# COLLOIDAL DISPERSION

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# CONTENT

Classification of dispersed systems and their general characteristics, size and shapes of colloidal particles, classification of colloids and comparative account of their general properties. Optical, kinetic and electrical properties. Effect of electrolytes, coacervation, peptization and protective action.

# INTRODUCTION

- Dispersed systems are defined as systems in which particles are dispersed with the aid of an agent to lower interfacial system.

- Dispersed phase (internal phase) dispersed in the dispersion medium (continuous phase)

| Medium/Phases | | Dispersed Phase | | |
|---|---|---|---|---|
| | | Gas | Liquid | Solid |
| Dispersion Medium | Gas | None (All gases are mutually miscible) | Liquid Aerosol Example: fog | |
| | Liquid | Foam Example: whipped creams | Emulsion Example : milk | Sol Example: blood |
| | Solid | Solid Foam Example: styrofoam | Gel Example:gelatin | Solid Sol Example: cranbery glass |

| Size | Less than 0.1nm | 1.0 nm to 1.0 μm | Greater than 1 μm |
|---|---|---|---|
| Dispersed System | Molecular Dispersion | Colloidal Dispersion | Coarse Dispersion |
| Example | Sucrose Solution | Solution of acacia | Calamine suspension |

solution      colloid      suspension

smallest ⟷ largest
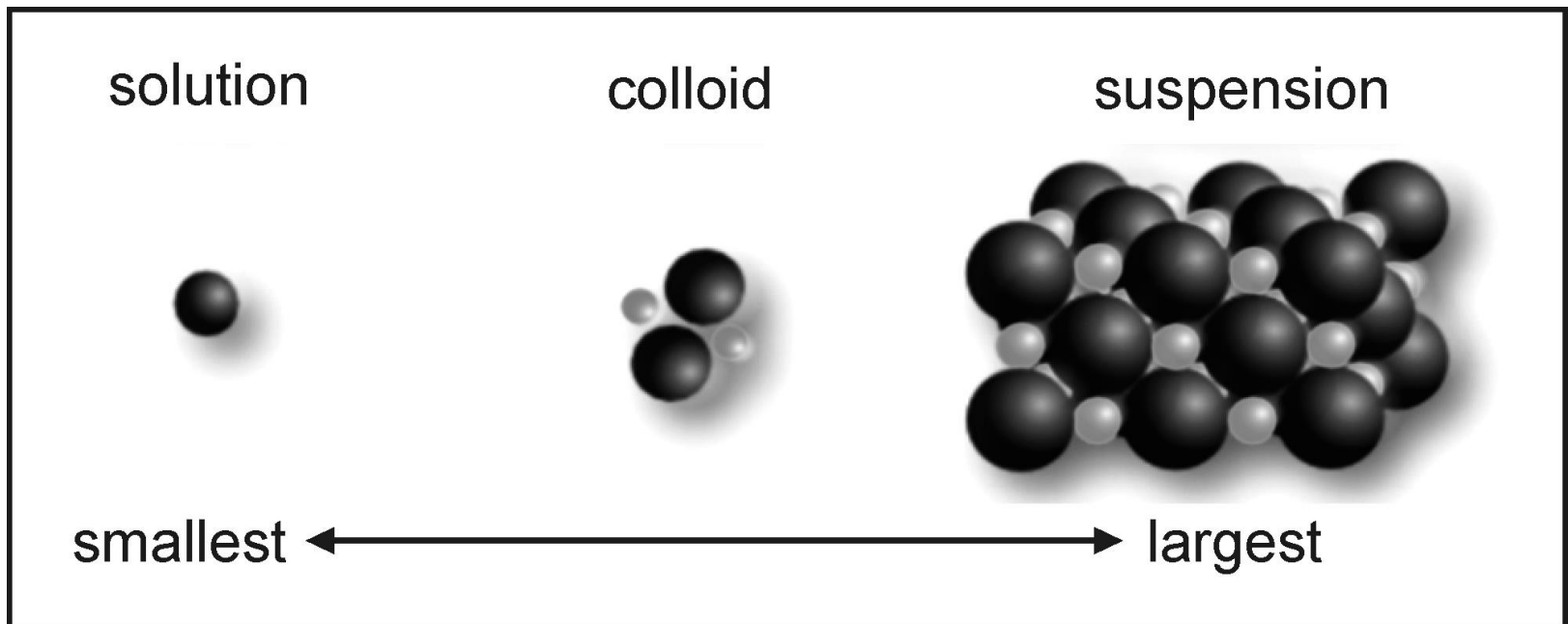
# CLASSIFICATION OF DISPERSED SYSTEM

- **ON THE BASIS OF DIFFUSION RATE**
    - Crystalloids: High diffusion rate
    - Colloids: Slow diffusion rate

- **ON THE BASIS OF MEAN PARTICLE DIAMETER**
    - Molecular
    - Colloidal
    - Coarse

- **ON THE BASIS OF DISPERSION MEDIUM**
    - Hydrosol: water as a dispersion medium
    - Alcosol: Alcohol as a dispersion medium
    - Benzosol: Benzene as a dispersion medium
    - Aerosol: Air or gas as a dispersion medium

# CHARACTERSISTICS OF DISPERSED SYSTEM

| Characteristic | Dispersed system | | |
|---|---|---|---|
| | Molecular dispersion | Colloidal dispersion | Coarse dispersion |
| **Particle size** | Less than 0.1nm | 1.0 nm to 1.0 μm | Greater than 1 μm |
| **Setting by ultracentrifuge** | no settling | Settles | settles |
| **Visibility** | not visible with an electron microscope | visible by ultra microscope | visible to naked eye |
| **Filtration** | Filtered | Filtered | cannot filter |
| **Light scattering** | No | Yes | no |
| **Diffusion** | Yes | No | no |
| **Diffusion rate** | Rapid | Slow | do not diffuse |
| **Example** | sugar solution | polymeric solution | Suspension |

# SIZE OF COLLOIDAL PARTICLES

- Colloidal systems are generally of a polydispersed nature

- dimension scale ranging from nanometers to micrometers (1nm-1000nm )

- Colloidal solutions are not only formed by certain specific substances as mentioned above but they can be obtained from any substance by subdividing or aggregating its particles in the size range.
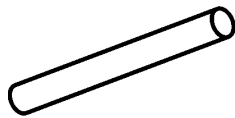
# SHAPE OF COLLOIDAL PARTICLES

- The exact shape of colloidal particle is may be complex.

- Colloidal particles can be classified according to shape as corpuscular, laminar or linear.
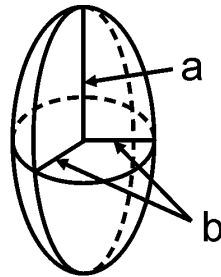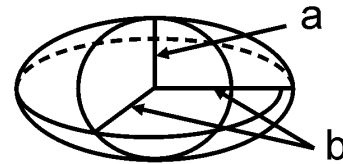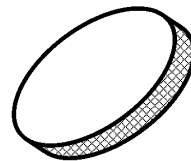


Prolate ellipsoid     Oblate ellipsoid

Rod     Disc     Random coil

# SHAPE OF COLLOIDAL PARTICLES

- Many colloidal systems do contain spherical or nearly spherical particles.

- Corpuscular particles which deviate from spherical shape can often be treated theoretically as ellipsoids of revolution.

- High-polymeric material usually exists in the form of long threadlike straight or branched-chain molecules.

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# CLASSIFICATION OF COLLOIDS

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# Classification based on interaction between dispersed phase

- **<u>Lyophilic colloids:</u>** The substances which when mixed with a suitable dispersion medium readily form colloidal solutions are called lyophilic colloids or intrinsic colloids.

- **<u>Lyophobic Colloids:</u>** The substances which do not pass much affinity for the dispersion medium and do not readily pass into the sol state when mixed with the medium are called hydrophobic colloids or extrinsic colloids

- **<u>Association Colloids:</u>** Association colloids are those colloids which behave as normal strong electrolytes at low concentrations but exhibit colloidal properties at higher concentrations due to the formation of aggregated particles.

# Classification based on charge present on surface of particles

- **Positive solution:** The colloids carrying positive charge are called as positive sols.

- **Negative solution:** The colloids carrying negative charge are called as negative sols.

# Comparative account of their general property

| Property | Lyophilic | Lyophobic | Association |
|---|---|---|---|
| **Solvent** | Loving | Hating | Amphiphilic |
| **Nature** | The considerable attraction between the dispersed phase and the aqueous phase | Less affinity between the dispersed phase and the aqueous phase | Interaction of polar or nonpolar part of a particle depends on types of dispersion medium |
| **Method of preparation** | Spontaneous dissolution in a solvent | special methods like dispersion or condensation | aggregation of particle |
| **Concentration** | The high concentration of dispersed phase in medium | --- | depends on the concentration of surface |
| **Stability** | more stable due to formation of the sheath around the colloidal particle | Less stable due to charge on the surface. | Medium |

# Comparative account of their general property

| Property | Lyophilic | Lyophobic | Association |
|---|---|---|---|
| **Particle size** | Small | large | Small |
| **Viscosity** | Greater than dispersion medium | Less than dispersion medium | Increases with the concentration of micelle |
| **Surface tension** | Less than dispersion medium | Equal to the dispersion medium | Less than dispersion medium |
| **Reversibility** | Reversible with temperature | Non-reversible with temperature | Reversible with temperature |
| **Charge** | Depends on the pH of the medium | Does not depend on the pH of the medium | Charged but solvated micelle |

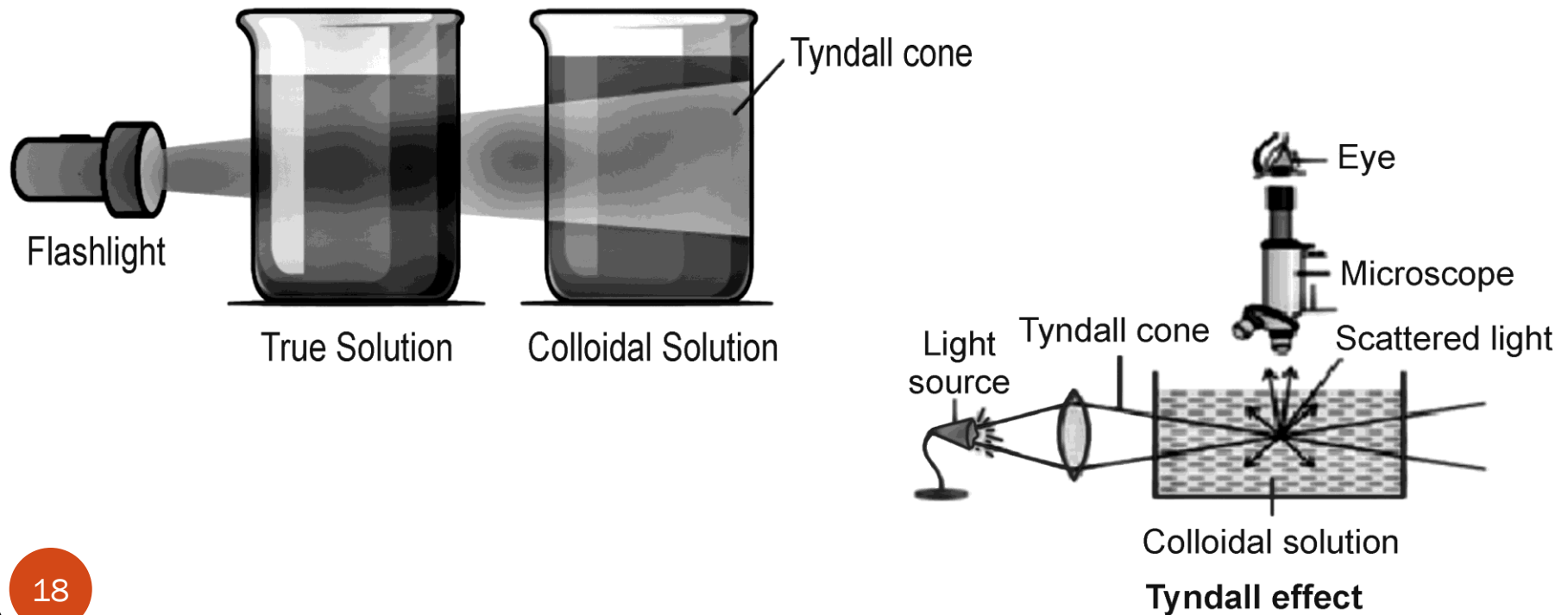# OPTICAL PROPERTIES OF COLLOIDS

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- The optical properties of a material define how it interacts with light.

- **Light scattering:** The resultant refraction or illumination of light upon passing through colloidal solution underlines the light scattering phenomenon. Refractive index effects on light scattering. In a crystal clear medium, light passes without deflection and scatters if particles of different refractive indices are present in a solution.

Scatterers in solution (Brownian motion)

Laser at $f_o$

Scattered light
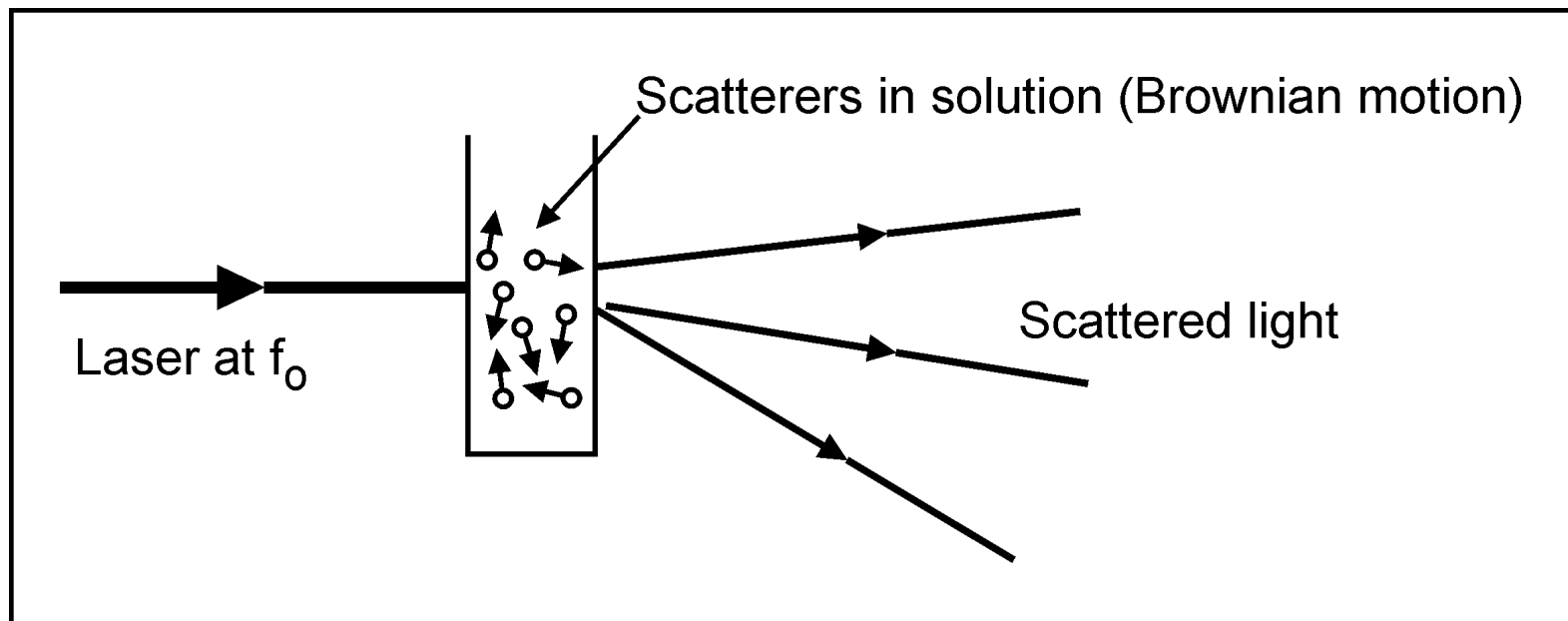
- **Tyndall effect**: When a strong beam of light is passed through the colloidal solution kept in dark and observes the path of the beam, its path is visible due to scattering of light by the colloidal particles. The effect is called as "Tyndall Effect" and the scattered beam is called "Tyndall beam". This beam is most visible against a dark background.
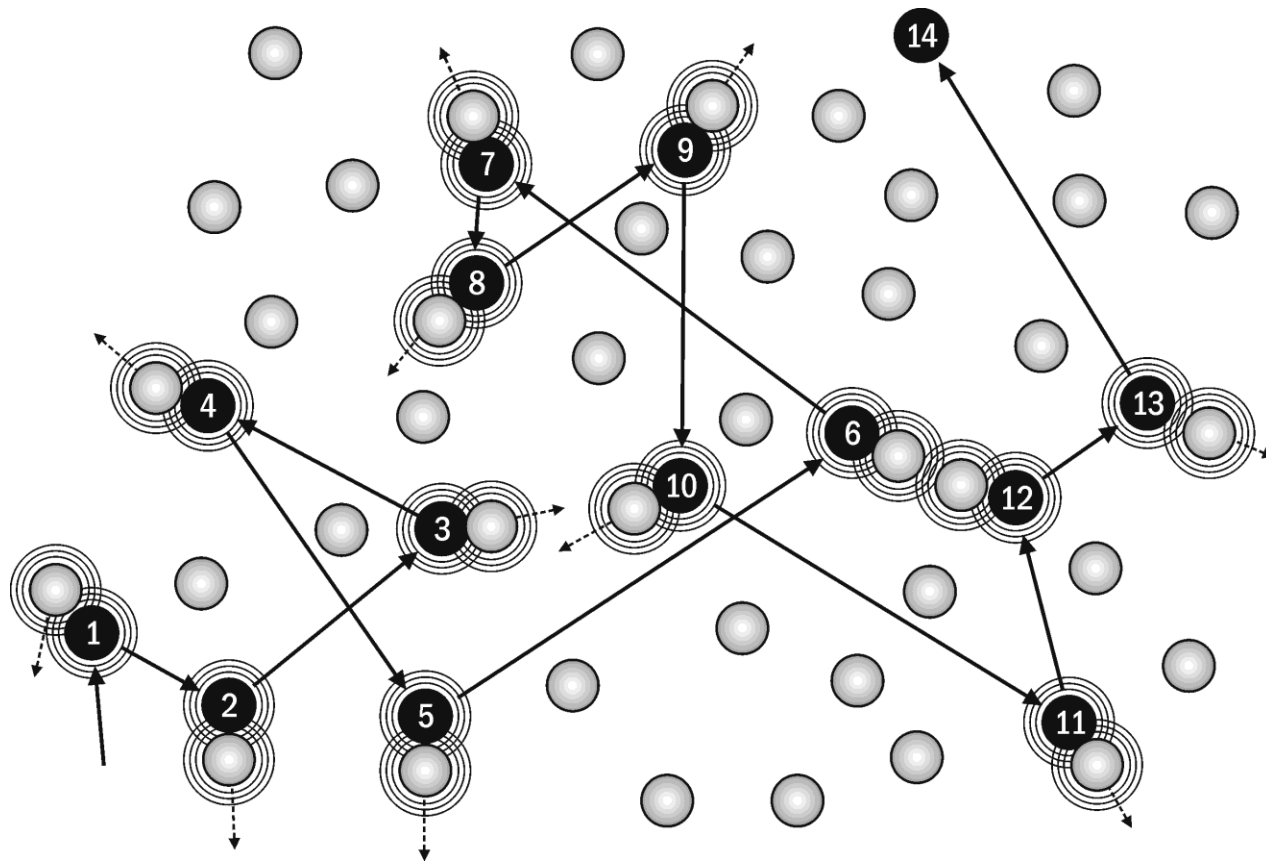


Tyndall effect

# KINETIC PROPERTIES OF COLLOIDS

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- **Brownian motion**: When a colloidal solution is viewed under an ultramicroscope, the colloidal particles are seen continuously moving in a zigzag path

- **Diffusion**: Particles diffuse spontaneously from the region of higher concentration to lower concentration until equilibrium reaches. Diffusion is a direct result of the Brownian movement. According to Fick's First Law, the amount of substance (dq) diffusing in time (dt) across a plane of area (S) is directly proportional to the change of concentration (dc) with distance travelled (dx).

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

- **Sedimentation**: The velocity of sedimentation of the spherical particle is given by Stoke's Law. The lower size limit of particle obeying Stoke's equation is about 0.5 $\mu$ because Brownian movement becomes significant and tends to offset sedimentation due to gravity and promotes mixing. In order to bring sedimentation, stronger force must be applied.

$$v = \frac{r^2 (\rho_s - \rho_o) g}{18 \eta_o}$$

- **Viscosity**: Viscosity is an expression of resistance to the flow of a system under applied stress. More the viscous liquid, greater the applied force required to make inflow at a particular rate. Viscosity studies of dilute colloidal system and how the viscosity data can be used to obtain the molecular weight of material comprising the disperse phase. Viscosity studies also provide information regarding the shape of particles in solution.
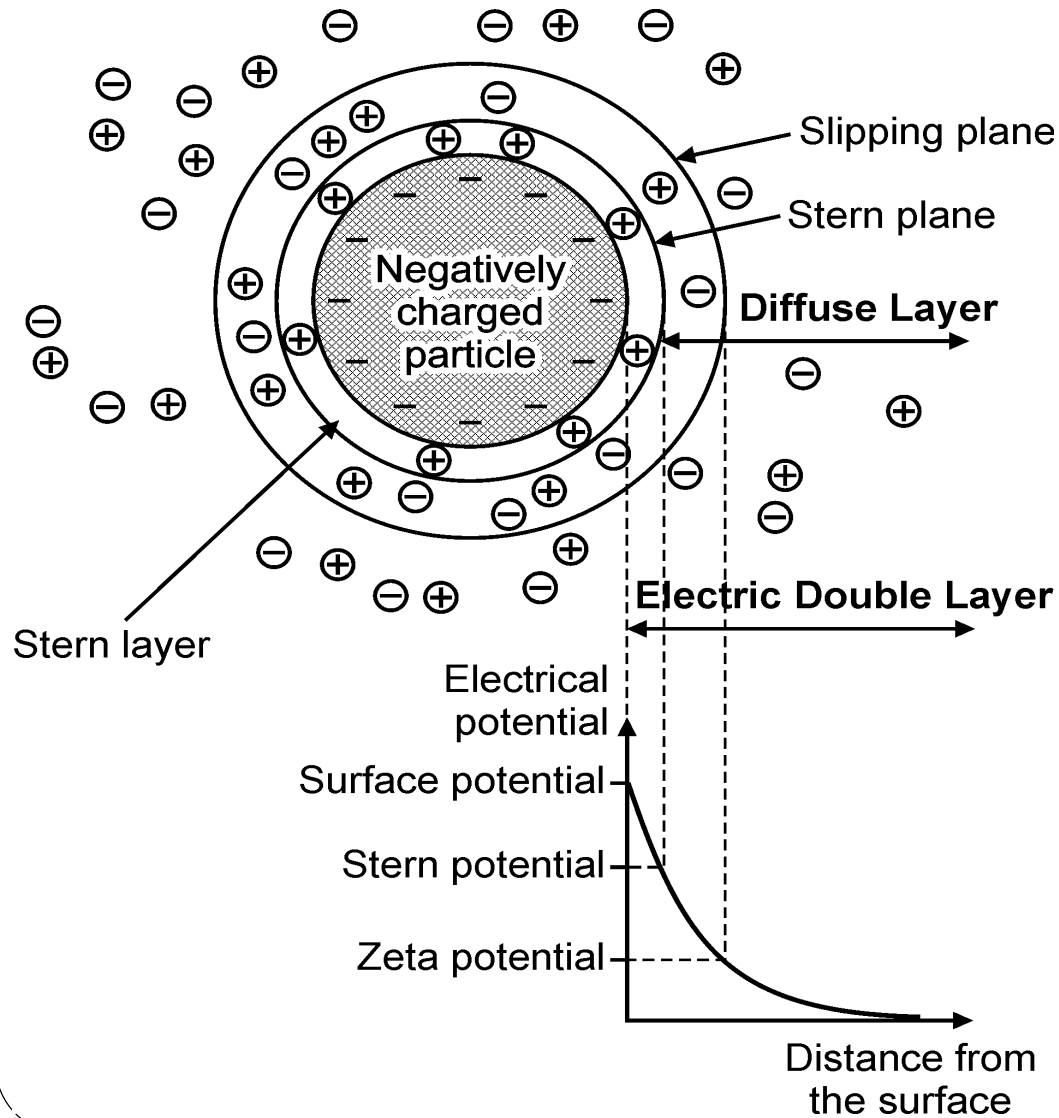
# ELECTRIC PROPERTIES OF COLLOIDS

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- The colloidal particles acquire charge due to dissociation of the adsorbed molecular electrolytes, due to the dissociation of molecules forming colloidal aggregates or due to preferential adsorption of ions from solutions. The charge on colloidal particles is balanced by that of the dispersion medium and the **colloidal solution as a whole is electrically neutral.**

- **Electric double layer**:    **Zeta potential & Nernst Potential**

Slipping plane

Stern plane

Negatively charged particle

**Diffuse Layer**

Stern layer

**Electric Double Layer**

Electrical potential

Surface potential

Stern potential

Zeta potential

Distance from the surface

$$\zeta = \frac{4\pi\eta}{\varepsilon} \times U \times 300 \times 300 \times 100$$

$\zeta$ = Zeta potential (mV)

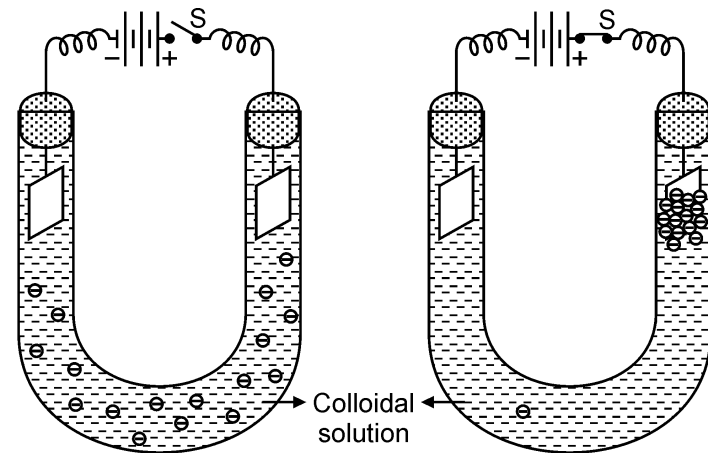$\eta$ = Viscosity of solution

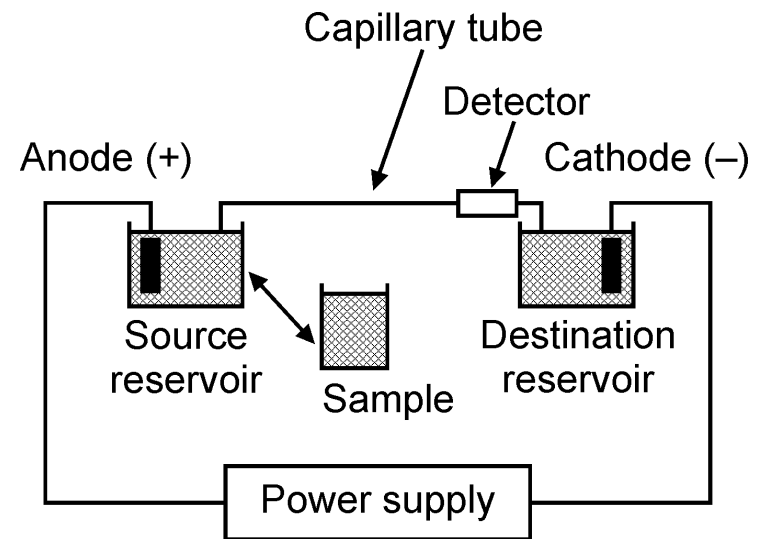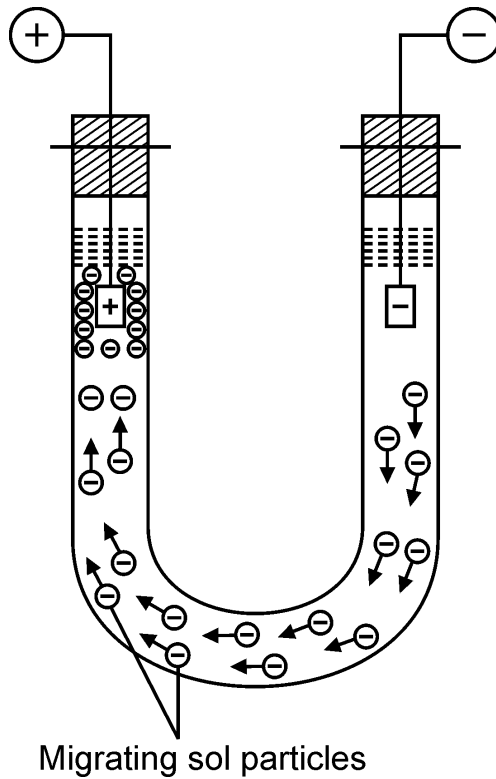$\varepsilon$ = Dielectric constant

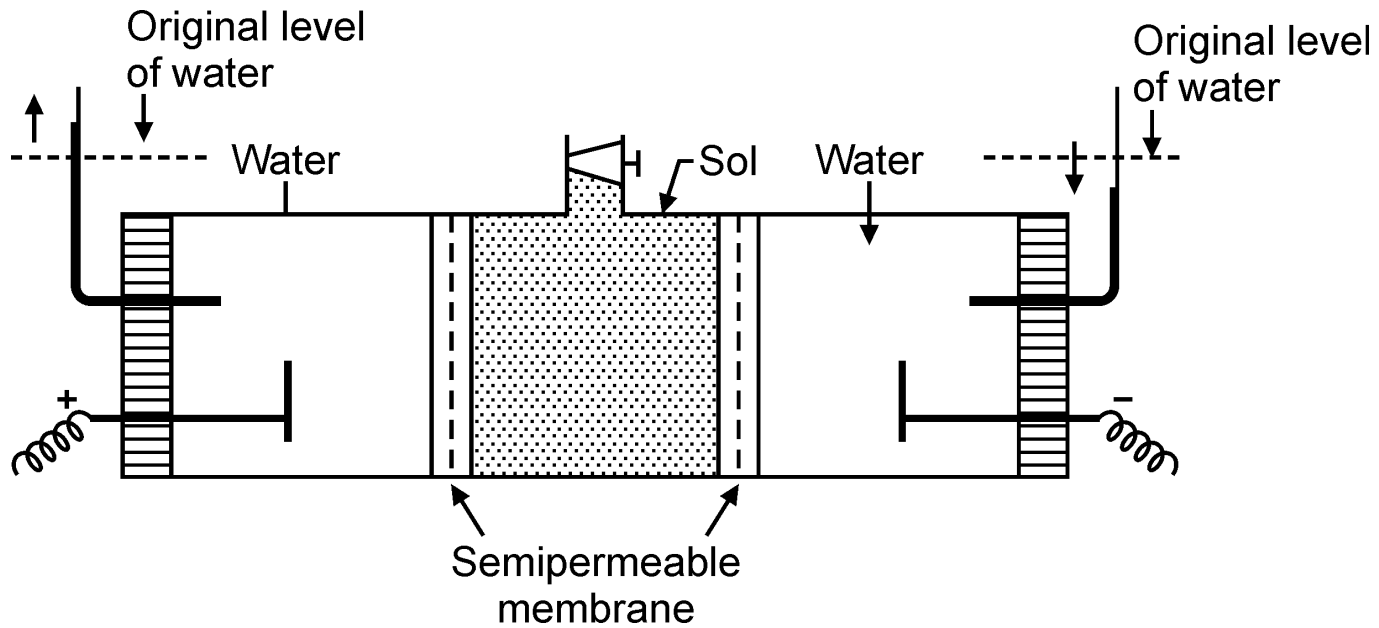$U = \dfrac{v}{V/L}$ : Electrophoretic mobility

$v$ = Speed of Particle (cm/sec)

$V$ = Voltage (V)

$L$ = The distance of Electrode

## Electrophoresis

Anode (+)    Capillary tube    Detector    Cathode (−)

Source reservoir    Sample    Destination reservoir

Power supply

Migrating sol particles

**(a) Before electrophoresis**    **(b) After electrophoresis**

Colloidal solution

## Electro-osmosis

# DONAN MEMBRANE EQUILIBRIUM

- Frederic Donnan published on thermodynamic equilibrium involving ions and polyelectrolytes.

- If NaCl is placed in solution on one side of a semi-permeable membrane and negatively charged colloid together with its counter ion R-Na+ on the other side, the Na+ and Cl- can pass freely across the Barrier except for colloidal anionic particles

| Outside | Inside |
|---------|--------|
|         | R-     |
| $Na^+$  | $Na^+$ |
| $Cl^-$  | $Cl^-$ |
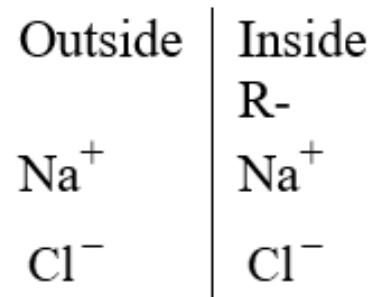
- After equilibrium has been established the concentration must be same on both side of membrane.   i.e. $[Na^+]_o\,[Cl^-]_o = [Na^+]i\,[Cl^-]i$

# COACERVATION

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- According to IUPAC, Coacervation is defined as the separation of colloidal systems into two liquid phases.

- It was suggested by Oparin that Coacervates might have played a significant role in the evolution of cells.
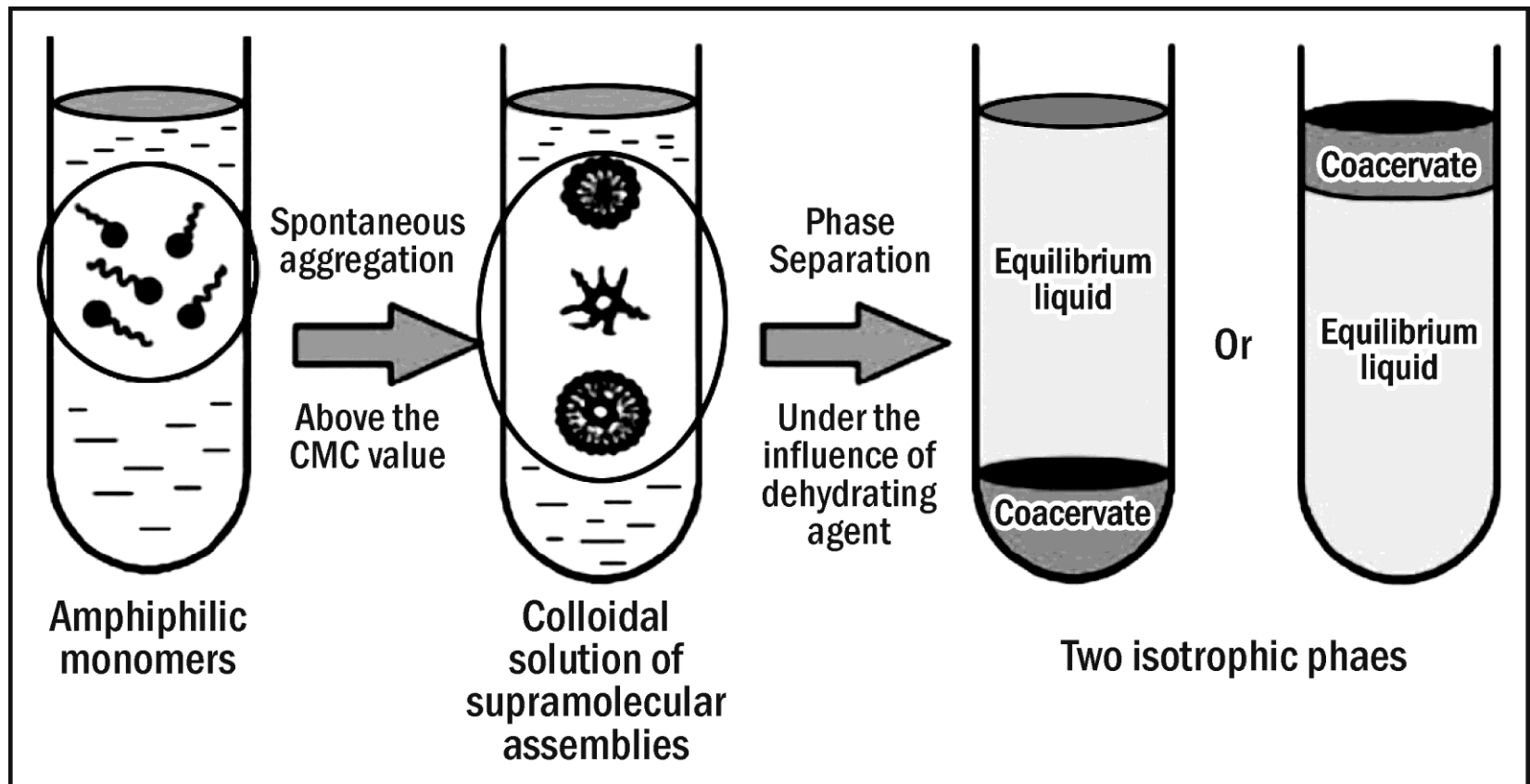
- Coacervation is a chemical method for producing polymer droplets in dispersion based on the separation of two liquid phases into one concentrated colloidal phase, being the coacervate, and another highly dilute colloidal phase.

- Coacervates could be regarded as a liquid, which had lost its free mobility to a certain degree and this explanation was mainly of the simple coacervation phenomenon.

- Coacervation uses the principle of difference in ionic forces to cause the polymer(s) to form droplets and drop out of solution. The role of physiochemical parameters, such as ionic strength and pH, on the coacervation formation, highlighted that the coacervation was a consequence of electrostatic interactions.

- Coacervation is an electrostatic interaction between two aqueous media in which the liquid-to-gel transition occurs at normal conditions.

- Coacervation requires elimination of the stability factors, charge and hydration.

- Phase separation in simple coacervation is brought about by addition of a salt, pH or temperature change in the polymeric solution while in complex coacervation is brought about by anion–cation interactions. Complex coacervate gels can be formed by mixing of a polyanion with a polycation.

# STABILITY OF COLLOIDS

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- **Stabilization can be accomplished by:**

    - Providing charge to dispersed particle suitable for lyophobic solution.

    - Forming sheath surrounding dispersed particle suitable for lyophilic solution.

- **Electrostatic stabilization and steric stabilization are the two main mechanisms for stabilization against aggregation.**

    - Electrostatic stabilization is based on the mutual repulsion of like electrical charges.

    - Steric stabilization consists of covering the particles in polymers which prevents the particle to get close in the range of attractive forces.

    - A combination of the two mechanisms is also possible (electrosteric stabilization).

- The flocculation and settling of discharged particles (sedimentation) are called as coagulation or precipitation of the sol.

- When a sol is colloidally unstable (i.e. the rate of aggregation is not negligible) the formation of aggregates is called coagulation or flocculation.

- The reversal of coagulation or flocculation, i.e. the dispersion of aggregates to form a colloidally stable suspension is called deflocculation (sometimes peptization).

- Sedimentation is the settling of suspended particles under the action of gravity or a centrifugal field.
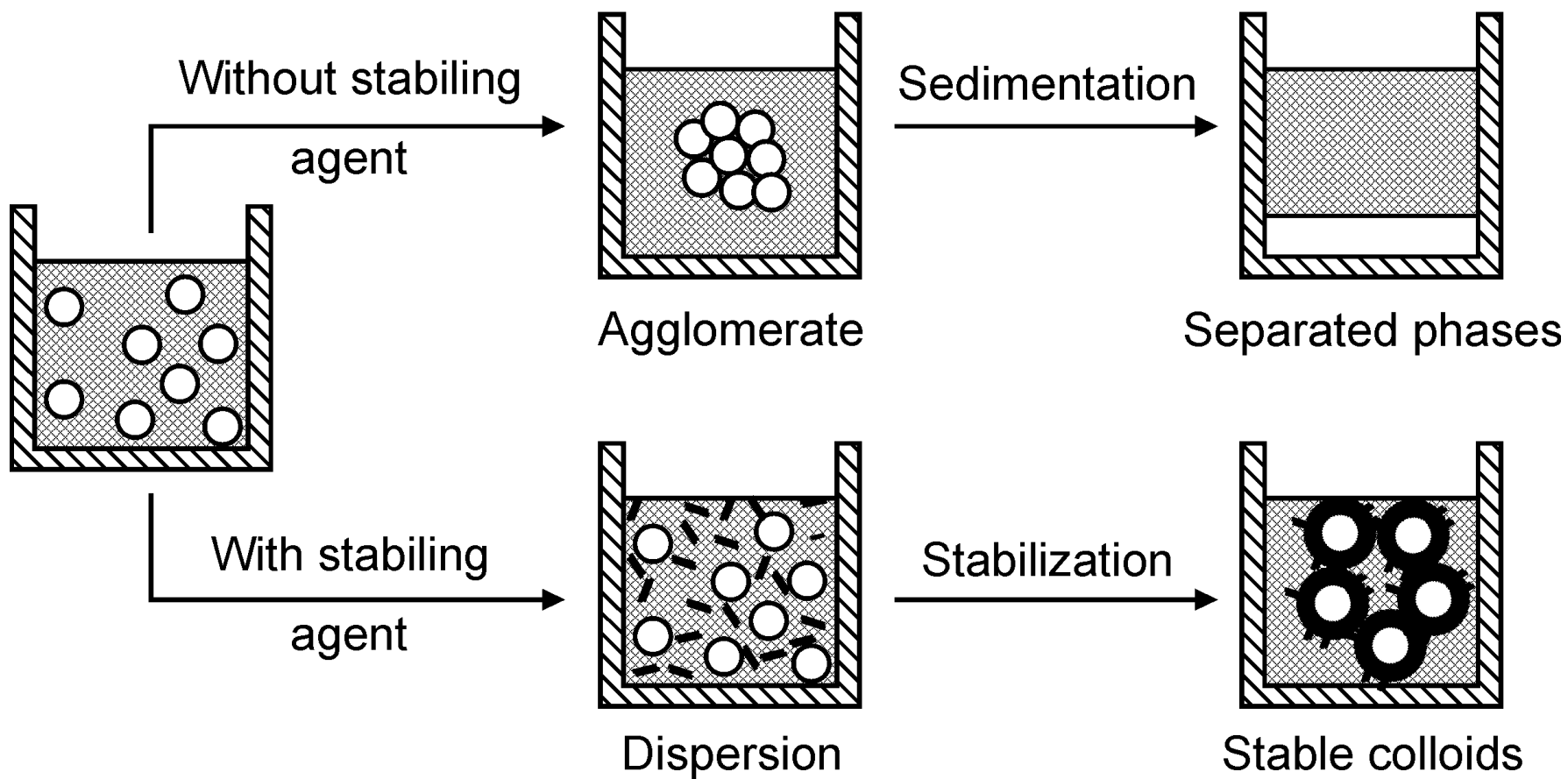
- Particle sedimentation and also floating arises from a difference in the density of the dispersed and the continuous phase.

- The higher the difference in densities, the faster the particle settling.

- A lyophobic solution is thermodynamically unstable and particles are made stable by the presence of charges on their surface. Like charges produce repulsion among them and result in Brownian motion and thus prevent coagulation.

- Addition of small amount of electrolyte to lyophobic solution tends to stabilize the system by imparting a charge to particles and to maintain zeta potential above a critical value (zeta potential below critical value can cause accumulation of ions).

- The minimum amount of an electrolyte (mmole) that must be added to one liter of the colloidal solution to bring complete coagulation is coagulation value of electrolyte.

- Smaller the coagulation value, greater the precipitating power.

# PROTECTIVE COLLOIDAL ACTION

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- Protective colloid is a lyophilic colloid that when present in small quantities keeps lyophobic colloids from precipitating under the coagulating action of electrolytes.

- Higher concentrations of the same hydrophilic colloid usually protect the hydrophobic sol from flocculation. This is considered to be due to reduction of zeta potential below the critical value. This phenomenon is called protective action.

- The particles of a protective colloid are believed to be adsorbed by lyophobic colloidal particles and thus form a covering over the surface of lyophobic colloidal particles. The lyophobic colloid thus behaves as lyophilic colloid and is precipitated less easily by electrolytes. The adsorption so occurred prevents precipitating ion to reach solution particle and thus coagulation prevented.

- Now entire colloid can act as hydrophilic colloid which is thermodynamically stable. The hydrophilic sol or lyophilic used to protect a hydrophobic sol or lyophobic sol from precipitation is referred to as protective colloids.

- It may be noted that protective colloid not only increases the stability of lyophobic colloids but it also makes them reversible.

Protective colloidal particles

Lyophobic particles
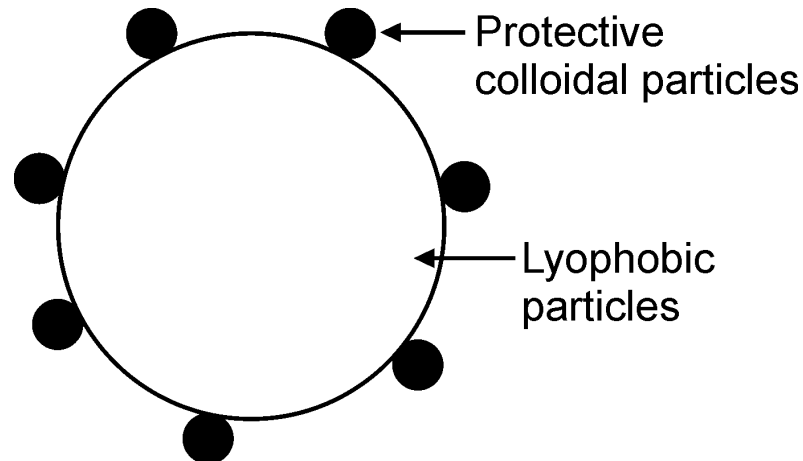
- Protective property of colloid is expressed in a gold number.

- Gold number is defined as the minimum amount of protective colloid required to prevent color change from red to violets in 10 ml of a gold solution on addition of 1 ml of 10% NaCl solution.

- Gold solution is hydrophobic colloid red in color changes to violet on addition of NaCl solution.

- Lower the gold number greater protective action.

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