

COLLOIDAL SYSTEM-SOL

11.1. INTRODUCTION

An ordinary solution consists of two components - a solute and a solvent. The particles of the solute are usually normal molecules or ions. For example, when sugar or common salt is added to water, a true solution is formed. On the other hand when substances like sand, powdered glass etc. are added to water, they settle down, such solutions are called *coarse suspensions*. Between these two extremes of true solutions and coarse suspensions exist systems called *colloidal solutions* or colloids. They occupy an intermediate position between true solutions on one hand and suspensions on the other. The word *colloids* is of Greek origin. (Kolla = glue and eiōds = like). Thomas Graham is usually regarded as the founder of Colloid Science who studied the diffusion of various substances from solution region to solvent region across a permeable membrane and observed that some substances have ability to diffuse through permeable membrane while other cannot pass through it. The substances which had ability to pass through permeable membrane were called crystalloids while those which could not pass through permeable membrane were names as colloids. The IUPAC definition of colloid is "The colloidal state is the state of subdivision in which molecules or polymolecular particles having at least one dimension in the range of 1 nm and 1 μm , are dispersed in some medium".

A colloidal solution, therefore, consists of particles which are larger than the normal molecules but not large enough to be seen by a microscope. However, there is no sharp line of demarcation between the true solution and the colloidal solution on one hand, and between colloidal solution and coarse suspension on the other. In a colloidal solution, the dispersed phase particle size (at least one dimension) lies in the range of 1 nm-1000 nm (1 μm). Thus, the essential difference between the solutions, colloids and coarse suspensions lies in their relative particle size. A colloidal solution cannot always be distinguished from a true solution with the naked eye. The particles of a colloidal solution can pass through an ordinary filter paper. A *colloidal solution* is defined as a heterogeneous system consisting of phases.

- (i) a dispersed phase (internal phase/inner phase/discontinuous phase) which consists of the colloidal particles, and
- (ii) a dispersion medium two (external phase/outer phase/continuous phase) in which the dispersion of particles takes place.

The dispersion medium usually forms the large fraction of colloids. Each of the two phases making a colloid may be a gas, liquid or a solid. For example, the dispersion of As_2S_3 , gold or oil in water forms a colloidal solution.

Some of the distinguishing characteristics of solution, colloid, and suspension are given in Table 21.1.

Table 21.1. Distinguishing Characteristics of Colloid, Suspension and Solution

S. No.	Properties	Suspension	Colloid	Solution
1.	Particle size	> 100 nm	1 nm - 100 nm	< 1 nm
2.	Separation			
	(i) Ordinary filtration	Possible	Not possible	Not possible
	(ii) Ultrafiltration	Possible	Possible	Not possible
3.	Setting	Settles under gravity	Settles on centrifugation	Does not settle
4.	Appearance	Opaque	Generally clear	Clear
5.	Diffusion	Not possible	Diffuses slowly	Diffuses rapidly
6.	Brownian motion	Shows	Shows	Not observable
7.	Tyndal effect	Shows	Shows	Not observable
8.	Phase	Heterogeneous	Heterogeneous	Homogeneous
9.	Charge on particles	Positively or negatively charged or neutral particles	Positively or negatively charged	Positive and negative ions or neutral molecules
10.	Examples	Sand or mud suspension	Milk, blood, fog	Urea or salt solution

21.2. CLASSIFICATION OF COLLOIDS

For the classification of colloids, a number of criteria have been employed. These are:

(a) Based on the physical State of Two Phases

Based on the physical state of dispersed phase and dispersion medium, colloidal systems are classified to eight different classes as shown in Table 21.2. A gas in a gas colloidal system cannot exist because mixing of two gases forms a homogeneous mixture. Sol (solid in liquid colloidal system), emulsion (liquid in liquid colloidal system) and gel (liquid in solid colloidal system) are three major classes of colloids and have gained a lot of attention with respect to their potential applications in various fields. This chapter deals with classification, synthesis, properties and application of sol which is also

known as colloidal solution. So, in this chapter, we shall mainly deal with colloidal systems in which the dispersed phase is a solid and the dispersion medium is a liquid. If the dispersion medium is water, they are called *hydrosols* or *aquasols*. If solid particles are dispersed in benzene then it may be called as *benzosol*. When alcohol is dispersion medium then sol is known as *alcosol*. Names of colloidal systems are also given on the basis of names of material of dispersed phase. For example, a system containing silver nanoparticles dispersed in aqueous medium is called *silver sol*. A colloidal system of emulsions and gels have been discussed in chapter 11.

Based on type of particles of dispersed phase

(c)

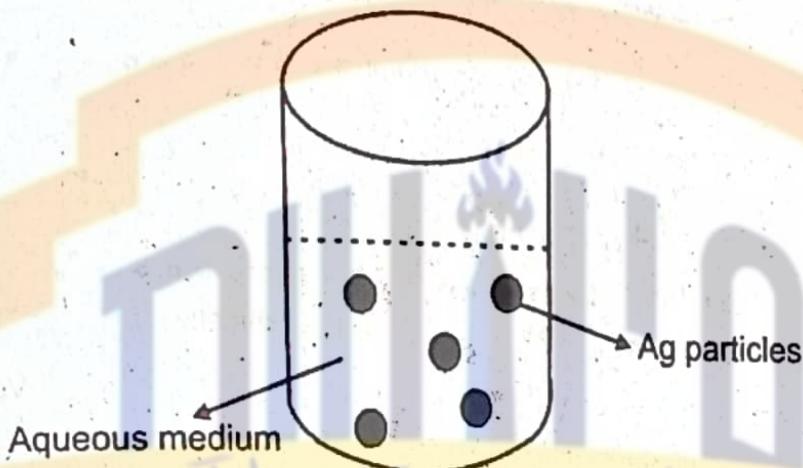


Fig. 21.1 Ag sol: Silver nanoparticles dispersed in aqueous medium.

Colloidal system may also be classified on the basis of type of particles of dispersed phase into multi-molecular, macromolecular and associated colloids (Fig. 21.2). A large number of small molecules or atoms of a substance are added together to form particles having size in the colloidal range. Such kind of particles dispersed in another medium are known as multi-molecular colloids. The aqueous dispersion of gold nanoparticles is an example of multi-molecular colloids. Each metal nanoparticle is made of thousands gold atoms. In macromolecular colloid, the macromolecule forms a solution with a solvent. The size of each macromolecule having large molecular mass remains in the range of colloidal size. Dispersion of starch, protein or cellulose in water is an example of macromolecular colloid. An aqueous solution of a high molecular weight polymeric substance can be treated as macromolecular colloid. Few amphiphilic substances are soluble in a solvent at their low concentration to form a true solution. In case of their true solution, amphiphilic substance units exist as individual units called unimers. At their high concentration, unimers aggregate with each other to form assemblies/particles called micelles. Micelles dispersed in a solvent have their size in colloidal range and are termed as associated colloids. The formation of micelles occurs above a certain temperature called critical solution temperature and specific concentration called critical micelle concentration (CMC). These colloids can be reverted by diluting micellar solution. Dispersion of a surfactant in aqueous medium having surfactant concentration \geq CMC is an example of associated colloids. Associated colloidal particles may have various shapes

like spherical, elliptical, bilayer, vesical reverse micelle as shown in Fig. 21.2 (d). The process of formation of associated colloids has been discussed in chapter 11.

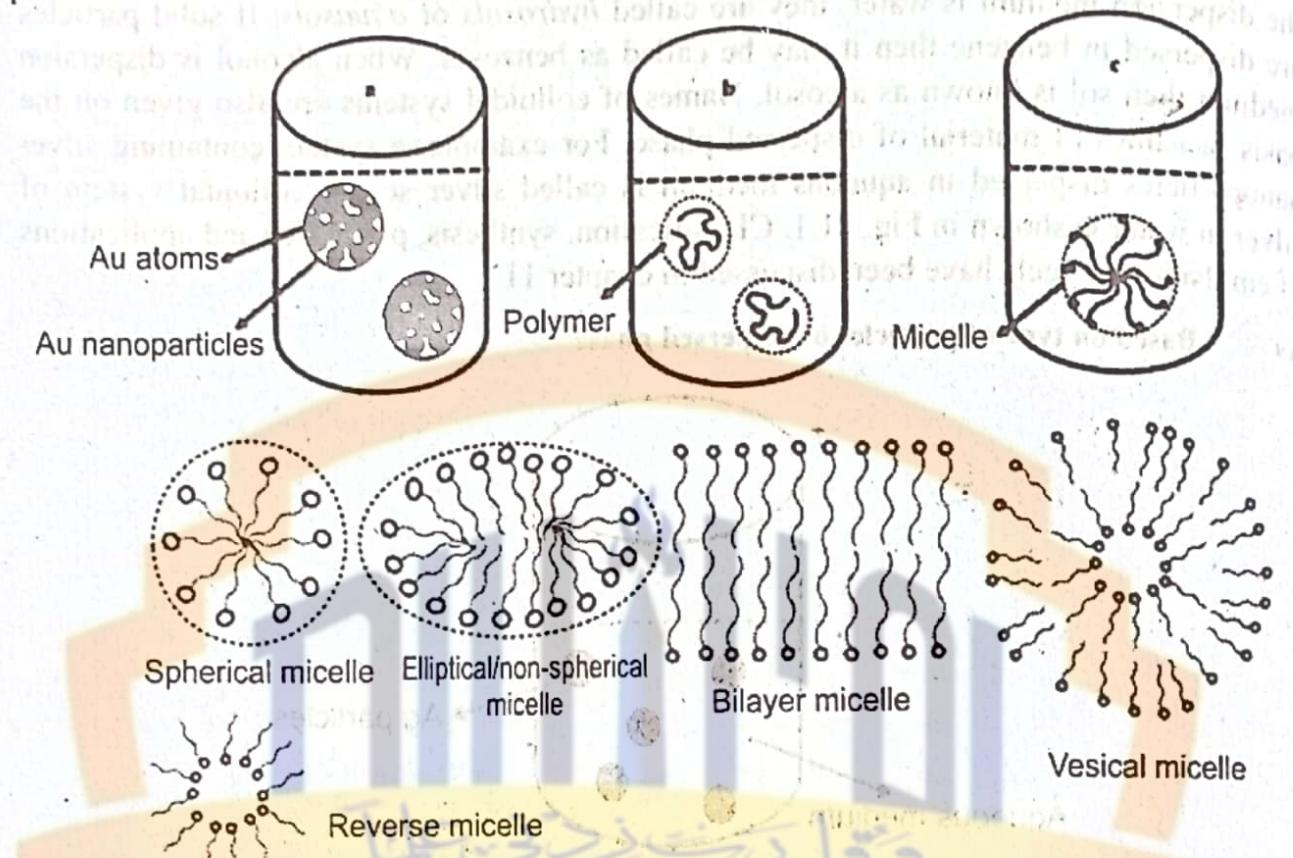


Fig. 21.2 (a) Multi-molecular (b) Macromolecular (c) Associated colloids and (d) various shapes of associated colloids

Table 21.2. Classification of Colloidal Solutions

S.No.	Dispersed Medium	Dispersion Phase	Name	Examples
1.	Gas	Liquid	Aerosol	Fog, mist, clouds.
2.	"	Solid	Aerosol	Smoke, dust.
3.	Liquid	Gas	Foam	Froath, whipped cream
4.	"	Liquid	Emulsion	Milk, oil in water.
5.	"	Solid	Sols	AgCl, As ₂ S ₃ in water.
6.	Solid	Gas	Solid foam	Pumice stone, ice cream
7.	"	Liquid	Gels	Jellies, curd.
8.	"	Solid	Solid sols	Ruby, gem.

(c) Based on Interaction of Phases

On the basis of affinity between the dispersed phase and the dispersion medium, sols can be divided into two categories, lyophobic and lyophilic sols. *Lyophobic* (solvent hating) sols have little attraction between the dispersed phase and dispersion medium,

Because of the poor interactions, lyophobic sols are less stable, precipitate out easily and which cannot be reconverted into sols either by adding solvent or by warming. Typical examples of such colloids are sols of metals, sulphur and silver halides. *Lyophilic* (solvent loving) sols on the other hand are systems in which the dispersed phase shows some definite affinity for the medium. Lyophilic sols are easily formed and are generally reversible, e.g., gums, starch etc.

When the liquid dispersion medium is water, the terms employed are *hydrophobic* and *hydrophilic* sols. Other essential differences between the two types of sols are given in Table 21.3.

Table 21.3. Distinguishing Characteristics of Lyophobic and Lyophilic Sols

S. No.	Lyophobic Sols	Lyophilic Sols
1.	These are generally unstable, get easily coagulated on adding electrolytes.	These are very stable and are not easily coagulated by electrolytes.
2.	These are irreversible in character.	These are reversible in character.
3.	Prepared by indirect methods.	Usually prepared by simple solution methods.
4.	Viscosity of the colloidal dispersion is same as that of the solvent.	These are highly viscous systems.
S. No.	Lyophobic Sols	Lyophilic Sols
5.	These are generally inorganic materials i.e., metals sulphide and oxide sols.	Mostly organic materials, e.g., starch, gum and proteins.
6.	Surface tension is similar to that of the dispersion medium.	Surface tension is lower than that of the dispersion medium.
7.	Particles carry positive or negative charge.	Particles may have little or no charge at all.
8.	Particles are easily detected under an ultramicroscope.	The particles cannot be readily detected under an ultramicroscope.
9.	There is no solvation of the lyophobic sol particles.	Lyophilic sol particles are solvated due their interaction with solvent.
10.	Examples. Gold or As_2S_3 in water.	Examples: Gum, starch, proteins.

(d) Based on Size Distribution of dispersed particles

Based on size distribution of dispersed particles, colloidal system may be classified into monodisperse colloidal system and poly-disperse colloidal system. The colloidal system with narrow size distribution of dispersed particles is called monodisperse colloidal system while the colloidal system with broad size distribution of dispersed particles is called poly-disperse colloidal system. It has been observed that monodisperse colloidal system is more stable than poly-disperse colloidal system.

(d) Based on Size of disperse phase particles

Based on size of disperse phase particles, colloidal system may be divided into nano-colloidal system and micro-colloidal system. In case of nano-colloids, at least one dimension of disperse phase particles lies in the range of 1-100 nm while in micro colloids, it lies in the range of 100-1000 nm.

21.3. PREPARATION OF SOLS

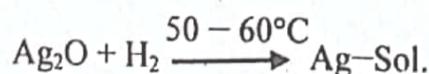
Many substances such as gelatin, starch and other high molar mass polymers when warmed with a suitable dispersion medium go into the solution form, forming a colloidal solution. Such sols are stable, reversible and are called *lyophilic sols*. *Lyophobic sols*, on the other hand, are unstable, irreversible and therefore, have to be prepared by special methods. Two methods are generally used for their preparations:

- (a) Condensation methods in which the particles present in the true solution as ions or molecules are allowed to grow in size to particles of colloidal dimensions. Such methods are also known as bottom up approaches.
- (b) Dispersion methods in which the bigger particles are disintegrated into particles of colloidal dimensions which remain in the dispersion medium. Such methods are sometime called top down approaches.

A. Condensation Methods (Bottom up approach)

The substance which is to be dispersed in the medium is obtained by chemical reactions or sometimes by physical changes under controlled conditions of temperature and concentration. The process of fabrication of particles is carried out in the presence of some suitable stabilizing system to prevent aggregation of colloidal particles. The various methods employed are:

- (i) **Reduction.** This method is generally used for the preparation of metal sols and is of historical interest. This method involves the reduction of soluble salts of metals by reducing agents such as hydrogen, formaldehyde, hydrazine, NaBH_4 etc. A silver sol may be prepared by passing a current of pure hydrogen through a saturated solution of silver oxide at 50 - 60°C.



Ag sol can also be prepared by chemical reduction of AgNO_3 by NaBH_4 in the presence of some suitable capping agent in aqueous medium.

(ii) **Oxidation.** Colloidal sulfur may be prepared by the oxidation of hydrogen sulfide. H_2S is passed into a solution of sulfur dioxide in water until all the odour of sulfur dioxide has been removed.



(iii) **Hydrolysis.** This method is used to obtain sols of oxides or hydroxides of weakly electropositive metals like iron, aluminum etc. A solution of ferric oxide is prepared by adding a small quantity of ferric chloride into a large volume of boiling water.



(iv) **Double Decomposition.** A silver chloride sol can be obtained by mixing dilute solutions of AgNO_3 and KCl in nearly equal amounts. The precipitate of AgCl is stabilized by the excess of Ag^+ or Cl^- ions.



Arsenious sulphide sol is obtained by mixing solutions of arsenious oxide and hydrogen sulphide.



(v) **Exchange of Solvent.** This method is based on the principle that if a substance A is insoluble in one solvent, say X, but soluble in other solvent, say Y, then the colloidal solutions of that substance is prepared by dissolving the substance A in Y and then pouring the solution into an excess of solvent X. This method is used to prepare sulphur or phosphorus sols by first dissolving them in alcohol and then pouring their alcoholic solutions into water. Such sols are unstable and are stabilized by the addition of some stabilizers.

Dispersion Methods (Top down approach)

In dispersion methods, a bulk material is converted into particles of colloidal dimension which are dispersed and stabilized in a liquid to form sol. Dispersion methods are also known as disintegration methods. Various dispersion methods used are:

(i) **Mechanical Disintegration.** Many substances can be disintegrated into particles of colloidal size in a colloid mill. The colloid mill consists of two steel discs each rotating in opposite direction at a speed of about 7000 rpm. The dispersion medium along with the dispersed substance and a protective substance is allowed to pass through the mill where a colloidal solution results (Fig.21.3).

SUSPENSION

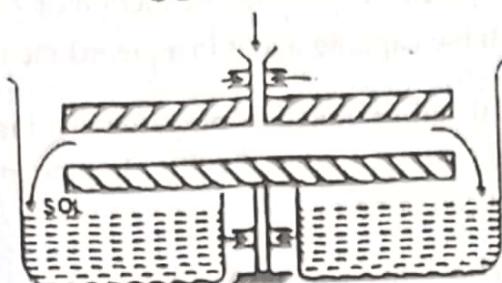


Fig. 21.3 A Colloid mill for fabrication of sol via mechanical disintegration.

- (ii) **Peptization.** The process of dispersing a precipitate into a colloidal solution by adding small quantity of an electrolyte is called *peptization*. The electrolyte added is called a *peptizing agent*. For example, freshly precipitated Fe(OH)_3 can be peptized by addition of dilute solution of ferric chloride into aqueous medium having Fe(OH)_3 precipitates. The Fe^{3+} ions coming from FeCl_3 are adsorbed on the surface of neutral Fe(OH)_3 particles and convert them into positively charged Fe(OH)_3 particles which are dispersed in aqueous medium due to electrostatic repulsion among all dispersed particles.



Similarly precipitates of many sulphides can be dispersed by passing H_2S through water in which they are suspended. Peptization is reverse of coagulation. Peptizing agent should have ions common to precipitates used for sol preparation.

- (iii) **Bredig's Arc Method.** This method is employed in preparing colloidal solutions of metals like Au, Pt, Ag etc. It consists in striking an electric arc between the electrodes of metal in water (Fig. 21.4). The metal electrodes are connected to source of high voltage to produce an arc in water between dipped electrodes. The heat of the arc evaporates the metal and the metal vapors are condensed in cold water as internal vessel is placed in an outer vessel containing ice. Traces of alkali metal hydroxide (usually KOH) are necessary to stabilize the colloidal metal particles. Actually, OH^- ions coming from KOH are adsorbed on the surface of metal particles to prevent their aggregation via electrostatic repulsion between the negatively charged metal particles. This method was improved by passing an alternating current by T. Svedberg who succeeded in obtaining organosols, hydrosols of metals and nonmetals.

- (iv) **Ultrasonic dispersion method.** The sound waves of high frequency are usually called ultra-sonic waves. Ultrasonic waves are passed through the solution containing bulk material and some suitable stabilizing agent. They break down bulk material into particles of colloidal dimension. The colloidal particles are then stabilized by stabilizing agent already present in solution.

Metal Electrodes

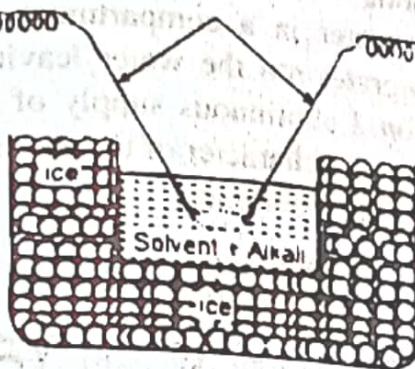


Fig. 21.4 Setup of Bredig's arc method used for preparation of metal particles.

PURIFICATION OF COLLOIDS

A sol prepared by any one of the above methods may often contain other materials besides the colloidal particles. It is often desirable to remove these impurities, particularly when they are electrolytes as they reduce the stability of the sol. The most commonly employed techniques are

(i) Dialysis and (ii) Ultrafiltration.

Dialysis

This method makes use of the fact that there is a significant difference in size between colloidal particles and the dissolved molecules or ions. The sol is filled in a porous membrane tubing and is suspended in a vessel containing distilled water. Solloid gets passed through the pores of membrane due to concentration gradient and colloidal particles are retained within porous tubing due to large particle size. This process of removing crystalloids or other impurities from a sol by diffusion through a semipermeable membrane is known as *dialysis*. The process of purification of sol via dialysis is shown in Fig. 21.5.

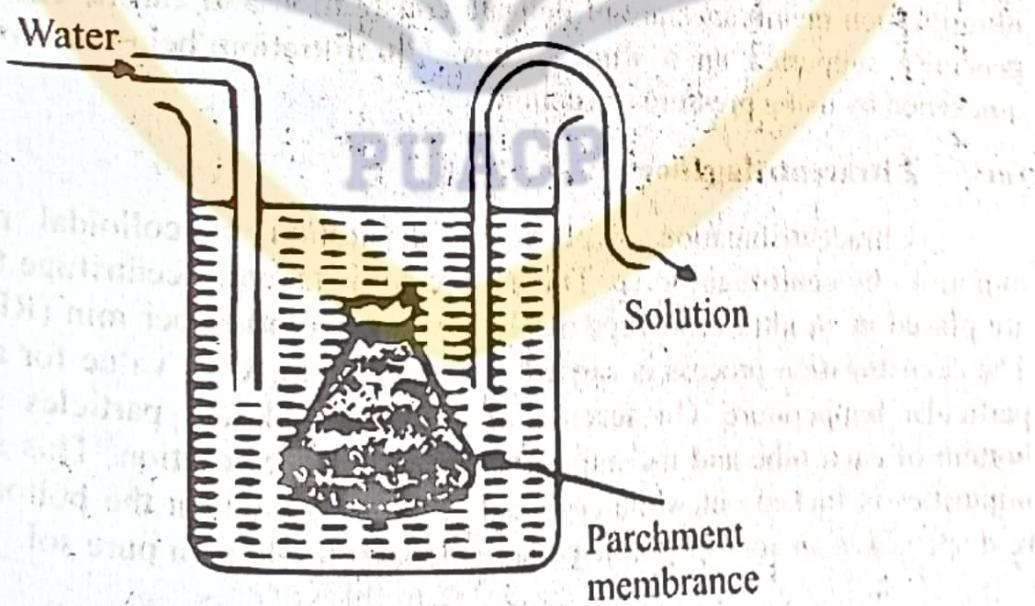


Fig. 21.5 Purification of sol via dialysis

The water in the tank is changed periodically. The process of dialysis can be quickened by applying an electric field. This process is called *electro-dialysis* and is shown in Fig.

21.6. The colloidal solution along with unwanted electrolyte is placed between two dialyzing membranes and pure water in a compartment on each side. When a high potential is applied, the ions migrate into the water leaving behind the pure colloidal solutions. For effective separation a continuous supply of water should be maintained. The process of dialysis depends on the character of the aggregates involved, the nature of the fluid and semi-permeability of the membrane.

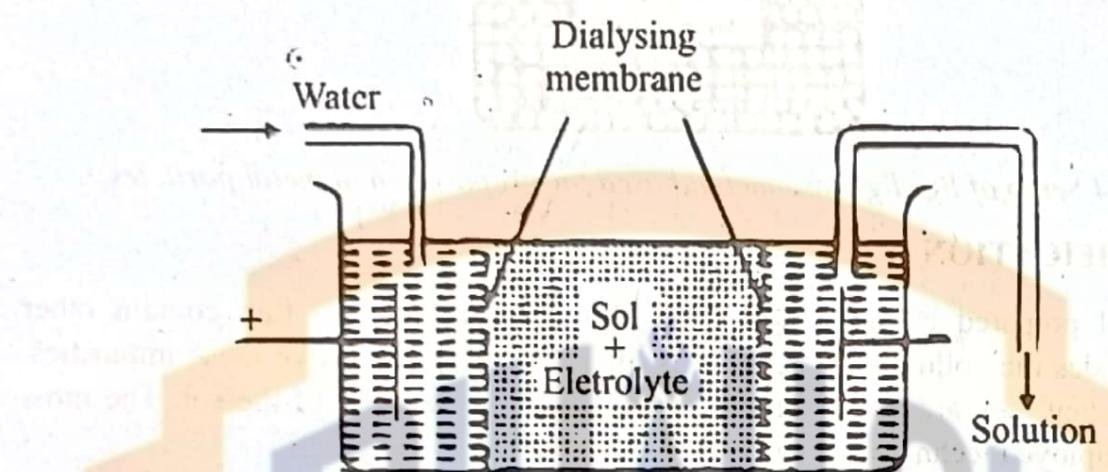


Fig. 21.6 Electro dialysis apparatus for rapid purification of sol.

(ii) Ultrafiltration

This is another important method for purifying sols. The process of ultrafiltration is similar to the filtration of an ordinary precipitate except with the difference that the membrane used here is designed in such a way that it will permit the passage of only electrolytes and medium, and not of colloidal particles. Colloidal particles thus can be separated from the medium containing electrolytes. Such membranes are made by impregnating ordinary filter paper with collodion or a regenerated cellulose. Since ultrafiltration membranes are of delicate constitution and can be easily broken, they are generally supported on a wire screens. Ultrafiltration being a slow process can be quickened by using pressure or suction.

(iii) Ultracentrifugation

Ultracentrifugation involves the separation of colloidal particles from the impurities by centrifugal force. The impure sol is taken in centrifuge tubes and the tubes are placed in an ultra-centrifuge machine with revolution per min (RPM) value ≥ 15000 . The centrifugation process is carried out on required RPM value for a specific period at particular temperature. On account of this, the colloidal particles settle down at the bottom of each tube and the impurities remain in the solution. This solution containing impurities is sucked out while colloidal particles present in the bottom of each tube are re-dispersed in an appropriate dispersing medium to obtain a pure sol.

21.5. PROPERTIES OF COLLOIDS

1. Color

Colloidal solutions are invariably colored. The color of the sol depends on the size and shape of the colloidal particles, the absorption power of the dispersed phase and dispersion medium and the wavelength of the light falling on it. For example a gold sol with different particle-size shows different colors.

2. Heterogeneity

Colloidal particles being larger than the molecules or ions, form heterogeneous mixtures consisting of particles of dispersed phase and dispersion medium.

3. Non-Settling

Colloidal solutions are quite stable systems and the suspended particles remain suspended indefinitely. Only some large particles may settle but very slowly.

4. Filterability

Colloidal particles pass through an ordinary filter paper, which cannot, therefore, be used for removing the dispersed phase. Ultrafilters are used for the purpose. These are made up of unglazed porcelain which retain the colloidal particles and allow the molecules of dispersion medium to pass through.

5. Optical Properties of Sol (Tyndall effect)

An important characteristic of colloids is the scattering of light. If a beam of light is passed through a medium which is optically clear that is, it contains no particles of large size than the molecules of true solution; it is difficult to detect the path of light. But when light is passed through a colloidal system, in which the particle size is large, the rays are scattered. This phenomenon of scattering of light by particles was studied by Tyndall and is generally known as the *Tyndall Effect*. An illuminated light beam passing through a colloidal solution is visible while the same beam passing through true solution cannot be seen because solute molecules cannot scatter light as illustrated in Fig. 21.7. The bright cone of scattered light is called Tyndall cone. A true solution does not show the Tyndall effect and is said to be optically void.

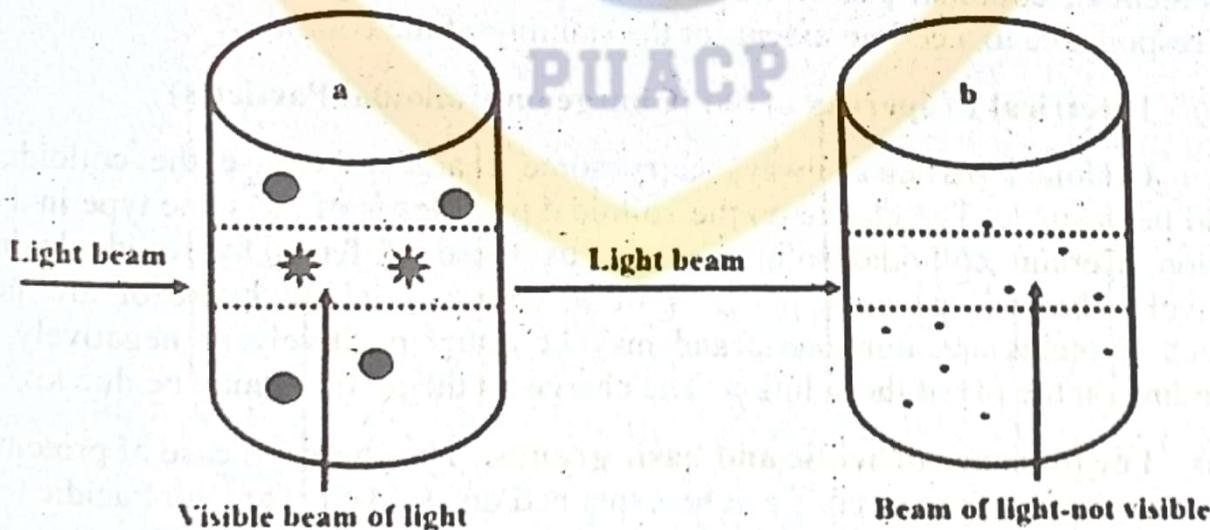


Fig. 21.7. Illustration of Tyndall Effect to differentiate (a) colloidal solution from (b) true solution.

If a beam of light is passed through a colloidal solution in a dark room, solution becomes luminescent when viewed through a microscope at right angle to the path of incident light. Quantitative study of the Tyndall effect and other kinetic properties has been rendered possible with the help of ultra-microscope introduced by Richard Zsigmondy in 1903. The arrangement of the system is shown in Fig. 21.8.

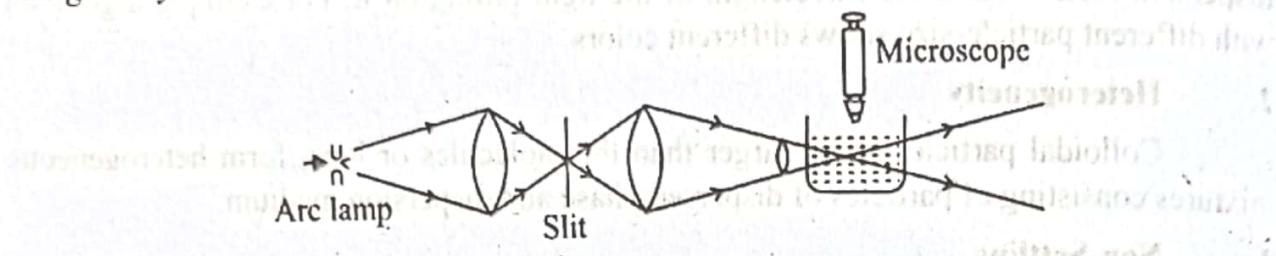


Fig. 21.8. Arrangement of ultra-microscope.

A strong beam of light is passed through a cell containing colloidal solution and is viewed through a microscope. Zsigmondy showed that if the colloidal particles are seen from directions at right angles to the incident light, the colloidal particles appear as bright spot against a dark background.

6. Kinetic Properties of Sol (Brownian movement)

Robert Brown (1927), a botanist, observed that pollen grains when suspended in a liquid and are observed under a microscope exhibit a ceaseless random motion and traveled a zig-zag path. It has been found that colloidal particles exhibit random zig-zag motion when seen under ultramicroscope. This random zig-zag motion of colloidal particles is known as **Brownian movement**. This movement is due to the bombardment of the colloidal particles by the molecules of the dispersion medium. When an unequal number of molecules of the medium strike the colloidal particle from opposite directions, then the colloidal particle begins to start his random motion. The Brownian movement of colloidal particles counteracts the force of gravity acting on them and is thus responsible to a certain extent for the stability of the colloids.

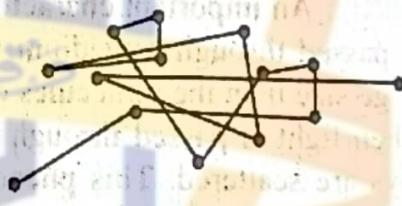


Fig. 21.9. Brownian movement.

7. Electrical Properties of Sol (Charge on Colloidal Particles)

Colloidal particles always carry some charge otherwise the colloidal system would be unstable. The charge on the colloidal particles is of the same type in a colloidal solution. Certain colloidal solutions such as those of ferric hydroxide hydrosol are positively charged, whereas particles of arsenious sulphide hydrosol are negatively charged. Proteins are amphoteric and may be either positively or negatively charged, depending on the pH of the solution. The charge on the particles may be due to:

- (a) **The presence of acidic and basic groups.** The charge in case of proteins, amino acids, polypeptides etc. can be explained due to the presence of acidic ($-COOH$) and basic ($-NH_2$) groups in the molecule. In acidic solution, the molecules will have positive charge due to the protonation of basic groups, while in alkaline

solution the, molecules will be negatively charged due to the ionization of acidic groups as shown below.

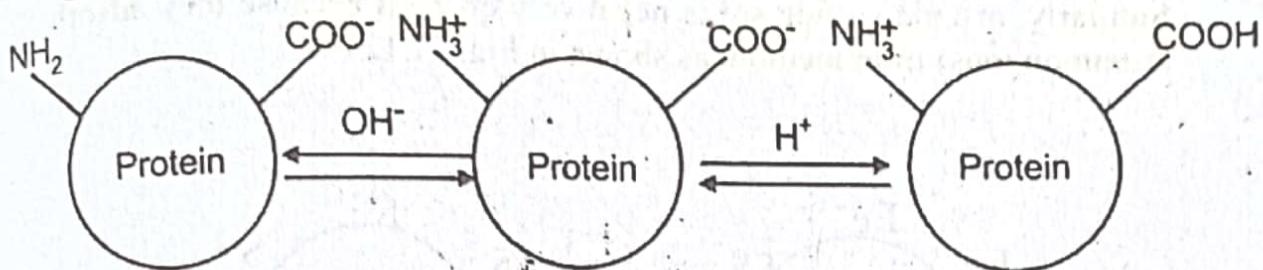


Fig. 21.10. The variation in charge of protein sol with change in pH of the medium.

It is clear that the charge in such cases is a function of pH of the medium. The pH at which the net charge on the molecule is zero is called the *isoelectric point*. The molecules at the isoelectric point exist as *Zwitter ions*. A lyophilic colloid has minimum stability at this pH. The direction of movement of protein sol particles in electrophoresis can be used for determination of sign of charge on protein particles.

- (b) Due to the formation of micelles of ionic surfactants. Colloidal electrolytes such as soaps, $C_{15}H_{31}COO^-Na^+$ (sodium palmitate) dissociate in solution giving positively charged metal ions and negatively charged carboxylate ions with long hydrocarbon chain. The hydrocarbon parts of anions have a marked affinity for one another and they are drawn together in aqueous medium. Thus the negative ions (the palmitate ions) aggregate to form an ionic micelle which is of colloidal size. This accounts for the presence of negative charge on the colloidal soap particles as shown in Fig 21.11. Similarly cationic surfactant form positively charged micelles of colloidal size.

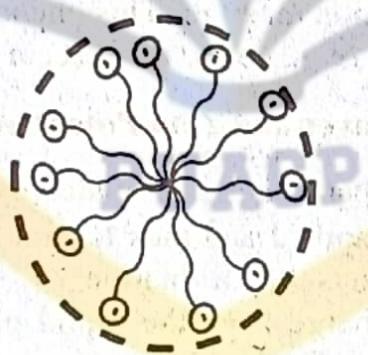
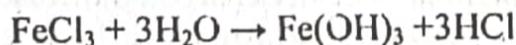


Fig. 21.11 Micelle of anionic surfactant indicating negative charged on particle.

- (c) Due to preferential adsorption of ions. The charge on the colloidal particles in some cases results from adsorption of either positive or negative ions from the medium in which they are prepared. The particles constituting the dispersed phase of a colloidal solution adsorb those ions preferentially which are common with their own lattice ions. For example, ferric hydroxide red sol system is obtained by hydrolysis of $FeCl_3$ as shown below:



Ferric hydroxide red sol is positively charged because Fe(OH)_3 particles adsorb common ions (Fe^{+3} ions) from aqueous medium as shown in Fig. 21.12 (a). Similarly, arsenic sulfide sol is negatively charged because they adsorb S^{2-} ions (common ions) from medium as shown in Fig. 21.12 (b).

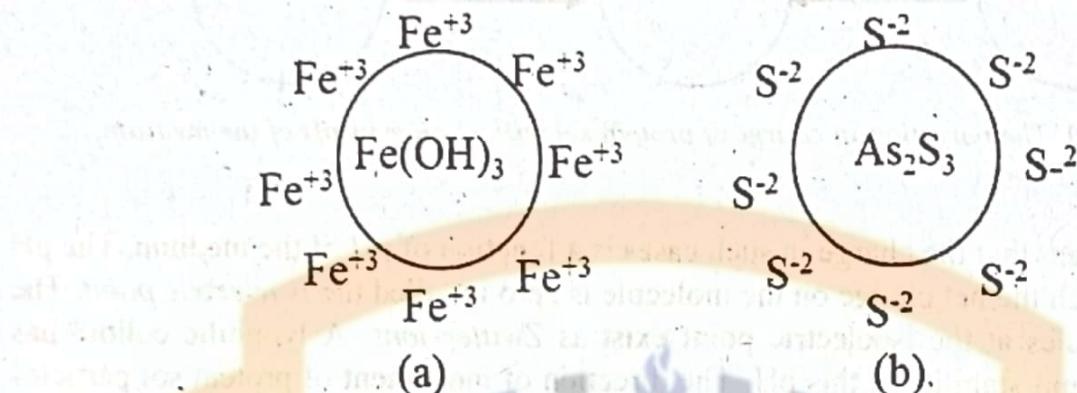


Fig. 21.12 (a) Positively charged Fe(OH)_3 sol and negatively charged As_2S_3 sol resulting from preferential adsorption of common cations and anions respectively

It is not necessary that a particular sol particles adsorb same kind of ions. Adsorption of ions on sol particles depends upon their concentration. The ions in excess are preferably adsorbed on sol particle surface. For example, if silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide (AgI) will adsorb iodide ions (I^-) from the dispersion medium and negatively charged colloidal solution will result. However, if silver iodide is formed by adding potassium iodide to silver nitrate solution, we will get a positively charged suspension due to the preferential adsorption of silver ions (Ag^+) which are present in the dispersion medium. This phenomenon forms the basis of the use of adsorption indicators (e.g., eosin, fluorescein etc.) in volumetric analysis.

7.1 Electrical Double Layer and Zeta Potential

A charged colloidal particle is surrounded by ions of opposite kind. The ions of one type (+ve or -ve) get adsorbed and thus form a fixed charged layer on the colloidal particle. Fig. 21.13 (a) depicts the formation of +ve fixed layer at the solid-liquid interface. Ions of opposite charge from the liquid phase tend to approach this layer in order to neutralize the charge. Due to thermal agitations in the liquid phase, however, these ions cannot remain fixed. That is why, it is called mobile layer. This concept was initially given by a German Chemist, Helmholtz. Therefore, charged pattern around colloidal particle (combination of positive and negative layer) shown in Fig. 21.13 is known as Helmholtz double layer. Stern (a colloid expert) further investigated the structure of electrical double layer. According to his concept, electrical double layer is made of two layers called compact layer and diffused layer. The compact layer consists of positive and negative charges forming a capacitor (charge storage device) while outer layer is diffused layer/mobile layer. The charges in diffused layer are statistically distributed towards bulk medium. The net charge on diffused layer is equal and opposite of that on the fixed layer. The potential difference between the compact layer and the

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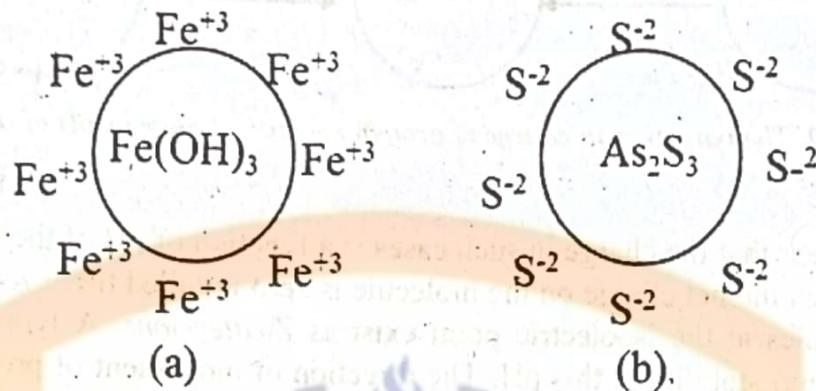


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It is not necessary that a particular sol particles adsorb same kind of ions. Adsorption of ions on sol particles depends upon their concentration. The ions in excess are preferably adsorbed on sol particle surface. For example, if silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide (AgI) will adsorb iodide ions (I^-) from the dispersion medium and negatively charged colloidal solution will result. However, if silver iodide is formed by adding potassium iodide to silver nitrate solution, we will get a positively charged suspension due to the preferential adsorption of silver ions (Ag^+) which are present in the dispersion medium. This phenomenon forms the basis of the use of adsorption indicators (e.g., eosin, fluorescein etc.) in volumetric analysis.

7.1 Electrical Double Layer and Zeta Potential

A charged colloidal particle is surrounded by ions of opposite kind. The ions of one type (+ve or -ve) get adsorbed and thus form a fixed charged layer on the colloidal particle. Fig. 21.13 (a) depicts the formation of +ve fixed layer at the solid-liquid interface. Ions of opposite charge from the liquid phase tend to approach this layer in order to neutralize the charge. Due to thermal agitations in the liquid phase, however, these ions cannot remain fixed. That is why, it is called mobile layer. This concept was initially given by a German Chemist, Helmholtz. Therefore, charged pattern around colloidal particle (combination of positive and negative layer) shown in Fig. 21.13 is known as Helmholtz double layer. Stern (a colloid expert) further investigated the structure of electrical double layer. According to his concept, electrical double layer is made of two layers called compact layer and diffused layer. The compact layer consists of positive and negative charges forming a capacitor (charge storage device) while outer layer is diffused layer/mobile layer. The charges in diffused layer are statistically distributed towards bulk medium. The net charge on diffused layer is equal and opposite of that on the fixed layer. The potential difference between the compact layer and the

bulk liquid across the diffused layer is termed as *electrokinetic potential* or *zeta potential*. The zeta potential measurement can be used to find the stability of charged colloidal particles. The theory of electrical double layer proposed by Stern along with concept of zeta potential is shown in Fig. 21.13 (b).

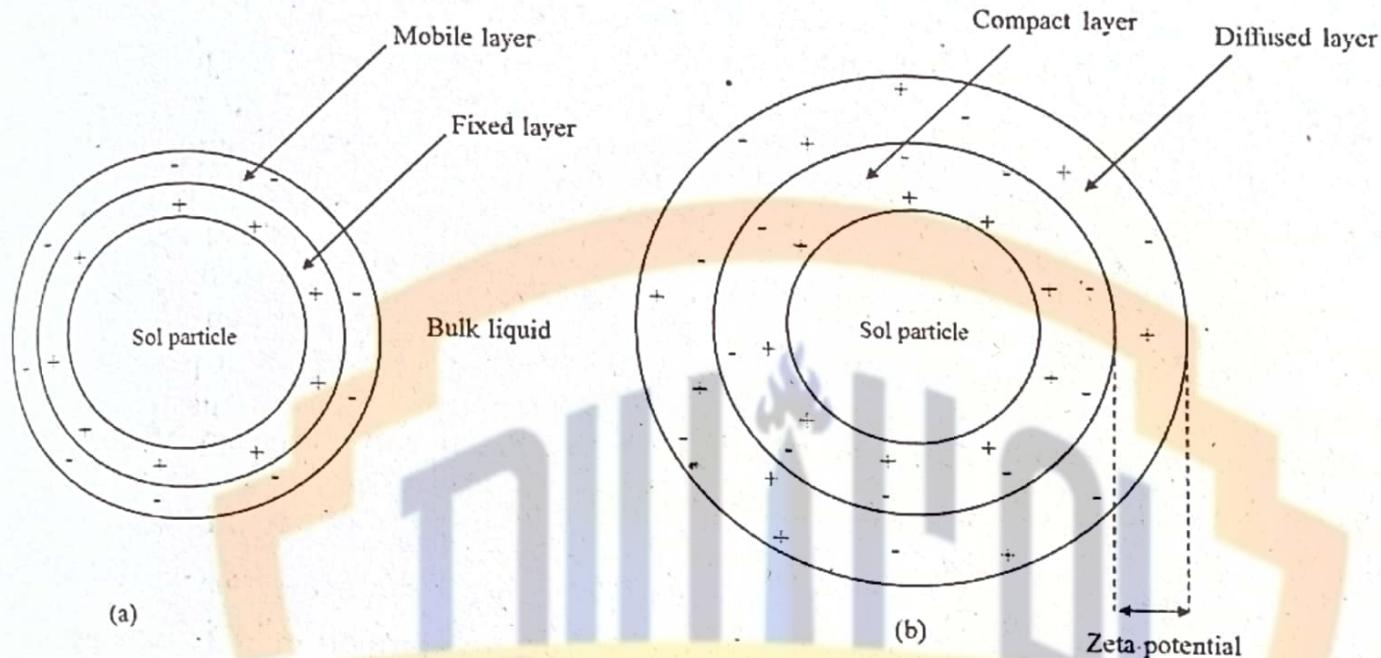


Fig. 21.13. (a) Helmholtz double layer and (b) Stern electrical double layer around a sol particle dispersed in liquid medium.

8. Electrophoresis

Since colloidal particles are charged and when placed in an electric field, these particles migrate either towards the cathode or anode depending upon their charges. This phenomenon of migration of colloidal particles in an electric field is called *electrophoresis* or *cataphoresis*. The speed/velocity (v) of colloidal particles per unit electric field strength (electric field intensity, E) is called electrophoretic mobility. It is denoted by μ and mathematically may be expressed as

$$\mu = \frac{v}{E} \quad (21.1)$$

The SI units of electrophoretic mobility are $m^2 S^{-1} V^{-1}$. The electrophoretic mobility depends upon the viscosity of the medium and charge and size of the colloidal particle. The mathematical relation between electrophoretic mobility and aforementioned parameters for movement of spherical colloidal particles can be established by balancing the electrostatic and drag forces. Charged colloidal particles moving towards electrode under electric field experience two forces: electrostatic force (F_e) and drag force (F_d). The electrostatic force in term of electric field intensity can be written as:

$$F_e = ZeE \quad (21.2)$$

Where Z is number of charges on colloidal particles, e is electronic charge while E is electric field intensity. According to Stokes law, drag force experienced by colloidal particle moving in a fluid is given as:

$$F_d = 6\pi\eta rv \quad (21.3)$$

Where η is the viscosity of the medium and r is the radius of colloidal particles. Under steady state condition, particles moves with constant velocity called terminal velocity and eq. 21.2 and eq. 21.3 can be combined as:

$$ZeE = 6\pi\eta rv \quad (21.4)$$

By rearranging eq. 21.4 and using eq. 21.1, we get

$$Ze = 6\pi\eta r \left(\frac{v}{E} \right)$$

$$Ze = 6\pi\eta r\mu$$

So electrophoretic mobility in term of charge on colloidal particles, size of colloidal particles and viscosity of the medium can be written as

$$\mu = \frac{Ze}{6\pi\eta r} \quad (21.5)$$

Eq. 21.5 depicts that electrophoretic mobility is directly proportional to charge on colloidal particles and is inversely proportional to radius of colloidal particles and viscosity of the medium. Eq. 21.5 is in fact principle of electrophoresis. The apparatus used for electrophoresis is shown in Fig. 21.14. It consists of a U-tube containing a hydrosol (ferric hydroxide, a positively charged sol) covered by a pure dispersion medium (water) in which the electrodes are dipped and connected to a source of suitable E.M.F. On applying a high potential, the boundary between the colloid and water begins to move towards the cathode. The level of the sol falls gradually on the positive electrode side and rise simultaneously on the negative electrode side. Conversely, if the sol particles are negatively charged, the reverse process occurs. The potential gradient is known from the applied E.M.F. and dimensions of the apparatus. Hence the velocity of the particles under a potential gradient of 1 volt cm^{-1} can be calculated. Electrophoresis can also be utilized for quantitative measurement of the rate of migration of sol particles. The type of charge on colloidal particles can be determined by electrophoresis as positively charged colloidal particles moves towards cathode while negatively charged particles moves towards anode under electric field. The electrophoretic mobility is zero when charge on colloidal particle is zero. The pH at which net charge on colloidal particle is zero is called isoelectric point. Electrophoresis (electrophoretic mobility measurements) can be used for determination of isoelectric point of Biomacromolecules. The electrophoretic mobility of colloidal particles depends upon their size/ molar mass. Therefore electrophoresis can be used for separation of mixture of Biomacromolecules with different molar masses. By avoiding convective mixing of separated components, the process of electrophoresis is carried out using suitable supporting medium. Depending upon the supporting medium, electrophoresis can be classified as paper electrophoresis and gel electrophoresis.

Example 21.1

Using eq. 21.1, prove that electrophoretic mobility has units = $\text{m}^2 \text{ S}^{-1} \text{ V}^{-1}$.

Solution

The SI units of velocity are m S^{-1} while E is the force per unit charge. So it can be expressed as

$$\beta = \frac{F}{q}$$

Multiplying and dividing above equation by displacement (d), we get

$$\beta = \frac{F \cdot d}{q \cdot d}$$

The product $F \cdot d$ is work (W), so

$$\beta = \frac{W}{q \cdot d}$$

The work per unit charge is potential, so

$$\beta = \frac{V}{d}$$

$\therefore E$ is a potential gradient and its units are Vm^{-1} . By inserting units of v (m S^{-1}) and E (Vm^{-1}) in eq. 21.1, units of μ can be obtained that are $\text{m}^2 \text{ S}^{-1} \text{ V}^{-1}$.

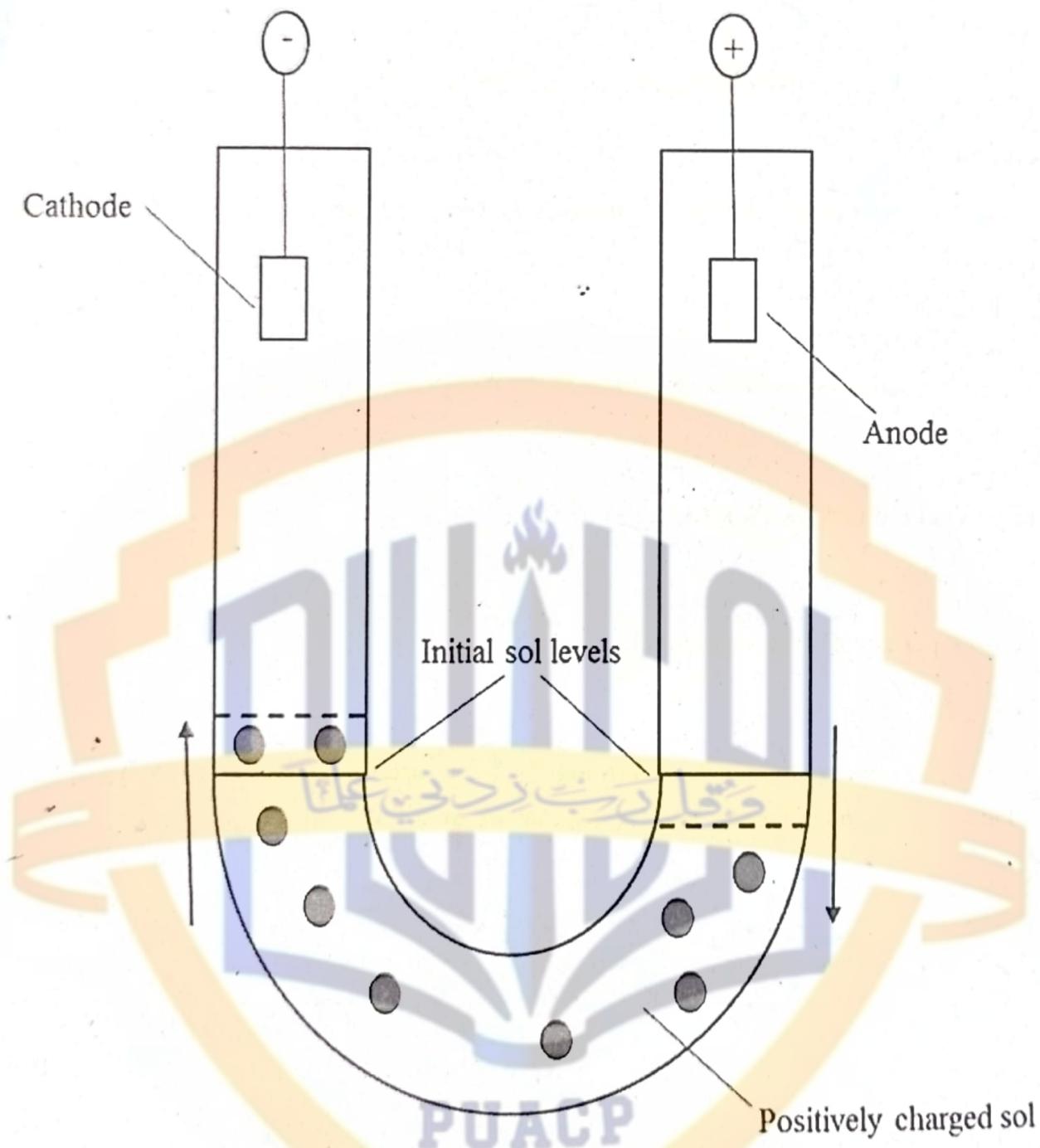


Fig. 21.14 Schematic illustration of electrophoresis of a positively charged sol.

9. Electro-osmosis

The movement of dispersion medium under the influence of electric field when the dispersed particles are prevented from moving is known as *electro-osmosis*.

In electrophoresis, the particles move but the dispersion medium remains stationary. In electro-osmosis, the opposite occurs; the liquid moves through a porous material under the influence of an applied electric field. Apparatus shown in Fig. 21.15 is used for demonstrating the phenomenon of electro-osmosis in the laboratory. Two dotted lines shown in bottom of U-shaped tube representing a porous membrane which divide the apparatus into three compartments. The middle compartment is filled with sol, while

the side compartments are filled with two electrodes and are filled with pure water. When an electric field is applied across the two electrodes, the water is observed to move towards one or the other electrode depending on the charge of the sol. In Fig. 21.15, negatively charged sol has been used as an example. On applying electric field, water level in right arm (cathode side) rises along with fall in water level in left arm (anode side) because of flow of dispersion medium opposite to the direction of flow of colloidal particles. This phenomenon of electro-osmosis is used technically in the removal of water from peat, in dewatering moist clay and in drying dye pastes. Electro-osmosis is used in microfluidic devices.

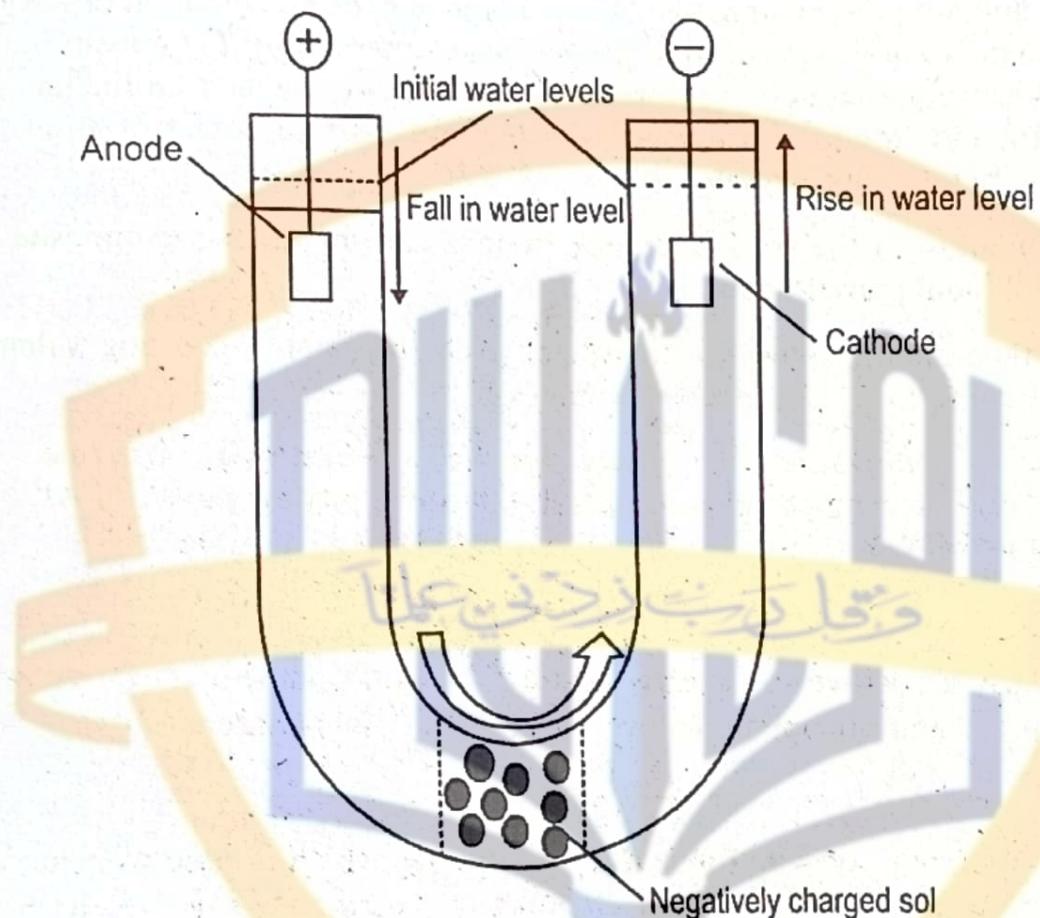


Fig.21.15 Illustration of electro-osmosis using negatively charged aqueous sol.

21.6. COAGULATION OF COLLOIDS

Coagulation is the process of breaking up of a colloidal solution resulting in the precipitation of the particles of the dispersed phase. The stability of a colloidal solution is mainly due to charge on the particles of the sol. Removal of charge in hydrophobic sols would lead to coagulation of sols, while to coagulate hydrophilic sol, both the charge and salvation must be removed. Compared to the *hydrophilic sols*, *hydrophobic sols* are readily precipitated. This may be achieved in following different ways.

(a) By Electrophoresis

In electrophoresis, the particles of the dispersed phase move towards the oppositely charged electrodes. If the process is allowed to continue for a definite period of time, these particles touch the electrode, loss their charge and get coagulated.

(b) By Mutual Precipitation

When two oppositely charged sols (e.g., Fe(OH)_3 and As_2S_3 /sols) are mixed in nearly equal proportions, their charges neutralize each other and the dispersed phases of both the sols coagulate and settle down. This is termed as mutual precipitation.

(c) By the Addition of Electrolytes

Traces of electrolytes are essential for the stability of a sol, while the addition of comparatively large amounts of electrolytes make the sol unstable. The colloidal particles grow in size and are precipitated out. This phenomenon of precipitation or coagulation of the sol particles is known as *flocculation* and was observed by T. Graham in 1861. The amounts of electrolytes required to precipitate a given sol depend on the nature of both the sol and the electrolyte. For a given sol, the precipitation power of an electrolyte is determined by two factors, namely,

- (i) Coagulation of the sol is effective by ions carrying a charge opposite to that of the colloidal particles, and
- (ii) The precipitating power increases considerably with increasing valence of the coagulating ion.

These generalizations are often known as *Hardy-Schulze* rule. Thus for precipitating As_2S_3 sol (negatively charged sol), the precipitating power of Al^{3+} , Mg^{2+} and K^+ ions is in the following order.



Similarly a positive sol, such as Fe(OH)_3 is precipitated by negative ions as Br^- , PO_4^{3-} , SO_4^{2-} etc. Their precipitating power is in the following order:



The minimum concentration of an electrolyte which is able to bring about the flocculation of a sol is called its *flocculation* or *precipitation value*. It is generally expressed in milli moles of electrolyte per dm^3 of sol. Table 8.4 shows the flocculation values for a positively charged sol and a negative charged sol.

Table 21.4. Flocculation Values of Different Electrolytes

Fe(OH) ₃ (Positive) Sol			As ₂ S ₃ (negative) Sol		
Electrolyte	Anion Valence	Flocculation Value	Electrolyte	Cation Valence	Flocculation Value
KCl	1	103	NaCl	1	51
KBr	1	138	KCl	1	50
K_2CrO_4	2	0.325	CaCl_2	2	0.65
$\text{K}_2\text{Fe(CN)}_6$	3	0.096	AlCl_3	3	0.093

It is clear from the table that on increasing the valence (charge) of the precipitating ion the flocculation value decreases. The precipitating effect of a trivalent ion is about 600 to 1000 times more than that of a monovalent ion.

By Persistent Dialysis

(d) Stability of a colloid is due to the presence of traces of electrolytes invariably present. On prolonged dialysis, these traces of electrolytes are removed and the colloid becomes unstable and gets precipitated.

Precipitation of Hydrophilic Sols is most difficult than hydrophobic sols. This is because in such sols the dispersed phase is heavily hydrated. The degree of hydration must be greatly decreased before coagulation. This is usually done by adding a second solvent which is miscible with water (alcohol). The solvent removes water from the sol which changes into lyophobic colloid and is readily precipitated on adding small amount of an electrolyte.

21.7. PROTECTIVE ACTION OF COLLOIDS

When a lyophilic sol is added to a lyophobic sol, the latter becomes more stable and less sensitive towards aggregation to be caused by electrolytes. In other words, a lyophobic sol is prevented from precipitation/coagulation/flocculation. This property of lyophilic sol itself is known as *protection* and the lyophilic sol thus plays a protective role, usually by forming an adsorbed layer completely covering the particles of the lyophobic sol, so that it virtually behaves like a lyophilic sol. The protective capacity of various lyophilic sols is expressed by Zsigmondy in terms of '*Gold Number*'. It is defined as the number of milligrams of the protective colloid that just prevents the coagulation (i.e., change of color from red to blue) of 10 cm^3 of a gold sol on the addition of 1 cm^3 of 10 per cent sodium chloride solution. The change in color initiates the initiation of coagulation. Smaller the gold number, greater is the protective action of a lyophilic colloid. Gelatin, agar, albumin etc. have low gold numbers and thus have high protective powers. Values of gold numbers for a few protective colloids are given in the Table 21.5.

Table 21.5. Gold Number of Some Protective Colloids

Protective Colloid	Gold Number
Gelatin	0.005 - 0.01
Hemoglobin	0.03 - 0.07
Albumin	0.1 - 0.2
Dextrin	6 - 20
Potato starch	25

Protective action is a very important phenomenon. It enables colloids to be kept for a long time when otherwise spontaneous change would take place. In the preparation of ice cream, little gelatin when added as a protective colloid gives the cream a smooth paste. Besides gold number, the iron number in which the sols of Fe_2O_3 are used and the rubin number, which involves sols of congo red, have also been introduced to measure

protective characteristics of the substances. The protective action of various sols is not clearly understood but it is reasonably certain that the particles of two sols are associated or united in some manner. Metal sols (aqueous dispersions of metal nanoparticles) are stabilized by suitable protecting agents. The protecting agents may be natural or synthetic materials. For long term protection of metal nanoparticles from their aggregation, a protecting agent should have ability to cover metal nanoparticles. It should have a good affinity towards dispersion medium. The presence of charges on protecting agent causes electrostatic repulsion between particles and does allow them to approach each other to make aggregates. Natural polymers, synthetic polymers, crosslinked polymeric systems, block copolymers, polyelectrolytes, conventional surfactants and dendrimers are usually used to protect metal particles from their aggregation as shown in Fig. 21.16.

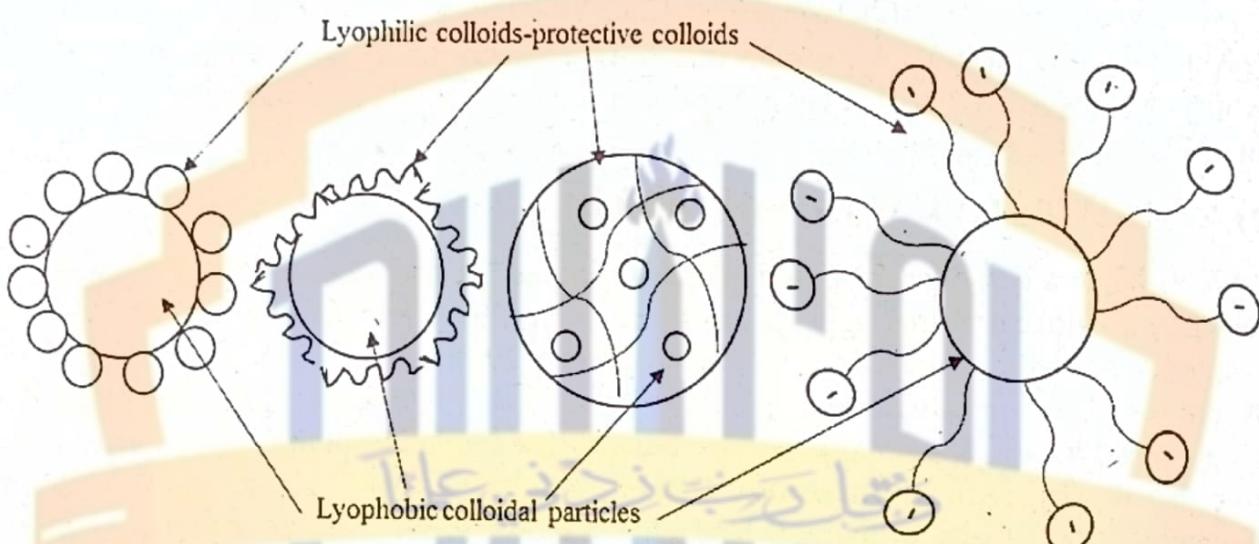


Fig.21.16. Various architectures of protective colloids used for stabilization of lyophobic colloidal particles.

21.8. APPLICATIONS OF COLLOIDS

There are a number of important processes in which colloids play an important role.

- (a) Leather tanning is a process which utilizes colloidal properties. Raw hides contain giant molecules arranged in long tangled fibers. Tanning materials which include tannin and compounds of chromium and aluminum are in colloidal state and the positively charged protein fibers adsorb negative charges from these metallic ingredients. Tanning imparts hardness to leather and prevents it from putrefaction.
- (b) A very useful application is in Cottrell precipitation, as purification process for industrial smoke. The air near the factories and industrial plants is frequently contaminated with smoke and gases which result from the manufacturing processes. The smoke is laden with colloidal particles, such as cement dust, arsenic compounds and metallic powder which are irritating and even poisonous. The Cottrell precipitator (Fig. 21.17) removes colloidal particles from the flue gases by means of electrical precipitation. In the Cottrell precipitator, flue gases

are passed over wires maintained at high voltage where suspended particles acquire an electric charge. A collecting plate of opposite charge attracts the charged particles which lose their charge and fall to the bottom. The air pollution is thus reduced to a minimum.

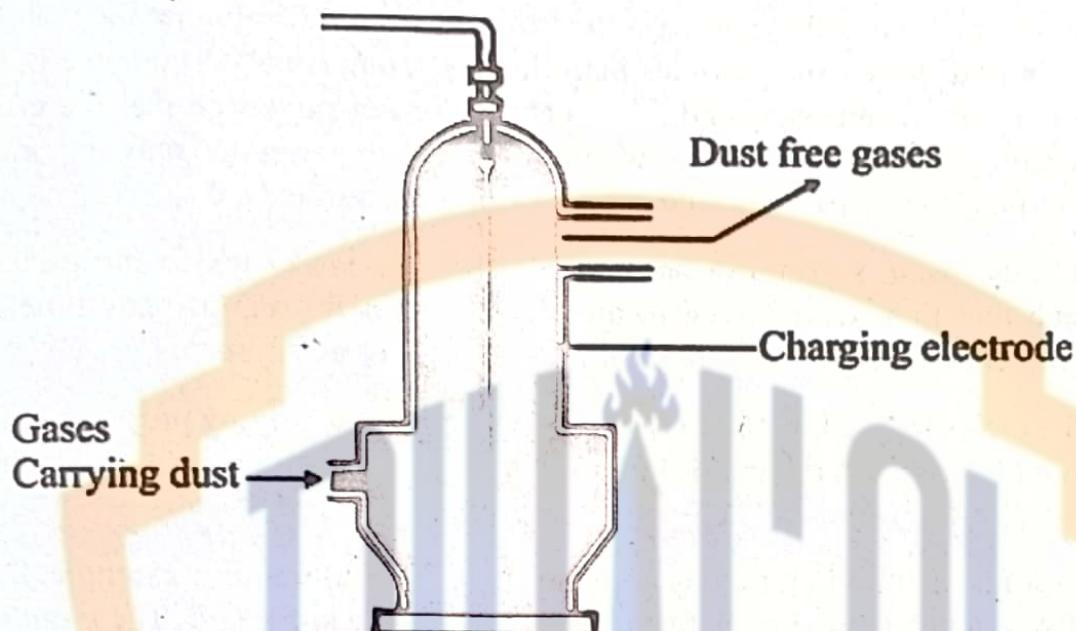
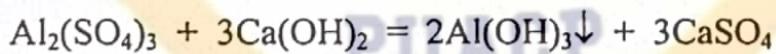


Fig. 21.16, Cottrell precipitator.

- (c) In textile dyeing, colloidal substances called mordants are used to fasten dyes.
- (d) In purification of water, aluminum sulphate and lime are added to form a flocculent precipitate of aluminum hydroxide. This precipitate will adsorb very fine particles of clay or other suspended matter and carry them to the settling tank. The reaction can be symbolized as



Extensive deposits of silt or clay formed at the mouth of rivers by colloidal action are called *deltas*.

- (e) Smoke screens consist of titanium dioxide particles dispersed in air and are used in warfare for the purpose of concealment.
- (f) "Fire-foam" is a carbon dioxide froth made by mixing solution of sodium bicarbonate and alum. A protective colloid such as glue, dextrin or saponin is added to stabilize the foam and keep the bubbles in finely dispersed form.
- (g) The disposal of sewage water by passing it into a tank fitted with metallic electrodes at high voltage. The suspended particles which are charged, move towards oppositely charged electrodes get discharged and are precipitated out.

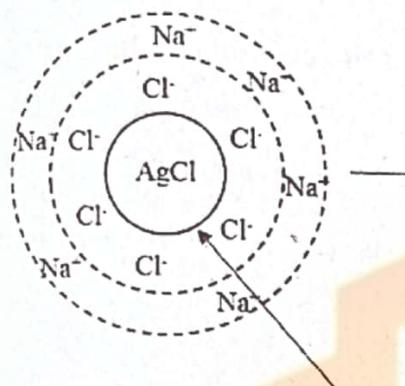
- (h) In drilling deep well or tube-wells, a colloidal solution is used to prevent the rock chips cut by the drill from forming a compact mass.
- (i) Colloids are of great importance in living systems. For example, protoplasm itself is a gel. It contains considerable amount of protein, glycogen and phospholipids; all are lyophilic materials. Molecules of these substances exhibit imbibition, that is they attract water strongly and so firmly that the water is said to be bound. When the particles in colloids rearrange and force some of the bound water out, syneresis is said to occur. It has been suggested that the efficiency of certain substances used in pharmaceutical preparations may be increased if colloidal forms are used, since these have large surface areas.
- Blood plasma substitutes are colloidal dispersions in which the particle size is such that they are retained in the blood vessels for an adequate time. Colloidal gold, calcium and silver are used in medicines or as ointments.
- (j) The cleansing action of detergents is due to its emulsifying properties. They form an emulsion with oil and dirt particles in water, which is carried away by moving water.
- (k) Colloids also find numerous applications in agriculture. For example, the fertility of soil depends on the relative amount of colloids in the soil. The humus and clay are the important ingredients of soil. If the ratio of these components is greater in the soil, then it will hold water and plant nutrients in a better way.
- (l) Delta is a landform created at the mouth of river by the deposition of sediments carried by river water. Formation of delta can be explained on the basis of coagulation of soil particles (colloidal particles) caused by metal ions present in sea water. When river water containing negatively charged colloidal particles (sand/clay particles) enters to sea water containing positively charged metal ions then coagulation of colloidal particles occurs due to removal of charge from colloidal particles which result in formation of deltas.
- (m) The process of titration of NaCl and AgNO_3 using adsorption indicator (Fluorescein) can be explained on the basis of colloidal chemistry. When AgNO_3 solution taken in burette is added into solution of NaCl and fluorescein (adsorption indicator) taken in a conical flask then following reaction occurs:

AgCl units formed are aggregated to form colloidal particles. Initially Cl^- ions are in excess in comparison to Ag^+ ions. Therefore Cl^- ions are adsorbed on AgCl surface to generate negatively charged colloidal particles (AgCl/Cl^-). Anions of fluorescein (denoted as Fl^-) cannot attach to AgCl/Cl^- sol particles because of electrostatic repulsion. Therefore precipitates remain white. However upon dropwise further addition of AgNO_3 solution into NaCl solution results in decrease in Cl^- ions concentration and increase in Ag^+ ions concentration in the flask. Due to unavailability of Cl^- ions and excess of Ag^+ ions in conical flask, positively charged colloidal particles (AgCl/Ag^+) are formed which attract negatively charged fluorescein anions (Fl^-) as shown in Fig. 21. 17. The formation of $\text{AgCl}/\text{Ag}^+/\text{Fl}^-$ results in color change from white to pink color. The appearance of pink

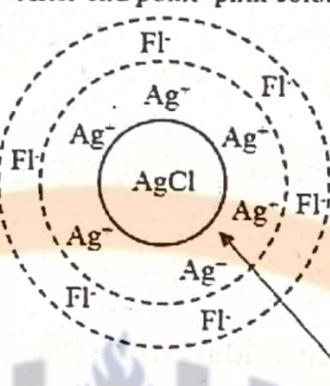


color (end point) is an indication of completion of reaction.

Before end point-greenish yellow color



After end point- pink color



Negatively charged sol surrounded by Na^+ ions

Positively charged sol surrounded by Fl^- ions

Fig. 21.17 Physical chemistry of adsorption indicator (fluorescein) used for titration of NaCl with AgNO_3 .

QUESTIONS

- Q. 1.** What do you understand by colloidal state of matter? Bring out the difference between a colloidal solution and a true solution.
- Q. 2.** What are the various methods available for preparing the colloidal solutions?
- Q. 3.** Distinguish between lyophobic and lyophilic colloids.
- Q. 4.** Explain the use of (a) *dialysis* (b) *electro-dialysis* (c) *ultrafiltration* in the purification of colloidal solutions.
- Q. 5.** Write short notes on the following:
- (i) Brownian movement.
 - (ii) Cataphoresis.
 - (iii) Gold number.
 - (iv) Tyndall effect.
- Q. 6.** What are protective colloids? What is meant by gold number? Discuss how a lyophilic colloid protects a lyophobic colloid.
- Q. 7.** What are sols? How are they prepared? Discuss the methods of purification of sols.
- Q. 8.** Discuss the origin of charge on colloidal particles. How would you determine the charge on a colloid?
- Q. 9.** Explain the following terms:
- (a) Sols
 - (b) Aerosols
 - (c) Protective colloids.
 - (d) Zeta potential

(e) Schulze-Hardy Rule.

Q.10. Discuss some important applications of colloids in daily life.

Q.11. What is isolectric point? How is it determined?

Q.12. Briefly answer the following questions.

- (i) What is the difference between a true solution and a colloidal solution?
- (ii) What are Lyophobic and lyophytic sols?
- (iii) How do colloids differ from crystalloids?
- (iv) Define Tyndall effect.
- (v) What is precipitation value?
- (vi) Explain the difference between suspension and emulsion.
- (vii) How would you prepare colloids?
- (viii) What are protective colloids? Explain their mechanism of action.
- (ix) Write some applications of colloids in daily life.
- (x) Explain the term zeta potential.
- (xi) What is river delta? Explain its formation on the basis of colloidal chemistry.