# Lecture 8. Colloid systems. Micelles

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# What kind of systems are colloid systems?

- Many definitions exist:
- Those systems in which the surface plays significant role in their behaviour.
- **Colloids** are those **(disperse) systems** which consist ***particles in size of 1 nm-500 nm*** (1nm = $10^{-9}$ m) The colloid state is independent on the chemical nature, every condensed phase can be turned into colloidal system.

# What is a colloid?

**Finely-divided dispersion of one phase in another**

**Size of dispersed ("solute-like") entity >> ordinary molecules**

**Example: blood cell in water.**

**Solution**
**homogeneous**
**particles** are molecules

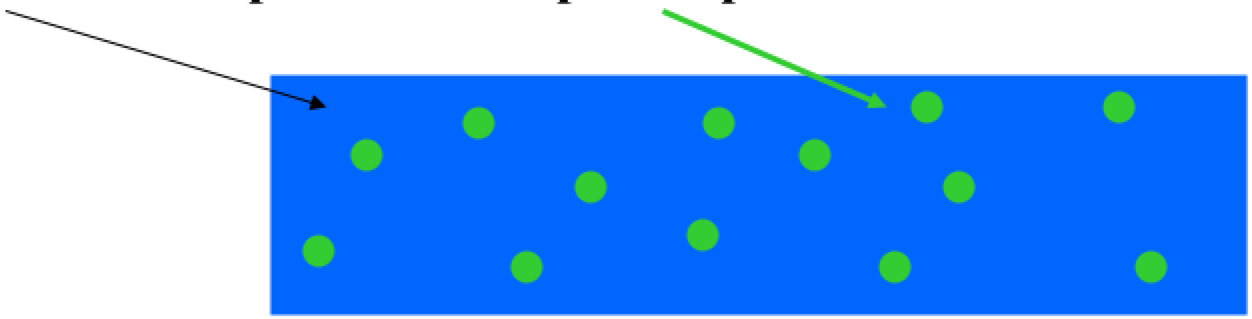
**Suspension**
**heterogeneous**
**particles** settle out

**Colloid**
**size 1–1000 nm**
particles remain suspended

| Property | True solution | Suspension | Colloidal solution |
|---|---|---|---|
| Nature | Homogeneous | Heterogeneous | Appears to be homogenous but actually heterogeneous |
| Particle size | < $10^{-9}$ A° (1 nm) | > 1000 A° (100 nm) | Between 10 A° (1 nm) to 1000 A° (100 nm) |
| Sedimentation | Do not settle | Settle on standing | Do not settle |
| Diffusion | Diffuse quickly | Unable to diffuse | Diffuse slowly |
| Visibility | Particles invisible | Particles visible by naked eye or under microscope | Particles scatter light and can be observed under ultramicroscope |
| Filterability | Pass easily through animal membrane and filter paper | Unable to pass through animal membrane or filter paper | Pass through filter paper but not through animal membrane |
| Appearance | Clear and transparent | Opaque | Translucent |

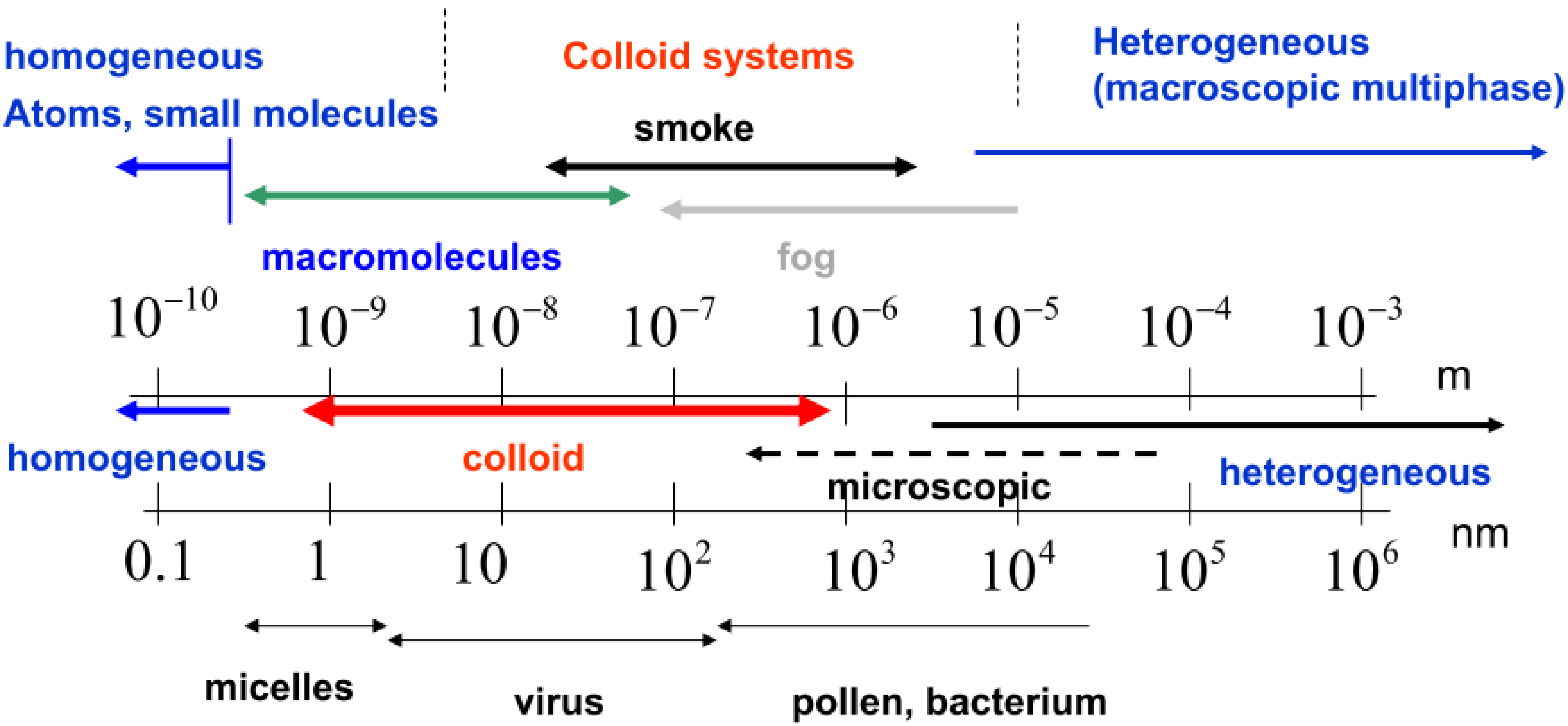
# Characteristics of colloids

- Continuous phase and dispersed phase



- Thermodynamically unstable but kinetically stable (i.e. they are stable indefinitely)
- Classified in terms of dispersed substance (solid, liquid, gas) in dispersing medium (solid, liquid, gas)
- Dispersed phase 10–1000 nm particles:
  - Large surface area to volume ratio
  - Size appropriate for scattering light
  - May have charged surfaces
- The name: Greek *kolla* = glue, *eidos*= like

# Are the colloid systems are homogeneous or heterogeneous?



# 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 - o.5 um)*

- 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, naural and synthetic polymers

*3- Coarse dispersions (> 0.5 um)*

- 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

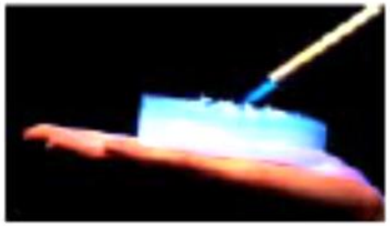
# Examples of colloidal systems from daily life

Foams

Milk

Fog, smoke


Detergents



Aerogel

Blood

Paints


Cosmetics

# Classification of colloids

Colloid systems

- INCOHERENT
  „fluid like"
  (individual particles)
  The attraction (coherent forces) is weaker than thermal energy
  - Colloidal dispersions (sols)
  - Solution of macromolecules
    proteins
    DNA, RNA
    polymers
  - Association colloids
    Association of small molecules
- COHERENT
  „solid" like
  (network structure)
  The attraction is stronger than the thermal energy (because of cross-links)
  - Porodin (porous materials)
  - Reticular (cross-linked fibrils)
  - Spongoid „sponge"-like systems

# Classification of colloids

Colloidal dispersions (sols)

**Aerosols** (the medium is gas)

- L/G: fog, mists, spray
- S/G: smoke, colloidal powder
- S/L/G: smog

**Liosols** (the medium is liquid)

- G/L: foam (whipped cream)
- L/L: emulsion (milk)
- S/L: suspension (toothpaste, mud)

**Xerosols** (the medium is solid)

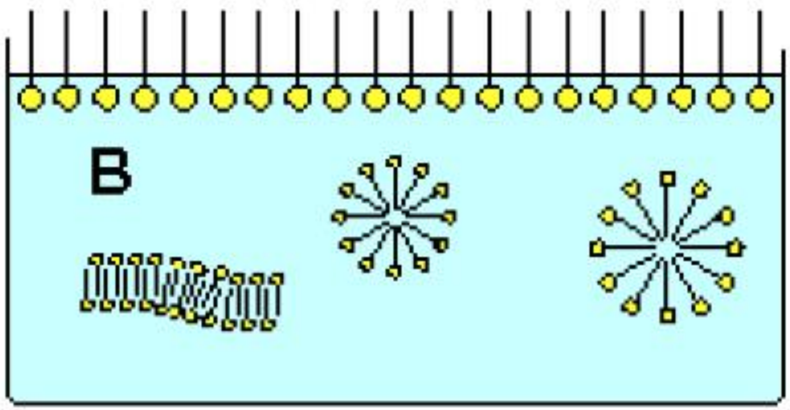
- G/S: solid foam (bread)
- L/S: solid emulsion (opals, pearls)
- S/S: solid suspensions (pigmented plastics)

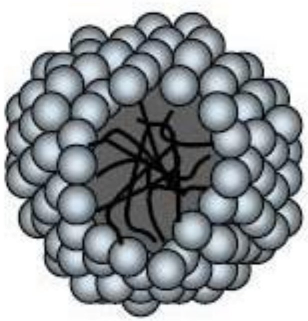
# Comparison of colloidal sols

| Lyophilic | Associated | Lyophobic |
|---|---|---|
| Dispersed phase (large organic mole. With colloidal size) | Dispersed phase (micelles of organic molec. Or ion –size below the colloidal range) | Dispersed phase (Inorganic particles as gold) |
| Molec. of dispersed phase are solvated<br>Formed spontaneously | Hydrophilic and lyophilic portion are solvated ,<br>Formed at conc. above CMC | Not formed spontaneously |
| The viscosity ↑ with ↑ the dispersed phase conc. | The viscosity ↑ with ↑ the micelles conc. | Not greatly increase |
| Stable dispersion in presence of electrolytes | CMC↓ with electrolytes | Unstable dispersion in presence of electrolytes |

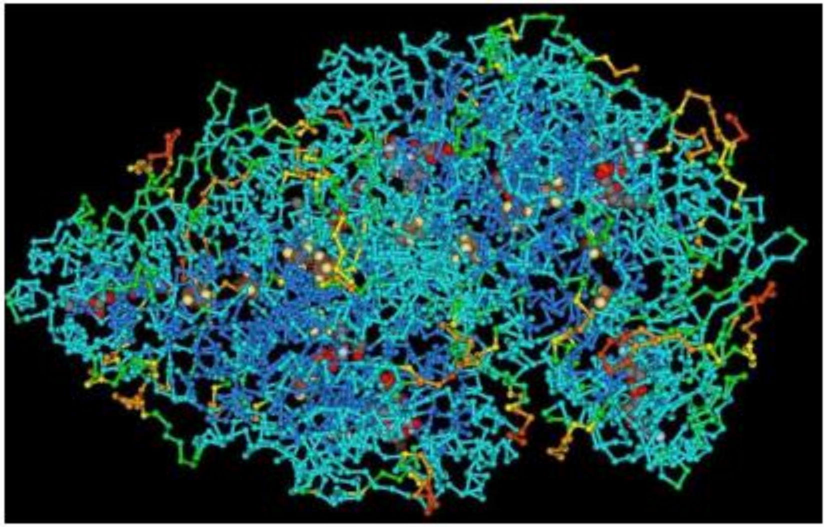
# Classification of colloids

Association colloids



Macromolecular colloids

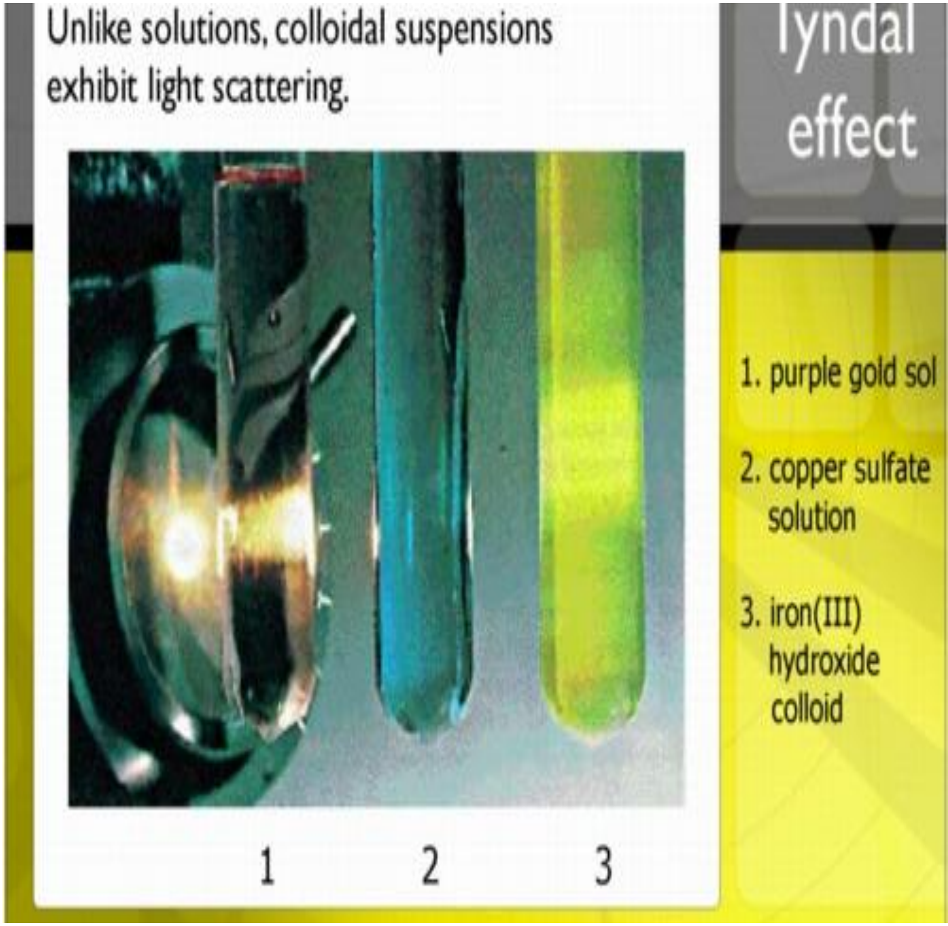


# Optical Properties of Colloids

**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).

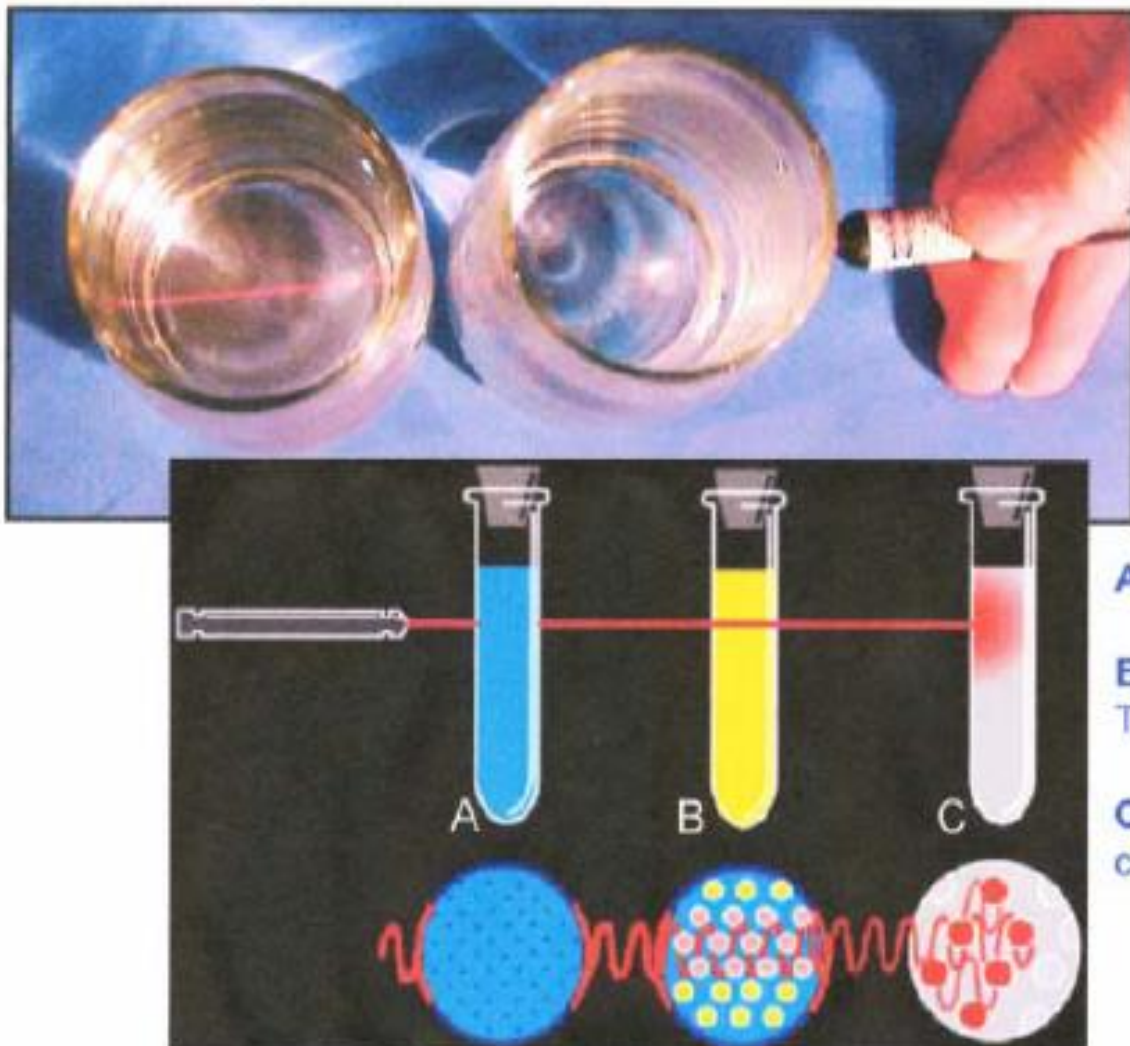
- This phenomenon resulting from the scattering of light by the colloidal particles.



# 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

# Characterization by stability

## Thermodynamic

**Stable (lyophilic colloids)**

$G_{colloid} < G_{initial}$

Association and macromolecular colloids

**Unstable (lyophobic colloids)**

$G_{colloid} > G_{initial}$

Colloidal dispersions

## Kinetic

**Stable**

NO change during the examination

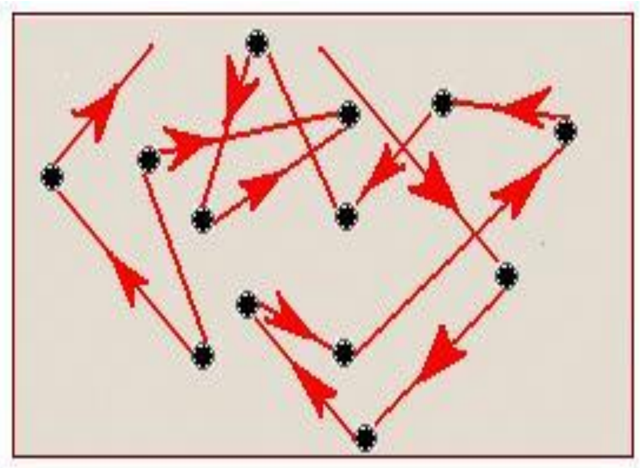
**Unstable**

Significant change can be observed Within the examination

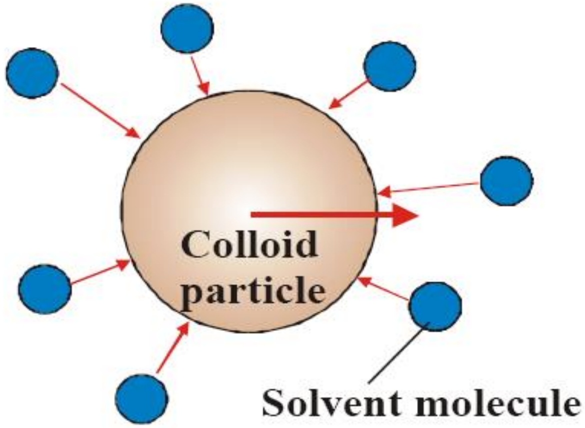
# Kinetic Properties of Colloids

## 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 coeffecient 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

$\pi$ = osmotic pressure
R= molar gas constant

**4- Sedimentation**

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

$$v = d2\ (\rho i - \rho e) g / 18\eta$$

V = rate of sedimentation
D = diameter of particles
$\rho$ = density of internal phase and external phase
g = gravitational constant
$\eta$ = 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

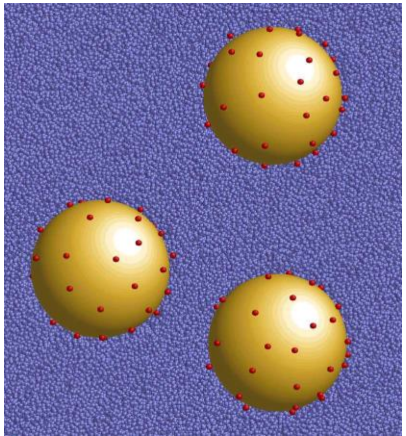
- The particles of a colloidal solution are electrically charged and carry the same type of charge, either negative or positive.
- The colloidal particles therefore repel each other and do not cluster together to settle down.
- The charge on colloidal particles arises because of the dissociation of the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

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

Due to self dissociation and loss of $OH^-$

to the medium, so they become $[Fe(OH)_3]$ $Fe^{+3}$



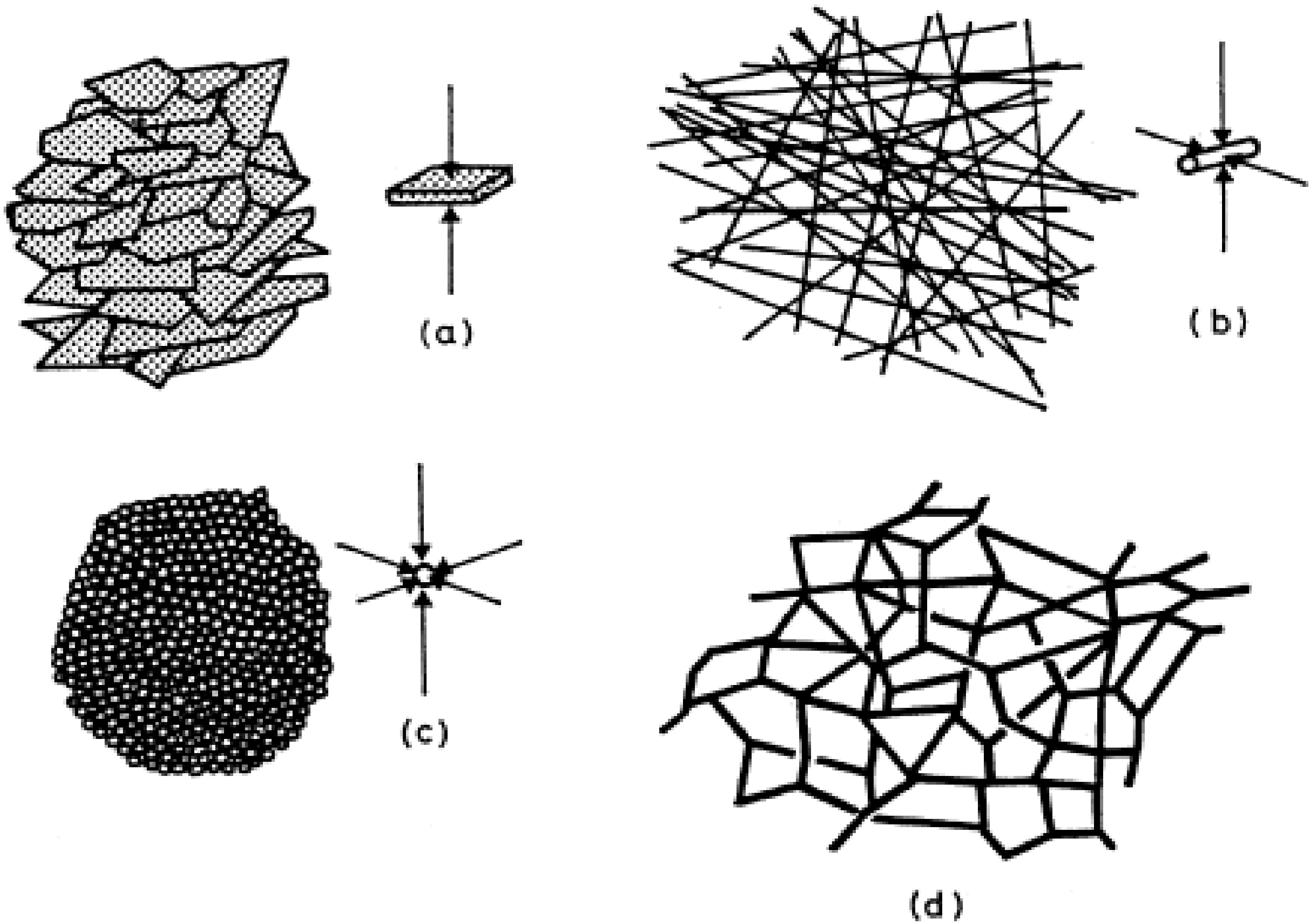
# Size and shape of colloids:

- 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.

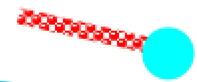
- Flow, sedimentation and osmotic pressure of the colloidal system affected by the shape of colloidal particles.
- Particle shape may also influence the pharmacologic action.

# Different shapes of colloids



# Surfactants

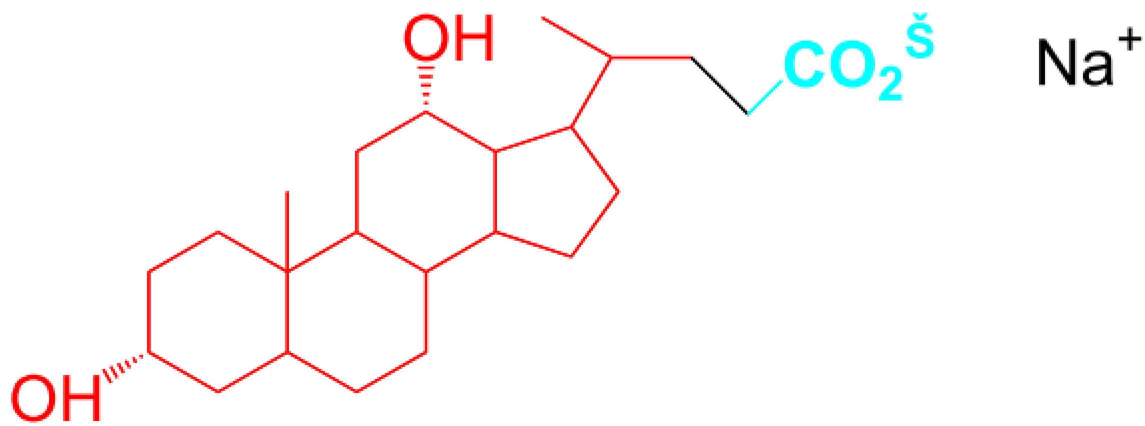
- Important in colloid and surface chemistry and biology
- <u>Sur</u>face-<u>act</u>ive <u>ag</u>e<u>nt</u>: molecule with
  hydrophobic (= lipophilic) and
  hydrophilic (= lipophobic) portions.



- e.g: (a) sodium dodecyl sulfate

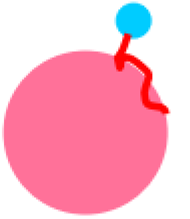
  $CH_3(CH_2)_{11}–OSO_3^- \ Na^+$

  (b)salts of bile acids – sodium deoxycholate



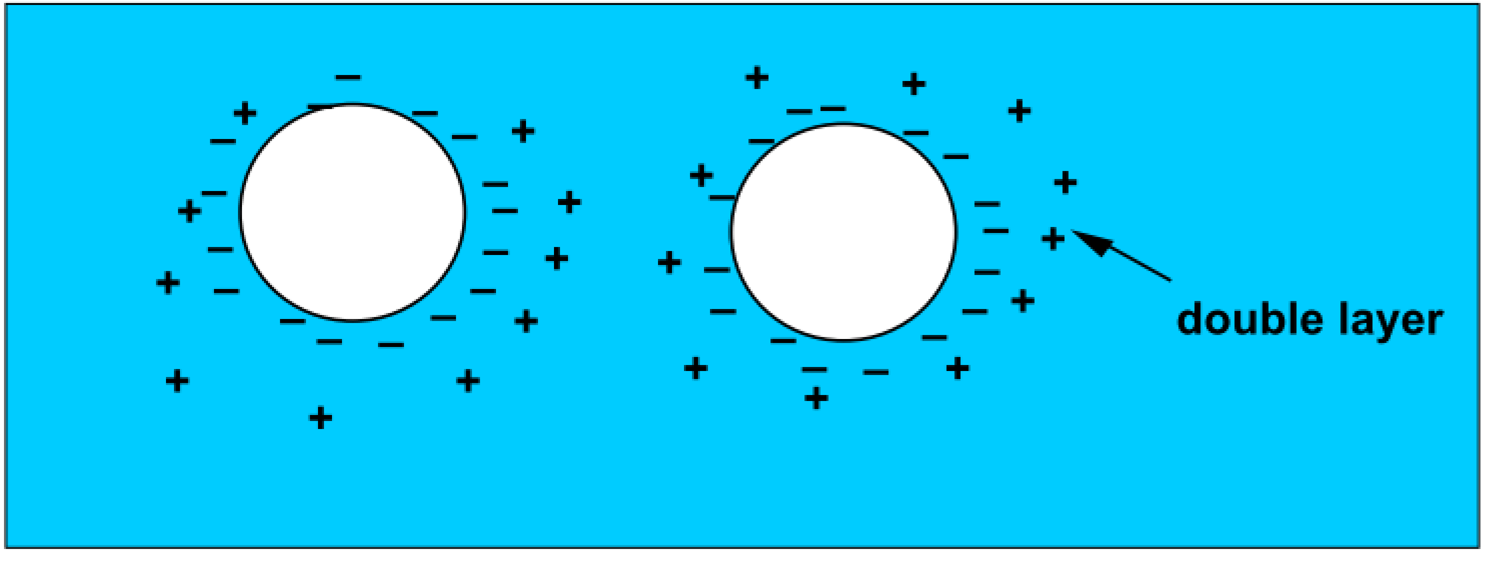

- Can also be cationic, e.g. $C_{14}H_{29}NH_3^+ \ Br^-$ (a common disinfectant)

# Ionic surfactants



- Ionic surfactants: e.g. sodium dodecyl sulfate
- Adsorbs onto a (hydrophobic) colloid: hydrophobic part in/on (organic) colloid, hydrophilic part in water: thermodynamically advantageous.
- Colloidal stability through electrostatic repulsion

**Negative charge from adsorbed surfactant attracts opposite charge: double layer**
**Repulsion between double layers keeps particles apart (colloidal stability)**



# Micelles

- Fatty acids: $C_{12}$ = dodecyl, $C_{18}$ = stearic
- Ions have long nonpolar tail and polar head

•Soap solution:

individual fatty acid anions dispersed in water
can group: micelles
hydrophilic part in water, hydrophobic tails with other hydrophobic tails: thermodynamically advantageous

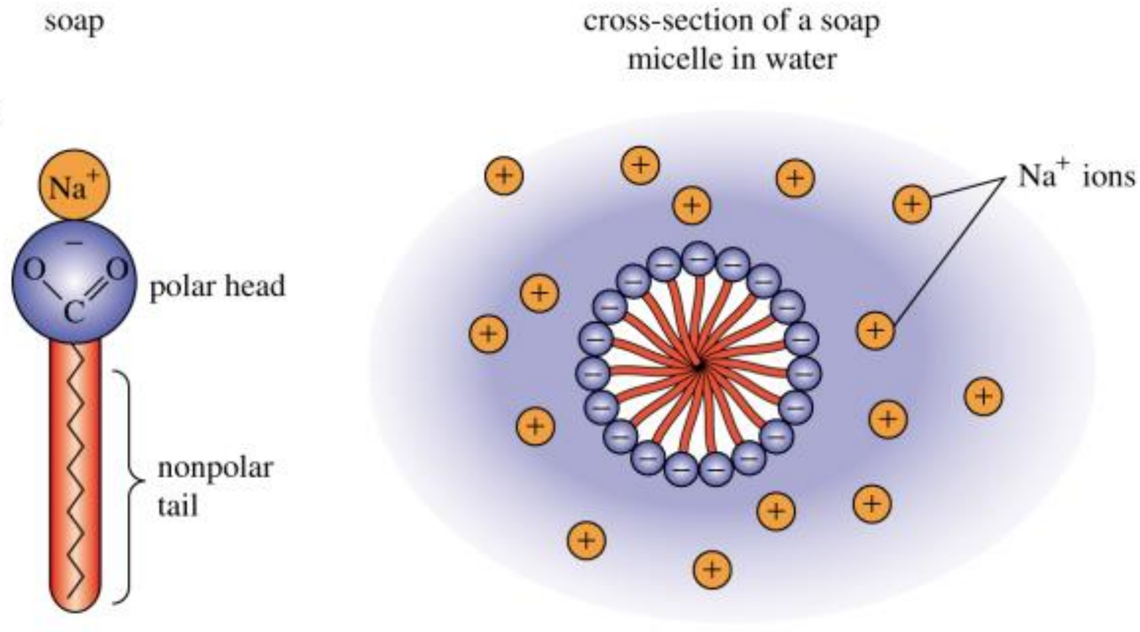


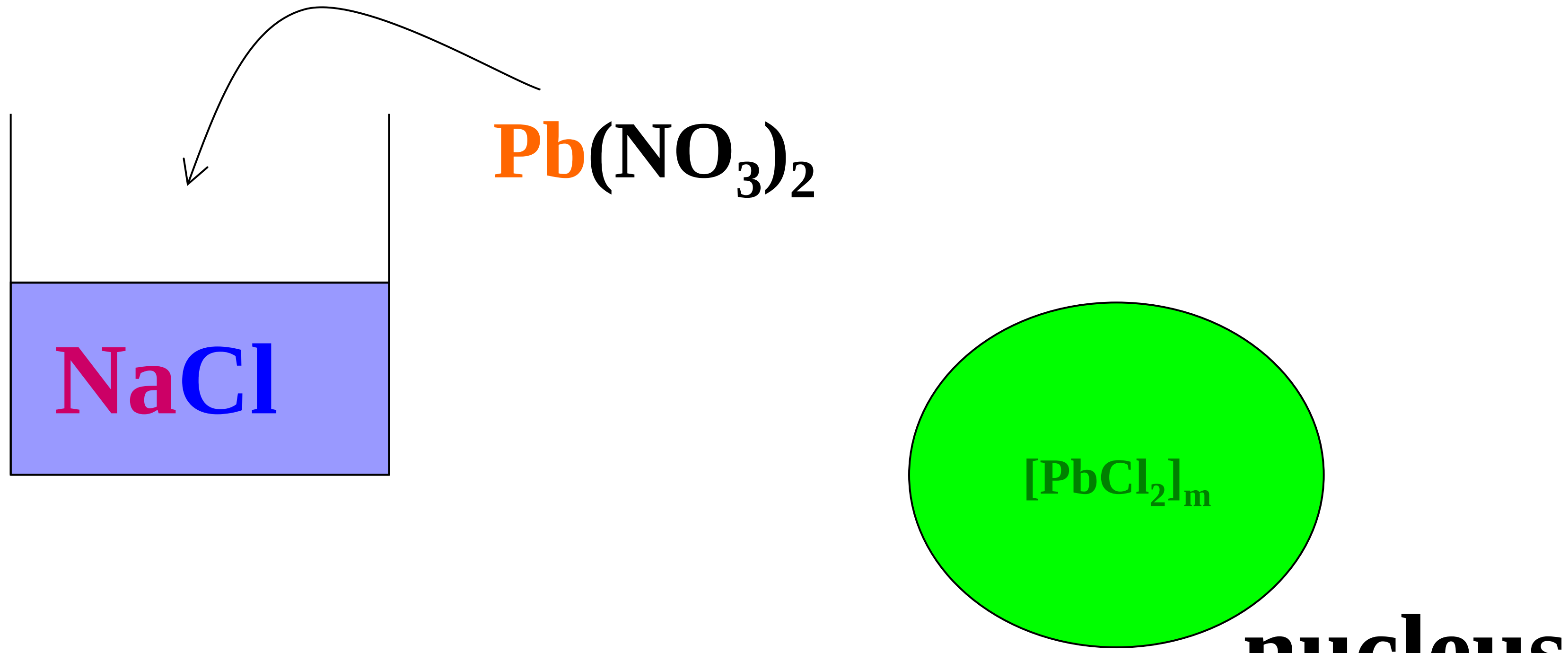

Figure 22.3 Blackman

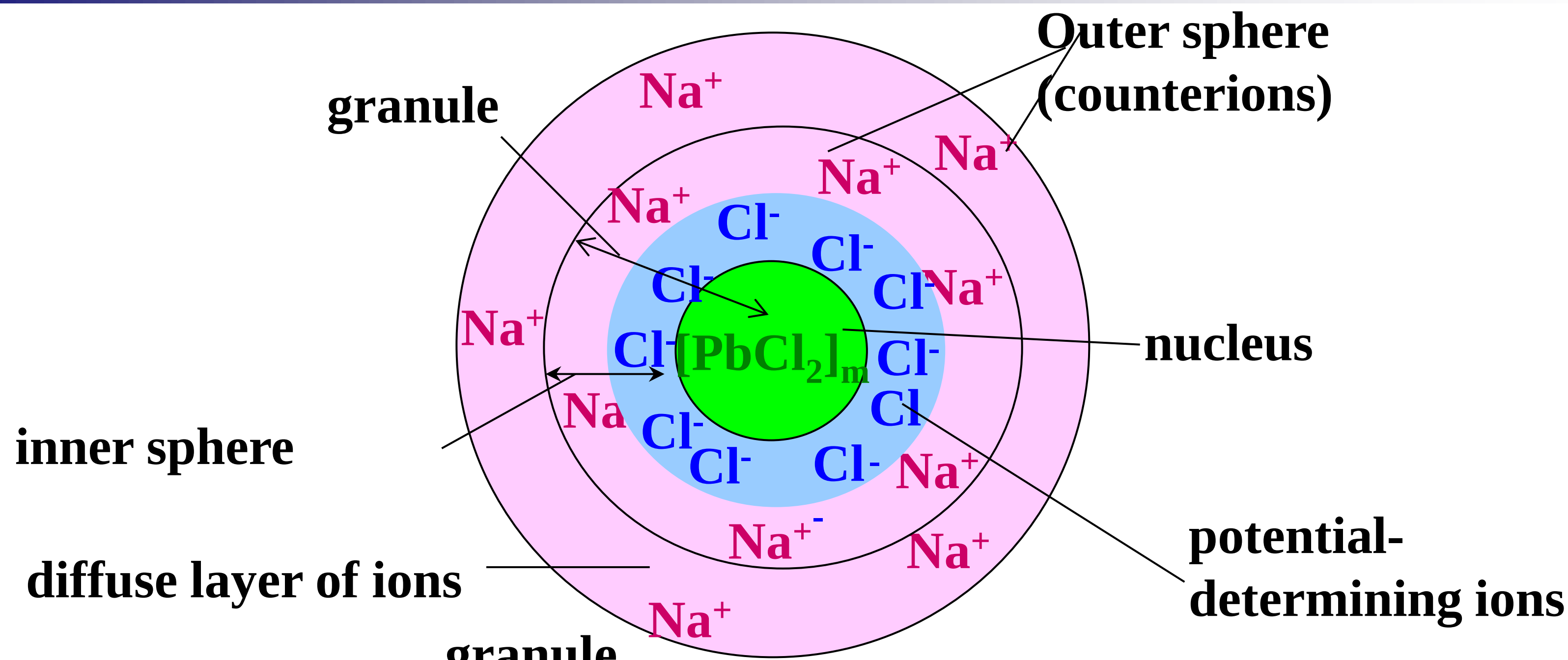
Micelles form above Critical Micelle Concentration (CMC)

- Soap-water mixture: suspension of micelles in water.
- Relatively large micelles scatter light (colloidal) so soapy water looks cloudy

# Structure of colloidal particle (micelle)

$$Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2\downarrow + 2NaNO_3$$






granule

$$\{[PbCl_2]_m nCl^-(n-x)Na^+\}^{-x} xNa^+$$

nucleus

potential-determining ions

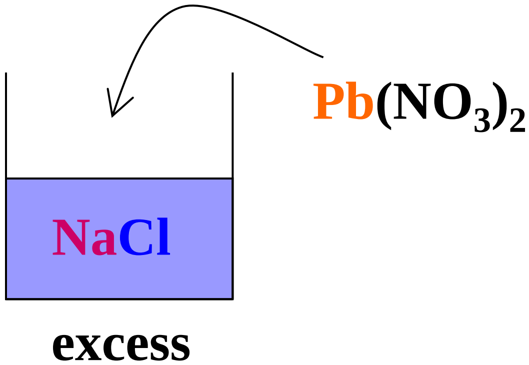
inner layer of ions

Counter ions

diffuse layer of ions

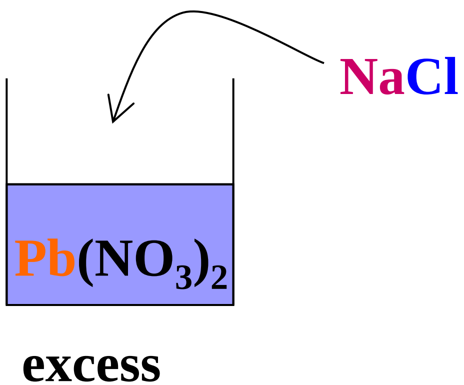
**Micelles with different granule charges could be obtained depending on the substance which is present in excess.**

$$Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2\downarrow + 2NaNO_3$$




$$\{[PbCl_2]_m nCl^-(n-x)Na^+\}^{-x} xNa^+$$

**Negatively charged sol**



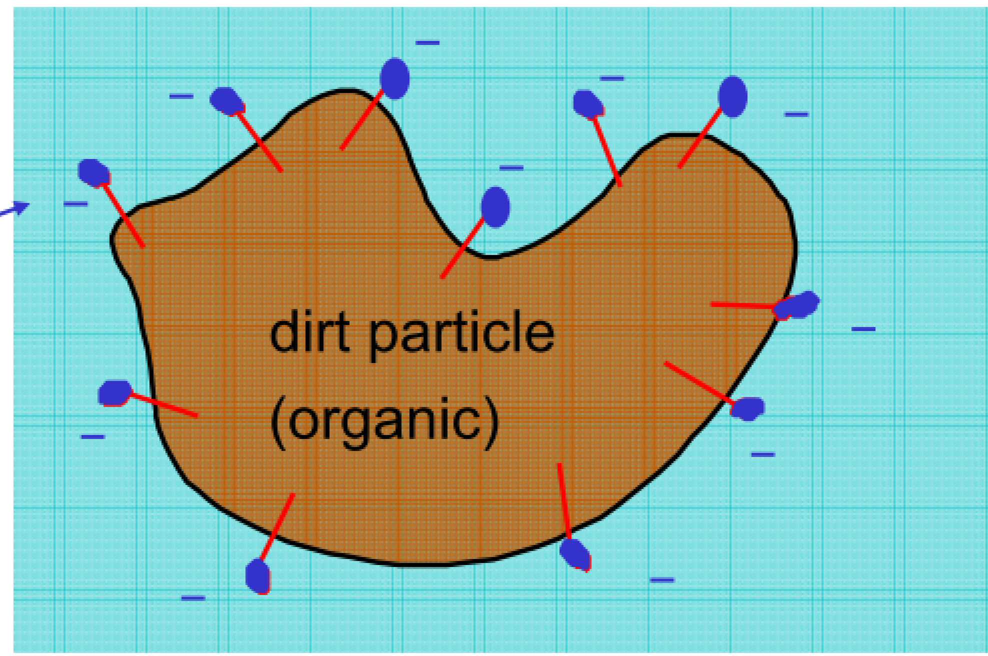

$$\{[PbCl_2]_m nPb^{2+}(2n-x)NO_3^-\}^{+x}\ xNO_3^-$$

**Positively charged sol**

# Surfactants

- "Dirt" is non-polar. Grease = long chain hydrocarbons
- However water is very polar and will not dissolve 'greasy dirt'
- Soaps, detergents (e.g. sodium dodecyl sulfate): emulsifying agent
  - Suspend normally incompatible grease in water

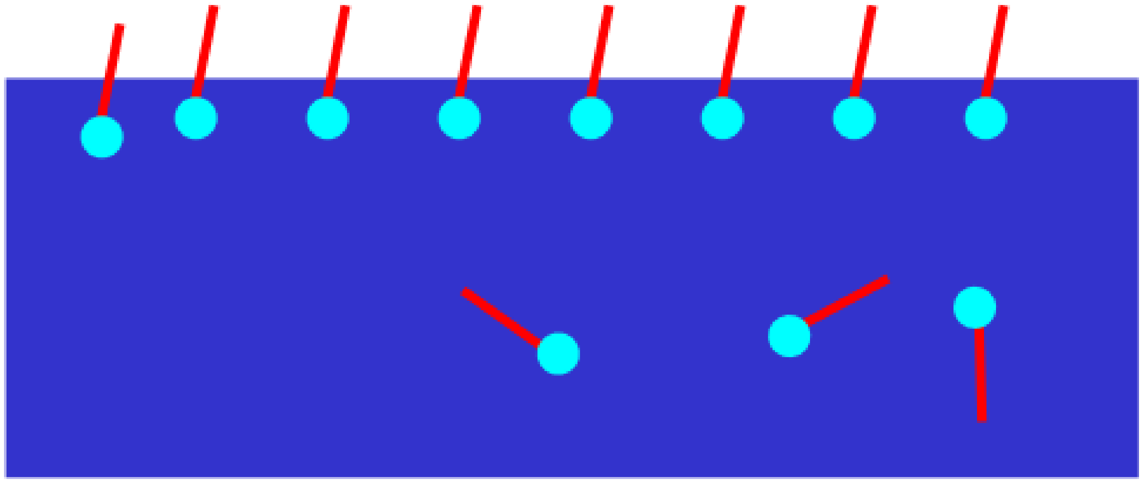
charges on outside from surfactant solubilise particle in water




- Hence called wetting agent or surfactant (= surface-active agent)

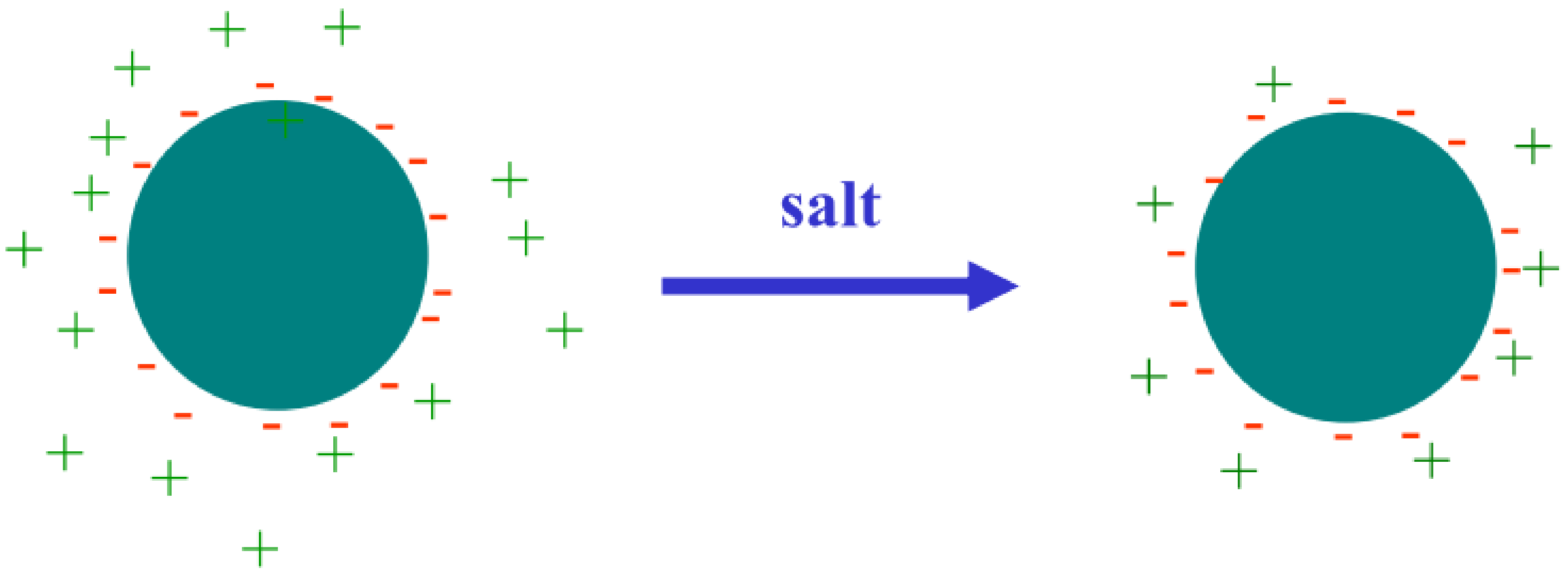
# Surfactants at the interface

- Surfactants have hydrophobic and hydrophilic parts
- Hence both parts "happy" in micelles
  ("happy" = low free energy)
- Hydrophobic part also makes them accumulate at air-water interface
  (hydrophobic part is at least out of the water)



# Ions and colloidal stability

- Another effect of ions: they cause perturbation of double layer which gives electrostatically-stabilised colloids their stability




- Reduces electrostatic barrier
- Can cause coagulation

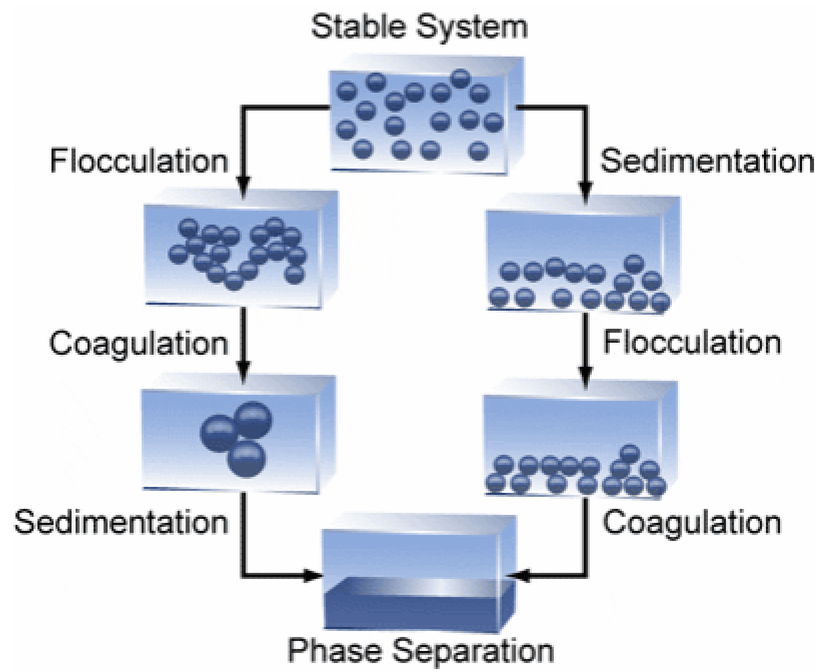
# Stabilisation of colloids

- A stable colloidal system is one in which the particles resist flocculation or aggregation and exhibits a long shelf-life.

- Depends upon the balance of the repulsive and attractive forces that exist between particles as they approach one another.

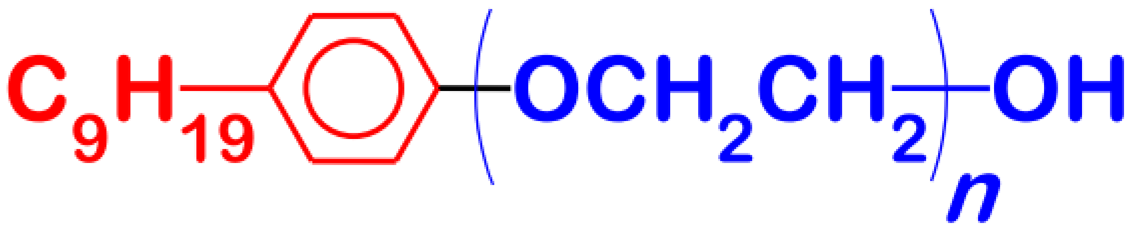
- If all the particles have a mutual repulsion then the dispersion will remain stable.

- If the particles have little or no repulsive force then some instability mechanism will eventually take place e.g. flocculation, aggregation etc.



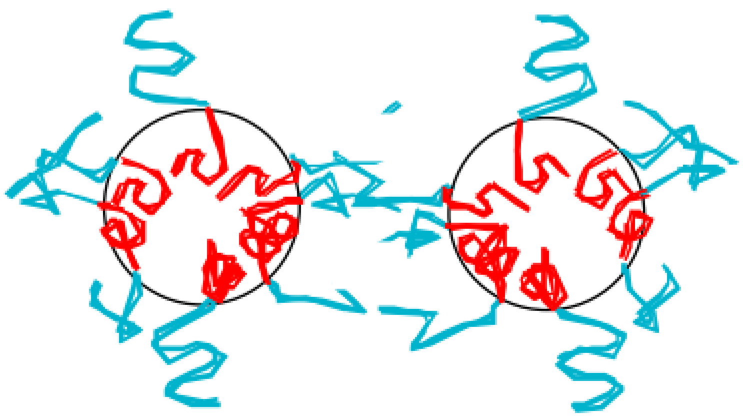
# Polymeric surfactants (stabilisers)

- **Polymer with hydrophobic & hydrophilic parts**




**$n$ is typically 10 – 40**

**Surrounds particle as "hairy layer"**



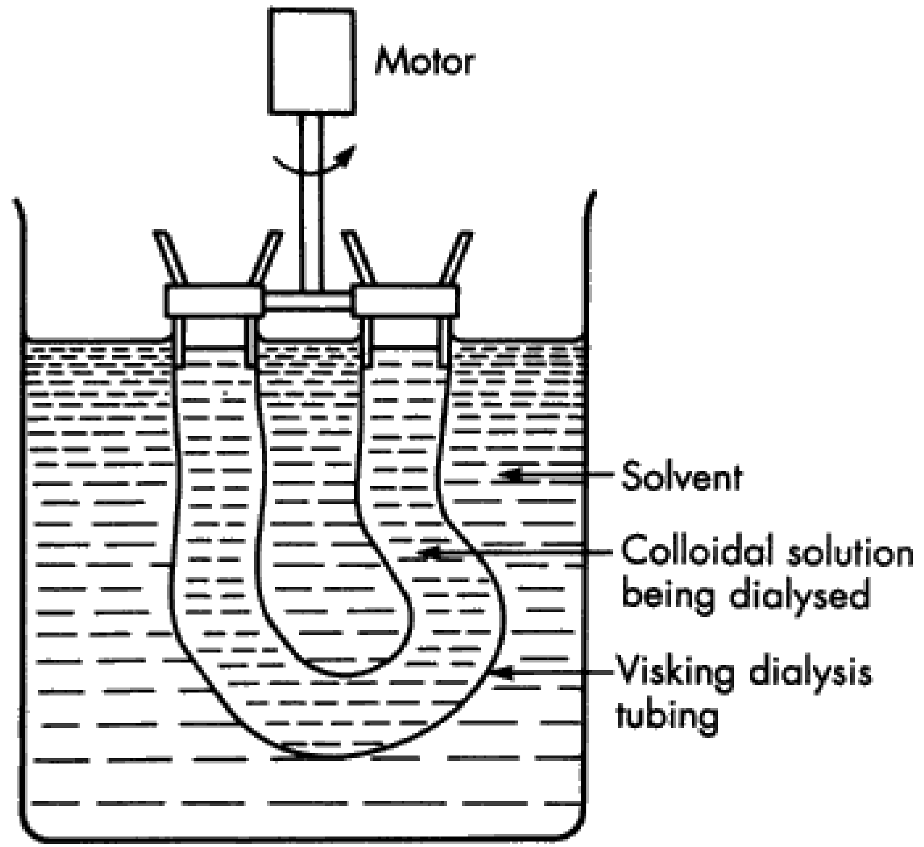
A **steric (or polymeric) stabiliser:**
**the *other type of stabiliser***

# 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:**

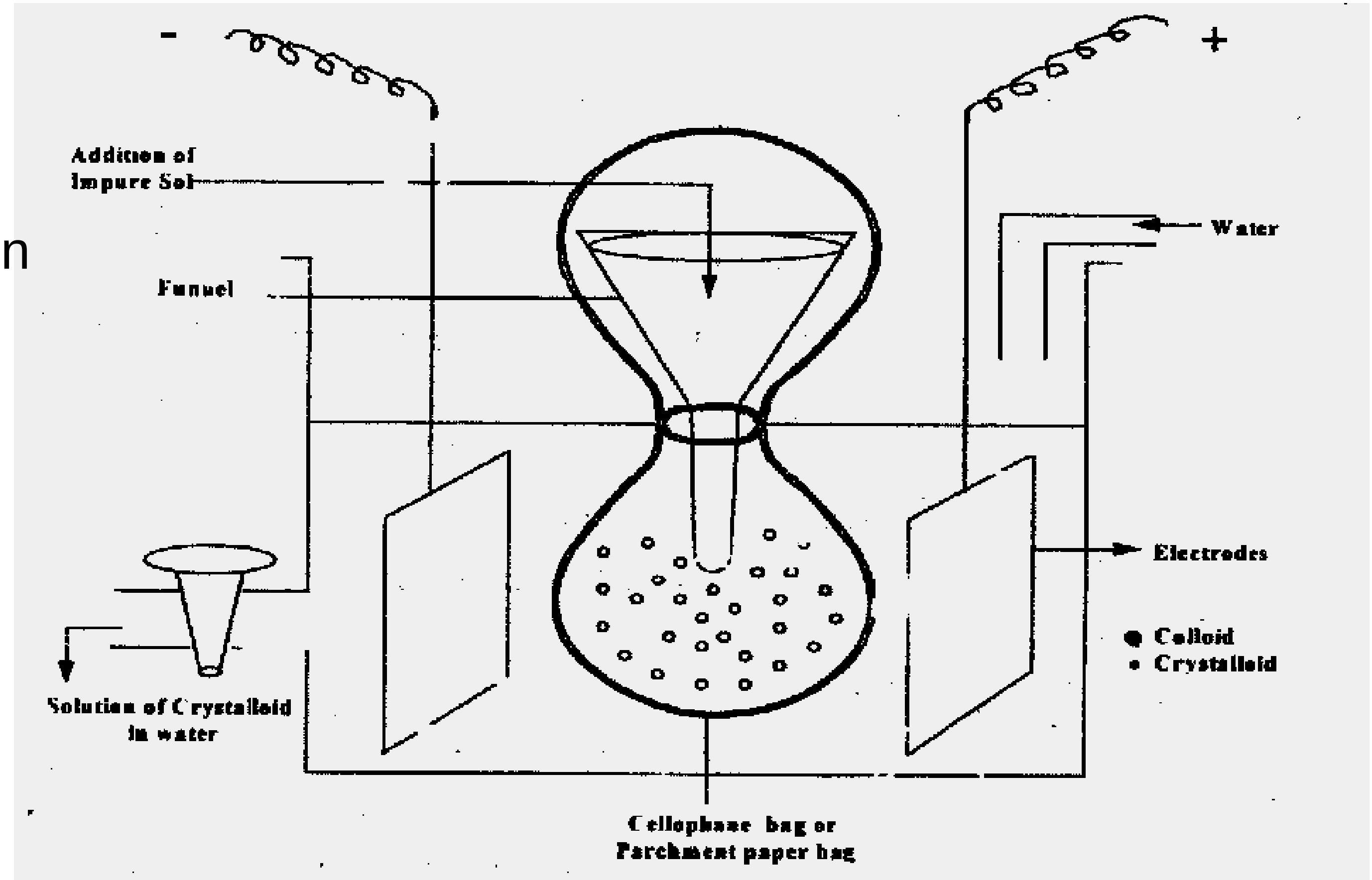
- Semipermeable cellophane membrane prevent the passage of colloidal particles, yet allow the passage of small molecules or electrolytes.



## 2- Electrodialysis:

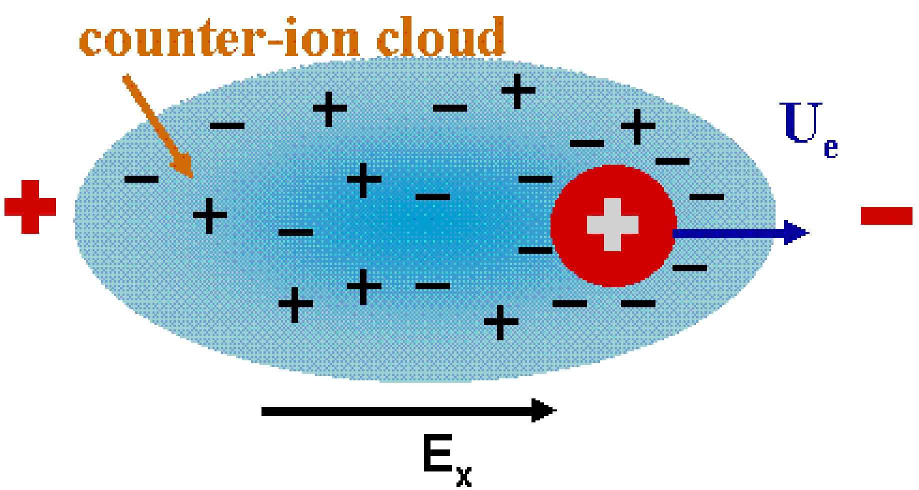
- In the dialysis unit, the movement of ions across the membrane can be speeded up by applying an electric current through the electrodes induced in the solution.
- The dialysis membrane allows small particles (ions) to pass through but the colloidal size particles (haemoglobin) do not pass through the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

-The most important use of dialysis is the purification of blood in artificial kidney machines.



# 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.



# 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:

3- **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

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

# Applications of colloidal solutions:

**5- *Photography:***

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

**6- *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.

# Thank you for attention!