Physical
pharmacy II

وزارة التعليم العالي والبحث العلمي
جامعة بغداد
University of Baghdad
كلية الصيدلة
COLLEGE OF PHARMACY
1936

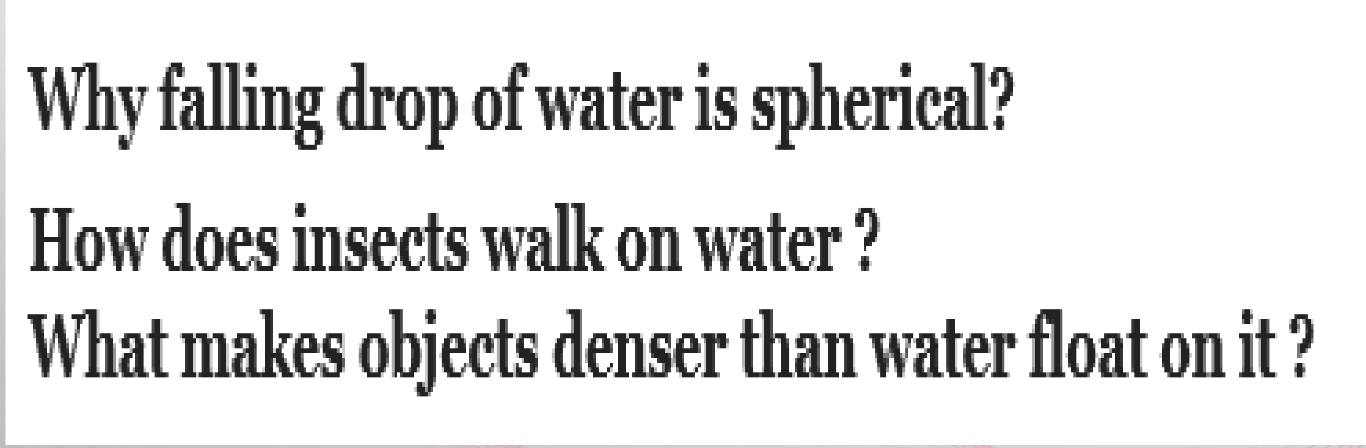
By:
Asst. Professor
Lena M. Thomas

INTERFACIAL PHENOMENA
(PART 1)

MEANING OF INTERFACIAL PHENOMENA

Interfacial phenomena are
**behaviors that occur at the interface
or boundary surface**
of two different phases of matter

It explains a variety of phenomena such as:



Why falling drop of water is spherical?

How does insects walk on water ?

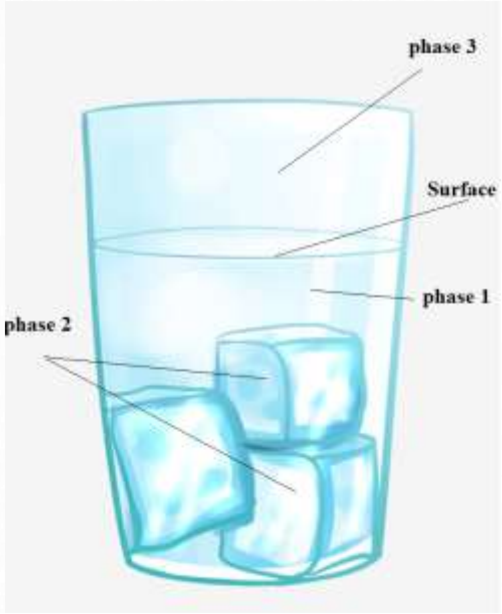
What makes objects denser than water float on it ?

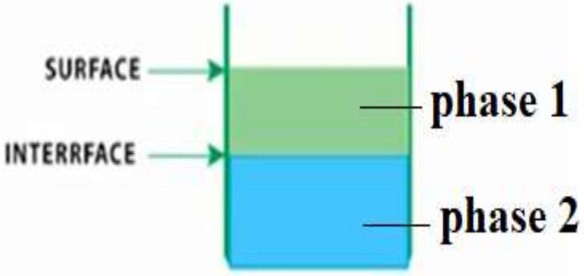
Interfacial phenomena

In this lecture, you'll learn:

- **Definition** of "surface" and "interface"
- **Types of interfaces**: emphasis on liquid interfaces
- **Definition** of "Surface tension" and "interfacial tension" and difference between them
- **Factors affecting on surface and interfacial tensions**
- **Importance** of interfacial phenomena in pharmacy and medicine

BASIC DEFINITIONS

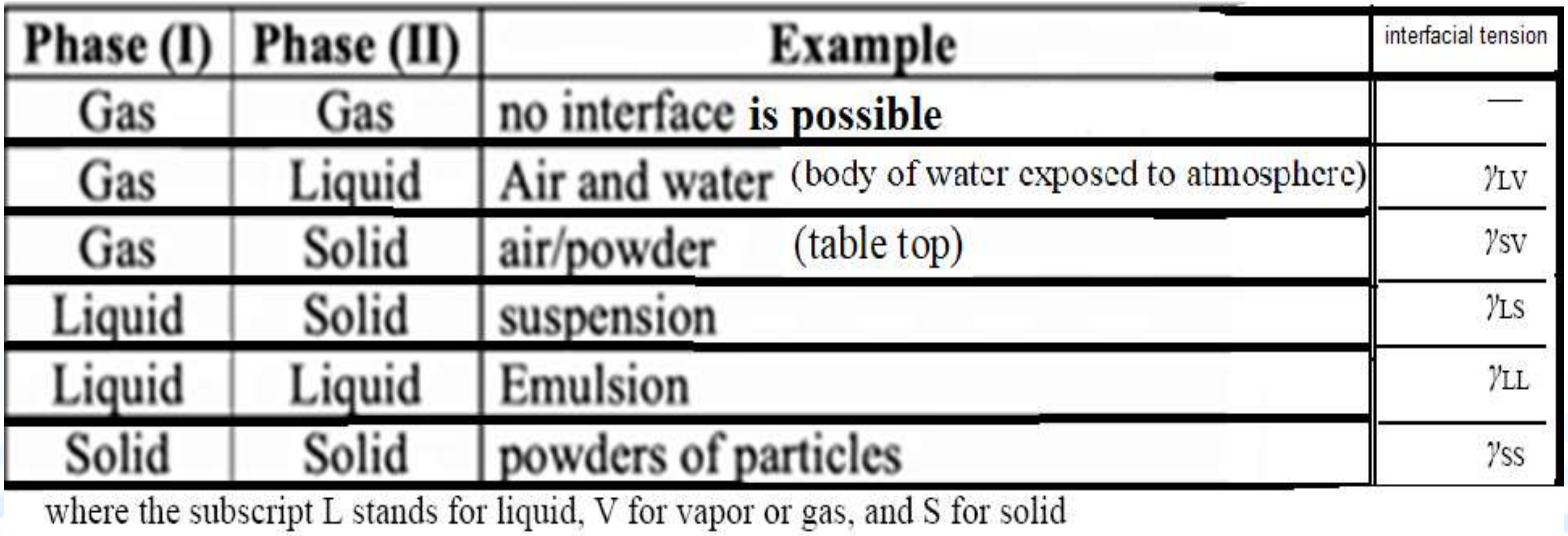




- **PHASE:** is chemically and physically uniform or homogeneous quantity of matter that can be separated mechanically from a mixture.
    - it may consist of a one or more substances.
- **INTERFACE:** is the boundary between two phases existing together. It surrounds each physical entity (be it a cell, a bacterium, a colloid, a granule, or a human) and separate it from its surroundings.
- **SURFACE:** is the outermost or uppermost layer of physical object. It represents the part on which other materials first interact and can be perceived by touch.
- EVERY SURFACE IS AN INTERFACE.
- HOWEVER, THE TERM “SURFACE” IS CUSTOMARILY USED WHEN REFERRING TO EITHER:
    - A **GAS–SOLID INTERFACE** (E.G., A TABLE TOP SURFACE FORMS A GAS–SOLID INTERFACE WITH THE ATMOSPHERE ABOVE IT)
    - A **GAS–LIQUID INTERFACE** (E.G., THE SURFACE OF A WATER IN OCEANS).

Classification of Interfaces

Several types of interface can exist, depending on whether the two adjacent phases are in the solid, liquid, or gaseous state as shown in the table



Phase (I)	Phase (II)	Example	interfacial tension
Gas	Gas	no interface is possible	—
Gas	Liquid	Air and water (body of water exposed to atmosphere)	γ_{LV}
Gas	Solid	air/powder (table top)	γ_{SV}
Liquid	Solid	suspension	γ_{LS}
Liquid	Liquid	Emulsion	γ_{LL}
Solid	Solid	powders of particles	γ_{SS}

where the subscript L stands for liquid, V for vapor or gas, and S for solid

Classification of Interfaces

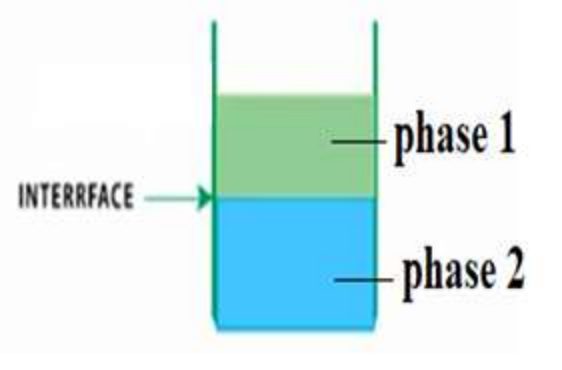
For convenience, these various combinations are divided into two groups:

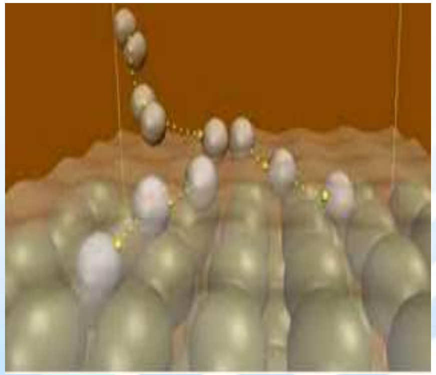
Liquid interfaces

- Deal with systems of a liquid-gas or liquid-liquid interfaces

Solid interfaces

- Deal with systems containing solid–gas, solid–liquid and solid-solid interfaces



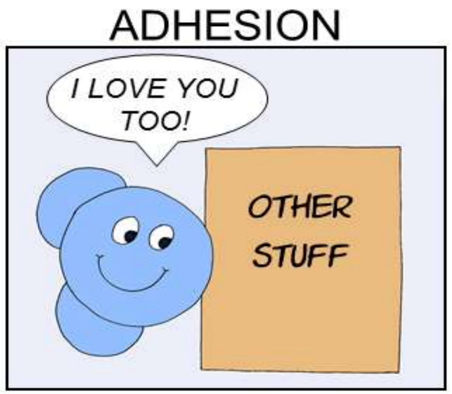


Although solid–solid interfaces have practical significance in pharmacy, little information is available to quantify these interactions and therefore, **only liquid interfaces will be discussed**

Surface and Interfacial Tension

Are they the same ?

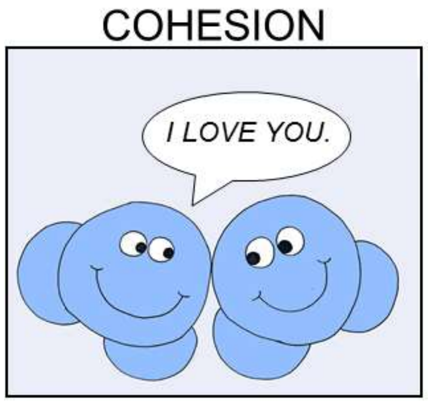
Before going to Surface and Interfacial Tension we need to understand about Cohesion and Adhesion



Electrostatic forces and Van der Waals forces between similar molecules cause adhesion

Cohesion causes the formation of water drops when it rains.

Adhesion causes the drops to cling to other surfaces.

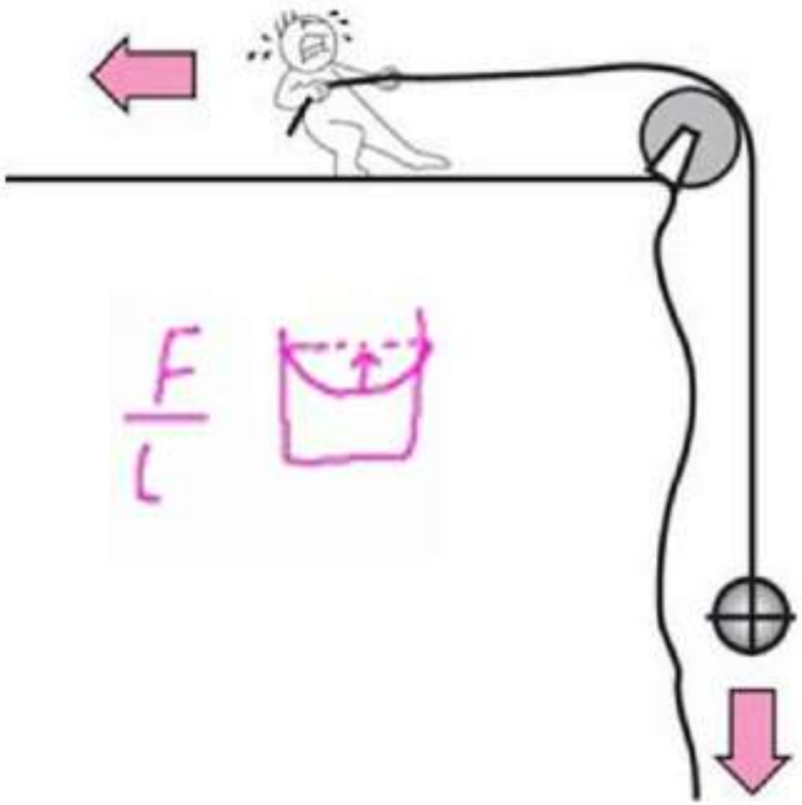


is a type of intermolecular force that occurs between two identical molecules

A. Surface tension

(symbolized by lower case gamma (γ))

- Surface tension is one of the principle **properties of fluids**.
- It is defined as " **the force per unit length that must be applied *parallel* to the surface so as to counterbalance the net inward pull**"



- It is similar to the situation that exists when an object dangling over the edge of a cliff on a length of rope is pulled upward by a man holding the rope and walking away from the edge of the top of the cliff.

Unit of Surface Tension

Surface tension, has the units of force/unit area

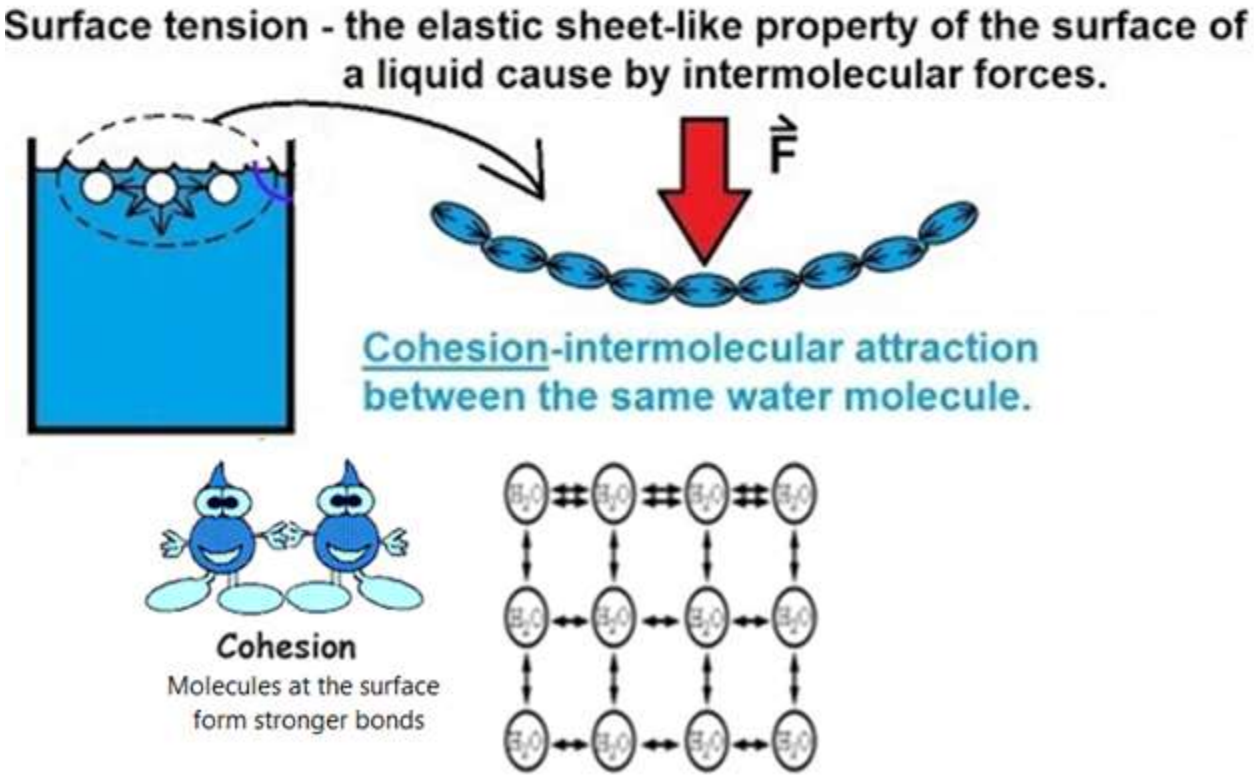
in the cgs system	dynes/cm
in the SI system	N/m

A. Surface tension

(symbolized by lower case gamma (γ))

- It is responsible for **making surface of liquids behave** as an **elastic sheet or a stretched film of rubber** (capable of stretching vertically and horizontally without breaking: similar to tramboline).

- It is **caused by the attraction between liquid molecules (Cohesion)** by various intermolecular forces.
- The higher the attraction forces, the higher the surface tension will be.



Surface tension - the elastic sheet-like property of the surface of a liquid cause by intermolecular forces.

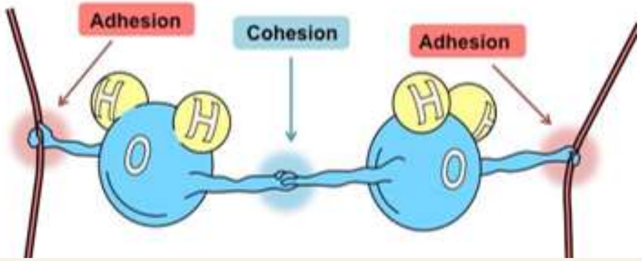
Cohesion-intermolecular attraction between the same water molecule.

Cohesion

Molecules at the surface form stronger bonds

The molecules lying inside (in the bulk) are attracted equally on all the directions by similar molecules around them therefore the net force acting on them becomes zero.

The molecules at the surface do not have similar liquid molecules above them to attract them upwards (although there is gas molecules, the adhesive forces between the liquid–gas interface is small); however, there are liquid molecules below, so there is a net **downward force** pulling the surface molecules towards the bulk, as a result, the surface will contract and lead to the formation of meniscus and resulting in a surface tension.



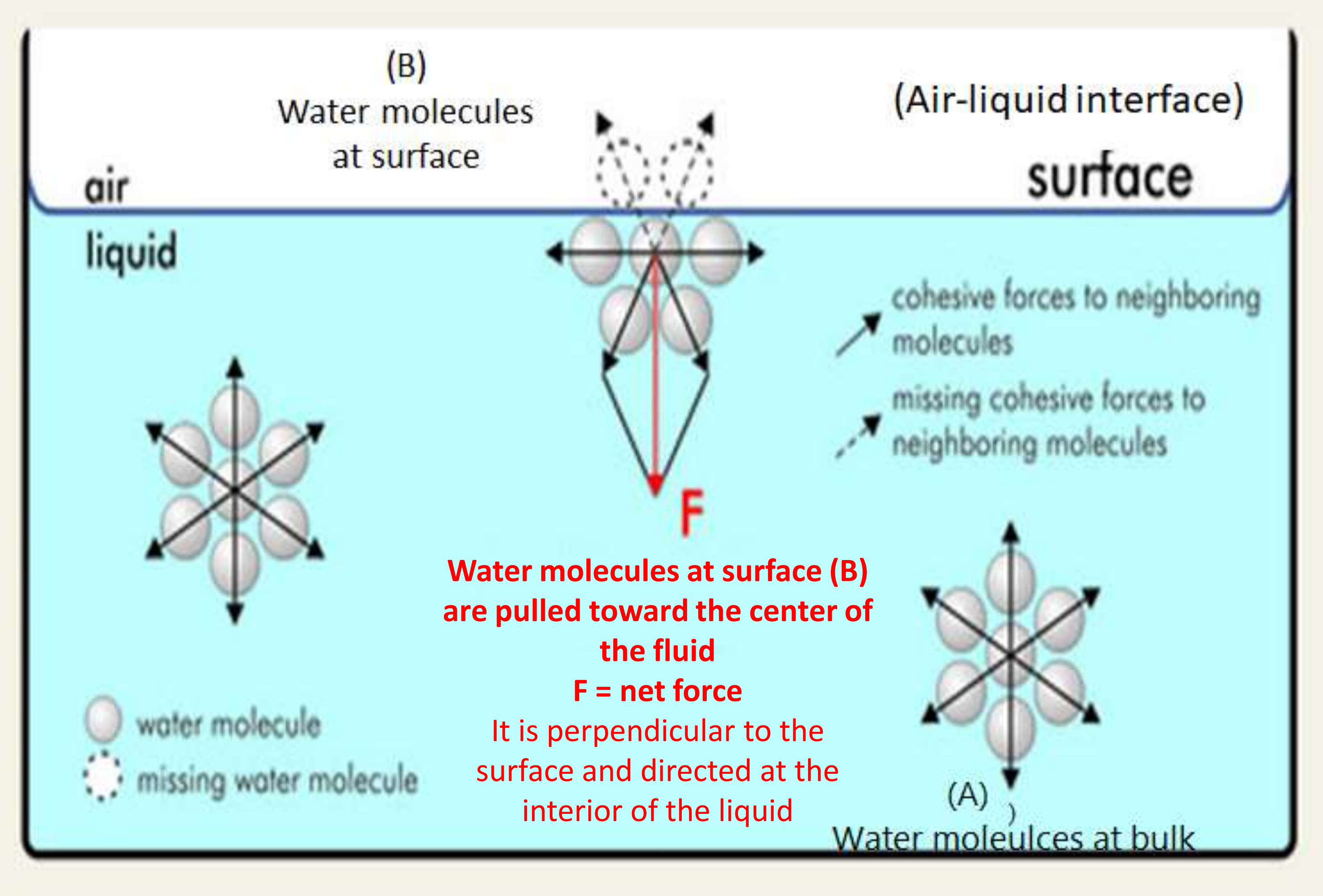
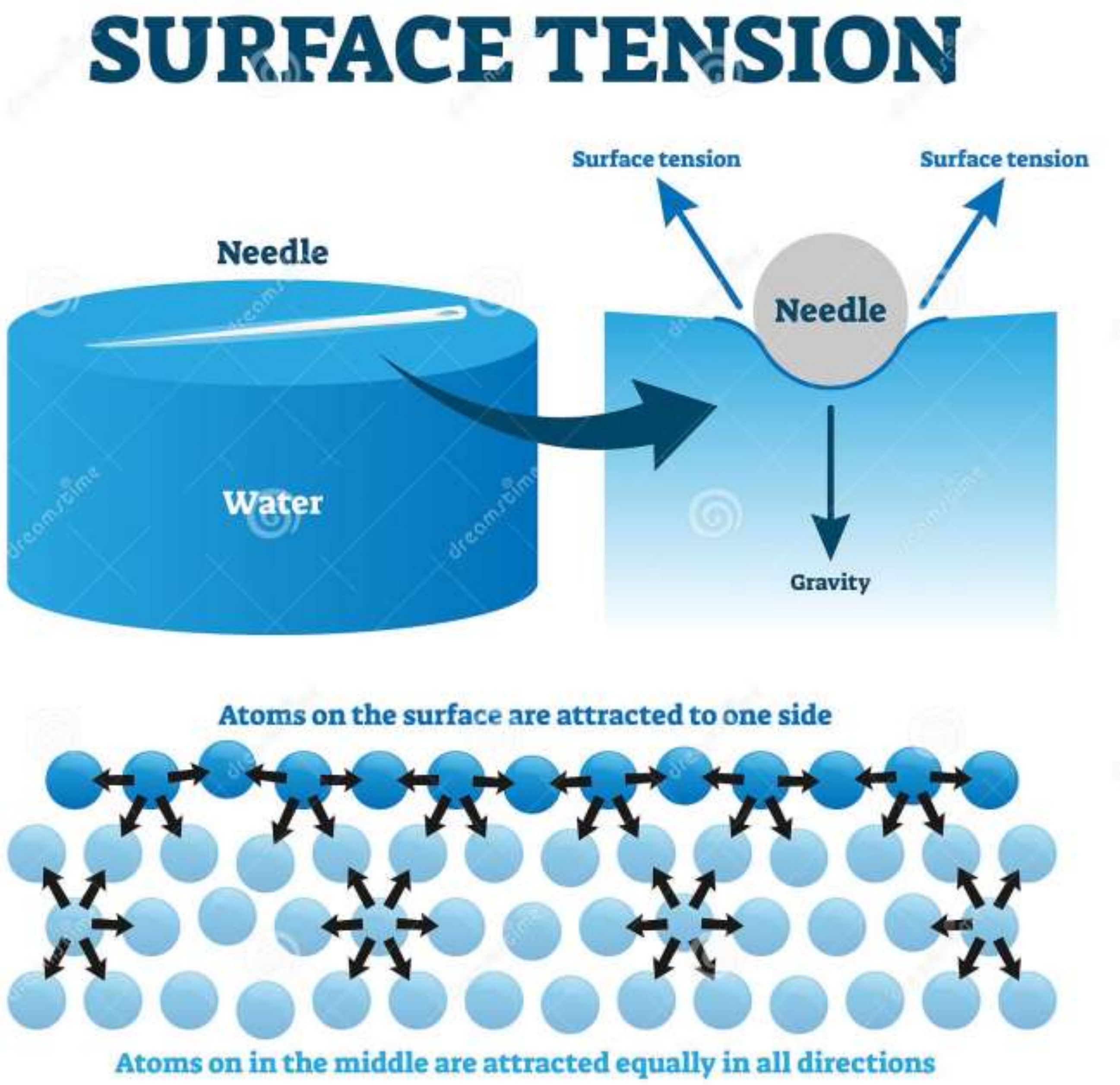
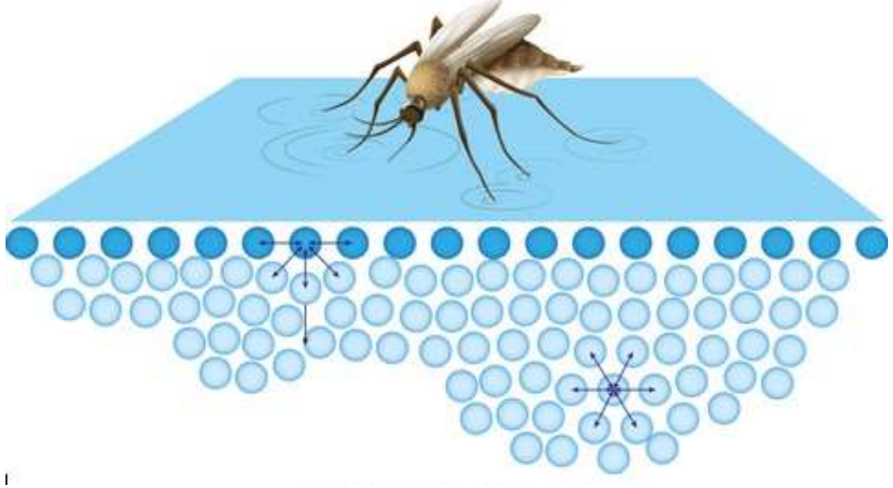


Figure 1: Representation of the unequal attractive forces acting on molecules at the surface of a liquid as compared with molecular forces in the bulk of the liquid

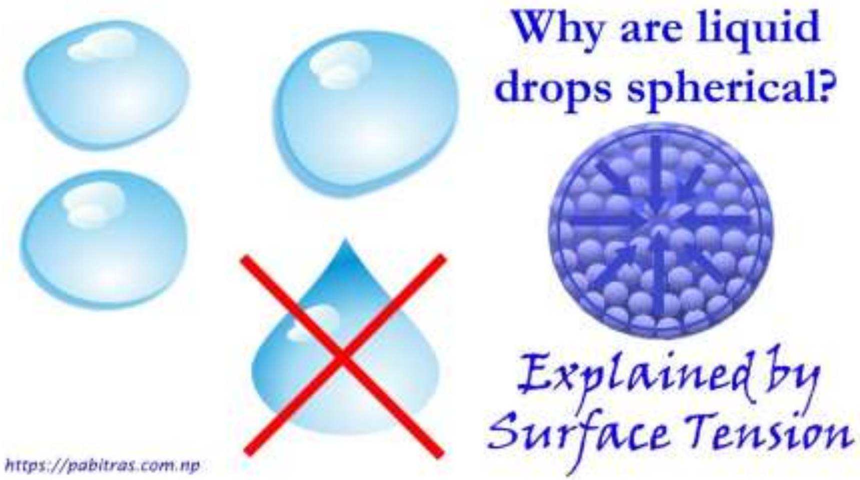
للاطلاع





The **surface molecules cohere more strongly** together by strong inter-molecular bonding and will result in a “surface film” which makes it more difficult to penetrate and move an object through the surface than to move it when it is completely dipped inside and is responsible for the ability of water surface to bear the weight of insects or low density objects over its surface.

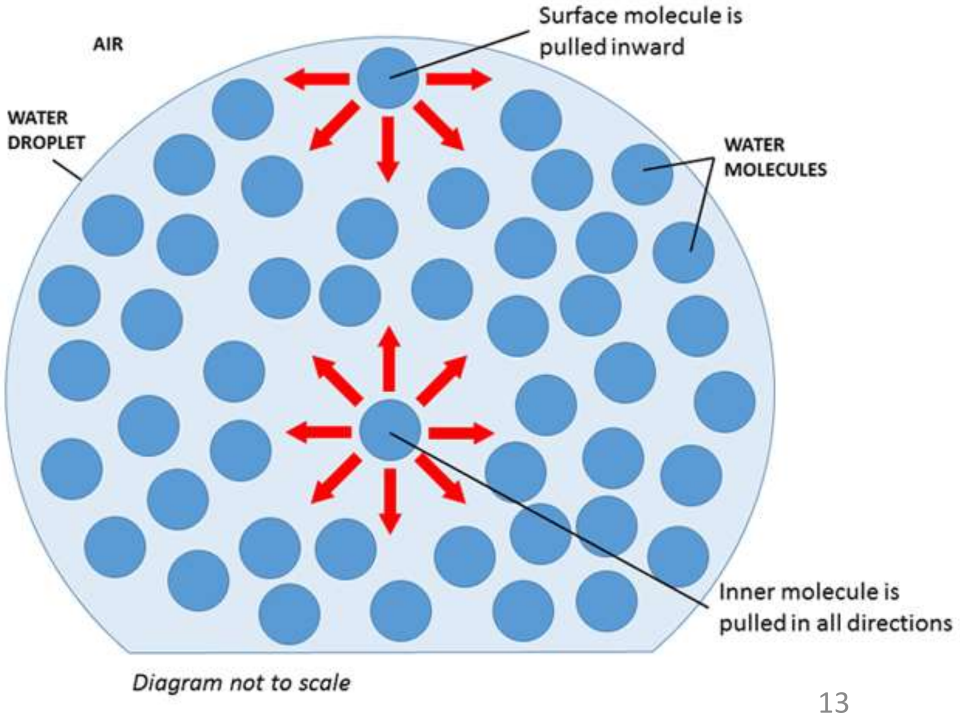
If we replace the water with ethanol, then the insect will get drawn into the water. It is because the **ethanol’s surface tension is very low as compared to that of the water.**

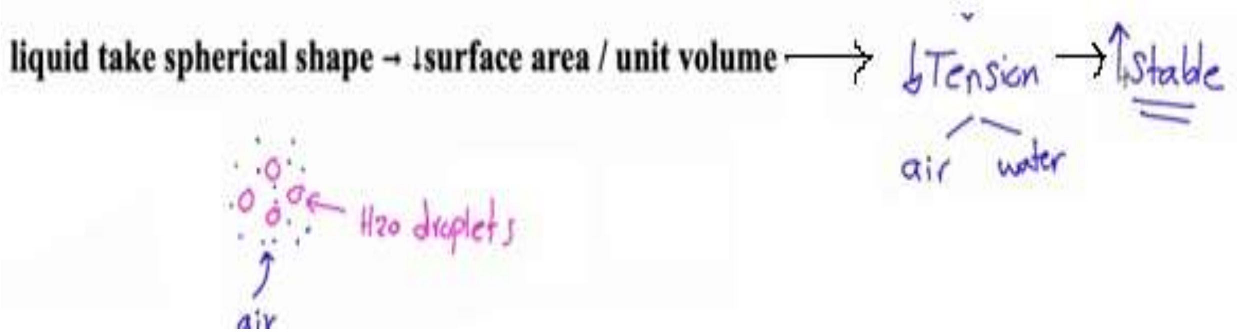


للاطلاع

- Surface tension (the inward pulling force) is the only reason due to which the water comes down a faucet or as rain in a spherical shape as it falls freely.
- The liquid droplets tend to have a spherical-shape since a sphere has the smallest surface area per unit volume (compared to different shape objects with the same area)

Any liquid surface always try to minimize the surface area





liquid take spherical shape → ↓surface area / unit volume → ↓Tension → ↑Stable

air water

H2o droplets

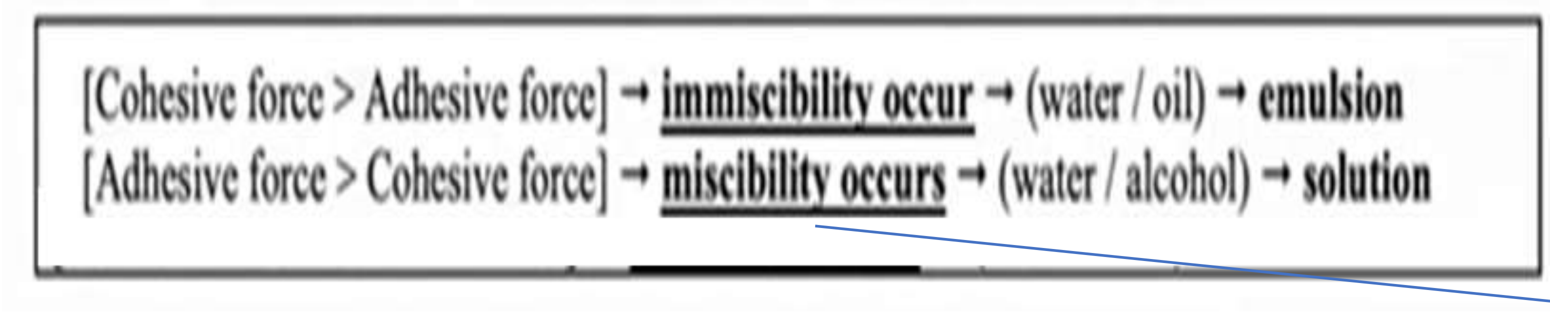
air

B. Interfacial tension

- Interfacial tension is the force per unit length existing at the interface between two immiscible liquid phases.
- Like surface tension, has the units of **dynes/cm.**

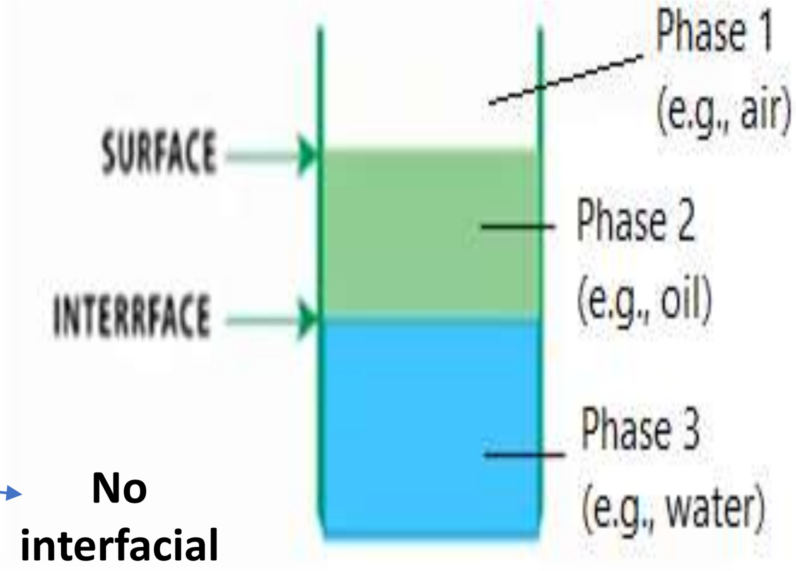
- Values of interfacial tensions reflects adhesion forces and the differences in chemical structure of the two phases involved: the greater the adhesion (higher tendency to interact and the more are the chemical groups capable of hydrogen bonding), the less interfacial tension.

Depending on the strength of forces at the interface:



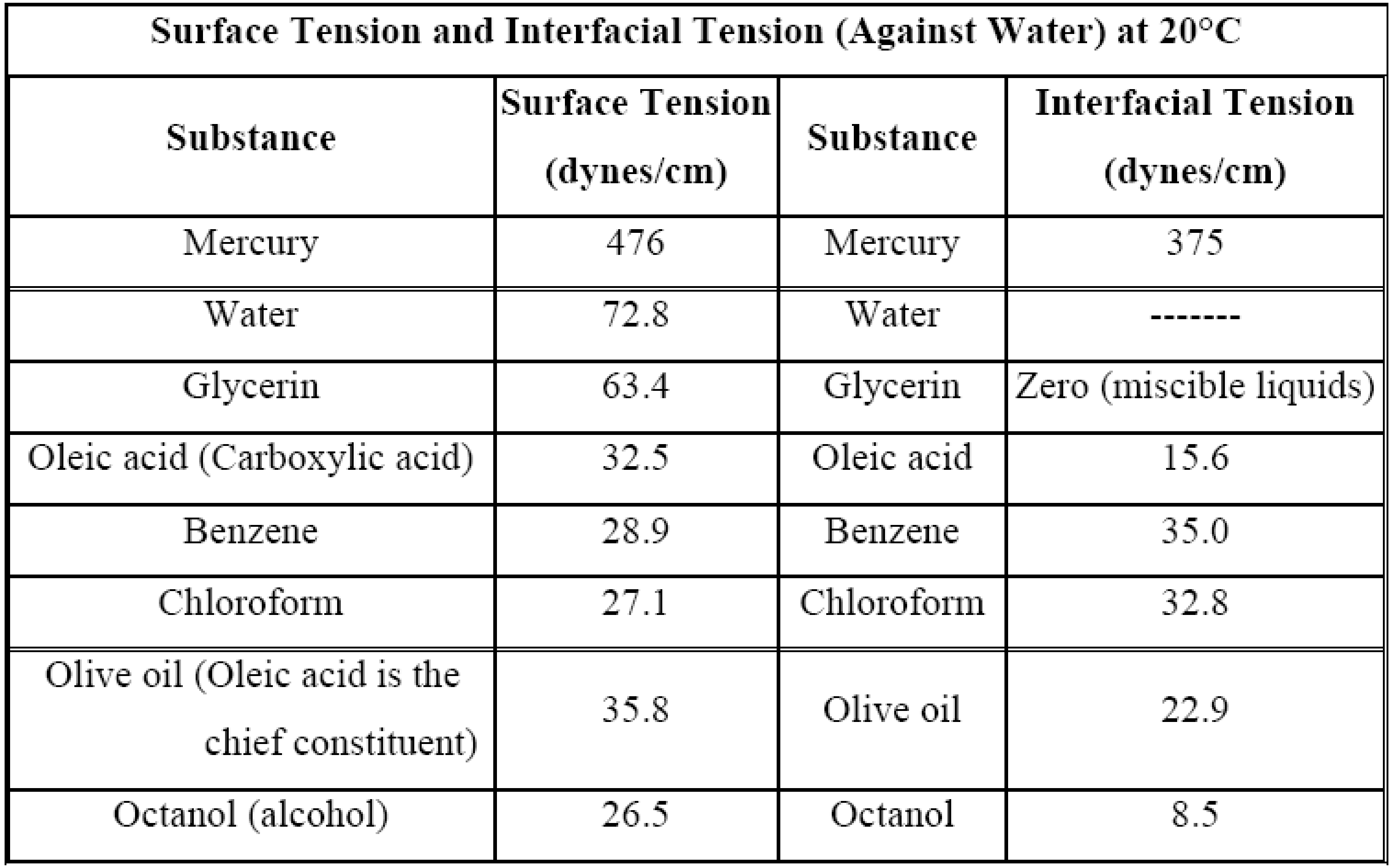
[Cohesive force > Adhesive force] → **immiscibility occur** → (water / oil) → **emulsion**
[Adhesive force > Cohesive force] → **miscibility occurs** → (water / alcohol) → **solution**

No interfacial tension



Ordinarily, interfacial tensions are less than surface tensions because the adhesive forces between two liquid phases forming an interface are greater than when a liquid and a gas phase exist together.

Some representative surface and interfacial tensions are listed in the following table



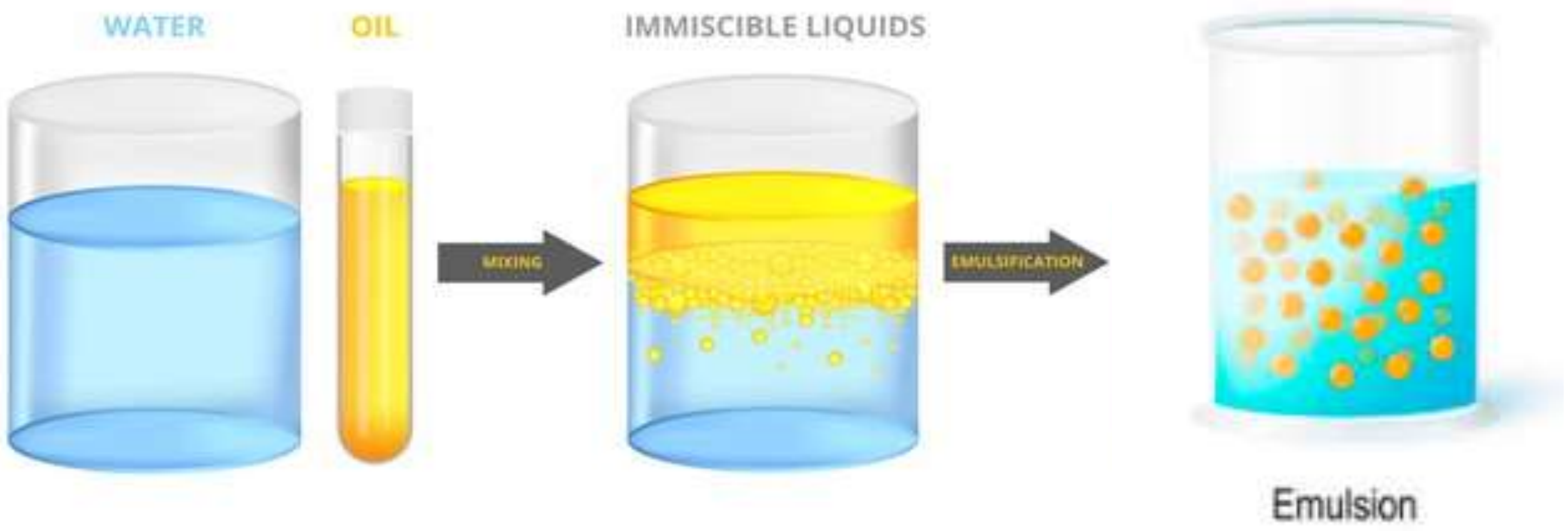
Surface Tension and Interfacial Tension (Against Water) at 20°C

Substance	Surface Tension (dynes/cm)	Substance	Interfacial Tension (dynes/cm)
Mercury	476	Mercury	375
Water	72.8	Water	-------
Glycerin	63.4	Glycerin	Zero (miscible liquids)
Oleic acid (Carboxylic acid)	32.5	Oleic acid	15.6
Benzene	28.9	Benzene	35.0
Chloroform	27.1	Chloroform	32.8
Olive oil (Oleic acid is the chief constituent)	35.8	Olive oil	22.9
Octanol (alcohol)	26.5	Octanol	8.5

الارقام في الجدول للاطلاع

How to reduce Interfacial tension ?

- To dispense one immiscible liquid in the other, it is necessary to introduce another kind of molecule that has affinity for both liquids. This type of molecule is called surface active agent (S.A.A). These molecules when placed at the interface of the immiscible liquids, they decrease the interfacial tension, allowing these liquids to mix.



Factors affecting on surface and interfacial tension

The type of the liquid

The surface tensions reflects the differences in chemical structure
Mercury(metallic bonds) > water(H bonds) > benzene (London forces)

The interfacial tension reflects presence of chemical groups capable of hydrogen bonding: increase H-bonding, markedly decrease interfacial tension

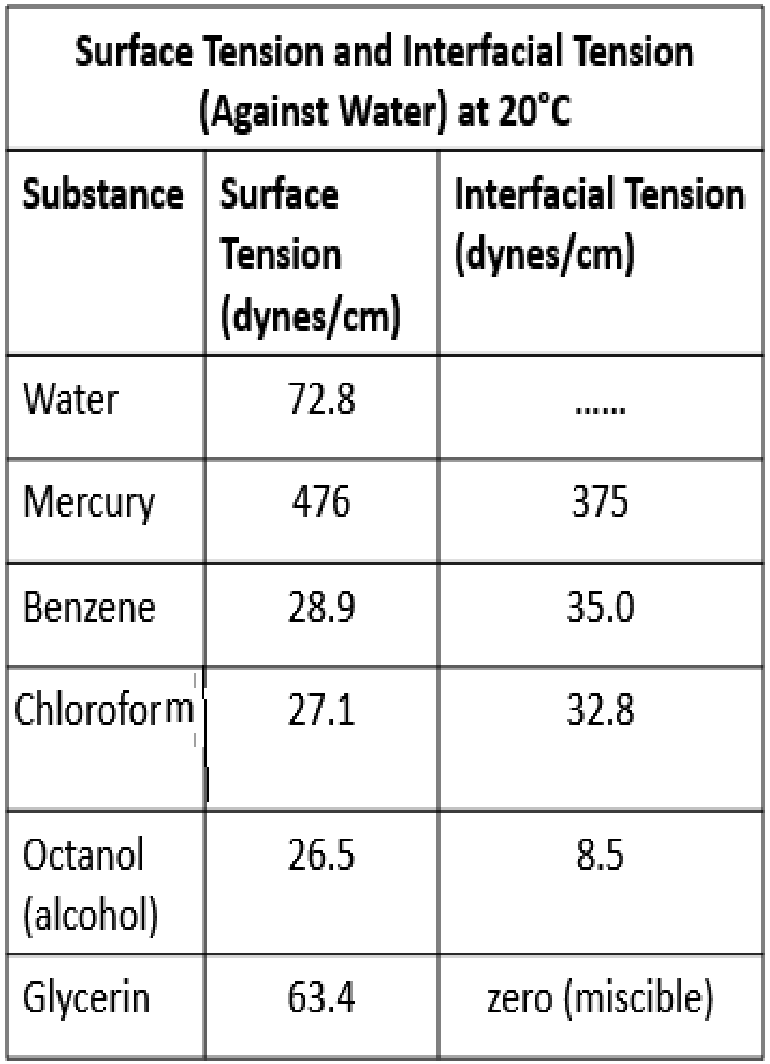
Temperature

↑Increasing temperature ↓reduces surface and interfacial tension.

This is the reason for the higher ability of hot water compared to cold water in cleaning: the surface tension of cold water is about 72 dyne/cm at 25°C but goes down to less than 60 dyne/cm at 100°C.

What is mixed with the liquid

- Electrolytes slightly ↑ increase surface tension
- Surface active agents (e.g., soap and detergents) ↓ decrease surface and interfacial tension



Surface Tension and Interfacial Tension (Against Water) at 20°C

Substance	Surface Tension (dynes/cm)	Interfacial Tension (dynes/cm)
Water	72.8	……
Mercury	476	375
Benzene	28.9	35.0
Chloroform	27.1	32.8
Octanol (alcohol)	26.5	8.5
Glycerin	63.4	zero (miscible)

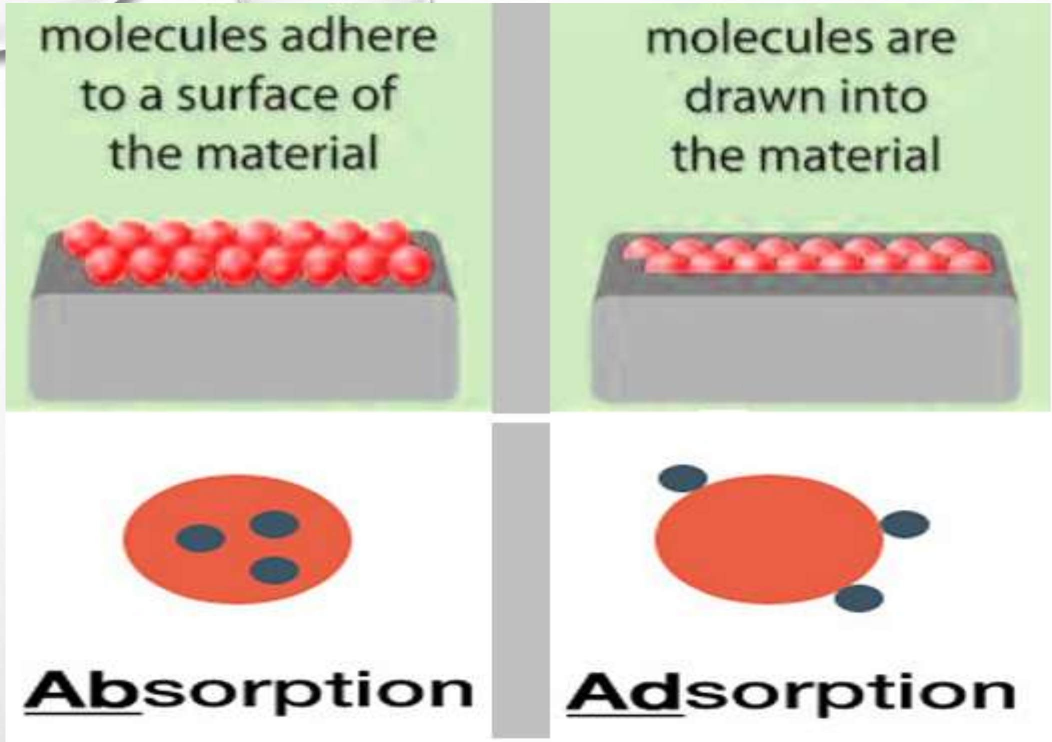
Factors affecting on surface and interfacial tension

Try it at home

Importance of Interfacial phenomena in pharmacy and medicine

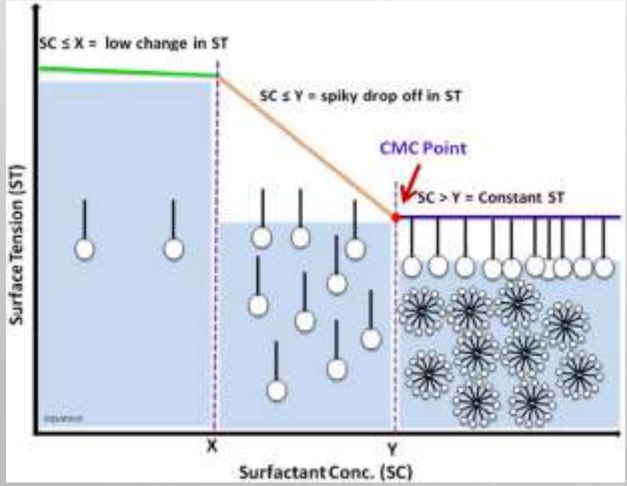
Interfacial phenomena will influence on:

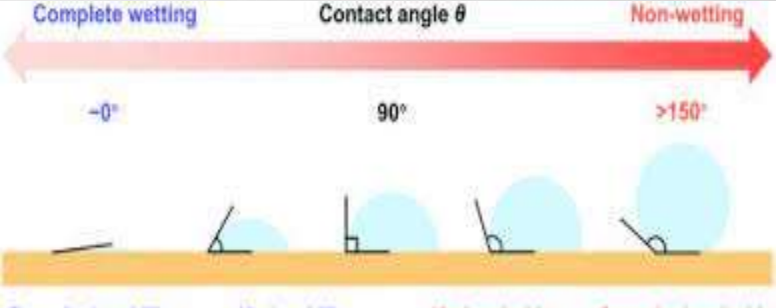
- ✓ The dispersion of insoluble particles in liquid media to form suspensions
- ✓ Emulsion formation and stability
- ✓ Adsorption of drugs onto solid particles in dosage forms
- ✓ The flow of particles and adhesion between granules
- ✓ The preparation of layered tablets
- ✓ The penetration of molecules through biologic membranes
- ✓ The interfacial properties of a surface-active agent lining the alveoli of the lung are responsible for the efficient operation of this organ



Physical pharmacy II

By:
Asst. Professor
Lena M. Thomas





INTERFACIAL PHENOMENA (PART 2)

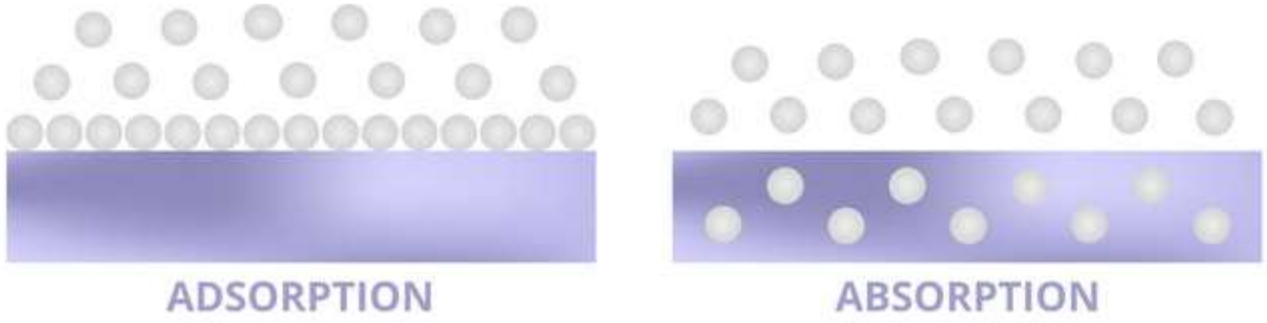
Interfacial phenomena

In this lecture, you'll learn:

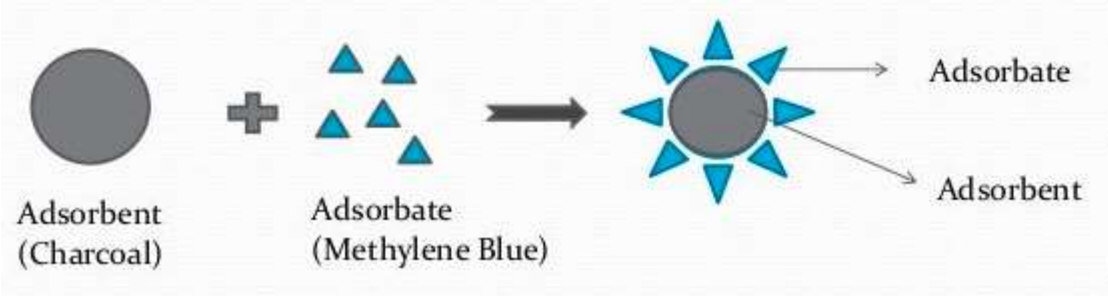
- Meaning of “absorption” and “adsorption”
- Adsorption at interfaces (liquid + solid)
- Surfactants: overview and their role regarding interfacial phenomena
- Meaning of “wetting”, “wettability” and their relation with “contact angle”
- Applications of wetting phenomena in pharmacy

Adsorption is a surface effect, it is a spontaneous phenomena that involves the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. Example: adsorption of drugs by charcoal.

This process differs from absorption, in which a fluid is dissolved by or permeates the capillary spaces of the absorbing medium. Example: taking up of water by a sponge.



- The substance on which adsorbate is adsorbed is called **adsorbent**
- A material that has been or is capable of being adsorbed is known as **adsorbate**.
- The process of adsorption creates a film of the adsorbate on the surface of the adsorbent.



To adsorb more adsorbate, an adsorbent of a given mass should have the greatest possible surface area.

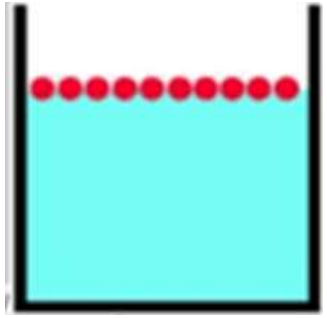
- Adsorption can occur at liquid interfaces as well as solid interfaces

A. Adsorption at Liquid Interfaces

Certain molecules and ions, when dispersed in the liquid will partition (or move towards)

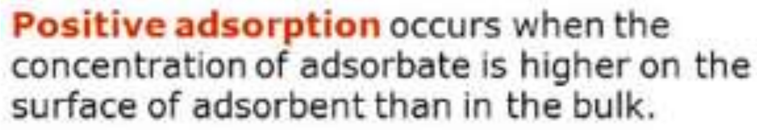
Surface/Interface > bulk

e.g., Surfactants



Positive Adsorption

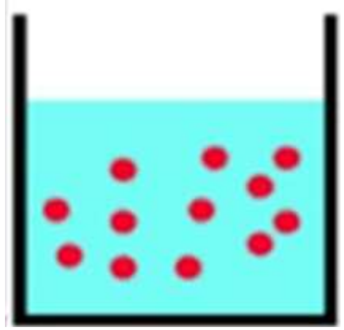
↓ surface free energy and surface tension



Positive adsorption occurs when the concentration of adsorbate is higher on the surface of adsorbent than in the bulk.

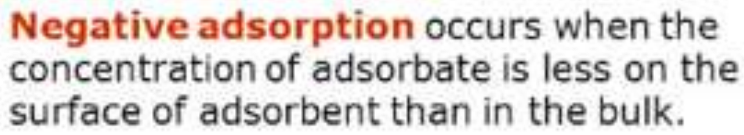
Surface/Interface < bulk

e.g., Inorganic electrolytes such as NaCl and sugar



Negative Adsorption

↑ surface free energy and surface tension



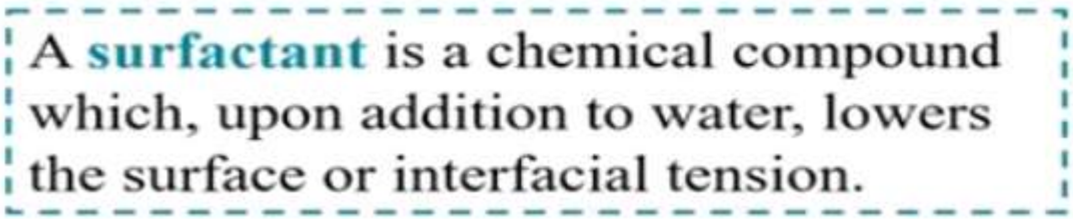
Negative adsorption occurs when the concentration of adsorbate is less on the surface of adsorbent than in the bulk.

A. Adsorption at Liquid Interfaces

Positive Adsorption

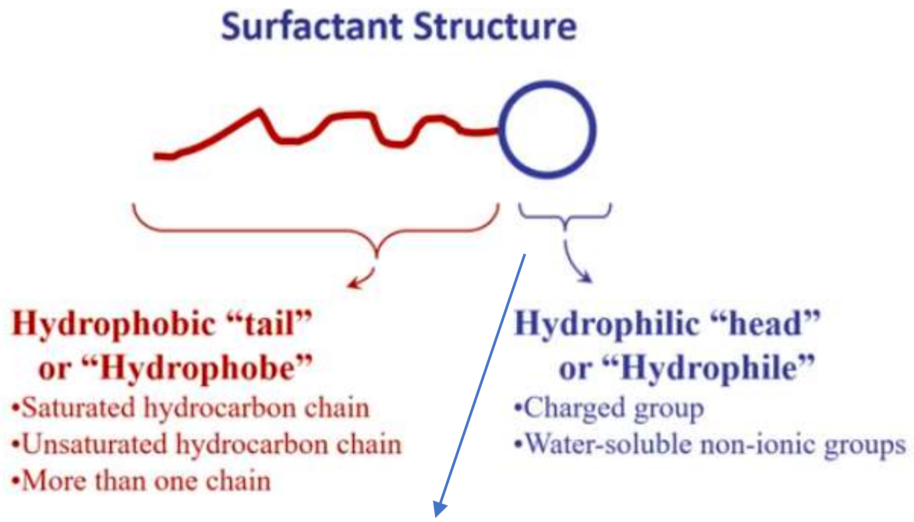
Surfactant Background

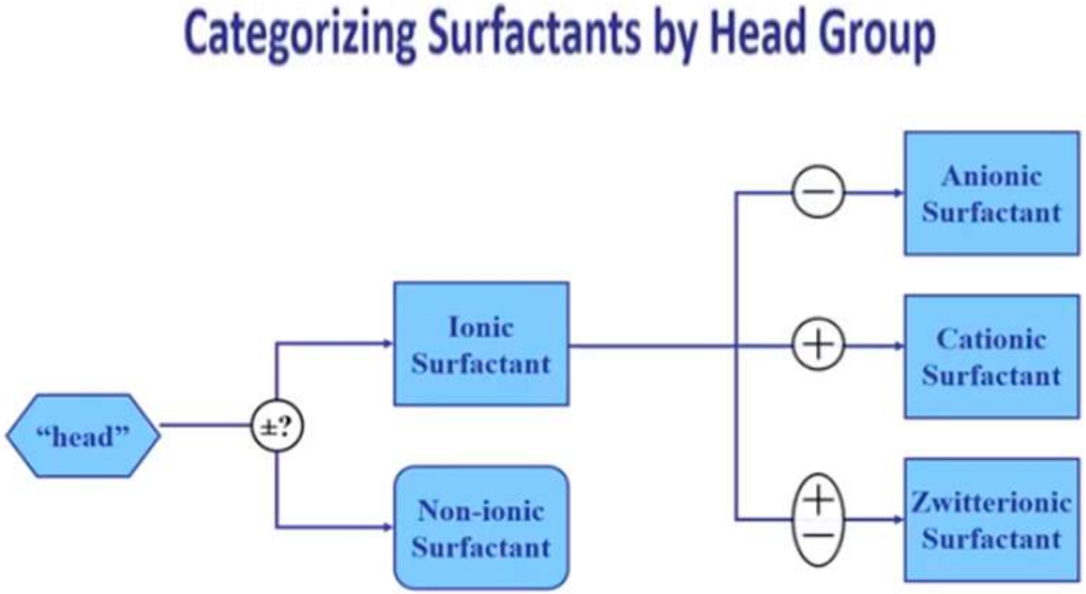
What are Surface-active agents (SAA) or “Surfactants” ?



A **surfactant** is a chemical compound which, upon addition to water, lowers the surface or interfacial tension.

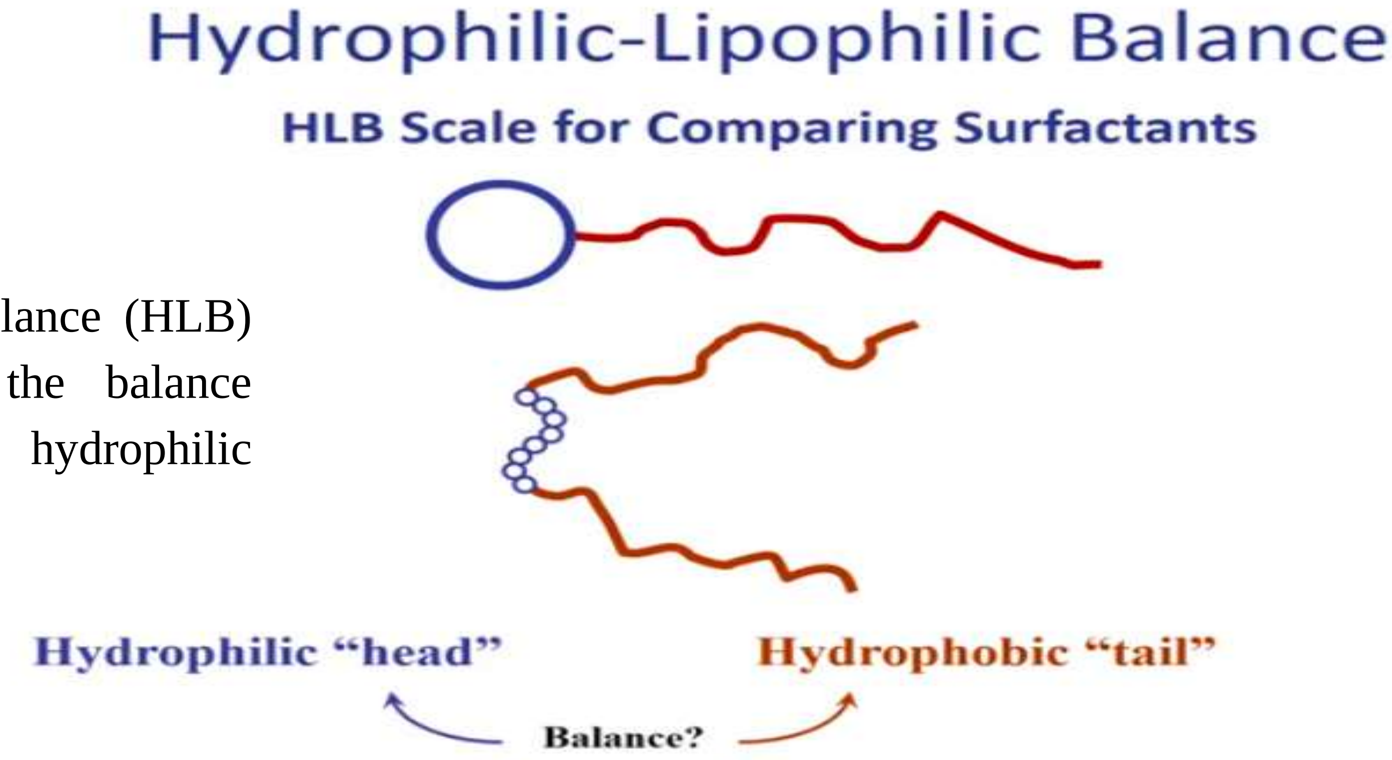
It is the amphiphilic nature of surface-active agents that causes them to be adsorbed at interfaces, whether these are liquid–gas or liquid–liquid interfaces.

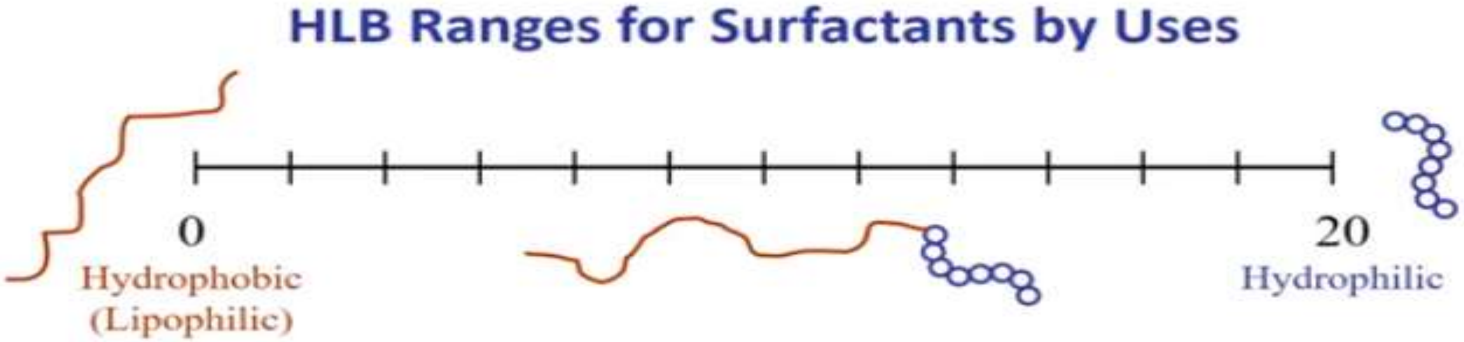




Surfactant Background

The hydrophilic–lipophilic balance (HLB) number is a measure of the balance between hydrophobic and hydrophilic portions of a surfactant.





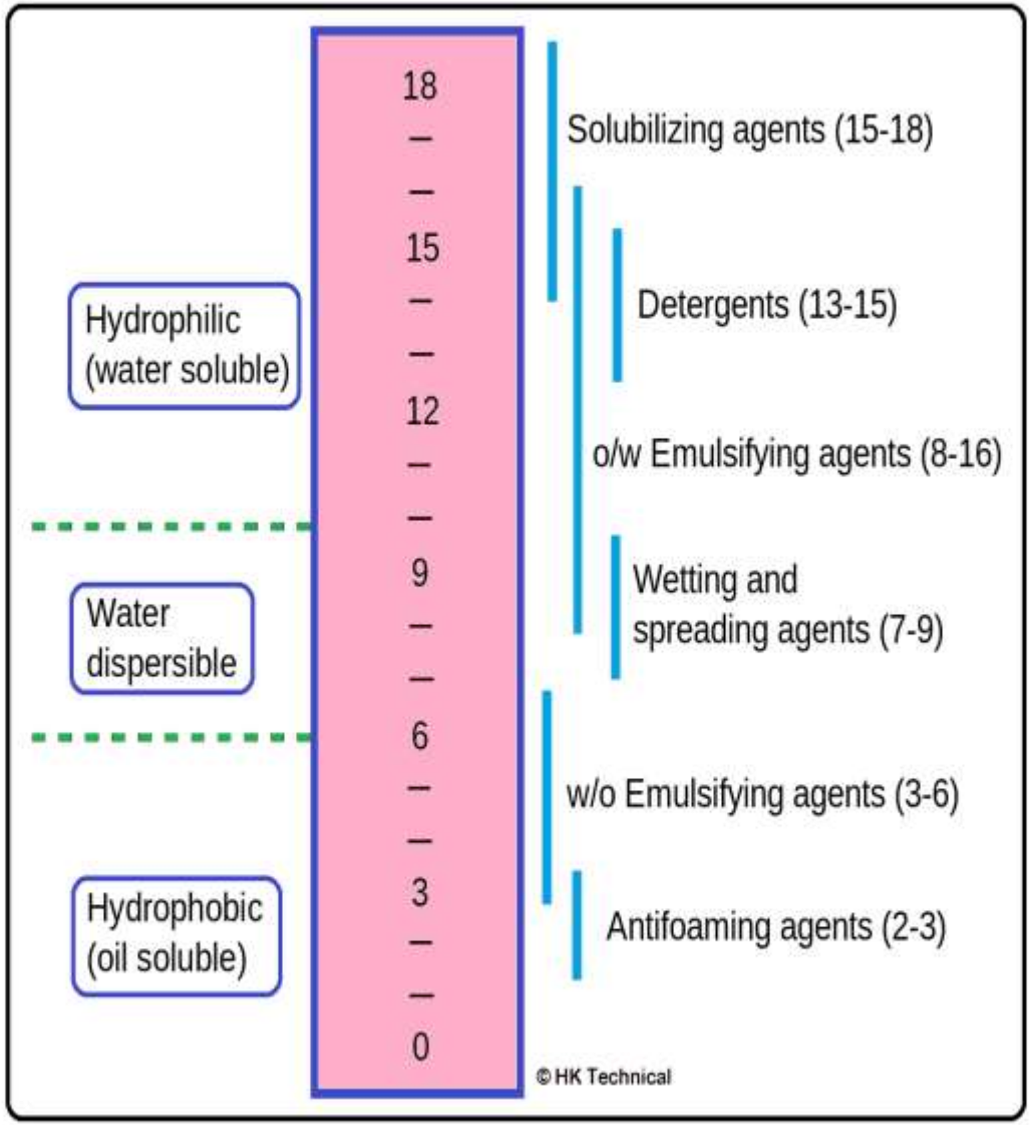
The HLB of a surfactant is expressed using an arbitrary scale which ranges from 0 to 20

Applications of Surfactants

1. As solubilizing agents by formation of micelles
2. As detergents used for removal of dirt
3. As emulsifying agents by decreasing interfacial tension
4. As wetting and spreading agents by increasing spreadability and decreasing the contact angle
5. As antifoaming agents
6. A surfactant may exert a drug action:

   both G +ve and G –ve organisms are susceptible to the action of the cationic quaternary compounds which act as surfactants.

   These agents are adsorbed on the cell surface and kill the micro-organism by increasing the permeability or “leakiness” of their lipid cell membrane.



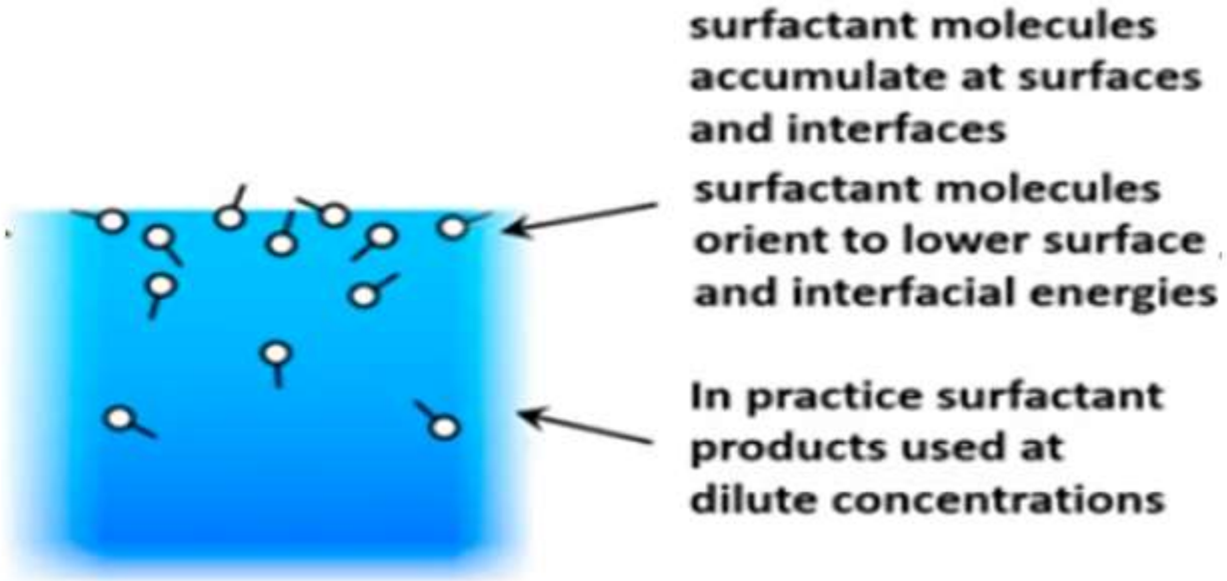
© HK Technical

Effect of Surface active agents on surface and interfacial tension of water

Adsorption of surfactant 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.

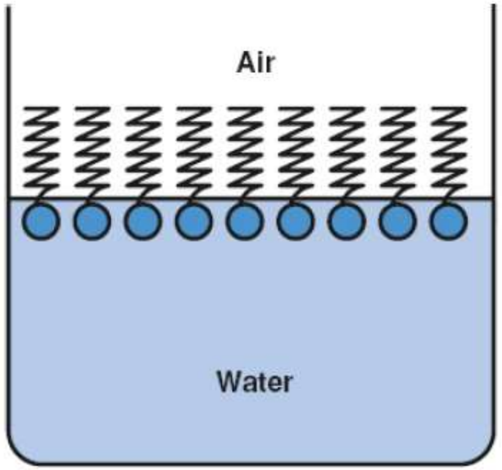
- If the molecule is too hydrophilic, it remains within the body of the aqueous phase and exerts no effect at the interface.
- Likewise, if it is too lipophilic, it dissolves completely in the oil phase and little appears at the interface.



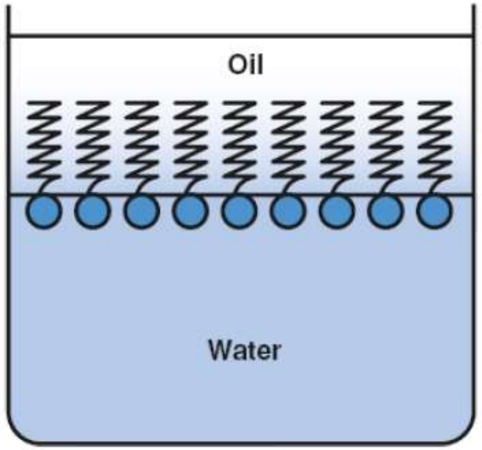
surfactant molecules accumulate at surfaces and interfaces

surfactant molecules orient to lower surface and interfacial energies

In practice surfactant products used at dilute concentrations



At the air–water interface, the lipophilic chains of surfactants are directed upward into the air



At the oil–water interface, lipophilic chains of surfactants are associated with the oil phase

Effect of surfactant on surface tension

Surfactant adsorb at the water surface, and reduce surface tension because they replace some of the water molecules in the surface and the forces of attraction between surfactant and water molecules are less than those between two water molecules (interfere with hydrogen of water), hence the contraction force is reduced.

The process is concentration dependent as follows:

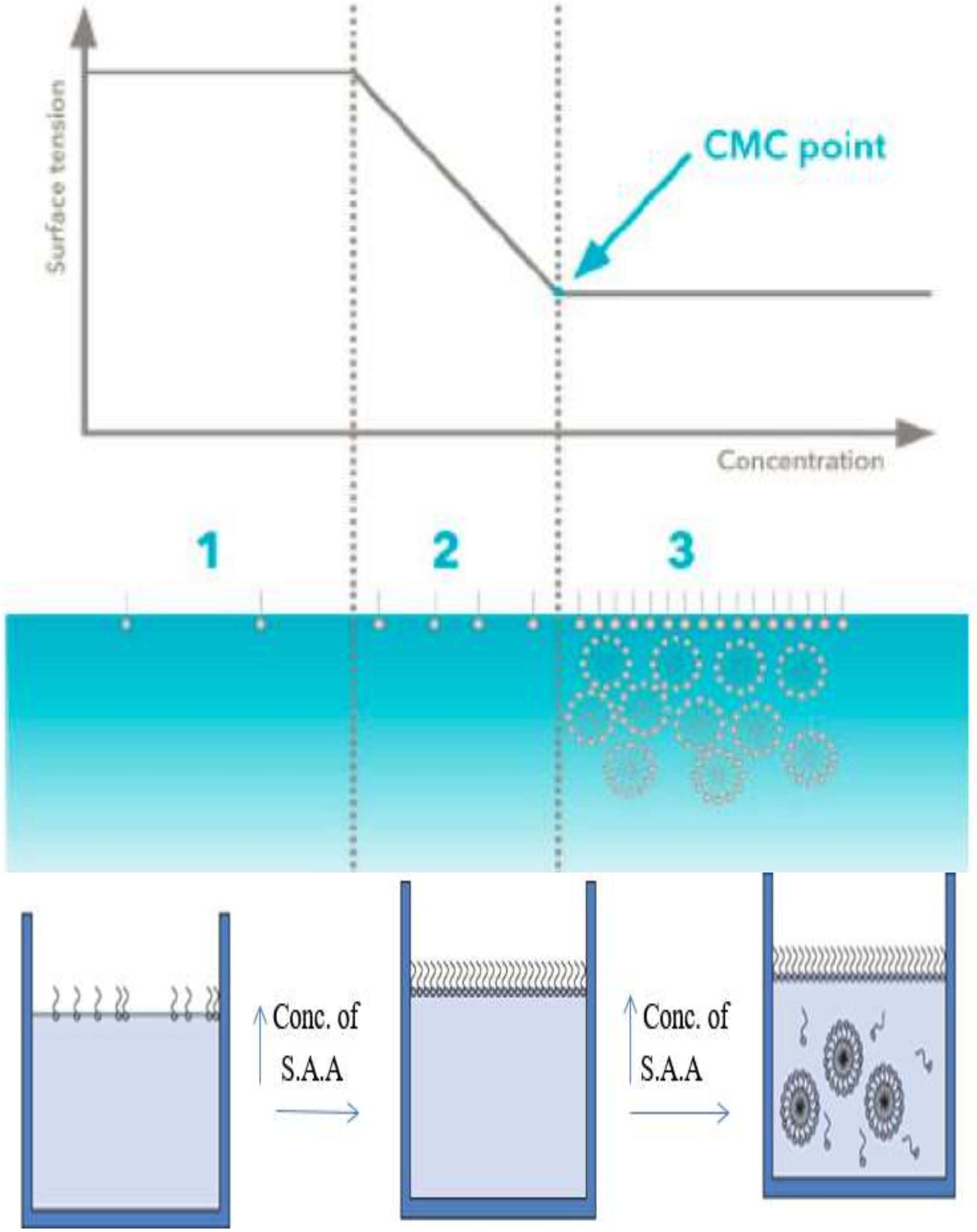
1. At very low surfactant concentration only slight change in surface tension is detected.
2. Addition of surfactant decreases the surface tension drastically
3. However, at critical micelle concentration (CMC), surface becomes saturated, and the addition of surfactant molecules do not affect on surface tension and plateau is reached.

Why surface tension stops decreasing and reaches a plateau?

When reaching critical micelle concentration (CMC), the surface becomes saturated with surface active molecules and any increase in their concentration will cause them to form **micelles** in the bulk

Why micelles are formed?

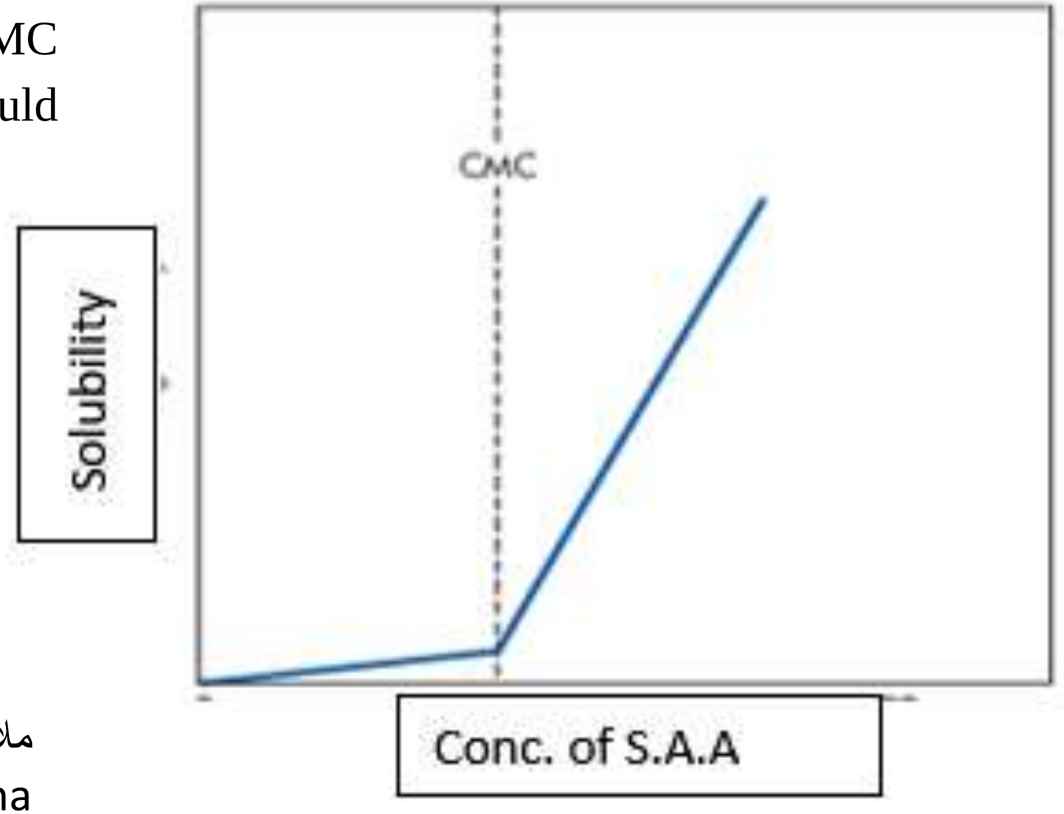
To protect their hydrophobic groups from the aqueous environment



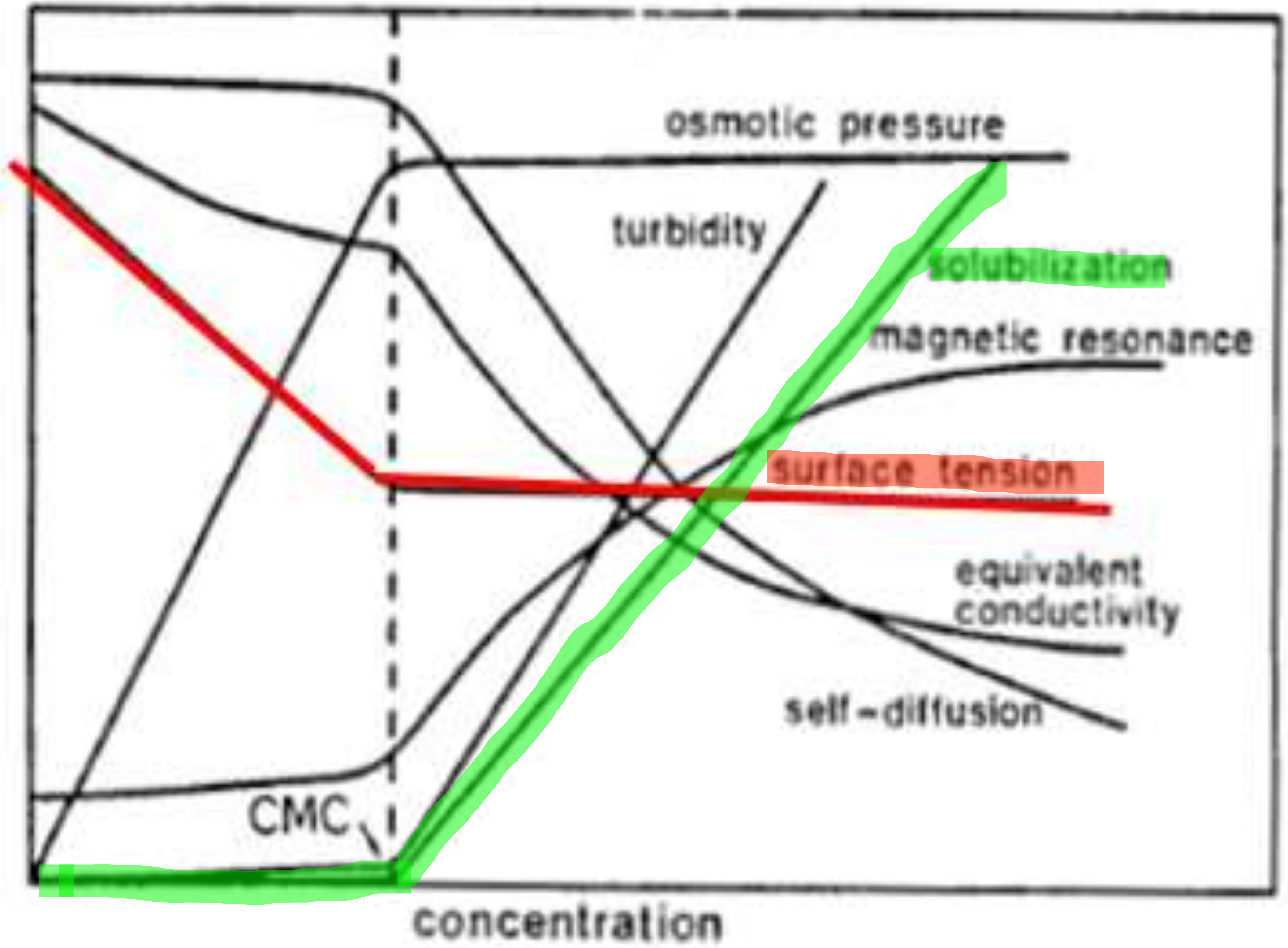
Surface tension against the surfactant concentration (logarithmic scale)

Effect of surfactant on solubility of slightly soluble substance

The ability of the solution to solubilize a drug, increase sharply when the concentration of the surface active agent increases beyond the CMC concentration since the non-polar molecules in aqueous systems would be located in the hydrocarbon core of the micelle



ملاحظة: هذا الموضوع لا يخص موضوع ال
interfacial phenomena
بل يخص موضوع ال
Solubility
لكن تم ذكره فقط للتنويه لاهمية ال
surfactants



osmotic pressure
turbidity
solubilization
magnetic resonance
surface tension
equivalent conductivity
self-diffusion
CMC
concentration

B. Adsorption at Solid Interfaces

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

The principles of solid–air adsorption can be applied in:

- the removal of objectionable odors from rooms and food,
- the operation of gas masks

The principles of solid–liquid adsorption can be applied in:

- Decolorizing solutions,
- Detergency, and wetting

An example of a substance that can adsorb enormous amounts of gases or liquids is activated charcoal.

It is used as an antidote for poisonings due to many drugs (drugs such as dyes, alkaloids, fatty acids, and even inorganic acids and bases can be adsorbed from solution onto solids such as charcoal and alumina).

Wetting phenomena and wetting agents

Adsorption at solid surfaces is involved in the phenomena of wetting and detergency.

Wettability: is a property which indicates the affinity between solid and fluid phase.

When a liquid comes into contact with the solid, the forces of attraction of molecules in the liquid (cohesion) and the forces of attraction between the liquid and the solid phases (adhesion) begin to play a significant role.

Mechanism of wetting:

In order for wetting of solid to occur, the **liquid must displace air** and spread over the surface of the solid, otherwise, we say that the solid is NOT wetted.

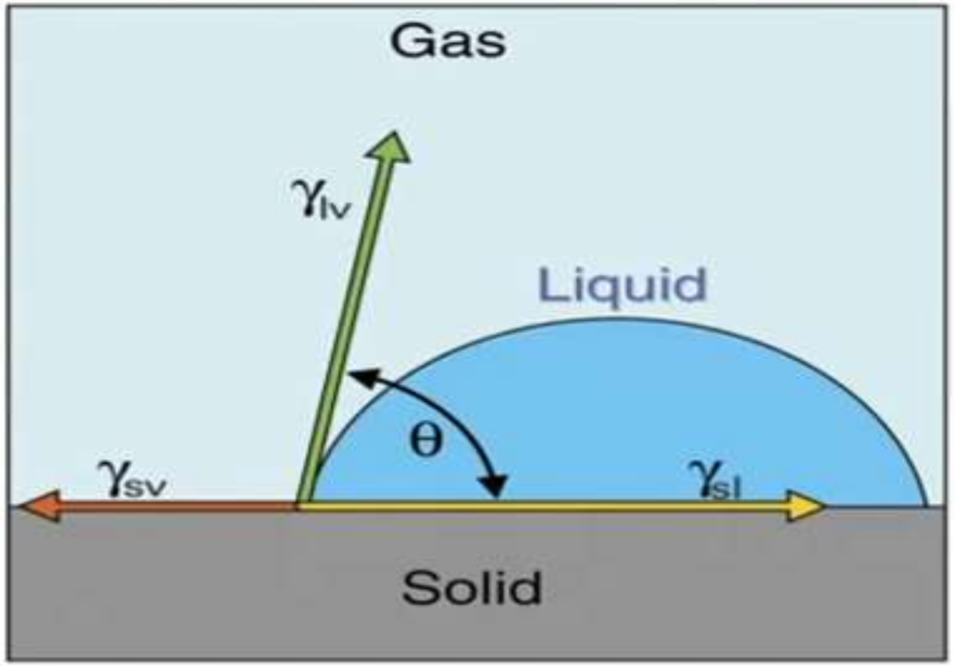
For example: talc or charcoal sprinkled on the surface of water are not wetted and they will float despite the fact that their densities are higher than that of water.

The parameter that reflects the degree of wetting is known as contact angle.

Contact angle and wettability

Contact angle is the angle between a liquid droplet and the surface over which it spreads.

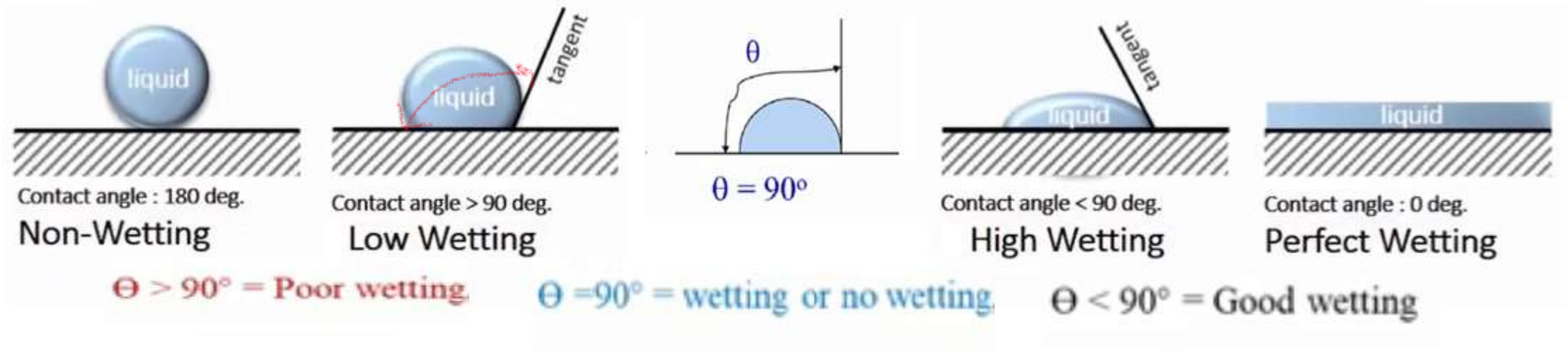
- It is defined by the angle between the tangent drawn to the liquid surface to a point of contact of liquid and solid inside the liquid.



θ is the contact angle

γ^{sl} is the solid/liquid surface tension
γ^{sv} is the solid/vapor surface free energy
γ^{lv} is the liquid/vapor surface tension

Contact angle is an inverse measure of wettability: the higher the contact angle, the lower is the wettability



Surfaces can be classified according to their wettability to:

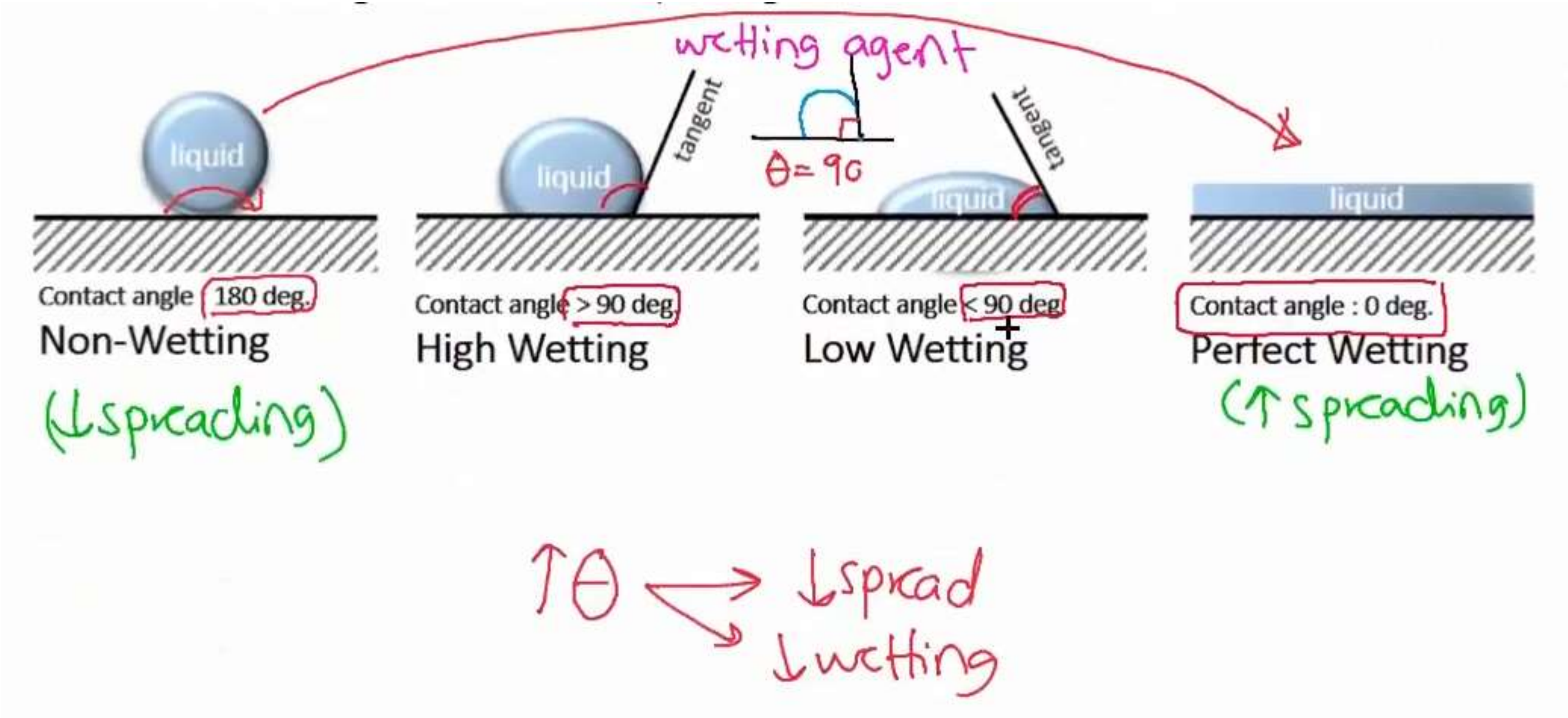
Superhydrophobic
Contact angle > 150°

Hydrophobic
Contact angle > 90°

Hydrophilic
Contact angle < 90°

Hydrophobic material have large contact angle

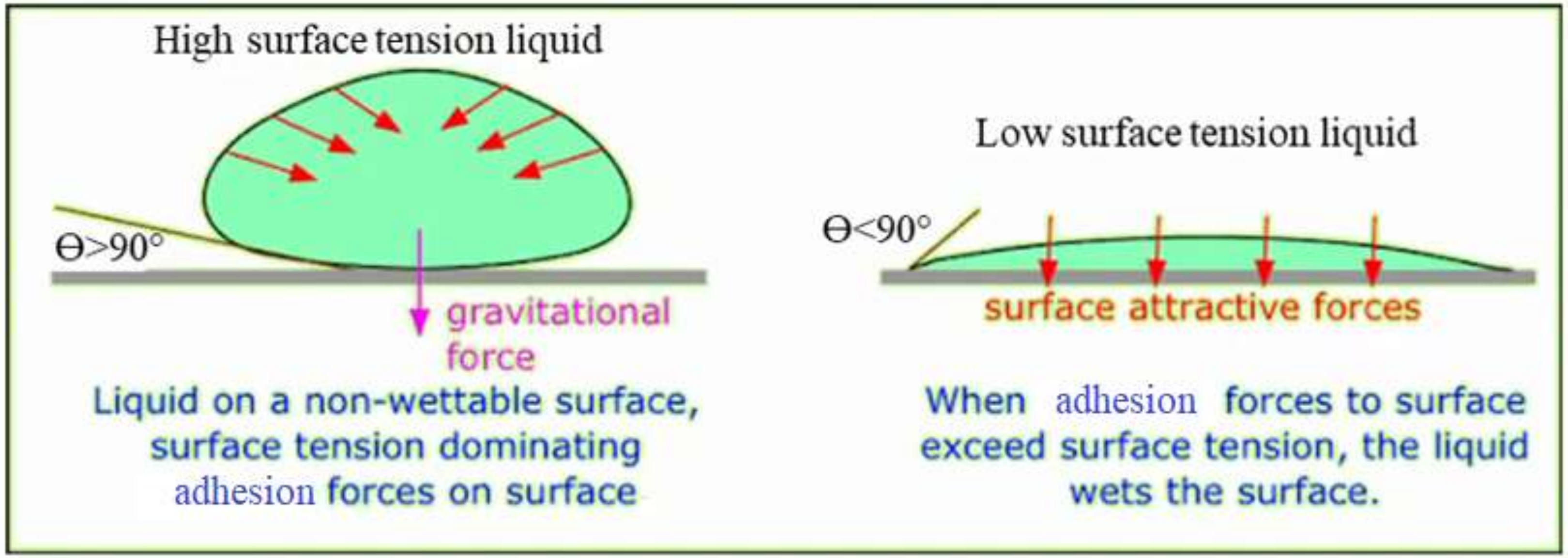
Hydrophilic material have small contact angle with water



To increase ↑wetting, the contact angle (ϴ) should be ↓decreased this is done by adding surfactant which is called **wetting agent**

A wetting agent is a surfactant that, when dissolved in water, lowers the contact angle, aids in displacing an air phase at the surface, and replaces it with a liquid phase.

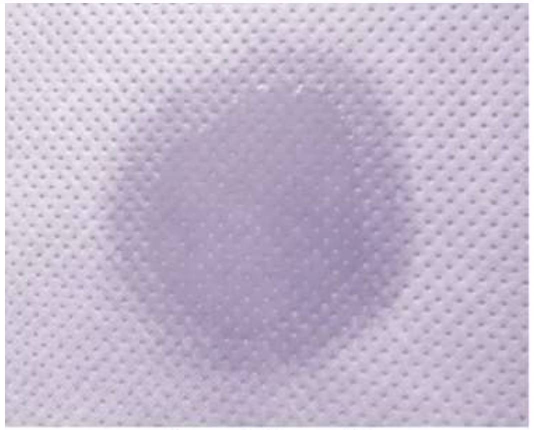
Relationship between surface tension and contact angle



Liquid on a non-wettable surface, surface tension dominating adhesion forces on surface

When adhesion forces to surface exceed surface tension, the liquid wets the surface.

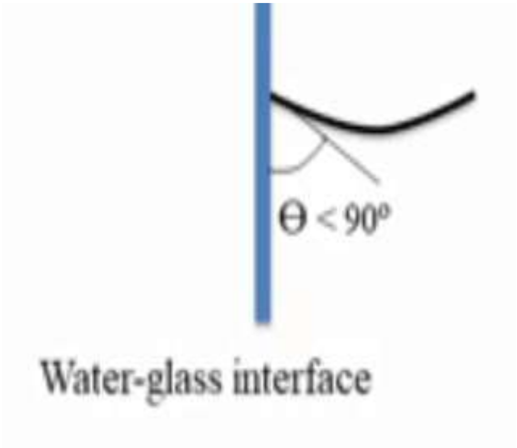
Non-wetting



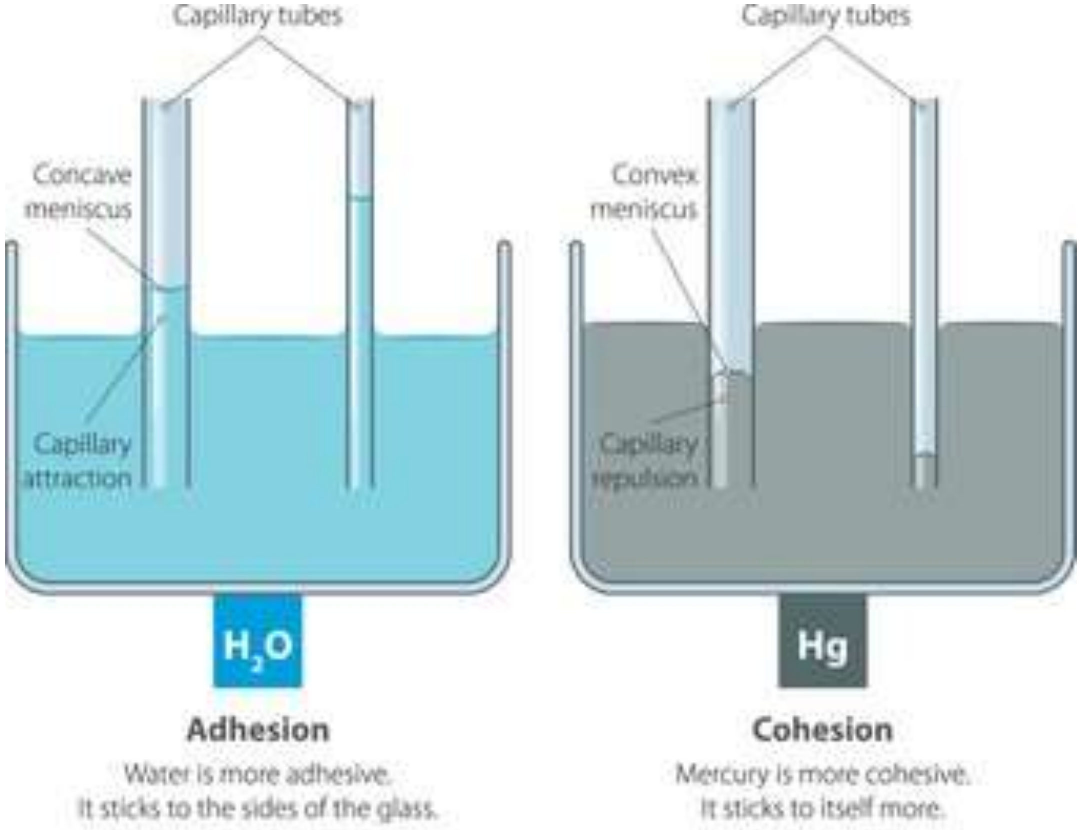
Complete wetting

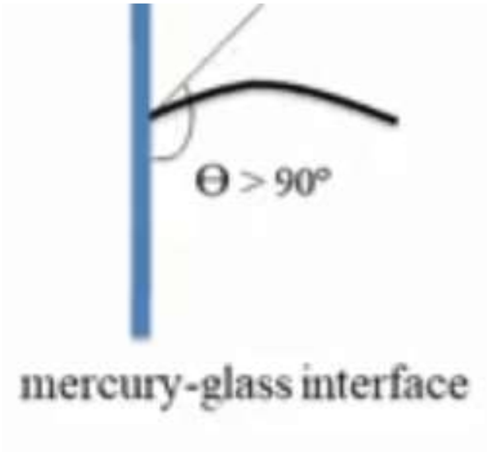
High surface tension of liquid
High contact angle

Low surface tension of liquid
low contact angle



Water rise inside the capillary tube as concave meniscus





Mercury rise inside the capillary tube as convex meniscus

Contact angle of water with glass < 90

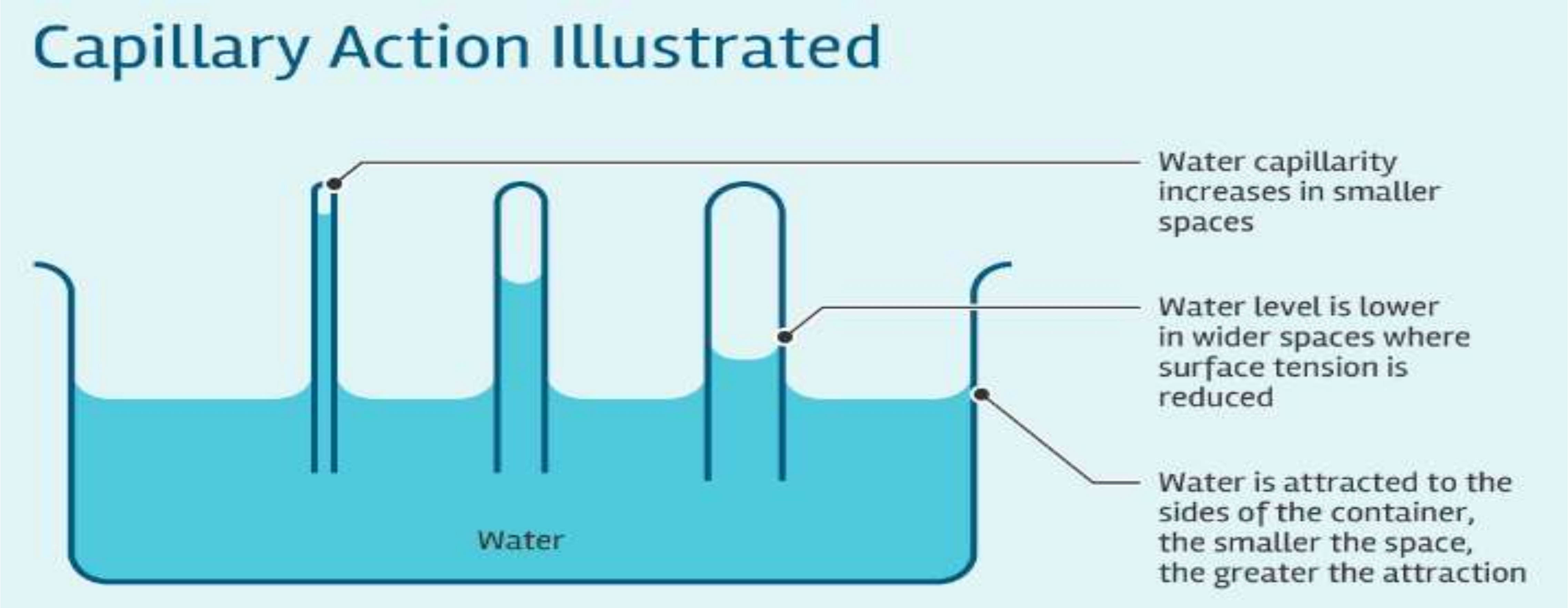
Contact angle of mercury with glass > 90

Water can wet the glass because

Adhesive forces between the glass and water molecules > Cohesive forces between water molecules themselves

Mercury cannot wet the glass because

Adhesive forces between the glass and mercury molecules < Cohesive forces between mercury molecules themselves



The rise of water in a thin tube inserted in water is caused by forces of attraction between the molecules of water and the glass walls and among the molecules of water themselves. These attractive forces just balance the force of gravity of the column of water that has risen to a characteristic height.

The narrower the bore of the capillary tube, the higher the water rises.

Examples of the application of wetting to pharmacy and medicine

- ✓ The **preparation of suspension** requires that the fine solid particles immersed and then dispersed in a liquid vehicle, this mean that the solid particles have to be wetted in order to be dispersed in a liquid
- ✓ The **displacement of air from the surface of powders** such as sulfur, charcoal, and others for the purpose of dispersing these drugs in liquid vehicles
- ✓ The **displacement of dirt** by the use of detergents in the washing of wounds
- ✓ The **application of medicinal lotions and sprays** to the surface of the skin and mucous membranes

Physical pharmacy II

By:
Asst. Professor
Lena M. Thomas

INTERFACIAL PHENOMENA
(PART 3)

Interfacial phenomena

In this lecture, you'll learn:

- Meaning of “spreading and spreading coefficient”
- Meaning of “work of adhesion” and “work of cohesion”
- Importance of studying spreading coefficient in pharmacy
- Calculation of spreading coefficient
- Factors affecting on spreading coefficient

What do we mean by spreading ?

- Spreading describes the expansion of a liquid phase on a second liquid or solid phase (complete wetting).
- Spreading coefficient (S) is a measure of the wetting behavior of a liquid on a surface

Spreading depends on the **surface tension** of the liquids involved and on the **interfacial tension** between them:

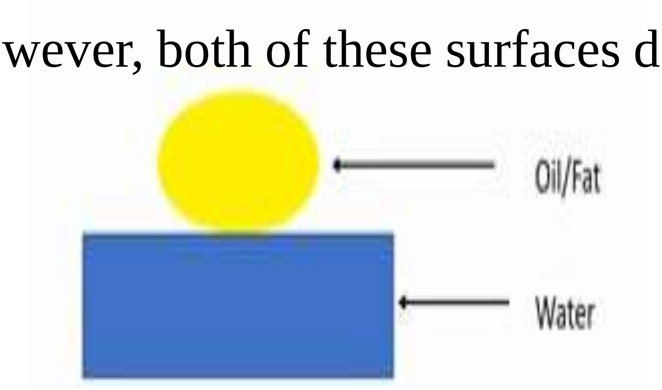
In other words: spreading **depends on the force of cohesion** and **force of adhesion**.

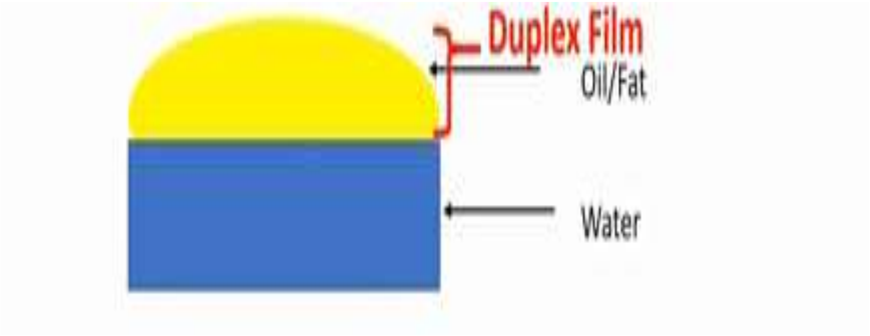
To understand spreading coefficient, consider a drop of oleic acid (type of oil) is placed on water:

As soon as oleic acid is placed on the surface of water:
it will initially form a **duplex film** (sufficiently thick film of 100 Å or more):

One of the surfaces of the oil is **exposed to spreading surface** (in our example water) and the other is **exposed to the atmospheric air**.

However, both of these surfaces do not interact with each other and do not affect on each other.



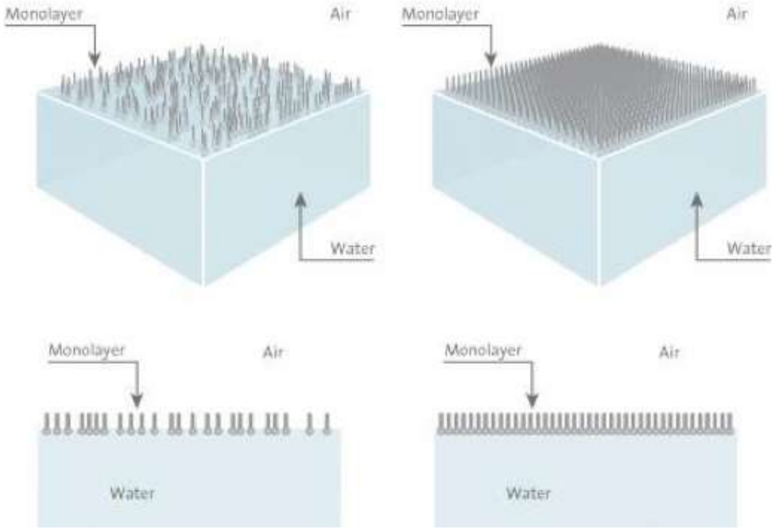


Spreading occurs if:

the adhesion force between the oleic acid molecules and the water molecules > the cohesion forces between the oleic acid molecules themselves

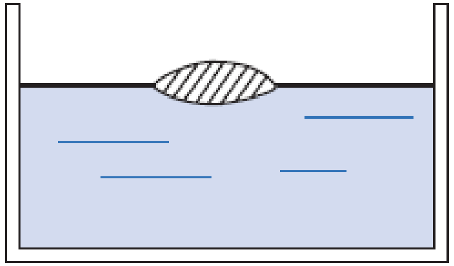
When a drop of oil is added on the surface of water, one of three things may happen:

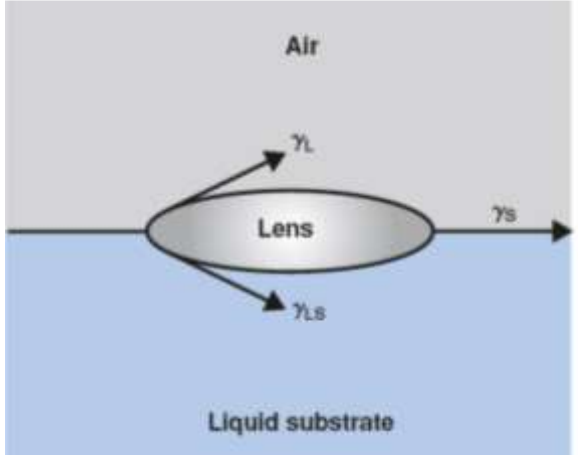
a. The drop may spread as a thin monolayer (molecular) film on the surface of water
b. If the oil cannot spread on the surface of water it may form a liquid lens
c. Combination of the above two cases is possible: the drop may spread as a monolayer film with remaining excess areas collecting as lenses



(a) Formation of a monolayer (molecular) film

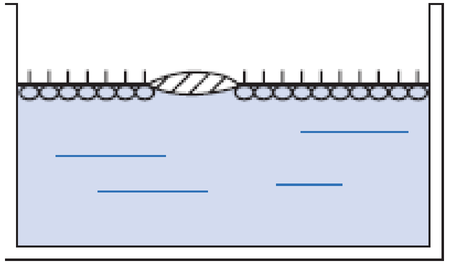
Contact angle between the two phases is 0°.





Forces existing at the surface of a lens floating in a substrate liquid

(b) Formation of a lens when a drop of oil is added to water



(c) Monolayer of oil with a lens

Can we calculate the value of spreading coefficient (S) ?

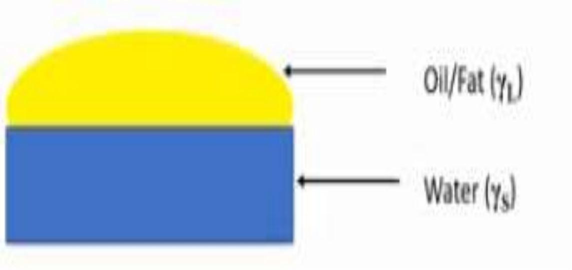
Yes !!
But you need to understand the following concepts before diving into **spreading coefficient:**

work of adhesion and work of cohesion

Work of adhesion (W_a):

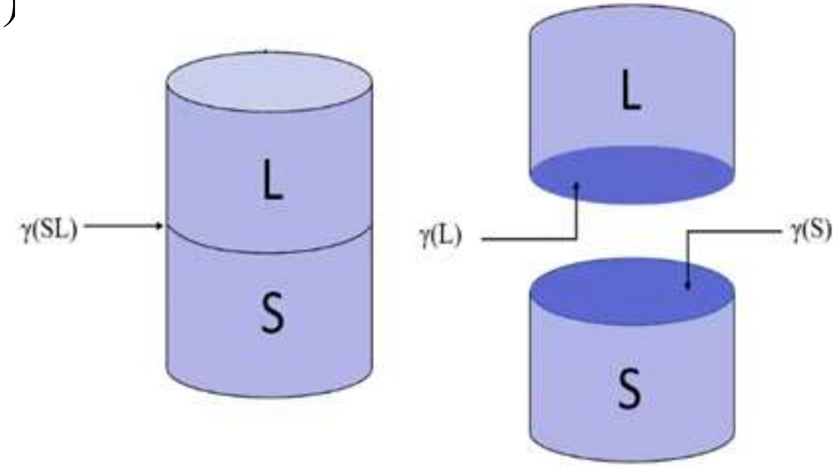
is the energy required to break the attraction between the unlike molecules.

(Or: the work required to separate two immiscible liquids which form an interface)



Suppose **L** is the <u>spreading liquid</u> and has surface tensions γ(L)
S is the <u>substrate</u> on which the liquid spreads and has surface tensions γ(S)
The γ(SL) is the interfacial tension between L and S

When the work of adhesion breaks the γ(SL) into two parts, it creates two new surfaces having surface tensions γ(S) and γ(L)



The work of adhesion : is equal to the newly created surface tensions, γL and γS, minus the interfacial tension, γLS, that has been destroyed in the process

Therefore our formula for **work of adhesion** (W_a) will be:

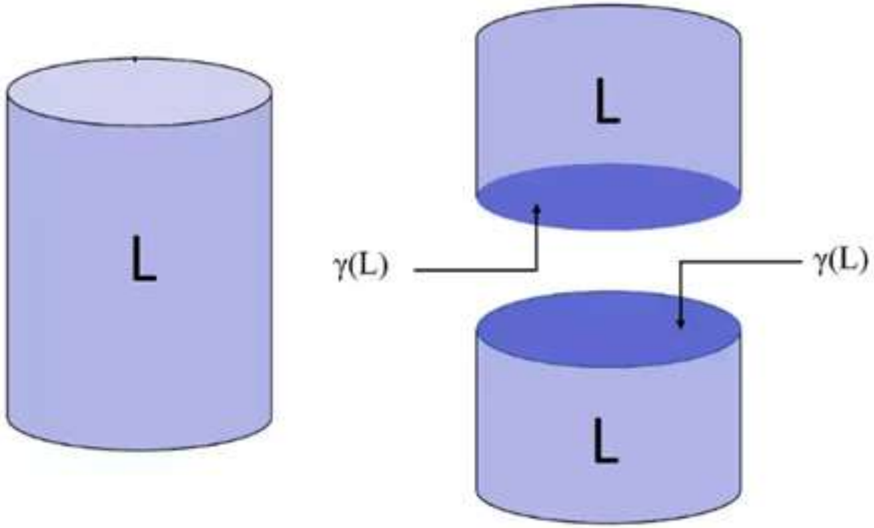
$$\boxed{W_a = \gamma_L + \gamma_S - \gamma_{LS}}$$

Work of cohesion (W_c):

is the work required to separate the molecules of the spreading liquid (L) so that it can flow over the substrate

When the work of cohesion breaks L into two parts, it creates two new surfaces having surface tension γ(L) each.

As we all know, interfacial tension does not exist within the like molecules so there is **NO** term like γ(LL)

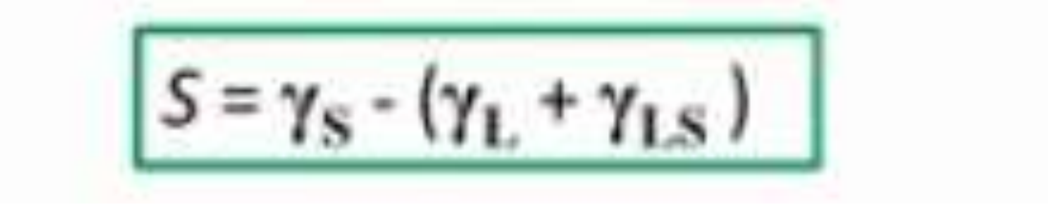


Therefore our formula for **work of cohesion** (W_c) will be:

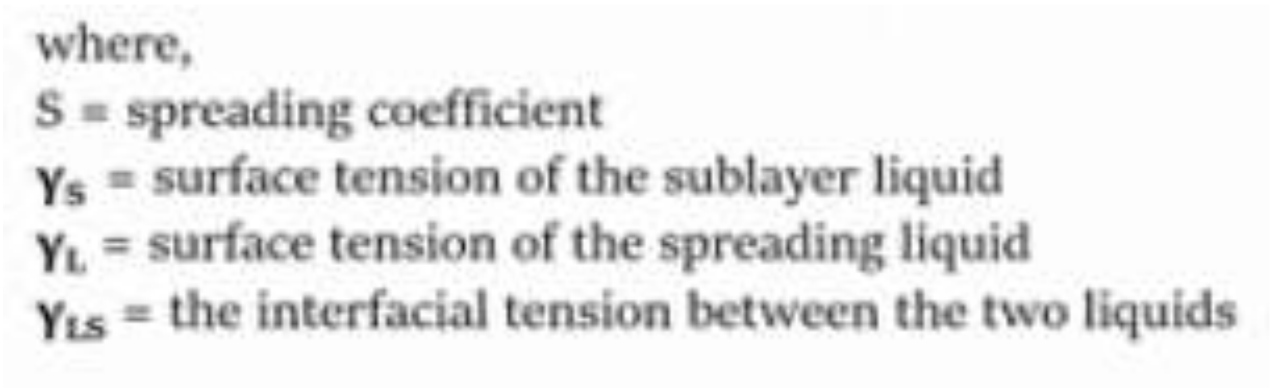
$$\boxed{W_c = 2\gamma_L}$$

Spreading coefficient formula:

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



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



where,
S = spreading coefficient
γ_S = surface tension of the sublayer liquid
γ_L = surface tension of the spreading liquid
γ_{LS} = the interfacial tension between the two liquids

Spreading will occur depending on the value of spreading coefficient (S):

Positive value of S

Spreading occurs

Wa > Wc

S is positive when $\gamma_S > (\gamma_{LS} + \gamma_L)$

(the surface tension of the sub-layer liquid (γ s) 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)

For Example, oleic acid on water.

Negative value of S

Spreading will not occur and substance will form globules or floating lens

S is negative when $\gamma_S < (\gamma_{LS} + \gamma_L)$

(the surface tension of the sub-layer liquid (γ s) is less than the sum of the surface tension of the spreading liquid and the interfacial tension between the sub-layer and the spreading liquid)

For Example, mineral oil on water.

Example:

If you know that the **surface tension** of organic liquid is 25 erg/cm^2, and of water is 72.8 erg/cm^2, and interfacial tension is 30 erg/cm^2 ,what is the

- **work of adhesion** between liquid and
- **work of cohesion** of organic liquid and
- what is the **spreading coefficient**?

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

$$Wa = 25 \quad + 72.8 - 30$$
$$= 67.8 \text{ erg/cm}^2$$

$$\boxed{W_c = 2\gamma_L}$$

$$Wc = 2 \times 25 = 50 \text{ erg/cm}^2$$

$$S = W_a - W_c$$
$$= 67.8 - 50 = 17.8 \text{ erg/cm}^2$$

Question:

Which liquid is spread over the other?

If you know that γ Hexane = 18 dyne/cm, γ water = 72.8 dyne/cm γ Hexane/water= 50.8 dyne/cm

---

If we want to spread hexane over water

Then: hexane is the spreading liquid and water is the substrate

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

$= 18 + 72.8 – 50.8 = 40$

$$\boxed{W_c = 2\gamma_L}$$

$= 2 \times 18 = 36$

$S = W_a - W_c$

$= 40 - 36 = 4$ dyne/cm (or erg/cm^2)

Hexane has low surface tension and low cohesive forces can spread over water

If we want to spread water over hexane

Then: water is the spreading liquid and hexane is the substrate

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

$= 72.8 + 18 – 50.8 = 40$

$$\boxed{W_c = 2\gamma_L}$$

$= 2 \times 72.8 = 145.6$

$S = W_a - W_c$

$= 40 - 145.6 = -105.6$ dyne/cm (or erg/cm^2)

Water has high surface tension which prevent its spreading over hexane

Home Work

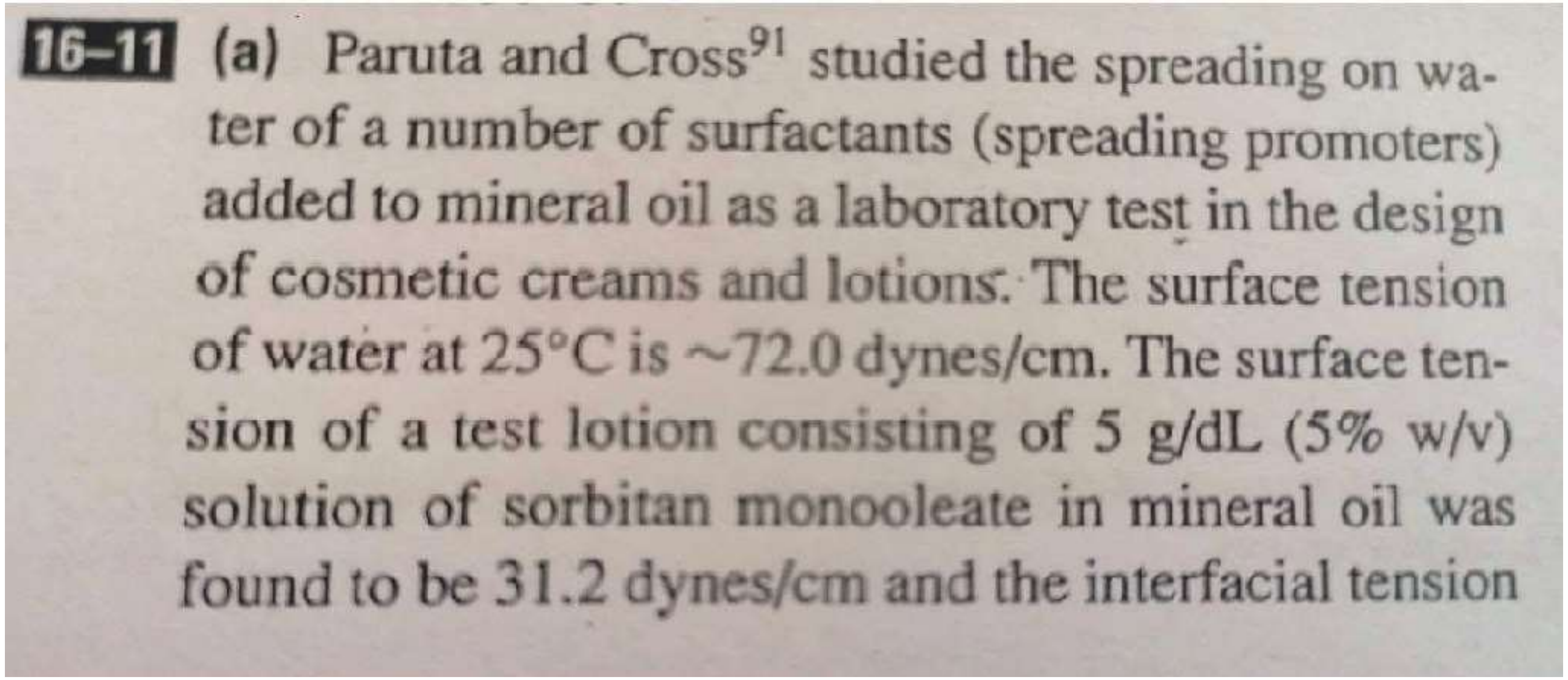
If you know that

$\gamma_{\text{water}} = 72.8$ dyne /cm $\gamma_{\text{oleic acid}} = 32.5$ dyne/cm

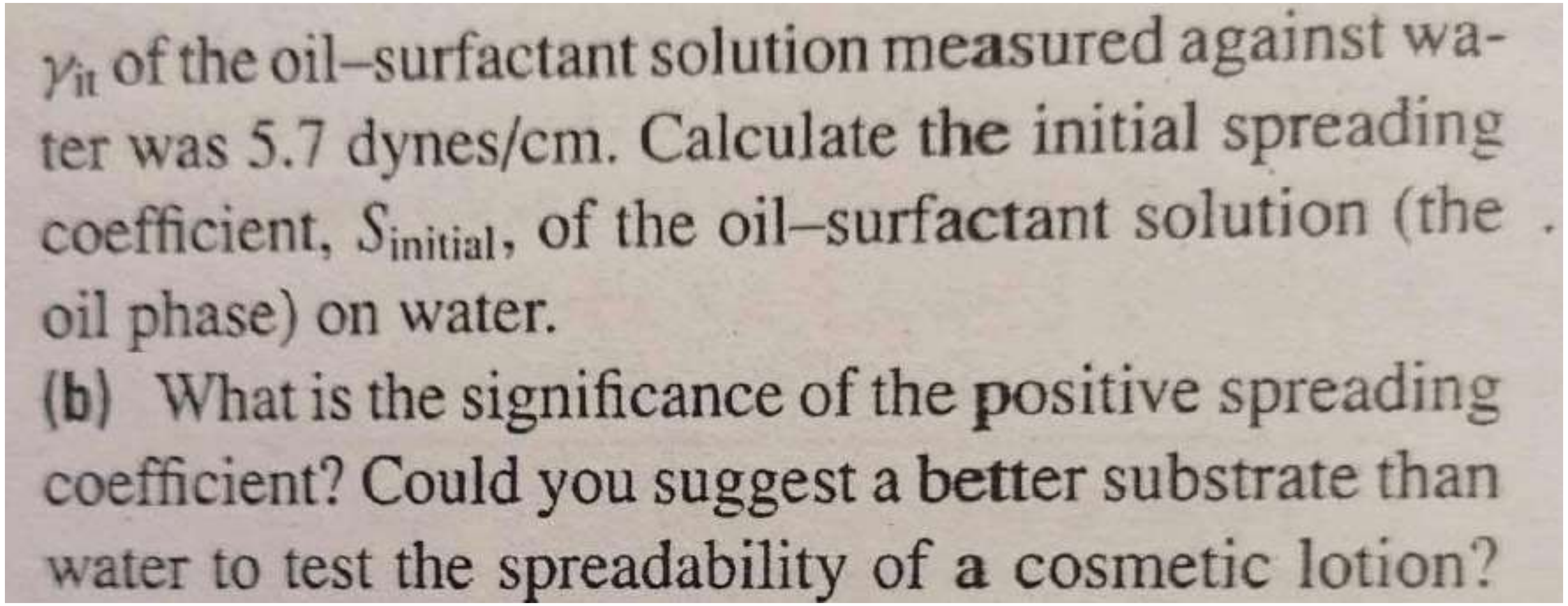
$\gamma_{\text{water/ oleic acid}} = 15.6$ dyne/cm

Which liquid can spread over the other ? Explain

السلايدين القادمين ايضا اسئلة يمكنكم محاولة حلها

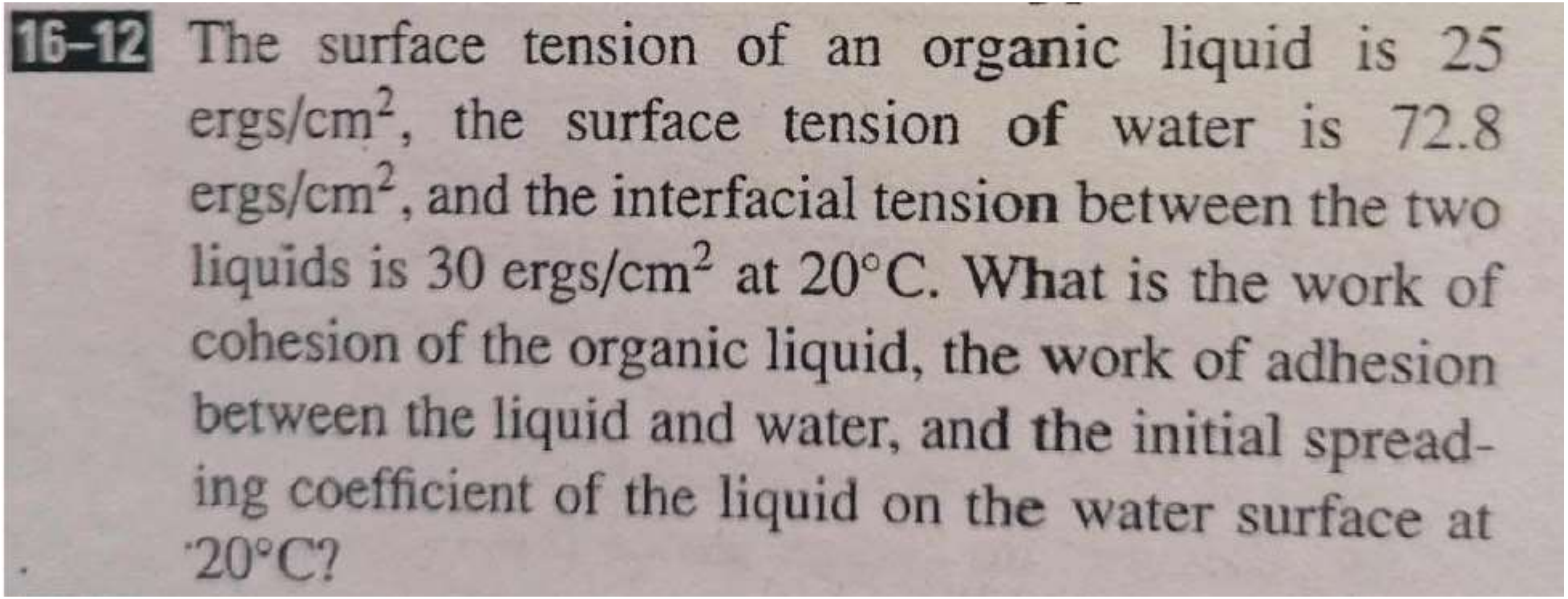


16–11 (a) Paruta and Cross[91] studied the spreading on water of a number of surfactants (spreading promoters) added to mineral oil as a laboratory test in the design of cosmetic creams and lotions. The surface tension of water at 25°C is ~72.0 dynes/cm. The surface tension of a test lotion consisting of 5 g/dL (5% w/v) solution of sorbitan monooleate in mineral oil was found to be 31.2 dynes/cm and the interfacial tension

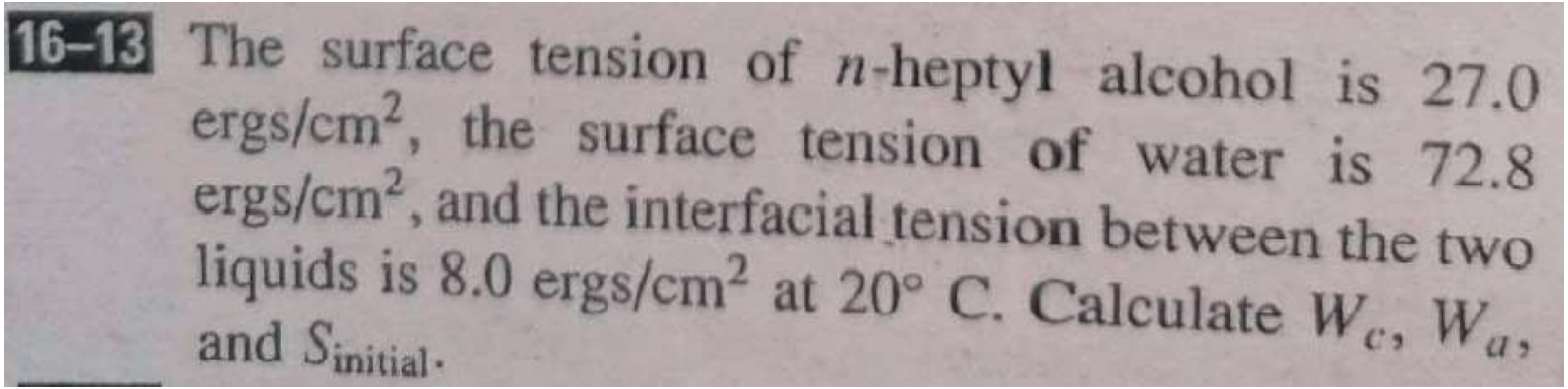


γ_{it} of the oil–surfactant solution measured against water was 5.7 dynes/cm. Calculate the initial spreading coefficient, $S_{initial}$, of the oil–surfactant solution (the oil phase) on water.

(b) What is the significance of the positive spreading coefficient? Could you suggest a better substrate than water to test the spreadability of a cosmetic lotion?



16–12 The surface tension of an organic liquid is 25 ergs/cm^2, the surface tension of water is 72.8 ergs/cm^2, and the interfacial tension between the two liquids is 30 ergs/cm^2 at 20°C. What is the work of cohesion of the organic liquid, the work of adhesion between the liquid and water, and the initial spreading coefficient of the liquid on the water surface at 20°C?



16–13 The surface tension of *n*-heptyl alcohol is 27.0 ergs/cm^2, the surface tension of water is 72.8 ergs/cm^2, and the interfacial tension between the two liquids is 8.0 ergs/cm^2 at 20° C. Calculate W_c, W_a, and S_{initial}.

Spreading Coefficient at equilibrium:

Till this point, we have only discussed *initial spreading*.

When both the surfaces become saturated with each other, the process achieves equilibrium. After reaching equilibrium, the value of **S** need not stay the same: the equilibrium can reduce the value of S or even make it negative. That means, initially spread liquid can also form coalescence afterward.

In case of organic liquids spreading on water, it is found that although the initial spreading coefficient may be positive or negative, the final spreading coefficient always has a negative value.

If we use a prime (′) to denote the values following equilibration (i.e., final rather than initial values), then the new surface tensions are $\gamma S'$ and $\gamma L'$.
Note: The $\gamma(SL)$ will not change because the interfacial tension is fixed under conditions of mutual saturations.

$$\boxed{S' = \gamma_{S}' - (\gamma_{L}' + \gamma_{LS})}$$

This reversal of spreading takes place when $\gamma S'$ becomes less than $(\gamma LS + \gamma L')$.

Example: Spreading of Benzene over Water

Find out the initial spreading coefficient using the following information:

- surface tension of water γ(S) is **72.8 dynes/cm** at 20◦C,
- surface tension of benzene, γ(L), **28.9 dynes/cm**,
- interfacial tension between benzene and water, γ(LS), is **35.0 dynes/cm**

Find the final spreading coefficient after the equilibration is achieved, knowing that:

- surface tension of water γ(S’) is **62.2 dynes/cm**
- surface tension of benzene γ(L’) is **28.8 dynes/cm**.

---

initial spreading coefficient

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

$$S = 72.8 - (28.9 + 35.0) = 8.9 \text{ dynes/cm (or } 8.9 \text{ ergs/cm}^2\text{)}$$

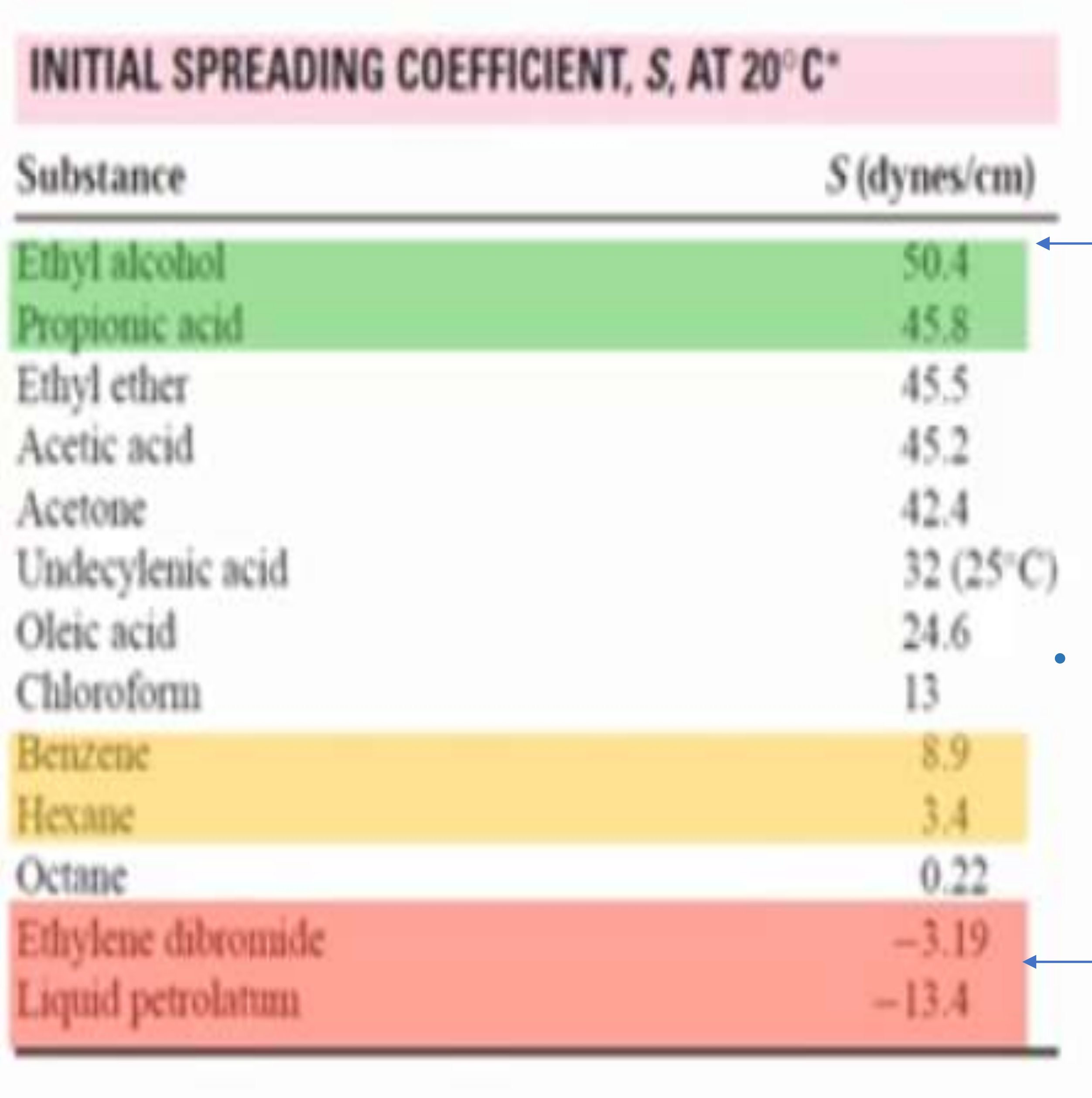
final spreading coefficient

$$S' = \gamma_{S'} - (\gamma_{L'} + \gamma_{LS})$$

$$S' = 62.2 - (28.8 + 35.0) = -\mathbf{1.6 \text{ dynes/cm}}$$

Because of this, benzene spreads initially on water,
but at equilibrium a saturated monolayer forms with the excess benzene (saturated with water) forming a lens.

Factors Affecting Spreading Coefficient



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

- **Molecular Structures**

  It is important to consider the types of molecular structures that lead to high spreading coefficient

The **greater the polarity** of the molecule , the more positive [S] e.g., ethanol and propionic acid

For organic acids, as oleic acid, the longer the carbon chain, the less polar character and therefore [S] decreases.
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 adhesive forces with water.

Non polar substances as Liquid petrolatum have negative [S] fail to spread on water

Applications of Spreading Coefficient in Pharmacy

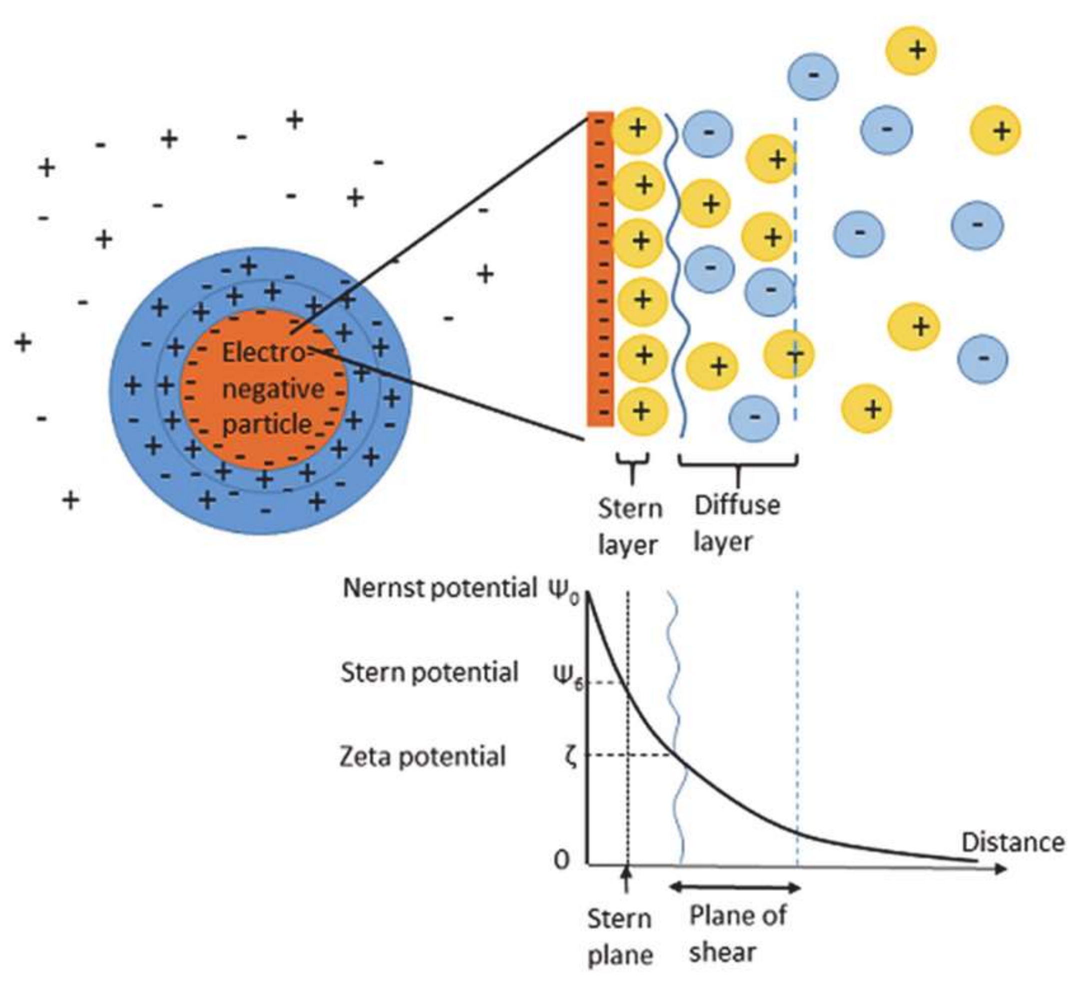
- ✓ **Spreading of film coats over the tablet surfaces**
- ✓ **Spreading of lotion on skin surface**
- ✓ **Spreading of ointment in the eye**
- ✓ **Spreading of disinfectant on the micro-organism surface**

Spreading of Skin Lotion

Like mixed fatty acids, our skin surface has an aqueous-oily layer where polar and non-polar molecules are mixed together.

Pharmaceutical lotion, having a mineral oil base needs to be spread freely and evenly on the skin. Therefore, we need to increase the polarity and eventually the surface coefficient of the lotion by adding a surfactant.

Physical pharmacy II



By:
Asst. Professor
Lena M. Thomas

INTERFACIAL PHENOMENA (PART 4)

Interfacial phenomena

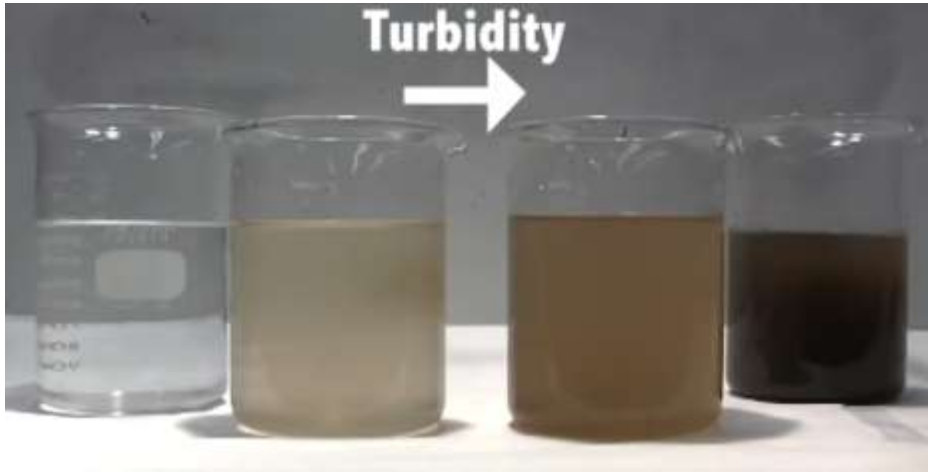
In this lecture, you'll learn:

- Overview on "electrical properties of interfaces" and meaning of "electrical double layer" and mechanism of its formation
- Meaning of "Nernest" and "Zeta potential",
- Applications of Zeta potential in practice

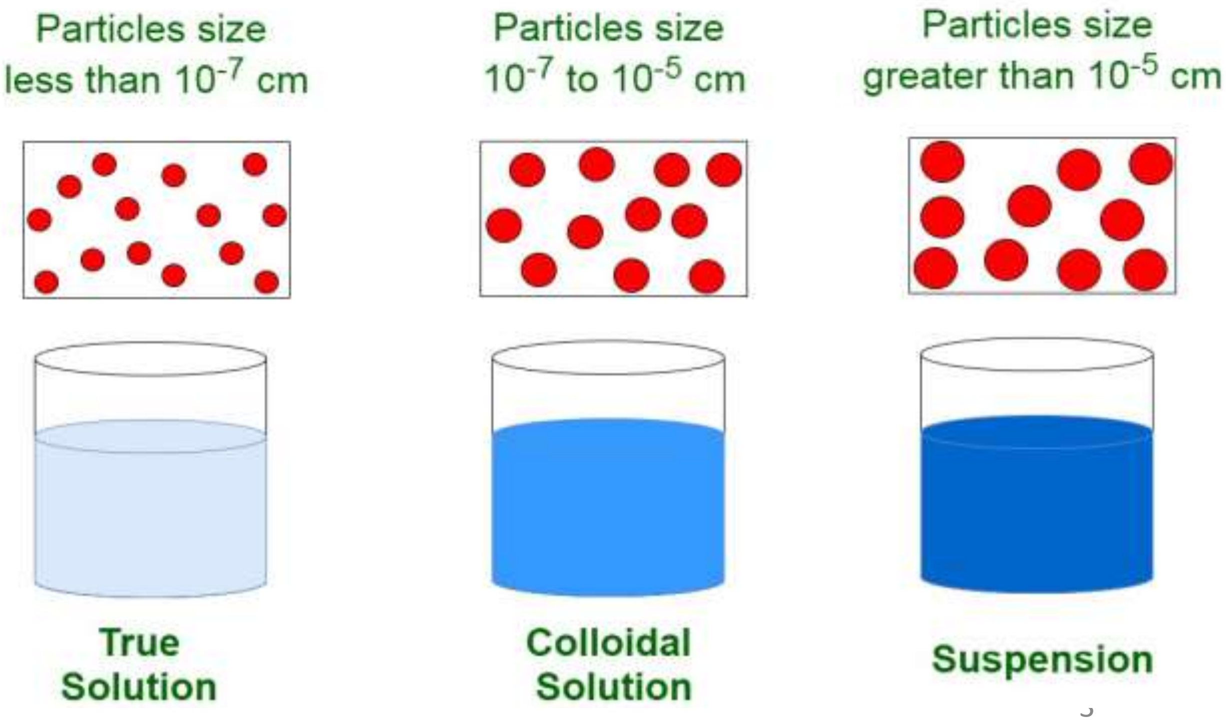
Supplementary material

An overview on Colloids

Colloidal systems is a two phases with dispersed phase consisting of microscopically dispersed insoluble particles (have a diameter of approximately 1 nm to 1 μm) that are too light to settle down in a dispersion medium.



Muddy water is an example of colloidal dispersion



ELECTRIC PROPERTIES OF INTERFACES

Origin of charge on the surface of a particle

Particles dispersed in liquid media may **become charged** mainly in one of two ways:

1. Selective adsorption of a particular ionic species present in solution, this comes form:
    - An ion added to the solution or,
    - In case of pure water, the hydronium or hydroxyl ion:
        - the majority of particles dispersed in water acquire a negative charge due to preferential adsorption of the hydroxyl ion to the surface of the particle (in comparison, the hydronium ion is more hydrated than hydroxyl ion , so they have greater tendency to be in the bulk of aqueous medium).

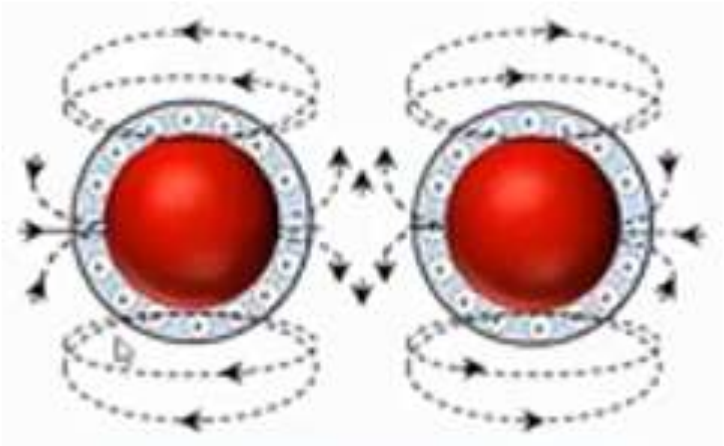
2. Charges on particles arise from ionization of groups (such as -COOH) that may be situated at the surface of the particle. The charge is a function of pK and pH.

Example: amino acid and protein (have -COOH and -NH_2) groups on their structure

- At low pH , the protein will have +ve charge due to ionization of -NH_2 groups to –NH_3^+
- At high pH the protein will have –ve charge due to ionization of –COOH groups to –COO^-
- At certain pH (specific for each protein), the total no. of +ve charge will be equal to the total no. of –ve charge and the net charge will be zero. This pH is termed as **isoelectric point of protein** and the protein exists as **Zwitter ion**.

ELECTRIC PROPERTIES OF INTERFACES

Practical applications



The concept of an "electrical properties of interfaces" , "presence of interfacial potentials" and "electrical double layer" (which will be discussed later) is essential in :

- **Describing behavior in all heterogeneous fluid-based systems** in every day life, such as blood, paint, ink, as well as food industry; for instance, homogenized milk exists only because fat droplets are covered with a electrical double layer that prevents their coagulation into butter.

- **Preparation of flocculated suspensions and stabilization of suspension and colloidal particles** (will be discussed in detail)

- **Existence of electrokinetic phenomena** (i.e, the motion of particles at a solid–liquid interface resulting from difference of electric potential)

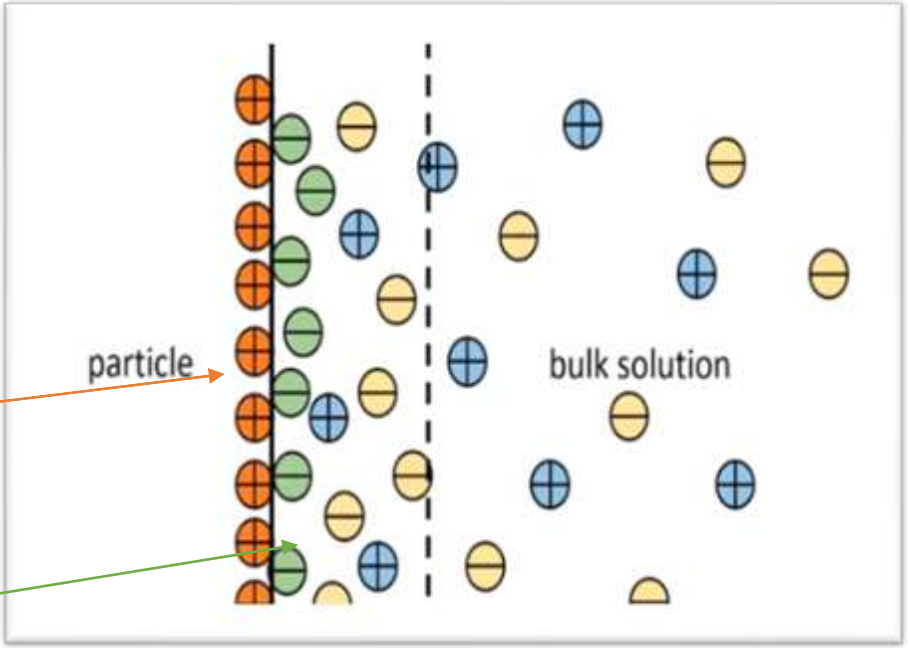
The Electric Double Layer (EDL)

what is it and how is it formed ?

Is a phenomena describing the presence of **two parallel layers** of electrical charges that surround a **charged particle** dispersed into an **electrolyte solution**.

When dispersed particles are in contact with an aqueous solution of an electrolyte, the particles may **selectively adsorb** one charge species.

- If the adsorbed species is **a cation** (as seen in this example), the **particles will be overall positively charged.**
  The adsorbed ions that give the particle surface its charge are referred to as the ***potential-determining ions*.**
- Remaining in solution are the rest of the anions plus the total number of cations. These ions, having a charge opposite to that of the potential-determining ions, are known as ***counterions*** or ***gegenions*.**



The counterions are attracted to the potential determining ions by **electric forces** and will repel the approach of any further ions to the particle surface once the adsorption is complete.

Electrical Double layer (EDD)

Particle surface

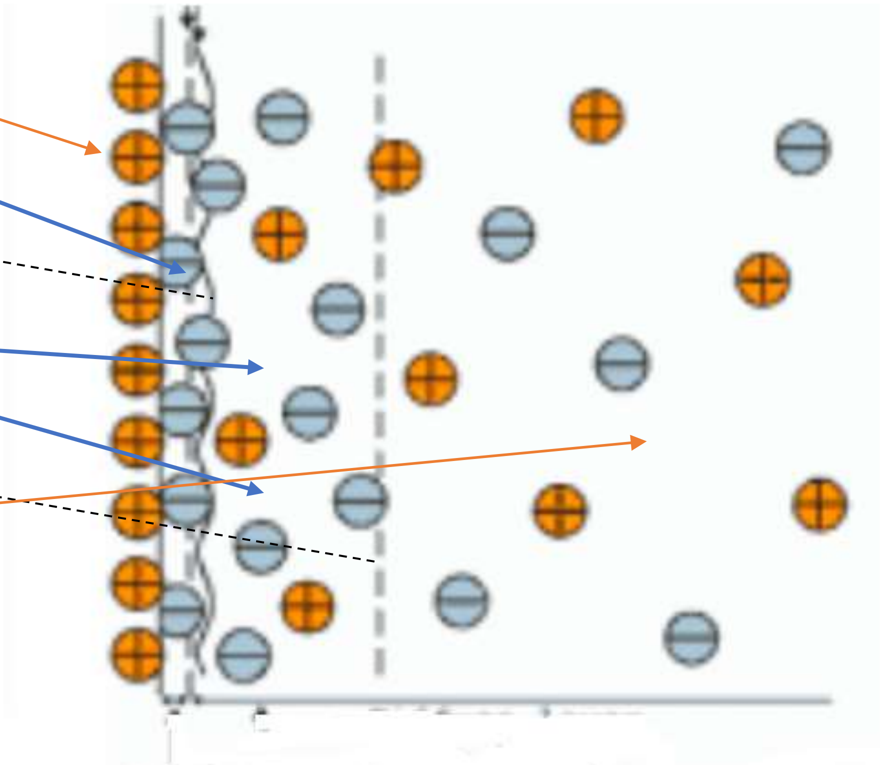
1. Stern layer (aa’-bb’)

Stern plane

2. Diffuse layer (bb’-cc’)

Slipping (shear) plane

Bulk solution

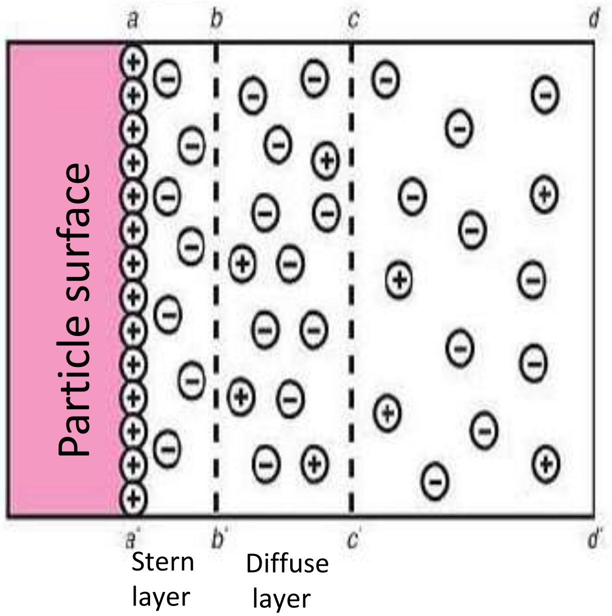


The double layer consist of:

- **The first layer** called **“stern layer”** : **(aa’-bb’)**
  it is a **tightly bound layer** made of accumulating counterions to the particle surface. The plane associated with this layer is called “**stern plane**”.

- **The second layer** called **“diffuse layer”**: **(bb’-cc’)**
  It is composed of free ions that move in the fluid and are **loosely attracted** to the surface charge via electrostatic force. The plane associated with this layer is called “**slipping plane**” or “**shear plane**”.

The presence of **“Stern layer”** and **“diffuse layer”** will lead to formation of **“electrical double layer ”**.



Electrical Double layer (EDL)

1. Stern layer (aa'-bb')

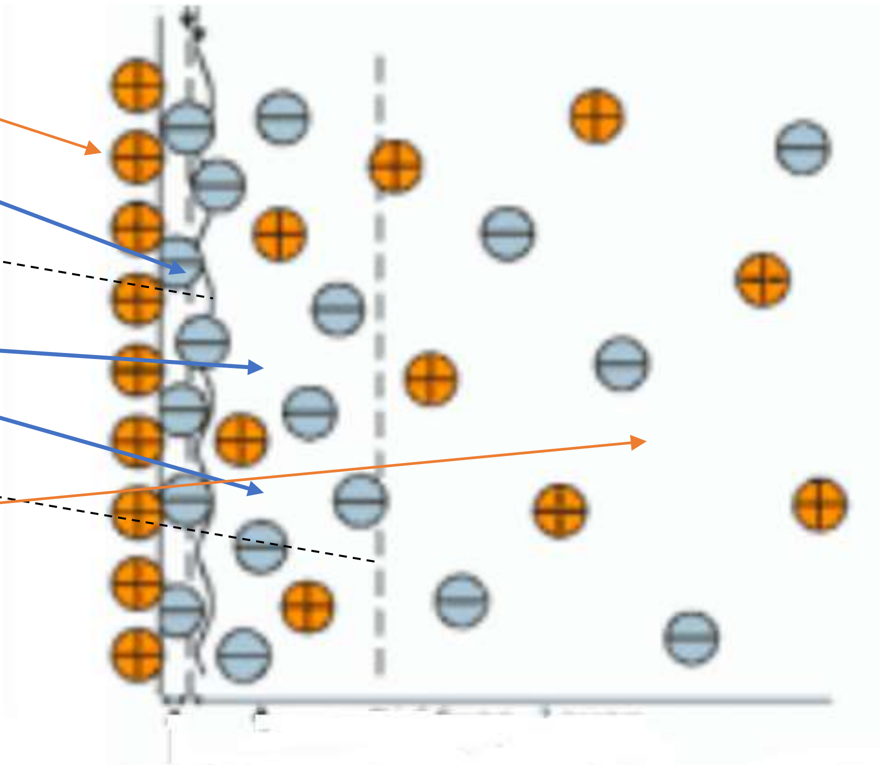
Stern plane (bb')

2. Diffusion layer (bb'-cc')

Slipping (shear) plane (cc')

Particle surface

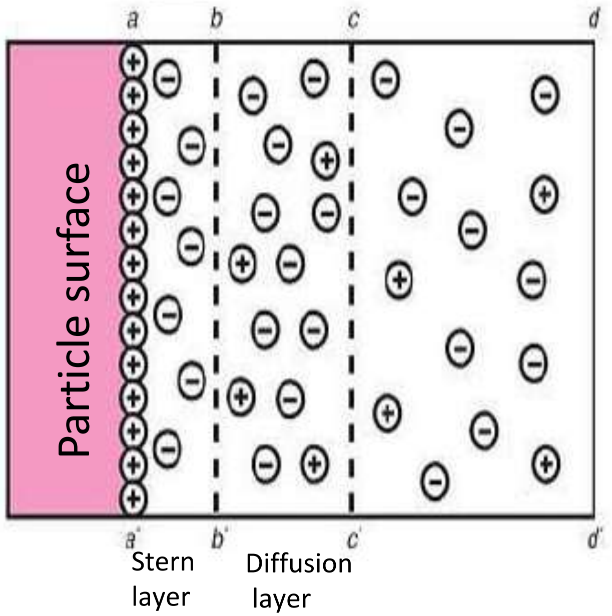
Bulk solution



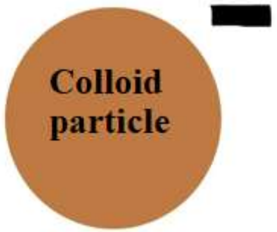
The EDL is electrically neutral.

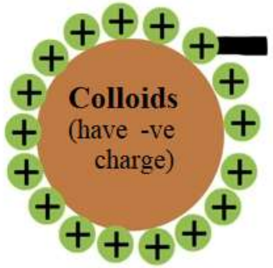
It essentially represents a wall of ions that surrounds the surface of an object placed in a dispersion medium in a way that it balances its charge and creates a repulsive force which prevents two colloidal particles from stacking to each other and make them move around to avoid collision with other colloids.

The thickness of the double layer depends upon the type and concentration of ions in solution.

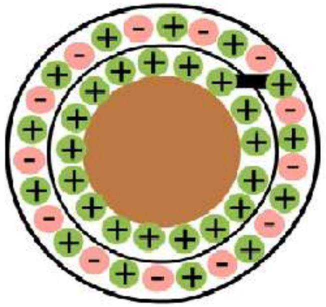


Graphical Summary for Mechanism of Formation of Electrical Double Layer (EDL)





Forming of first layer



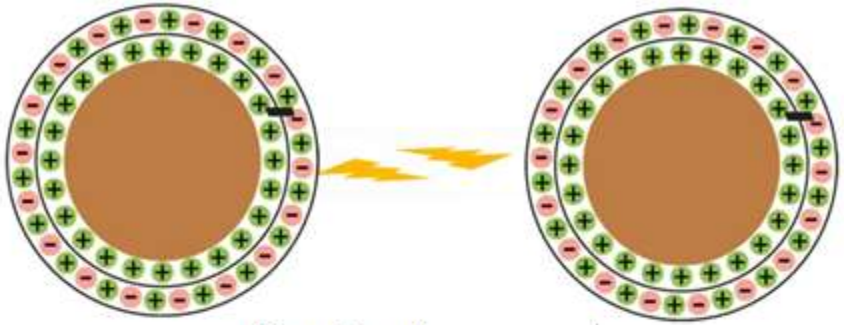
Double layer

In summary: the electric distribution at the solid–liquid interface can be visualized as a double layer of charge.

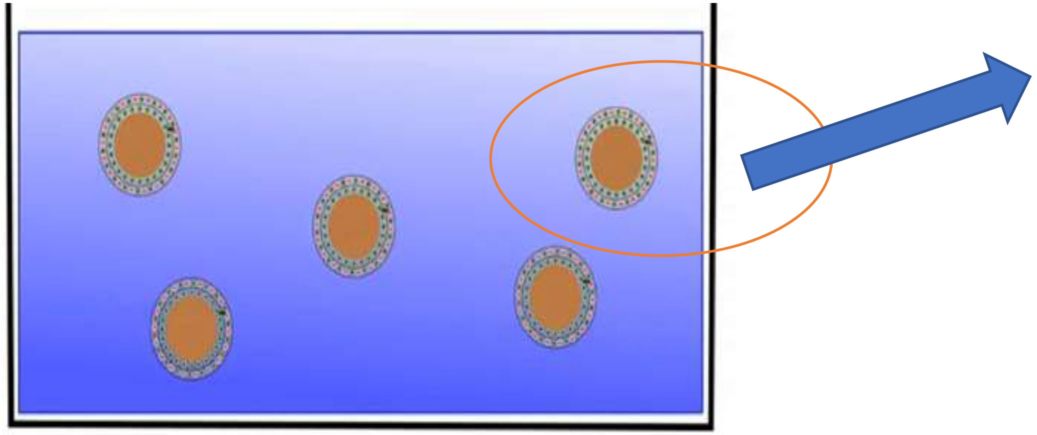
The Stern layer, the first layer is tightly bound to the solid surface and contains **mostly the counter-ions**.

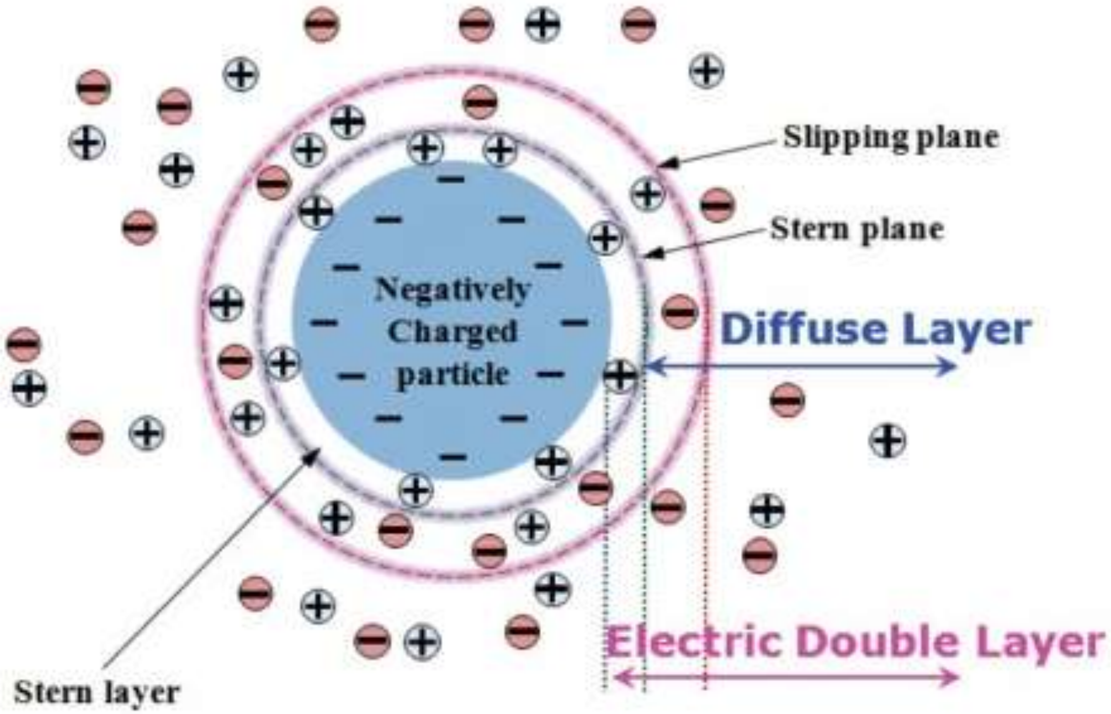
The second layer is more mobile containing **more counter-ions than co-ions.**

These two layers are commonly known as **“the electric double layer”.**



Repulsive force

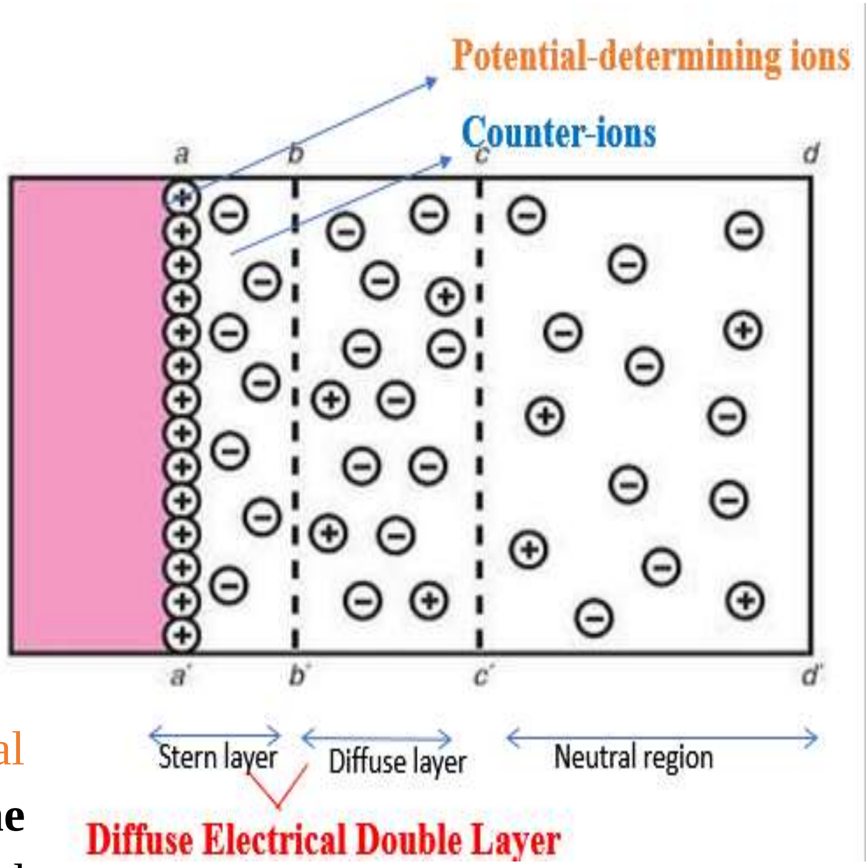




The Electric Double Layer (EDL)

Electric neutrality occurs where the mobile **“diffuse layer”** ends.
It is important to remember that even though there are regions of unequal distribution of anions and cations **the system as a whole** is electrically neutral and neutrality prevail throughout the remaining part of the dispersion medium.

This is because the **electric forces** and **thermal motion** of particles keeps an equal distribution of all the ions in solution. It results in an **equilibrium condition** where some of the excess cations approach the surface and the rest of the cations will be distributed in decreasing amounts as one moves away from the charged surface.



Two situations other than that represented by the figure are possible:

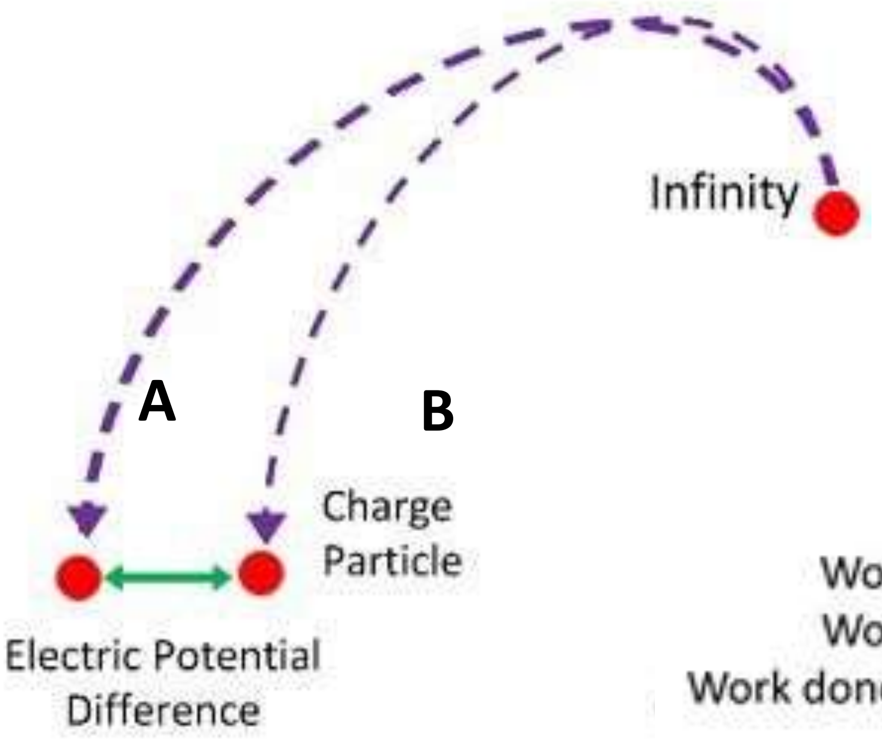
1. If the counterions in the tightly bound (stern solvated layer) **equal** the potential determining ions on the solid surface, then electric **neutrality occurs at the shear plane** bb′ rather than cc′ and there will be **only one layer** of medium and ions, instead of double layer
2. If the total charge of the counterions in the region aa′–bb′ **exceed** the charge due to the potential determining ions, then in this instance, the net charge at bb’ will be negative rather than positive, and for electric neutrality to be obtained at cc′, an excess of counterions must be present in the region bb′–cc′.

The Nernst and zeta potentials

We need to understand the general meaning of potential at first:

General definition of term “electrical potential”

Electric potential, is the amount of work needed to move a unit charge from a reference point to a specific point against an electric field.



Work done to bring charge from infinity to point A is electric potential at A.
Work done to bring charge from infinity to point B is electric potential at B.
Work done to move change from A to B is called the potential difference between A & B.

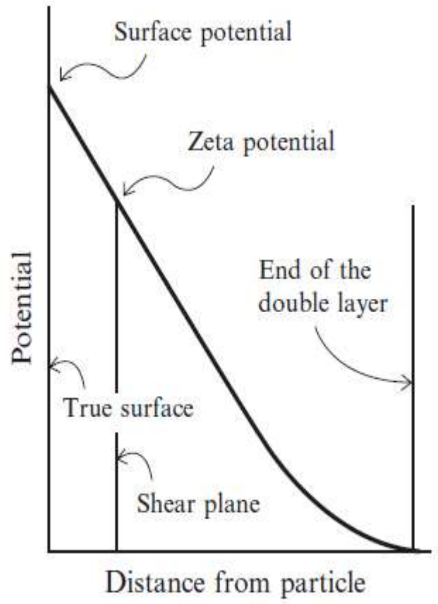
The Nernst and zeta potentials

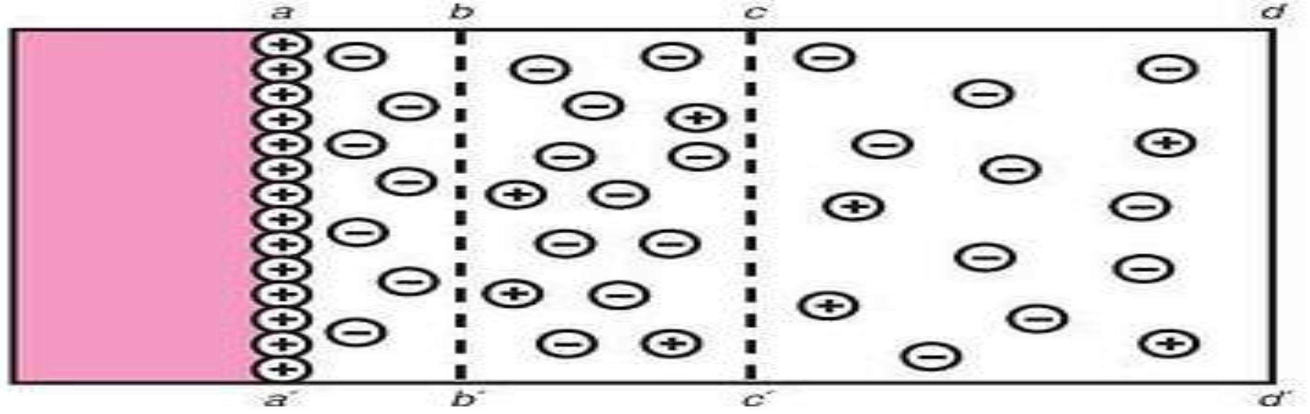
Electrokinetic potential curve at solid–liquid boundaries

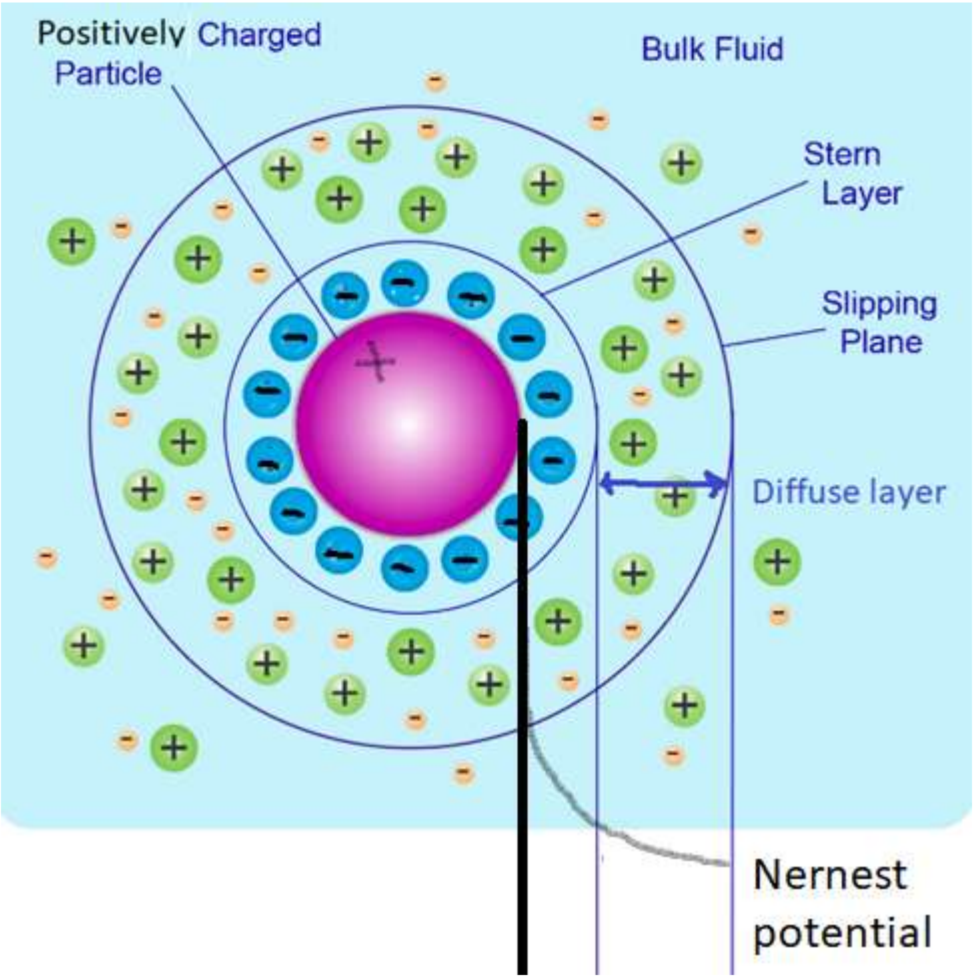
A graph of **electrical potential** as a function of **distance** gives an idea about the **magnitude of electrostatic repulsion between particles**.

When measuring the potential we see that: the potential initially drops off rapidly, followed by a more gradual decrease as the distance from the surface increases.

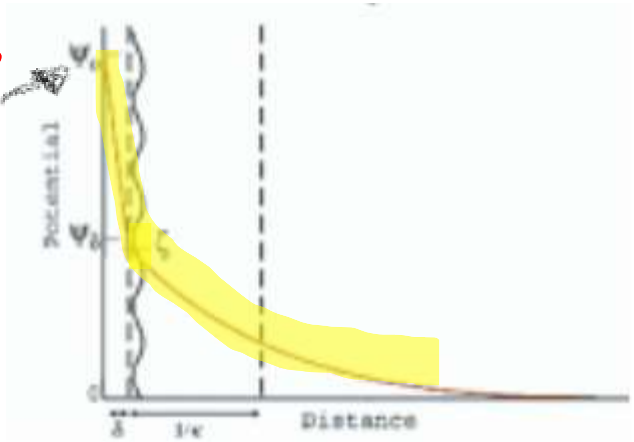
This is because the counterions close to the surface act as a screen that reduces the electrostatic attraction between the charged surface and those counterions further away from the surface



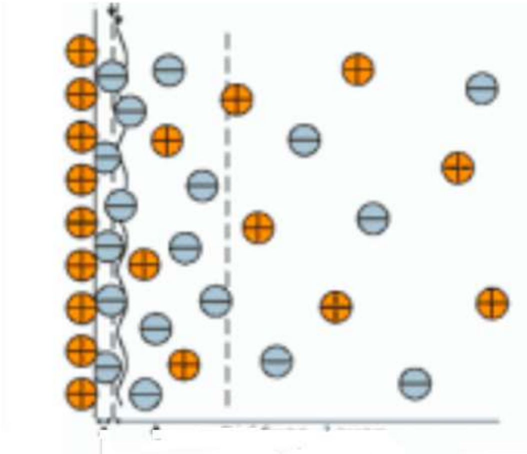


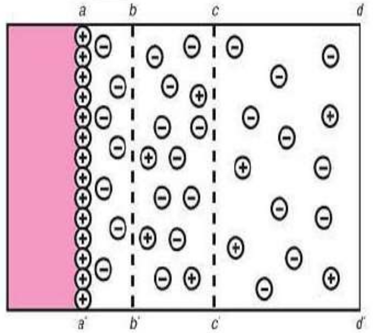


- **Surface or Nernst potential (E), electrothermodynamic potential**

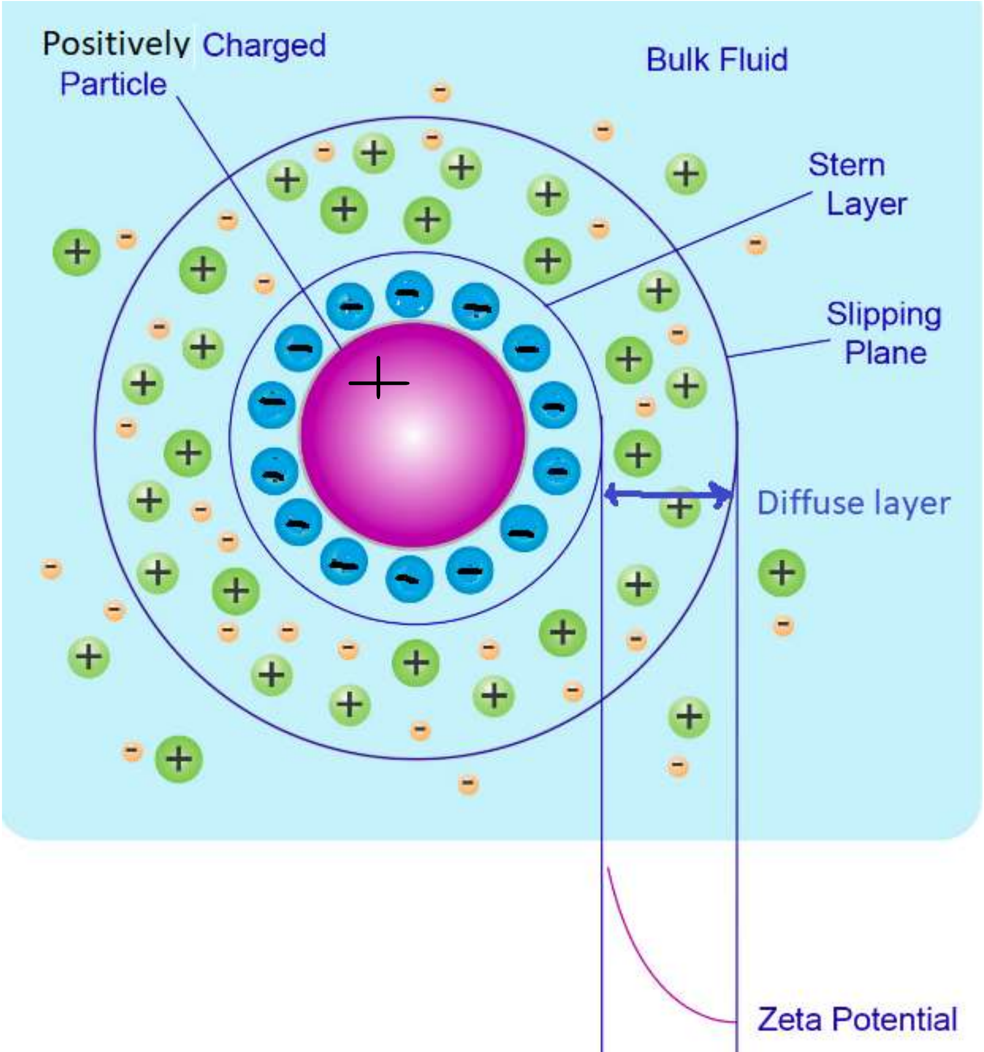


Represents the **potential at the solid surface** aa′ due to the potential-determining ion.



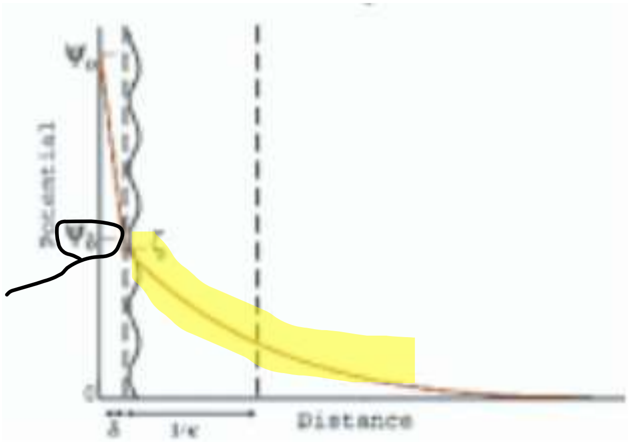


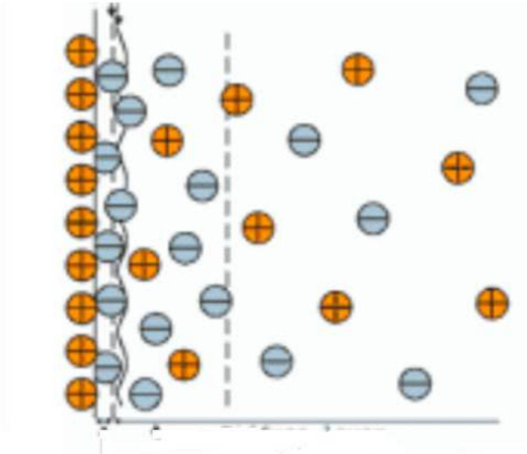
It is defined as **the difference in potential between the actual surface and the electro-neutral region of the solution”.**

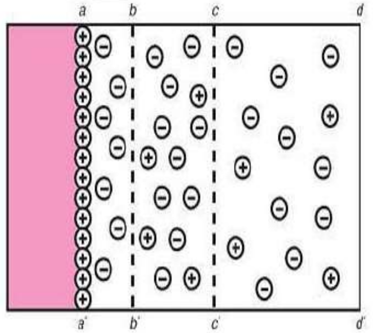


- **Zeta potential or electrokinetic potential (ζ)**

It is the electrical potential located at the slipping (shear) plane





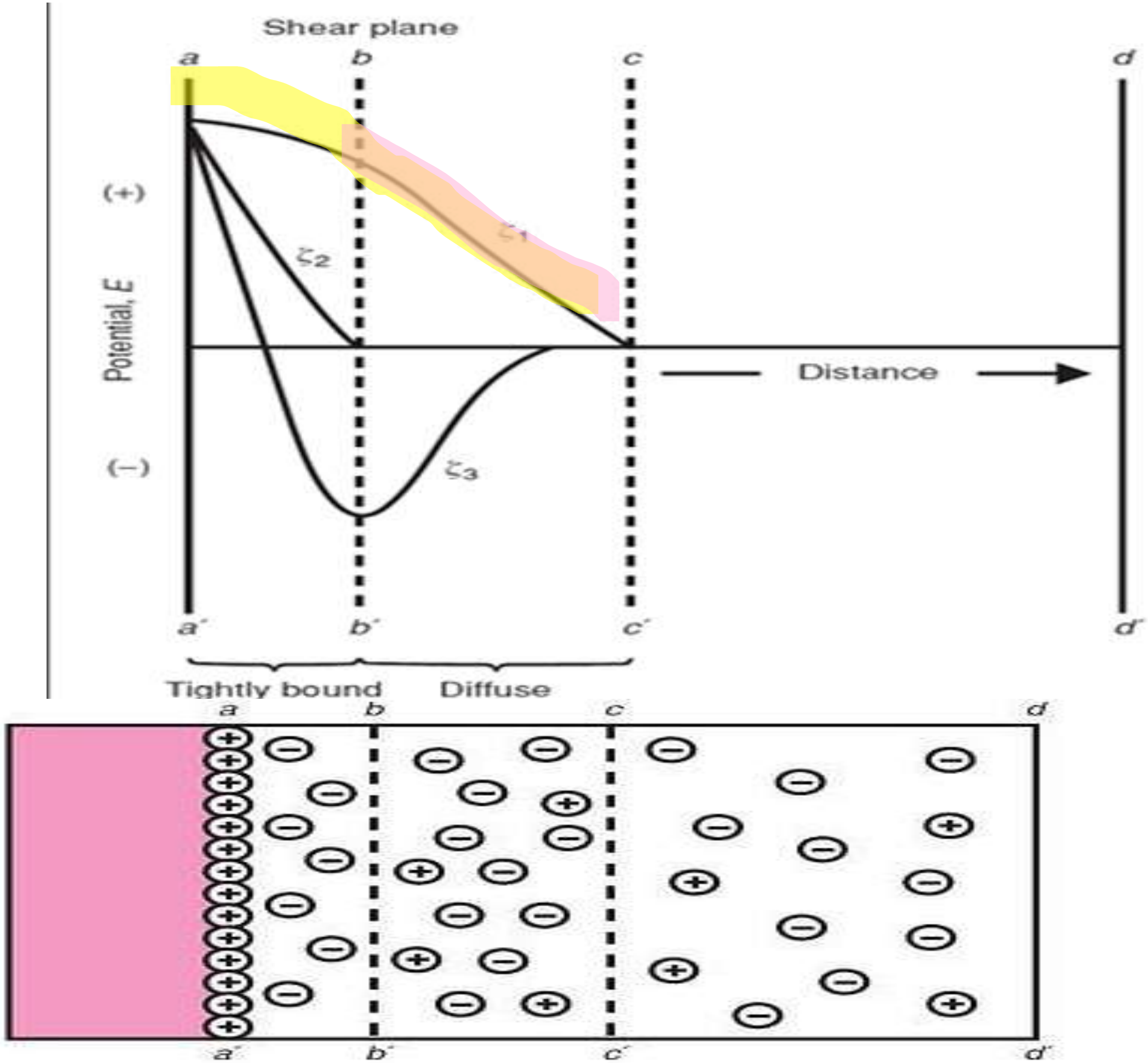


Its value could be

- - ve
- zero
- +ve

It is defined as "**difference in potential between the surface of the tightly bound layer and the electroneutral region of the solution.**

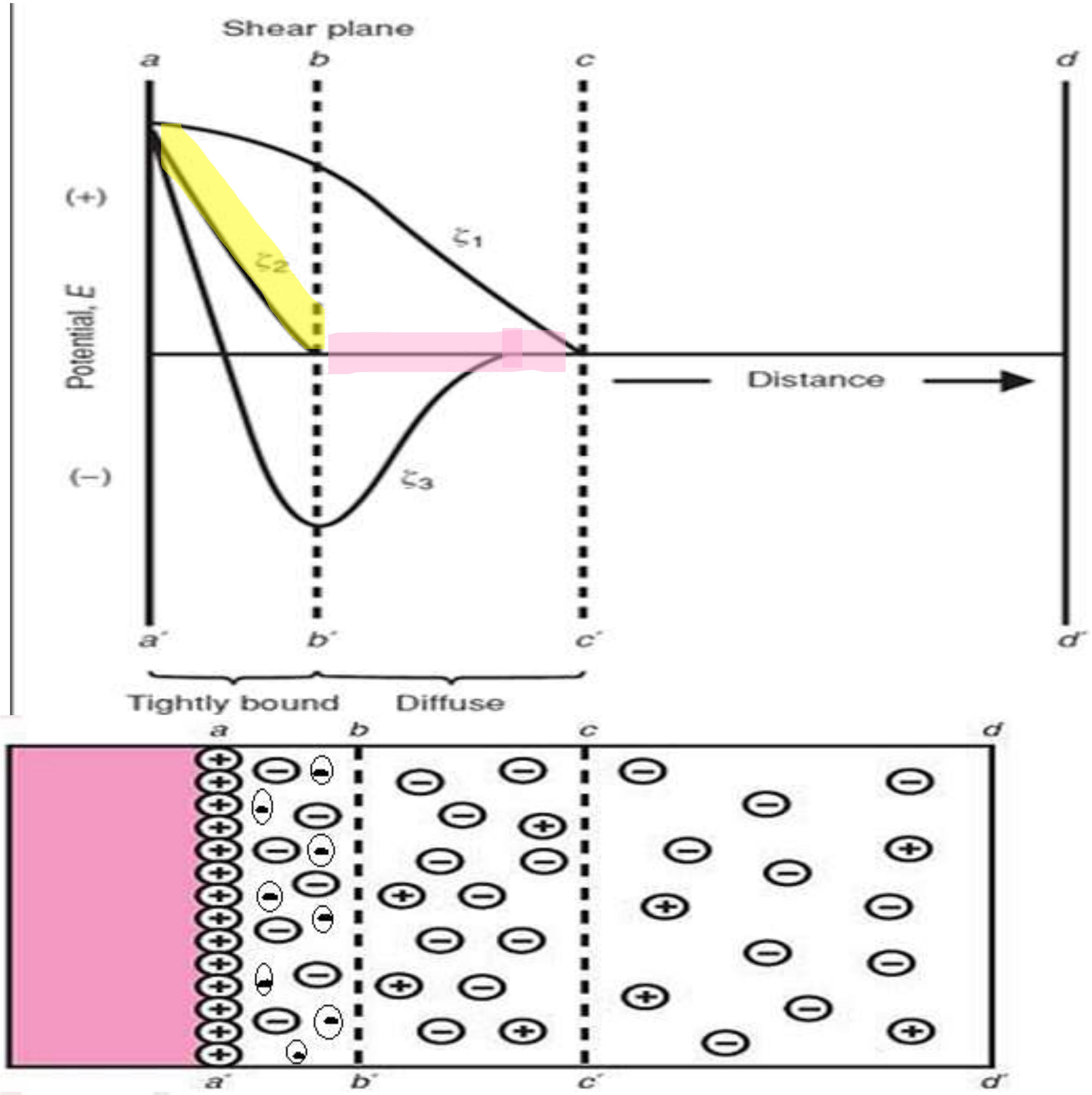
Curves are shown for three cases characteristic of the ions or molecules in the liquid phase.



Note that although E is the same in all three cases, the zeta potentials are positive (ζ_1), zero (ζ_2) and negative (ζ_3), as follows:

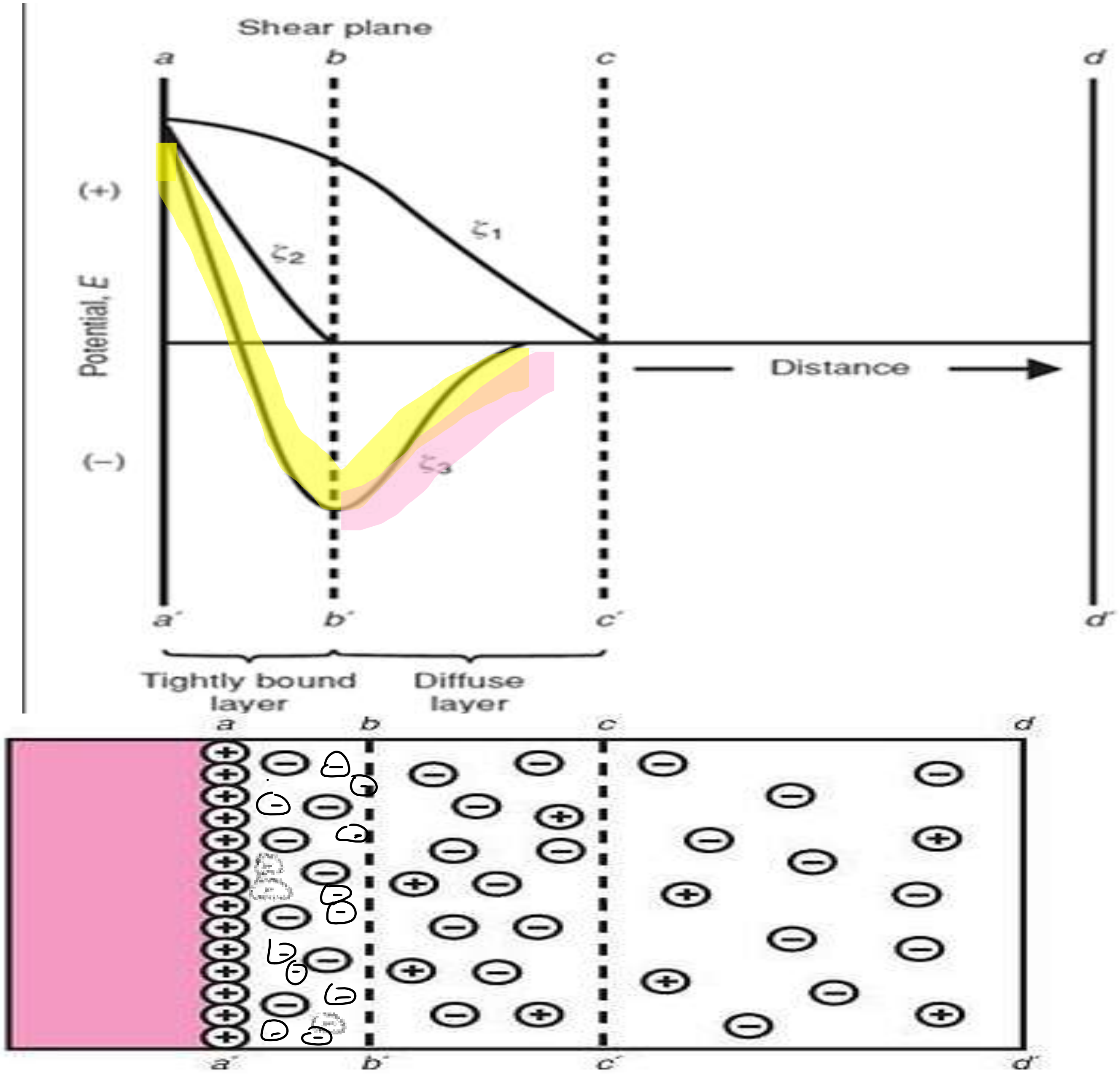
1. **Positive zeta potential (ζ1):**

It means that the dispersed particles have a positive charge.
The potential **at (bb') layer is positive** because there are **fewer anions** than cations.
From bb' to cc' there is excess negative ions but the potential is still positive, and beyond cc' the ions are uniformly distributed, and electrical neutrality is obtained



2. Zero zeta potential (ζ2):

The potential at (bb') layer is equal to zero. It is observed when the adsorbed counterions in the tightly bound solvated layer is **equal to** the potential determining ions on the solid surface.

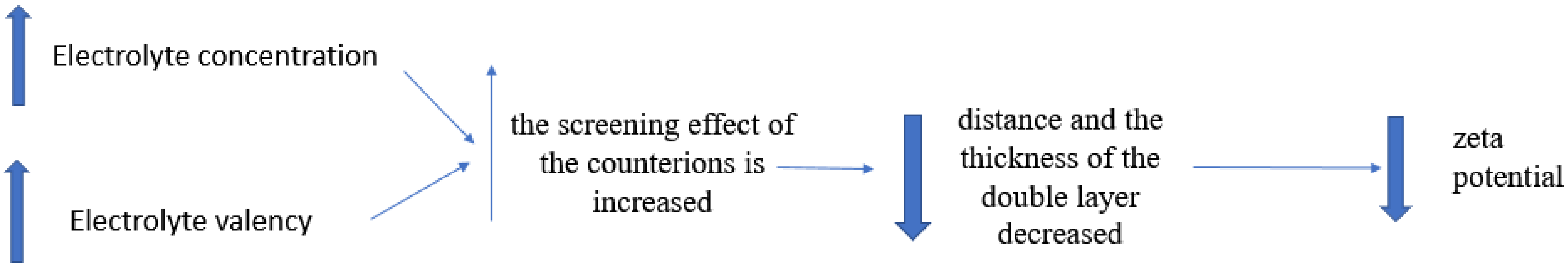


3. Negative zeta potential (ζ3):

The potential at (bb’) layer is negative because there are **more anions** than cations. It means that the dispersed particles have a negative charge.

From bb’ to cc’ there is less negative ions but the potential is still negative, and beyond cc’ the ions are uniformly distributed, and electrical neutrality is obtained

Factors affecting on Zeta Potential



Electrolyte concentration

Electrolyte valency

the screening effect of the counterions is increased

distance and the thickness of the double layer decreased

zeta potential

Importance and applications of Zeta Potential

The **magnitude of the zeta potential** indicates the **degree of electrostatic repulsion** between adjacent, similarly charged particles in a dispersion, and is a parameter in the theory of interaction of colloidal particles and is important for quantifying the magnitude of surface charge during formulations.

So, colloids with **high zeta potential *** (negative or positive) **are electrically stabilized** since repulsive forces between particles exceed the attractive forces and they resist aggregation

In colloids with **low zeta potentials** the attractive forces between particles due to van der Waals' force may exceed repulsion and therefore such particles tend to coagulate or flocculate.

*** Controlled to certain limit**

Importance and applications of Zeta Potential

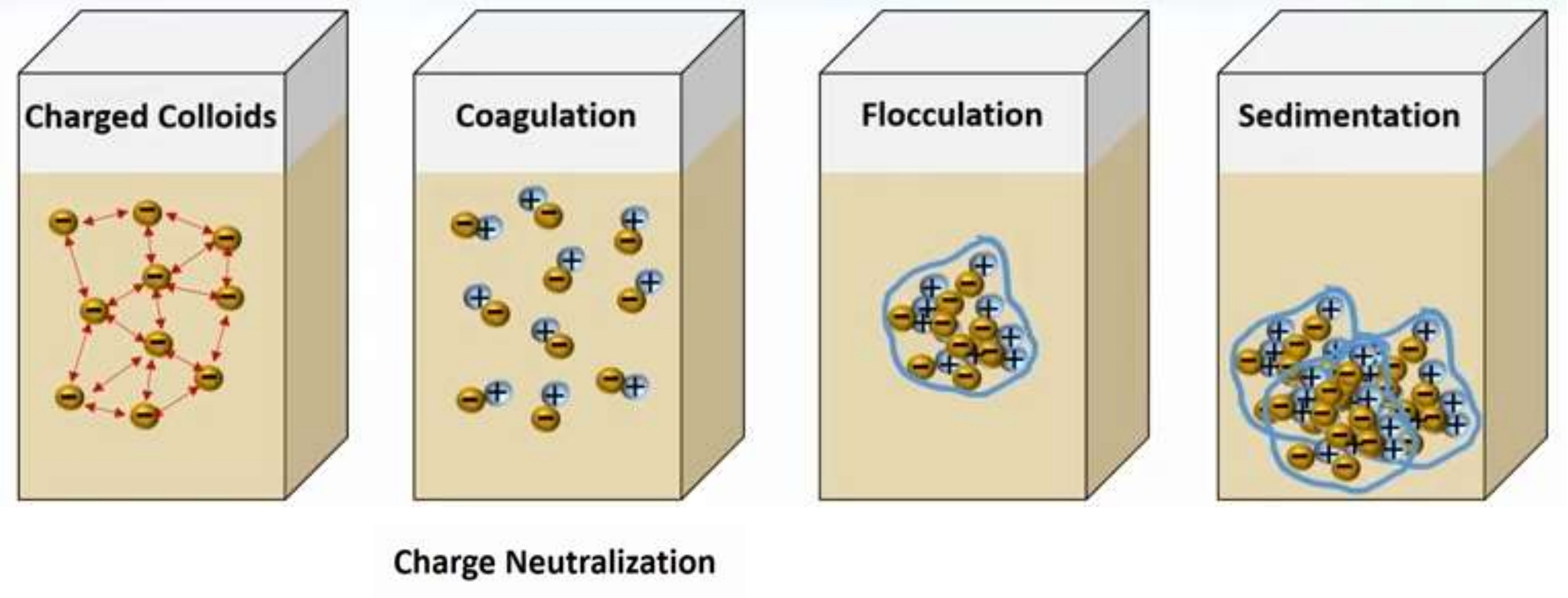
1. Interfacial Properties of Suspended Particles

We can keep particles suspended in a suspension by keeping them charged:
Charged particles act like magnets and repel each other

To prepare a **stable suspension**, it must have a **proper zeta potential** such that the suspended particles **are “flocculated”**

A very high +ve or –ve zeta potential is not preferred in preparation of suspension, but its value should be controlled within certain limit (as will be shown in the coming figures).

Explanatory material



by addition of flocculating agent

Flocculation and Deflocculation

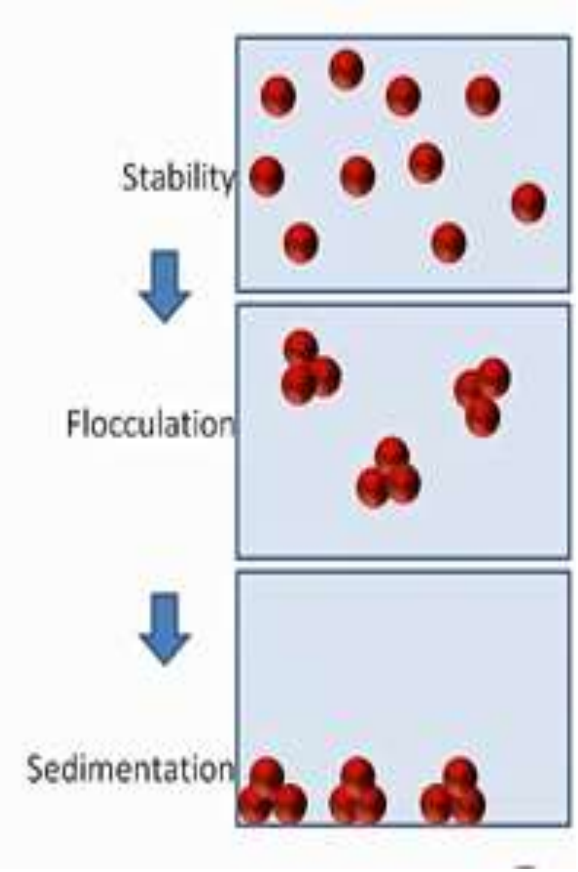
Flocculation is a process by which colloidal particles come out of suspension to sediment under the form of floc or flake, either spontaneously or due to the addition of a flocculating agent (e.g, KH_2PO_4) or by using flocculating agents other than electrolytes (e.g., nonionic surfactants).

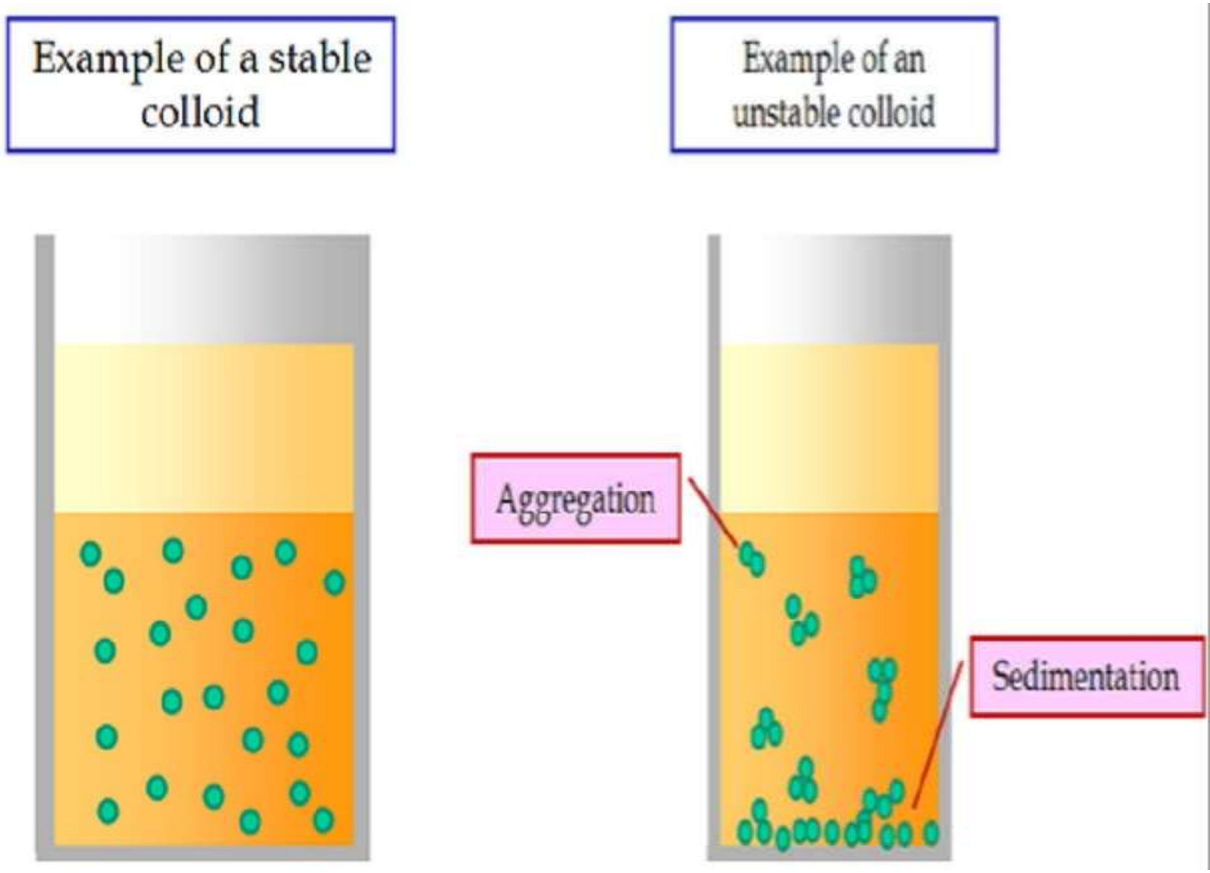
Flocculated particles are light, fluffy weakly bonded conglomerates, that are held together by weak van der Waals forces. They settle rapidly, do not form a cake, and are easily resuspended.

Under certain conditions, the flocculated particles may adhere by stronger forces to form what are termed **aggregates** or **cake**

Explanatory material

Figures showing colloidal stability





Caking diagram, showing the flocculation of suspension by means of the flocculating agent monobasic potassium phosphate (KH_2PO_4)

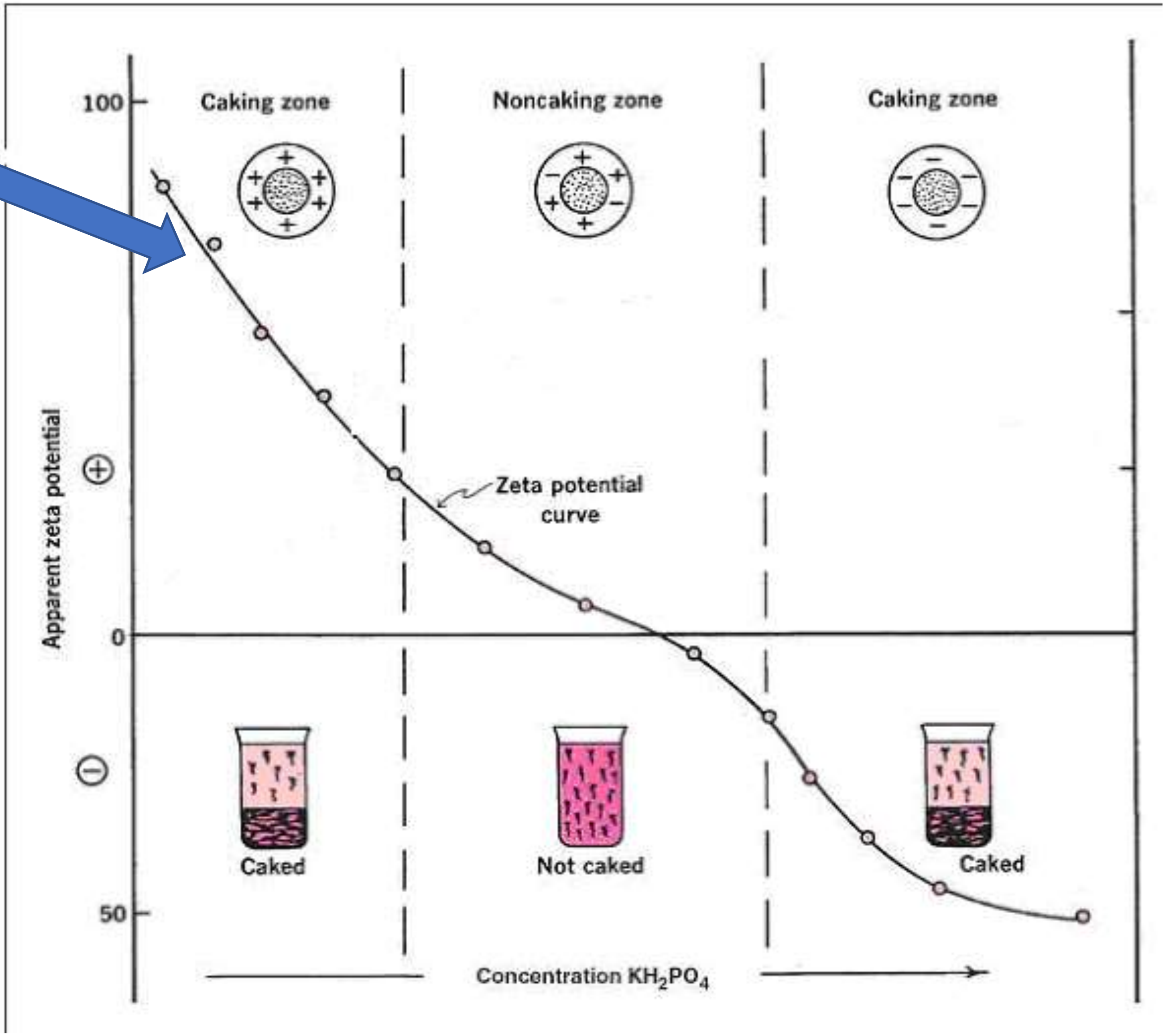
When the repulsion energy (zeta potential) is high, the collision of the particles is opposed.

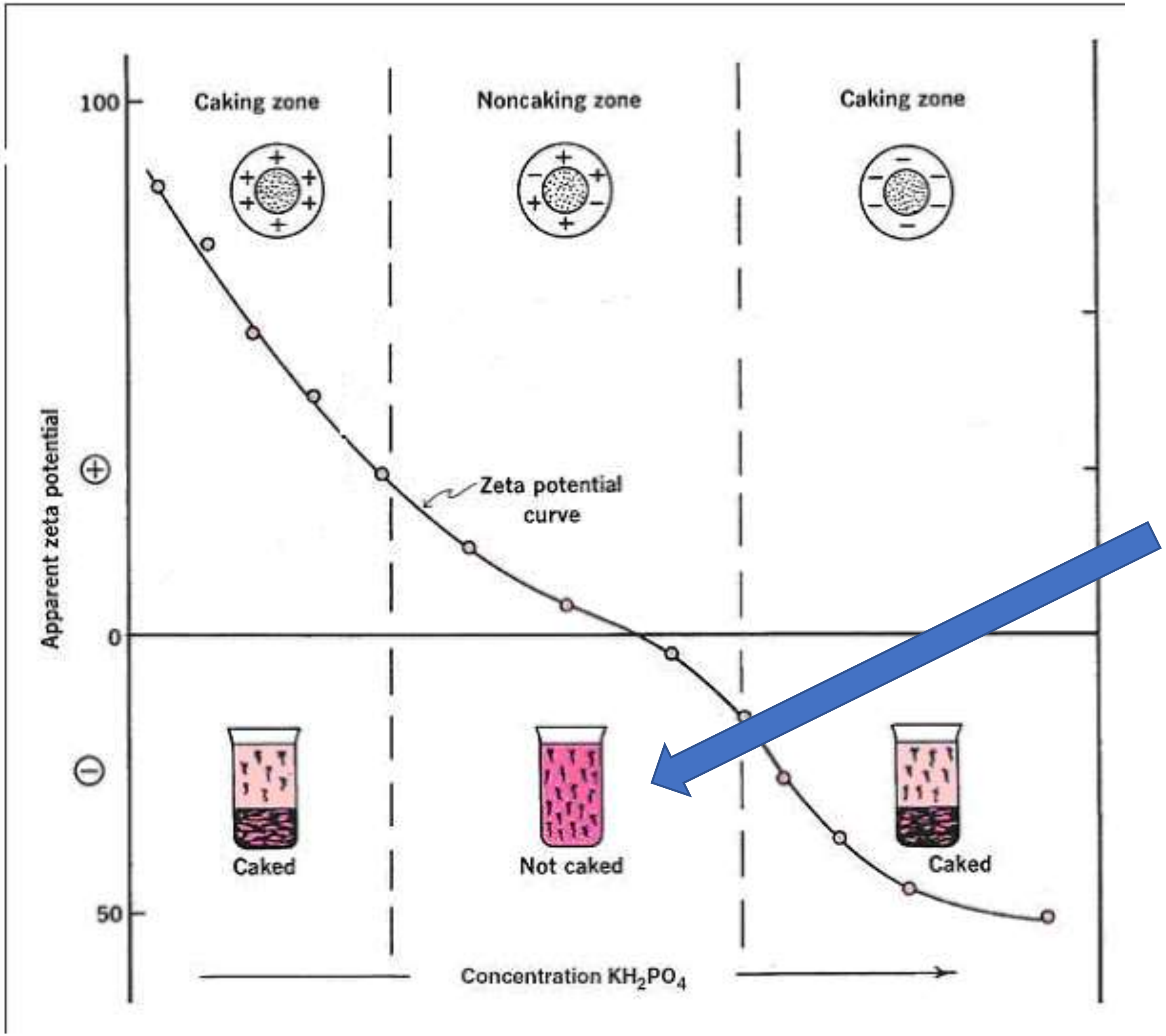
A **deflocculated system** has a zeta potential higher than the critical value when the repulsive forces exceed the attractive forces.

Particles in this type of systems remains suspended for a long period of time, and only a small portion of the solid is found in the sediment due to the force of gravitation.

During sedimentation, the smaller particles fill the void between the larger ones; and the particles lowest in the sediment are **gradually pressed together** by the weight of the particles above. Both situations increase the closeness of the particles; and, thus, they are **attracted by a large amount of van der Waals'-London force.**

To resuspend and redisperse these particles, it is again necessary to overcome these forces. Because this **is not easily achieved by agitation**, the particles tend to remain strongly attracted to each other and **form a hard cake** which is difficult, if not impossible, to redisperse

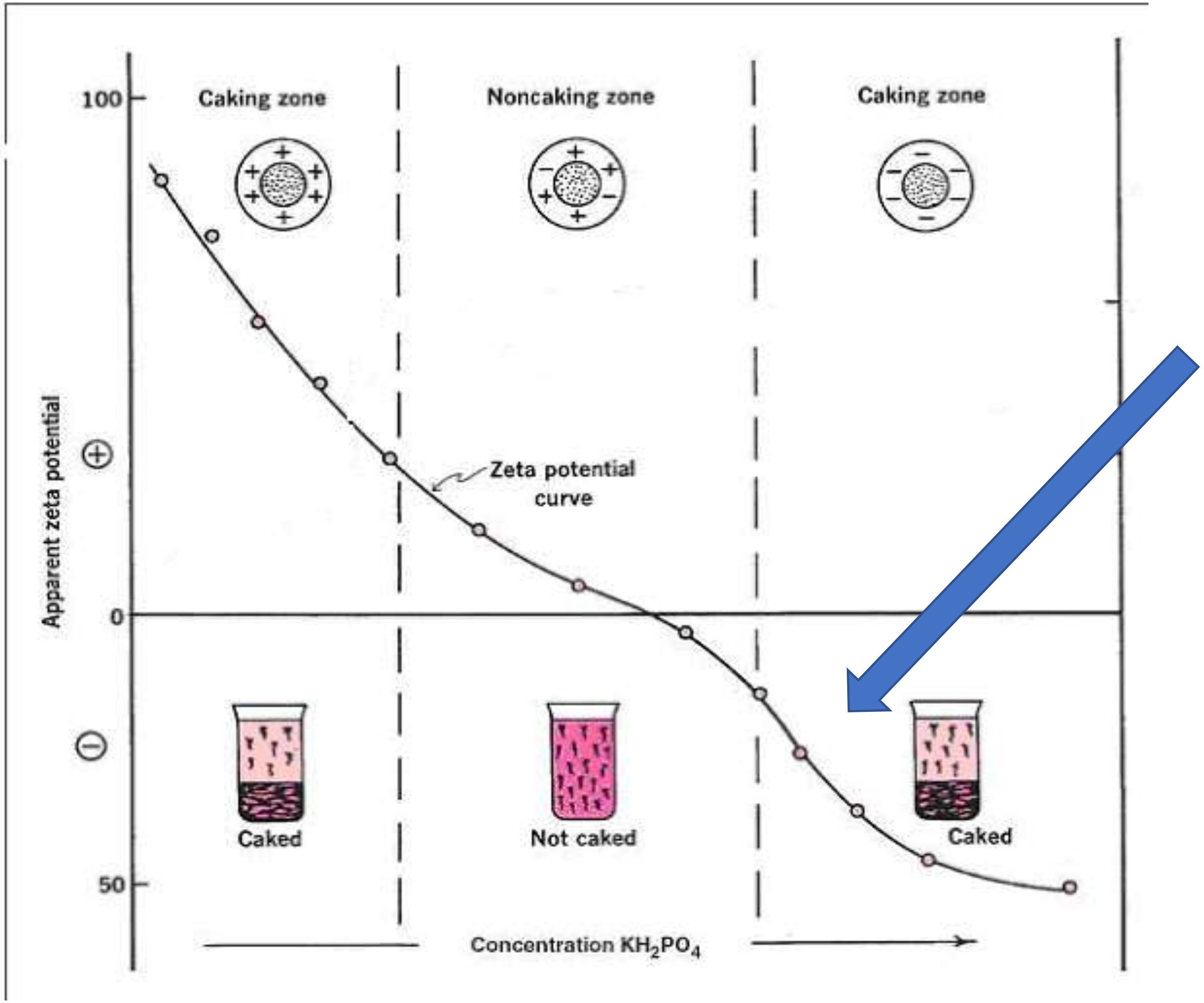




Upon the addition of a small amount of electrolyte **(flocculating agent),** the zeta potential of the system reduces.
Once it is below the critical value, the attractive forces supersede the repulsive forces, **producing flocculation (i.e.,** when the particles collide, **loosely packed aggregates of particles or flocs are created)**.

Being larger and heavier than individual particles, these flocs **get settled faster** than the deflocculated particles. However, since the flocs are loose structures, they will not form hard, cake-like deflocculated suspensions and will resuspend with minute agitation.

Generally a clear supernatant liquid is found at the top of the **flocculated suspensions**



If the zeta potential is reduced below a certain value (which depends on the particular system being used), the attractive forces exceed the repulsive forces, and **the particles come together forming a hard to disperse flocculated particles (caked system)**

Importance and applications of Zeta Potential

2. Electrokinetic Phenomena

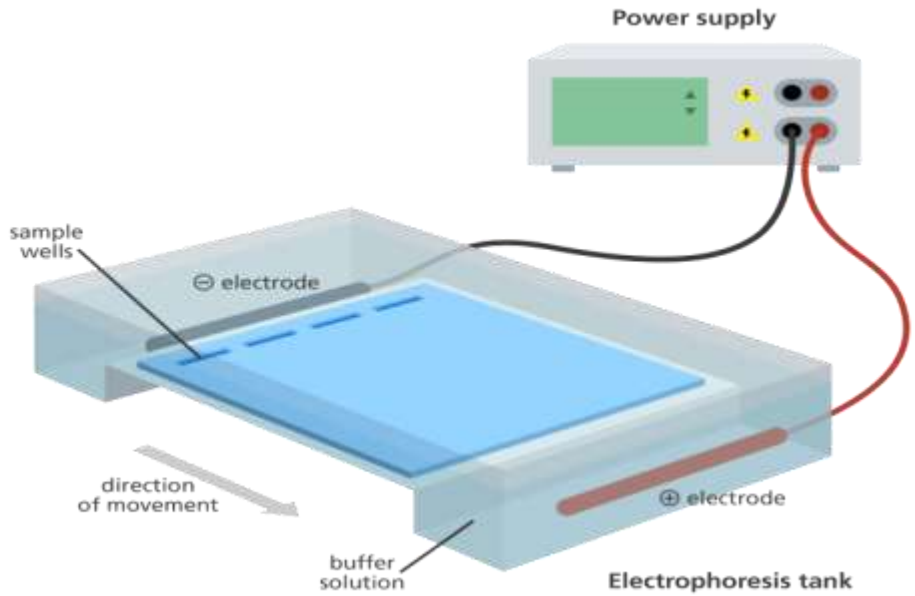
ELECTROKINETICS is a branch of physics **dealing with phenomena in which electric charge causes movement**.

The most important application of this phenomena is **electrophoresis**

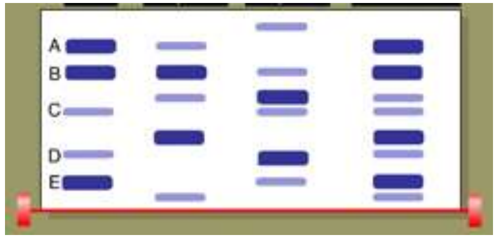
Electrophoresis

This is a phenomena which involves the movement of a charged particle through a liquid under the influence of an applied electrical field (potential difference).

- Electrophoresis is mainly **used for separation of plasma protein**.
- An electrophoresis cell fitted with two electrodes contains the dispersion.
- When electrical field is applied by using two oppositely charged electrodes (a potential difference exist), the particles migrate to the oppositely charged electrode and the plasma proteins can be separated in this way.



Electrophoresis tank



Electrophoresis sheet

وزارة التعليم العالي والبحث العلمي
جامعة بغداد
University of Baghdad
College of Pharmacy
كلية الصيدلة
1936

Physical pharmacy II

By:
Asst. Professor
Lena M. Thomas

Part 1

Rheology

In this lecture, you'll learn:

- Terminology associated with rheology
- Applications of rheology in the field of pharmacy
- Principles of viscosity
- Newton’s Law of Flow
- Dynamic Viscosity vs Kinematic Viscosity
- Factors Affecting Viscosity

Definitions

Rheology

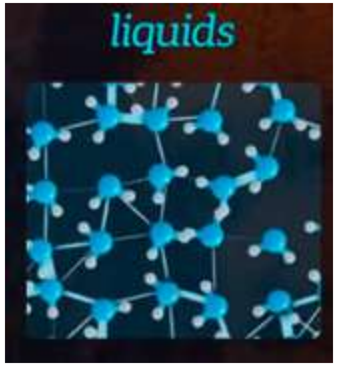
It is the science that deals with the change in flow characteristics of liquids and the deformation of solids under applied stress or force.

Rheology is derived from the Greek *rheo* (flow) and *logos* (science).

Viscosity

It is an expression describing the resistance of a fluid to flow or deformation under an applied stress.

In everyday terms, viscosity is a **property of liquids** which describes **"the thickness"** or **"the resistance"** of a liquid to flow. It represents the "**tendency of a liquid to oppose any adjustment in its shape or movement".**

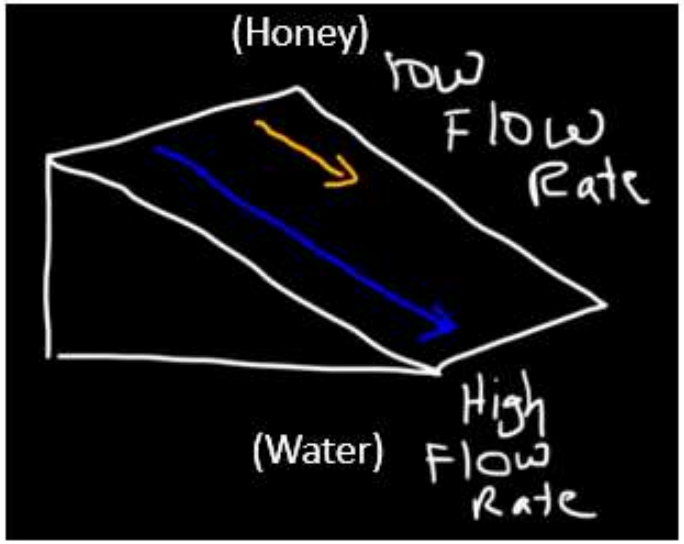


Viscosity in liquids generally arises due to cohesion of molecules together so that it impedes the flow of the fluid.

A liquid with **higher cohesion force** between its molecules will have **higher viscosity and lower flow rate**.

Viscosity in gases arises due to intermolecular collisions which creates interactions between adjacent layers of fluid.

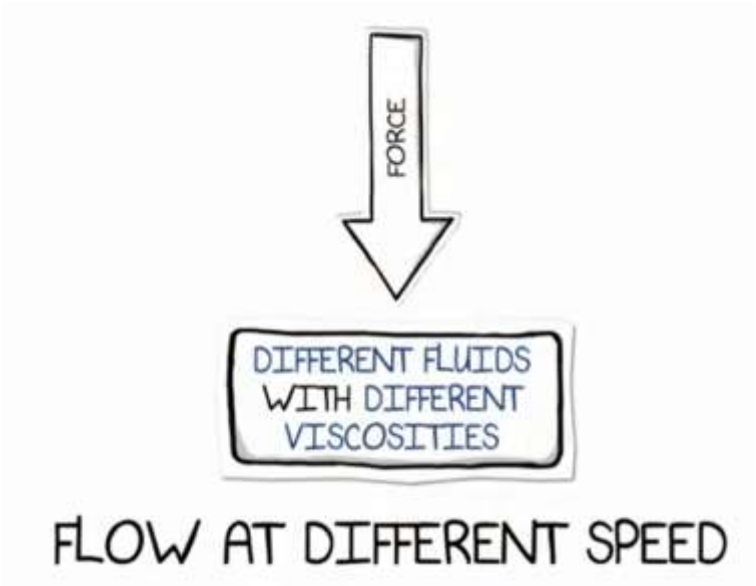
Water



If you poured both water and honey down a slope:
flow rate of water >> the flow rate of honey

Honey

Two fluids with different viscosities will flow at different speeds
when the same amount of force is applied:
the higher the viscosity,
the greater is the resistance,
and the slower is the flow.



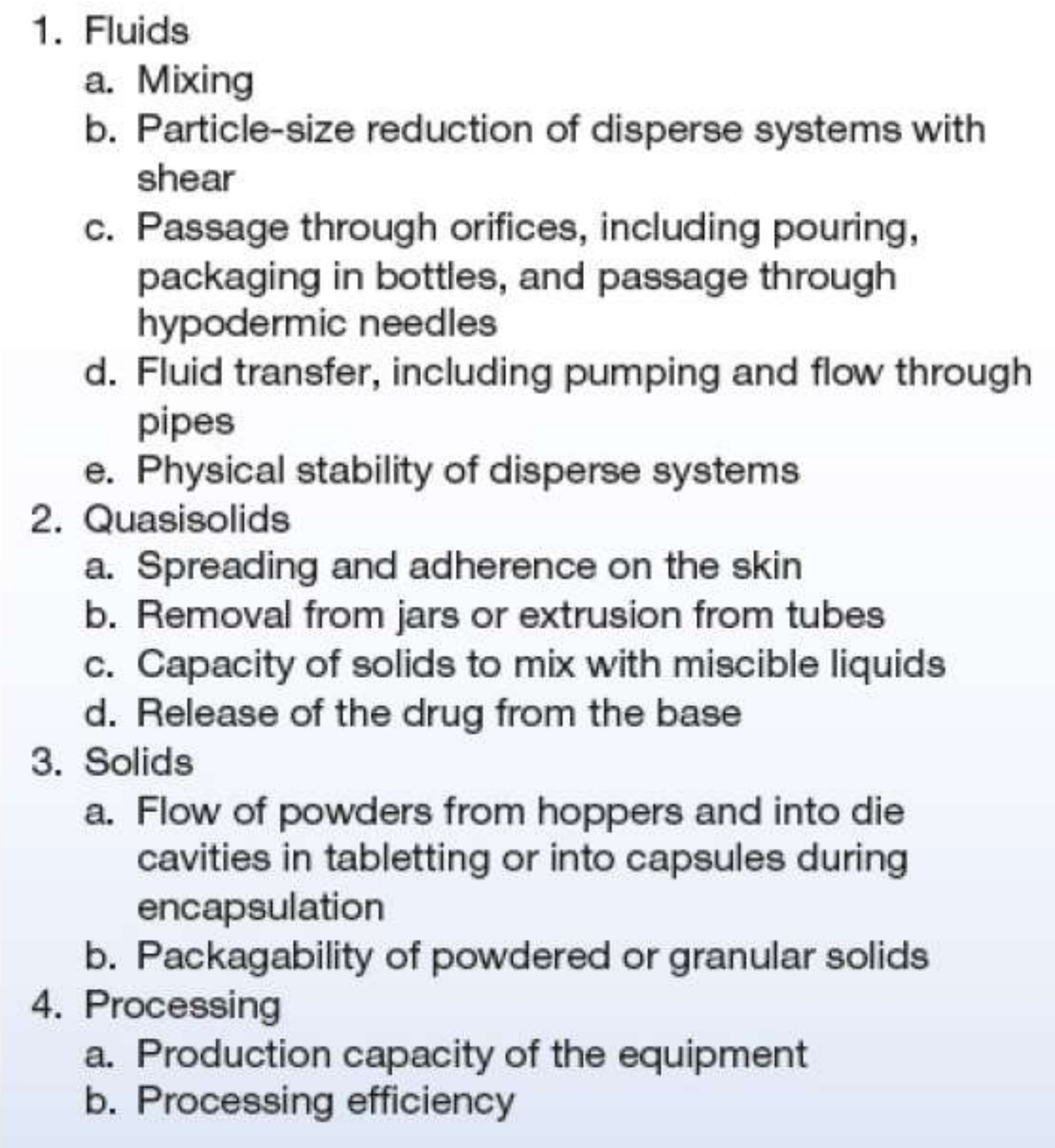
Pharmaceutical Areas in which Rheology Is significant (applications of rheology in pharmacy)

Fundamental principles of rheology are used to study paints, inks, doughs, road-building materials, cosmetics, dairy products, and other materials.

In the pharmaceutical sciences, rheology widely has a role in:

- Formulation of cosmetic as well as medicinal products such as emulsions, lotions, creams, pastes, suppositories, and tablet coatings.
- Selection of processing equipment used in pharmaceutical formulation manufacture as it is involved in the mixing and flow of materials, their packaging into containers, their removal prior to use, whether by pouring from a bottle, extrusion from a tube, or passage through a syringe needle.
- The rheology of product can affect the final consistency of the product and therefore patient acceptability, physical stability of the product, and even biologic availability. For example, viscosity has been shown to affect absorption rates of drugs from the gastrointestinal tract.

In other words

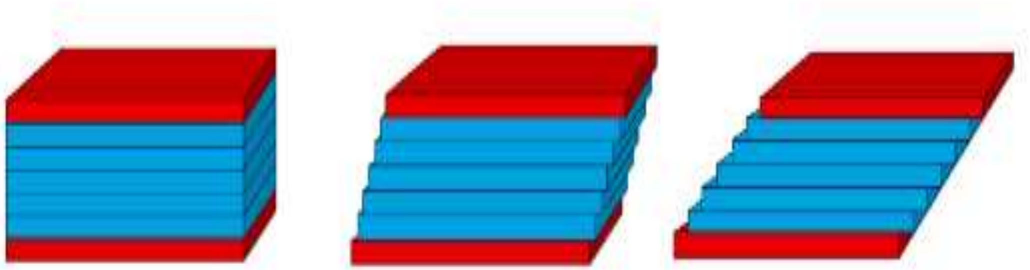


1. Fluids
   a. Mixing
   b. Particle-size reduction of disperse systems with shear
   c. Passage through orifices, including pouring, packaging in bottles, and passage through hypodermic needles
   d. Fluid transfer, including pumping and flow through pipes
   e. Physical stability of disperse systems
2. Quasisolids
   a. Spreading and adherence on the skin
   b. Removal from jars or extrusion from tubes
   c. Capacity of solids to mix with miscible liquids
   d. Release of the drug from the base
3. Solids
   a. Flow of powders from hoppers and into die cavities in tabletting or into capsules during encapsulation
   b. Packagability of powdered or granular solids
4. Processing
   a. Production capacity of the equipment
   b. Processing efficiency

Principles of Viscosity

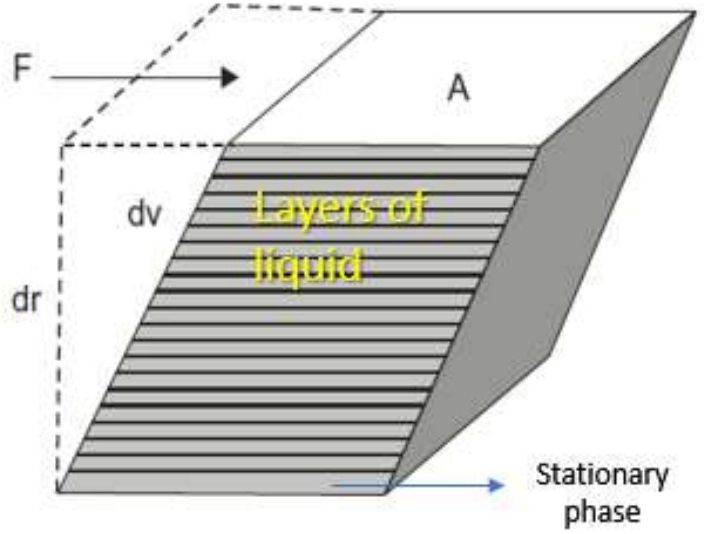
Basic concept

Let's consider a "cube of liquid" consisting of parallel layers of liquid stacked on one another (similar to deck of cards), with the surface area of each side equal to A



If we apply a force equal to F on the top plate, it starts moving with a velocity v.

The plate below this top plate, moves at velocity lower than v and the plate on the base does not move at all (stationary phase)

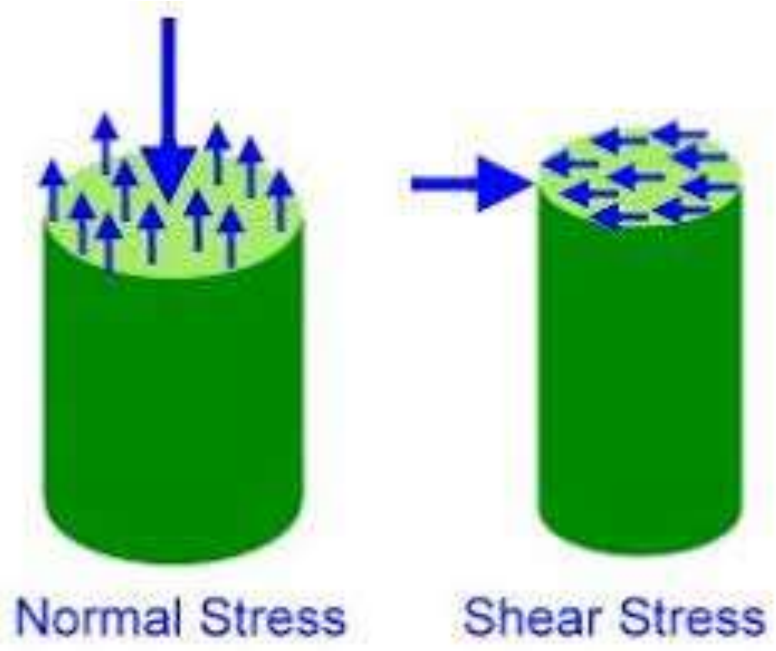


Parallel plates of fluid move in the same direction of applied force at different velocities
The velocity of fluid movement decreases with distance from the top plate

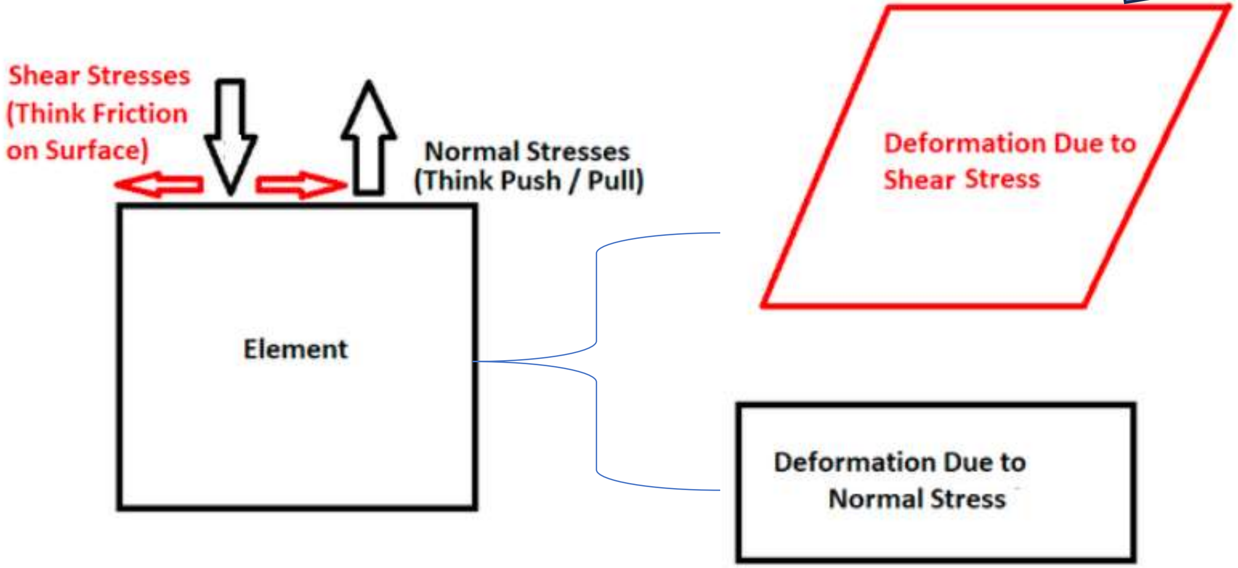
When a layer of fluid is subjected to move upon a surface or another layer of the same fluid, the fluid particles tend to oppose such movement.
This opposing force developed by a liquid is called viscosity.

Types of stress

مادة اثرائية



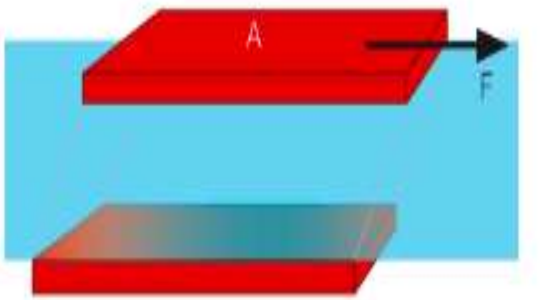
We are interested in shear stress during our study for concept of viscosity



Principles of Viscosity
Basic terminology

Shear stress (F or τ) :

Is the tangential force per unit area applied to a fluid layer, causing it to deform (or flow).

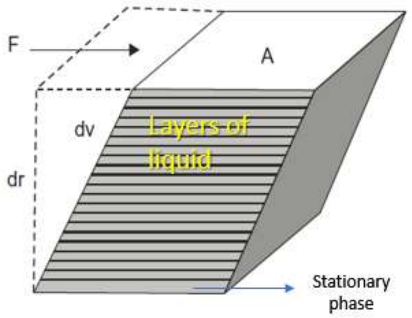


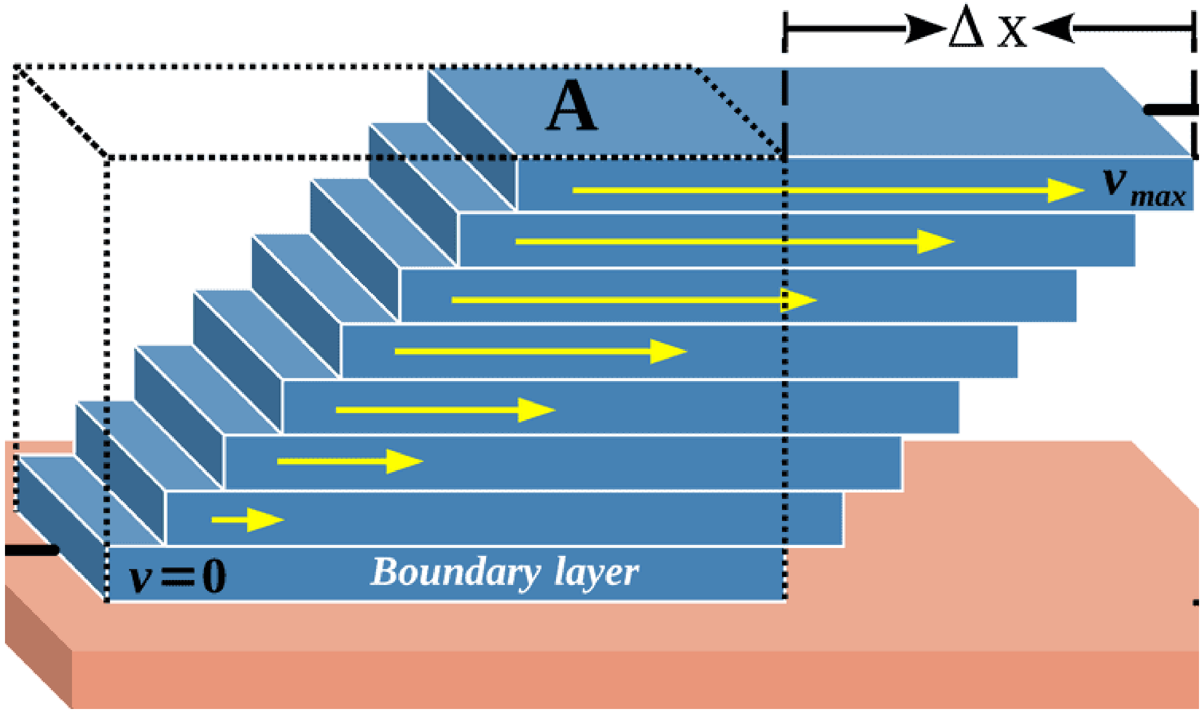
Imagine placing a layer of fluid between two horizontal plates, where the top plate is moving horizontally relative to the bottom plate. The force applied by the moving plate to the fluid layer represents the shear stress

Mathematically it is represented by $\tau = F'/A$

where τ is the shear stress,
F is the applied force, and
A is the cross-sectional area parallel to the direction of the applied force

The **unit for shear stress** is Pa (pascal) = N/m^2

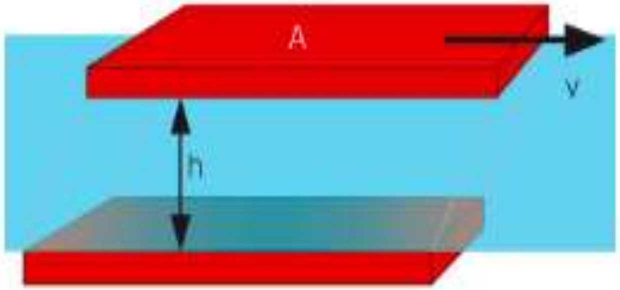




Principles of Viscosity

Basic terminology

Shear rate or velocity gradient (G) or ($\dot{\gamma}$) :



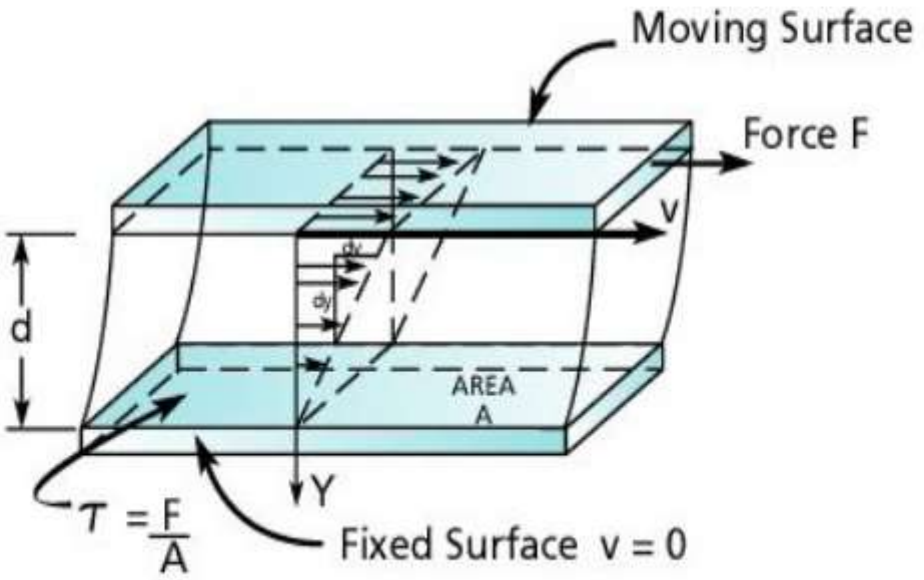
Is the rate of deformation of the fluid layer under shear stress
(velocity of flow as a function of distance);
It describes how fast the layers of the fluid are moving relative to each other.

It represents the difference of velocity, ***dv***, between two planes of liquid separated by an infinitesimal distance ***dr (or dh)***

Mathematically it is represented as $\dot{\gamma}$ **= dv/dr**

Where $\dot{\gamma}$ is shear rate (s^{-1})
dv is the change in velocity (m/s)
dr is the change in distance (m)

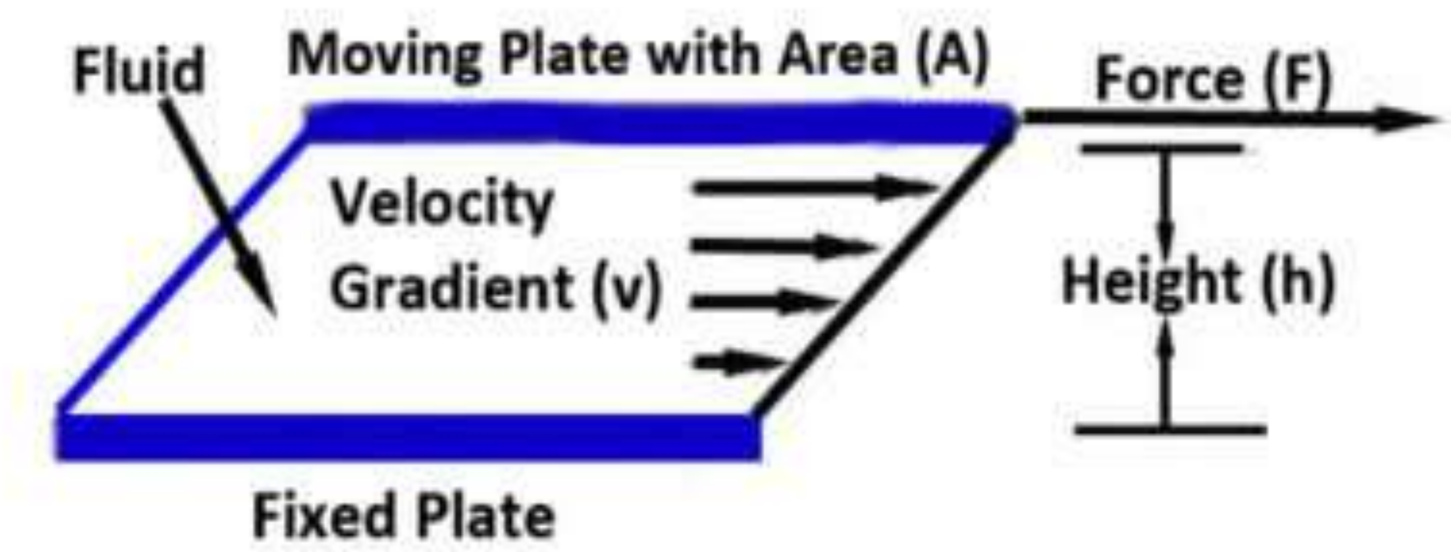
The **unit for shear rate** is reciprocal seconds (or **reciprocal of time**)
1/second = s^{-1}.

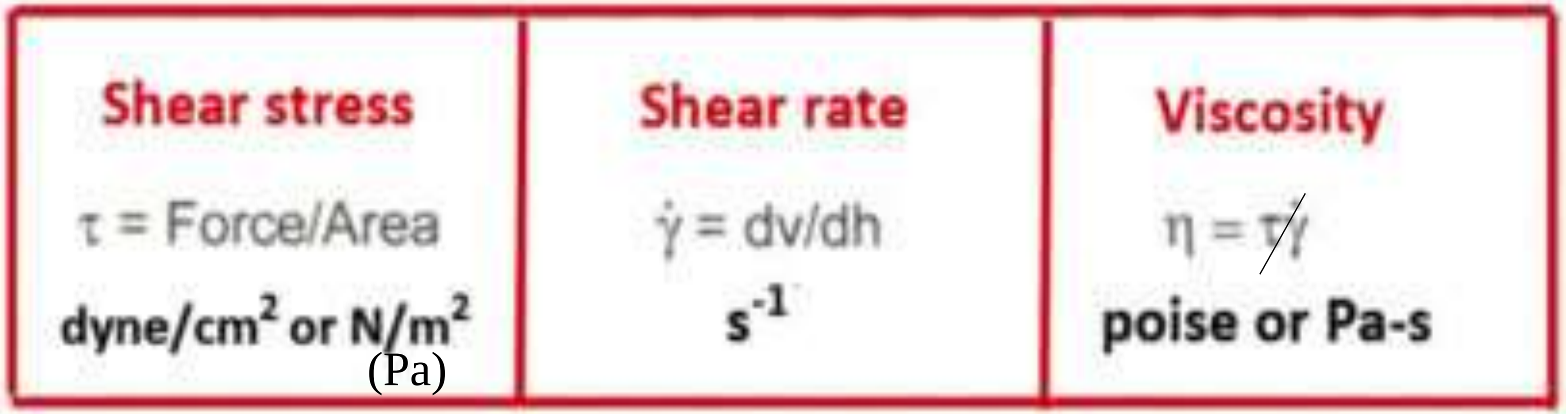


Principles of Viscosity

Basic terminology

The parameter that connects the shearing stress and shearing rate is the **viscosity.**





Shear stress	Shear rate	Viscosity
τ = Force/Area	$\dot{\gamma}$ = dv/dh	$\eta = \tau/\dot{\gamma}$
dyne/cm^2 or N/m^2 (Pa)	s^{-1}	poise or Pa-s

Principles of Viscosity

Law of viscosity

Newton's Law of Flow: Newton was the first to study flow properties of liquids in a quantitative way

He recognized that there is a **direct relationship between the shearing stress and the shearing rate**:
The higher the viscosity of a liquid, the greater is the force per unit area (shearing stress) required to produce a certain rate of shear (shearing rate).

The law of Newton may be represented mathematically as follows:

$$\frac{F'}{A} \propto \frac{dv}{dr} \rightarrow \frac{F'}{A} = \eta \frac{dv}{dr}$$

Where η (eta) is the coefficient of viscosity, or simply the **viscosity**.

Shearing stress (F) = viscosity (η) x rate of shear (G)

Or: Viscosity (η)= shearing stress (F) /shear rate (G)

Frequently written as:

$$\eta = \frac{F}{G}$$

Principles of Viscosity

There are two ways to report viscosity

While the relationship is straightforward, it's important to remember two fluids with the same dynamic viscosity values may have different densities and thus difference kinematic viscosity values.

Absolute or dynamic viscosity

- is a measure of a fluid's resistance to flow

Dynamic viscosity $\eta = \frac{F}{G}$

- The units used are poise (p) and centipoise (cp)

$$\eta = \frac{\text{Force/Area}}{\text{Velocity/distance}} = \frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cm/sec}} = \frac{\text{dyne sec}}{\text{cm}^2}$$

$(= \text{dyne. sec. cm}^{-2}) = \text{g cm}^{-1}\ \text{sec}^{-1}$

$= 1$ poise

$= 100$ centipoise (cp)

⇨ $1\ cp = 0.01$ poise

A more convenient unit
for most work

Kinematic viscosity

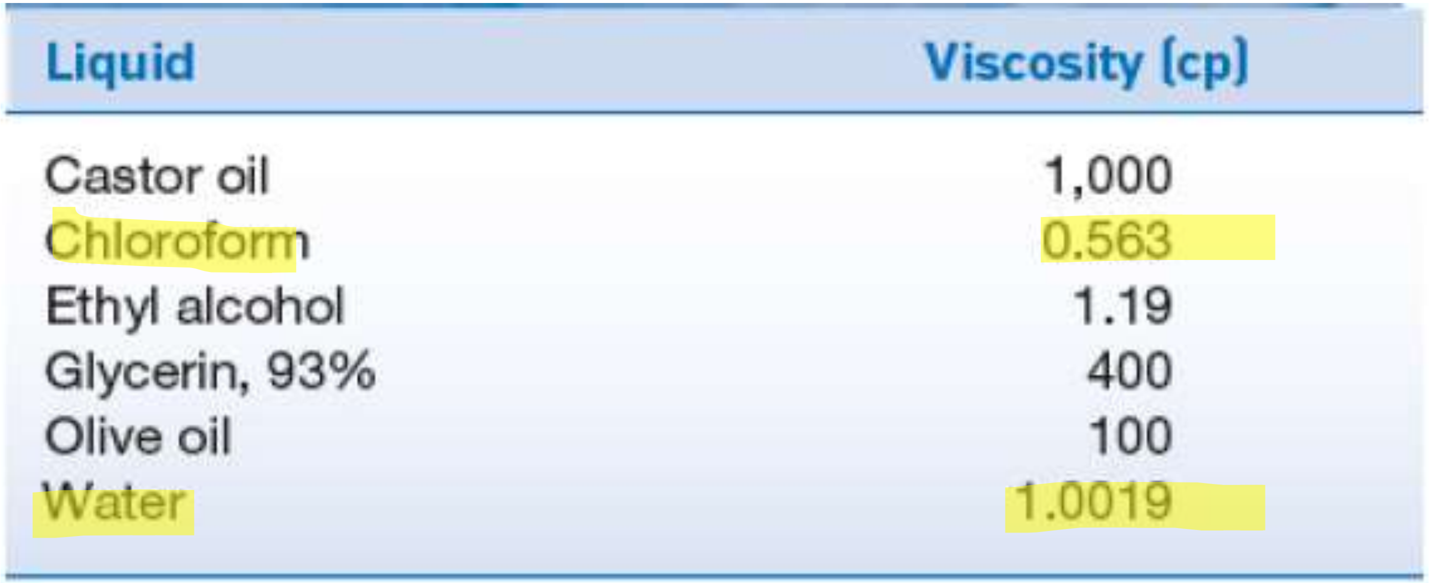
- is the ratio of dynamic viscosity to a fluid's density

$$\text{Kinematic viscosity} = \frac{\eta}{\rho}$$

- The units used are Stokes (s) and the centistoke (cs)

(after the British physicist George Gabriel Stokes)

Absolute Viscosity of Some Newtonian Liquids at 20°C



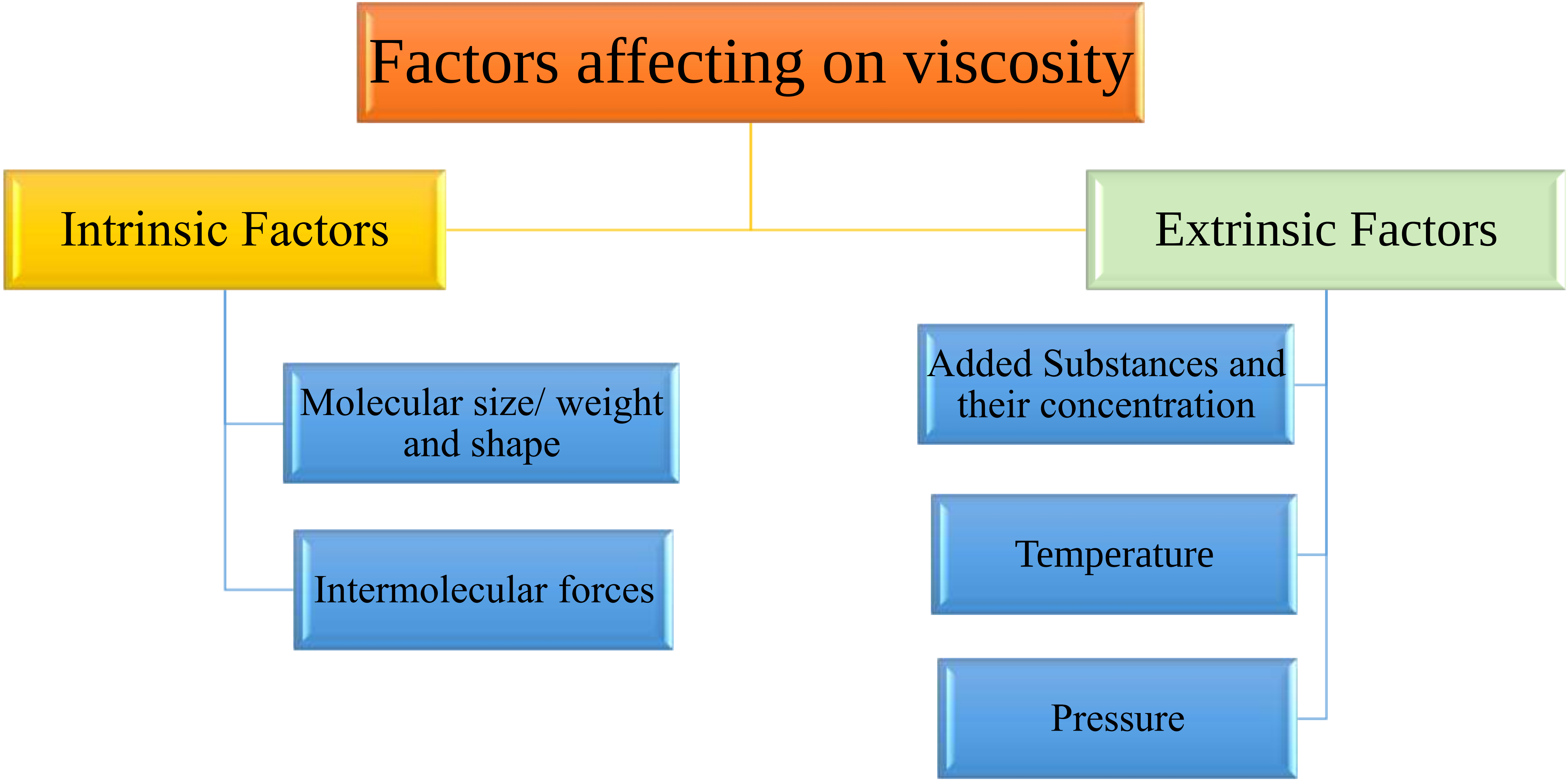
Liquid	Viscosity (cp)
Castor oil	1,000
Chloroform	0.563
Ethyl alcohol	1.19
Glycerin, 93%	400
Olive oil	100
Water	1.0019

Viscosity of Water

The viscosity of water is low, yet it is higher than that of most other liquids made of comparable-sized molecules. This is due to hydrogen bonding between neighboring water molecules.

لاحظ على سبيل المثال القيم
المؤشرة باللون الاصفر

The **dynamic (absolute) viscosity** of water is 1.0019 centipoise (cP) at 20 °C, whereas its **kinematic viscosity** is 1.0023 cs at 20 °C.



Factors affecting on viscosity

Intrinsic Factors

- Molecular size/ weight and shape
- Intermolecular forces

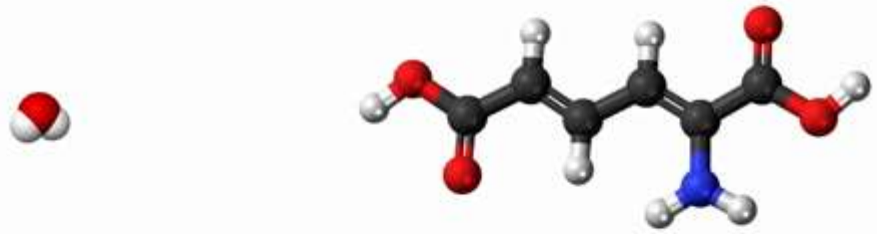
Extrinsic Factors

- Added Substances and their concentration
- Temperature
- Pressure

Factors affecting on viscosity

Intrinsic Factors

- size/shape of the molecule

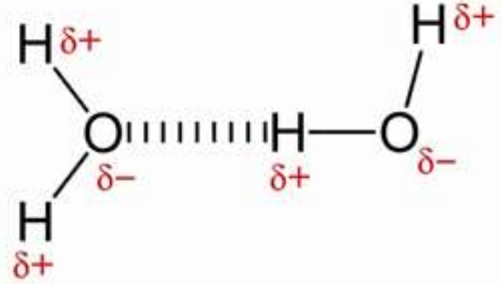


Small, symmetrical molecules move past each other more easily and therefore are less viscous

Large, irregularly shaped molecules move past each other less easily and therefore are more viscous

Spheroid colloids is less viscous than linear colloids, as the latter tend to form a network within the dispersion medium.

- strength of intermolecular forces



Viscosity is a reflection for the internal friction of a moving fluid

Stronger attractions (stronger intermolecular forces) make the molecules move less easily and the substance is more viscous

Factors affecting on viscosity

Extrinsic Factors

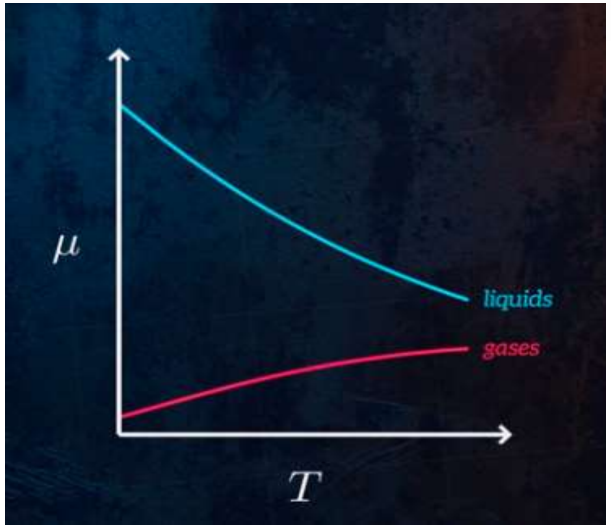
Both the **intensity** of the external force as well as the **duration** has an influence on the viscosity.

Temperature

Temperature has the greatest effect on viscosity.
Generally:
In a liquid, increasing temperature decreases viscosity because heat gives molecules enough energy to overcome intermolecular attraction.
For each 1 °C increase in temperature, there is 1-10% reduction in viscosity.

This is the reason for:

- Using different oils in hot and cold countries
- It is easier to pour skin lotion in summer than winter



Note:

In gases, the opposite occurs because temperature increases molecular collision

In some polymeric solutions such as methyl cellulose, increasing the temperature increases the viscosity

Factors affecting on viscosity

The dependence of the viscosity of a liquid on temperature is expressed approximately for many substances by an equation analogous to the Arrhenius equation of chemical kinetics:

Arrhenius equation:

$$\eta = Ae^{EvRT}$$

$$\log \eta = \text{Log } A + \frac{Ev}{2.303RT}$$

Or:

$$\ln\eta = \ln A + \frac{Ev}{R}\,\frac{1}{T}$$

A : constant depends on the molecular weight and molar volume of the liquid

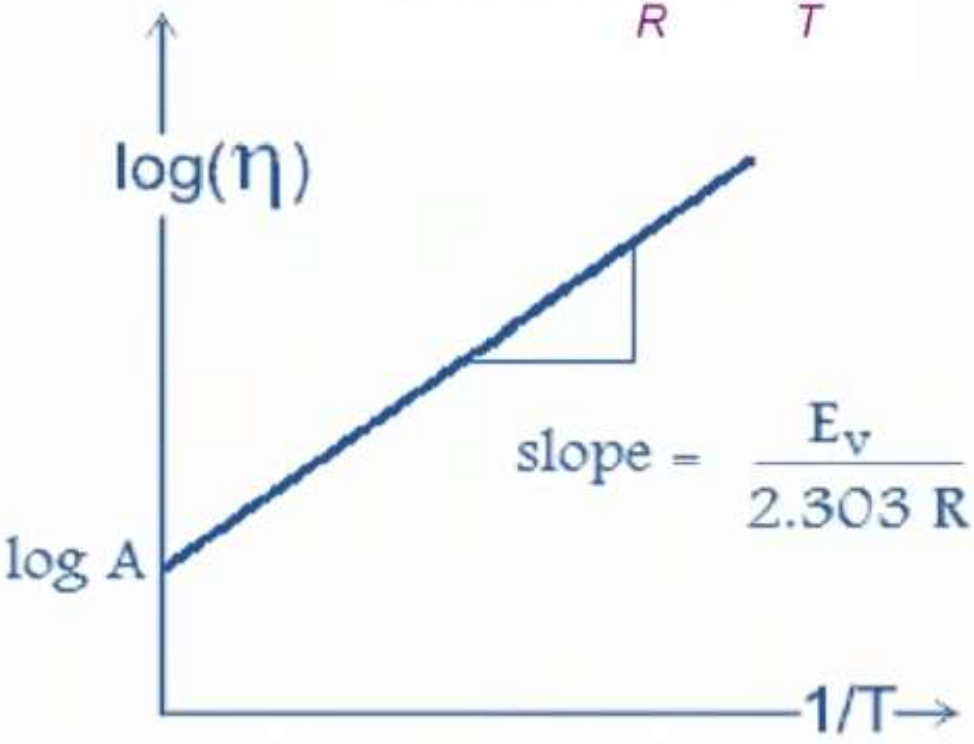
η: viscosity.

A: constant that depends on M.wt of liquid

Eν: activation energy → energy required to initiate the flow between molecules.

R: gas constant (1.987 cal/mole.Deg & 8.314 joule/mole.deg)

T: absolute temperature (in Kelvin)



Factors affecting on viscosity

Extrinsic Factors

-Added substances

The effect of adding molecules can be significant.

In general, addition of small quantities of non electrolytes such as glycerin, alcohol, sugar to water makes it much more viscous. Similarly, polymers and other macromolecules enhance the viscosity of solvents such as water.

On the other hand, small amounts of strong electrolytes decrease the viscosity.

-Pressure:

An increase in pressure enhances the cohesive forces of interaction leading to an increase in viscosity. However, the effect of pressure on liquids is small and often ignored.

Physical pharmacy II

2021-2022

By:
Asst. Professor
Lena M. Thomas

Part 2

Rheology

In this lecture, you'll learn:

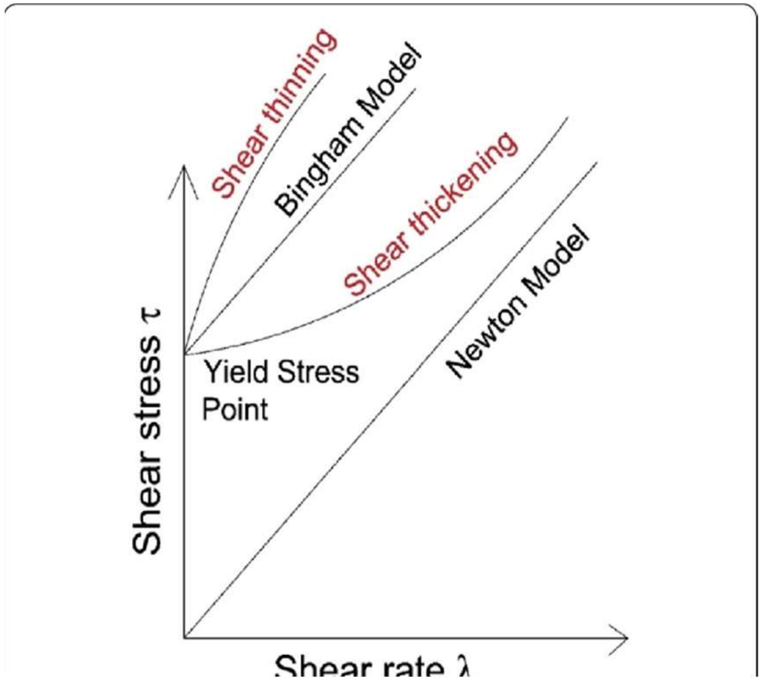
- Classification of systems according to their type of flow
- Meaning of flow curves and their types
- Laws used to calculate viscosity of different systems

Flow curves = Consistency curves= Rheograms

- It is a graphical representation of a fluid's behavior under different shear rates.
- Usually, this is a plot of **shear stress** **(F or τ)** represented on one axis versus **shear rate** **(G or γ̇)** on the other.

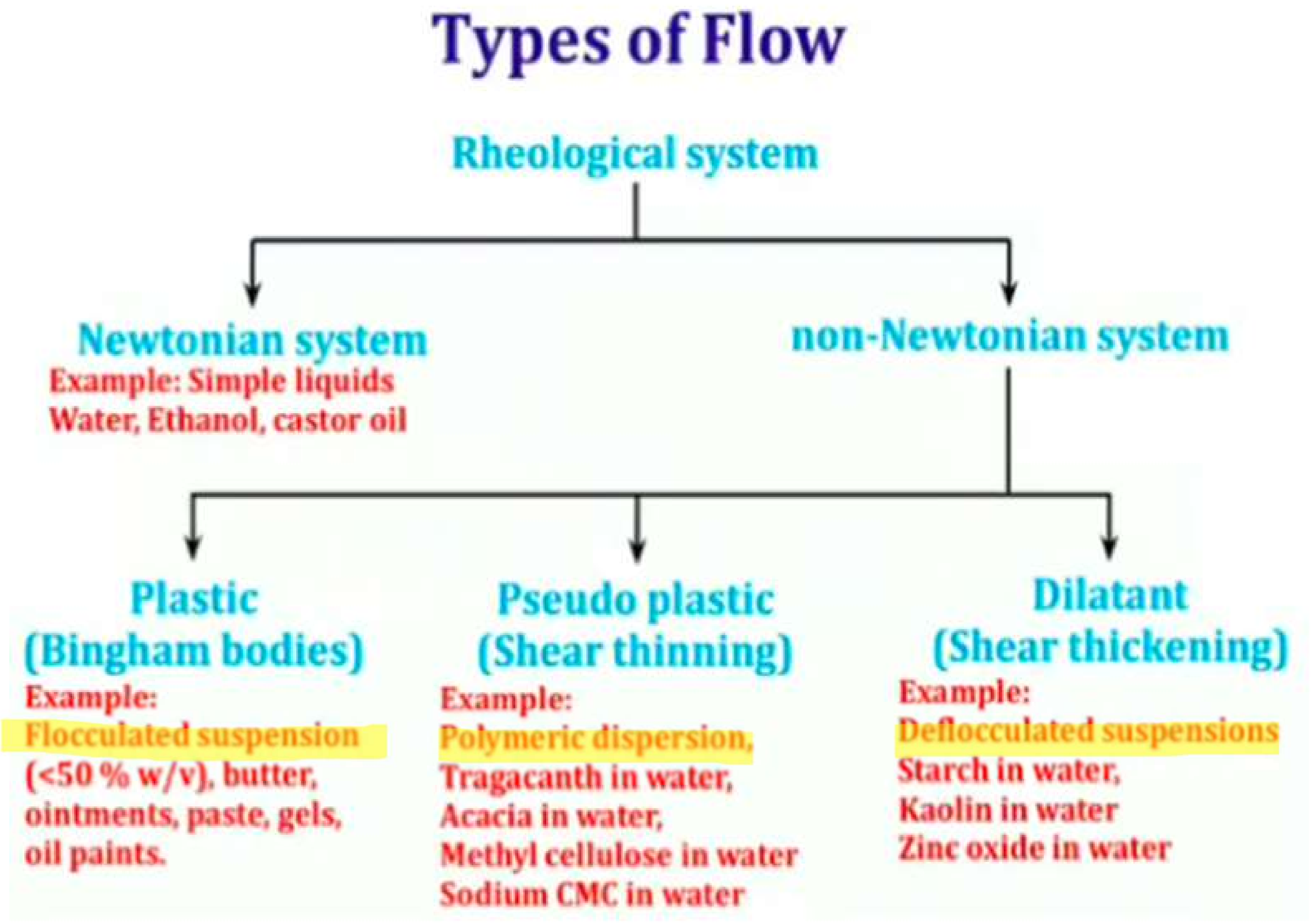
When we run the test on a sample in the beaker at fixed temperature using certain shear stress we get a value of shear rate that can be represented on the graph

By analyzing the shape of the flow curve, we can determine the **type of fluid** and then obtain its **viscosity**



ملاحظة: ننوه انه يمكن التبديل بين مواقع المحاور السيني والصادي عما تم تمثيله بالرسم اعلاه وهذا ما سيتم ملاحظته لاحقا في المحاضرة
بحيث يكون شكل الرسومات مختلفا. وينصح باتباع نسق واحد كان يكون دائما
Shear stress on x-axis and shear rate on y axis

Classification of Materials in Terms of Their Flow



Types of Flow

Rheological system

Newtonian system

Example: Simple liquids
Water, Ethanol, castor oil

non-Newtonian system

Plastic (Bingham bodies)

Example:
Flocculated suspension (<50 % w/v), butter, ointments, paste, gels, oil paints.

Pseudo plastic (Shear thinning)

Example:
Polymeric dispersion,
Tragacanth in water,
Acacia in water,
Methyl cellulose in water
Sodium CMC in water

Dilatant (Shear thickening)

Example:
Deflocculated suspensions
Starch in water,
Kaolin in water
Zinc oxide in water

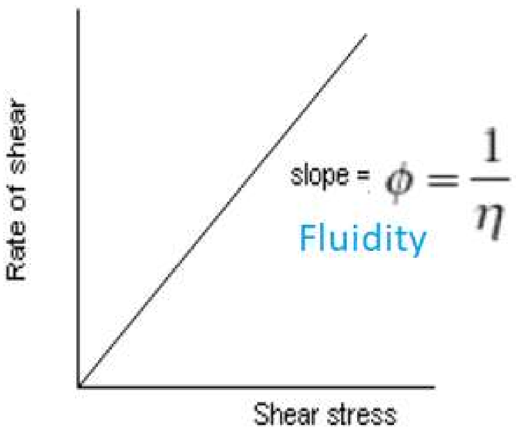
Note:

The next two slides are a summary of different systems with their flow curves and laws of viscosity associated with each type.

It is positioned in this sequence to have a complete picture to what you will learn in the lecture

To understand it fully, you must read the details of each system in the upcoming slides and then refer to this slide as a summary

Newtonian systems

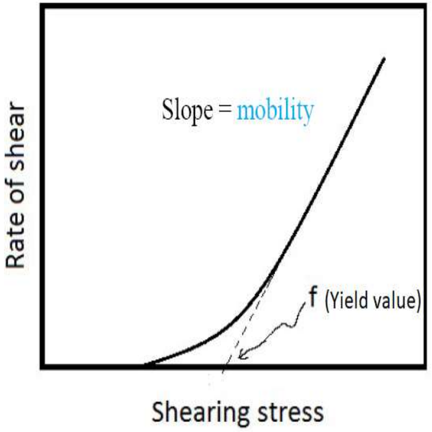


- A plot of shear rate (G) versus shear stress (F) gives **a straight line that passes through the origin**
- The **slope of the straight line** in the curve is referred to as **Fluidity** and its reciprocal is known as **viscosity** (η)
- The greater the slope of the line, the greater is the fluidity and the lower is the viscosity

$$\boxed{\eta = \frac{F}{G}}$$

Non-Newtonian systems

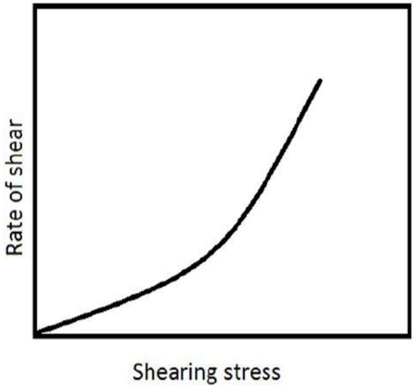
Plastic systems (Bingham Bodies)



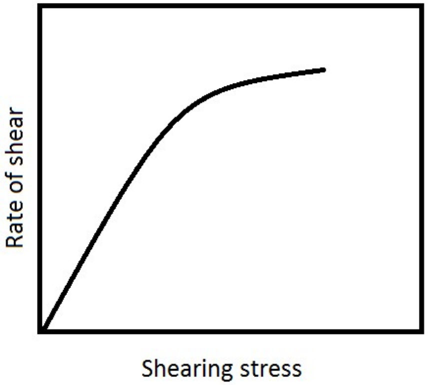
- A plot of shear rate (G) versus shear stress (F) gives a curve that **does not pass through the origin** but intersects the shearing stress axis at particular point known as **yield value (f)**
- The **slope of the straight line in the curve** is referred to as mobility, and its reciprocal is known as plastic viscosity (U)

$$\boxed{U = \frac{F - f}{G}}$$

Pseudo plastic systems (shear thinning systems)



Dilatant systems (shear thickening systems)



- A plot of shear rate (G) versus shear stress (F) gives a curve that **begins from the origin**

An "apparent viscosity" can be obtained at any rate of shear from the slope of the tangent to the curve at the specified point

$$\eta' \text{ or } \eta_{pp} = \frac{F^N}{G}$$

$$\eta' \text{ or } \eta_D = \frac{F^N}{G}$$

The constant N:

N depend on the type of material

- N less than 1 → Dilatant flow
- N more than 1 → pseudo plastic flow
- N equals 1 → Newtonian flow

Newtonian systems

Example

Water-
Alcohol-
Glycerin-
Benzene-
Chloroform

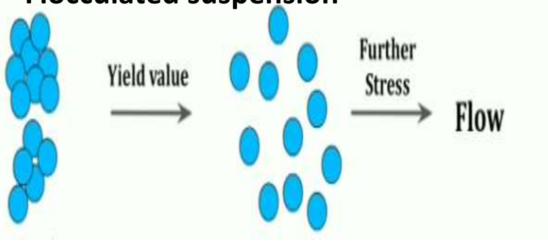
Non-Newtonian systems

Plastic systems (Bingham Bodies)

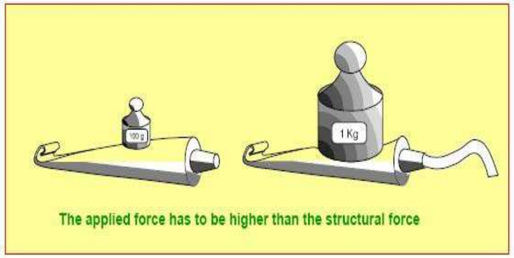
Examples:

1. Suspension of zinc oxide in mineral oils
2. Certain paints
3. Most ointments
4. Jelly
5. Tooth paste

Flocculated suspension



A certain shear stress has to be applied in order to let the sample flow



The applied force has to be higher than the structural force

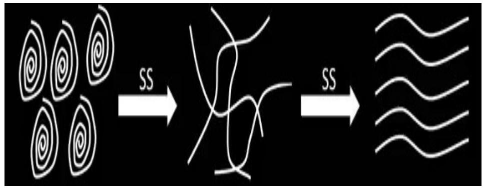
Examples:
Pastes (tomato paste, chilli paste, tooth pastes)

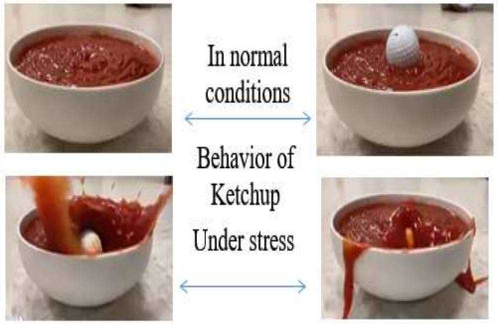
Pseudo plastic systems (shear thinning systems)

Examples:

Liquid dispersions of natural and synthetic gums such as:

1. Liquid dispersion of tragacanth
2. Sodium alginate
3. Methyl cellulose
4. Sodium carboxy methyl cellulose (Na CMC)

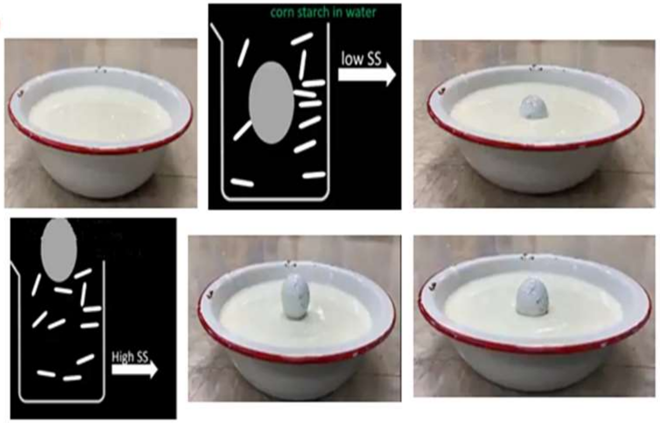




Dilatant systems (shear thickening systems)

Example

Suspensions containing a high concentration (> 50 %) of small, dispersed, **deflocculated particles**



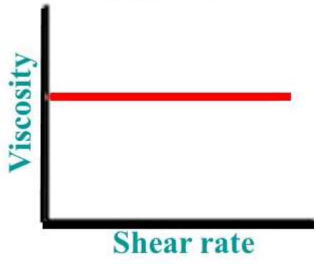
Example: a system consisting of 2:1 corn starch: water

I. Newtonian Systems

Liquids that always show the same viscosity
(same resistance to flow)at different rates of shear

A **Newtonian fluid** is a fluid that obeys Newton’s law of friction

Examples: Water-Alcohol-Glycerin-Benzene-Chloroform

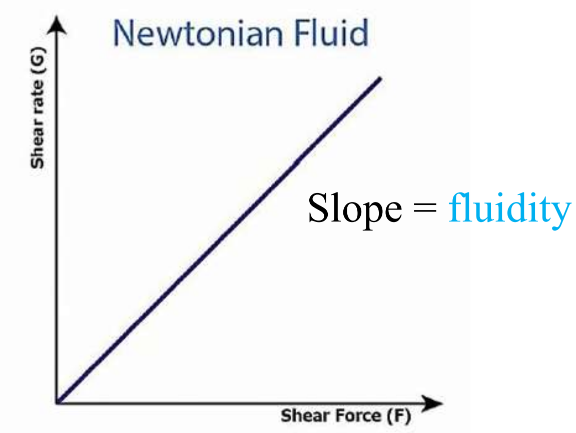


- Liquids that demonstrate Newtonian flow represent an idealized type of flow and obey Newton’s law of flow which states that: the rate of shear (G) is directly proportional to shearing force (F).

F α G

Consistency curves of Newtonian systems:

- A plot of shear rate (G) versus shear stress (F) gives **a straight line that passes through the origin**
- The **slope of the straight line** in the curve is referred to as **Fluidity** and its reciprocal is known as **viscosity** (η)



Slope = fluidity

Equation:

$$\eta = \frac{F}{G}$$

The reciprocal of viscosity is **fluidity**.

Fluidity $\phi = \frac{1}{\eta}$

The greater the slope of the line, the greater is the fluidity or, conversely, the lower is the viscosity

II. Non-Newtonian Systems

Liquids exhibit a change in viscosity upon shear stress

- A **non-Newtonian fluid** is one which does not obey Newton's law of flow (the relationship between shear rate and shear stress is not a constant)

- Such behavior is exhibited by liquid and solid heterogeneous dispersions such as colloidal solutions, emulsions, liquid suspensions, and ointments.

- There are **different** ways to deviate from Newtonian behavior, and when non-Newtonian materials are analyzed in a rotational viscometer and results are plotted, we can get **various shapes of rheograms** in which the plot does not pass through the origin or is non-linear, or both.

- Therefore we can classify flow in non-Newtonian systems to three types as:

a. Plastic flow
b. Pseudoplastic flow (shear thinning systems)
c. Dilatant flow (shear thickening systems)

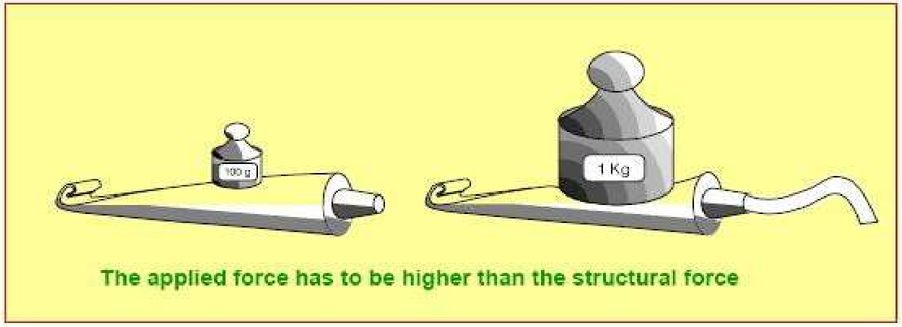
II. Non-Newtonian Systems

a. Plastic systems (Bingham bodies)

Examples:

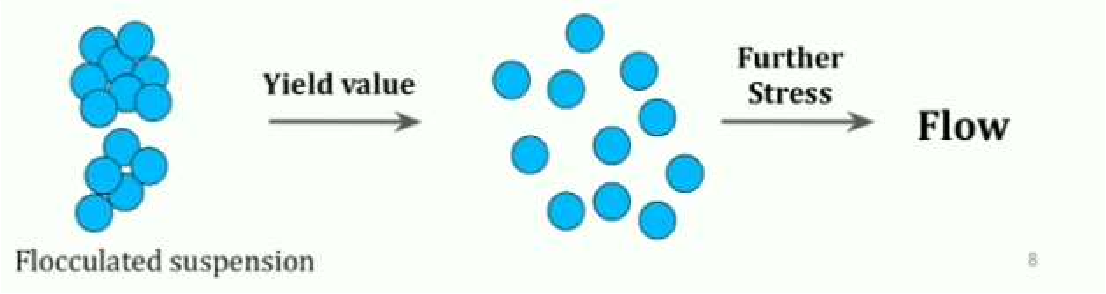
1. Suspension of zinc oxide in mineral oils
2. Certain paints
3. Most ointments
4. Jelly
5. Tooth paste

A certain shear stress has to be applied in order to let the sample flow



The applied force has to be higher than the structural force

Examples:
Pastes (tomato paste, chilli paste, tooth pastes)



Plastic flow is associated with the presence of **flocculated (aggregated) particles** in concentrated suspensions. These particles contact with each other at rest (by van der Waals forces).
When stress is applied, the interparticle contact is broken, and only above a certain value of stress applied (known as yield value), the particles get separated and behaves individually, and flow will begin.

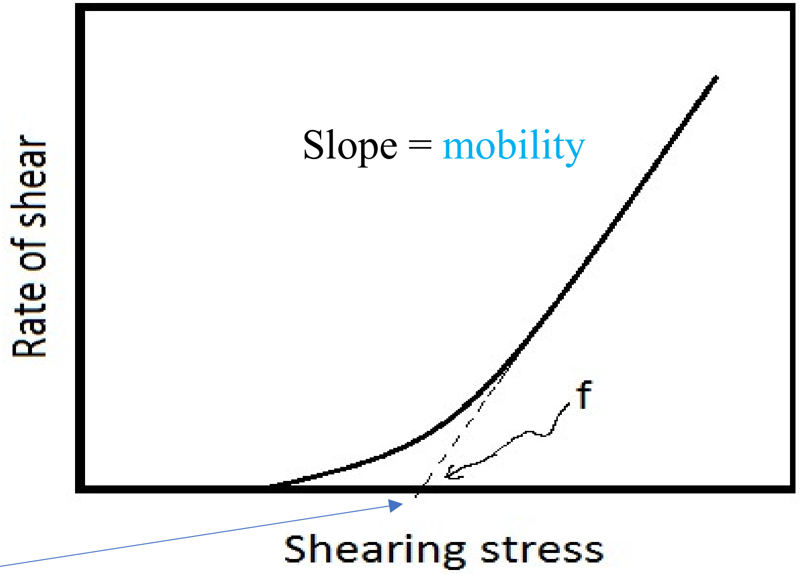
Thus, yield value is a measure of force of flocculation: the higher the yield value, the higher the flocculated is the suspension.

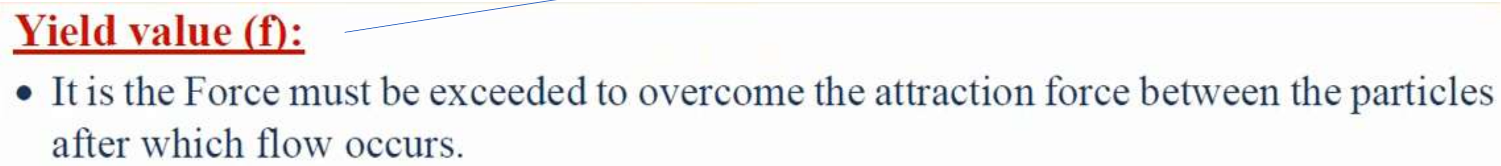
II. Non-Newtonian Systems

a. Plastic systems (Bingham bodies)

Consistency curves of plastic systems:

- The curve **does not pass through the origin** but intersects the shearing stress axis at particular point known as (**yield value (f)**)
- The flow of plastic materials occur only after application of sufficient force that exceeds the yield value
- At stresses below the yield value, the substance acts as an elastic material.
- At a value of shearing stress above the yield value, the shear stress will become directly proportional to rate of shear (i.e., the system will resemble Newtonian systems above the yield value) and flow occurs.





Yield value (f):

- It is the Force must be exceeded to overcome the attraction force between the particles after which flow occurs.

The **slope of the rheograms** in plastic flow is termed as the mobility, which is analogous to fluidity in Newtonian system, and its reciprocal is known as plastic viscosity (U)

Equation:

$$U = \frac{F-f}{G}$$

F : is the shearing stress.
G: is the shearing rate.
f : is the yield value. (dynes/cm^2)

Example:

A plastic material was found to have a yield value of 5,200 dynes/cm2. At shearing stresses above the yield value, *F* was found to increase linearly with *G*. If the rate of shear was 150 sec^{-1} when *F* was 8,000 dynes/cm2, calculate *U*, the plastic viscosity of the sample.

$$U = \frac{F - f}{G}$$

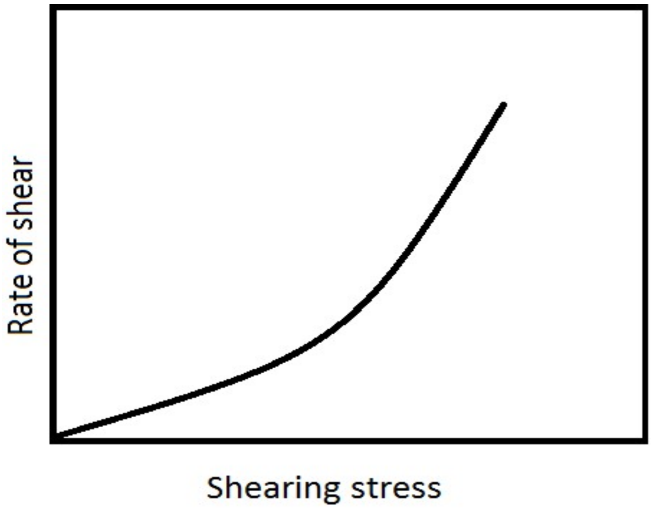
$$\begin{aligned} U &= (8{,}000 - 5{,}200)/150 \\ &= 2{,}800/150 \\ &= 18.67\ \text{poise} \end{aligned}$$

II. Non-Newtonian Systems

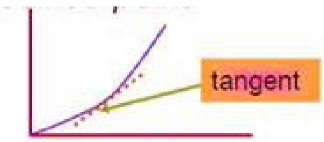
b. Pseudo plastic systems (shear thinning systems)

Consistency curves of pseudo plastic systems:

- The consistency curve for a pseudoplastic material **begins at the origin** (similar to Newtonian systems) and there is **no yield value** as there is in a plastic system
- Viscosity decrease with shearing: such systems are therefore called "shear thinning systems".



- The viscosity of the pseudoplastic material can not be expressed by any single value because no part of the curve is linear. An "apparent viscosity" can be obtained at any rate of shear from the slope of the tangent to the curve at the specified point. However, The most satisfactory representation for a pseudoplastic material, is probably a graphic plot of the entire consistency curve.



Equation:

The exponential formula can be used to compare rheology of pseudoplastic materials to be compared as follows:

$$F^N = \eta' G$$

Rearranged to →

$$\eta' \text{ or } \eta_{pp} = \frac{F^N}{G}$$

Or:

$$\log G = N \log F - \log \eta'$$

N is constant depends on the material and must be more than 1 for the system to be a pseudoplastic system
(When N = 1, the flow is Newtonian)

II. Non-Newtonian

b. Pseudo plastic systems (shear thinning systems)

Examples:

Liquid dispersions of natural and synthetic gums such as:

1. Liquid dispersion of tragacanth
2. Sodium alginate
3. Methyl cellulose
4. Sodium carboxy methyl cellulose (Na CMC)

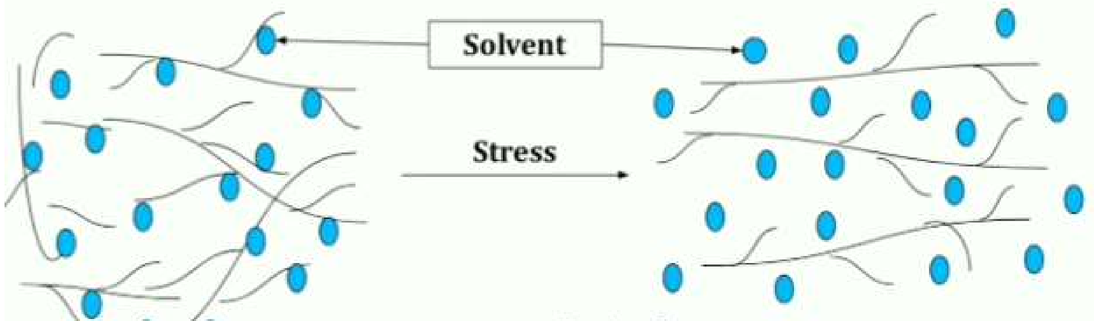
Under normal conditions the polymeric molecules are randomly arranged in dispersion.

On application of force, the molecules start to arrange in the direction of stress applied leading to a decrease in internal resistance of material and allows a greater rate of shear at each successive shearing stress.

In addition, the solvent molecules associated with the polymeric molecules will be liberated, leading to lowering of the concentration of dispersed molecules.

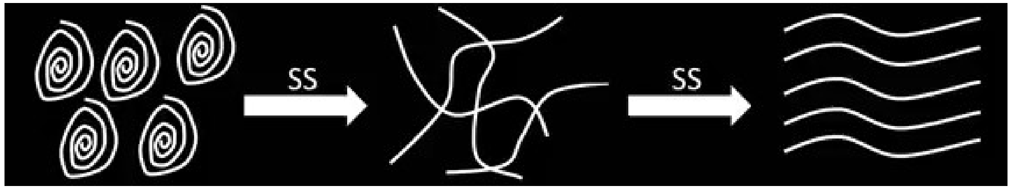
Curly hairs:
Randomly oriented hairs
Offers more resistance while comb

- Straight hairs:
- Hairs are oriented in one direction
- Offers less resistance while comb



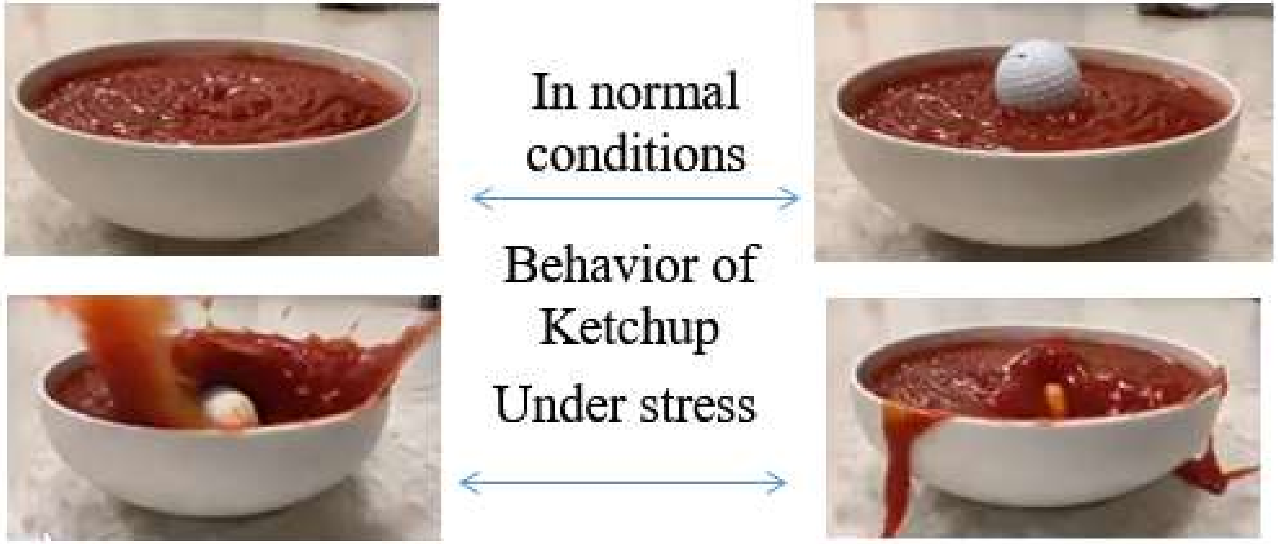
At rest:
Random arrangement & solvent is bound

During flow:
Polymer long axes align in the direction of force applied & water is released



II. Non-Newtonian Systems

b. Pseudo plastic systems (shear thinning systems)



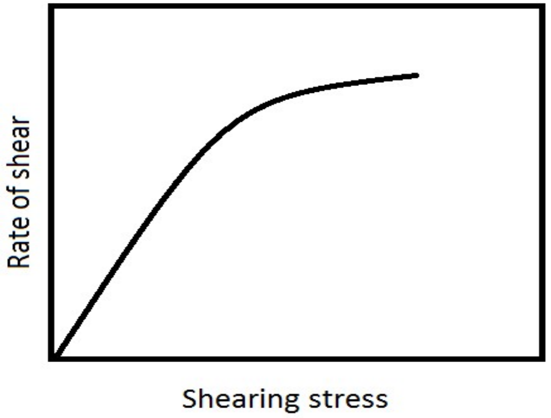
Ketchup is a shear-thinning fluid
When you throw a ball at small force, it stays on the surface,
When you mix the system and then throw a ball at high shear, it will penetrate the surface as the viscosity will be reduced
Als, when you shake a bottle of ketchup, it becomes runnier because the shaking forces the molecules to align, which reduces the viscosity.

II. Non-Newtonian Systems

c. Dilatant systems (shear thickening systems)

Consistency curves of dilatant systems:

- The consistency curve for a dilatant systems **begins at the origin** (similar to Newtonian systems) and there is no yield value as there is in a plastic system
- The type of flow is the inverse of that possessed by pseudoplastic systems
- Viscosity increase as shear increase: such systems are therefore called "shear thickening systems".



Equation:

The exponential formula can be used to describe dilatancy quantitatively and compare rheology of dilatant materials to be compared as follows:

$$F^N = \eta' G \xrightarrow{\text{Rearranged to}} \eta' \text{ or } \eta_D = \frac{F^N}{G}$$

N is constant depends on the material and must be less than 1 for the system to be a pseudoplastic system
(When N = 1, the flow is Newtonian)

$$F^N = \eta \, 'G$$

The constant N:

N depend on the type of material

- N less than 1 → Dilatant flow
- N more than 1 → pseudo plastic flow
- N equals 1→ Newtonian flow

II. Non-Newtonian Systems

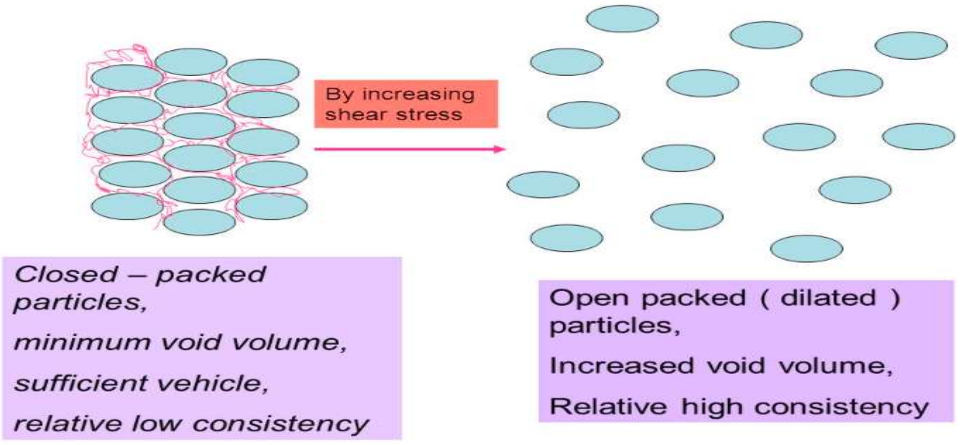
c. Dilatant systems (shear thickening systems)

Example:

Suspensions containing a high concentration (about 50 % or greater) of small, dispersed, **deflocculated particles**

- **Normally:** particles are closely packed with minimal interparticle volume (void). The amount of vehicle is sufficient to fill the voids and permits particles to move relative to one another at low rate of shear. Thus, a dilatant suspension can be poured from a bottle because under these conditions it is reasonably fluid.
- **As shear stress is increased:** the particles, in an attempt to move quickly past each other, take an open form of packing which leads to a significant increase in interparticle void volume. The amount of vehicle remains constant and at some point, it becomes insufficient to fill the increased voids between particles and particles are no longer completely wetted by the vehicle.

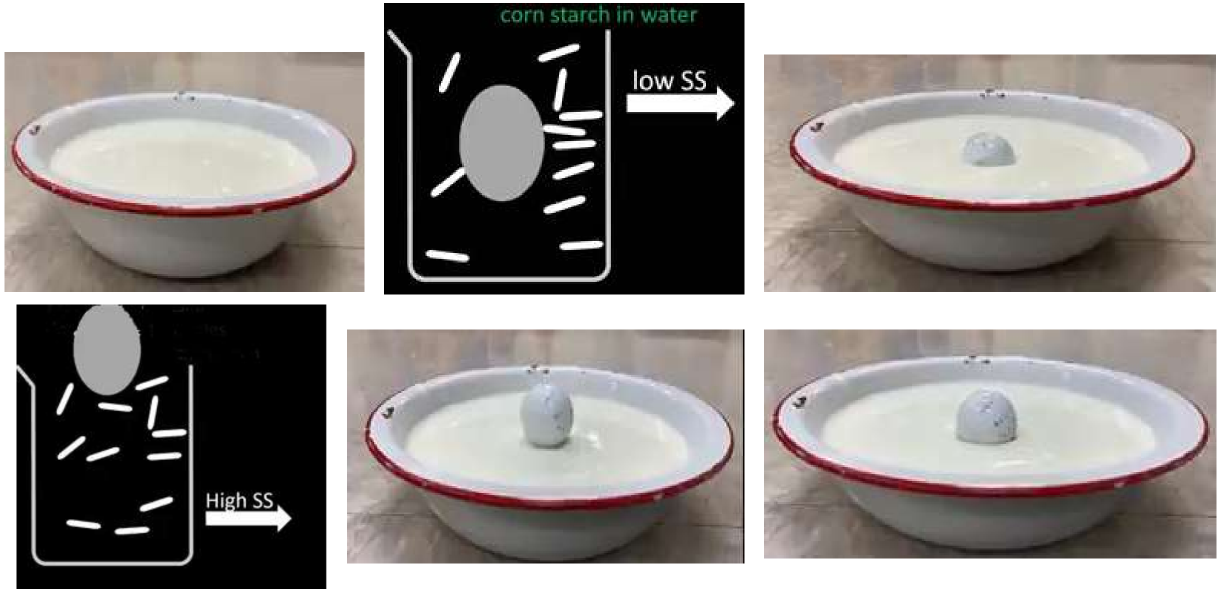
  The system actually increases in volume (and are hence termed dilatant) and the **resistant to flow will increase** and eventually the suspension will set up as firm paste.
- **When stress is removed**, a dilatant system returns to its original state of fluidity.



Caution:
Dilatant materials may solidify during mixing and milling under high shear, thereby overloading and damaging processing equipment.

II. Non-Newtonian Systems

c. Dilatant systems (shear thickening systems)



Examples:

A system consisting of
2:1 corn starch: water

When you throw a ball at low shear stress, the system initially has low viscosity and most of the ball will be immersed in the liquid.

When you mix the system and then throw a ball at high shear, the system will have high viscosity and the ball will not be immersed but remain on the surface mainly because of the high viscosity of the system.

Another example: Quicksand is a dilatant fluid. When you step on quicksand, it becomes more difficult to walk through because the grains of sand pack together and create more resistance

Physical pharmacy II

By:
Asst. Professor
Lena M. Thomas

Part 3

Rheology

In this lecture, you'll learn:

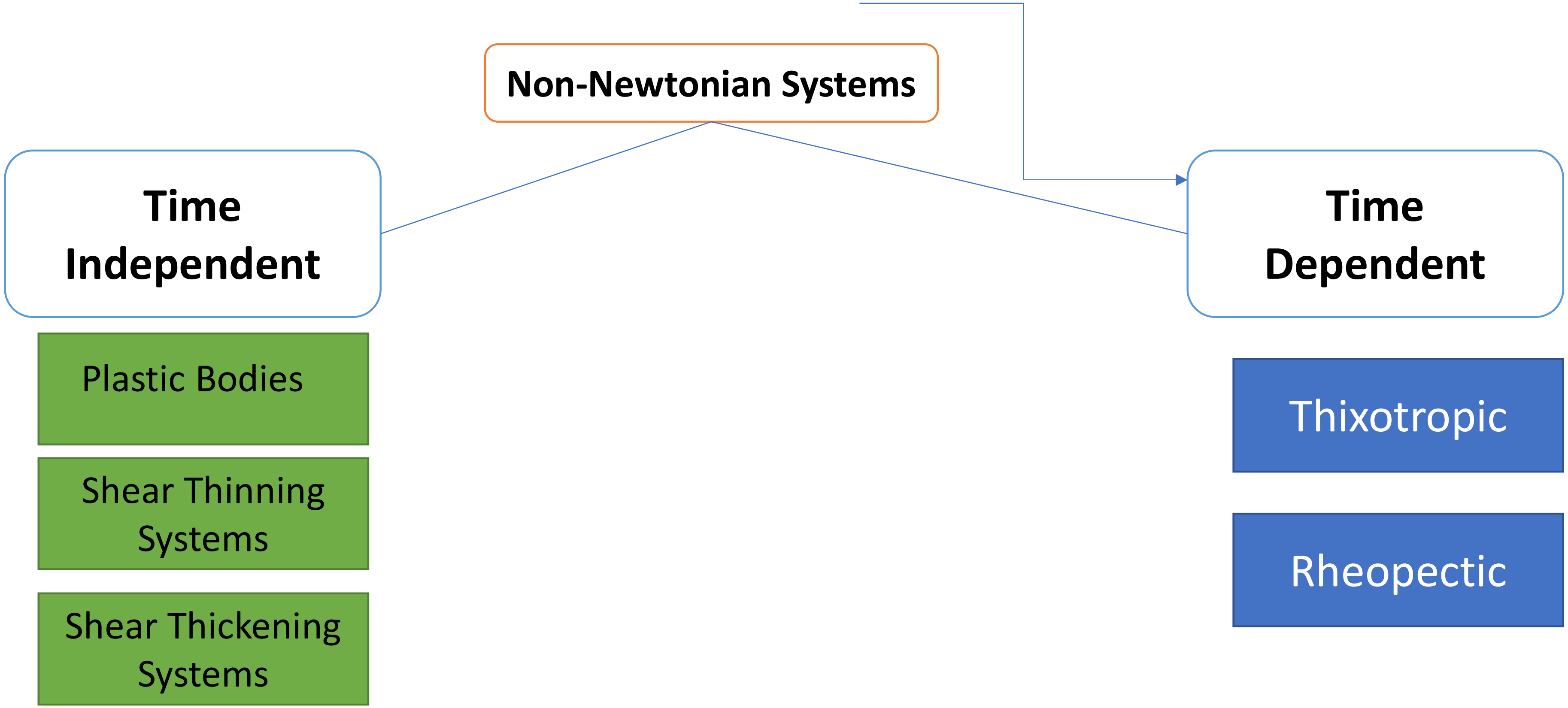
Time dependent classification of Non-Newtonian systems:

- Thixotropic and rheopectic systems

Time-dependent viscosity

Time-dependent viscosity is a property of fluids whose viscosity changes as a function of time.

Depending upon the response of a material to shear over a period of time, it is customary to sub-divide time-dependent fluid behavior into two types, namely, thixotropy and rheopexy.



Non-Newtonian Systems

Time Independent

- Plastic Bodies
- Shear Thinning Systems
- Shear Thickening Systems

Time Dependent

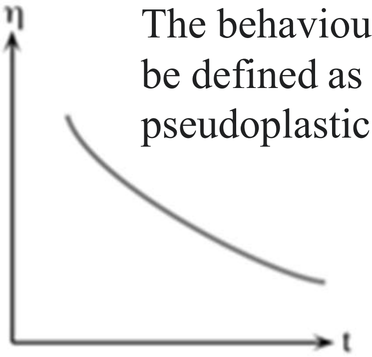
- Thixotropic
- Rheopectic

THIXOTROPY and RHEOPEXY

Thixotropy and rheopexy are two properties exhibited by **certain non-Newtonian fluids**,
whose viscosity changes over time under applied shear stress.
Once the stress is removed, the fluid regains its original viscosity over time,
as the internal structure rebuilds itself

Thixotropy is the more common of the two.

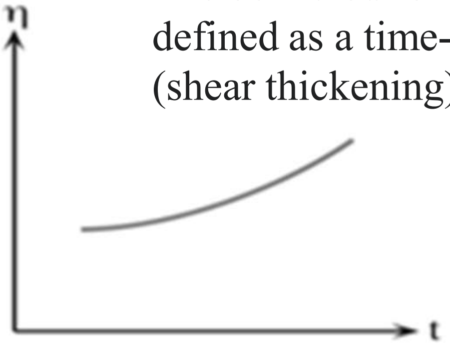
Thixotropy



The behaviour of thixotropic fluids can be defined as a time-dependent pseudoplastic (shear thinning) behaviour.

In thixotropic fluids, the **viscosity** of the fluid **decreases** with **stress over time**
(a thixotropic fluid becomes thinner and flows more easily the more it is stressed or agitated)

Rheopexy (also called Rheopecty)



The behaviour of rhopectic fluids can be defined as a time-dependent dilatent (shear thickening) behaviour.

In rheopectic fluids, the **viscosity** of the fluid **increases** with **stress over time**.
(a rheopectic system thicken or solidify when shaken or agitated; the longer it undergo a shearing force, the higher the viscosity becomes)

ملاحظة: سيكون التركيز في الشرح على الظاهرة الاكثر شيوعا وهي الThixotropy

Thixotropy, can be defined as "an isothermal and comparatively slow recovery, on standing of a material, of a consistency lost through shearing."

In simpler terms, a thixotropic fluid becomes thinner and flows more easily the more it is stressed or agitated. Once the stress is removed, the fluid regains its original viscosity over time, as the internal structure rebuilds itself.

It refers to the time-dependent decrease in viscosity of a fluid when it experiences shear stress (agitation, shaking, or stirring).

Ketchup is a good example of a thixotropic substance. It does not flow even when the bottle is held upside down.

However, when the bottle is struck (vibrated), the ketchup temporarily liquefies and flows.

Once the vibration stops, the ketchup returns to its original viscous state.

Thixotropic systems

Examples

- **Suspensions, emulsions, protein solutions**
- **Ketchup:** When undisturbed, ketchup appears thick and ketchup. But when you shake the bottle, it flows more easily.
- **Honey:** Honey also exhibits thixotropy. Pure honey will flow more easily if you stir it.
- **Toothpaste:** Toothpaste is formulated to be thixotropic. This makes it easy to dispense from the tube but keeps it from oozing out.
- **Paint:** Many paints are thixotropic. When left sitting in the can they are viscous. Stirring them reduces their viscosity and allows them to be easily applied to a brush or roller. After stirring is stopped, they become thicker preventing them from running or dripping after application.

Rheopectic systems

- **Certain slurries:** Concentrated suspensions of clay, gypsum pastes or cement.
- **Lubricants**
- **Printer inks**
- **Body armor and combat vehicle armor** are key areas where efforts are being made to use rheopectic materials.

Both thixotropy and rheopexy have important applications in various industries

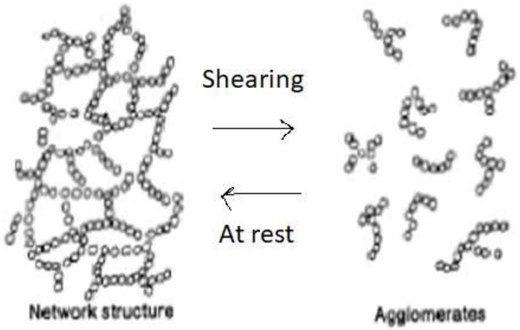
Thixotropy is desirable in liquid preparations:
A suspension or an emulsion, for example, could be in a settled form in a container, in viscous state, but when sheared for certain time, it will have sol-like properties and will flow and is easily dispensed. When shear is removed, the product re-settle in the container

Rheopectic properties can be useful in applications where a fluid needs to thicken under shear stress, such as in some types of coatings.

Thixotropy

Gel → Sol → Gel

- **At rest:** Systems showing thixotropic behavior usually contain **asymmetric particles** that through numerous points of contact set up a **loose three dimensional network** throughout the sample. Such structure confers **some degree of rigidity** on the system and it **resembles a gel** when it is at rest for a period of time (increase in viscosity).



Particle interaction in thixotropic dispersions

- **If sufficient shear stress is exerted** (e.g., shaken, agitated), the structure is broken (viscosity is reduced) and the material undergoes a **gel-to-sol transformation**
- **On removal of shear stress applied after certain time**, there is **slow recovery** of a consistency or viscosity (**sol-to-gel transformation**) and regain its consistency (return to their initial viscous state). This occurs because **asymmetric particles come into contact with each other** by undergoing random Brownian movement restoring the consistency of the system and does not reform immediately when stress is removed or reduced

Rheopexy

Sol → Gel → Sol

Rheopectic fluids, when shaken gently (i.e, under influence of shear stress), the rocking motion will cause randomly arranged particles or molecules to align or aggregate, leading to an increase in viscosity and the sol forms a gel more readily when gently shaken than when allowed to form the gel if it is kept at rest.

How can you detect thixotropic/rheopectic behavior ?

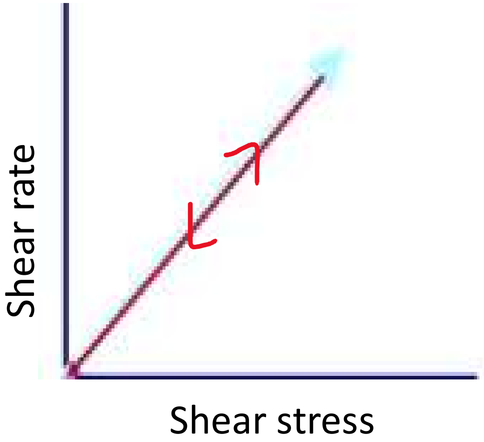
Thixotropic/rheopectic systems show **hysteresis loops** when shear rate is plotted against shear stress (thus, hysteresis loops is the area between the upcurve and down curve of rheograms)

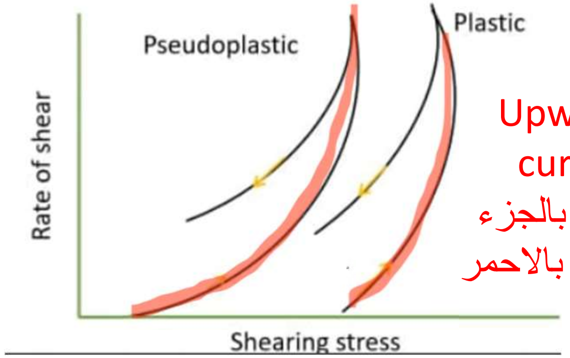
When we apply a gradually increasing shear rate for certain time and record the resulting shear stress, then decrease the shear rate back to zero and observe the behavior, the resulting graph wouldn't be a simple straight line or curve but instead, it would form a loop.

Note

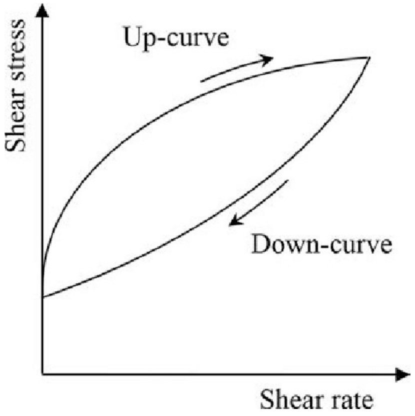
For Newtonian systems, the down curve would be identical with, and superimposable on the up curve

No hysteresis loop is observed, that is, the enclosed area of the loop is zero





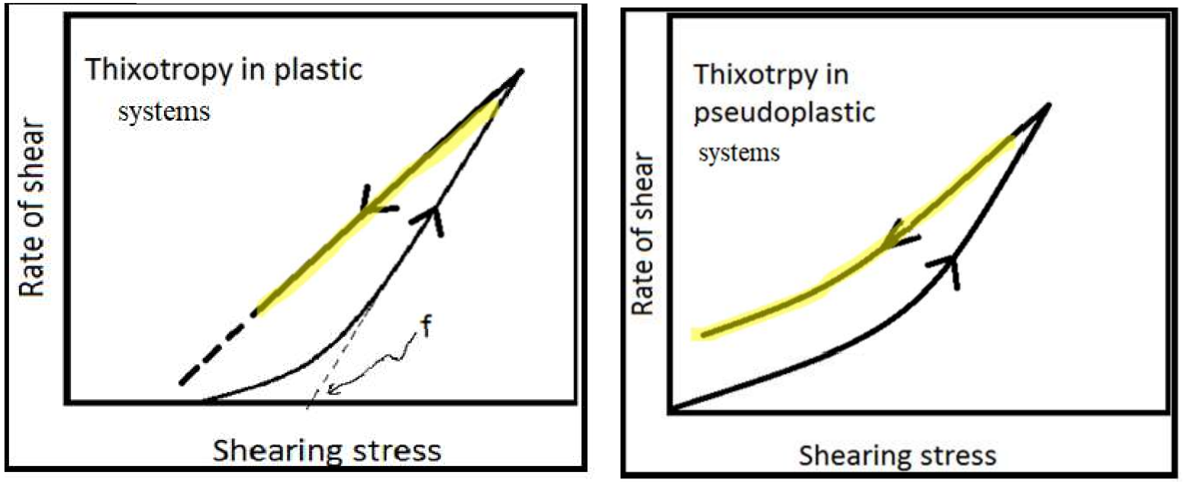
Upward curve
متمثل بالجزء المؤشر بالاحمر



للاطلاع:
الرسم هنا وضع مسميات المحاور بالتعاكس فاصبح الرسم بالعكس

How can you detect thixotropic/rheopectic behavior ?

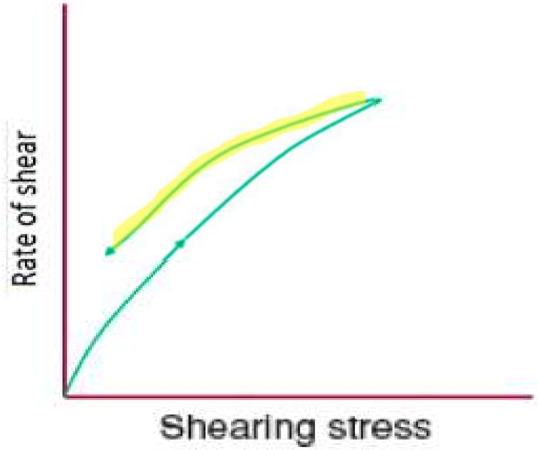
Thixotropy Rheogram or Flow Curve



At rest — At equilibrium — At rest

Gel → Applied Shear → Sol → Shear removal → Gel

Rheopexy Rheogram or Flow Curve



At rest — At equilibrium — At rest

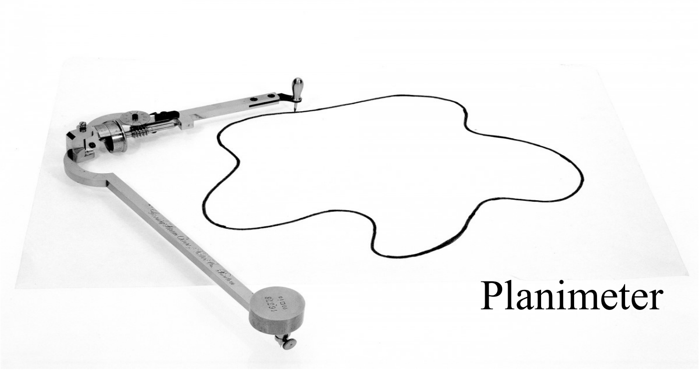
Sol → Applied Shear → Gel → Shear removal → Sol

The down curve is not superimposed on up curve but is frequently displaced to the left of the up curve showing that the material has a lower consistency (lower shear stress) at any one rate of shear on the down curve than it had on the upcurve.

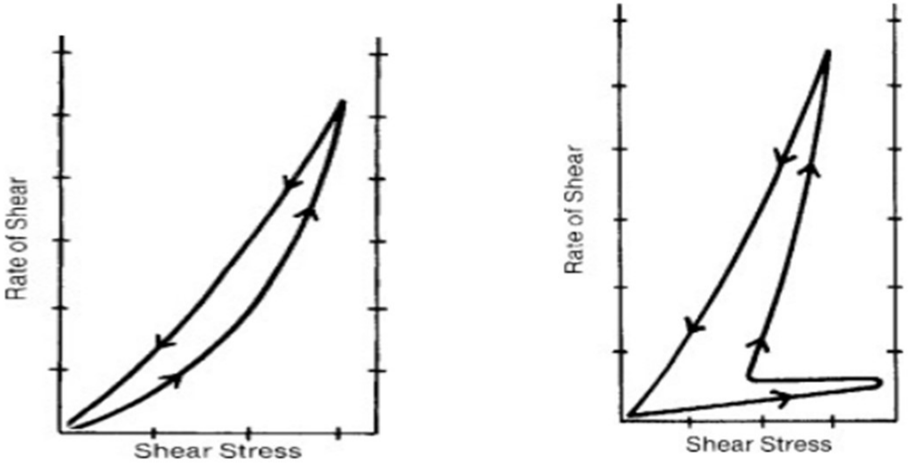
Thixotropic flow is type of non-Newtonian, shear-thinning flow but the changes observed occur in a time-dependent manner (only after a measurable time interval which can range from fractions of a second to hours), rather than instantaneously.

Measurement of Thixotropy

- Rheograms are used to obtain a quantitative measure of thixotropy.
- The area of hysteresis has been proposed as a measure of thixotropic breakdown; it can be obtained readily by means of a planimeter or other suitable technique.



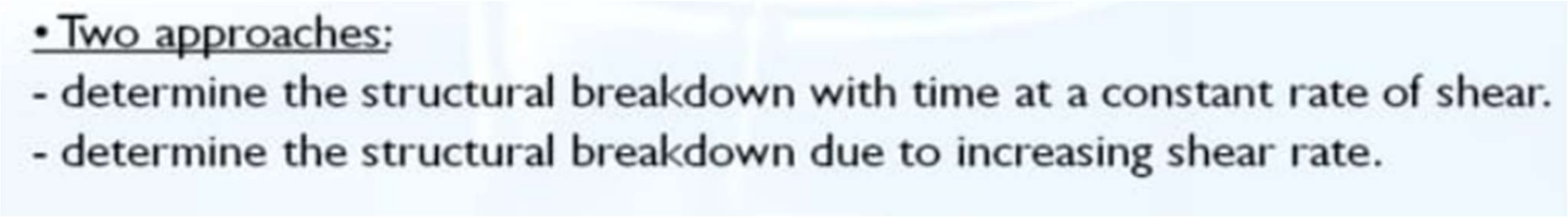
Planimeter



- It is important to remember that the rheogram of a thixotropic material is not unique and the degree of thixotropy is a function of:
    - **the degree of structure in the sample** (degree of substitution of polymer, concentration of polymer).
    - **rheologic history of the sample :** it is highly dependent on the rate at which shear is increased or decreased, as well as the length of time a sample is subjected to any one rate of shear
    - **Approach used in obtaining the rheogram**.

Measurement of Thixotropy

With plastic (Bingham) bodies, to estimate degree of structural breakdown with time we have:



- Two approaches:

- determine the structural breakdown with time at a constant rate of shear.
- determine the structural breakdown due to increasing shear rate.

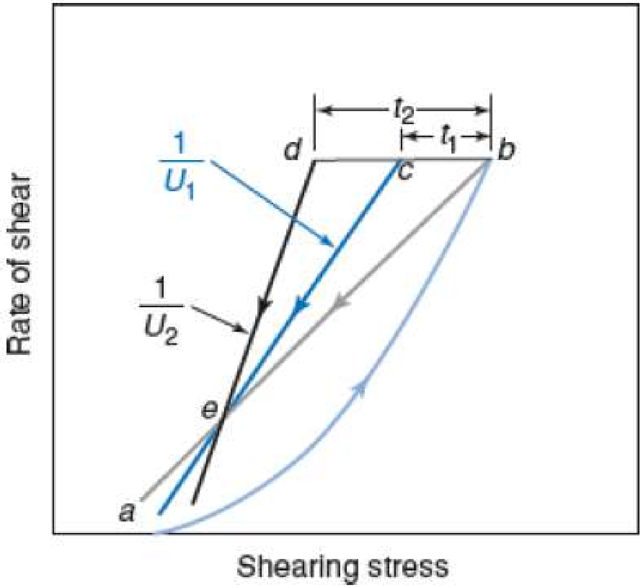
Limitations

-Does not take into account the shape of up-and down curves

-Two different materials may have loops of similar area and will have different flow behavior due to different shapes

Measurement of Thixotropy

Approach 1: determine structural breakdown with time at a *constant* shear rate (the choice of shear rate is arbitrary).



Suppose that the shear rate of a thixotropic material is increased in a constant manner from point *a* to point *b* and is then decreased at the same rate back to *e.*
Typically, this would result in the so-called *hysteresis loop abe.*

If, however, the sample was taken to point *b* and the shear rate held constant for a certain period of time (say, t_1 seconds), shearing stress, and hence consistency, would decrease to an extent depending on time of shear, rate of shear, and degree of structure in the sample.

Decreasing the shear rate would then result in the *hysteresis loop abce.* If the sample had been held at the same rate of shear for t_2 seconds, the loop *abcde* would have been observed

Based on a rheograms obtained for a plastic system to which **stress is applied at certain rate and time and then removed**, a **thixotropic coefficient, *B*,** the rate of breakdown with time at constant shear rate, is calculated as follows:

$$B = \frac{U_1 - U_2}{\ln \frac{t_2}{t_1}}$$

where U_1 and U_2 are the **plastic viscosities** of the two down curves, calculated from equation after shearing at a constant rate for t_1 and t_2 seconds, respectively.

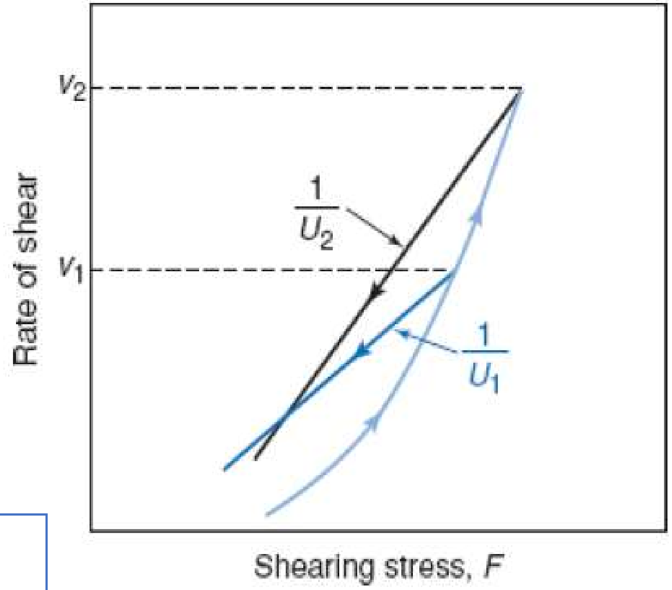
$$U = \frac{F - f}{G}$$

Measurement of Thixotropy

Approach 2: determine the structural breakdown due to *increasing* shear rate.

This is a more meaningful, though time-consuming method for characterizing thixotropic behavior, and involves measuring fall in stress with time at several rates of shear.

In this case, two hysteresis loops are obtained having different maximum rates of shear, v_1 and v_2.



In this case, a **thixotropic coefficient, M**, the loss in shearing stress per unit increase in shear rate, is obtained from:

$$M = \frac{U_1 - U_2}{\ln(v_2/v_1)}$$

where M is in dynes sec/cm^2 and U_1 and U_2 are the plastic viscosities for two separate down curves having maximum shearing rates of v_1 and v_2, respectively.

A criticism of this technique is that the two rates of shear, v_1 and v_2, are chosen arbitrarily; the value of M will depend on the rate of shear chosen because these shear rates will affect the down curves and hence the values of U that are calculated.

وزارة التعليم العالي والبحث العلمي
جامعة بغداد University of Baghdad
كلية الصيدلة COLLEGE OF PHARMACY
1936

Physical pharmacy II

By:
Asst. Professor
Lena M. Thomas

Part 4

Rheology

In this lecture, you'll learn:

- Negative Thixotropy
- Types of viscometers and choice of viscometer

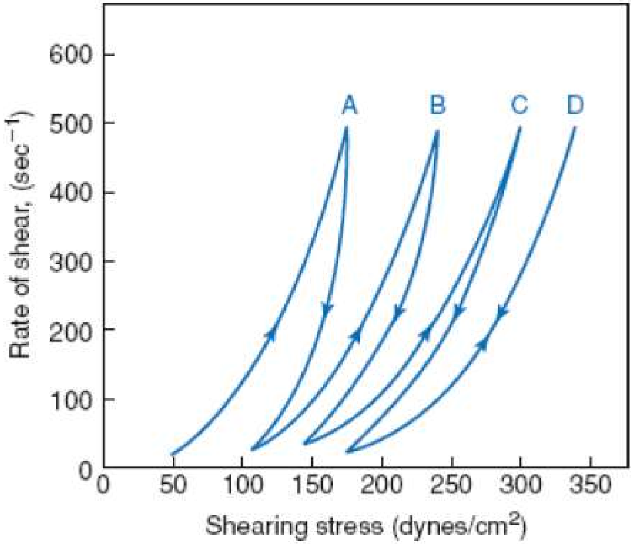
Negative Thixotropy (anti-thixotropy)

Is a phenomena of **increase in thickness (viscosity)** or resistance to flow **with increase in time of shear**, followed by a **gradual recovery** when the shear is removed

Example: such behavior was observed with clay suspensions and **magnesia magma.**
It was detected at shear rates of greater than 30 sec^{-1}; below 30 sec^{-1} the magma showed normal thixotropy.

In rheograms, there is an increase rather than a decrease in consistency on the down curve (shifting of the down curve to the right)

When this system was alternately sheared at repeated increasing and then at decreasing rates of shear, the magma continuously thickened (an increase in shearing stress per unit shear rate) but at a decreasing rate, and it finally reached an equilibrium state in which further cycles of increasing–decreasing shear rates no longer increased the consistency of the material (seen at point D in the rheograms) and the upcurves and down curves coincided.



Negative Thixotropy (anti-thixotropy)

Antithixotropy **results from an increased collision frequency** of dispersed particles or polymer molecules in suspension, **resulting in increased interparticle bonding with time**. This **changes an original state** consisting of a large number of individual particles and **small floccules** to an eventual **equilibrium state consisting of a small number of relatively large floccules**. At rest, the large floccules break up and gradually return to the original state of small floccules and individual particles.

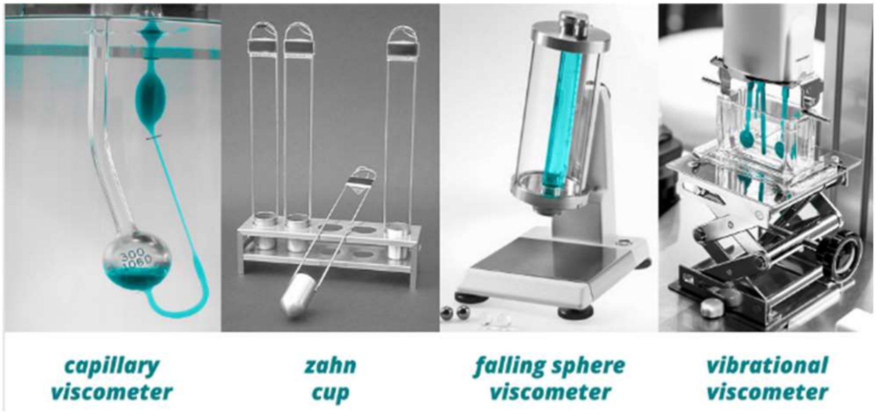
Note:

Anti-thixotropy or negative thixotropy should not be confused with dilatancy or rheopexy.

- Dilatant systems are deflocculated suspensions and ordinarily contain greater than 50% by volume of solid dispersed phase, whereas anti-thixotropic systems have low solids content (1% to 10%) and are flocculated suspensions
- In a rheopectic system, the gel is the equilibrium form, whereas in antithixotropy, the equilibrium state is the sol.

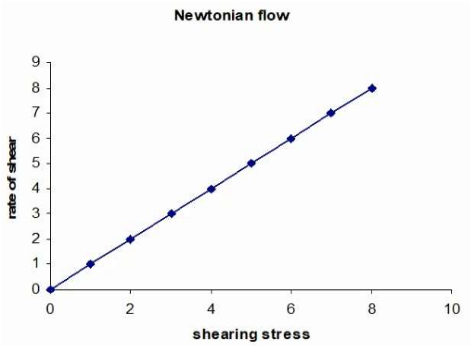
Measurement of Viscosity and Choice of Viscometer

- There are many different ways to measure viscosity. Each method corresponds to a particular type of system and requires certain type of viscometer.
- Successful determination and evaluation of rheologic properties of any particular system depend, in large part, on choosing the correct instrumental method.
- Factors that influence the viscosity measurement are **temperature**, **time**, and **shear stress**



“Single-point” instruments

- Application: Newtonian systems.
- Uses single rate of shear.
- Provide one point on the rheograms; extrapolation of a line through this point to the origin will result in a complete rheogram.



Equipment:

1) Capillary viscometers.
2) Falling sphere viscometer.

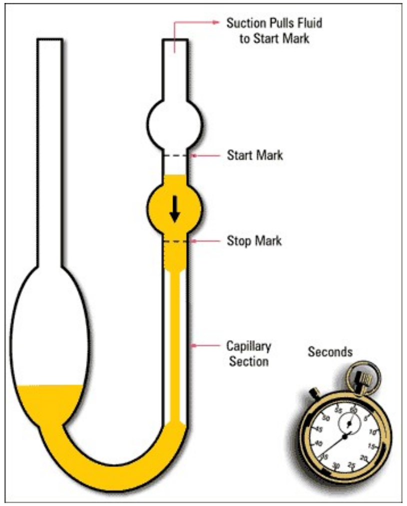
“Multi-point” instruments

- Application: Newtonian and non-Newtonian systems
- Uses several rates of shear.
- Provide many points on the viscosity curve will result in a complete rheograms
- Viscometers that can characterize non-Newtonian fluids are usually called rheometers. There distinctively different types of rheometers:

❑ Rotational (shear rheometers): Measures the flow behavior of a material under rotational shear stress or shear rate.

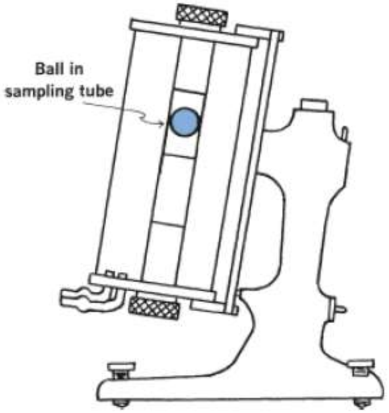
❑ Extensional (elongational) rheometers: Measures the flow behavior of a material under elongational stress or strain.

“Single-point” instruments



Capillary Viscometers (U-tube viscometers)

viscosity is measured by timing how long it takes the fluid to pass through the tube



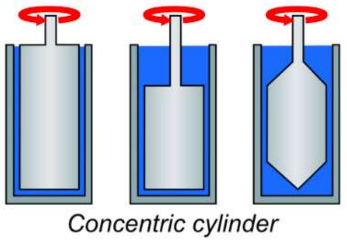
Falling-Sphere (falling ball) Viscometer

viscosity is measured by timing how long it takes a stainless steel ball to pass through the liquid in the tube

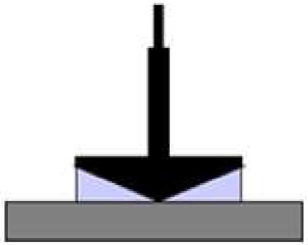
“Multi-point” instruments

Rotational rheometers

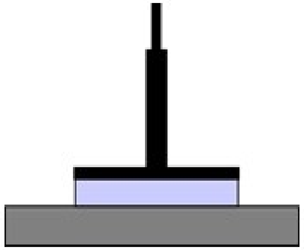
Continuous shear produced by rotational viscometers does not keep the material being tested in its rheologic “ground state” but yields large deformation and alteration of the material during measurement.



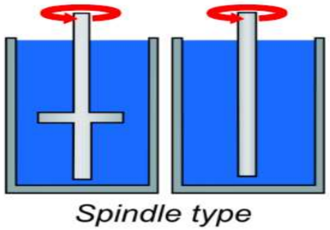
Cup-and-Bob rheometer (Concentric cylinder rheometer)



Cone and plate rheometer



Parallel plates rheometer



Spindle rheometer

“Multi-point” instruments

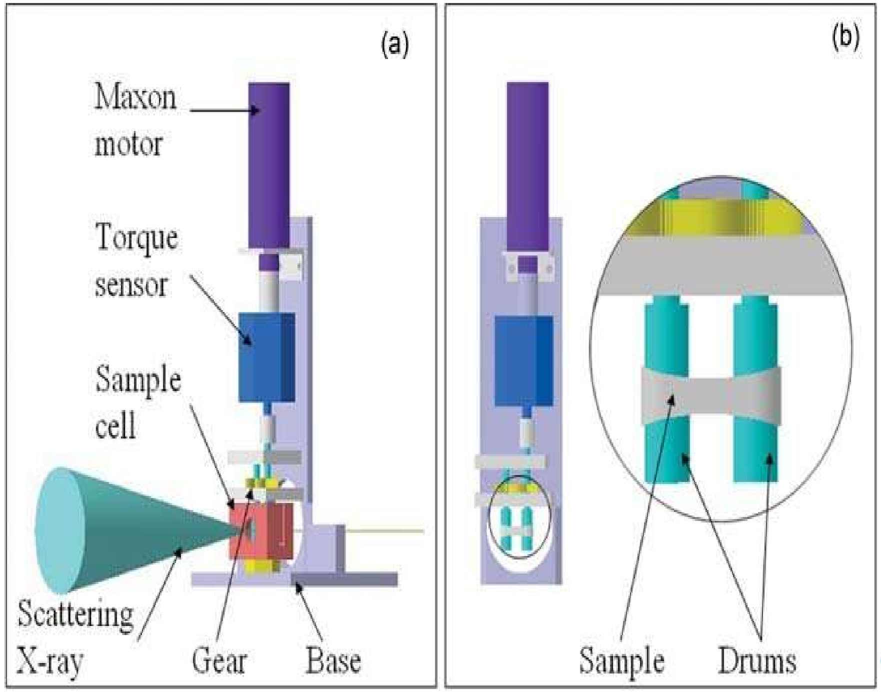
للاطلاع فقط

Extensional (elongational) rheometers

The Capillary Breakup Extensional Rheometer (CaBER) is the only commercially available rheometer for measuring extensional properties

Complex flows that contain strong extensional components occur in many industrial processes and applications.

Some examples are extrusion flows, coating flows, contraction flows and fiber spinning flows.

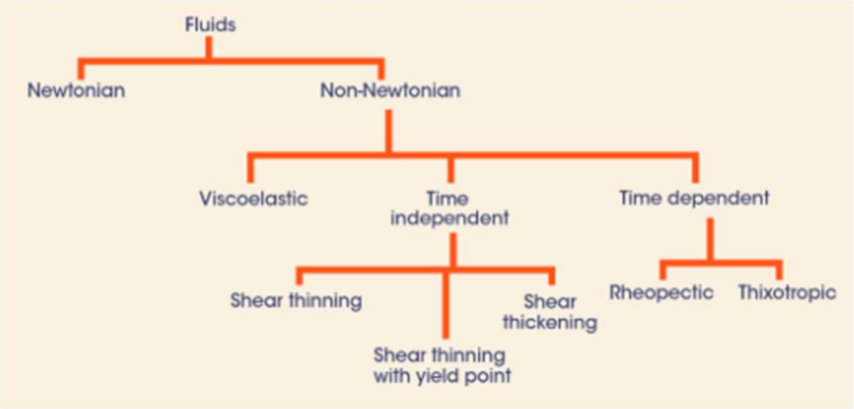


Three-dimensional view of the extensional rheometer

Viscoelasticity, Viscoelastic materials and measurement of their viscosity

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation

- There are many biological materials that exhibit viscoelastic properties, such as blood, cervical fluid, sputum, tissue, skin and cartilage.
- Many of the systems studied in pharmacy belong to this class, examples being creams, lotions, ointments, suppositories, suspensions, and the colloidal dispersing, emulsifying, and suspending agents



Viscous materials, like honey or syrup, resist shear flow and when stress is applied, they strain linearly with time

Elastic materials, like rubber bands, strain when stretched and immediately return to their original state once the stress is removed

Viscoelastic materials behave both like a liquid and a solid and that it has a time-dependent strain.

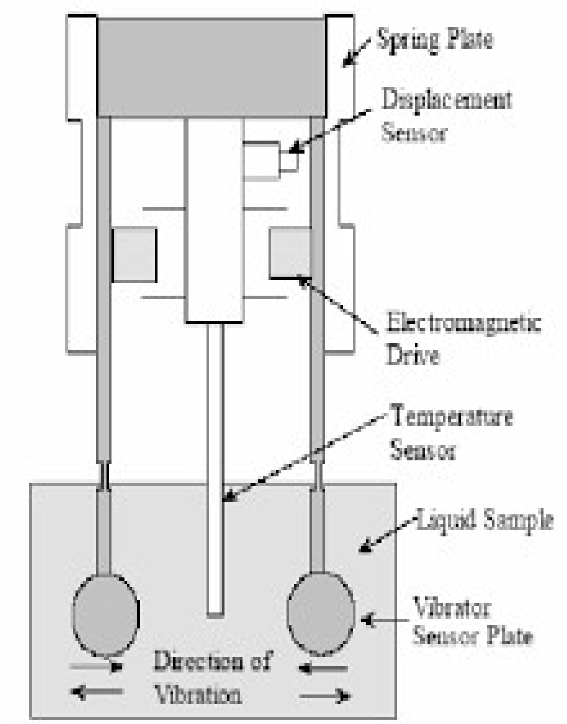
Vibrational (oscillatory) rheometers:

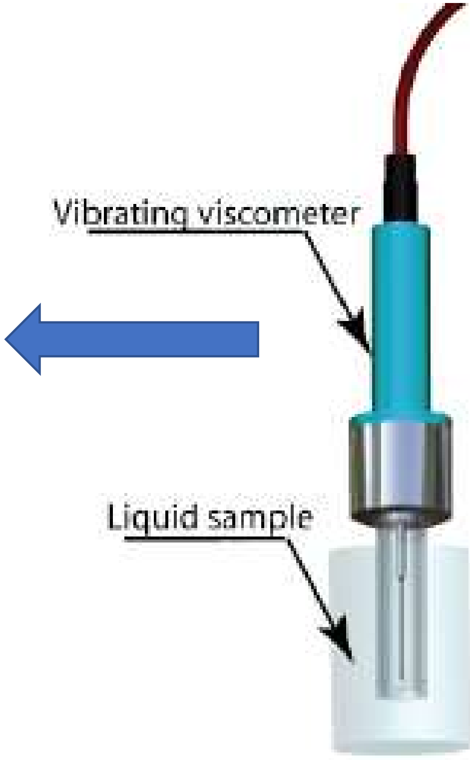
Measures the response of a material to a small, oscillating shear stress or strain.

It operates by measuring the damping of an oscillating electromechanical resonator immersed in a fluid whose viscosity is to be determined.

Scheme and physical principle of the vibrational viscometer

للاطلاع فقط





Vibrational viscometer operates by measuring the damping of an oscillating electromechanical resonator immersed in a fluid whose viscosity is to be determined.
The resonator generally oscillates in torsion or transversely (as a cantilever beam or tuning fork).
The higher the viscosity, the larger the damping imposed on the resonator.

University of Baghdad
College of Pharmacy
1936

Physical pharmacy II

COLLOIDAL DISPERSIONS

Part 1

By:
Asst. Professor
Lena M. Thomas

Colloidal Dispersions

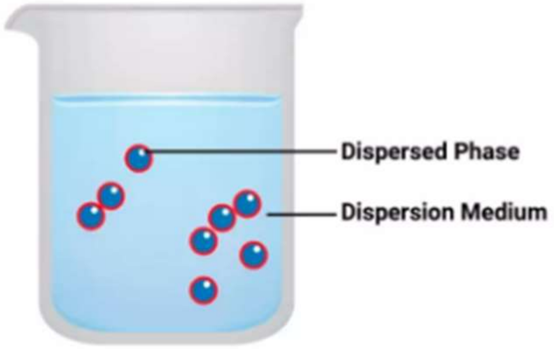
In this lecture, you'll learn:

- Definition and types of dispersed systems
- Characteristics of dispersed systems
- Classification of colloidal dispersions

Dispersed Systems

- Dispersed systems consist of particulate matter, known as the dispersed phase, distributed throughout a continous or dispersion medium.

- The dispersed material may range in size from particles of atomic & molecular dimensions to particles whose size is measured in millimeters.

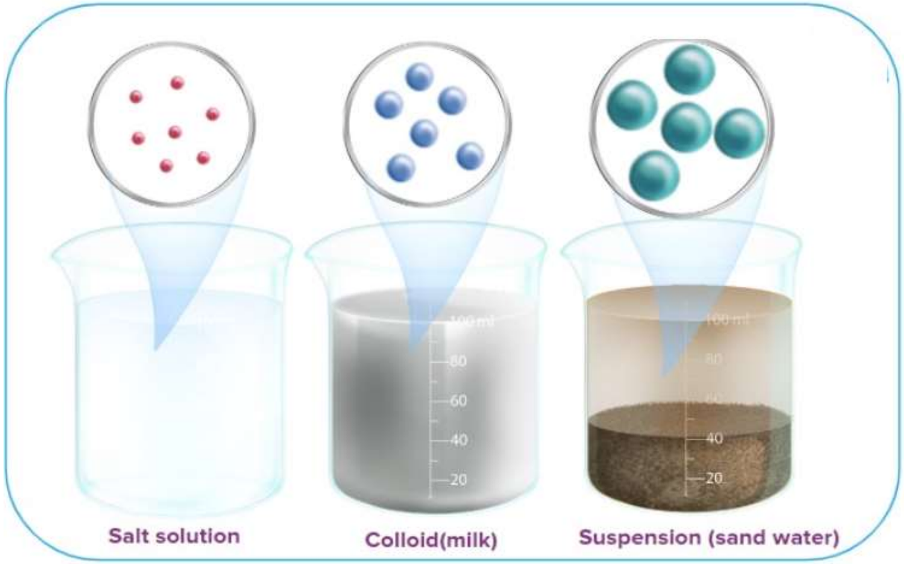


Classification of dispersed systems

(on the basis of the mean particle size of the dispersed material)

There are three kind of Dispersed Systems:

1. Molecular
2. Colloidal
3. Coarse

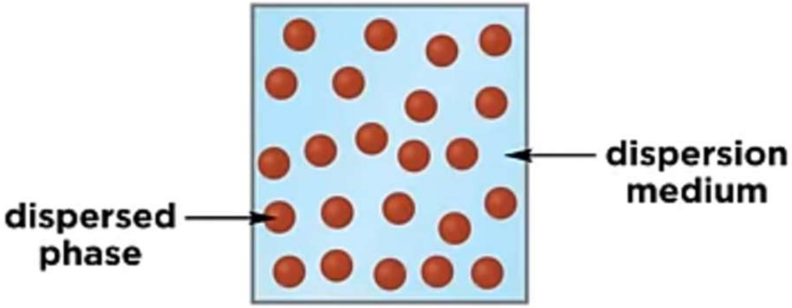


Colloid: type of mixture that falls between homogenous and heterogeneous systems

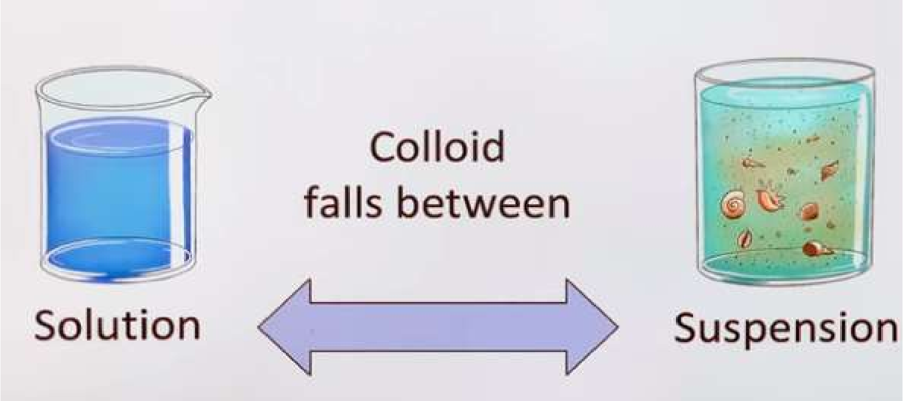
It is a **heterogenous system** consisting of 2 phases:

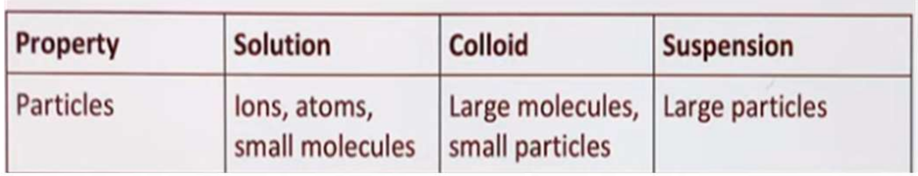
- Dispersed phase of colloidal particles
- Dispersion medium

components of a colloid



these can both be of **any phase**





Property	Solution	Colloid	Suspension
Particles	Ions, atoms, small molecules	Large molecules, small particles	Large particles

solution

salt in water

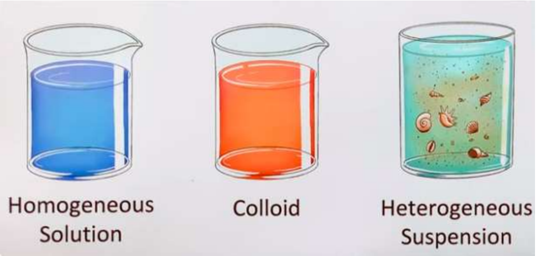
colloid

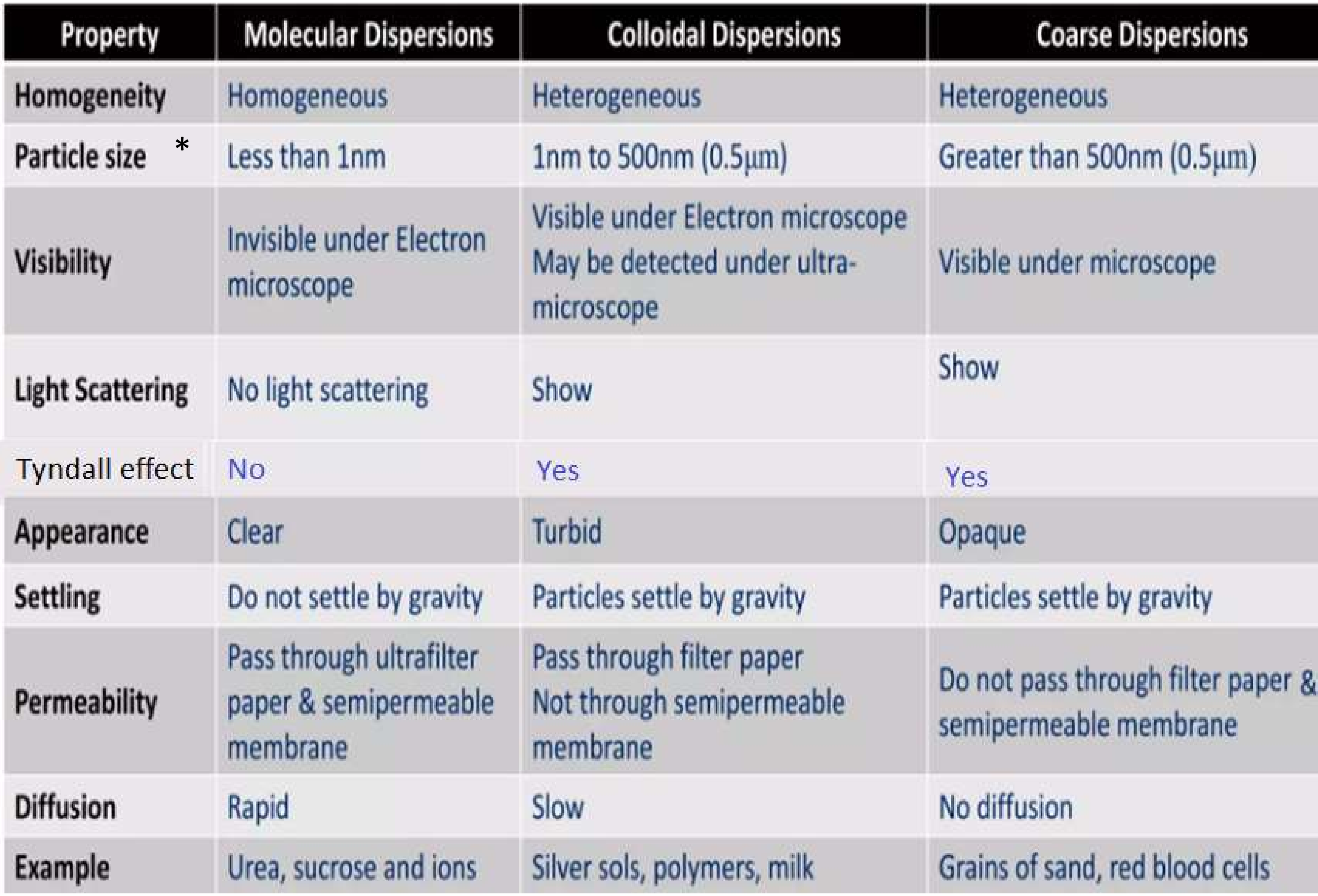
milk

suspension

mud in water

Properties or characteristics of Dispersed Systems

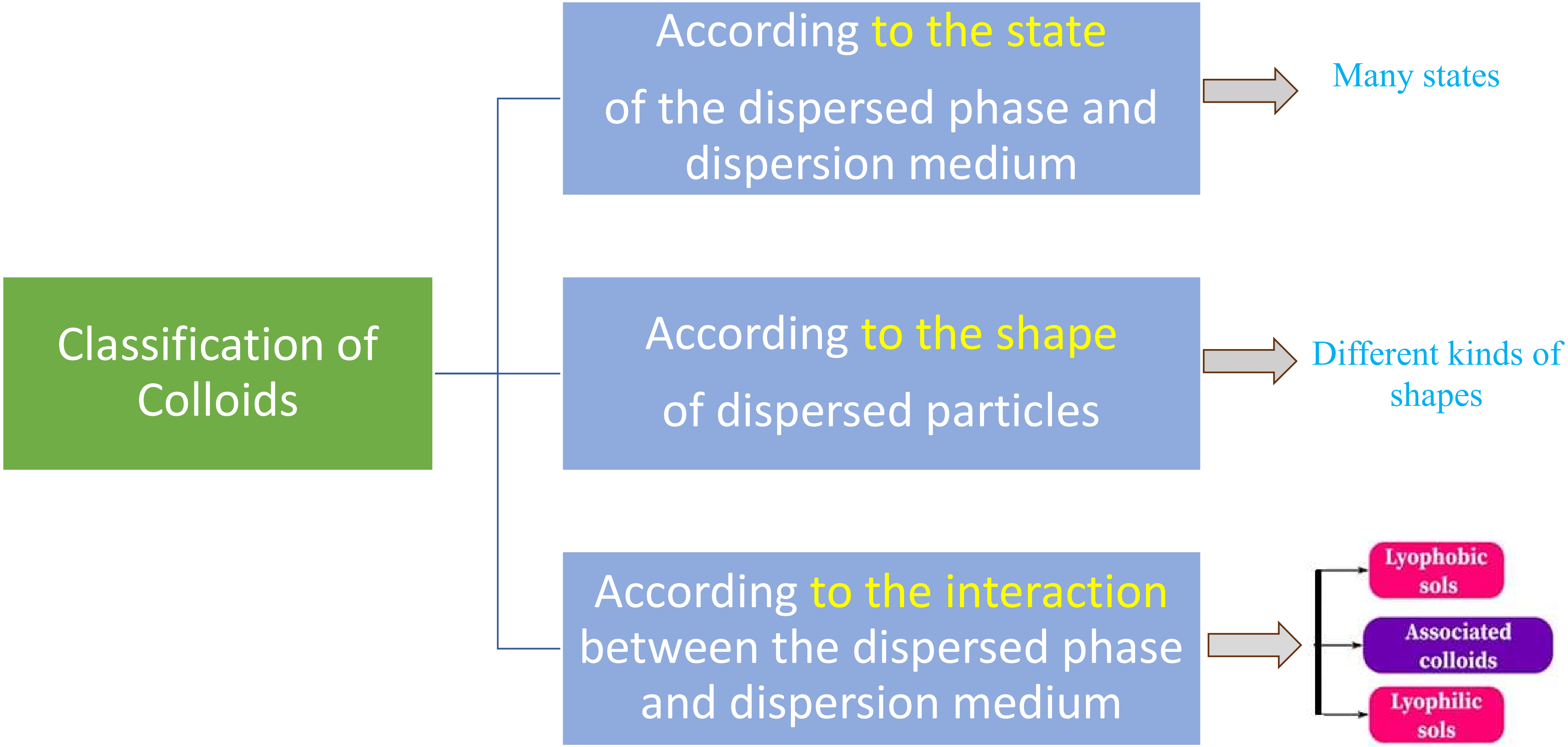




Property	Molecular Dispersions	Colloidal Dispersions	Coarse Dispersions
Homogeneity	Homogeneous	Heterogeneous	Heterogeneous
Particle size *	Less than 1nm	1nm to 500nm (0.5μm)	Greater than 500nm (0.5μm)
Visibility	Invisible under Electron microscope	Visible under Electron microscope May be detected under ultra-microscope	Visible under microscope
Light Scattering	No light scattering	Show	Show
Tyndall effect	No	Yes	Yes
Appearance	Clear	Turbid	Opaque
Settling	Do not settle by gravity	Particles settle by gravity	Particles settle by gravity
Permeability	Pass through ultrafilter paper & semipermeable membrane	Pass through filter paper Not through semipermeable membrane	Do not pass through filter paper & semipermeable membrane
Diffusion	Rapid	Slow	No diffusion
Example	Urea, sucrose and ions	Silver sols, polymers, milk	Grains of sand, red blood cells

* 1 nm (nanometer) = 10^{-9} m; 1 μm (micrometer) = 10^{-6} m

Classification (types) of colloids



Classification of Colloids

According to the state of the dispersed phase and dispersion medium

Many states

According to the shape of dispersed particles

Different kinds of shapes

According to the interaction between the dispersed phase and dispersion medium

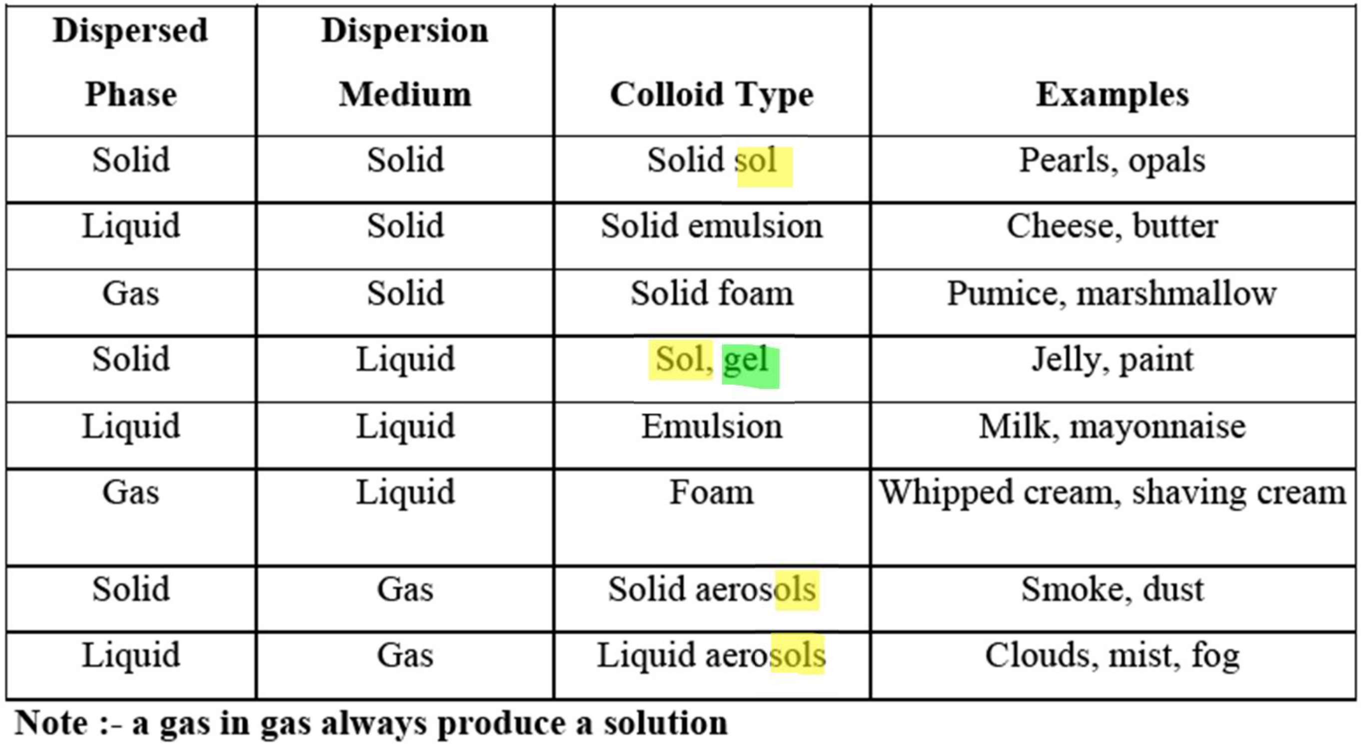
Lyophobic sols

Associated colloids

Lyophilic sols

Classification or types of colloids

A. According to the state of the dispersed phase and dispersion medium



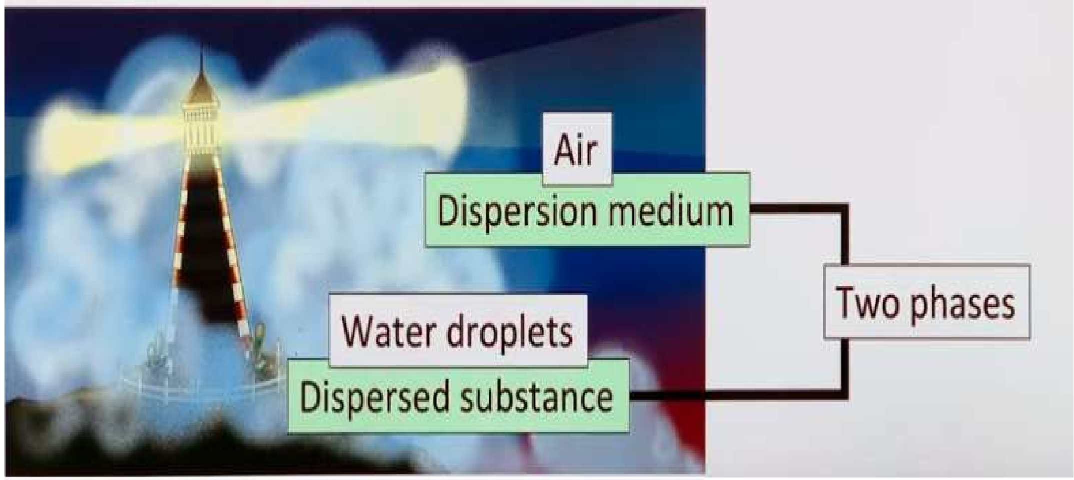
Dispersed Phase	Dispersion Medium	Colloid Type	Examples
Solid	Solid	Solid sol	Pearls, opals
Liquid	Solid	Solid emulsion	Cheese, butter
Gas	Solid	Solid foam	Pumice, marshmallow
Solid	Liquid	Sol, gel	Jelly, paint
Liquid	Liquid	Emulsion	Milk, mayonnaise
Gas	Liquid	Foam	Whipped cream, shaving cream
Solid	Gas	Solid aerosols	Smoke, dust
Liquid	Gas	Liquid aerosols	Clouds, mist, fog

Note :- a gas in gas always produce a solution

Note: Most of the lectures on colloidal systems will be oriented to discussing sols

The terms *sols* and *gels* are often applied to colloidal dispersions of a solid in a liquid or gaseous medium.

- Sols tend to have a lower viscosity and are liquid. If the solid particles form bridged structures possessing some mechanical strength, the system is then called a gel.
- **Prefixes** typically **designate the dispersion medium**. For example, hydrosol (or hydrogel), alcosol (or alcogel), and aerosol (or aerogel) designate water, alcohol, and air, respectively.



Air

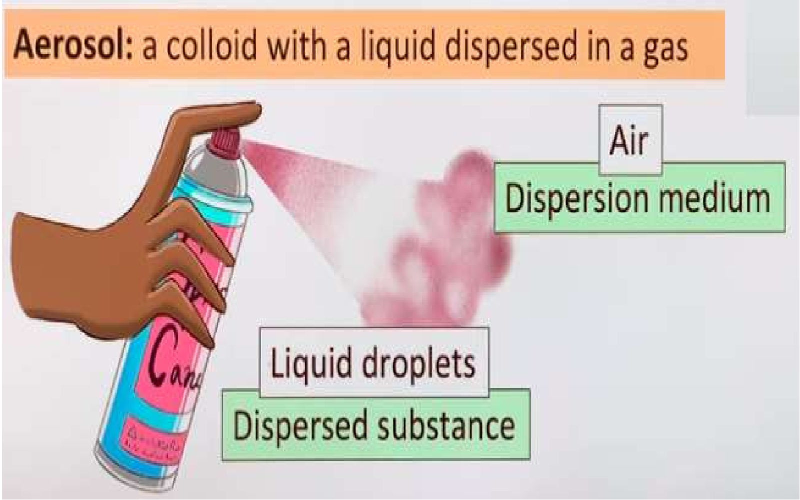
Dispersion medium

Water droplets

Dispersed substance

Two phases

Fog is tiny droplets of water dispersed in air



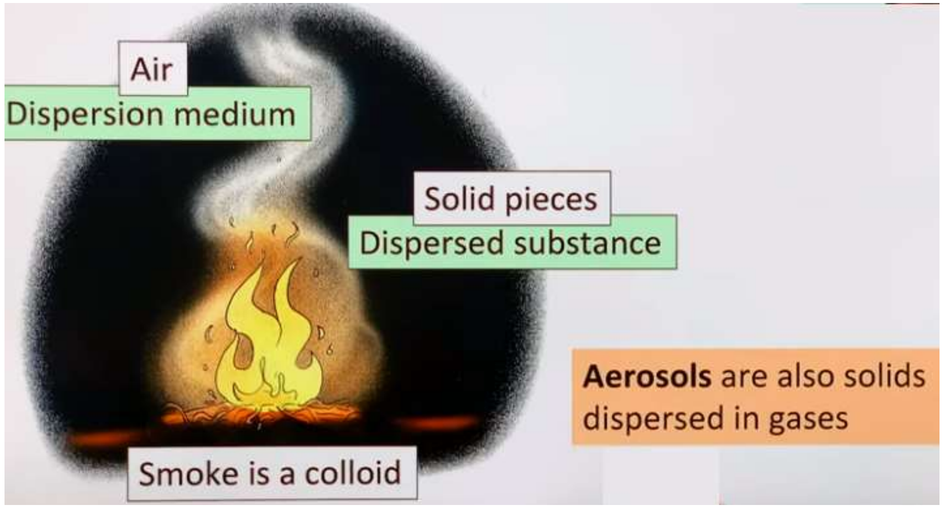
Aerosol: a colloid with a liquid dispersed in a gas

Air

Dispersion medium

Liquid droplets

Dispersed substance



Air

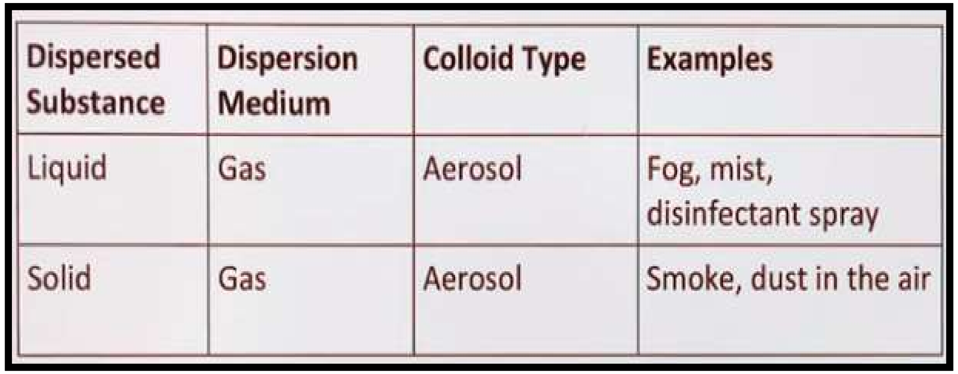
Dispersion medium

Solid pieces

Dispersed substance

Aerosols are also solids dispersed in gases

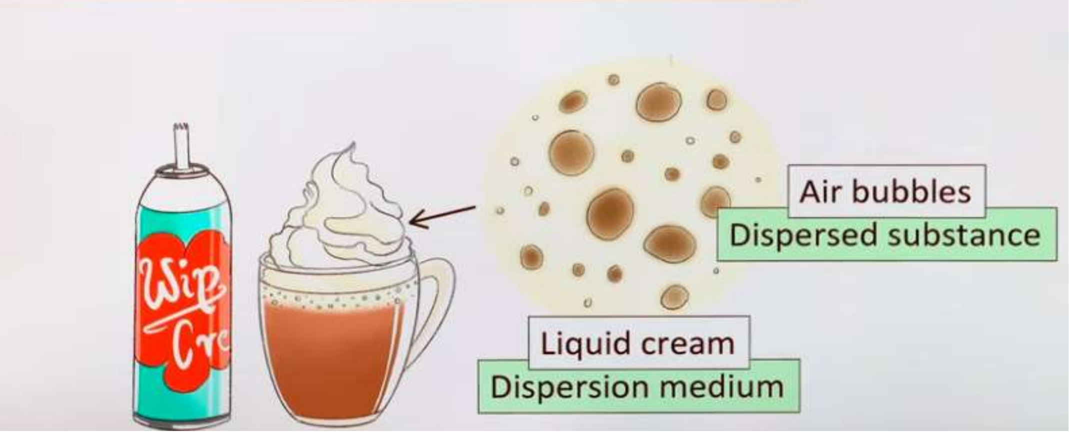
Smoke is a colloid



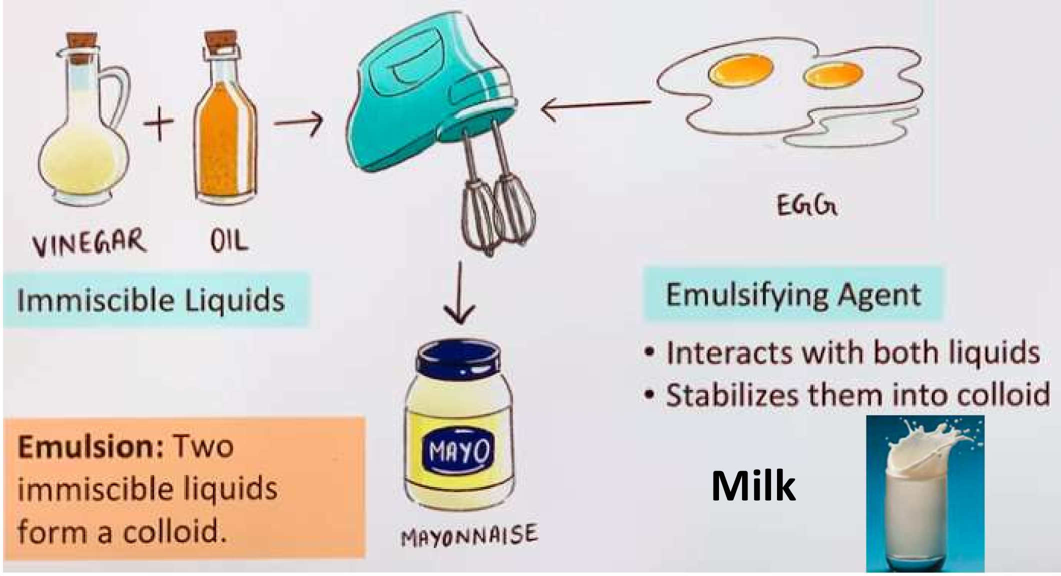
Dispersed Substance	**Dispersion Medium**	**Colloid Type**	**Examples**
Liquid	Gas	Aerosol	Fog, mist, disinfectant spray
Solid	Gas	Aerosol	Smoke, dust in the air

Marshmallow and polysterene foams: **Gas in Solid systems**

Foam: a colloid with a gas dispersed in a liquid



Gel: colloid with a solid dispersed in a liquid



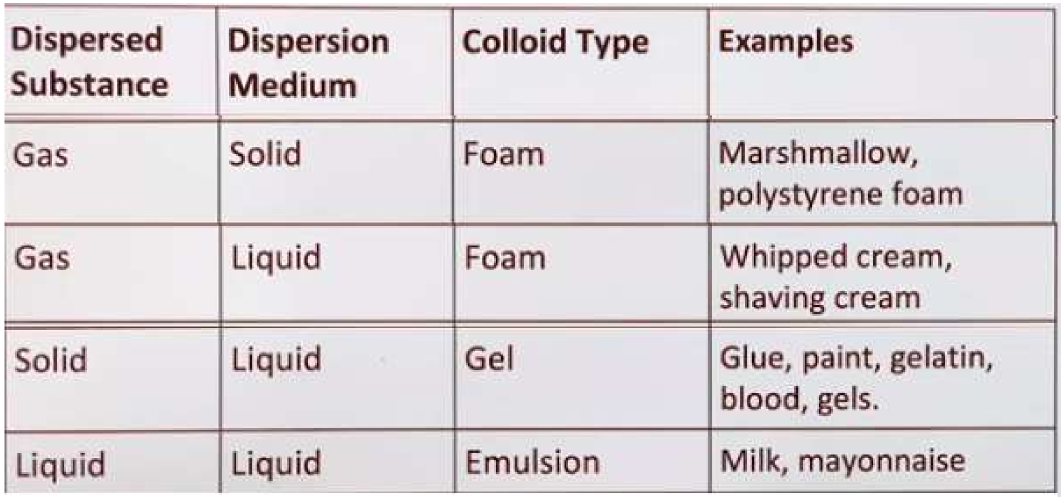
Immiscible Liquids

Emulsifying Agent

- Interacts with both liquids
- Stabilizes them into colloid

Emulsion: Two immiscible liquids form a colloid.

Milk



Dispersed Substance	**Dispersion Medium**	**Colloid Type**	**Examples**
Gas	Solid	Foam	Marshmallow, polystyrene foam
Gas	Liquid	Foam	Whipped cream, shaving cream
Solid	Liquid	Gel	Glue, paint, gelatin, blood, gels.
Liquid	Liquid	Emulsion	Milk, mayonnaise

Classification or types of colloids

B. According to the shape of dispersed particles

Primary particles of colloidal systems exist in a wide variety of shapes (all kinds of shapes), and their aggregation produces an even wider variety of shapes and structures

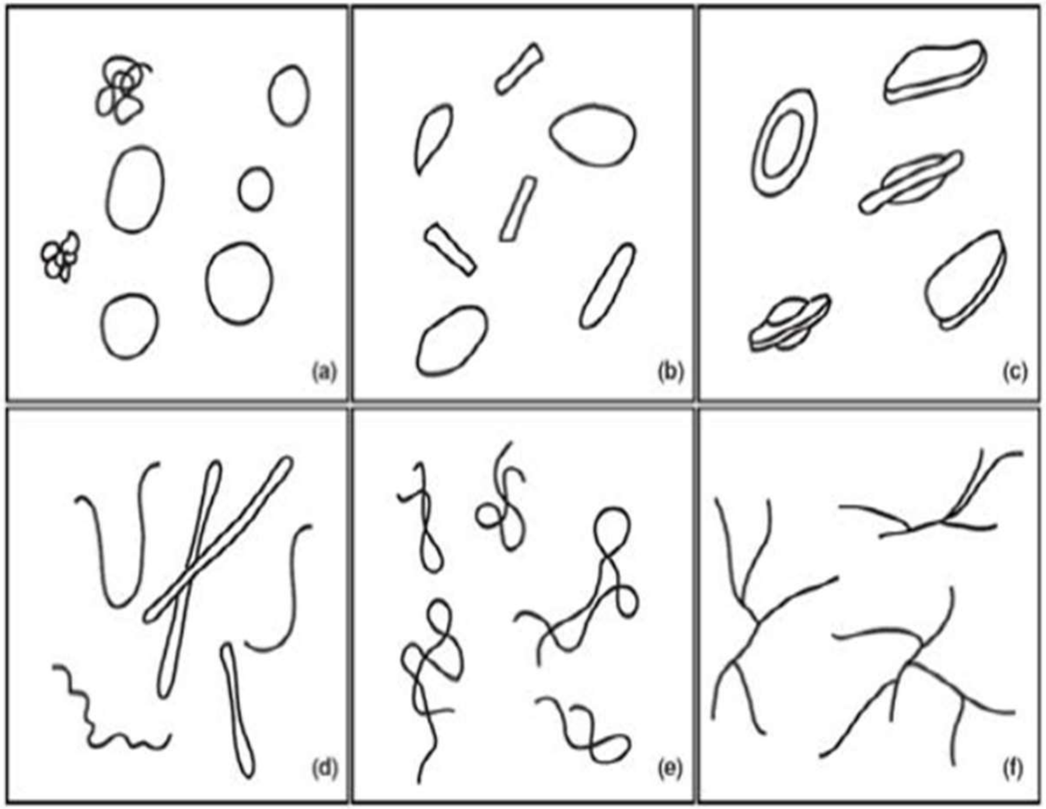
To compare the surface areas quantitatively, the term **specific surface** is used.

Specific surface: the surface area per unit weight or volume of material.

The specific surface area increases as the material is broken into a larger number of smaller and smaller spheres (i.e, the specific surface area is larger for a more finely dispersed system)

The shape of colloidal particles in dispersion is important:

The more extended the particle → the greater its specific surface → the greater the attractive force between the particles of the dispersed phase and the dispersion medium.



Spheres and globules

Short rods and prolate ellipsoids

Oblate ellipsoids and flakes

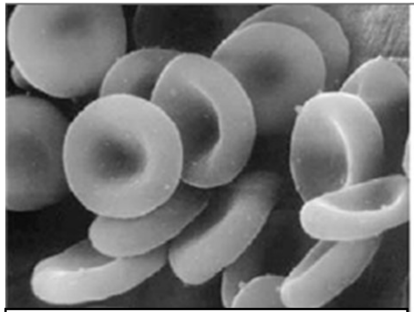
Long rods and threads

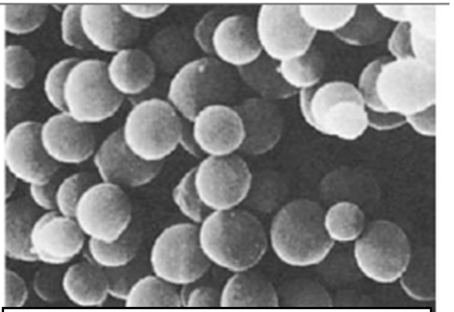
Loosely coiled threads

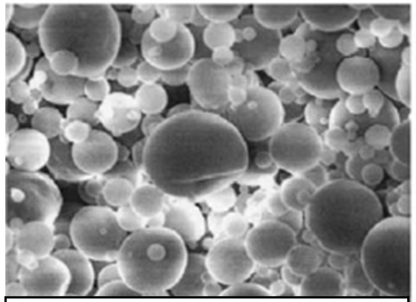
Branched threads

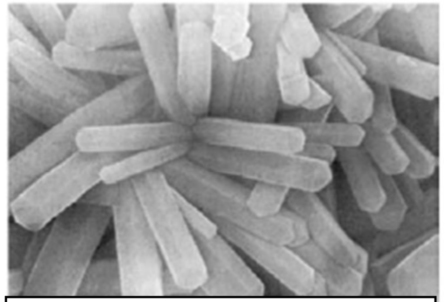
Different shapes of biocolloidal particles

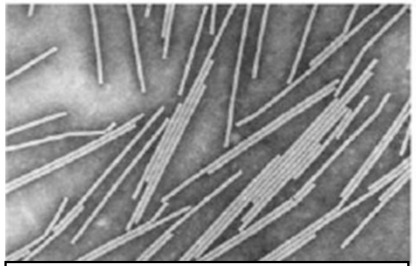
للاطلاع

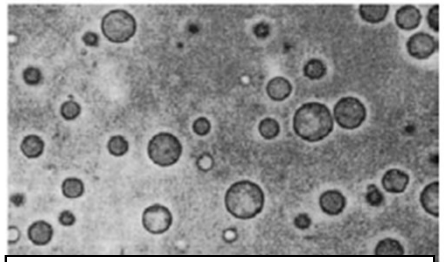

Erythrocytes


Staphylococcus aureus


Trehalose particles


Hydroxyapatite crystal


Tobacco mosaic virus


Fat globules in milk

Classification or types of colloids

C. According to the interaction between the dispersed phase and dispersion medium

This classification refers mostly to solid-in-liquid dispersions

Lyophilic Sols (solvent-loving colloids)

There is considerable attraction between the dispersed phase and the dispersion medium (i.e., extensive solvation).
One of the most important property of lyophilic colloid is the presence of solvent sheath.

Molecules disperse spontaneously to form colloidal dispersions and lyophilic sols are obtained simply by dispersing/dissolving the material in the solvent being used.

Associated colloids

Lyophobic Sols (solvent-hating colloids)

There is little attraction between the dispersed phase and the dispersion medium.
This is primarily due to the absence of a solvent sheath around the particle

It is necessary to use special methods to prepare lyophobic colloids.

Examples of hydrophobic materials include:

- Non-ionized inorganic substances (e.g., sulfur, silver chloride, and gold)
- Organic compounds consisting largely of hydrocarbon portions with few, if any, hydrophilic functional groups (e.g., cholesterol and other steroids);
- Oleophilic materials such as organic lipophilic drugs, paraffin wax, magnesium stearate, and cottonseed or soybean oils.

Classification or types of colloids

C. According to the interaction between the dispersed phase and dispersion medium

Lyophilic Sols (solvent-loving colloids)

if the dispersion medium is water

The system is said to be *hydrophilic colloidal dispersion* or *hydrosol,* and the dispersed phase is called *hydrophilic colloid*

Solvation process (association of solvent (water) with solute) is called hydration

Most lyophilic colloids are organic molecules.
Such systems can be classified into 3 types:

- **True solutions**: when using water soluble polymers such as acacia and povidone
- **Gelled solutions or jellies**: such as gelatin, starch or methyl cellulose solutions; these will have low water solubility when present at high concentration
- **Particulate dispersions**: such as bentonite in water

if the dispersion medium is not water

The system is said to be *oleophilic or Lipophilic* colloidal *dispersion* and the dispersed phase is known as *lipophilic or oleophilic colloid*

Examples:

- Polymers such as rubber or polystyrene dissolved in benzene,
- Magnesium, or aluminum stearate dissolved or dispersed in cottonseed oil

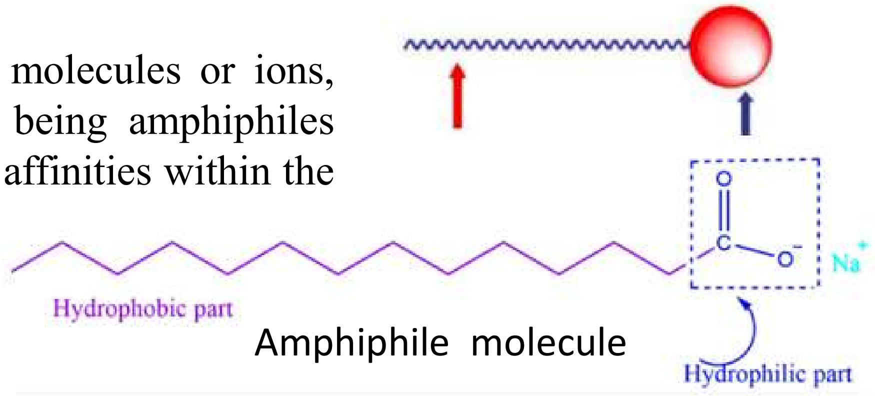
Note:
A material that forms a lyophilic colloidal system in one liquid (e.g., water) may not do so in another liquid (e.g., benzene).

Classification or types of colloids

C. According to the interaction between the dispersed phase and dispersion medium

Associated (Amphiphilic) Colloids

This group of colloids includes certain organic molecules or ions, termed **surface-active agents** characterized by being amphiphiles (having two distinct regions of opposing solution affinities within the same molecule or ion.)



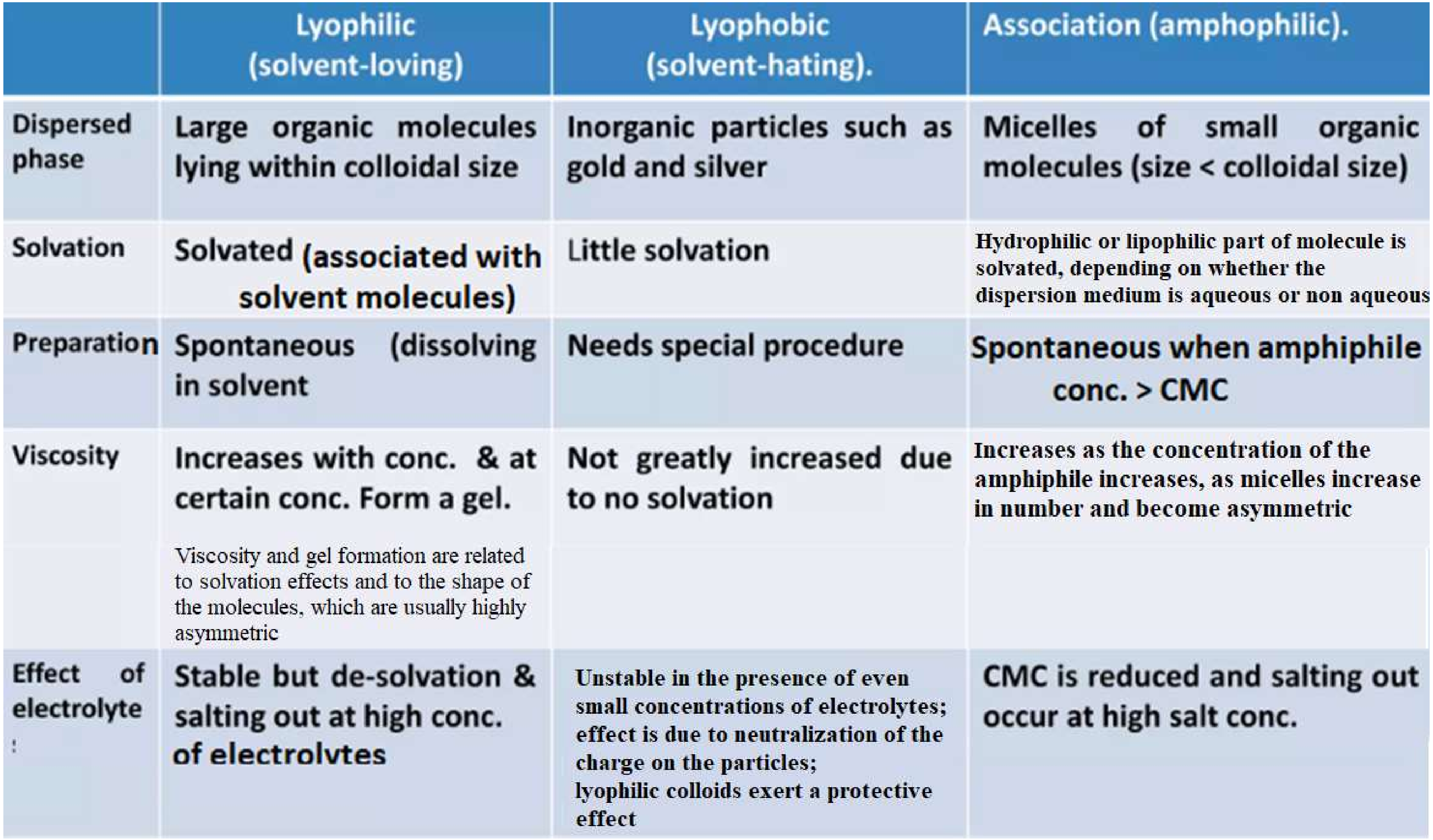
Amphiphile molecule

When present in a liquid medium at low concentrations, the amphiphiles exist separately and are of such a size as to be subcolloidal.

As the concentration of amphiphilic molecules is increased, enough small amphiphilic molecules aggregate over a narrow concentration range and association colloids are formed. These aggregates, which may contain 50 or more monomers, are called micelles.

Micelles are “association colloids” because the diameter of each micelle is of the order of 50 Å, which lie within the size range of colloidal particles.

Comparison of Properties of Colloidal Sols



	Lyophilic (solvent-loving)	Lyophobic (solvent-hating).	Association (amphophilic).
Dispersed phase	Large organic molecules lying within colloidal size	Inorganic particles such as gold and silver	Micelles of small organic molecules (size < colloidal size)
Solvation	Solvated (associated with solvent molecules)	Little solvation	Hydrophilic or lipophilic part of molecule is solvated, depending on whether the dispersion medium is aqueous or non aqueous
Preparation	Spontaneous (dissolving in solvent	Needs special procedure	Spontaneous when amphiphile conc. > CMC
Viscosity	Increases with conc. & at certain conc. Form a gel. Viscosity and gel formation are related to solvation effects and to the shape of the molecules, which are usually highly asymmetric	Not greatly increased due to no solvation	Increases as the concentration of the amphiphile increases, as micelles increase in number and become asymmetric
Effect of electrolyte	Stable but de-solvation & salting out at high conc. of electrolytes	Unstable in the presence of even small concentrations of electrolytes; effect is due to neutralization of the charge on the particles; lyophilic colloids exert a protective effect	CMC is reduced and salting out occur at high salt conc.

Physical pharmacy II

COLLOIDAL DISPERSIONS

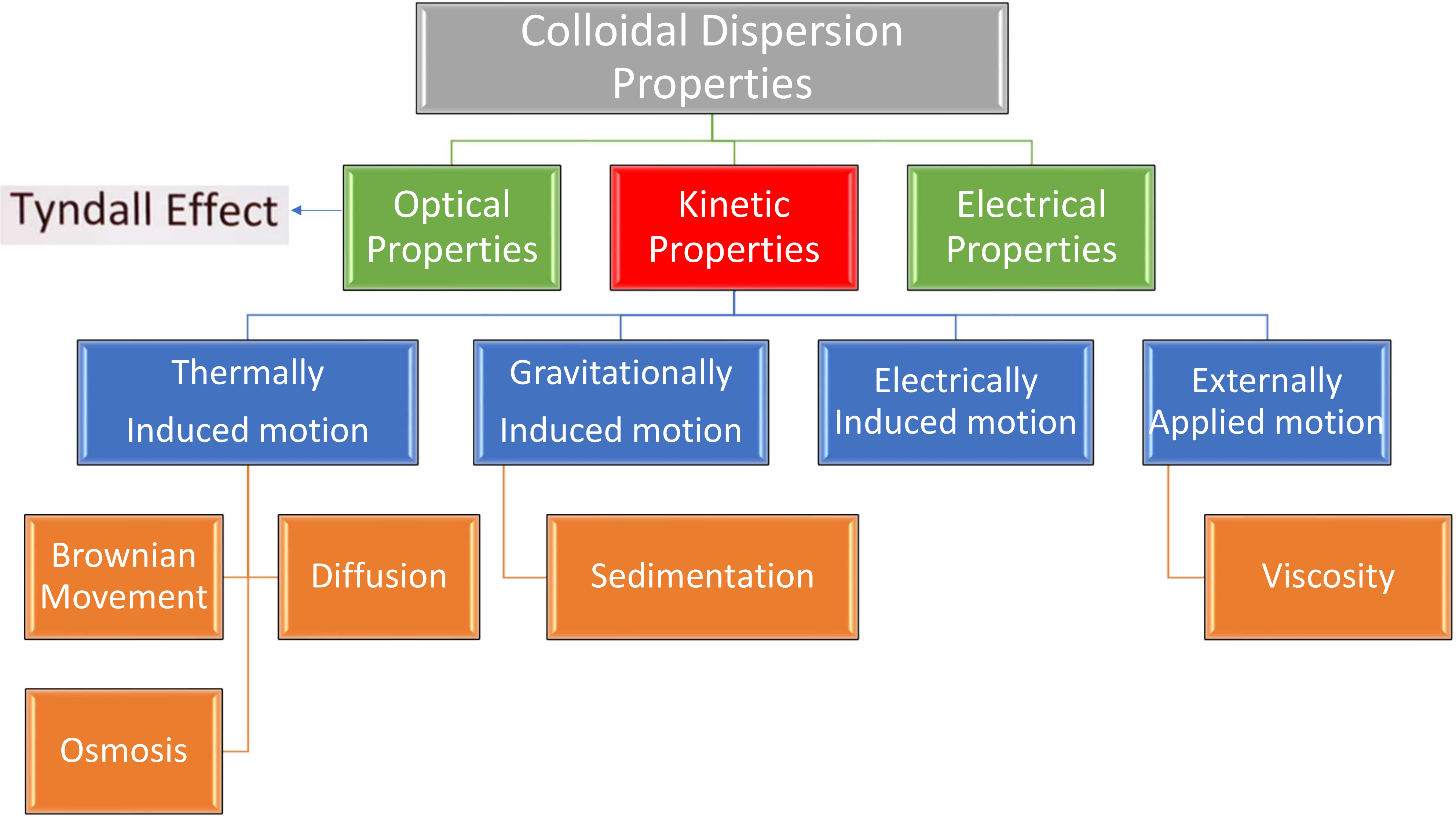
Part 2

By:
Asst. Professor
Lena M. Thomas

Colloidal Dispersions

In this lecture, you'll learn:

- Properties of colloidal dispersions
  - Emphasis on Kinetic Properties
    - Thermally induced motion (Brownian movement)
      - Diffusion
      - Dialysis
      - Osmosis



Colloidal Dispersion Properties

- Optical Properties
  - Tyndall Effect
- Kinetic Properties
  - Thermally Induced motion
    - Brownian Movement
    - Diffusion
    - Osmosis
  - Gravitationally Induced motion
    - Sedimentation
  - Electrically Induced motion
  - Externally Applied motion
    - Viscosity
- Electrical Properties

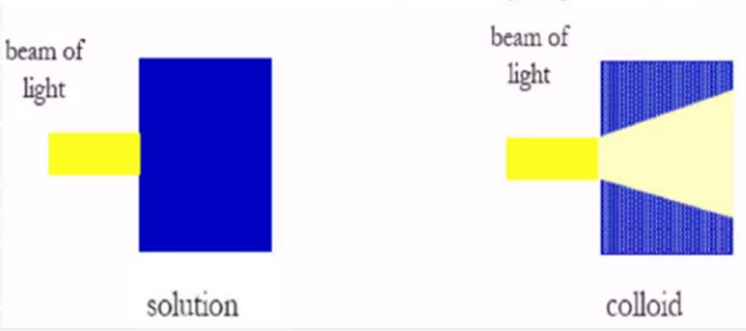
للاطلاع

Optical Properties of Colloids

Colloids reflect or scatter light

When a strong beam of light is passed through colloidal dispersions, the light rays form a visible cone (Tyndall cone) resulting from the light scattered by colloidal particles.

- ✓ This is called the Faraday-Tyndall effect



Particles are too small to scatter light

Particles are large enough to scatter light

Tyndall Effect

Scattering of light by dispersed particles

Examples:

- Headlights in fog
- Sun in dusty air

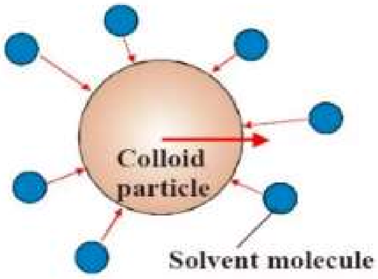
kinetic Properties of Colloids

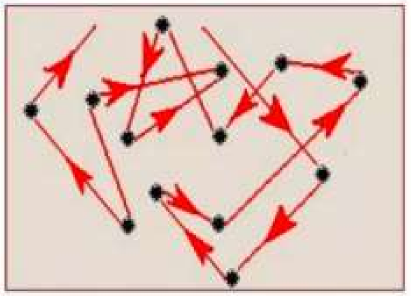
1.Thermally induced motion (increased by increasing temp)

Bombardment of the colloidal particles by dispersion medium molecules makes colloidal particles move randomly, and this is described by **Brownian motion.**

The motion of the molecules cannot be observed, of course, because the molecules are too small to see.

- ✓ This motion is affected by different factors including
  - ✓ **Temperature**: generally enhances Brownian motion
  - ✓ **Particles size**: smaller particles move faster
  - ✓ **Viscosity**: high viscosity limits Brownian motion.





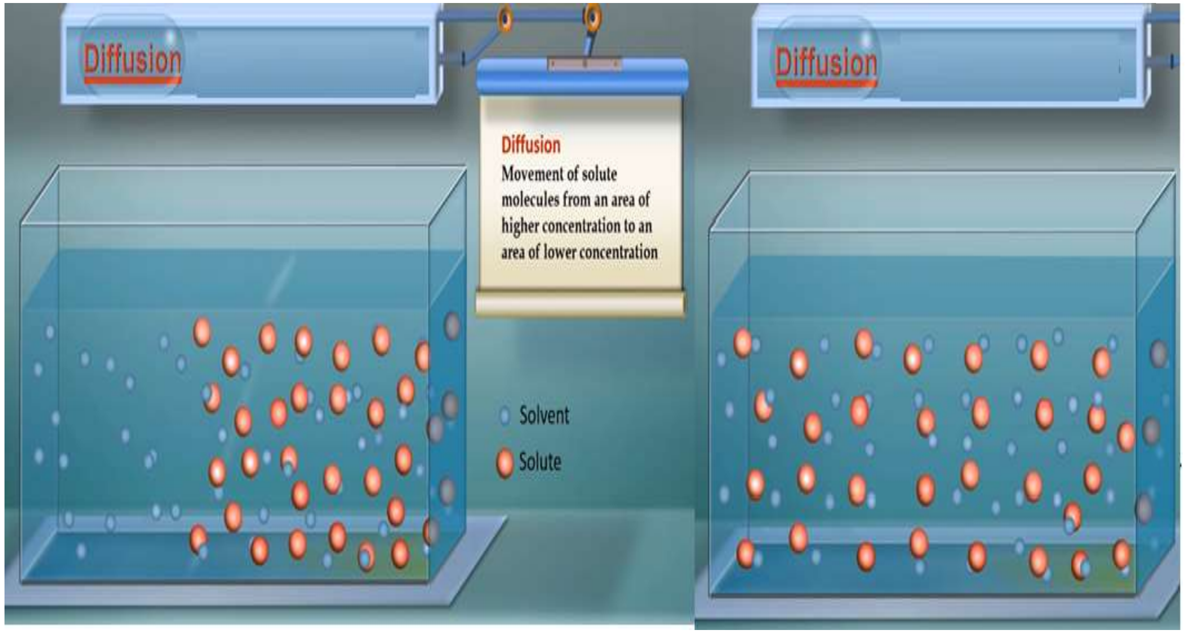
- ✓ As a consequence of Brownian motion in a stable colloidal system:
  - The gravitational force (sedimentation) is counteracted
  - Colloidal particles diffuse from high to low concentration

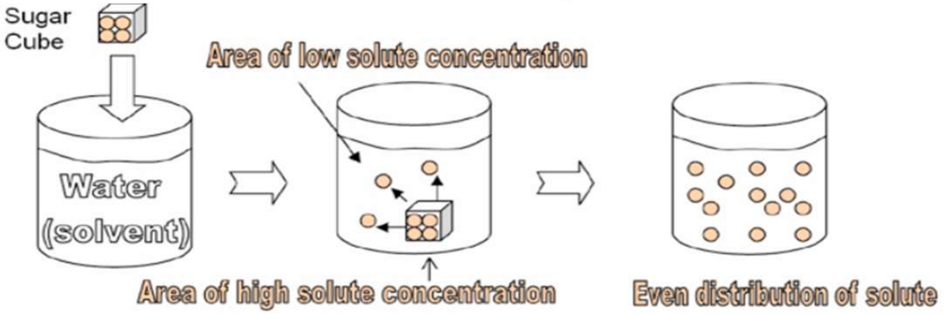
kinetic Properties of Colloids

Thermally induced motion

Diffusion

It is a spontaneous movement of solute particles from a higher to a lower concentration until a system is uniform throughout.





What are the rules of diffusion?

1. Particles always move from an area of high concentration to areas of lower concentration.
2. Particles will continue to move until their concentration within a container, or on each side of a membrane, is equally distributed.
3. Diffusion is passive, meaning it does not require energy in order to occur.
4. Smaller molecules diffuse faster in a given medium

Diffusion is a direct result of **Brownian movement** therefore all factors affecting Brownian movement will affect diffusion.

kinetic Properties of Colloids

Thermally induced motion

Diffusion **According to *Fick's first law***

The rate of movement of particles from high to low concentration (**diffusive flux; J)** is directly proportional to the particle's concentration gradient.

OR: **the amount** *dq*, of substance **diffusing in time**, *dt*, **across a plane of area**, *S*, is directly proportional to the **change of concentration**, *dc*, with **distance traveled**, *dx.*

Fick's law is written as

$$dq = -DS\frac{dc}{dx}dt$$

Or

$$J = -D\frac{dc}{dx}$$

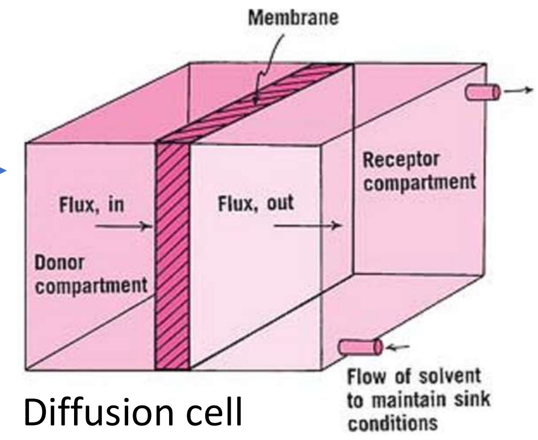
- **J** is the diffusion flux (number of particles passing through a unit area per unit time); its units are g/cm^2 sec. It is always a positive quantity. Diffusion will stop when the concentration gradient no longer exists (i.e., when dc/dx = 0).
- **D** is the **diffusion coefficient or diffusivity**(a constant that depends on the specific particle and the medium it's in); it represents the amount of material diffusing per unit time across a unit area when the concentration gradient (dc/dx) is unity. It has dimensions of unit area per time $\rightarrow\rightarrow$ $D = cm^2 / sec.$
- **q** is the **mass** given in grams or moles**, C** is **concentration** in g/cm^3, ***S*** is the **surface area** in cm^2, **t,** is the **time** in seconds, and **x** is the **distance** in centimeter of movement perpendicular to the surface of the barrier, and **dc/dx** is the concentration gradient (the rate of change of concentration with respect to position).
- **The negative sign** indicates that the diffusion happens down the concentration gradient, from high to low concentration.

kinetic Properties of Colloids

Thermally induced motion

Diffusion

Diffusion cell showing the donor compartment contains diffusant at concentration C

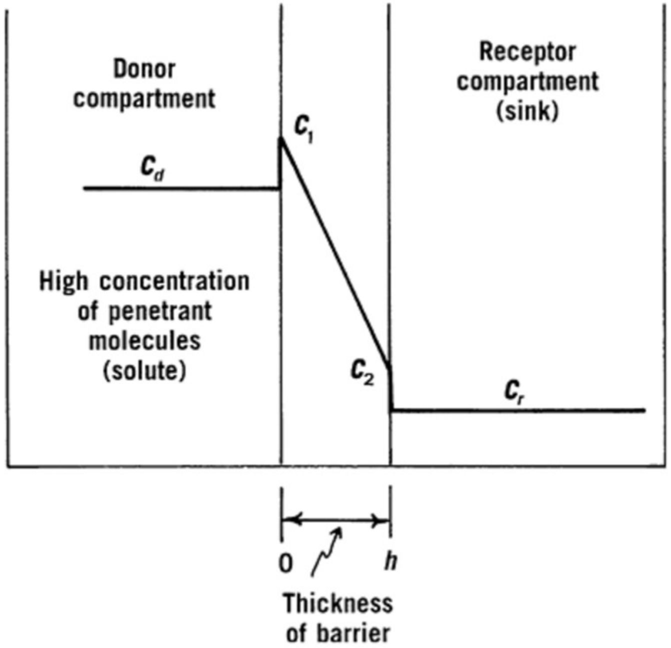


Diffusion cell

In diffusion experiments, the solution in the receptor compartment is constantly removed and replaced with fresh solvent to keep the concentration at a low level. This is referred to as “sink conditions,” the left compartment being the source and the right compartment the sink.

Originally, the diffusant concentration will fall in the left compartment and rise in the right compartment until the system comes to equilibrium, based on the rate of removal of diffusant from the sink and the nature of the barrier.
When the system has been in existence a sufficient time, the concentration of diffusant in the solutions at the left and right of the barrier becomes constant with respect to time but obviously not the same in the two compartments.

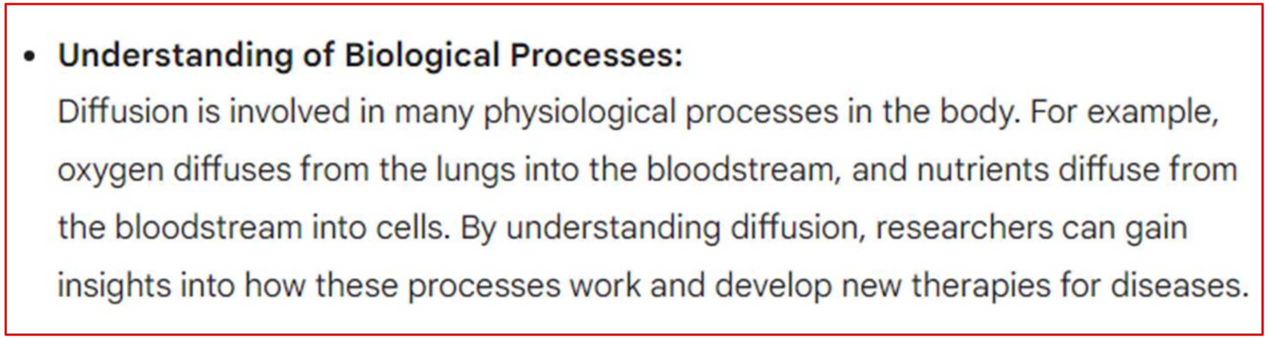
In the figure to the right, we see that concentration gradient of diffusant across the diaphragm of a diffusion cell. It is normal for the concentration curve to increase or decrease sharply at the boundaries of the barrier because, in general, C_1 is different from C_d, and C_2 is different from C_r.



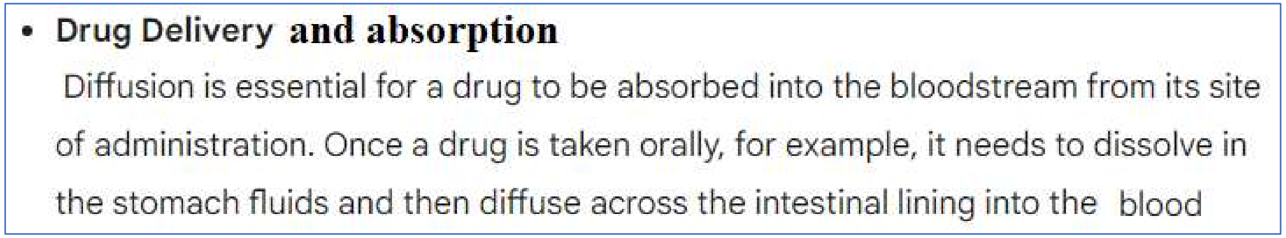
kinetic Properties of Colloids

Importance of Diffusion in pharmacy and medicine

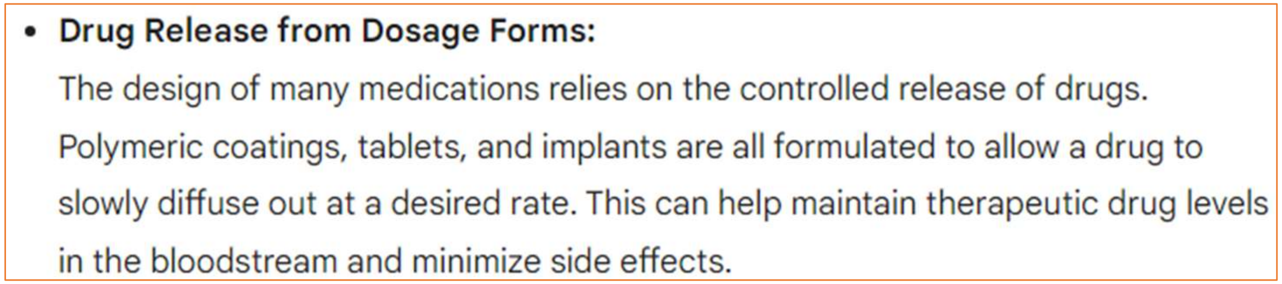
Diffusion is a fundamental process in pharmacy and medicine, and some key applications include:



- **Understanding of Biological Processes:**
  Diffusion is involved in many physiological processes in the body. For example, oxygen diffuses from the lungs into the bloodstream, and nutrients diffuse from the bloodstream into cells. By understanding diffusion, researchers can gain insights into how these processes work and develop new therapies for diseases.

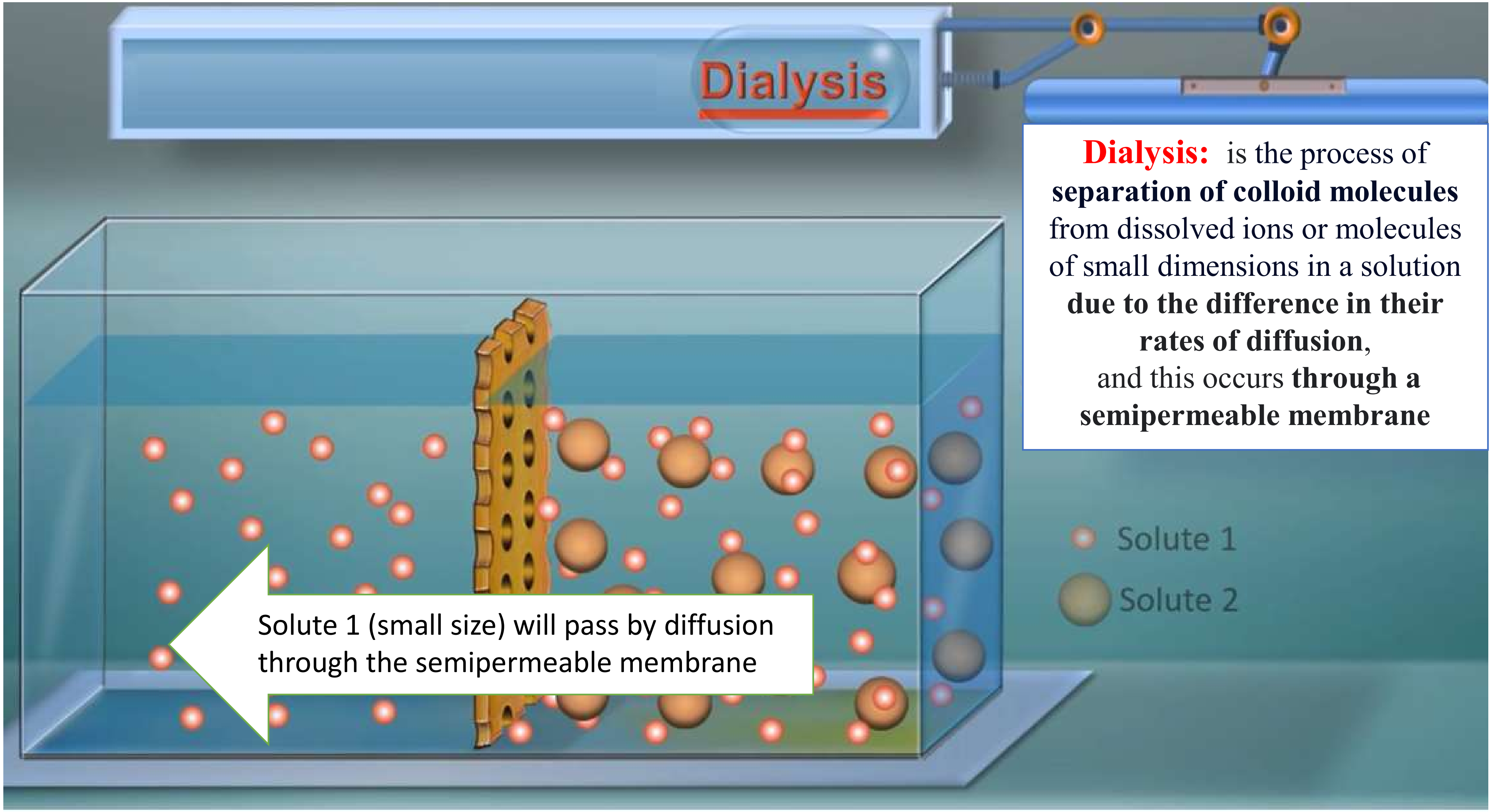


- **Drug Delivery and absorption**
  Diffusion is essential for a drug to be absorbed into the bloodstream from its site of administration. Once a drug is taken orally, for example, it needs to dissolve in the stomach fluids and then diffuse across the intestinal lining into the blood



- **Drug Release from Dosage Forms:**
  The design of many medications relies on the controlled release of drugs. Polymeric coatings, tablets, and implants are all formulated to allow a drug to slowly diffuse out at a desired rate. This can help maintain therapeutic drug levels in the bloodstream and minimize side effects.

Importance of Diffusion in pharmacy and medicine

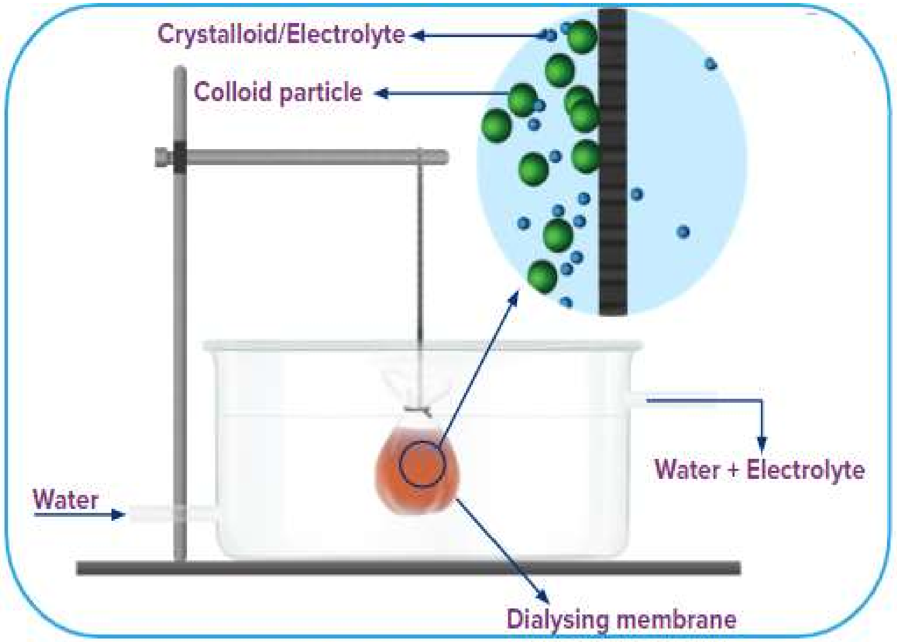


Dialysis: is the process of **separation of colloid molecules** from dissolved ions or molecules of small dimensions in a solution **due to the difference in their rates of diffusion**, and this occurs **through a semipermeable membrane**

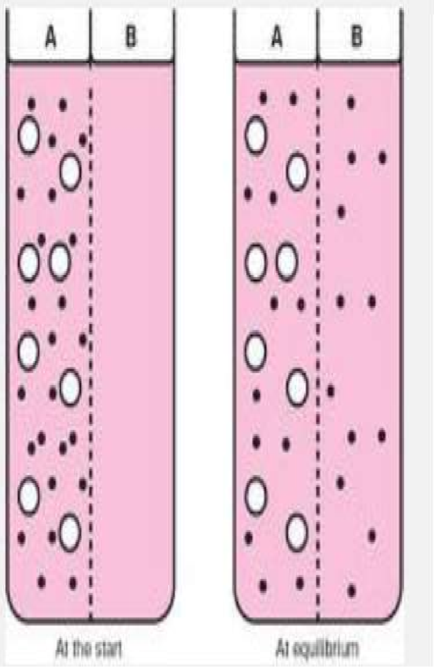
Solute 1 (small size) will pass by diffusion through the semipermeable membrane

Importance of Diffusion in pharmacy and medicine

Because of their size, colloidal particles can be separated from molecular particles with relative ease.
The technique of separation, known as dialysis uses a semipermeable membrane, the pore size of which will prevent the passage of colloidal particles, yet permit small molecules and ions, such as urea, glucose, and sodium chloride, to pass through



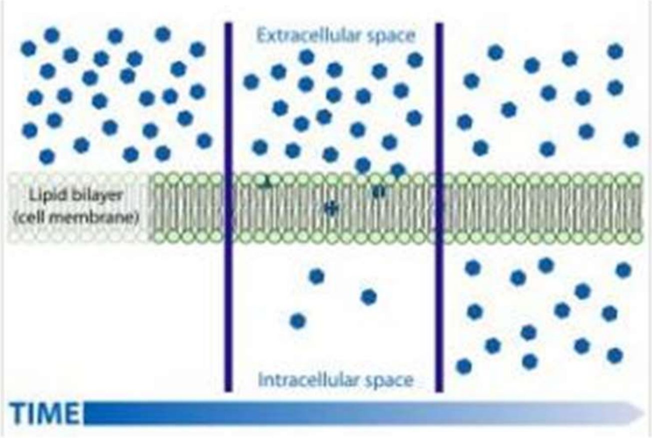
Dialysis



Sketch showing the removal of electrolytes from colloidal material by diffusion through a semipermeable membrane. Conditions on the two sides, A and B, of the membrane are shown at the start and at equilibrium. The open circles are the colloidal particles that are too large to pass through the membrane. The solid dots are the electrolyte particles that pass through the pores of the membrane.

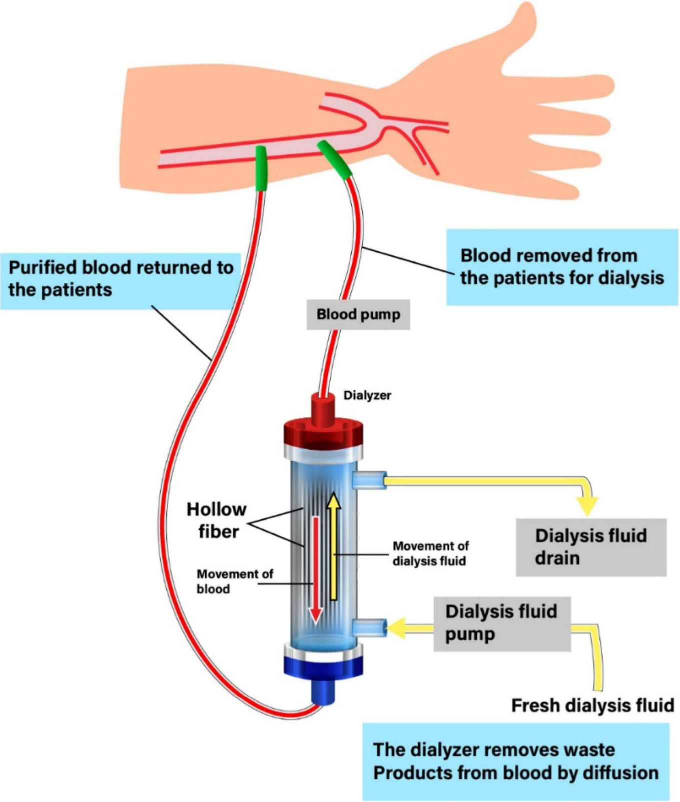
Dialysis Process

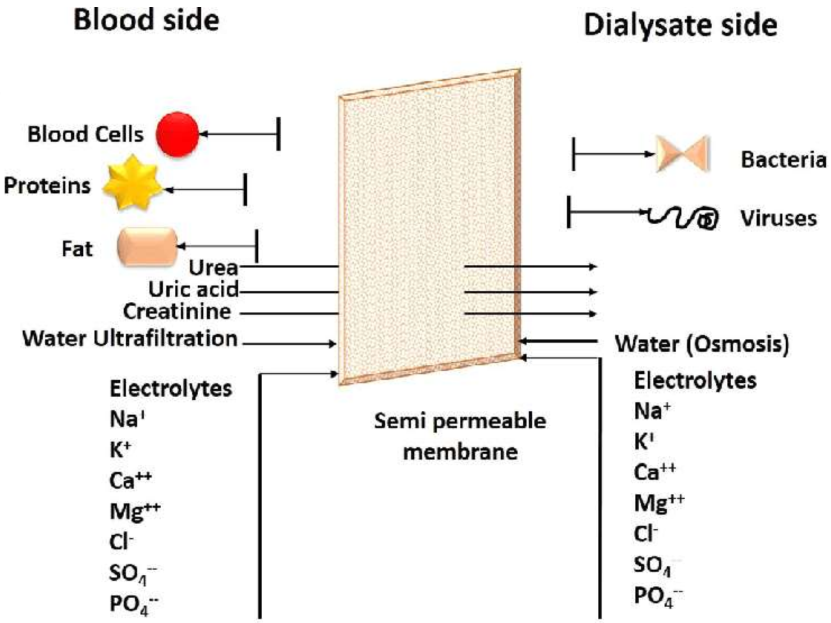
- Dialysis occurs *in vivo*. Thus, ions and small molecules pass readily from the blood, through a natural semipermeable membrane, to the tissue fluids; the colloidal components of the blood remain within the capillary system.



- Dialysis is a life saving treatment for people with kidney failure. It uses the principles of diffusion to remove waste products and excess fluids from the blood.

  During dialysis, blood is passed through a dialyzer, which separates blood from a dialysis solution. Waste products (low–molecular-weight impurities) diffuse from the blood across a semipermeable membrane into the dialysis solution, which is then discarded.





Physical pharmacy II

COLLOIDAL DISPERSIONS

Part 3

By:
Asst. Professor
Lena M. Thomas

Colloidal Dispersions

In this lecture, you'll learn:

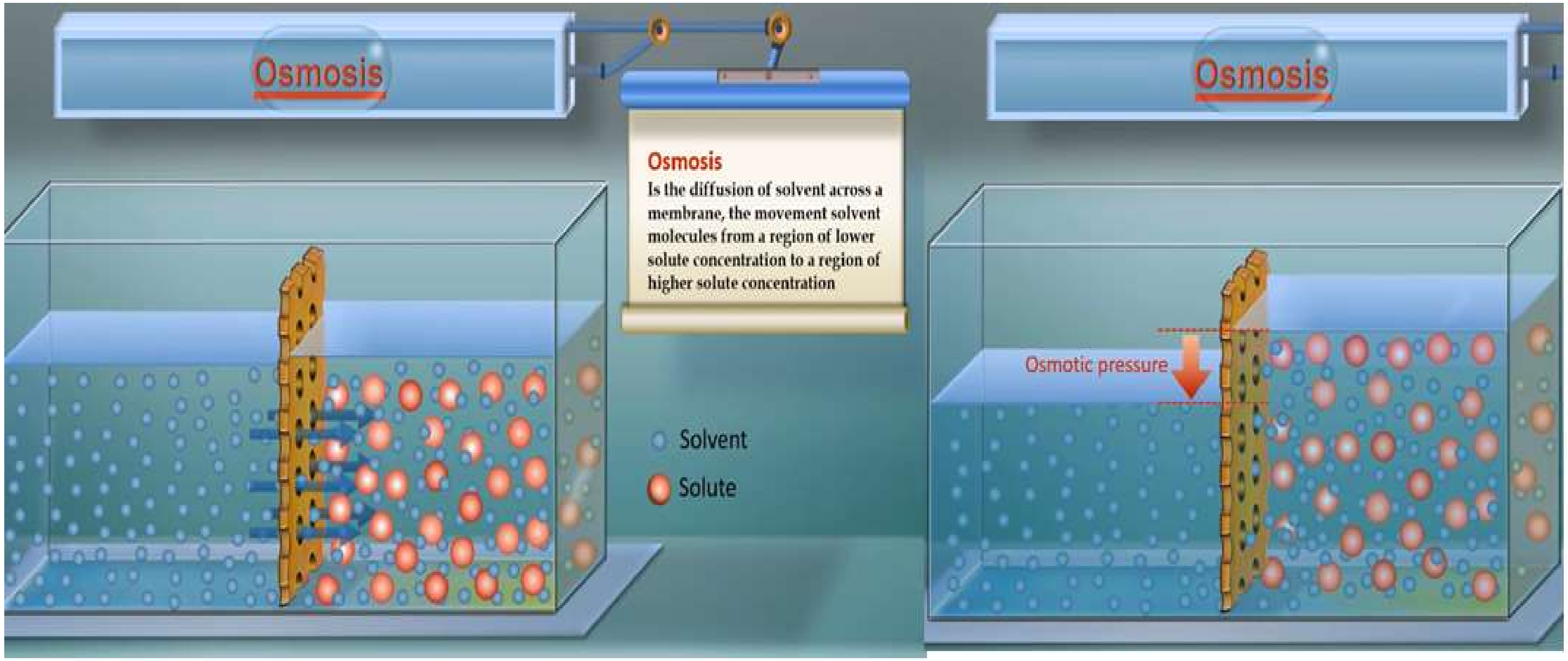
- Properties of colloidal dispersions
    - **Emphasis on Kinetic Properties**
        - **Thermally induced motion** (Brownian movement)
            - Diffusion
            - Dialysis
            - Osmosis
        - **Gravitationally induced motion**
            - Sedimentation and factors affecting it
        - **Externally affected motion (role of viscosity)**
        - **Electrically induced motion (discussed earlier)**

kinetic Properties of Colloids

Thermally induced motion

Osmosis

It is defined as the spontaneous net movement or diffusion of solvent molecules through a selectively-permeable membrane from a region of high solvent (usually water) concentration (low solute concentration) to a region of low solvent concentration. This movement continues until the concentrations on both sides of the membrane become equal, reaching an equilibrium.



Osmosis

Is the diffusion of solvent across a membrane, the movement solvent molecules from a region of lower solute concentration to a region of higher solute concentration

kinetic Properties of Colloids

Thermally induced motion

Osmotic Pressure:

Osmotic pressure is the force that opposes osmosis.

It's the minimum external pressure required to prevent the flow of solvent molecules across the semipermeable membrane from the dilute solution to the concentrated solution.

- ✓ It is the driving force in osmosis as is the concentration gradient for diffusion.
- ✓ The osmotic pressure of a dilute colloidal dispersion can be described by van't Hoff's equation

$$\pi = cRT$$

where **π** is the osmotic pressure,

c is molar concentration of solute ,
R is the gas constant = 0.082 atm.mole/ L.deg
T is the absolute temperature (kelvin)

This equation can be used to calculate the molecular weight of a colloid in a dilute solution. Replacing c with c_g/M in equation, in which c_g is the grams of solute per liter of solution and M is the molecular weight, we obtain:

$$\boxed{\pi = \frac{c_g}{M}RT}$$

kinetic Properties of Colloids

Gravitationally induced motion

Sedimentation

Refers to the process where suspended particles settle out of a liquid medium due to the influence of gravity

Useful Applications of Sedimentation

للاطلاع

- ✓ **Water Treatment:** Sedimentation is a primary method for removing suspended solids from water during water purification.

- ✓ **Blood Analysis:** In blood tests, sedimentation rate is a measure of how quickly red blood cells settle out of unclotted blood. Abnormal sedimentation rates can indicate inflammation or other health conditions
- ✓ **Ultracentrifugation process:** use of ultracentrifuge that provides a force one million times that of gravity will produce sedimentation of colloidal particles.

kinetic Properties of Colloids

Gravitationally induced motion

Sedimentation

Factors Affecting Sedimentation:

The velocity, v, of sedimentation of spherical particles having a density ρ in a medium of density ρ_0 and a viscosity η_0 is given by Stokes's law:

$$v = \frac{2r^2(\rho - \rho_0)g}{9\eta_0}$$

Where
v= velocity of sedimentation of spherical particles
r = radius of particle,
ρ = density of particle,
ρ_0 = density of the dispersion medium
η_0 = viscosity of the dispersion medium,
g = is the acceleration due to gravity

kinetic Properties of Colloids

Gravitationally induced motion

Sedimentation

$$v = \frac{2r^2(\rho - \rho_0)g}{9\eta_0}$$

Factors Affecting Sedimentation:

- **Particle size : (r):** Larger particles have higher mass and therefore settle faster than smaller particles since they are more affected by gravity. The lower size limit of particles obeying Stokes's equation is about 0.5 µm. This is because Brownian movement becomes significant and tends to offset sedimentation due to gravity and promotes mixing When Brownian motion diminishes with increasing particle size, the tendency of particles to sediment is increased.
- **Particle shape:** spherical particles settle faster than irregularly shaped particles. This is because irregularly shaped particles have more drag, which slows down their settling rate.
- **Particles concentration:** If there are too many particles in a fluid, they may start to bump into each other, which can slow down the settling rate.
- **Particle density:** (ρ) Denser particles settle faster than less dense particles. This is because denser particles have more mass per unit volume and are therefore more affected by gravity.

  As difference between the densities of the dispersed particles and the dispersion medium increases so does the sedimentation rate increase (↑ difference → ↑ sedimentation)
- **Fluid viscosity:** (η): Fluids with higher viscosity will slow the rate of sedimentation. For example, particles will settle more slowly in honey than in water.
- **Temperature:** As the temperature of a fluid increases, the viscosity of the fluid decreases. This means that particles will settle faster in warmer fluids than in colder fluids.

kinetic Properties of Colloids

Externally affected motion

Viscosity

Viscosity is an expression of the resistance to flow of a system under an applied stress. The more viscous a liquid is, the greater is the applied force required to make it flow at a particular rate

In this lecture were are concerned with how can viscosity data be used to obtain:

A. Shape of the particles in dispersion

- **The shapes of particles of the disperse phase affect the viscosity of colloidal dispersions**:
  Spherocolloids form dispersions of relatively low viscosity, whereas systems containing linear particles are more viscous

- **The relationship of shape and viscosity reflects the degree of solvation of the particles**:
  If a linear colloid is placed in a solvent for which it has a low affinity, it tends to “ball up,” that is, to assume a spherical shape, and the viscosity falls. This provides a means of detecting changes in the shape of flexible colloidal particles and macromolecules.

kinetic Properties of Colloids

Externally affected motion

Viscosity

B. Molecular weight of material comprising the disperse phase

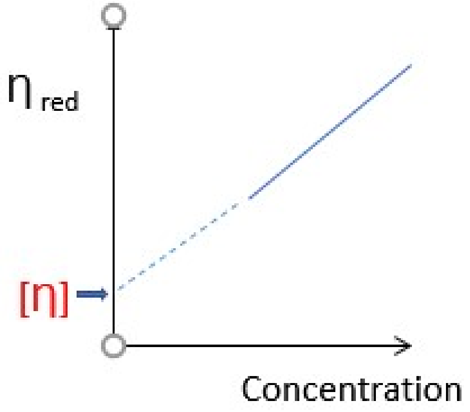
By determining the viscosity of different concentration of polymeric solution and knowing the viscosity of dispersion medium, we can find the **reduced viscosity**. When **reduced viscosity** is plotted against **concentration**, the intercept of such plot to the y-axis will give us the **intrinsic viscosity** [η], this obtained value can be applied according to the so-called Mark–Houwink equation used to calculate the M.wt:

$$[\eta] = KM^{\alpha}$$

Where K, α are constants related to the polymer-solvent system
M: is the molecular weight of the polymer

الرسم والجدول للاطلاع

Concentration (C)	Viscosity of polymeric solution	Relative viscosity $(\eta_{rel}) = \eta/\eta_o$	Specific viscosity $(\eta_{sp.}) = (\eta_{rel}) - 1$	Reduced viscosity $(\eta_{red.}) = (\eta_{sp})/C$
c_1	η_1	η_{rel1}	η_{sp1}	η_{red1}
c_2	η_2	η_{rel2}	η_{sp2}	η_{red2}
c_3	η_3	η_{rel3}	η_{sp3}	η_{red3}



kinetic Properties of Colloids

Electrically induced motion

It is the movement of charged surface of colloidal particles with respect to an adjacent liquid phase.

One of the most important application for such movement is the electrophoresis

Electrophoresis involves the movement of a charged particle through a liquid under the influence of an applied potential difference. An electrophoresis cell fitted with two electrodes contains the dispersion.
When a potential is applied across the electrodes, the particles migrate to the oppositely charged electrode

Physical pharmacy II

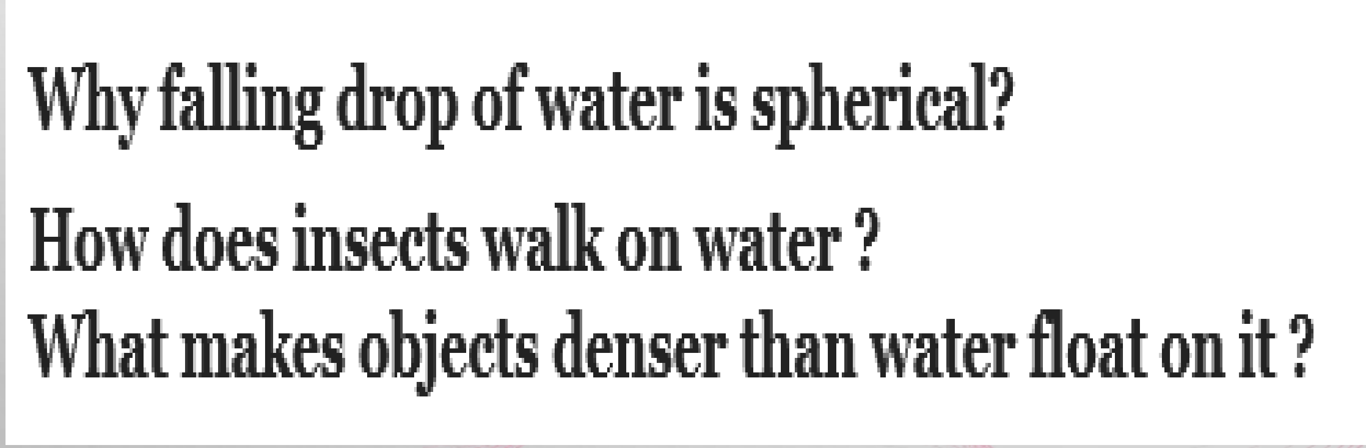
By:
Asst. Professor
Lena M. Thomas

INTERFACIAL PHENOMENA
(PART 1)

MEANING OF INTERFACIAL PHENOMENA

Interfacial phenomena are
behaviors that occur at the interface
or boundary surface
of two different phases of matter

It explains a variety of phenomena such as:



Why falling drop of water is spherical?

How does insects walk on water ?

What makes objects denser than water float on it ?

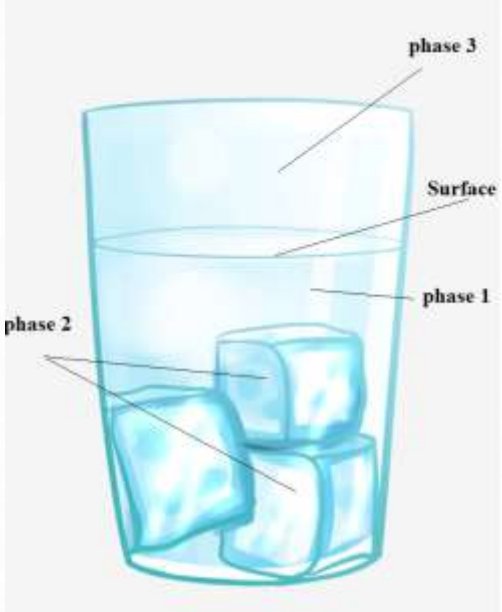
Interfacial phenomena

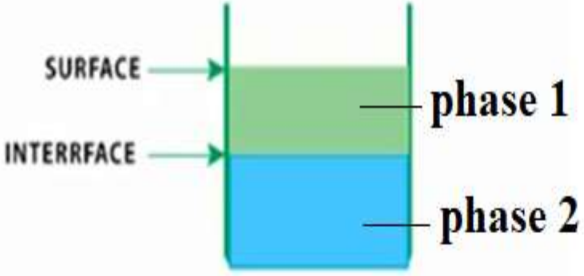
In this lecture, you'll learn:

- **Definition** of "surface" and "interface"
- **Types of interfaces**: emphasis on liquid interfaces
- **Definition** of "Surface tension" and "interfacial tension" and difference between them
- **Factors affecting on surface and interfacial tensions**
- **Importance** of interfacial phenomena in pharmacy and medicine

BASIC DEFINITIONS

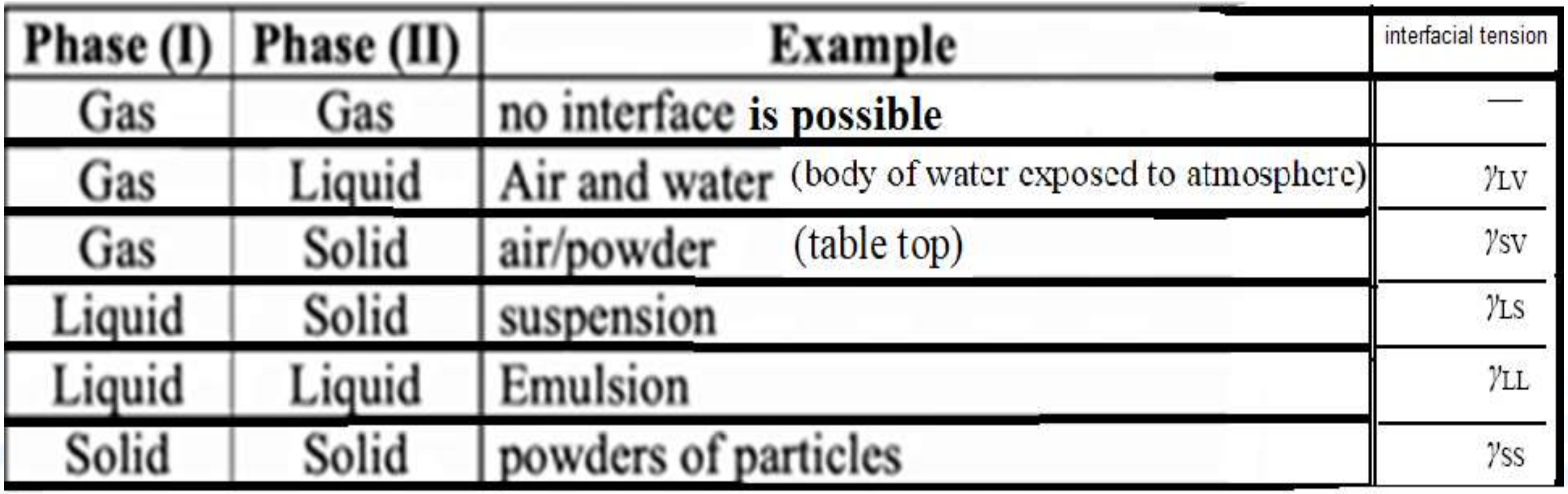
- **PHASE:** is chemically and physically uniform or homogeneous quantity of matter that can be separated mechanically from a mixture.
  - it may consist of a one or more substances.
- **INTERFACE:** is the boundary between two phases existing together. It surrounds each physical entity (be it a cell, a bacterium, a colloid, a granule, or a human) and separate it from its surroundings.
- **SURFACE:** is the outermost or uppermost layer of physical object. It represents the part on which other materials first interact and can be perceived by touch.
- EVERY SURFACE IS AN INTERFACE.
- HOWEVER, THE TERM “SURFACE” IS CUSTOMARILY USED WHEN REFERRING TO EITHER:
  - A **GAS–SOLID INTERFACE** (E.G., A TABLE TOP SURFACE FORMS A GAS–SOLID INTERFACE WITH THE ATMOSPHERE ABOVE IT)
  - A **GAS–LIQUID INTERFACE** (E.G., THE SURFACE OF A WATER IN OCEANS).





Classification of Interfaces

Several types of interface can exist, depending on whether the two adjacent phases are in the solid, liquid, or gaseous state as shown in the table



Phase (I)	Phase (II)	Example	interfacial tension
Gas	Gas	no interface is possible	—
Gas	Liquid	Air and water (body of water exposed to atmosphere)	γ_{LV}
Gas	Solid	air/powder (table top)	γ_{SV}
Liquid	Solid	suspension	γ_{LS}
Liquid	Liquid	Emulsion	γ_{LL}
Solid	Solid	powders of particles	γ_{SS}

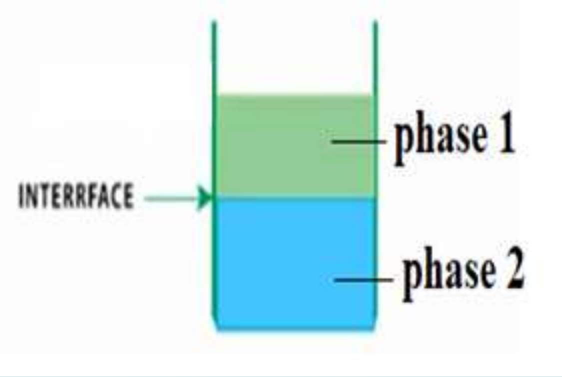
where the subscript L stands for liquid, V for vapor or gas, and S for solid

Classification of Interfaces

For convenience, these various combinations are divided into two groups:

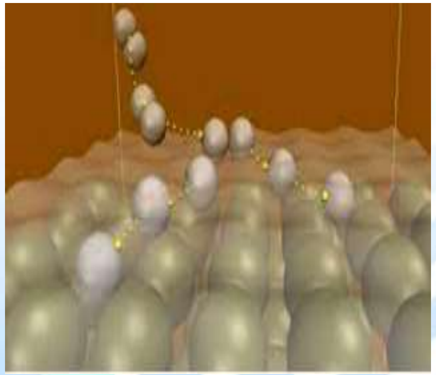
Liquid interfaces

- Deal with systems of a liquid-gas or liquid-liquid interfaces



Solid interfaces

- Deal with systems containing solid–gas, solid–liquid and solid-solid interfaces

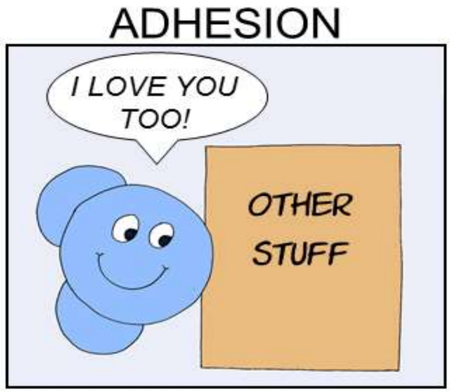


Although solid–solid interfaces have practical significance in pharmacy, little information is available to quantify these interactions and therefore, **only liquid interfaces will be discussed**

Surface and Interfacial Tension

Are they the same ?

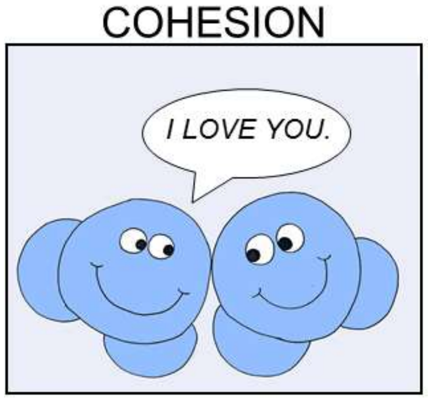
Before going to Surface and Interfacial Tension we need to understand about Cohesion and Adhesion



Electrostatic forces and Van der Waals forces between similar molecules cause adhesion

Cohesion causes the formation of water drops when it rains.

Adhesion causes the drops to cling to other surfaces.

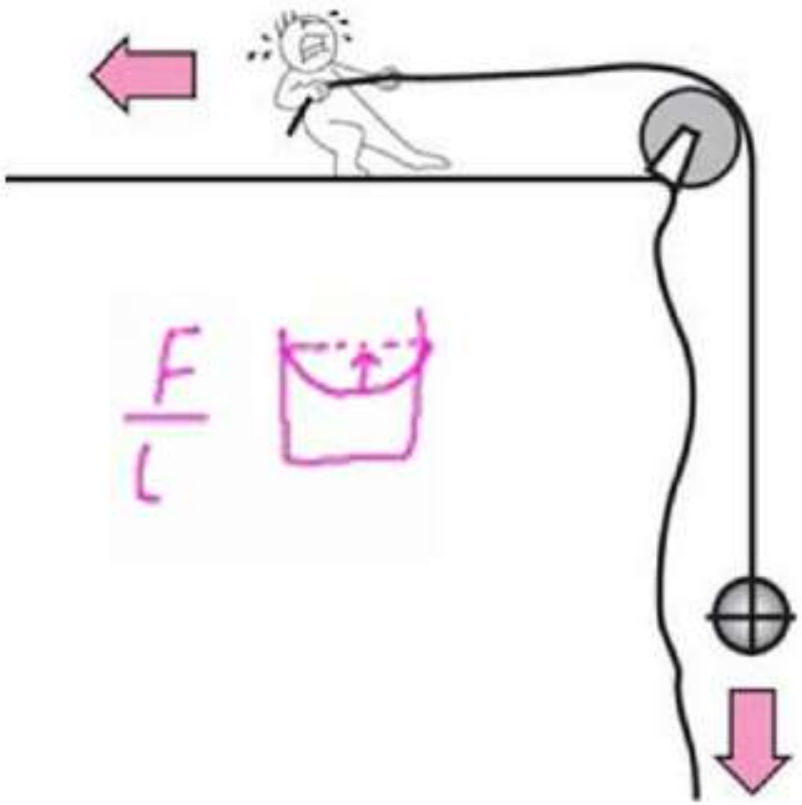


is a type of intermolecular force that occurs between two identical molecules

A. Surface tension

(symbolized by lower case gamma (γ))

- Surface tension is one of the principle **properties of fluids**.
- It is defined as “ **the force per unit length that must be applied *parallel* to the surface so as to counterbalance the net inward pull”**



- It is similar to the situation that exists when an object dangling over the edge of a cliff on a length of rope is pulled upward by a man holding the rope and walking away from the edge of the top of the cliff.

Unit of Surface Tension

Surface tension, has the units of force/unit area

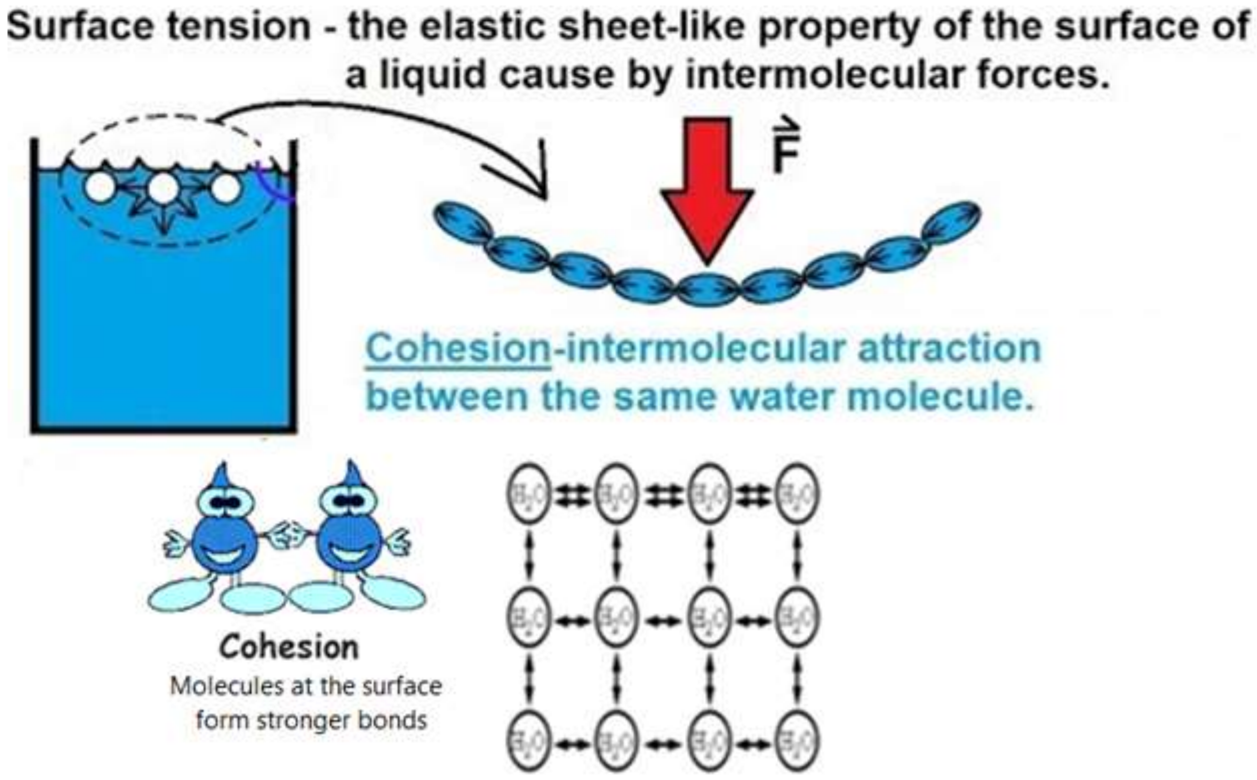
- in the cgs system dynes/cm
- in the SI system N/m

A. Surface tension

(symbolized by lower case gamma (γ))

- It is responsible for **making surface of liquids behave** as an **elastic sheet or a stretched film of rubber** (capable of stretching vertically and horizontally without breaking: similar to tramboline).

- It is **caused by the attraction between liquid molecules (Cohesion)** by various intermolecular forces.
- The higher the attraction forces, the higher the surface tension will be.



Surface tension - the elastic sheet-like property of the surface of a liquid cause by intermolecular forces.

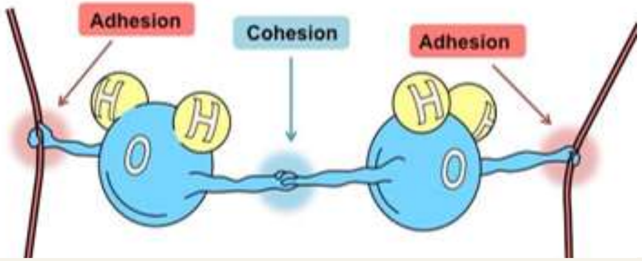
Cohesion-intermolecular attraction between the same water molecule.

Cohesion

Molecules at the surface form stronger bonds

The molecules lying inside (in the bulk) are attracted equally on all the directions by similar molecules around them therefore the net force acting on them becomes zero.

The molecules at the surface do not have similar liquid molecules above them to attract them upwards (although there is gas molecules, the adhesive forces between the liquid–gas interface is small); however, there are liquid molecules below, so there is a net **downward force** pulling the surface molecules towards the bulk, as a result, the surface will contract and lead to the formation of meniscus and resulting in a surface tension.



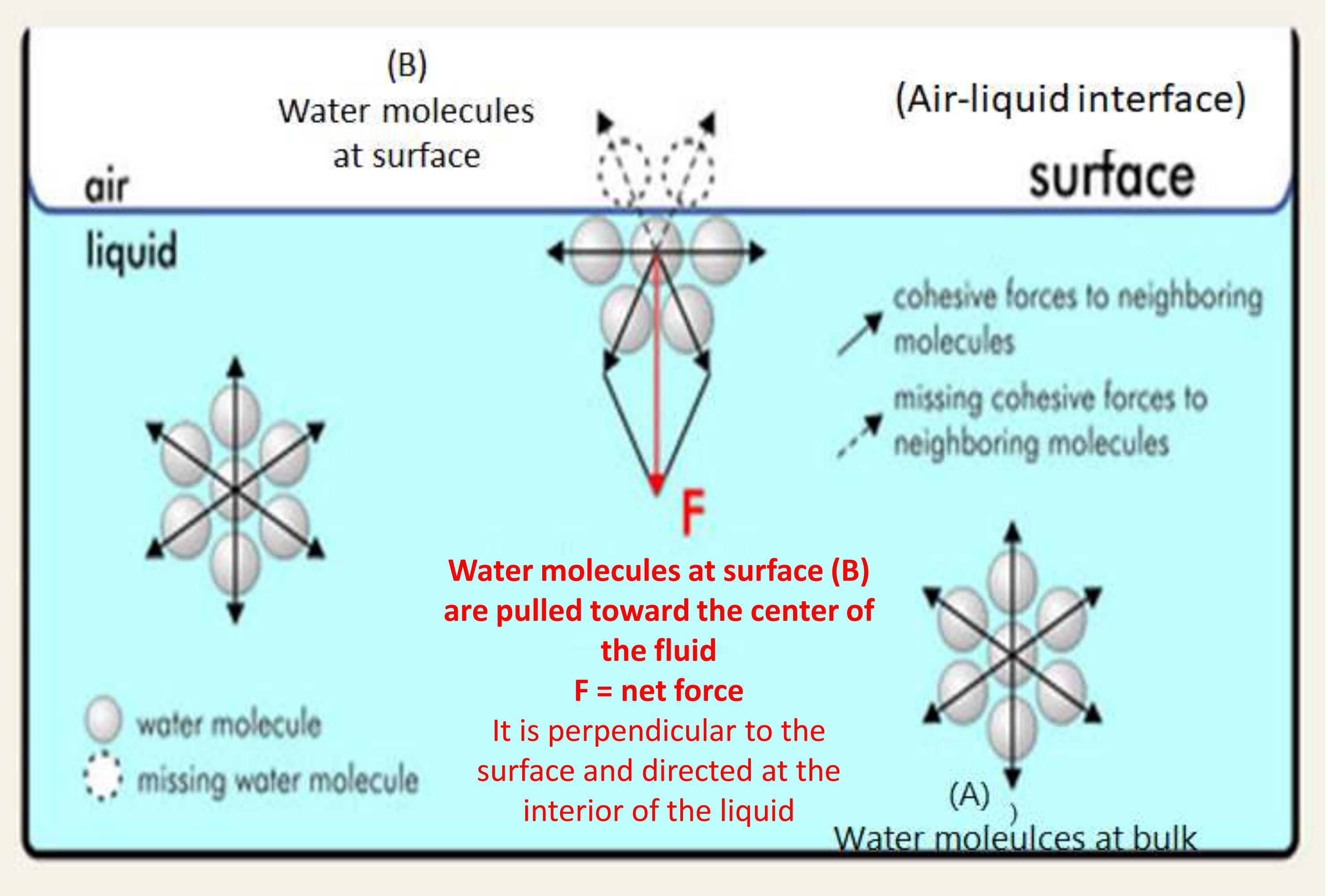
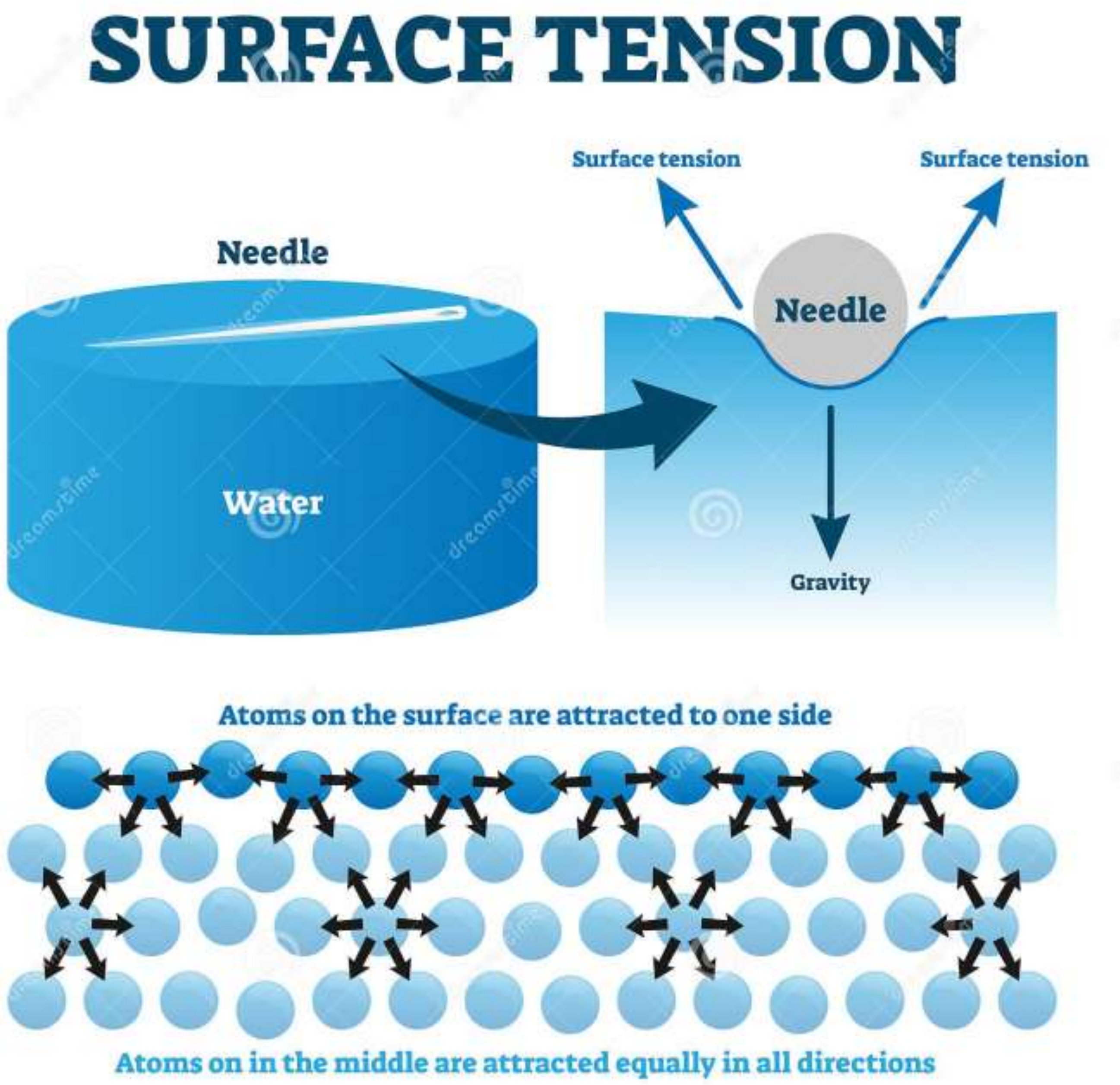
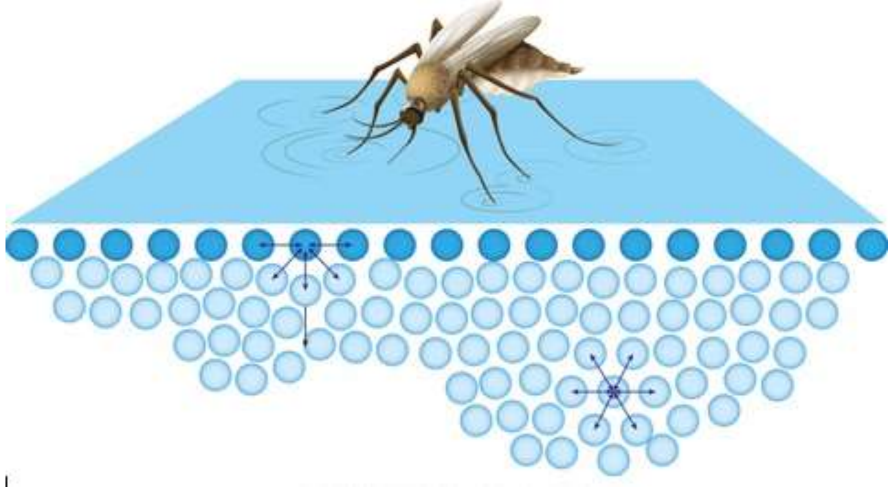


Figure 1: Representation of the unequal attractive forces acting on molecules at the surface of a liquid as compared with molecular forces in the bulk of the liquid

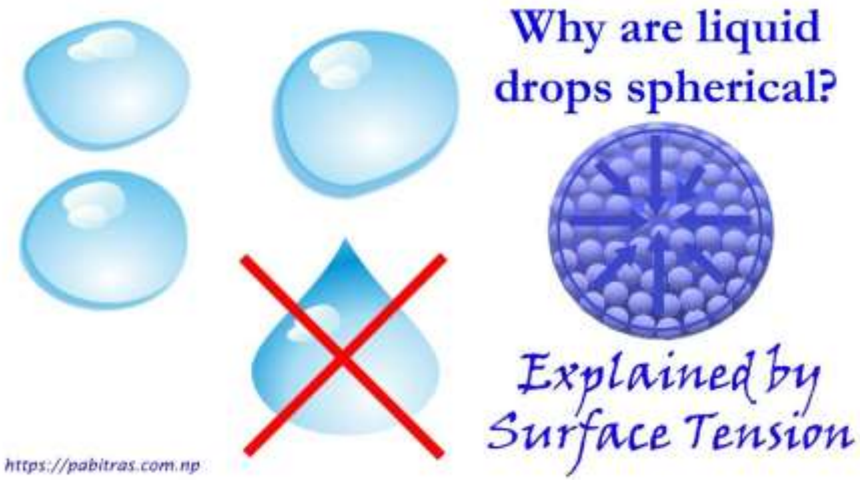


للاطلاع



The **surface molecules cohere more strongly** together by strong inter-molecular bonding and will result in a “surface film” which makes it more difficult to penetrate and move an object through the surface than to move it when it is completely dipped inside and is responsible for the ability of water surface to bear the weight of insects or low density objects over its surface.

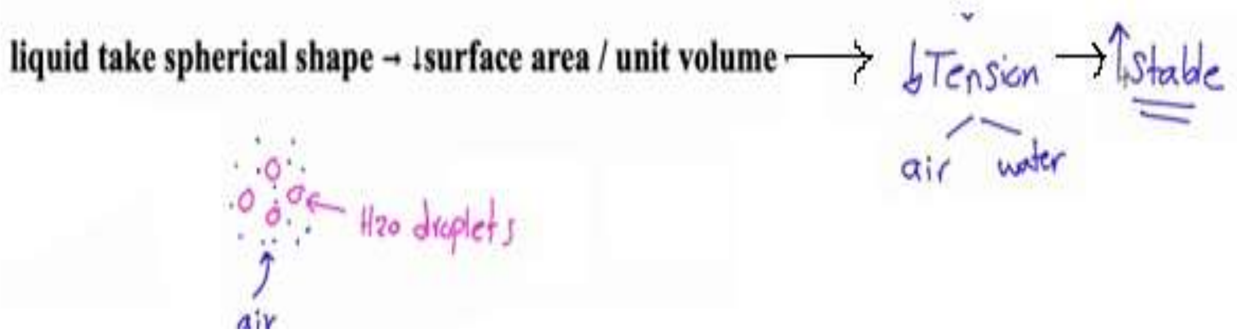
If we replace the water with ethanol, then the insect will get drawn into the water. It is because the **ethanol’s surface tension is very low as compared to that of the water.**



للاطلاع

- Surface tension (the inward pulling force) is the only reason due to which the water comes down a faucet or as rain in a spherical shape as it falls freely.
- The liquid droplets tend to have a spherical-shape since a sphere has the smallest surface area per unit volume (compared to different shape objects with the same area)

Any liquid surface always try to minimize the surface area



liquid take spherical shape → ↓surface area / unit volume → ↓Tension → ↑Stable

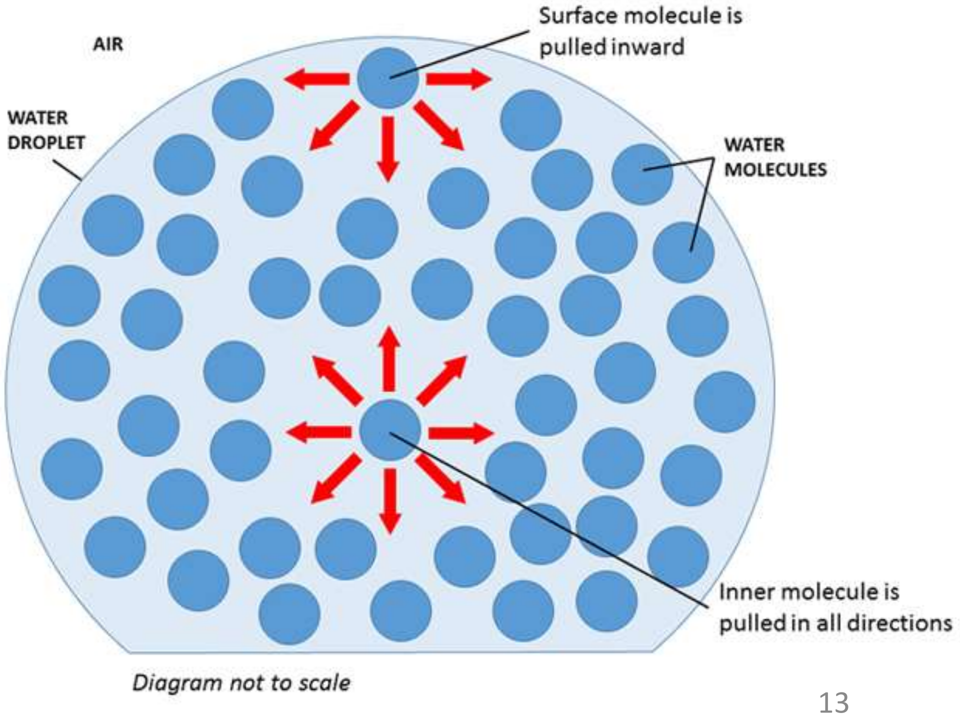


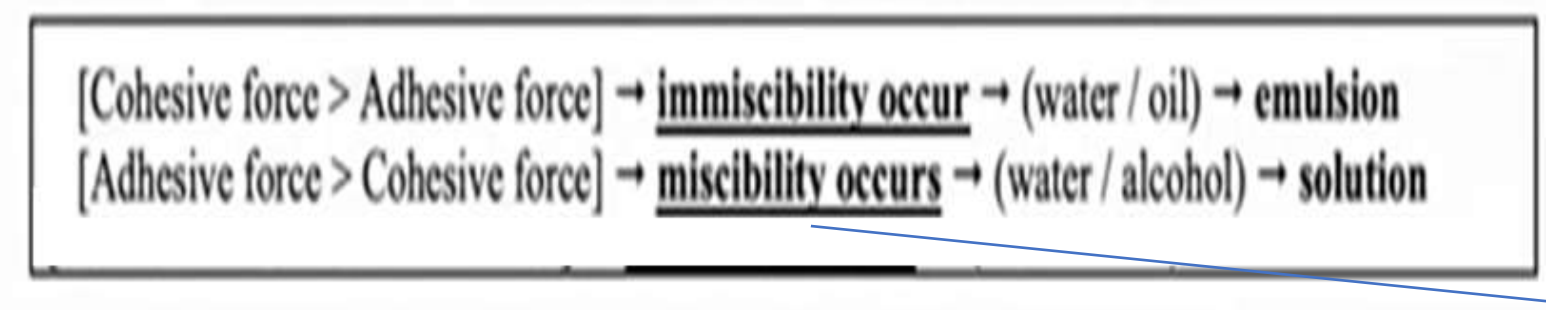
Diagram not to scale

B. Interfacial tension

- Interfacial tension is the force per unit length existing at the interface between two immiscible liquid phases.
- Like surface tension, has the units of **dynes/cm.**

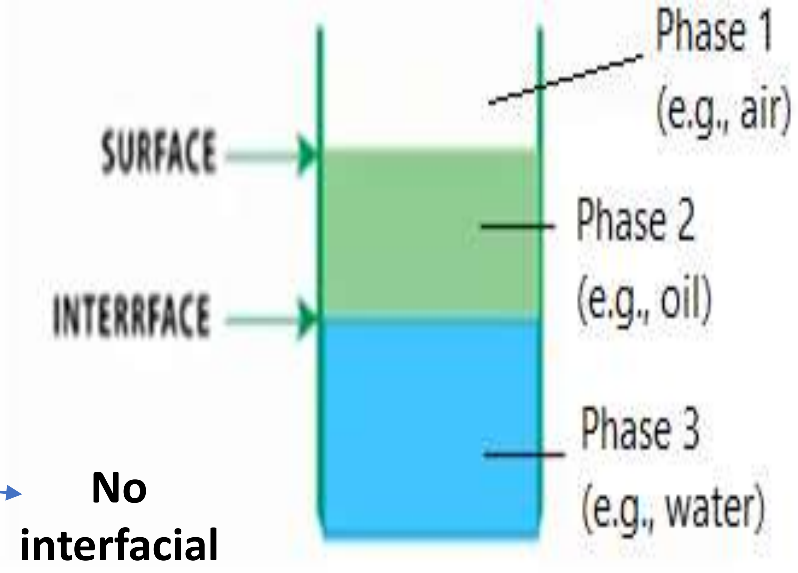
- Values of interfacial tensions reflects adhesion forces and the differences in chemical structure of the two phases involved: the greater the adhesion (higher tendency to interact and the more are the chemical groups capable of hydrogen bonding), the less interfacial tension.

Depending on the strength of forces at the interface:



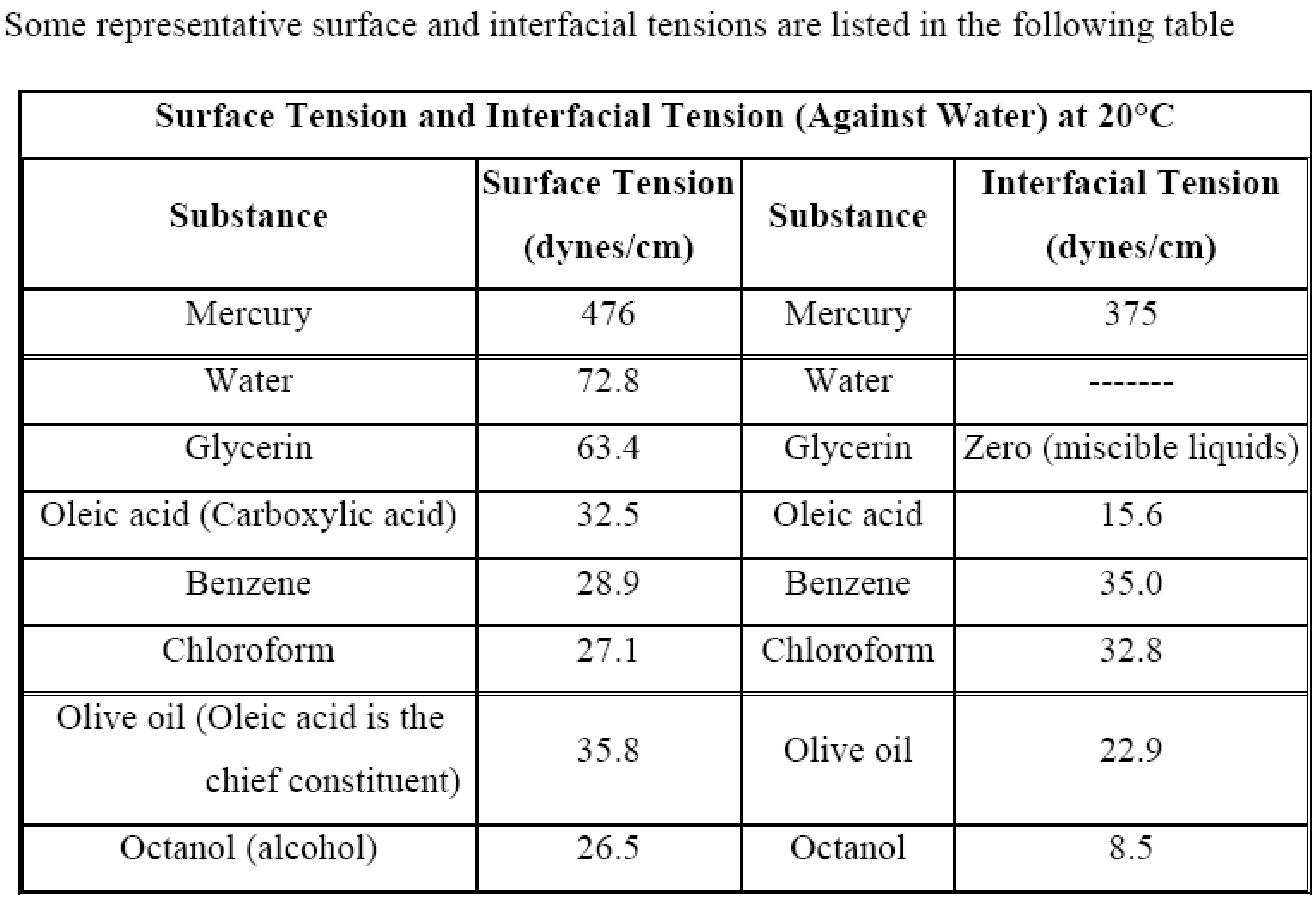
[Cohesive force > Adhesive force] → **immiscibility occur** → (water / oil) → **emulsion**

[Adhesive force > Cohesive force] → **miscibility occurs** → (water / alcohol) → **solution**



No interfacial tension

Ordinarily, interfacial tensions are less than surface tensions because the adhesive forces between two liquid phases forming an interface are greater than when a liquid and a gas phase exist together.



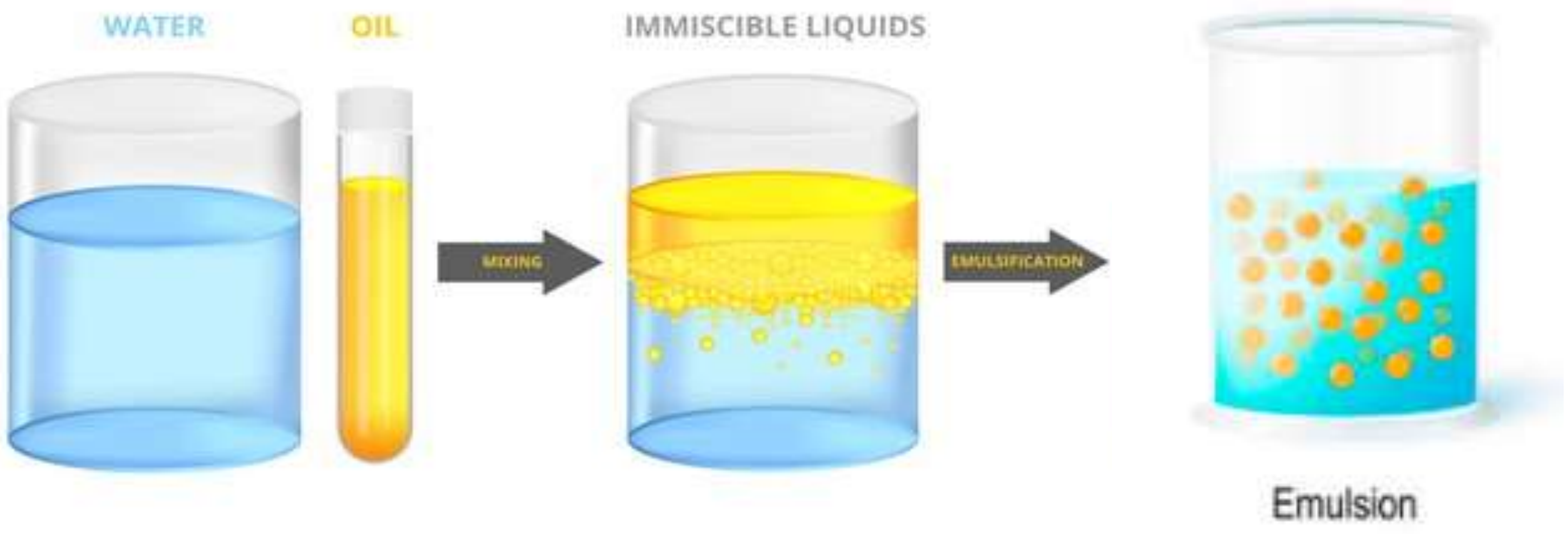
Some representative surface and interfacial tensions are listed in the following table

Surface Tension and Interfacial Tension (Against Water) at 20°C			
Substance	**Surface Tension (dynes/cm)**	**Substance**	**Interfacial Tension (dynes/cm)**
Mercury	476	Mercury	375
Water	72.8	Water	-------
Glycerin	63.4	Glycerin	Zero (miscible liquids)
Oleic acid (Carboxylic acid)	32.5	Oleic acid	15.6
Benzene	28.9	Benzene	35.0
Chloroform	27.1	Chloroform	32.8
Olive oil (Oleic acid is the chief constituent)	35.8	Olive oil	22.9
Octanol (alcohol)	26.5	Octanol	8.5

الارقام في الجدول للاطلاع

How to reduce Interfacial tension ?

- To dispense one immiscible liquid in the other, it is necessary to introduce another kind of molecule that has affinity for both liquids. This type of molecule is called surface active agent (S.A.A). These molecules when placed at the interface of the immiscible liquids, they decrease the interfacial tension, allowing these liquids to mix.



Factors affecting on surface and interfacial tension

The type of the liquid

The surface tensions reflects the differences in chemical structure
Mercury(metallic bonds) > water(H bonds) > benzene (London forces)

The interfacial tension reflects presence of chemical groups capable of hydrogen bonding: increase H-bonding, markedly decrease interfacial tension

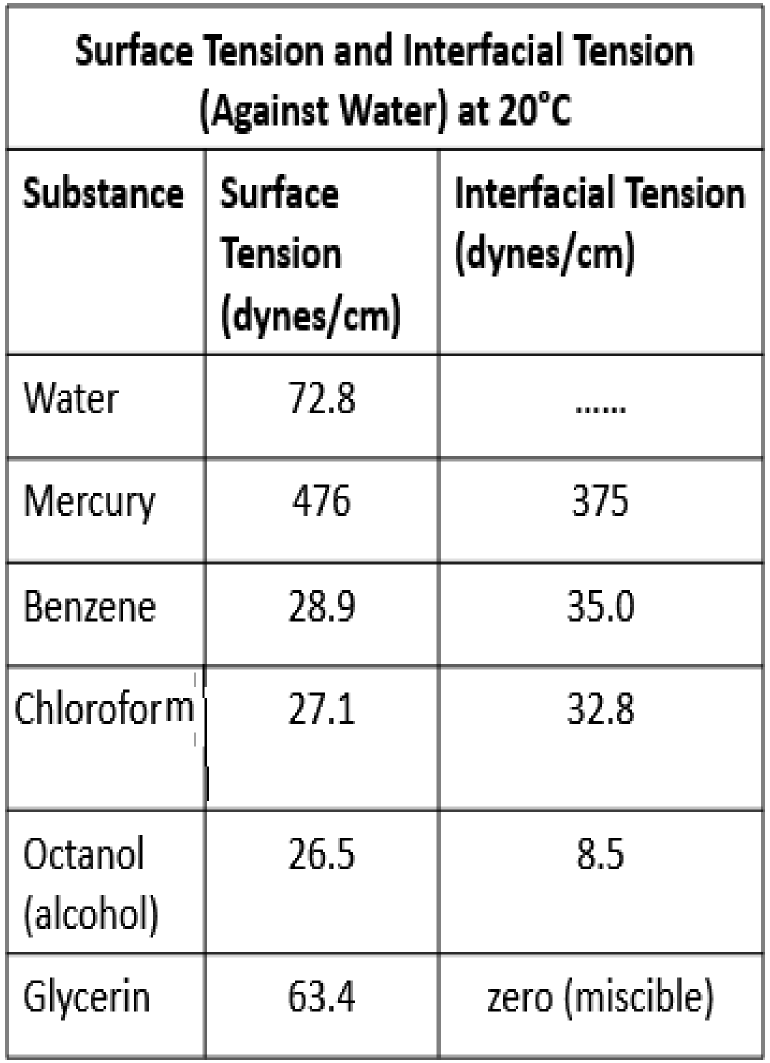
Temperature

↑Increasing temperature↓reduces surface and interfacial tension.

This is the reason for the higher ability of hot water compared to cold water in cleaning: the surface tension of cold water is about 72 dyne/cm at 25°C but goes down to less than 60 dyne/cm at 100°C.

What is mixed with the liquid

- Electrolytes slightly↑increase surface tension
- Surface active agents (e.g., soap and detergents)↓decrease surface and interfacial tension



Surface Tension and Interfacial Tension (Against Water) at 20°C

Substance	Surface Tension (dynes/cm)	Interfacial Tension (dynes/cm)
Water	72.8	......
Mercury	476	375
Benzene	28.9	35.0
Chloroform	27.1	32.8
Octanol (alcohol)	26.5	8.5
Glycerin	63.4	zero (miscible)

Factors affecting on surface and interfacial tension

Try it at home

Importance of Interfacial phenomena in pharmacy and medicine

Interfacial phenomena will influence on:

- ✓ The dispersion of insoluble particles in liquid media to form suspensions
- ✓ Emulsion formation and stability
- ✓ Adsorption of drugs onto solid particles in dosage forms
- ✓ The flow of particles and adhesion between granules
- ✓ The preparation of layered tablets
- ✓ The penetration of molecules through biologic membranes
- ✓ The interfacial properties of a surface-active agent lining the alveoli of the lung are responsible for the efficient operation of this organ