The Colloidal State

Introduction:

A colloid is one of the three primary types of mixtures, with the other two being a solution and suspension. A colloid is a solution that has particles ranging between 1 and 1000 nanometers in diameter, yet are still able to remain evenly distributed throughout the solution. These are also known as colloidal dispersions because the substances remain dispersed and do not settle to the bottom of the container. In colloids, one substance is evenly dispersed in another. The substance being dispersed is referred to as being in the dispersed phase, while the substance in which it is dispersed is in the continuous phase.

When a dispersed phase is dispersed in a dispersion medium then depending on the degree of dispersion, the systems are classed as i) true solution, ii) colloidal solution, and iii) suspension

Properties	True solution	Colloidal solution	Suspension
Particle size	1 Å – 10 Å	10 Å – 1000 Å	More than 1000 Å
Appearance	Clear	Generally clear	Opaque
Nature	Homogeneous	Heterogeneous	Heterogeneous
Separation by filtration	Not possible	Not possible	Possible
Separation by cellophane paper	Not possible	Possible	Possible
Visibility	Not visible under microscope	Visible under ultra-microscope	Visible to naked eye
Brownian motion	Not observable	Occurs	May occur

Example of colloids

Colloidal AgCl, AgI, Ag proteinate (effective germicide), colloidal sulphur. Many natural and synthetic polymers are important in pharmaceutical practice.

Polymers: These are macromolecules formed by polymerization or condensation of small non-colloidal molecules e.g. proteins, natural colloids, plasma proteins which are responsible for binding certain drug molecules so that the pharmacological action of the drug molecule is affected by them. Starch and hydroxymethylallulose, cyclodeztrin are also examples.

Dispersion Medium	Dispersed Phase	Type of Colloid	Example
Solid	Solid	Solid sol	Ruby glass
Solid	Liquid	Solid emulsion/gel	Pearl, cheese
Solid	Gas	Solid foam	Lava, pumice
Liquid	Solid	Sol	Paints, cell fluids
Liquid	Liquid	Emulsion	Milk, oil in water
Liquid	Gas	Foam	Soap suds, whipped cream
Gas	Solid	Aerosol	Smoke
Gas	Liquid	Aerosol	Fog, mist

Classification

Lyophilic colloids (solvent loving): They are so called because of affinity of particles for the dispersion medium. Solutions of lyophiles are prepared by simply dissolving the material in the solvent. Because of attraction between the dispersed phase and dispersion medium, salvation (hydration in case of water) of the particles occur. Most of these colloids are organic n nature e.g. gelatin, acacia, insulin, albumin. The solution is viscous because of strong affinity for water (called gels).

Lyophobic colloid (solvent hating): The dispersed phase has little attraction to the solvent (solvent hating). Their properties differ from the lyophilic (hydrophilic). They are usually inorganic n nature e.g. gold, silver, sulphur. In contrast to lyophilic colloid, it is necessary to use special method to prepare hydrophobic colloid.

Hydrophilic sol: For lyophilic sol when the dispersion medium is water then it is called then they are called hydrophilic sols. Such as starch, glue, proteins, gelatin and certain other organic compounds.

Hydrophobic sols: For lyophobic sol when the dispersion medium is water then it is called then they are called hydrophobic sols. Examples are sol of metals, metal sulphides, metal hydroxides, suipher, phosphorous and other inorganic substances.

Properties	Lyophobic sols or Hydrophobic sol	Lyophilic sols or hydrophilic sol
Detection of particles	The particles may be readily detected by means of an ultra-microscope	The particles are not detected by means of an utra-microscope
Viscosity	Hardly differs from that of the dispersion medium	Much higher than that of the dispersion medium
Electric charge	All particles in a sol have the same charge resulting from the adsorption of ions from solution	The charge on colloidal particles depends upon the pH of the medium, since the particles readily adsorb H+ or OH- ions. This charge is often due to the dissociation of the molecules of the disperse substance.
Migration of particles in the electric field	The particles migrates in one characteristic direction depending on the charge they bear	The particles may migrate in either direction or may not migrate at all, depending on the pH of the medium
Stability	Dispersed particles are precipitated by the addition of small amount of an electrolyte	Dispersed particles are not precipitated by small amounts of electrolytes although large quantities cause precipitation
Nature	When the liquid is removed, the resulting solid does not form sol again by the simple addition of the liquid	When the liquid is removed, resulting jelly-like solid is recoverted into sol by the addition of the liquid
Occurrence	Generally, do not occur naturally	Most of these occur naturally

Preparation of Colloids

We have two main types of methods for the preparation of colloidal solutions: 1) Dispersion, 2) Condensation.

1) **Dispersion method**: In the dispersion or disintegration methods, as the name suggests, particles of colloidal size are produced by disintegration of a bulk quantity of a hydrophobic material. These methods may involve the use of such mechanical methods as:

    i)   Mechanical dispersion.
    ii)   Electro-dispersion.
    iii)   Ultrasonic dispersion.
    iv)   Peptization

i)   Mechanical dispersion: The substance to be dispersed is ground as finely as possible by the usual methods. It is shaken with the dispersion medium and thus obtained in the form of a coarse suspension. This suspension is now passed through a colloid mill. The simplest type of colloid mill called disc mill, consists of two metal discs nearly touching each other and rotating in opposite directions at a very high speed. The suspension passing through these rotating discs is exposed to a powerful shearing force and the suspended particles are apart to yield particles of colloidal size. Colloid mill are widely used in the industrial preparation of paints, cement, food products, pharmaceutical products etc.
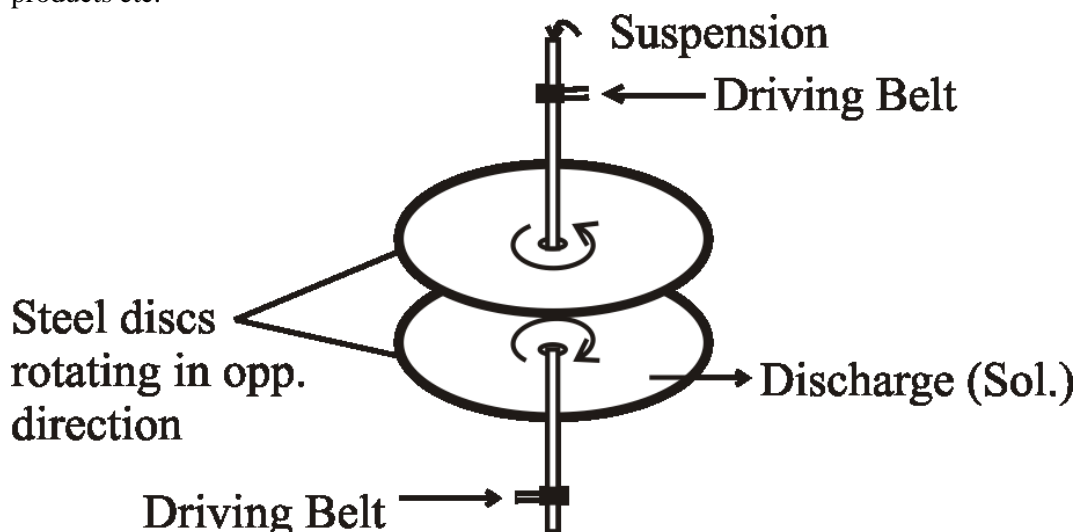

Figure: Mechanical dispersion

ii)   Electro-dispersion: These methods are employed for obtaining colloidal solutions of metals like gold, silver, platinum etc. An electric arc is struck between the two metallic electrodes placed in a container of water. The intense heat of the arc converts the metal into vapours, which are condensed immediately in the cold water bath. This results in the formation of particles of colloidal size. We call it as gold sol.
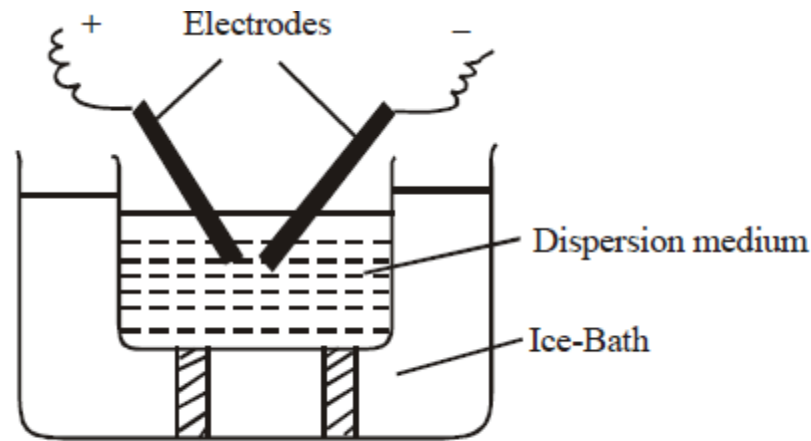
2 : Preparation of colloidal solution by Bredig's Arc Method

Figure: Bredig´s Arc method

iii)   Ultrasonic dispersion: Ultrasonic vibrations (having frequency more than the frequency of audible sound) could bring about the transformation of coarse suspension to colloidal dimensions. Claus obtained mercury sol by subjecting mercury to sufficiently high frequency ultrasonic vibration.
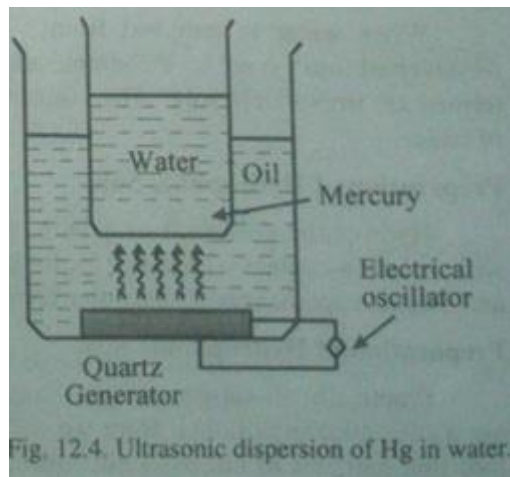

Fig. 12.4. Ultrasonic dispersion of Hg in water.

Figure: Ultrasonic dispersion

iv)   Peptization: Peptisation is the process of converting a freshly prepared precipitate into colloidal form by the addition of a suitable electrolyte. The electrolyte is called peptising agent. For example when ferric chloride is added to a precipitate of ferric hydroxide, ferric hydroxide gets converted into reddish brown coloured colloidal solution. This is due to preferential adsorption of cations of the electrolyte by the precipitate. When $FeCl_3$ is added to $Fe(OH)_3$, Fe^{3+} ions from $FeCl_3$ are adsorbed by $Fe(OH)_3$ particles. Thus the $Fe(OH)_3$ particles acquire + ve charge and they start repelling each other forming a colloidal solution.

2) **Condensation Methods**: Sulphur sol is obtained by bubbling H_2S gas through the solution of an oxidizing agent like HNO_3 or Br_2 water, etc. according to the following equation :

$$Br_2 + H_2S \rightarrow S + 2\,HBr$$

$$2\,HNO_3 + H_2S \rightarrow 2\,H_2O + 2\,NO_2 + S$$
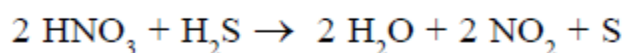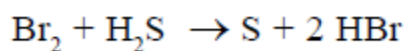
$Fe(OH)_3$ sol, As_2S_3 sol can also be prepared by chemical methods.

Purification of colloids:

When a colloidal solution is prepared it contains certain impurities. These impurities are mainly electrolytic in nature and they tend to destabilise the colloidal solutions. Therefore colloidal solutions are purified by the following methods:

(i) Dialysis
(ii) Electrodialysis

i) **Dialysis** : The process of dialysis is based on the fact that colloidal particles cannot pass through parchment or celloplane membrane while the ions of the electrolyte can. The colloidal solution is taken in a bag of cellophane which is suspended in a tub full of fresh water. The impurities diffuse out leaving pure coloidal solution in the bag. This process of separating the particles of colloids from impurities by means of diffusion through a suitable membrane is called *dialysis*.
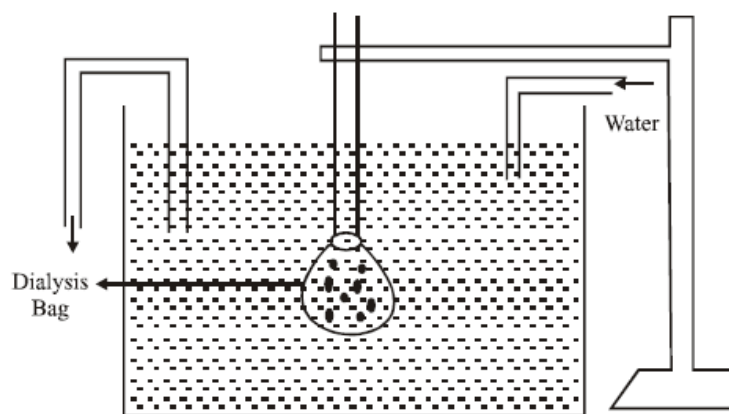

Figure: dialysis

ii) **Electro-dialysis**: The dialysis process is slow and to speed up its rate, it is carried out in the presence of an electrical field. When the electric field is applied through the electrodes, the ions of the electrolyte present as impurity diffuse towards oppositely charged electrodes at a fast rate. The dialysis carried out in the presence of electric field is known as electro-dialysis.
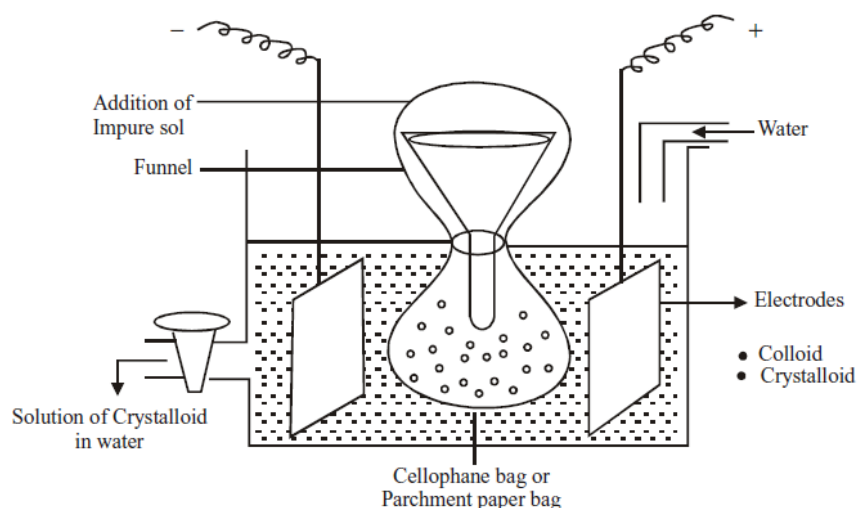
Figure: Electro-dialysis

Origin of charge in colloidal particles:

The charge on a colloidal particle is developed due to the following reasons:

i) Self-dissociation: Colloidal electrolytes such as sodium stearate (soap) dissociate in solution giving $C_{17}H_{35}COO^-$ and Na^+ ions. The hydrocarbon parts of the ions have marked affinity for one another, thus they cluster together developing a negative charge on the colloidal soap particles.

ii) Presence of acid or basic groups: Proteins have a carboxyl group and a basic amino group (RNH_2COOH). Thus in acid solution colloidal particles of protein develop a positive charge whereas in alkaline solution a negative charge is developed due to ionization.

iii) Selective adsorption of ions: The origin of charge on the sol particles in most cases has been demonstrated to be the selective adsorption of a certain type of ions present in the dispersion medium. The negative charge on the metal sols is due to the adsorption of hydroxyl ions furnished by traces of alkali used to produce stable sols.

When two or more ions are present in the dispersion medium, selective adsorption of the ion common to the colloidal particles usually takes place. For example, the negative charge on As_2S_3 sol is due to the preferential adsorption of sulphide ions (S^{2-}) produced by the ionisation of hydrogen sulphide used in the preparation of the sol ($H_2S = 2H^+ + S^{2-}$). Ferric hydroxide sol is positively charged because the sol particles adsorb the ferric ions in preference to the chloride ions.

Stability of colloids:

Colloidal particles, though larger than ions and molecules, yet are stable, and do not settle under gravity. There are at least three good reasons for the stability of colloidal sols.

i) Brownian motion: like the molecules or ions in a solution, the colloidal particles of a sol are in a state of continuous rapid motion. The intensity of Brownian motion falls rapidly with increase in the particle size, yet it is high enough to offset of gravity in case of colloidal particles.

ii)   Electric charge: As we know that the colloidal particles in a sol are all either positively charged or negatively charged. Therefore, the force of repulsion keeps the particles scattered and even upon close approach they will not collide and coalesce. Hence similar charge on all the particles of a colloid accounts for the stability due to mutual repulsion in the solution.

iii)   Solvation: The colloidal particles of a sol are often highly hydrated in solution. The resulting hydrated ´´shell´´ prevents close contact and cohesion od colloidal particles. Comparatively the addition of small amounts of a lyophilic colloid called protective colloids.

Properties of Colloids:

In order to be classified as a colloid, the substance in the dispersed phase must be larger than the size of a molecule but smaller than what can be seen with the naked eye. This can be more precisely quantified as one or more of the substance's dimensions must be between 1 and 1000 nanometers. If the dimensions are smaller than this the substance is considered a solution and if they are larger than the substance is a suspension.

A common method of classifying colloids is based on the phase of the dispersed substance and what phase it is dispersed in. The types of colloids include sol, emulsion, foam, and aerosol.

Sol is a colloidal suspension with solid particles in a liquid.

Emulsion is between two liquids.

Foam is formed when many gas particles are trapped in a liquid or solid.

Aerosol contains small particles of liquid or solid dispersed in a gas.

When the dispersion medium is water, the collodial system is often referred to as a hydrocolloid. The particles in the dispersed phase can take place in different phases depending on how much water is available. For example, Jello powder mixed in with water creates a hydrocolloid. A common use for hydrocolloids is in the creation of medical dressings.

In general colloids have the following properties:
1.   The particles of the dispersed phase are relatively large, however they pass through ordinary filter media.
2.   The dispersed phase doesn't dissolve in the dispersion medium.
3.   They scatter light (Tyndal effect).
4.   Particles show random motion (Brownian motion), due to collision with molecules of the dispersion medium.
5.   Particles adsorb ions (its own ions in preference to others).
6.   Particles may have an electrical charge which leads to repulsive forces which stabilize the colloid dispersion and prevent its coagulation.
7.   When the particles of the dispersion phase join together, they coagulate and separate due to gravity.
8.   Particles have large surface area.
9.   Colloidal suspensions have negligible effects on colligative properties.

i)   Kinetic properties:

Brownian movement: It is also termed as Brownian motion and is named after its discoverer Robert Brown (a Botanist.) Brownian motion is the zig-zag movement of colloidal particles in continuous random manner. Brownian motion arises because of the impact of the molecules of the dispersion

medium on the particles of dispersed phase. The forces are unequal in different directions. Hence it causes the particles to move in a zig-zag way.
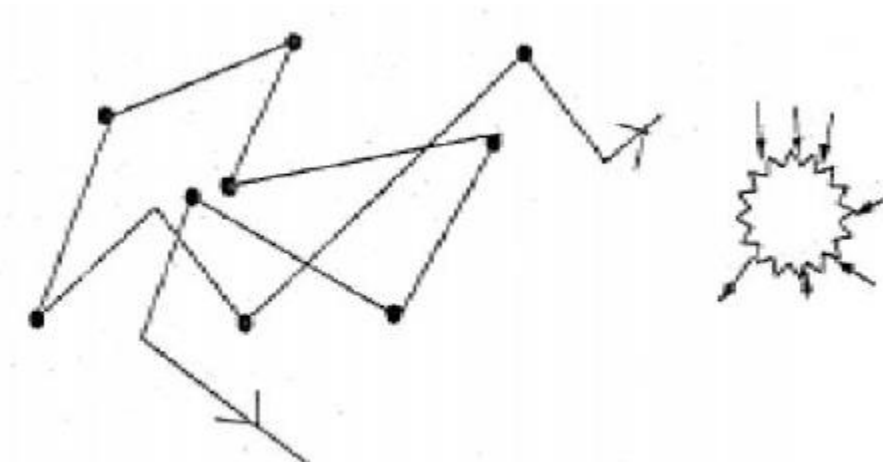

Figure: Brownian movement

ii)   Optical properties:

Tyndall Effect: Tyndall in 1869, observed that if a strong beam of light is passed through a colloidal solution then the path of light is illuminated. This phenomenon is called Tyndall Effect. This phenomenon is due to scattering of light by colloidal particles. The same effect is noticed when a beam of light enters a dark room through a slit and becomes visible. This happens due to the scattering of light by particles of dust in the air.
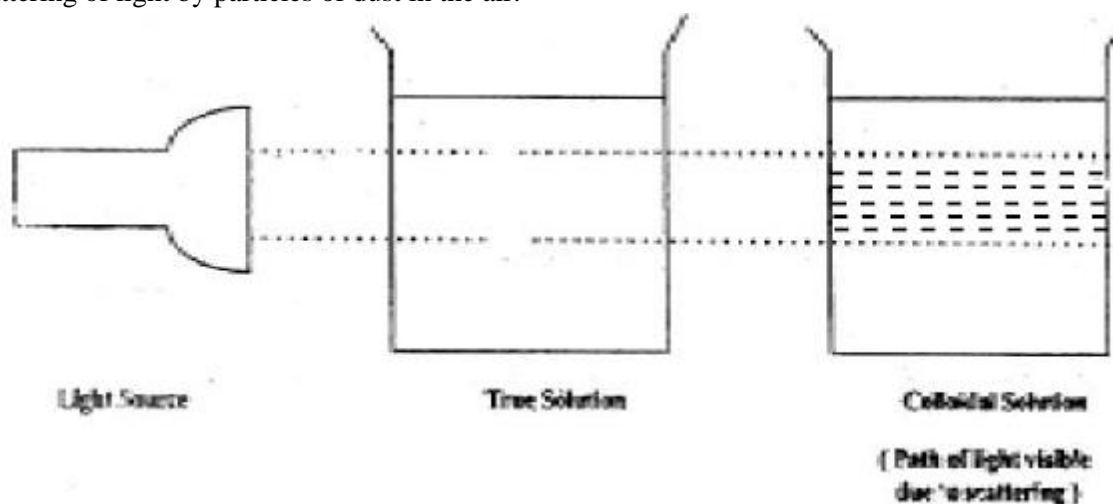

Light Source   True Solution   Colloidal Solution

(Path of light visible
due to scattering)

Figure: Tyndall effect

iii)   Electrical properties:

The particles of a colloidal solution are electrically charged and carry the same type of charge, either negative or positive. The dispersion medium has an equal and opposite charge. The colloidal particles therefore repel each other and do not cluster together to settle down. For example, arsenious sulphide sol, gold sol, silver sol, etc. contain negatively charged colloidal particles whereas ferric hydroxide, aluminium hydroxide etc. contain positively charged colloidal particles.

Origin of charge on colloidal particles is due to:
(a) Preferential adsorption of cations or anions by colloidal particles.
(b) Miscelles carry a charge on them.
(c) During the formation of colloids especially by Bredig´s arc method, colloidal particles capture electrons and get charged.

a) Effect of addition of Lyophobic sols:

The quantity of the electrolyte which is required to coagulate a definite amount of a colloidal solution depends upon the valency of the coagulating ion(ion having a charge opposite to that of the colloidal particles). This observation of Hardy and Schulze is known as Hardy Schulze Law, the main points of which may be stated as follows:

(i) The effective ions of the electroyte in bringing about coagulation are thise which carry charge opposite to that of the colloidal particles. These ions are called coagulating ions or flocculating ions.
(ii) Greater is the valency of the coagulating or the flocculating ion, greater is its power to bring about coagulation.

b) Effect of applied field on lyophobic sols:

Electrophoresis:

When a potential difference (electric field) is applied across two platinum electrodes immersed in a colloidal solution, the particles of dispersed phase move towards either the positive or negative electrode. This observation was first discovered by Rauss in 1807 and was investigated later by Linder and Picton.
The movement of colloidal particles under the action of electric field is known as Electrophoresis.
If the colloidal particles move towards the positive electrode (Anode) they carry negative charge. On the other hand if the sol particles migrate towards negative electrode (Cathode), they are positively charged. From the direction of movement of colloidal particles it is possible to find out the charge on colloidals.
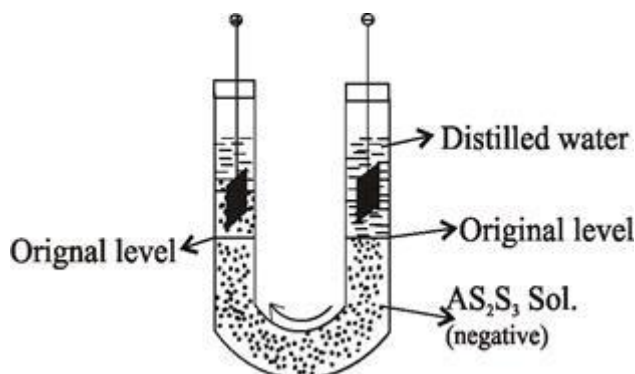

Figure: Electrophoresis

Demonstration of Electrophoresis
        The demonstration of electrophoresis is as follows:-

Take a colloidal sol say AS_2S_3 sol in a U – tube. Place an electrolyte, having density less than that of solution (say distilled water). The electrolyte provides distinct boundary between electrolyte and colloidal sol.

Place two platinum electrodes in two arms of U – tube such that they dip in the colloidal sol. When a high potential difference of about 100 volts is applied across the two platinum electrodes, it is observed that the level or Boundary of colloidal solution falls on the negative electrode side and rises up on positive electrode side. On reaching the positive electrode, the colloidal particles get discharged. As a result of neutralisation of charge, the colloidal particles aggregate and settle down at the bottom.

Electro-Osmosis:

A colloidal solution as a whole is electrically neutral in nature i.e., dispersion medium carries an equal and opposite charge to that of the particles of dispersed phase. When the movement of dispersed phase of colloidal solution is prevented by suitable means, the dispersion medium can be made to move under the influence of an applied electric field or potential. This phenomenon is referred to as Electro-Osmosis. Thus electro-osmosis may be defined as the movement of the dispersion medium under the influence of an applied electric field when the particles of dispersed phase are prevented from moving.
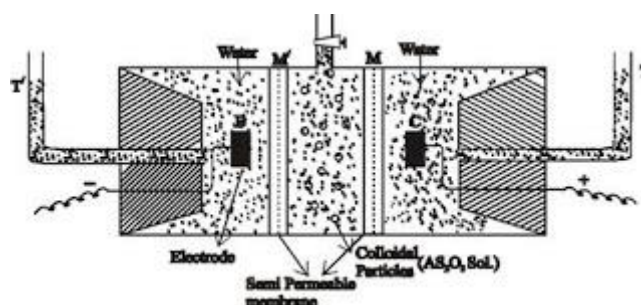

Figure: Electro-Osmosis

Demonstration of Electro-Osmosis: The phenomenon of electro-osmosis can be demonstrated experimentally as follows:-

The demonstration of electro-osmosis is carried out in a specially designed apparatus. The apparatus consists of a bigger tube having two side tubes T and T/ attached to its ends. The bigger tube is divided into three compartments A, B and C by means of two semi-permeable membranes. A tube carrying a stop-cock is attached to the central compartment A. Two platinum electrodes are inserted in the outer compartments B and C.

A colloidal dispersion is placed in the central compartment A and the outer compartments B and C are filled with water. The water in compartments B and C also extends to the side tube T and T/. The function of membrane is to prevent the movement of colloidal particles. Therefore, when a potential difference is applied across the electrodes held close to the membranes in the compartment B and C, dispersion medium begins to move.

If the particles carry positive charge, the dispersion medium would start moving towards the anode and the level of water in the side tube T would be seen to rise, indicating the presence of negative charge on the dispersion medium. If the particles carry negative charge, the dispersion medium would be seen to move towards cathode and water in the side tube T would start rising.

Electro osmosis is utilizing for dewatering moist clay and drying of dye pastes.

Electrokineticphenomena:

Electrophoresis is the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field. This electrokinetic phenomenon was observed for the first time in 1807 by Ferdinand Frederic Reuss (Moscow State University), who noticed that the application of a constant electric field caused clay particles dispersed in water to migrate. It is ultimately caused by the presence of a charged interface between the particle surface and the surrounding fluid. It is the basis for a number of analytical techniques used in biochemistry for separating molecules by size, charge, or binding affinity.

Electrophoresis of positively charged particles (cations) is called cataphoresis, while electrophoresis of negatively charged particles (anions) is called anaphoresis. Electrophoresis is a technique used in laboratories in order to separate macromolecules based on size. The technique applies a negative charge so proteins move towards a positive charge. This is used for both DNA and RNA analysis. Polyacrylamide gel electrophoresis has a clearer resolution than agarose and is more suitable for quantitative analysis. In this technique DNA foot-printing can identify how proteins bind to DNA. It can be used to separate proteins by size, density and purity. It can also be used for plasmid analysis, which develops our understanding of bacteria becoming resistant to antibiotics.

Suspended particles have an electric surface charge, strongly affected by surface adsorbed species, on which an external electric field exerts an electrostatic Coulomb force. According to the double layer theory, all surface charges in fluids are screened by a diffuse layer of ions, which has the same absolute charge but opposite sign with respect to that of the surface charge. The electric field also exerts a force on the ions in the diffuse layer which has direction opposite to that acting on the surface charge. This latter force is not actually applied to the particle, but to the ions in the diffuse layer located at some distance from the particle surface, and part of it is transferred all the way to the particle surface through viscous stress. This part of the force is also called electrophoretic retardation force. When the electric field is applied and the charged particle to be analyzed is at steady movement through the diffuse layer, the total resulting force is zero:

$$F_{tot} = 0 = F_{el} + F_f + F_{ret}$$

Considering the drag on the moving particles due to the viscosity of the dispersant, in the case of low Reynolds number and moderate electric field strength E, the drift velocity of a dispersed particle v is simply proportional to the applied field, which leaves the electrophoretic mobility μ_e defined as:

$$\mu_e = \frac{v}{E}.$$

The most well-known and widely used theory of electrophoresis was developed in 1903 by Smoluchowski

$$\mu_e = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta},$$

where ε_r is the dielectric constant of the dispersion medium, ε_0 is the permittivity of free space ($C^2\,N^{-1}\,m^{-2}$), η is dynamic viscosity of the dispersion medium (Pa s), and ζ is zeta potential (i.e., the electrokinetic potential of the slipping plane in the double layer).

The Smoluchowski theory is very powerful because it works for dispersed particles of any shape at any concentration. Unfortunately, it has limitations on its validity. It follows, for instance, from the fact that it does not include Debye length κ^{-1}. However, Debye length must be important for electrophoresis, as follows immediately from the Figure on the right. Increasing thickness of the double layer (DL) leads to removing point of retardation force further from the particle surface. The thicker DL, the smaller retardation force must be.

Detailed theoretical analysis proved that the Smoluchowski theory is valid only for sufficiently thin DL, when particle radius a is much greater than the Debye length :

$$a\kappa \gg 1.$$

This model of "thin Double Layer" offers tremendous simplifications not only for electrophoresis theory but for many other electrokinetic theories. This model is valid for mostaqueous systems, where the Debye length is usually only a few nanometers. It only breaks for nano-colloids in solution with ionic strength close to water.

The Smoluchowski theory also neglects the contributions from surface conductivity. This is expressed in modern theory as condition of small Dukhin number:

$$Du \ll 1$$

In the effort of expanding the range of validity of electrophoretic theories, the opposite asymptotic case was considered, when Debye length is larger than particle radius:

$$a\kappa < 1.$$

Under this condition of a "thick Double Layer", Hückel predicted the following relation for electrophoretic mobility:

$$\mu_e = \frac{2\varepsilon_r \varepsilon_0 \zeta}{3\eta}.$$

This model can be useful for some nanoparticles and non-polar fluids, where Debye length is much larger than in the usual cases.

There are several analytical theories that incorporate surface conductivity and eliminate the restriction of a small Dukhin number, pioneered by Overbeek and Booth. Modern, rigorous theories valid for any Zeta potential and often any $a\kappa$ stem mostly from Dukhin-Semenikhin theory. In the **thin Double Layer** limit, these theories confirm the numerical solution to the problem provided by O'Brien and White.

Various combinations of the driving force and moving phase determine various electrokinetic effects. According to J.Lyklema, the complete family of electrokinetic phenomena includes:

Electrophoresis, as motion of particles under influence of electric field;

Electro-osmosis, as motion of liquid in porous body under influence of electric field;

Diffusiophoresis, as motion of particles under influence of a chemical potential gradient;

Capillary osmosis, as motion of liquid in porous body under influence of the chemical potential gradient;

Sedimentation potential, as electric field generated by sedimenting colloid particles;

Streaming potential/current, as either electric potential or current generated by fluid moving through porous body, or relative to flat surface;

Colloid vibration current, as electric current generated by particles moving in fluid under influence of ultrasound; electric sonic amplitude, as ultrasound generated by colloidal particles in oscillating electric field.

Electrical double layer:

The model which gave rise to the term 'electrical double layer' was first put forward in the 1850's by Helmholtz. In this model he assumed that no electron transfer reactions occur at the electrode and the solution is composed only of electrolyte. The interactions between the ions in solution and the electrode surface were assumed to be electrostatic in nature and resulted from the fact that the electrode holds a charge density (qm) which arises from either an excess or deficiency of electrons at the electrode surface. In order for the interface to remain neutral the charge held on the electrode is balanced by the redistribution of ions close to the electrode surface. Helmholtz's view of this region is shown in the figure below
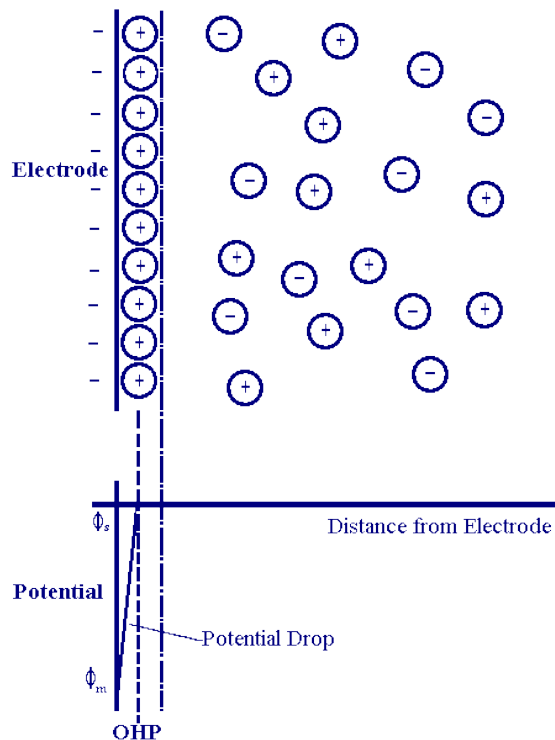
with the potential drop occurring in a linear manner between the two plates. It is perhaps no surprise that when impedance analysis is performed on electrochemical systems the response due to the electrolyte redistribution is modelled in terms of capacitive elements.

The model of Helmholtz while providing a basis for rationalising the behaviour of this region does not account for many factors such as, diffusion/mixing in solution, the possibility of absorption on to the surface and the interaction between solvent dipole moments and the electrode. A later model put forward by Stern begins to address some of these limitations now the ions are assumed to be able to move in solution and so the electrostatic interactions are in competition with Brownian motion. The

result is still a region close to the electrode surface (100×10^{-10} m) containing an excess of one type of ion but now the potential drop occurs over the region called the diffuse layer.
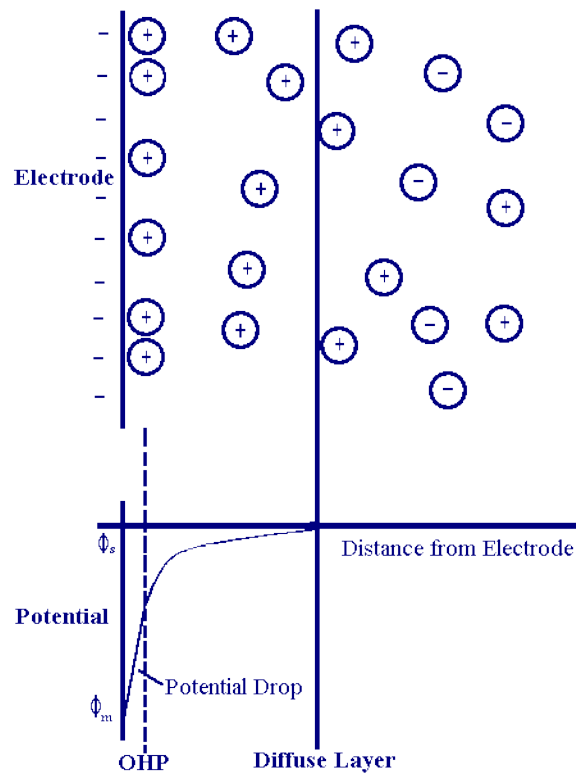
Many modifications and improvements have been made to these early models with the latest approaches using numerical modelling to follow the redistribution effects as the electrode potential is varied.

Ultracentrifuge:

The ultracentrifuge is a centrifuge optimized for spinning a rotor at very high speeds, capable of generating acceleration as high as $2\,000\,000$ g (approx. $19\,600$ km/s²). There are two kinds of ultracentrifuges, the preparative and the analytical ultracentrifuge. Both classes of instruments find important uses in molecular biology, biochemistry, and polymer science.

Molecular weight determination of macromolecules:

The Z – average molecular weight, $\overline{M}_z$ is expressed as :

$$\overline{M}_z = \frac{\Sigma\, N_i\, M_i^{\,3}}{\Sigma\, N_i\, M_i^{\,2}}$$

For a given molecular weight distribution, the various average molecular weights come in the order $\overline{M}_n < \overline{M}_v \leq \overline{M}_w < \overline{M}_z$. The Z-average molecular weight is commonly measured by sedimentation equilibrium method using an ultracentrifuge.

The ultra-centrifugation techniques are somewhat complicated and much less commonly employed for molecular weight measurements of synthetic polymers, even though, they are more commonly used for characterizing biological polymers such as proteins and enzymes.

Employing a low speed of rotation with the polymer solution in the cell held in position and operating the ultracentrifuge under constant conditions for a long period avoiding convection related disturbances within the cell, a state of equilibrium is reached. Under equilibrium condition, the polymer fractions get distributed in the cell according to size or molecular weight distribution. The force of sedimentation on a molecular species in solution is just balanced by its tendency to diffuse out. For dilute solutions closely approaching ideal behavior and for a monodisperse polymer, the molecular weight M is expressed as

$$M = \frac{2\,RT\,ln\,(\,c_2\,/\,c_1\,)}{(1 - v\,\rho)\,\omega^2\,(r_2{}^2 - r_1{}^2)}$$

where c_1 and c_2 are the concentration at two points corresponding to distances r_1 and r_2 in the cell and ω is the angular velocity of rotation, v, the partial specific volume of the polymer and ρ, the density of the medium. The solvent chosen should be preferably a poor solvent having a density far different from that of the polymer so as to facilitate sedimentation; the solvent and polymer must also differ in refractive index so as to facilitate easy measurement. For a poly disperse polymer, different approaches for measuring the concentration as a function of r yield different molecular weight averages ($\overline{M}_w$ or $\overline{M}_z$). Measurements based on refractive index yield $\overline{M}_z$. Preparative ultracentrifugation is utilized in fractionating polymer samples and in separating them from easily sedimented contaminants.