

COLLOIDAL STATE

8.1. 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 eiods = like). Thomas Graham is usually regarded as the founder of Colloid Science.

A colloidal solution, therefore, consists of solute 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 particle size lies in the range 1 nm to 100 nm. 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 two phases

- (i) a dispersed phase which consists of the colloidal particles, and
- (ii) a dispersion medium 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 8.1.

Table 8.1. 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	Possible	Not possible	Not possible
	(i) Ordinary filtration	Possible	Possible	Not possible
	(ii) Ultrafiltration	Settles under gravity	Settles on centrifugation	Does not settle
3.	Setting	Opaque	Generally clear	Clear
4.	Appearance	Not possible	Diffuses slowly	Diffuses rapidly
5.	Diffusion	Shows	Shows	Not observable
6.	Brownian motion	Shows	Shows	Not observable
7.	Tyndal effect	Heterogeneous	Heterogeneous	Homogeneous
8.	Phase	Positively or negatively charged or neutral particles	Positively or negatively charged	Positive and negative ions or neutral molecules
9.	Charge on particles	Sand or mud suspension	Milk, blood, fog	Urea or salt solution
10.	Examples			

8.2. CLASSIFICATION OF COLLOIDS

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

(a) Based on the State of Aggregation of Two Phases

Based on the state of aggregation of dispersed phase and dispersion medium, colloidal solutions are classified as shown in Table 8.2. Colloidal solutions are generally known as *sols*. We shall mainly deal with colloidal systems in which the dispersed phase is a solid and the dispersion medium a liquid. If the dispersion medium is water, they are called *hydrosols* or *aquasols*.

Table 8.2. Classification of Colloidal Solutions

S.No.	Disper- sion Medium	Dispersed 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_2S_3 in water.
6.	Solid	Gas	Solid foam	Pumice stone, ice cream
7.	"	Liquid	Gels	Jellies, curd.
8.	"	Solid	Solid sols	Ruby, gem.

(b) 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 are obtained with difficulty. On heating or cooling such a system, solids are obtained 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 *hydrphobic* and *hydrophilic*. Other essential differences between the two types of sols are given in Table 8.3.

Table 8.3. 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.
5.	These are generally inorganic materials i.e., metals sulphides 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.	Examples. Gold or As_2S_3 in water.	Examples: Gum, starch, proteins.

8.3. PREPARATION OF COLLOIDAL SOLUTIONS

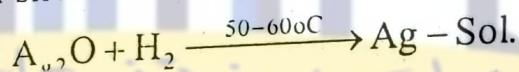
Many substances such as gelatin, starch and other high molar mass polymers when warmed with a suitable dispersion medium go into the solution form, forming a colloidal solution. Such sols are stable, reversible and are called *lyophilic sols*. *Lyophobic sols*, on the other hand, are unstable, irreversible 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.
- (b) Dispersion methods in which the bigger particles are disintegrated into particles of colloidal dimensions which remain in the dispersion medium.

A. Condensation Methods

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 various methods employed are:

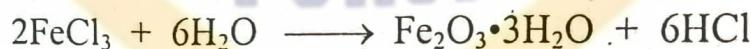
- (i) **Reduction.** This method is generally used for the preparation of metal sols and is of historical interest. This method involves the reduction of soluble salts of metals by reducing agents such as hydrogen, formaldehyde, hydrazine, tannin etc. A silver sol may be prepared by passing a current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



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



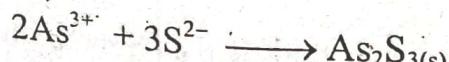
- (iii) **Hydrolysis.** This method is used to obtain sols of oxides or hydroxides of weakly electropositive metals like iron, aluminum etc. A solution of ferric oxide is prepared by adding a small quantity of ferric chloride into a large volume of boiling water.



- (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 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

Various methods used in dispersion 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.
- (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 a dilute solution of ferric chloride.



Sol.

Similarly precipitates of many sulphides can be dispersed by passing H_2S through water in which they are suspended.

Suspension

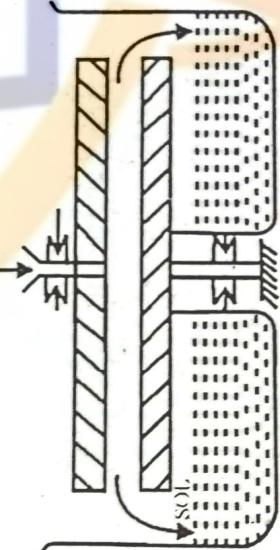
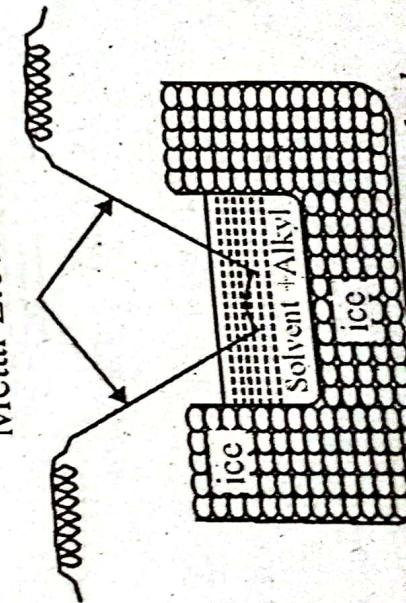


Fig. 8.1 A Colloid mill

- (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. 8.2). The heat of the arc evaporates the metal and the vapors are condensed in water. Traces of alkali metal hydroxide are necessary to stabilize the colloidal solution. This method was improved by passing an alternating current by T. Svedberg who succeeded in obtaining organosols, hydrosols of metals and nonmetals.



8.4. 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.

(i) 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 placed inside a dialyser which consists of a vessel open at both ends. The one end can be covered by a parchment or cellophane membrane. The dialyser is nearly filled with the colloidal solution and suspended in a vessel containing distilled water. Crystalloid gets through and the colloidal particles are retained. This process of removing crystalloids or other impurities from a sol by diffusion through a permeable membrane is known as *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. 8.3. 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.

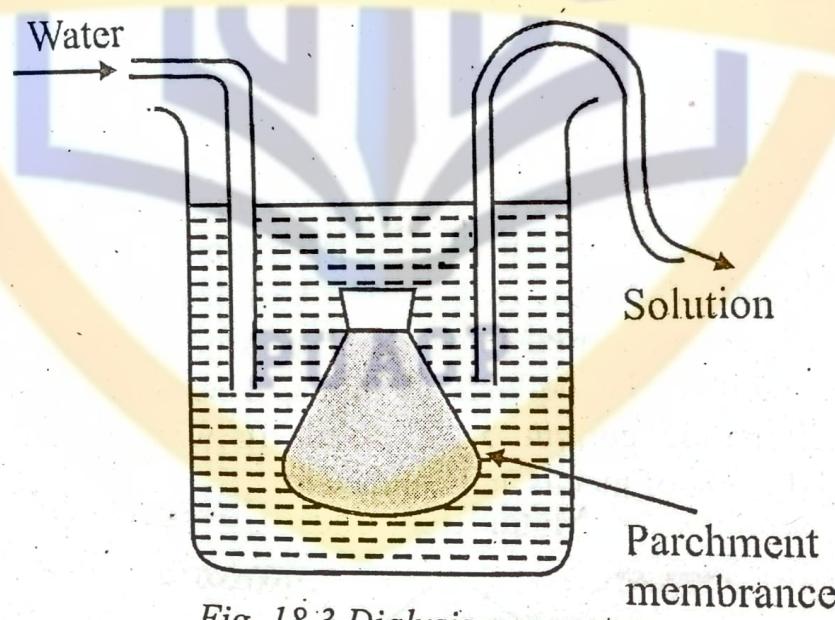


Fig. 18.3 Dialysis apparatus

(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.

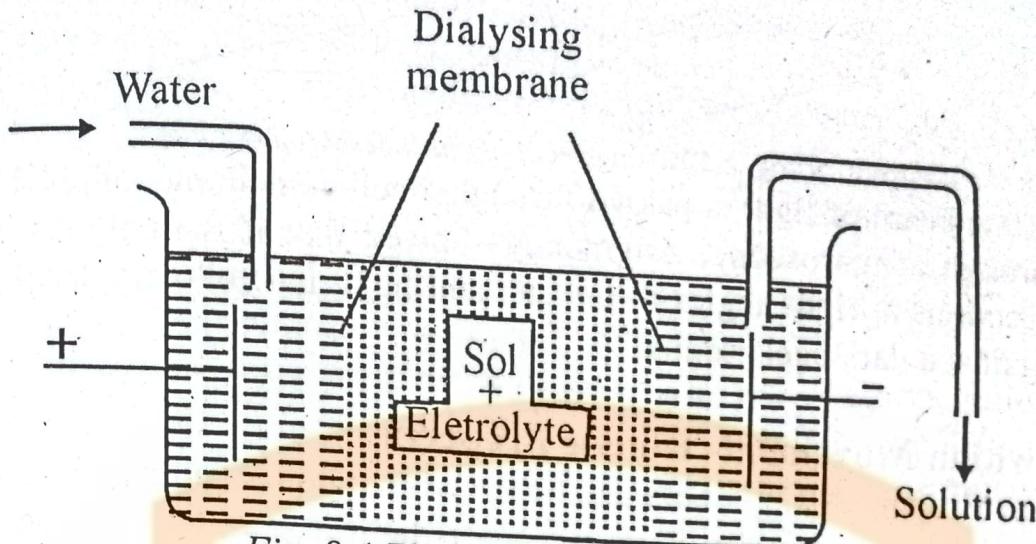


Fig. 8.4 Electro dialysis apparatus.

8.5. 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. Filtrability

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. Tydall Effect - Optical Properties

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*. The bright cone of scattered light is called Tyndall cone. A true solution does not show the Tyndal effect and is said to be optically void.

If a beam of light is passed through a colloidal solution in a dark room, solution becomes luminescent when viewed through a microscopic 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 ultramicroscope introduced by Zsigmondy in 1903. The arrangement of the system is shown in Fig. 8.5.

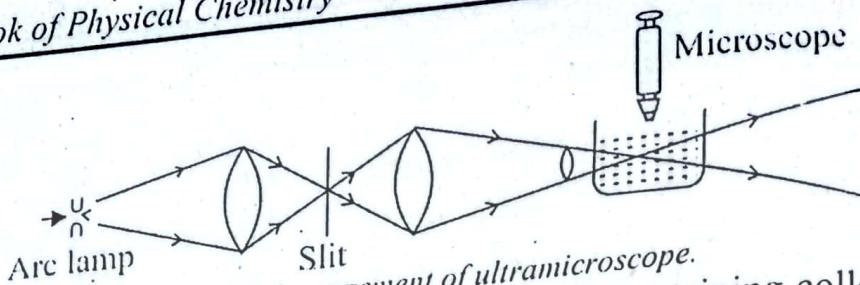


Fig. 8.5. Arrangement of ultramicroscope.

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. Brownian Movement- Kinetic Properties

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.

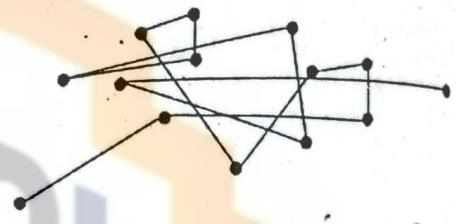
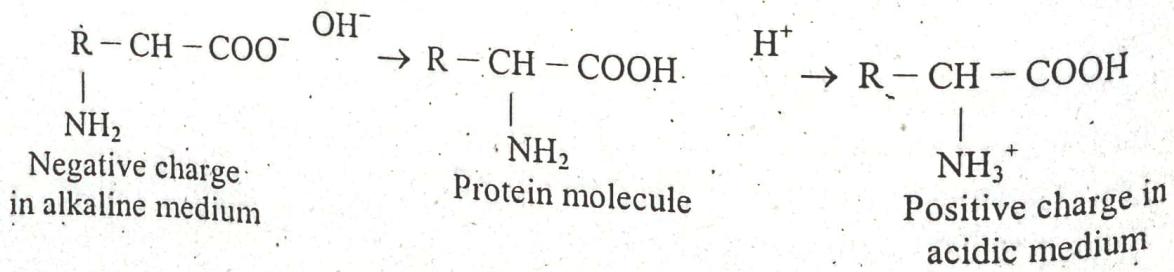


Fig. 8.6. Brownian movement.

7. Charge on Colloidal Particles - Electrical Properties

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.



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.

- (b) **Due to the dissociation of the surface molecules.** Colloidal electrolytes such as soaps, $C_{15}H_{31}COO^- Na^+$ (sodium palmitate) dissociate in solution giving ions. The hydrocarbon parts of the ions have a marked affinity for one another and they are drawn together. 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.
- (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, 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.

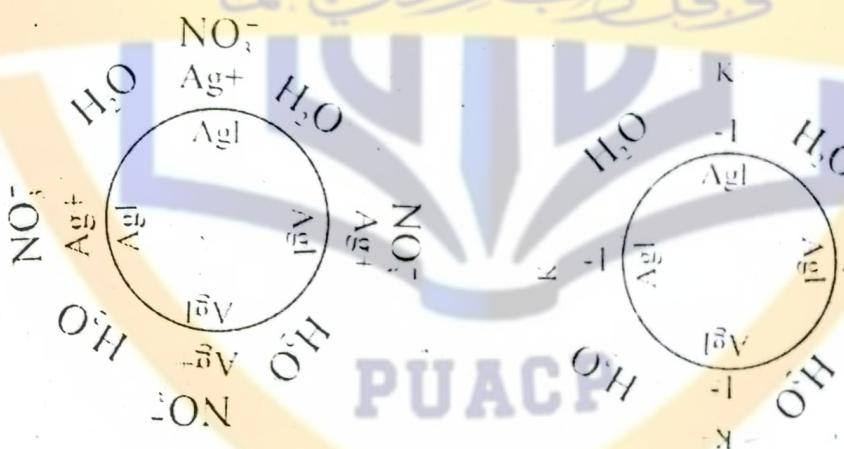


Fig. 8.7. Silver iodide sols stabilized by (a) iodide ions (b) silver ions.

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. Figure 8.8 depicts the formation of (a)-ve and (b) +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 to form a parallel plate. They, therefore, get statistically distributed forming what is called the diffused or mobile layer in such a way that its net charge is equal and opposite to that on the fixed layer. The two taken together is a *double layer system*. Since separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer result in the appearance of a

difference of potential between these layers. This potential difference between the fixed charged layer and the diffused layer having opposite charge is termed the *electrokinetic potential* or *zeta potential*. The electrical double layer theory proposed by Helmholtz and extended by Guey, Stern and others provides plausible explanation for many electrical properties of the colloidal system.

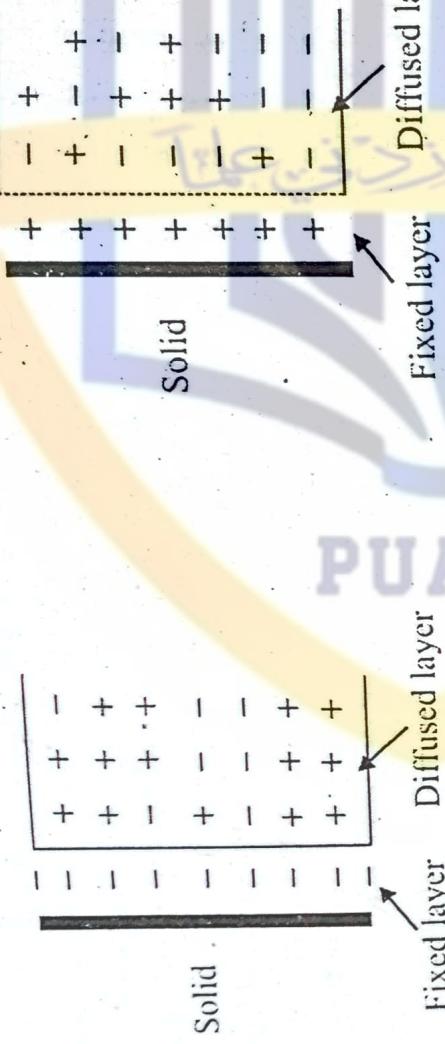


Fig. 8.8. The electrical double layer.

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 of colloidal particles when the applied field strength is 1 volt cm^{-1} is known as electrophoretic mobility. The electrophoretic mobility depends upon the molecular size of the colloidal particle. The difference in the electrophoretic mobilities is used in the separation of mixtures. The apparatus used for electrophoresis is shown in Fig. 8.10. It consists of a U-tube containing a hydrosol covered by a pure dispersion medium, e.g., ferric hydroxide sol and 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 and rise simultaneously on the negative electrode side. Conversely, if the solution particles are negatively charged, the reverse 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 of 1 volt cm^{-1} can be calculated. Electrophoresis can also be utilized for quantitative measurement of the rate of migration of sol particles.

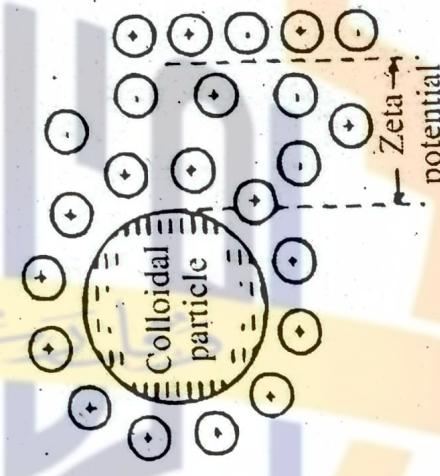


Fig. 8.9. Origin of Zeta potential.

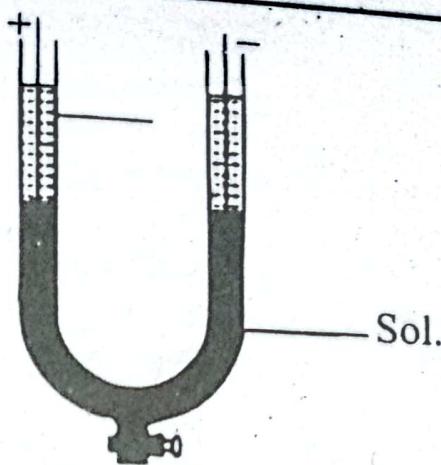


Fig. 8.10 Electrophoresis

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. 8.11 is used for demonstrating the phenomenon of electro-osmosis in the laboratory. In this D and D' are diaphragms 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. This phenomenon of electro-osmosis is used technically in the removal of water from peat, in dewatering moist clay and in drying dye pastes.

8.6. 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

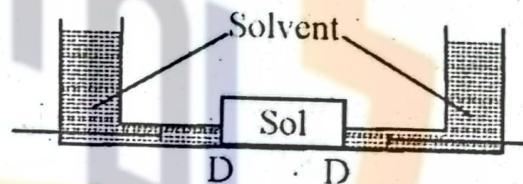


Fig. 8.11. Electro-osmosis.

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,

- Coagulation of the sol is effective by ions carrying a charge opposite to that of the colloidal particles, and
- 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 (-vely charged), the precipitating power of Al^{3+} , Mg^{2+} and K^+ ions is in the following order.



Similarly a positive sol, such as $\text{Fe}(\text{OH})_3$ 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 millimoles 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 8.4. Flocculation Values of Different Electrolytes

$\text{Fe}(\text{OH})_3$ (Positive) Sol			As_2S_3 (negative) Sol		
Electrolyte	Anion Valency	Flocculation Value	Electrolyte	Cation Valency	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
$\text{K}_2\text{Fe}(\text{CN})_6$	3	0.096	AlCl_3	3	0.093

It is clear from the table that on increasing the valency 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.

(d) By Persistent Dialysis

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.

8.7. PROTECTIVE ACTION OF COLLOIDS

When a hydrophilic sol is added to a hydrophobic sol, the latter becomes more stable and less sensitive towards electrolytes. In other words, a hydrophobic sol is prevented from precipitation. This property of hydrophilic sol to prevent the precipitation of hydrophobic sol is

called *protection* and the lyophilic sol itself is known as *protective colloid*. 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 cm³ of a gold sol on the addition of 1 cm³ 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 8.5.

Table 8.5. 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 Fe₂O₃ 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.

8.8. EMULSIONS

An emulsion is a dispersed system in which both the dispersed phase and the dispersion medium are liquids. Milk is a naturally occurring emulsion in which the particles (globules) of liquid fats are dispersed in water. In most emulsions, one of the liquids is water and the other liquid is immiscible with water such as oil or fat. Emulsion droplets are bigger than sol particles and can be seen under an ordinary microscope or sometimes even with a magnifying glass. There are two types of emulsions.

- (i) **Oil-in-Water Emulsion**, in which the dispersed phase is oil while water is the dispersion medium. For example, milk and vanishing cream.
- (ii) **Water-in-Oil Emulsion**, in which water is dispersed in oil. Common examples of this type of emulsions are butter and cold cream.

- (iii) **Ageing.** Colloidal systems usually exhibit slow spontaneous aggregation. This is referred to as ageing. In gels, ageing results in the gradual formation of a denser network of gelling agent.
- (iv) **Rheological Properties.** Gels exhibit the mechanical properties of rigidity, tensile strength, and elasticity that are characteristics of solids.

Uses of Gels

Gelatin gels are employed in the preparation of hard and soft capsules that may be used to mask the unpleasant tastes of solids and liquids. Agar and gelatin gels are used as solid media for the culture of micro-organisms. The diffusion of antibiotics, antiseptics, vitamins and enzymes through solid culture media is used in microbiological assay of these materials.

8.10. SURFACE-ACTIVE AGENTS AND MICELLIZATION

Macromolecules are the substances which composed of giant molecules and dissolve in suitable solvent to give colloidal solution. Such giant molecules are called macromolecules. The dimensions of macromolecule lie in the range of $10 - 1000 \text{ \AA}$. Gelatin, synthetic polymers, cellulose starch etc. are the examples of macromolecules. The solutions of macromolecules behave like a reversible colloid and are lyophilic sols. These have high viscosities and show weak Tyndal effect.

Surface-active agents or surfactants are the substances that lower the interfacial tension between the two liquids or phases. These are also known as colloidal electrolytes because their molecules aggregate (join up) spontaneously in a given solvent to form particles of colloidal dimensions. Soaps, detergents, gelatin etc. are the examples of surfactants.

Soaps are generally sodium and potassium salts of long chain fatty acids. The general formula of soap is $\text{RCOO}^- \text{Na}^+$. This molecule has two parts:

1. The long hydrocarbon part -R is lyophobic, which tries to keep away from solvent (water). This part is called 'tail'.
2. The other part is -COONa. It is called head. This is ionizable and lyophilic which tends to go into solvent (water) resulting into -COO^- and Na^+ ions.

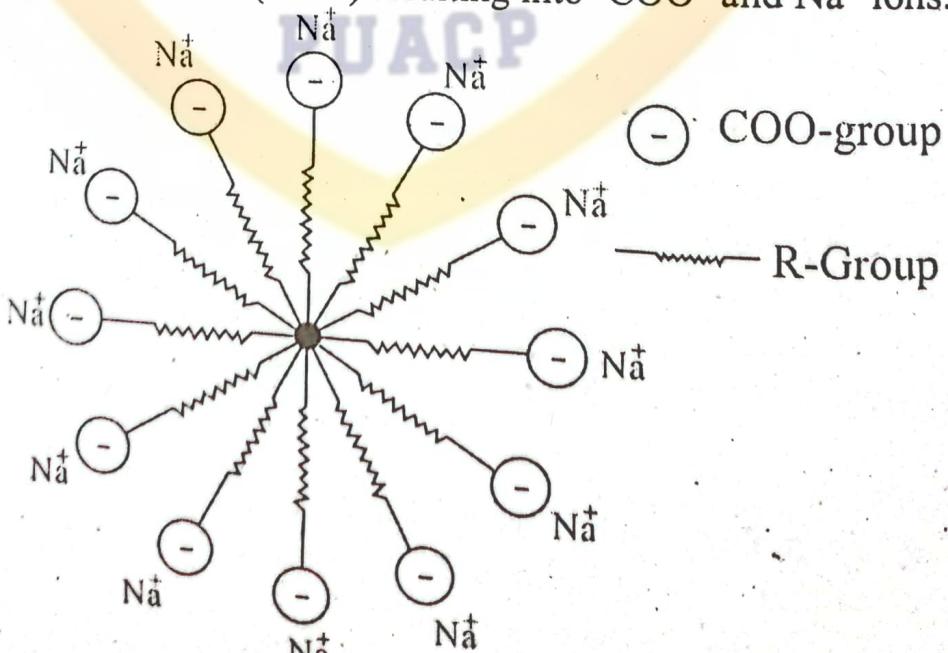


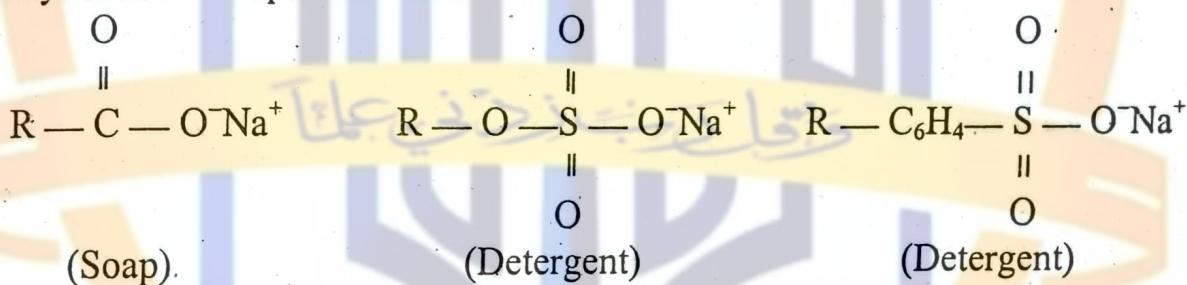
Fig. 8.15. Micelle formation.

Thus RCOO^- group will orient itself in a manner so as to make the COO^- end projecting outward in contact with solvent (water) and R end away from solvent. As the concentration of soap solution increases, $\text{RCOO}^- \text{Na}^+$ molecules come closer, the hydrophobic hydrocarbon parts ($-R$) approach each other (because they do not carry any charge hence do not repel each other) and form a cluster (aggregate) called *micelle* (Fig. 8.15). This micelle is supposed to be spherical, the $-R$ ends are in the interior and $-\text{COO}^-$ groups are projecting outward (i.e., on the surface of sphere) in contact with water. Usually 50 to 100 molecules take part in a micelle. Each micelle is solvated by a large number of solvent molecules.

The micelle has usually the size of colloidal particle, since it is charged, it is the colloidal ion and the parent substances a colloidal electrolyte.

In dilute solution, soap behaves as a simple electrolyte ionizing into positive (Na^+) and negative (RCOO^-) ions. Micellization does not take place at very low concentration. It occurs when a particular concentration is reached at a given temperature. The initial concentration at which micellization begins is called the critical micellization concentration (CMC). Every colloidal electrolyte has a definite CMC at a given temperature. Below this concentration the solute behaves like a strong electrolyte.

Detergents are either sodium salts of alkyl hydrogen sulphates or sodium salts of long chain alkyl benzene sulphonate acids.



Where R = alkyl group having a chain of 12 to 18 carbons.

The function of detergents is like soap but actually they are not soaps. Many colloidal electrolytes function as good detergent and emulsifying agents. The detergent action depends on their ability to retain water repellent dirt or dye particles inside the micelle cluster. Water insoluble dyes are solubilized in soap solutions and subsequently deposited uniformly on fabrics.

8.11 CRITICAL MICELLE CONCENTRATION

Micelle formation occurs due to association of surfactant molecules into bulk phase. "Single surfactant molecule is called unimer" and by the combination of unimers micelle formation occurs. "The number of surfactant molecules present in a micelle is called aggregation number". If the micelle is in spherical form, then its radius is called hydrodynamic radius.

Micelles are formed at a certain concentration of surfactant and "this minimum concentration at which process of micellization starts is called critical micelle concentration (CMC)". Below CMC micellization does not occur. Spherical micelle has two regions, hydrophilic region which is called corona and hydrophobic region which is called core as shown in Fig. 8.16. If the concentration of surfactant is less than the critical micelle concentration then it does not stabilize the emulsion.

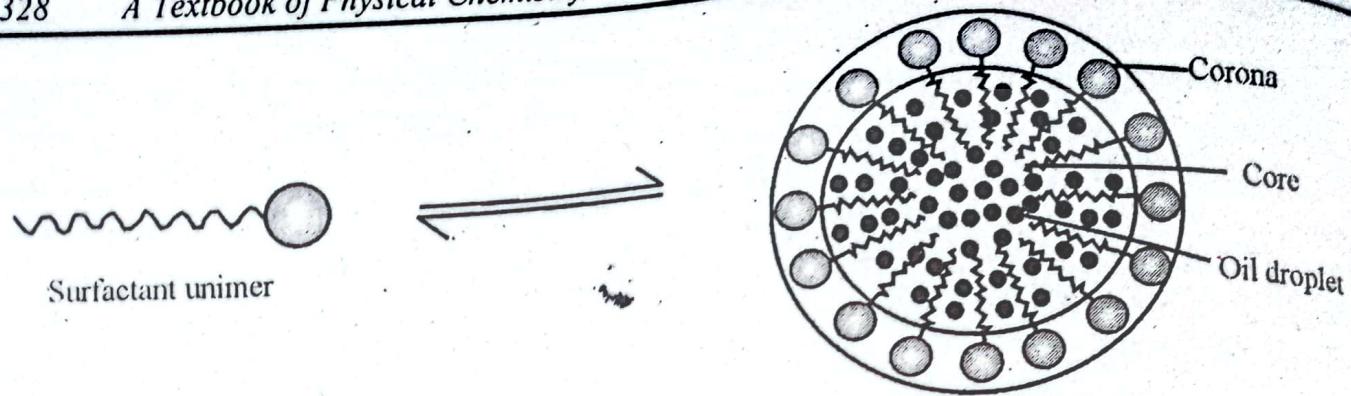


Fig. 8.16. Illustration of micellization and micelle structure

The value of CMC of a surfactant depends upon temperature, hydrophilic-lipophilic balance (HLB) of surfactant and nature of solvent.

Determination of CMC of a Surfactant

Different methods for the determination of CMC are discussed below

(1) Surface Tension Measurement

Solutions of different concentration of surfactant are prepared and the surface tension of each solution is measured and a graph is plotted between surface tension versus natural logarithm of concentration of surfactant as shown in Fig. 8.17. At initial stages surface tension will decrease with the increase in $\ln C$ but after a certain concentration, value of surface tension will become constant. The concentration at which the surface tension of solution becomes constant is called CMC. Because at this concentration micelle formation starts. This method is applicable generally for the determination of CMC of nonionic surfactants.

(2) Conductivity Measurements

Solutions of different surfactant concentrations are prepared and the conductivity of solutions is measured. A graph is plotted between conductivity versus concentration as shown in Fig. 8.18. At initial stage, conductivity and concentration are linear to each other. At certain concentration, conductivity versus conc. plot gives a break. This break will give the value of CMC. Conductivity depends upon the mobility of unimers. After CMC unimers combine and form micelle. Because the mobility of micelle is less than that of unimer so, slope of plot changes at CMC.

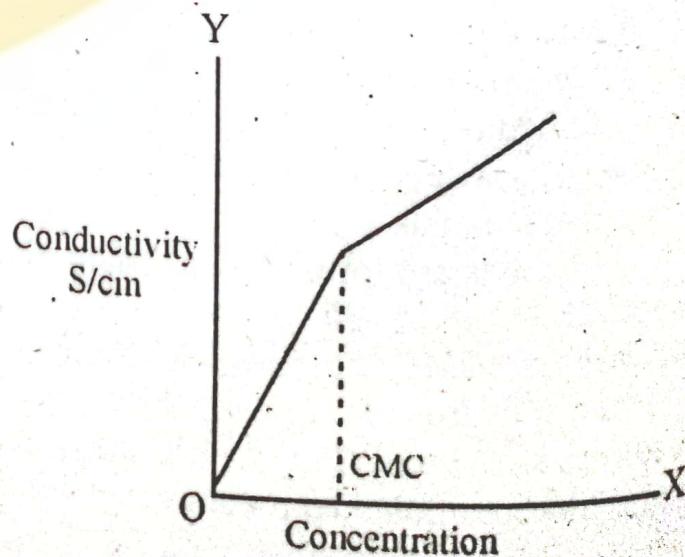
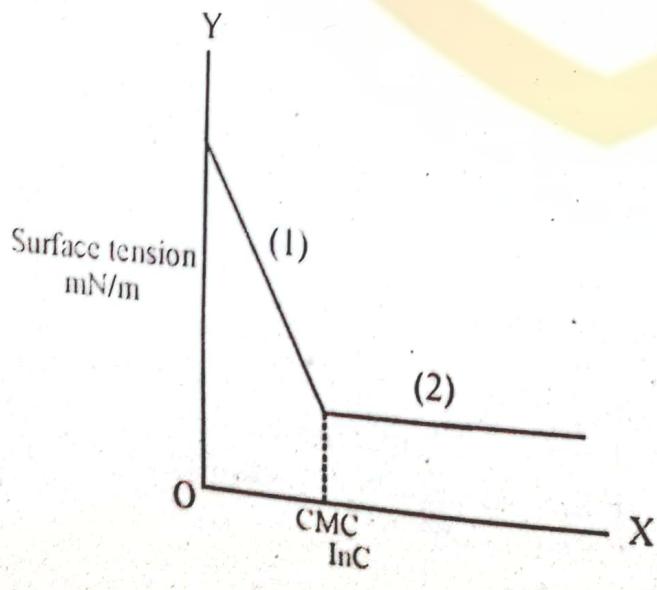


Fig. 8.17 Plot of surface tension versus $\ln C$

Fig. 8.18 Plot of conductivity versus concentration of surfactant

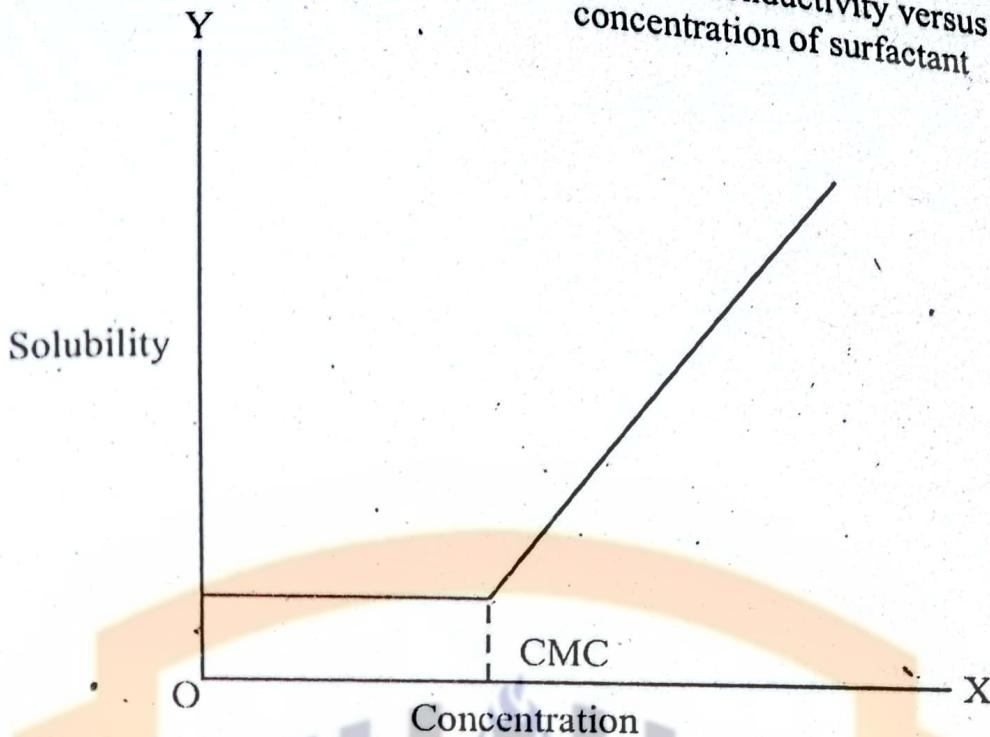


Fig. 8.19 Plot of solubility versus concentration of surfactant

(3) Solubility Measurements

A substance is taken that is insoluble in water. Solutions of different concentrations of surfactant are prepared and the substance that is insoluble in water is added. At lower concentration of surfactant the substance is not soluble because surfactant is present at interface only. But when concentration of surfactant approaches the CMC and surfactant molecules goes in to the bulk then they can solubilize the substance. As a result of which solubility of the substance increases rapidly. Break point of plot of solubility of the substance as function of concentration of surfactant gives the value of CMC of surfactant as shown in Fig. 8.19.

8.12. 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. 8.16) 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.

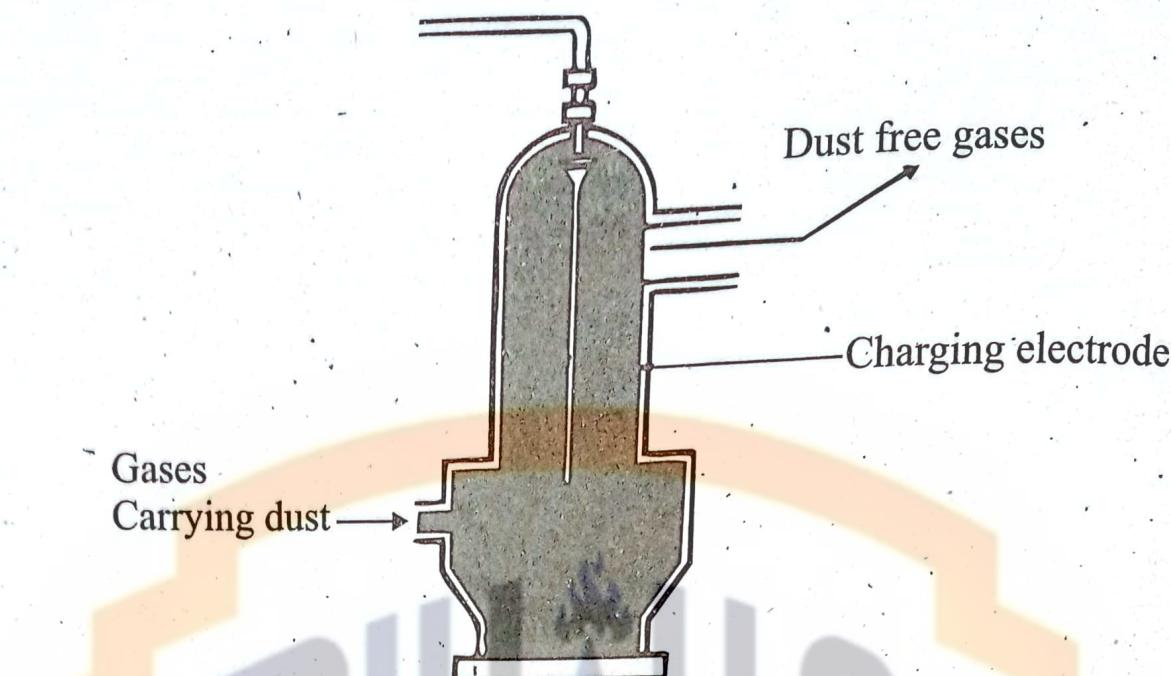
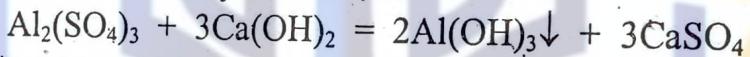


Fig. 8.20. Cottrell precipitator.

- (c) In textile dyeing, colloidal substances called mordants are used to fasten dyes.
- (d) In purification of water, aluminium 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.
- (i) 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.

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) electrodialysis (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 emulsions? How are they prepared? Discuss the role of emulsifier.
- 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) Gels,
 - (c) Surface-Active Agents.
 - (e) Schulze-Hardy Rule.
 - (b) Aerosols
 - (d) Thixotropy
- Q. 10. Discuss some important applications of colloids in daily life.
- Q. 11. What is micellization? How critical micelle concentration is 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 lyophilic sols?
 - (iii) How do colloids differ from crystalloids?
 - (iv) Define Tyndall effect.
 - (v) What is precipitation value?
 - (vi) What is the difference between suspension and emulsion.