

COLLOIDS

Examples of colloidal systems from daily life



Foams



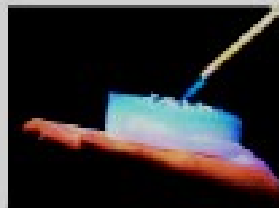
Milk



Fog, smoke



Detergents



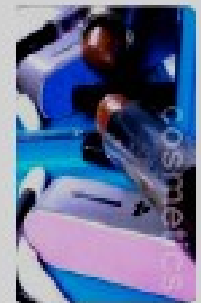
Aerogel



Blood



Paints



Cosmetics



Dispersed Systems:

- Dispersed systems consist of particulate matter (dispersed phase), distributed throughout a continuous phase (dispersion medium).
- They are classified according to the particle diameter of the dispersed material:

1- Molecular dispersions (less than 1 nm)

- Particles invisible in electron microscope
- Pass through semipermeable membranes and filter paper
- Particles do not settle down on standing
- Undergo rapid diffusion
- E.g. ordinary ions, glucose



Dispersed Systems:

2- Colloidal dispersions (1 nm - 0.5 μm)

- Particles not resolved by ordinary microscope, can be detected by electron microscope.
- Pass through filter paper but not pass through semipermeable membrane.
- Particles made to settle by centrifugation
- Diffuse very slowly
- E.g. colloidal silver sols, natural and synthetic polymers

3- Coarse dispersions (> 0.5 μm)

- Particles are visible under ordinary microscope
- Do not pass through filter paper or semipermeable membrane.
- Particles settle down under gravity
- Do not diffuse
- E.g. emulsions, suspensions, red blood cells



Dispersed Systems:

Classification Based on Size

Class	Size	Examples
Molecular dispersion	< 1.0 nm	Oxygen gas, ordinary ions, glucose
Colloidal dispersion	1.0 nm to 0.5 μm	Silver sols, natural and synthetic polymer latices
Coarse dispersion	> 0.5 μm	Sand, pharmaceutical emulsions & dispersions, red blood cells



Size and shape of colloids:

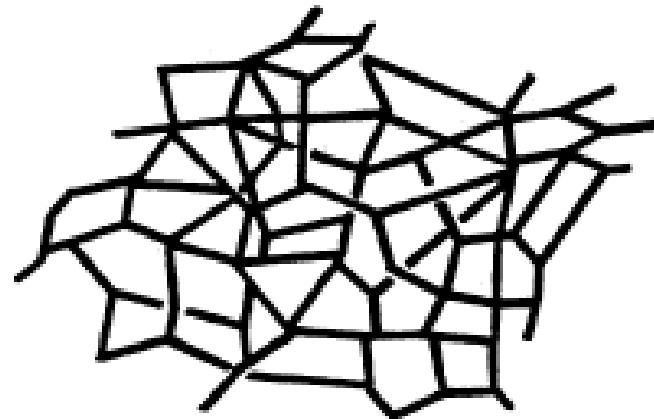
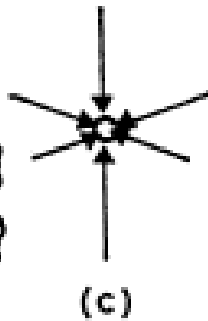
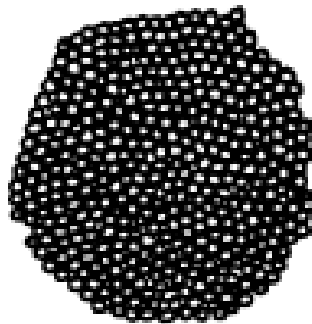
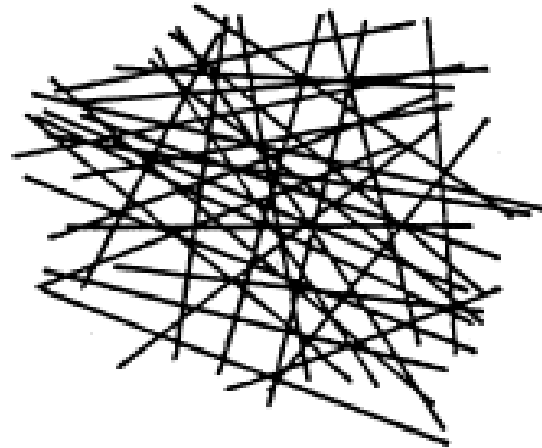
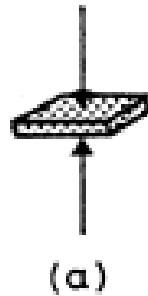
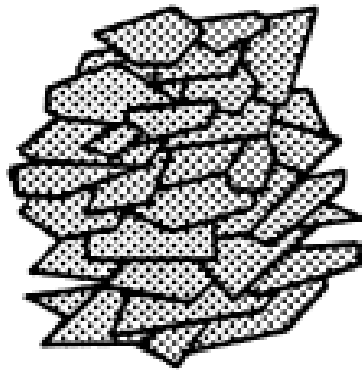
- Particles lying in the colloidal size have large surface area when compared with the surface area of an equal volume of larger particles.
 - **Specific surface:** the surface area per unit weight or volume of material.
 - **The possession of large specific surface results in:**
 - 1- platinum is effective as catalyst only when found in colloidal form due to large surface area which adsorb reactant on their surface.
 - 2- The colour of colloidal dispersion is related to the size of the particles
- e.g. red gold sol takes a blue colour when the particles increase in size



Size and shape of colloids:

- 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.
 - Flow, sedimentation and osmotic pressure of the colloidal system affected by the shape of colloidal particles.
 - Particle shape may also influence the pharmacologic action.

Different shapes of colloids



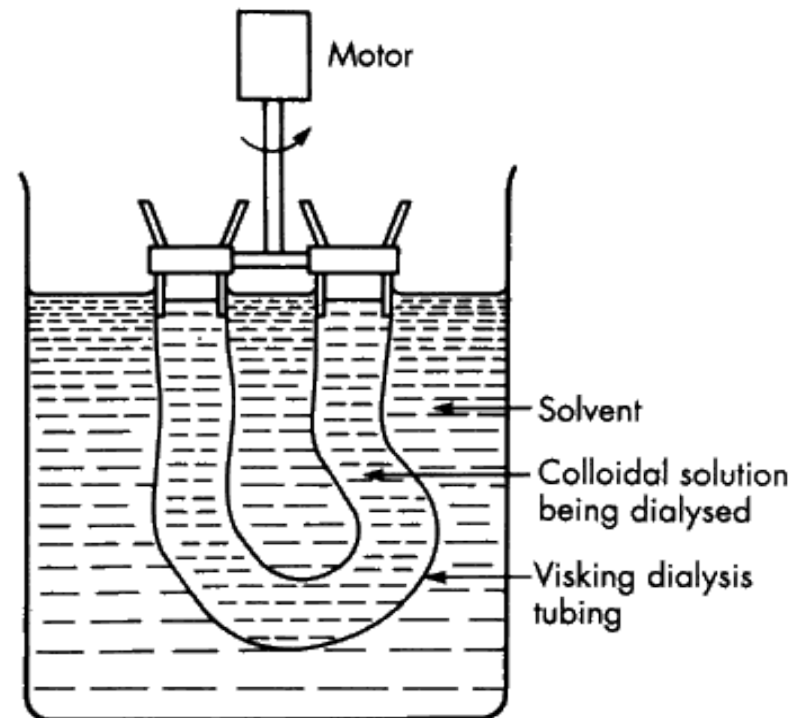
(d)

Purification of colloidal solutions:

- When a colloidal solution is prepared is often contains certain electrolytes which tend to destabilize it. The following methods are used for purification:

1- Dialysis:

- Semipermeable cellophane membrane prevent the passage of colloidal particles, yet allow the passage of small molecules or electrolytes.



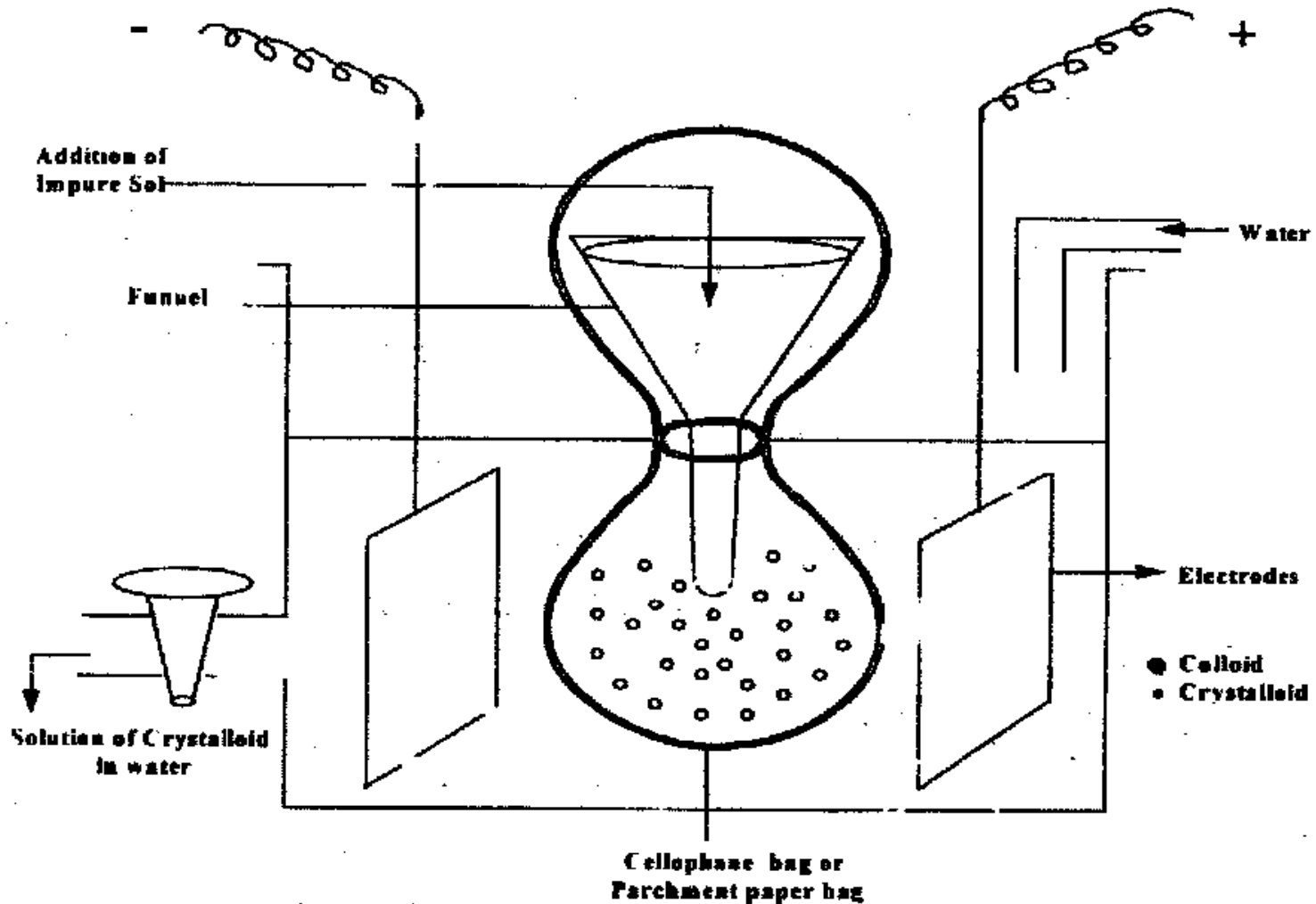
Purification of colloidal solutions:



2- Electrodialysis:

- In the dialysis unit, the movement of ions across the membrane can be speeded up by applying an electric current through the electrodes induced in the solution.
- The most important use of dialysis is the purification of blood in artificial kidney machines.
- The dialysis membrane allows small particles (ions) to pass through but the colloidal size particles (haemoglobin) do not pass through the membrane.

Electrodialysis:





Applications of colloidal solutions:

- 1- Therapy--- Colloidal system are used as therapeutic agents in different areas.
e.g- Silver colloid-germicidal
Copper colloid-anticancer
Mercury colloid-Antisyphilis
- 2- Stability---e.g. Lyophobic colloids prevent flocculation in suspensions.
e.g- Colloidal dispersion of gelatin is used in coating over tablets and granules which upon drying leaves a uniform dry film over them and protect them from adverse conditions of the atmosphere.



Applications of colloidal solutions:

4- Absorption--- As colloidal dimensions are small enough, they have a huge surface area. Hence, the drug constituted colloidal form is released in large amount.

e.g- sulphur colloid gives a large quantity of sulphur and this often leads to sulphur toxicity

5- Targeted Drug Delivery--- Liposomes are of colloidal dimensions and are preferentially taken up by the liver and spleen.



Applications of colloidal solutions:

6- Photography:

A colloidal solution of silver bromide in gelatine is applied on glass plates or celluloid films to form sensitive plates in photography.

7- Clotting of blood:

- Blood is a colloidal solution and is negatively charged.
- On applying a solution of FeCl_3 bleeding stops and blood clotting occurs as Fe^{+3} ions neutralize the ion charges on the colloidal particles.

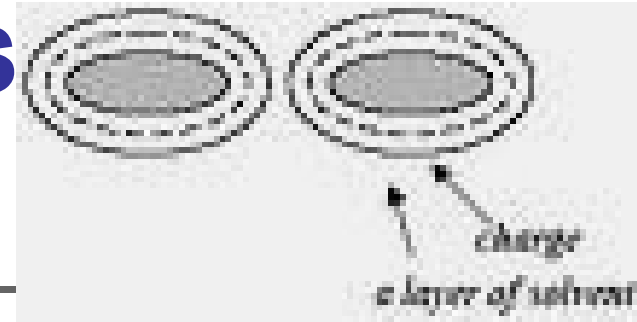
Types of colloids

Colloids are usually classified according to:

1- The original states of their constituent parts

Dispersed Phase	Dispersion Medium	Common Name	Examples
Solid	Solid	Solid Sol	Coloured gemstones, coloured glasses
Solid	Liquid	Sol	Paints, muddy water, gold sol, starch sol, arsenous sulphide sol
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Gellies, cheese
Liquid	Liquid	Emulsion	Milk, cod liver oil
Liquid	Gas	Liquid aerosol	Mist, fog, cloud
Gas	Solid	Solid foam	Foam rubber, pumice stone
Gas	Liquid	Foam	Froth, whipped cream

Types of colloids



2-The nature of interaction between dispersed phase and dispersion medium.

A-Lyophilic colloids (solvent attracting) (solvent loving) – The particles in a lyophilic system have a great affinity for the solvent.

- If water is the dispersing medium, it is often known as a hydrosol or hydrophilic.
- readily solvated (combined chemically or physically, with the solvent) and dispersed, even at high concentrations.
- More viscid

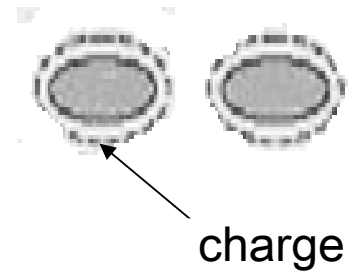


Types of colloids:

Examples of lyophilic sols include sols of gum, gelatin, starch, proteins and certain polymers (rubber) in organic solvents.

- the dispersed phase does not precipitate easily
- the sols are quite stable as the solute particle surrounded by two stability factors:
 - a- negative or positive charge
 - b- layer of solvent
- If the dispersion medium is separated from the dispersed phase, the sol can be reconstituted by simply remixing with the dispersion medium. Hence, these sols are called **reversible sols**.
- Prepared simply by dissolving the material in the solvent being used e.g. dissolution of acacia in water.

Types of colloids:



Lyophobic (solvent repelling) (solvent hating) - The particles resist solvation and dispersion in the solvent.

- The concentration of particles is usually relatively low.
- Less viscid
- These colloids are easily precipitated on the addition of small amounts of electrolytes, by heating or by shaking
- Less stable as the particles surrounded only with a layer of positive or negative charge
- Once precipitated, it is not easy to reconstitute the sol by simple mixing with the dispersion medium. Hence, these sols are called **irreversible sols**.
- Examples of lyophobic sols include **sols of metals and their insoluble compounds like sulphides and oxides**.

e.g. gold in water

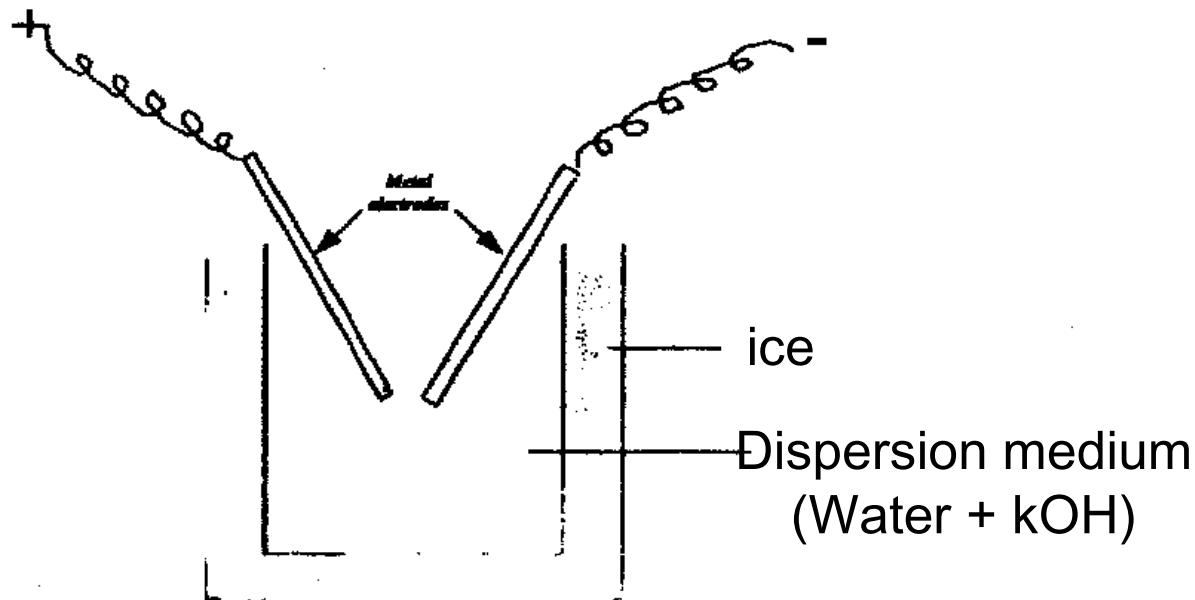


Types of colloids:

Prepared by:

1. Physical method (Bridge's arc method)

- This method is employed for obtaining colloidal solutions of metals e.g. silver, gold, platinum





I. Physical method (Bridge's arc method)

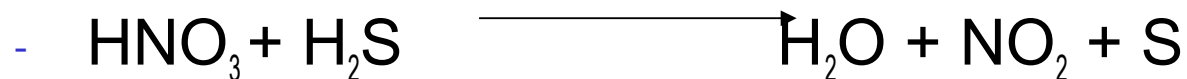
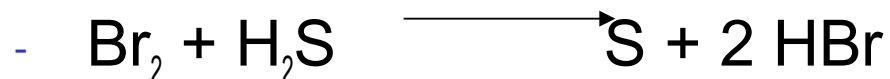
- An electric current is struck between two metallic electrodes placed in a container of water.
- The intense heat of the arc converts the metal into vapours which condensed immediately in the cold water bath.
- This results in the formation of particles of colloidal size.



Types of colloids:

II. Chemical method :by oxidation

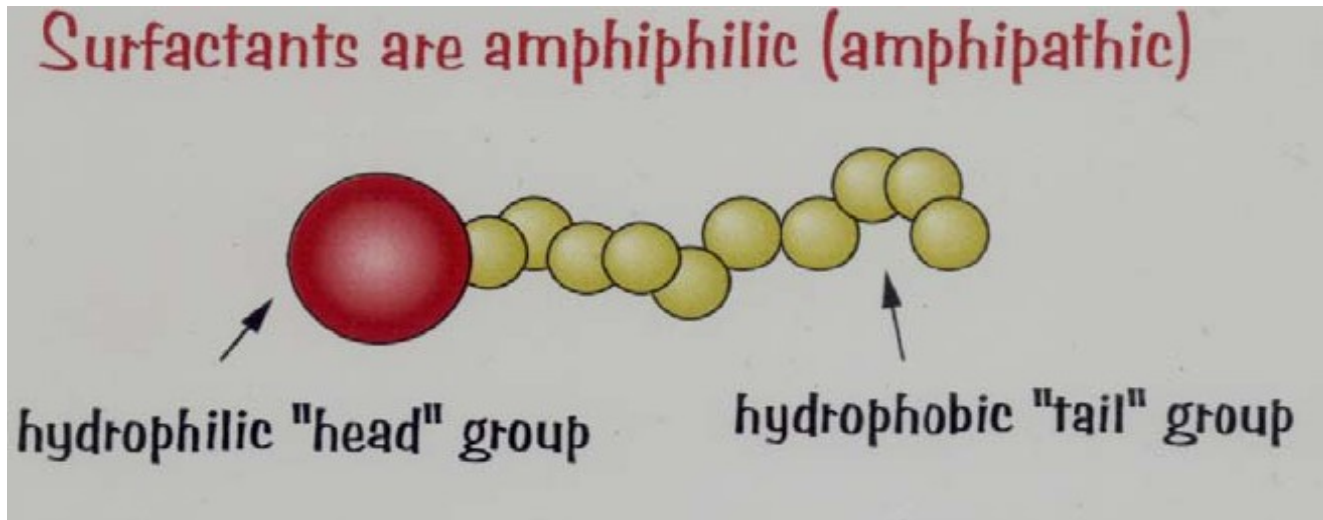
- Sulphur solution is obtained by bubbling H_2S gas through the solution of an oxidizing agent like HNO_3 or Br_2 in water , according to the following equations:



Types of colloids:

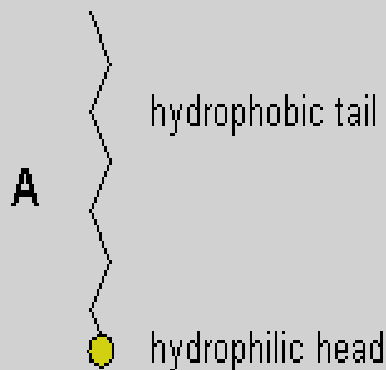
C- Association / amphiphilic colloids

- Certain molecules termed amphiphiles or surface active agents, characterized by two regions of opposing solution affinities within the same molecule.

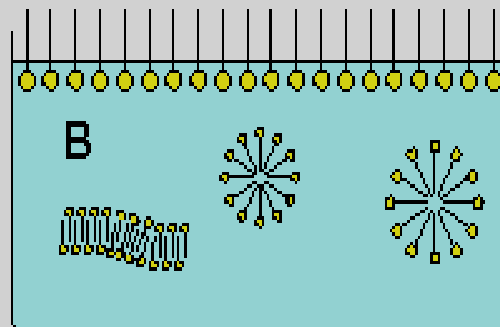


Types of colloids:

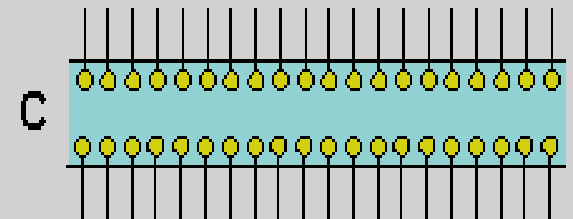
- **At low concentration:** amphiphiles exist separately (subcolloidal size)
- **At high concentration:** form aggregates or micelles (50 or more monomers) (colloidal size)



scheme of molecule of surfactant



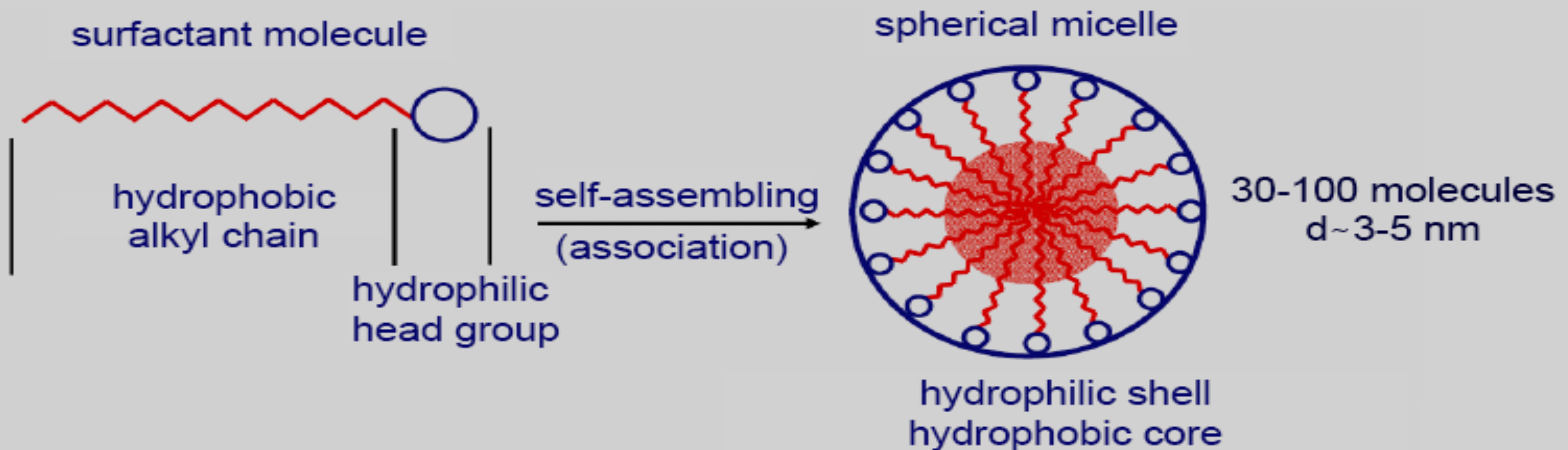
Surfactants arrange themselves on the water surface like a monolayer of molecules, and inside it as micelles and membranes tied by their hydrophobic tail. As the cohesion of these molecules is inferior to that of the molecules of water, the surface tension of water is lowered.



Layer of soapy water. The molecules of surfactant arrange themselves with the head in the water and the tail outside.

Association colloids

Surfactant micelles



cationic surfactant $\text{CH}_3(\text{CH}_2)_n\text{N}^+(\text{CH}_3)_3\text{Br}^-$
anionic surfactant $\text{CH}_3(\text{CH}_2)_n\text{SO}_3^- \text{Na}^+$
nonionic surfactant $\text{CH}_3(\text{CH}_2)_n(\text{CH}_2\text{CH}_2\text{O})_n\text{-OH}$

orientation \rightarrow energy minimum
Hardy-Harkins principle



Types of colloids:

Critical micelle concentration (C.M.C) : the concentration at which micelle form

- The phenomenon of micelle formation can be explained:

1- below C.M.C: amphiphiles are adsorbed at the air/water interface

2- As amphiphile concentration is raised: both the interphase and bulk phase become saturated with monomers (C.M.C)

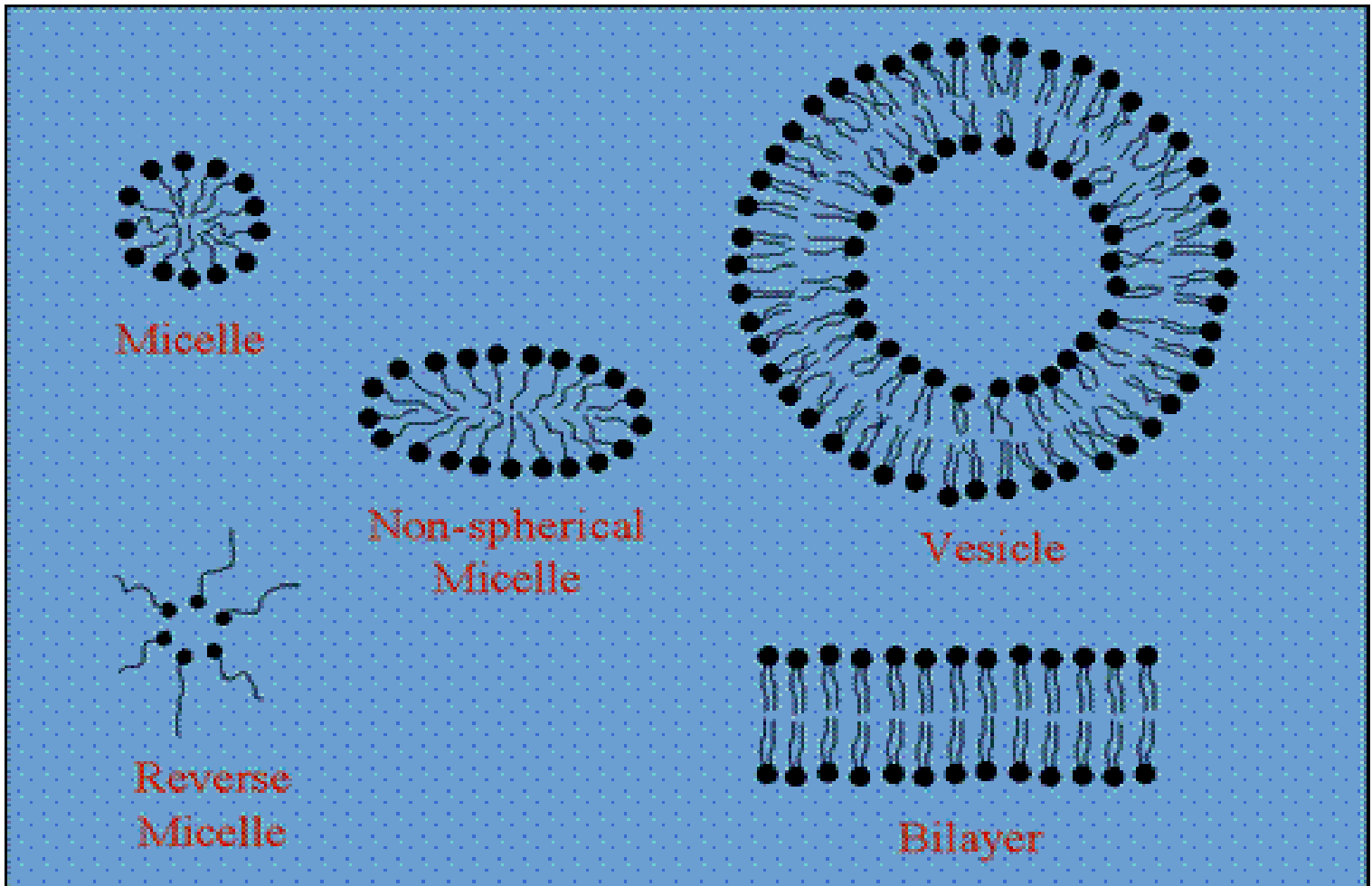
3- any further amphiphile added in excess: amphiphiles aggregate to form micelles



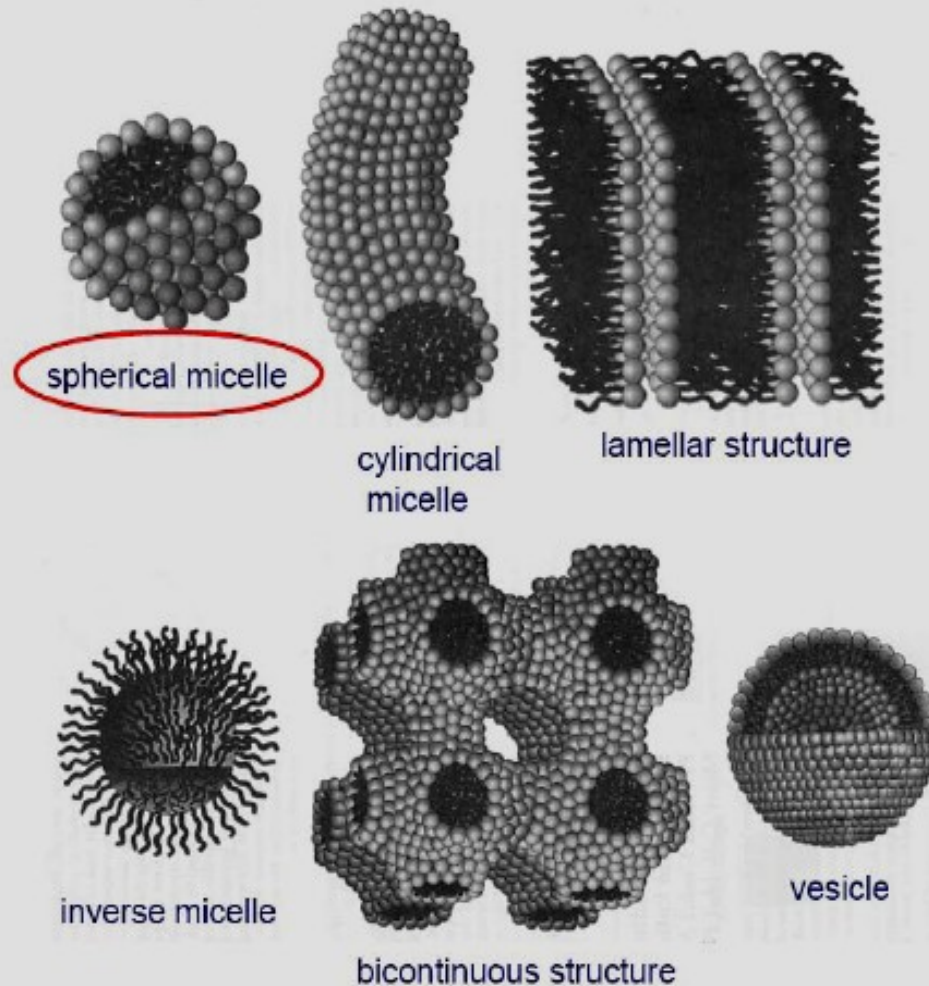
Types of colloids:

- **In water:** the hydrocarbon chains face inwards into the micelle forming hydrocarbon core and surrounded by the polar portions of the amphiphile associated with water molecules.
- **In non-polar liquid:** the polar heads facing inward and the hydrocarbon chains are associated with non-polar liquid.
- At concentrations close to C.M.C \longrightarrow spherical micelles
- At higher concentrations \longrightarrow lamellar micelles

Association Colloids



Shapes of surfactant aggregates





Types of colloids:

- The formation of association colloids is spontaneous, provided the concentration of amphiphile in solution exceed C.M.C.

Comparison of colloidal sols

Lyophilic

Dispersed phase
(large organic mole.
With colloidal size)

Molec. of dispersed
phase are solvated

Formed
spontaneously

The viscosity \uparrow with \uparrow
the dispersed phase
conc.

Stable dispersion in
presence of
electrolytes

Associated

Dispersed phase
(micelles of organic
molec. Or ion –size
below the colloidal
range)

Hydrophilic and lyophilic
portion are solvated ,

Formed at conc. above
CMC

The viscosity \uparrow with \uparrow
the micelles conc.

CMC \downarrow with electrolytes

Lyophobic

Dispersed phase
(Inorganic particles as
gold)

Not formed
spontaneously

Not greatly increase

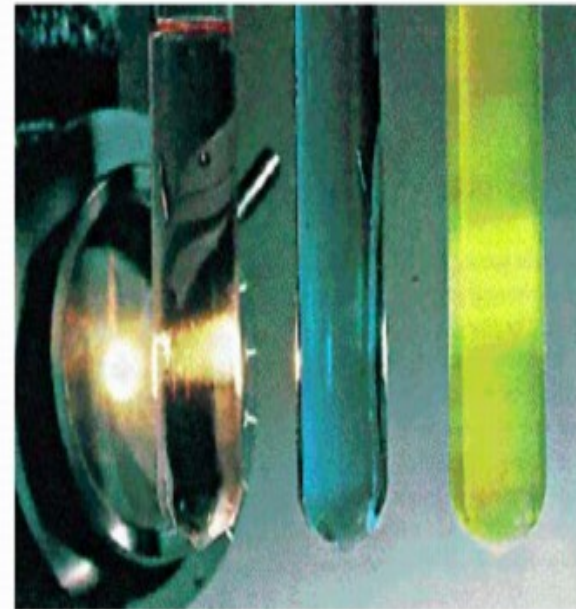
Unstable dispersion in
presence of
electrolytes

Optical Properties of Colloids

1-Faraday-Tyndall effect

- when a strong beam of light is passed through a colloidal sol, the path of light is illuminated (a visible cone formed).
- This phenomenon resulting from the scattering of light by the colloidal particles.

Unlike solutions, colloidal suspensions exhibit light scattering.

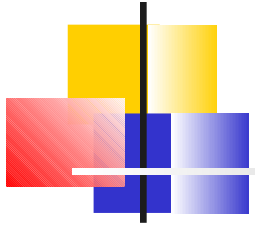


1 2 3

Tyndall effect

1. purple gold sol
2. copper sulfate solution
3. iron(III) hydroxide colloid

Optical Properties of Colloids

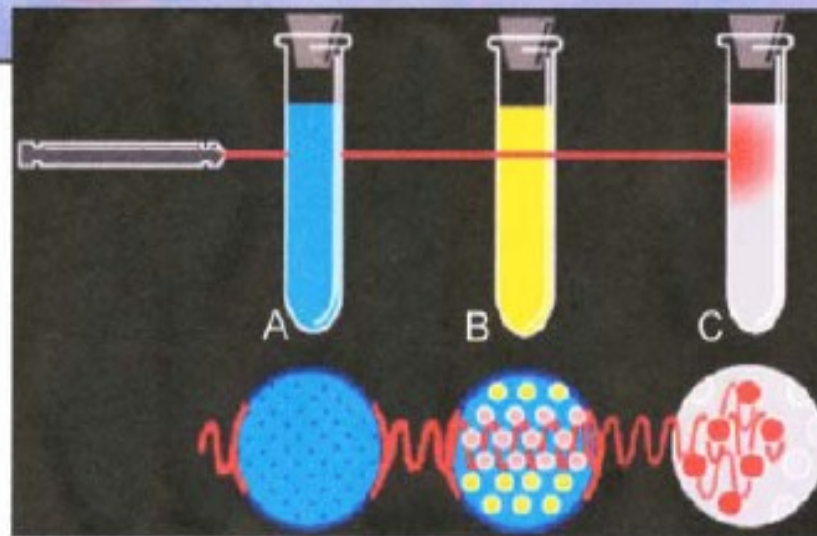


-
- The same effect is noticed when a beam of sunlight enters a dark room through a slit when the beam of light becomes visible through the room.
 - This happens due to the scattering of light by particles of dust in the air.

The Faraday-Tyndall effect



Tyndall Effect: Laser Pointer traveling through a solution (right) and through a colloidal suspension (left).



A: Solution

B: Colloidal Suspension
Transparent

C: Colloidal Suspension
completely absorbing light

Optical Properties of Colloids



2- Electron microscope

- Ultra-microscope has declined in recent years as it does not able to resolve lyophilic colloids.
- so electron microscope is capable of yielding pictures of actual particles size, shape and structure of colloidal particles.
- Electron microscope has high resolving power, as its radiation source is a beam of high energy electrons, while that of optical microscope is visible light.

Electron Microscope

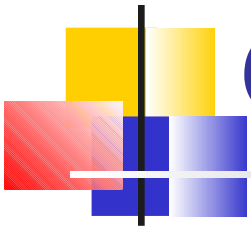




Optical Properties of Colloids

3- Light Scattering

- depend on tyndall effect.
- used to give information about particle size and shape and for determination of molecular weight of colloids.
- Used to study proteins, association colloids and lyophobic sols.
- Scattering described in terms of turbidity, T
- *Turbidity*: the fractional decrease in intensity due to scattering as the incident light passes through 1 cm of solution.
- Turbidity is proportional to the molecular weight of lyophilic colloid



Optical Properties of Colloids

$$H_c / T = 1/M + 2Bc$$

T: turbidity

C: conc of solute in gm / cc of solution

M: molecular weight

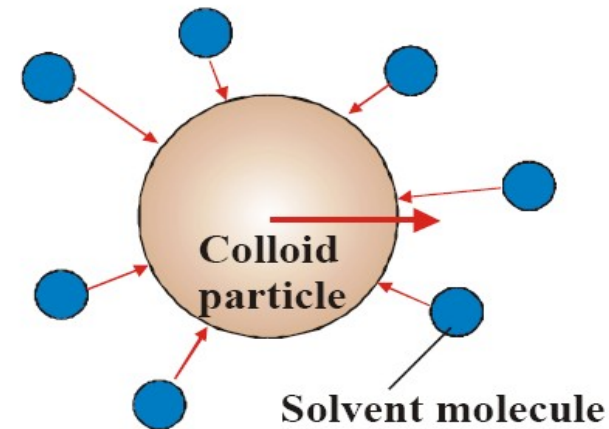
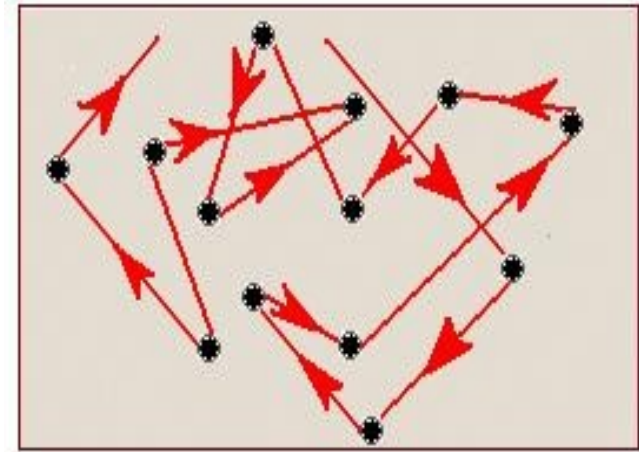
B: interaction constant

H: constant for a particular system

Kinetic Properties of Colloids

1-Brownian motion

- The zig-zag movement of colloidal particles continuously and randomly.
- This brownian motion arises due to the uneven distribution of the collisions between colloid particle and the solvent molecules.
- Brownian movement was more rapid for smaller particles.
- It decrease with increase the viscosity of the medium.





Kinetic Properties of Colloids

2- Diffusion

- Particles diffuse spontaneously from a region of higher conc. To one of lower conc. Until the conc. of the system is uniform throughout.
- Diffusion is a direct result of Brownian motion.
- *Fick's first law* used to describe the diffusion:
(The amount of Dq of substance diffusing in time dt across a plane of area A is directly proportional to the change of concentration dc with distance traveled)

$$dq = -DA (dc / dx) dt$$



Kinetic Properties of Colloids

D → diffusion coefficient

the amount of the material diffused per unit time across a unit area **when dc/dx** (conc. gradient) is unity.

- The measured diffusion coefficient can be used to determine the radius of particles or molecular weight.



Kinetic Properties of Colloids

3- Osmotic pressure

- van 't hoff equation:

$$\pi = cRT$$

- Can be used to determine the molecular weight of colloid in dilute solution.
- Replacing c by C / M (where C = the grams of solute / liter of solution, M = molecular weight)

$$\pi/C = RT/M$$



Kinetic Properties of Colloids

π = osmotic pressure

R = molar gas constant

4- Sedimentation

- The velocity of sedimentation is given by Stokes' Law:

$$v = \frac{d^2 (\rho_i - \rho_e)g}{18\eta}$$

V = rate of sedimentation

D = diameter of particles

ρ = density of internal phase and external phase

g = gravitational constant

η = viscosity of medium



Kinetic Properties of Colloids

5- Viscosity:

- It is the resistance to flow of system under an applied stress. The more viscous a liquid, the greater the applied force required to make it flow at a particular rate.
- The viscosity of colloidal dispersion is affected by the shape of particles of the disperse phase:

Spherocolloids → dispersions of low viscosity

Linear particles → more viscous dispersions

Electric Properties Of Colloids

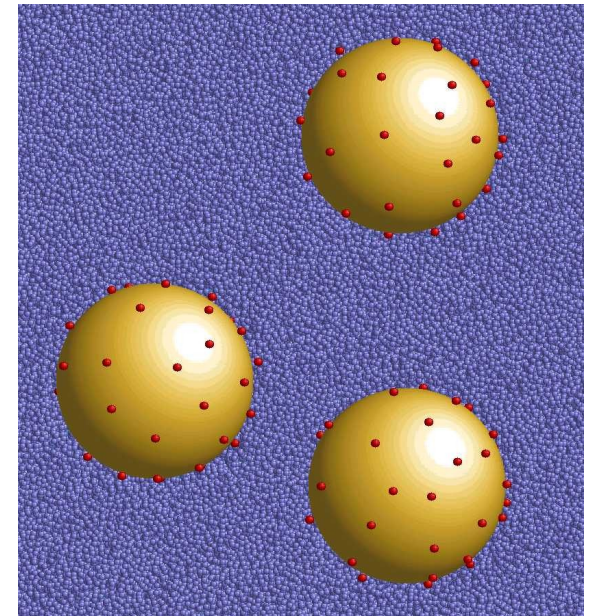
- The particles of a colloidal solution are electrically charged and carry the same type of charge, either negative or positive.
- The colloidal particles therefore repel each other and do not cluster together to settle down.
- The charge on colloidal particles arises because of the dissociation of the molecular electrolyte on the surface.
- *E.g. As_2S_3 has a negative charge*

During preparation of colloidal As_2S_3 , H_2S is absorbed on the surface and dissociate to H^+ (lost to the medium) and $.S^{-2}$ remain on the surface of colloid

Electric Properties Of Colloids

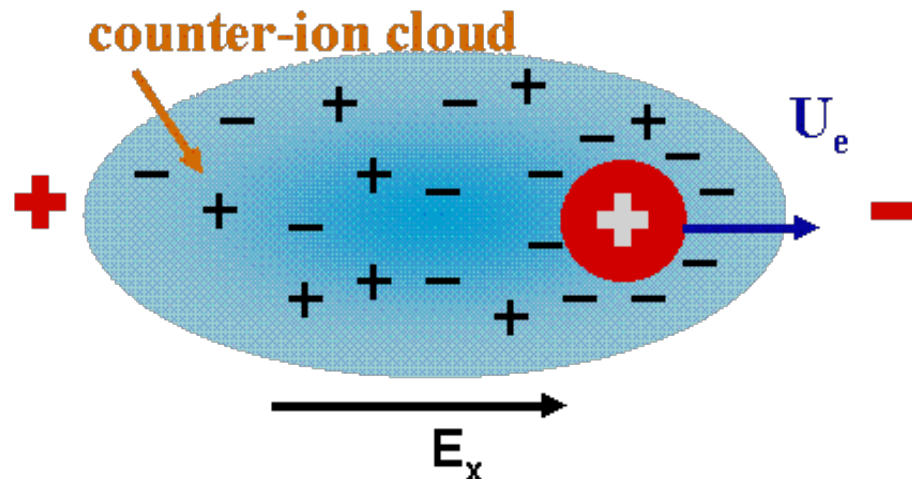
- *$Fe(OH)_3$ is positively charged*

Due to self dissociation and loss of OH^- to the medium, so they become $[Fe(OH)_3] Fe^{+3}$

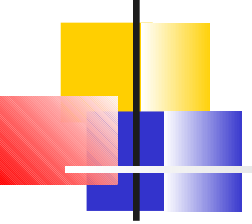


Electrophoresis

- Electrophoresis is the most known electrokinetic phenomena. It refers to the motion of charged particles related to the fluid under the influence of an applied electric field.
- If an electric potential is applied to a colloid, the charged colloidal particles move toward the oppositely charged electrode.



Electro-osmosis

- 
-
- It is the opposite in principle to that of electrophoresis.
 - When electrodes are placed across a clay mass and a direct current is applied, water in the clay pore space is transported to the cathodically charged electrode by electro-osmosis.
 - Electro-osmotic transport of water through a clay is a result of diffuse double layer cations in the clay pores being attracted to a negatively charged electrode or cathode. As these cations move toward the cathode, they bring with them water molecules that clump around the cations as a consequence of their dipolar nature.

Electro-osmosis

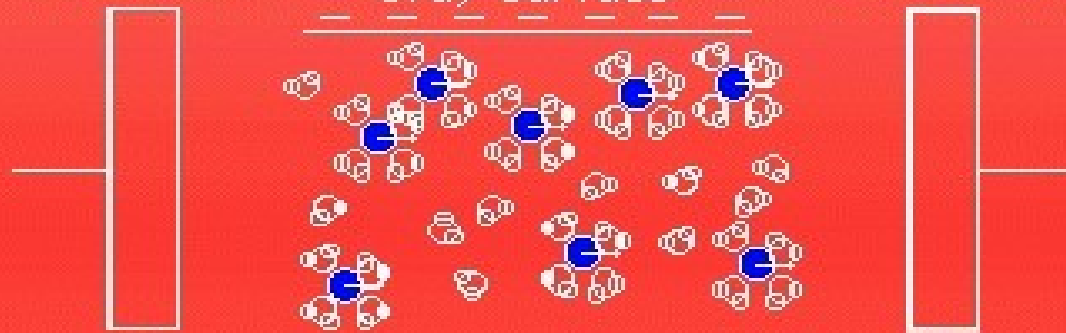


Model of water and salt movement by electric field

+ anode (Pt)

- cathode (Pt)

clay surface



+side

● Na

○ H₂O

-side

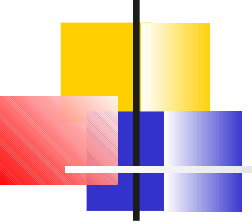


Mass flow $\frac{\partial M}{\partial t} = D \cdot \frac{\partial^2 M}{\partial x^2} + k \cdot \frac{\partial (M \cdot \psi_x)}{\partial x}$

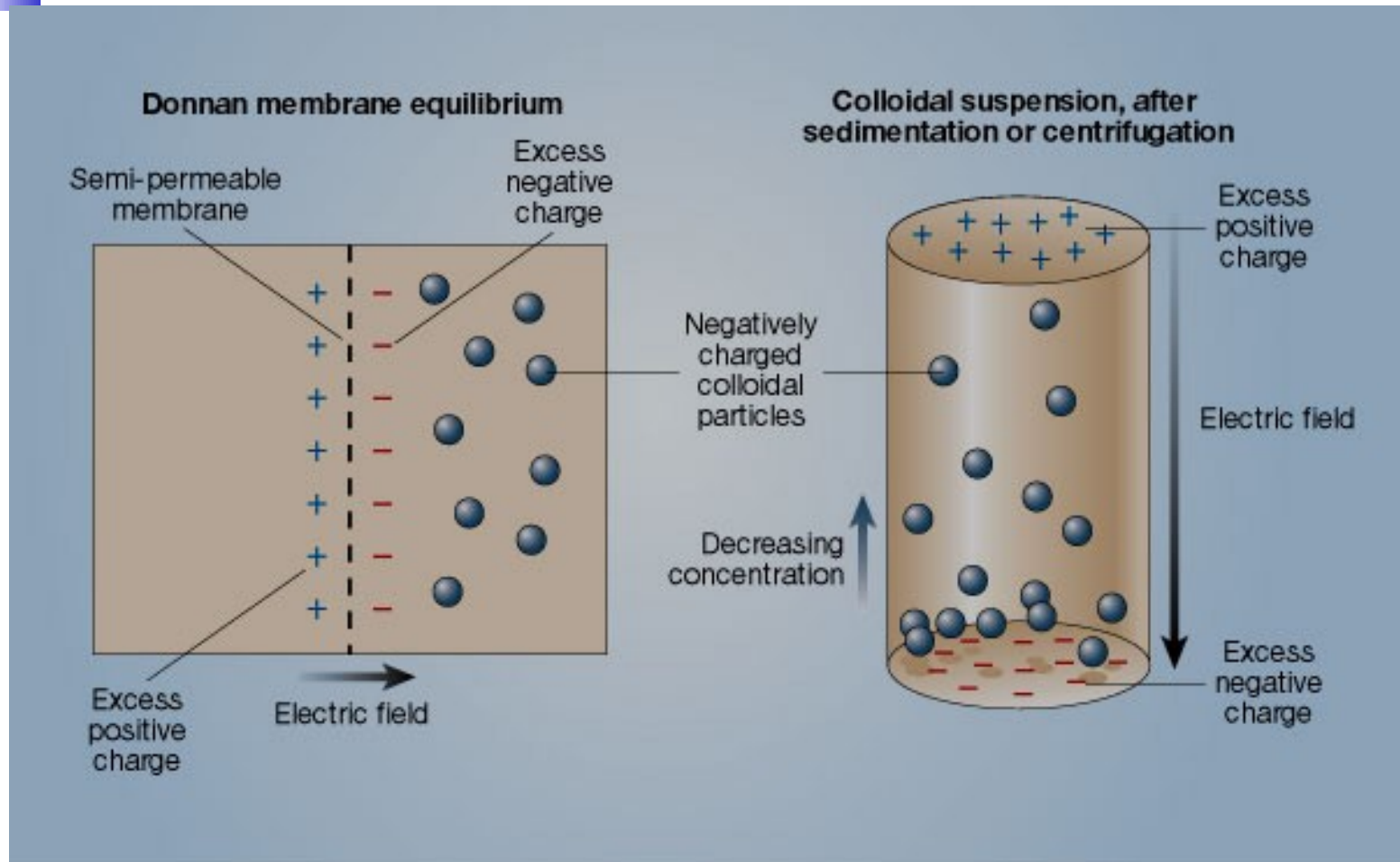
M : Na⁺, water t : time D : diffused coefficient k : coefficient

x : distance ψ_x : electric gradient

Sedimentation Potential

- 
-
- The sedimentation potential also called the *(Donnan effect)*.
 - It is the potential induced by the fall of a charged particle under an external force field.
 - It is analogous to electrophoresis in the sense that a local electric field is induced as a result of its motion.
 - if a colloidal suspension has a gradient of concentration (such as is produced in sedimentation or centrifugation), then a macroscopic electric field is generated by the charge imbalance appearing at the top and bottom of the sample column.

Sedimentation Potential

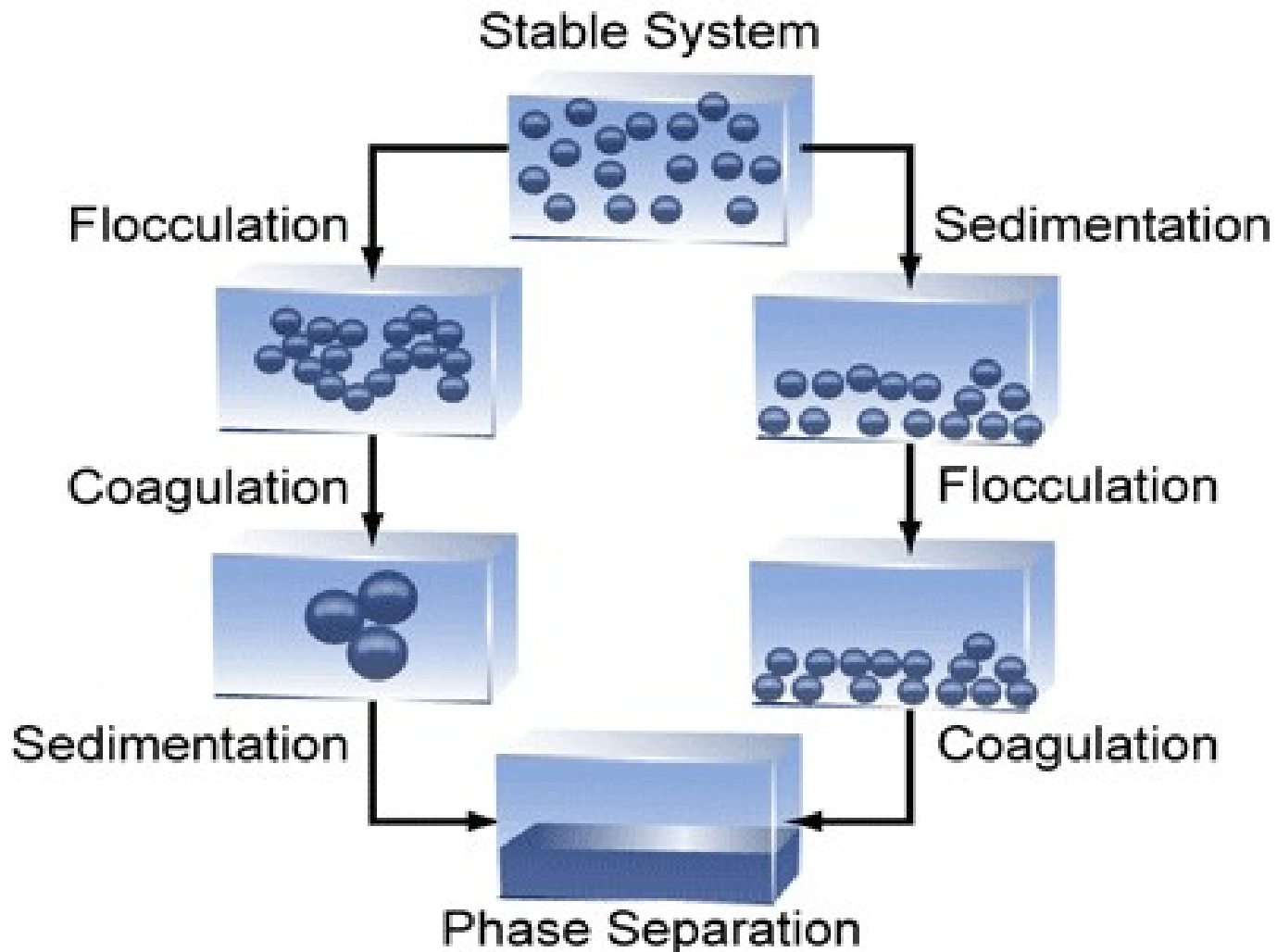




Streaming Potential

- Differs from electro-osmosis in that the potential is created by forcing a liquid to flow through a bed or plug of particles.

Stability of colloids





Stability of colloids

- Stabilization serves to prevent colloids from aggregation.
- The presence and magnitude, or absence of a charge on a colloidal particle is an important factor in the stability of colloids.
- Two main mechanisms for colloid stabilization:
 - 1-**Steric stabilization** i.e. surrounding each particle with a protective solvent sheath which prevent adherence due to Brownian movement
 - 2-**electrostatic stabilization** i.e. providing the particles with electric charge



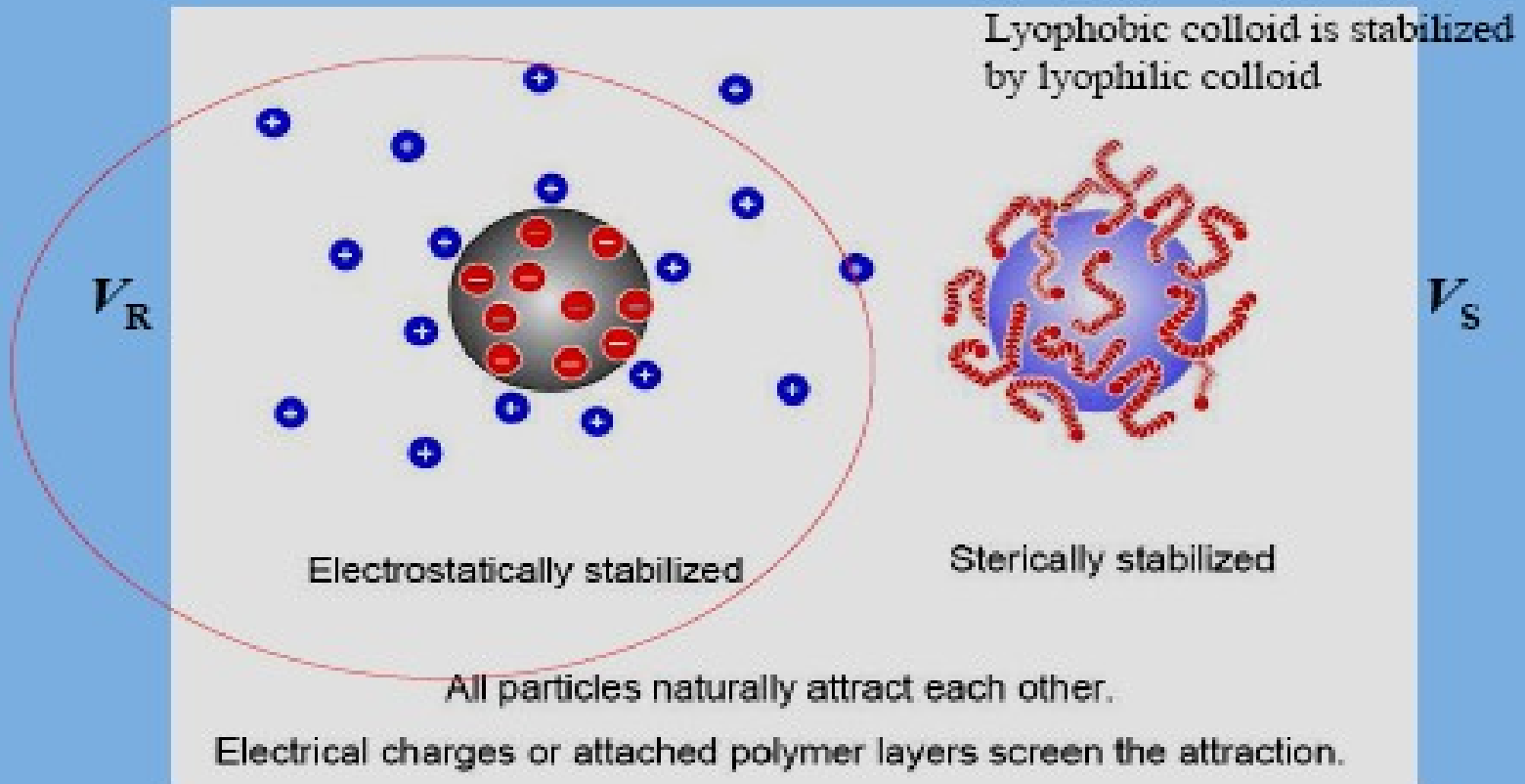
Stability of colloids

A- Lyophobic sols:

- Unstable.
- The particles stabilized only by the presence of electrical charges on their surfaces through the addition of small amount of electrolytes.
- The like charges produce repulsion which prevent coagulation of the particles and subsequent settling.
- Addition of electrolytes beyond necessary for maximum stability results in \longrightarrow accumulation of opposite ions and decrease zeta potential \longrightarrow coagulation \longrightarrow precipitation of colloids.

Stability of colloids

Colloidal stability requires a **repulsion force**:





Stability of colloids

- Coagulation also result from mixing of oppositely charged colloids.

B- Lyophilic sols and association colloids:

- Stable
- Present as true solution
- Addition of moderate amounts of electrolytes not cause coagulation (opposite lyophobic)

** Salting out:

Definition: agglomeration and precipitation of lyophilic colloids.



Stability of colloids

- This is obtained by:

1- Addition of large amounts of electrolytes

- Anions arranged in a decreasing order of precipitating power: citrate > tartrate > sulfate > acetate > chloride > nitrate > bromide > iodide
- The precipitation power is directly related to the hydration of the ion and its ability to separate water molecules from colloidal particles

2- addition of less polar solvent

- e.g. alcohol, acetone



Stability of colloids

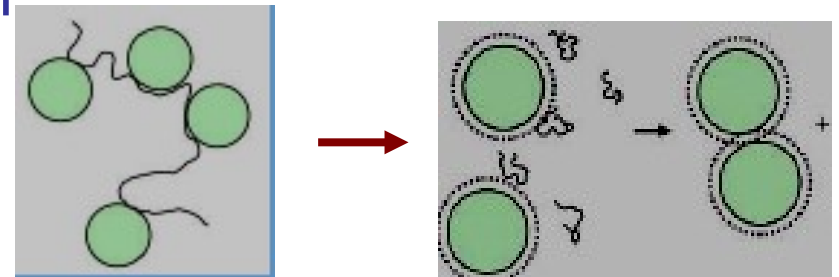
- The addition of less polar solvent renders the solvent mixture unfavourable for the colloids → ↓solubility

** Coacervation:

Definition: the process of mixing negatively and positively charged hydrophilic colloids, and hence the particles separate from the dispersion to form a layer rich in the colloidal aggregates (**coacervate**)

Sensitization and protective colloidal action:

- ***Sensitization:*** the addition of small amount of hydrophilic or hydrophobic colloid to a hydrophobic colloid of opposite charge tend to sensitize (coagulate) the particles.
- Polymer flocculants can bridge individual colloidal particles by attractive electrostatic interactions.
- For example, negatively-charged colloidal silica particles can be flocculated by the addition of a positively-charged polymer



Sensitization and protective colloidal action:

- *Protection*: the addition of large amount of hydrophilic colloid (**protective colloid**) to a hydrophobic colloid tend to stabilize the system.
- This may be due to:

The hydrophile is adsorbed as a monomolecular layer on the hydrophobic particles.

