5

COLLOIDS

(Glue)

5.1 INTRODUCTION

Selmi (1843)

Thomas Graham (1861) divided all substances, when treated with solvents, into two classes on the basis of their ability to diffuse into water across a permeable membrane:

(i) Crystaloids and (ii) Colloids.

(i) **Crystalloids.** The substances like sugars, salts etc., from which aqueous solutions are obtained, which can pass through the animal or vegetable membranes and can be crystallised readily from solutions are called **crystalloids**.

(ii) **Colloids.** The substances like glue , gelatin, starch etc., from which aqueous solutions are obtained , which can not pass through the animal or vegetable membranes are called **Colloids**. Graham thought that the difference in the behaviour of 'crystalliods' and 'colloids' is due to the particle size .

In a true solution, the solute particles are dispersed in the solvent as single molecules or ions. The size of the dispersed particles ranges from 0.1 – 1.0 nm . On the other hand, in a **suspension** , the dispersed particles are aggregates of million of molecules. The size of the dispersed particles is of the order of 1000 nm or more .

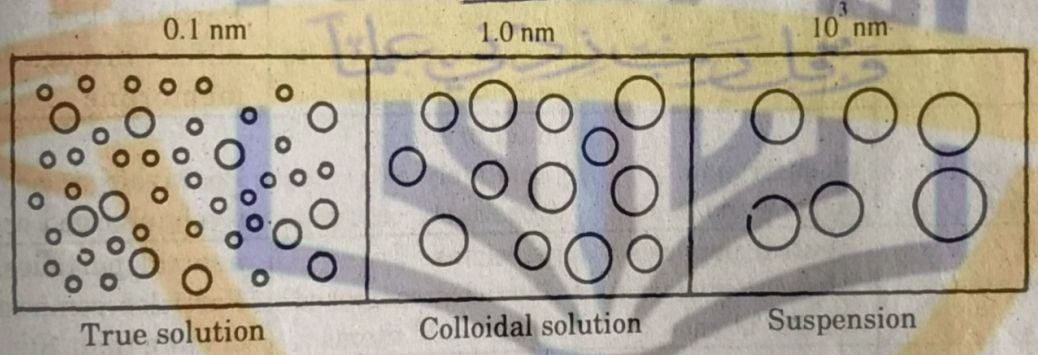

Fig.5.1. Particle size range of true solution, colloidal solution and suspension.

The colloidal solutions or colloidal suspensions *are intermediate between true solutions and coarse suspensions* (big Particles) . In other words, *the size of the dispersed particles in a colloidal dispersion is bigger than that of the solute particles in a true solution and smaller than that of a suspension.*

The colloidal solutions are frequency referred as **sols**. Unlike true solutions , colloidal solutions are heterogeneous system , consisting of two phases, a **dispersed phase** (or the inner phase) which consisted of the colloidal particles, and the other is the **dispersion medium** (or the outer phase) , in which the colloidal particles are dispersed,

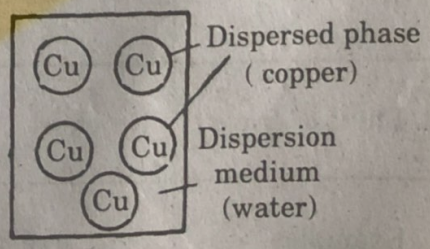

Fig. 5.2. Colloidal system of Cu in H_2O

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for example , a colloidal solution of Cu in water, consists of a dispersed phase (Cu) and the dispersion medium (water) .

The material with particle size in the colloidal range is said to be in the **colloidal state**. In a broader sense, we can say :

Colloids are dispersions of small particles of one material in another. 'Small' means around or less than 500nm in diameter. They are aggregate of numerous atoms or molecules which are too small to be seen with ordinary optical microscope. They pass through most filter papers but can be detected by light scattering, sedimentation and osmosis. Some distinctive properties of colloids are given and compared with true solutions and coarse suspensions in table 5.1.

Table 5.1 : Some properties of dispersed systems

Properties	*True solution*	*Colloidal dispersion*	*Coarse suspension*
1. Size of particles	0.1 – 1.0 nm	10 – 10^3 nm	≥ 10^3 nm
2. Phase	one-phase system	Two-phase system	Two-phase system
3. Shape	–	Linear, coiled, rod-shaped, ellipse or flat plates.	Irregular
4. Visibility	Molecules or ions invisible in electron microscope.	Particles visible in electron microscope, but invisible in ordinary microscope	Particles visible to the naked eye.
5. Diffusion	Diffuse rapidly through membrane.	Diffuse slowly or have no tendency to diffuse through membrane	Particles do not diffuse through membrane
6. Charge on particles	Positive and negative ions or neutral particles.	Positively or begatively charged particles.	Positively or negatively charged or neutral particles.
7. Aggregates	Molecules contain 2 – 10^3 atoms.	Particles composed of 10^3 – 10^9 atoms.	Particles composed of more than 10^{10} atoms.
8. Dispersion of light	Do not scatter light.	Scattering of light.	Scatter and reflect light.
9. Filtrability	Pass through ultrafilters.	Particles can pass through an ordinary filter paper, but are retained by ultra-filters.	Particles cannot pass through an ordinary filter paper.
10. Effect of gravity	No effect.	Do not settle down under the influence of gravity.	Settle down under the influence of gravity.
11. Examples	Salt, urea or sugar solutions.	Milk, rubber, soap, mist, fog, etc.	Mud or sand suspension.

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MACROMOLECULES

Macromolecules are very large molecules having molecular masses that may be several millions of atomic mass units. Despite their size, however, there is an underlying simplicity in the structures of the biological macromolecules. They are usually linear chains of small, similar molecules covalently bonded together.

Solution of macromolecules, which are true solutions of molecules so large that they fall into the colloidal range and exhibit many properties of colloidal solutions e.g. ability for dialysis and slow diffusion. Examples are aqueous solutions of proteins, polyvinyl alcohol, cellulose etc., or solutions of rubber and various other high–polymeric materials in organic solvents. However in low concentrations these solutions are homogeneous and true solution.

MICELLES

in water

When molecules or ions that have a hydrophobic and a hydrophilic end are dispersed in water, they associate, or aggregate, to form colloidal-sized particles or micelles. A ***micelle*** is a colloidal-sized particle formed in water by the association of molecules or ions that each have a hydrophobic end and a hydrophilic end. The hydrophobic ends point inward toward one another and the hydrophobic ends are on the outside of the micelle facing the water. *A colloid in which the dispersed phase consists of micelles is called an* **association colloids.** Ordinary soap in water provides an example of an association colloid.

e.g

Thus, colloids may be classified into three general categories depending on the manner in which the large size of the particles arise. These are (i) Colloidal dispersions (ii) Solutions of macromolecules (iii) Association colloids. These three general categories have been described above.

5.2 CLASSIFICATION OF COLLOIDS

A colloidal system is made up of two phases – a dispersed phase and the dispersion medium. Depending upon the nature of a dispersed phase and the dispersion medium, the colloidal systems may be classified into eight types as given in table 5.2 . A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular mixture.

Table 5.2 : Types of Colloidal Systems

Sr. No.	Dispersed phase	Dispersion medium	Nomen-clature	Examples
1.	Gas	Gas	–	Unknown.
2.	Gas	Liquid	Foam	Whipped cream, soap lather.
3.	Gas	Solid	Solid foam	Pumice stone, foam rubber.
4.	Liquid	Gas	Aerosol	Fog, mist, cloud.
5.	Liquid	Liquid	Emulsion	Oil in water, milk.
6.	Liquid	Solid	Gel or jelly	Jellies, butter, cheese.
7.	Solid	Gas	Smoke	Smokes, dust, iodine vapours in air.
8.	Solid	Liquid	Sol	AgCl, Au, As_2S_3 or S in H_2O.
9.	Solid	Solid	Solid sol	Alloys,ruby glass,mixed crystals,gems

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Of the eight types observed, those of particular interest and importance are sols, emulsions, gels and aerosols.

5.3 SOLS

To distinguish the colloidal solutions from ordinary solutions, they are called by a general name **'sol'**. Sols are colloidal system in which a solid is dispersed in a liquid. If the dispersion medium is water, the sols are called **Hydrosols** or **Equasols**. When the dispersion medium is alcohol or benzene, the sols are referred to as **'Alcosols'** and **'Benzosols'** respectively.

Sols can be subdivided into two classes :

(i) Lyophilic sols (solvent loving) (ii) Lyophobic sols (solvent hating)

(i) **Lyophilic sols** are those colloidal dispersions in which the dispersed phase shows a definite affinity or attraction for the dispersion medium or the solvent, and get solvated. When lyophilic sols are precipitated, they can easily be converted back into sols by the addition of the dispersed medium and are, therefore, termed as " **Reversible Sols**". Lyophilic sols are more stable than the lyophobic sols. The examples of lyophilic sols are dispersion of starch, gum, gelatin and proteins in water.

(ii) **Lyophobic sols** are those dispersions in which there is no or very little interactions between the dispersed phase and the solvent. Lyophobic sols can readily be precipitated from the colloidal solutions and they can not be easily converted back into the colloidal solutions by the addition of the dispersed medium, and are therefore, termed **Irreversible sols**. Lyophobic sols are not very stable. The examples of lyophobic sols are dispersion of gold, iron (III) hydroxide and sulphur in water.

When water is used as the dispersion medium, the colloidal systems are referred to as "**Hydrophilic**" or **Hydrophobic** " in stead of lyophilic or lyophobic.

Table 5.3 : Comparison (i.e. Properties of Lyophilic and Lyophobic sols)

Properties	*Lyophobic sols*	*Lyophilic sols*
1. Visibility in ultra-microscope	The particles can easily be detected in the ultra-microscope.	The particles cannot be readily detected in the ultra-microscope
2. Charge on particles	Particles carry positive or negative charge.	Particles may have little or no charge at all.
3. Salvation	No salvation of particles.	Particles are generally solvated.
4. Tyndall Effect	Exhibit Tyndall effect	Do not exhibit Tyndall effect
5.Migration in electric field	Particles migrate to either anode or cathode.	Particles migrate to either anode or cathode or remain stationary.
6. Precipitation by electro-lytes	Precipitated by low concen-tration of electrolytes.	Precipitated by high concentration of electrolytes

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Colloids

7. Viscosity	Viscosity almost the same as of the dispersion medium itself.	Viscosity higher than dispersion medium.
8. Surface tension	Similar to that of dispersion medium.	Generally lower than that of dispersion medium.

5.4 PREPARATION OF SOLS

L.Q

The lyophilic sols are prepared by simply dispersing the substance in a suitable solvent. For example, starch can be dispersed in water by adding a slurry of starch in the boiling water. Certain stabilizers are added to make these preparations stable. The lyophobic sols are prepared by special methods. These methods fall into two categories :

(a) **Dispersion Methods.** In these methods, the coarse particles are broken down to the colloidal size.

(b) **Condensation or Aggregation Methods.** The methods which involve the union of a larger number of molecules to form bigger particles of colloidal size called *condensation methods.*

(a) Dispersion Methods

1. **Mechanical Dispersion.** In these methods, the substance is finely ground and then it is shaken with a dispersion medium to get a coarse suspension. The suspension particles are broken down to colloidal size by means of a colloidal mill. The colloidal mill or disc mill consists of two metal discs nearly touching each otherand rotating in opposite directions with very high speeds. The suspension passes through the rotating discs and is broken down to particles of colloidal size and are then dispersed in the liquid to give sol. Colloidal graphite (a lubricant) and printing inks are made by this method.

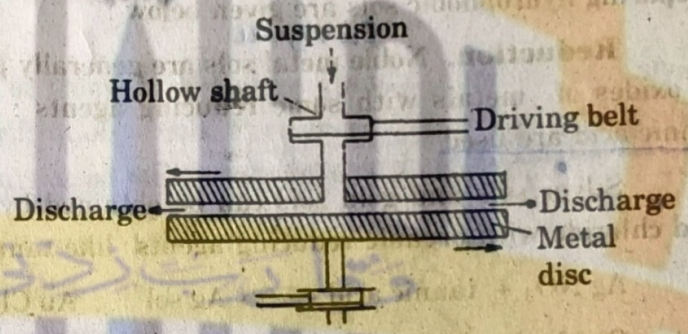

Fig.5.3. A colloidal mill.

2. **Electro – dispersion (Bredig's arc Method).** This method involves both dispersion and condensation processes. In this method, an electric arc is struck beneath conductivity water between the two electrodes of a metal to be dispersed. The intense heat of the arc turns the metal into the vapours which are immediately condensed by the ice cold water to give particles of colloidal size. A little KOH is added to water (dispersion medium) to stabilise the sol. It is used for preparing hydrosols of metals, e.g, Ag , Au, Pb, Cu and Pt .

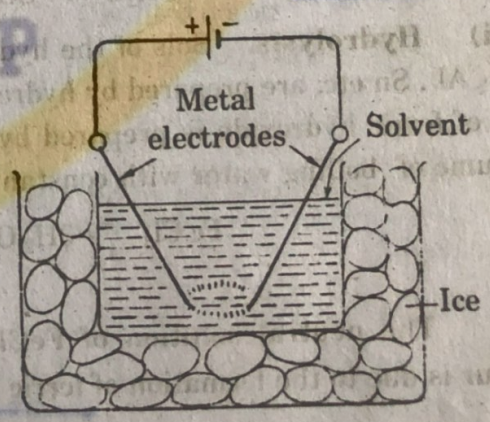

Fig. 5.4. Bredig's arc method.

Non metal sols can be made by suspending coarse particles of the substance in the dispersion medium and striking an arc between iron electrodes .

3. **Peptization.** Peptization is the reverse process of coagulation. *The dispersal of a precipitated material into colloidal solution by action of an electrolyte in the solution is called* ***peptization*** *and the electrolyte is called a* ***peptizting agent***. Some freshly precipitated ionic solids are dispersed into colloidal solution in water by the addition of small amounts of electrolytes, particularly those containing a common ion. The precipitate absorbs the common ion and electrically charged particles then split from the precipitate as colloidal particles. Freshly prepared precipitates of ferric hydroxide on treatment with a small amount of $FeCl_3$ solution (peptizing agent) forms a dark reddish brown sol.

In the preparation of lyophilic sols such as glue, gum, gelatin, starch, etc., dispersion medium water itself acts as a peptizing agent.

(b) Condensation or Aggregation Methods

The essential principle of these methods is that the ions or molecules originally present in a true solution are converted into insoluble colloidal size particles by means of a chemical reaction. The unwanted ions (spectator ions) present in the sol are removed by dialysis as these ions may eventually coagulate sol. The more important methods for preparing hydrophobic sols are given below :

(i) Reduction. Noble metal sols are generally prepared by the reduction of their salts or oxides of metals with some reducing agents : usually organic reducing agents like tannic acid are used.

Silver sols and gold sols can be obtained by treating dilute solution of $AgNO_3$ or gold chloride with organic reducing agents like tannic acid or methanal (HCHO).

$$AgNO_3 + \text{tannic acid} \longrightarrow Ag\ sol \quad ; \quad AuCl_3 + \text{tannic acid} \longrightarrow Au\ sol$$

(ii) Oxidation. A milky sulphur sol is frequently formed during qualitative analysis by the action of hydrogen sulphide with an oxidizing agent such as nitric acid or ferric ions.

$$H_2S + O \xrightarrow{HNO_3} H_2O + S\ (\text{colloidal})$$

A sulphur sol can be prepared by passing H_2S gas into a solution of sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + S\downarrow$$

(iii) Hydrolysis. Sols of the hydroxides of weakly electropositive metals such as Fe, Cr, Al, Sn etc; are prepared by hydrolysis of their salts in aqueous solutions. For example sol of ferric hydroxide is prepared by the addition of a few cm^3 of 33 % $FeCl_3$ to a large volume of boiling water with constant shaking.

$$FeCl_3 + 3H_2O \longrightarrow \underset{(\text{red sol})}{Fe(OH)_3} + 3HCl$$

The neutral solution of $FeCl_3$ becomes dark red on standing. This change in colour is due to the formation of ferric hydroxide sol by partial hydrolysis.

(iv) Double Decomposition. An arsenious sulphide (As_2S_3) sol is prepared by passing a slow stream of H_2S gas through a solution of arsenious oxide (As_2S_3)

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$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

The excess of hydrogen sulphide is removed by passing a stream of hydrogen.

(v) **Exchange of Solvent**. It is a general principle that if a substance *A* is soluble in *B* but is insoluble in *C*. *A* will form a colloidal suspension, when a solution of *A* in *B* is added to an excess of *C*. The two solvents *B* and *C* should be miscible. Thus a sulphur sol can be prepared by adding a saturated solution of sulphur in alcohol to water.

5.5 PURIFICATION OF SOLS

Sols prepared by the methods stated above contain appreciable amounts of electrolytes in addition to the colloidal particles . To obtain the pure sol these electrolytes have to be removed . This purification of sols can be accomplished by three methods:

(a) Dialysis (b) Electrodialysis (c) Ultrafiltration

(a) **Dialysis**. *The process of removing ions (or molecules) form a sol by diffusion through a permeable membrane is called* **Dialysis.** The apparatus used for dialysis is called a **Dialyser.**

Different forms (cylinder, bag or thimble) of dialysers and a numbers of dialysing materials have been used for the purification of sols. Parchment paper, cellophane sheet, cellulose acetate and animal bladder are used for membranes of dialysers.

Ordinary dialyser consists of a cylindrical vessel closed at one end with the membrane . The sol to be dialysed is placed in the cylinder which is then suspended in a large dish through which distilled water is made to circulate continuously . On prolonged contact with the distilled water, the ions in solution pass through the membrane into water , but the colloidal particles, are unable to pass through the membrane , are retained to yield a pure sol. Dialysis is a slow process and in some cases rapid removal of electrolytes become necessary to protect the sol particles from coagulation. This is achieved by *electrodialysis* .

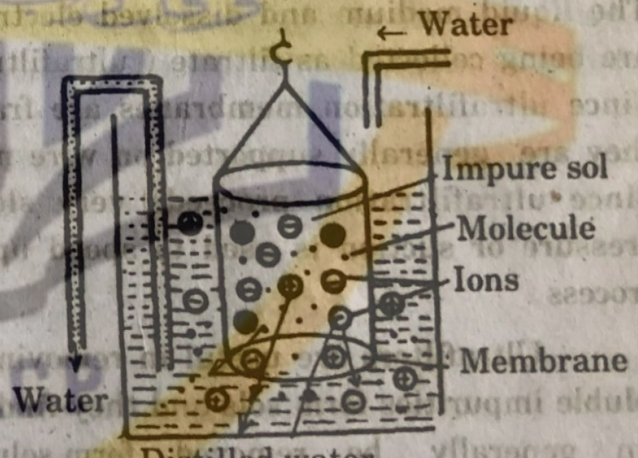

Fig.5.5. Dialyser.

(b) Electrodialysis.

The process of dialysis can be accelerated to facilitate the rapid diffusion of the electrolyte through the membrane under the influence of electric field and the process is called **Electrodialysis**. In this method, two electrodes are placed in the outer vessel containing water. The impure colloidal solution is taken in the shallow cylinder. When an electric field is applied across the membrane, ions in the sol move faster towards the opposite electrodes and are thereby removed from the sol rapidly.

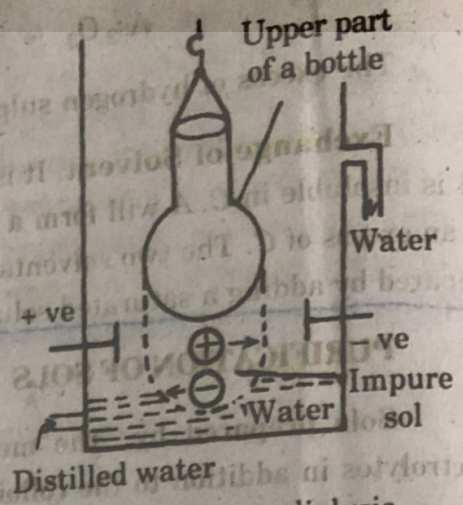

Fig.5.6. Electrodialysis.

(c) Ultrafiltration. *The separation of the sol particles from the liquid medium and electrolytes by filtration through an ultrafilter is called* **Ultrafiltration.**

Sols pass through an ordinary filter paper because the pores are too large to retain colloidal particles. For ultrafiltration, ordinary filter paper impregnated with collodion or cellophane membranes are employed to hold back colloidal particles. The liquid medium and dissolved electrolyte are being collected as filtrate (ultrafiltrate). Since ultrafiltration membranes are fragile, they are generally supported on wire mesh. Since ultrafiltration proceeds very slowly, pressure or suction is used to speed up the process.

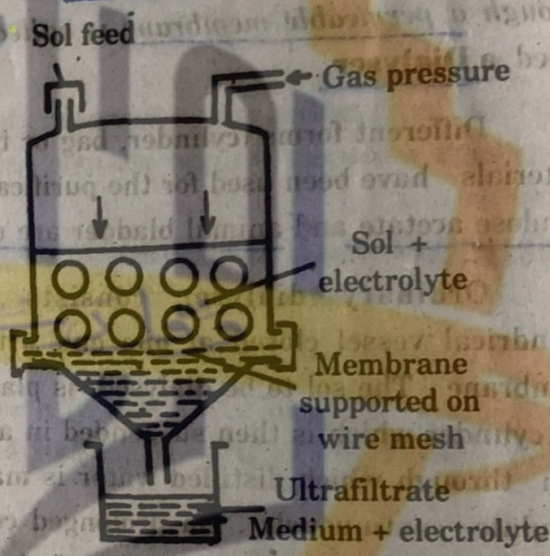

Fig.5.7. Ultrafiltration apparatus.

Ultrafilters are useful in removing soluble impurities form sols and they find extensive application in bacteriology as bacteria can generally be removed form solution by ultrafiltration.

5.6 PROPERTIES OF SOLS

Physical properties

1. **Filtrability**. The colloidal particles can easily pass through an ordinary filter paper, while coarse particles cannot do so. Colloidal particles are generally removed by ultrafilters.

2. **Diffusibility**. The colloidal particles have little power of diffusion, chiefly because of their large size as compared to solute particles in solution.

3. **Heterogeneity**. The colloidal system is heterogeneous in nature. The colloidal particles though invisible under the ordinary microscope but visible under the ultra-

microscope while the molecules or ions of true solutions are invisible in ultramicroscope or even in an electron microscope .

4. **Sedimentation.** Although colloidal solutions are found to be fairly stable over considerable periods of time, they do very slowly settle down under the influence of gravity–even though some of them may take years to do so. The rate of settling (or sedimentation as it is called) can be readily determined because the boundary line between the clear medium and the sol can be easily made out.

5. **Surface Tension and Viscosity.** The surface tension and viscosity of sols depend on whether the sols are lyophobic or lyophilic. For lyophobic sols, density , surface tension and viscosity are not very different form those of the medium. This is so because there is very slight interaction between suspended particles and medium . On the other hand , lyophilic sols show a high degree of solvation of the particles and as a result , the physical properties are modified . Thus the viscosity is much higher for the lyophilic sol than for the medium. Furthermore, the surface tension of the sol is generally lower than that of the pure medium .

6. **Sols exhibit Tyandall Effect.** *The phenomenon of the scattering of light, by the sol particles, is called Tyandall effect* . The illuminated beam or cone formed by the scattering of light by the sol particles is called **Tyndall cone**. When a beam of light enters a dark room through a small hole , the tiny dust particles , floating in air , scatter the light and as a result the beam is rendered visible when viewed at right angle . Similarly , when a strong beam of light passed through a sol, the sol particles absorbs light energy and part of the incident light is scattered in all directions and as a result a heavy beam or cone of illuminated particles appears.Zsigmondy (1903) used the Tyndall phenomenon to set up an apparatus called **Ultramicroscope**.

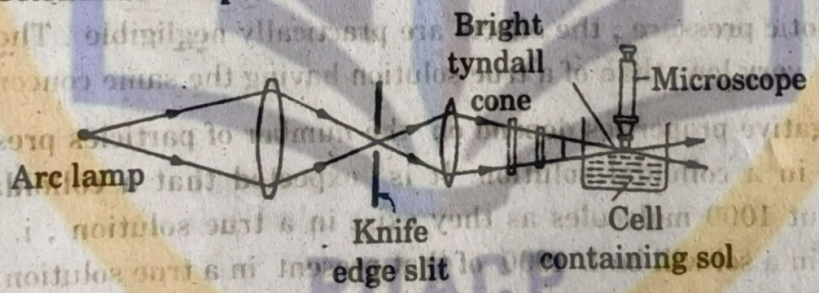

Fig.5.8. Tyndall effect.

True solutions do not show Tyndall effect. Since ions or solute molecules are too small to scatter light, the beam of light passing through a true solution is not visible when viewed from the side. Tyndall effect can be used to distinguish a colloidal solution from a true solution .

The amount of light scattered depends on three factors (i) the fourth power of the reciprocal of the wavelength of the incident light $\left(\frac{1}{\lambda^4}\right)$, (ii) the difference between the refractive index of the particles and that of medium (iii) the size and shape of the particles.

7. **Visibility.** Sol particles can be seen with an electron microscope. These particles have been found to be spheroid , rod - like, disc like or long filaments .

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KINETIC PROPERTIES

8. Brownian Movement. *The continuous rapid zig-zag movement executed by colloidal particles in the dispersion medium is called* ***Brownian Movement*** (after the name of the discoverer, **Sir Robert Brown**. Brownian movement is due to the bombardment of the colloidal particles by molecules of the medium . The movement of the particles is caused by unequal number of molecules of the medium striking it from opposite direction . When more molecules strike the particles on one side than on another side, the direction of movement is changed . Thus zig - zag motion of the colloidal particles can be observed through an ultramicroscope.

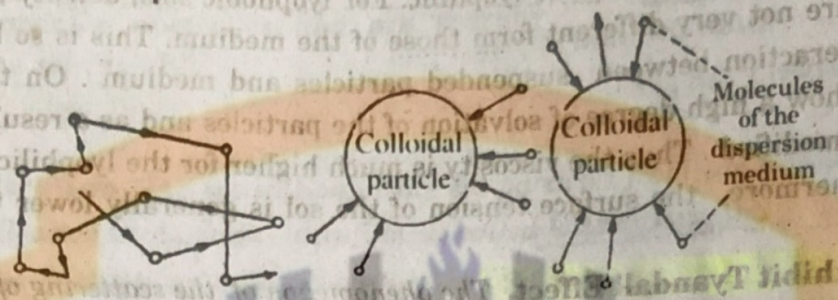

Fig.5.9. Brownian movement.

True solutions and suspensions do not exhibit Brownian movements .

The Brownian movement is , in part , responsible for the stability of colloidal dispersions , as it counteracts the force of gravity acting on the sol particles .

9. Colligative Properties. Sols show colligative properties e. g. , lowering of vapour pressure , depression in freezing point , boiling point elevation and osmotic pressure, but the effects observed are very much smaller than for true solutions . In fact , with the exception of osmotic pressure , the effects are practically negligible . The osmotic pressure of sols is usually very low than of a true solution having the same concentration .

The colligative properties depend on the number of particles present whether in a true solution or in a colloidal solution. It is expected that a colloidal particle is an aggregate of about 1000 molecules as they exist in a true solution , i. e., the number of particles present in a sol will be 1/ 1000 of that present in a true solution , having the same concentration . Hence the colligative effects will be reduced by the same amount . Such a decrease in the number of particles leads to practically no observable difference between colligative properties of the sol and true solution with the exception of osmotic pressure. Since the osmotic pressure, being larger in magnitude than the other collegative properties, can be measured with a reasonable accuracy, and hence is employed for the determination of the relative molecular mass of the dispersed particles.

Electrical Properties of Sols. The sol particles carry an electrical charge . All the suspended particles possess either a positive or negative charge. The charge on the particles is mainly responsible for the stability of the sols. Since the mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity .

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The sol particles acquire charge by preferential adsorption of + ve or – ve ions on the surface of the particles from the dispersion medium . For example , ferric hydroxide sol particles acquire a positive charge because they absorb the common ion Fe^{3+} (from $FeCl_3$ used in the preparation of the sol) from the dispersion medium.

$$Fe(OH)_3 + Fe^{3+} \longrightarrow Fe(OH)_3 / Fe^{3+} \text{ (positive ferric hydroxide sol particles)}$$

Since the sol as a whole is neutral, the charge on the particles is counterbalanced by positively charged ions termed as **counterions** (in this case Cl^-) furnished by the electrolyte in the medium .

Arsenious sulphide sol particles acquire a negative charge since they absorb the common ion S^{2-} (from H_2S) from the medium .

$$As_2S_3 + S^{2-} \longrightarrow As_2S_3 / S^{2-} \quad \text{(a negative sol particle)}$$

Electrical Double Layer. The surface of colloidal particles acquire a positive or negative charge by selective adsorption of a layer of + ve or – ve ions around it . This layer attracts counterions from the medium which forms a second layer of opposite charges. The combination of the two layers of + ve and –ve charges around the sol particles is called **Helmholtz Double layer**. Helmholtz thought that the charges next to the particle surface were fixed, while the compensating charges along with the medium (liquid) were mobile .

Fig .5.10. Helmholtz double layer.

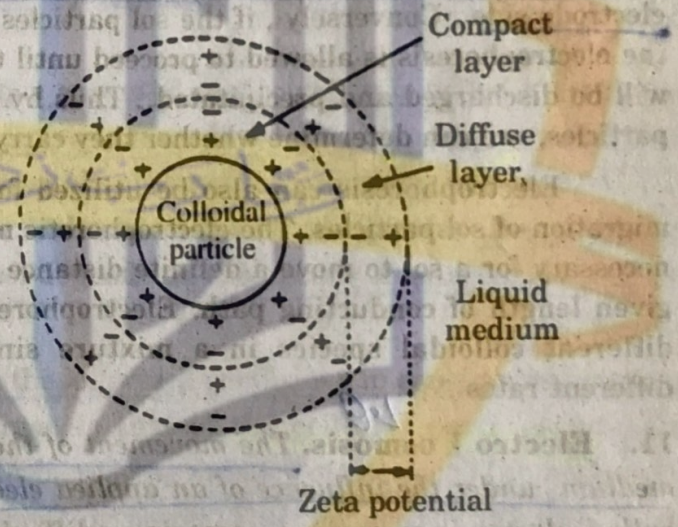

Fig.5.11. Electrical double layer (Stern).

More recent consideration have shown that the double layer is made of : (a) compact layer of + ve and –ve charges which are fixed firmly on to particle surface .

(a) **A Compact Layer** of +ve and –ve charges which are fixed firmly onto particle surface.

(b) **A Diffuse Layer** of counterions diffused into the medium containing opposite ions .

The combination of the compact and diffused layer is referred to as the **Stern double layer**. The diffuse layer is only loosely attached to the particle surface and moves just the opposite direction under an applied electric field. Because of the distribution of the charge around the particle , there is a difference in potential between the compact layer and the bulk of solution across the diffuse layer. This is called the **Electrokinetic or zeta potential**.

Zeta potential accounts for the electrical properties such as : (a) cataphoresis; and (b) Electro osmosis of colloids. The magnitude of the zeta potential can be determined with the help of these properties .

10. Electrophoresis or cataphoresis. *The movement of electrically charged sol particles under the influence of an applied electric field is called* **Electrophoresis.**

Electrophoretic effect can be conveniently studied in an apparatus shown in Fig.5.12 , called *Bruton tube* . The apparatus consists of a U- tube fitted with a stop - cock for drainage and a funnel-shaped filling tube with stop - cock (not shown) attached to the back of the U- tube. First , some quantity of pure dispersion medium , e.g. water is placed in the tube , and then sol is introduced through the funnel so as to displace the dispersion medium upward and produce sharp boundaries in the two arms. Electrodes are then inserted and connected to a source of potential that is a high voltage battery. The sol particles travel towards oppositely charged electrodes. If the sol particles are negatively charged, the level of the sol falls gradually on the negative electrode side and rises simultaneously on the positive electrode side . Conversely , if the sol particles are positively charged, the reverse occurs if the electrophoresis is allowed to proceed until the appropriate electrode is reached , the sol will be discharged and precipitated . Thus by noting the direction of movement of the sol particles, we can determine whether they carry a positive or negative charge .

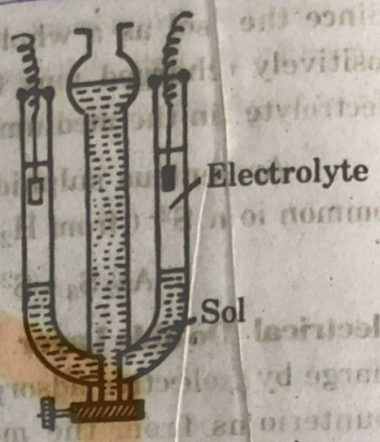

Fig.5.12. Electrophoresis.

Electrophoresis can also be utilized for quantitative measurement of the rate of migration of sol particles. The electrophoretic mobility can be calculated by noting the time necessary for a sol to move a definite distance under a potential difference applied over a given length of conducting path. Electrophoresis may be employed for the separation of different colloidal species in a mixture since different colloidal species move with different rates .

11. Electro - osmosis. *The movement of the dispersion medium under the influence of an applied electric field is called electro - osmosis,* (osmosis = diffusion through porous membrane).

A sol is electrically neutral. Therefore , the dispersion medium carries an equal but opposite charge to that of the dispersed particles. If sol particles are kept stationary by some suitable means, the dispersion medium would move to the electrode of opposite sign under the influence of an applied electric field. Electro- osmosis is a direct consequence of the existence of zeta potential between the sol particles and the medium.

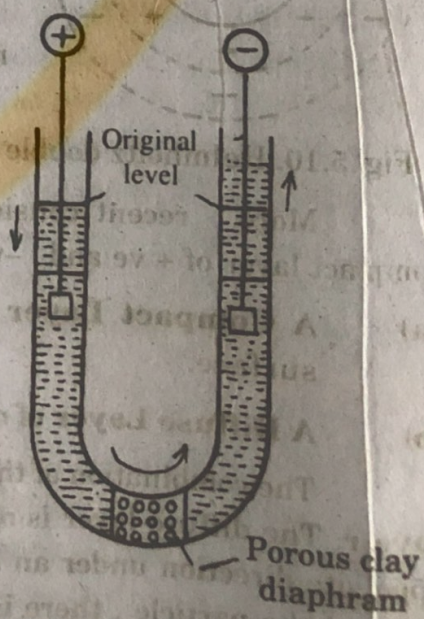

Fig.5.13. Electro-osmosis.

The phenomenon of electro-osmosis can be observed by fixing a porous diaphragm made of

colloidal particles (dispersed phase). Such as moist clay, in a U- tube containing the dispersion medium , water. When an electric current is applied across the two platinum electrodes immersed in water on each side of the clay (dispersed phase)(water) is observed to move towards one or the other electrode as shown in Fig.5.13. The direction of flow of the dispersion medium (water) depends on the charge of the colloid. The phenomenon of electro- osmosis is used technically in the removal of water from peat , in dewatering moist clay and in drying dye pastes.

12. **Precipitation or coagulation of sols.** The stability of a sol is mainly due to the electric charge on the sol particles. For **lyophobic sols**, the stability is due to their electric charge but for **lyophilic sols** stability is both due to their electric charge and their high hydration (solvation). Removal of charge in lyophobic sols would lead to precipitation of sols, while to precipitate a lyophilic sols, both the charge and solvation must be removed .

S.Q

The flocculation (or aggregation) and settling down of the discharged sol particles is called **coagulation or precipitation** of sol .

The precipitation of a lyophobic sol can be brought in four ways as given below:

(a) By addition of electrolytes (b) By electrophoresis (c) By mixing two oppositely charged sols (d) By boiling .

(a) **By addition of Electrolytes .** When excess of an electrolyte is added to a sol, the dispersed particles are precipitated . The electrolyte furnishes both + ve and – ve ions in the medium. The sol particles adsorb the oppositely charged ions and get neutralized. The electrically neutral particles then aggregate and settle down as precipitate. The amount of electrolyte required to precipitate a given sol depends on the nature of both the sol and the electrolyte added .

S.Q v.v.imp.

Hardy - Schulze Rule states that the ion which is effective in causing precipitation of a sol is the one carrying opposite charge to that of the colloidal particles; and the precipitating effect increases markedly with increasing valency of the ion. The higher the valency of the ion , the greater is its precipitating power. Thus for precipitating As_2S_3 sol (negatively charged) the precipitating power of Al^{3+} , Ba^{2+} and Na^+ ions is in the following order :

$$Al^{3+} > Ba^{2+} > Na^+$$

Similarly for precipitating $Fe(OH)_3$ sol (positively charged) the precipitating power of PO_4^{3-} , SO_4^{2-} , Cl^- ions is in the following order :

$$PO_4^{3-} > SO_4^{2-} > Cl^-$$

The minimum amount of an electrolyte required in millimoles to bring about the precipitation dm^{-3} (per litre) of the sol in two hours is called the **Precipitation or Flocculation value** . The smaller the precipitation value , the higher the precipitating power of an ion.

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Table 5.4 : Flocculation Values.

$Fe(OH)_3$ sol (+ve)		As_2S_3 sol (–ve)	
Electrolyte	Concentration (millimoles dm^{-3})	Electrolyte	Concentration (millimoles dm^{-3})
NaCl, (Cl^-)	9.30	NaCl, (Na^+)	51.00
KCl, (Cl^-)	9.00	KCl, (K^+)	50.00
K_2SO_4, (SO_4^{2-})	0.20	$BaCl_2$ (Ba^{2+})	0.69
$K_3Fe(CN)_6$, [$Fe(CN)_6$]$^{3-}$	0.096	$AlCl_3$(Al^{3+})	0.093

From the table 5.4, it is evident that the precipitating power of an electrolyte increases very rapidly with the increase of valence. The ratio for the mono, di, and trivalent anions or cations are approximately 1 : 40 : 90 for $Fe(OH)_3$ sol and 1: 70 : 500 for As_2S_3 sol.

From the table, it may be seen that Al^{3+} ions in alums are very effective and are used in styptic pencils for congealing of blood. When river water containing colloidal clay flows into the sea, brine induces coagulation and delta formation takes place.

(b) By Electrophorsis. In electrophorsis the charged sol particles migrate to the electrode of opposite sign under the influence of an electric field. As the charge particles come in contract with electrode, the particles are discharged and are precipitated.

(c) By Mixing of two oppositely charged sols. When two sols of opposite charges are mixed together in different proportions, their mutual precipitation can be affected. Ferric hydroxide (+ve sol) and arsenious sulphide (–ve sol) form such a pair and when mixed in the correct proportions they are precipitated.

(d) By Boiling. Sols such as sulphur and silver halides dispersed in water, may be coagulated by boiling.

Precipitation in Lyophilic sols may be brought about when solvents such as alcohol or acetone, which have a high affinity for water, are added to a hydrophilic sol, the disperse phase undergoes dehydration to yield particles whose stability is now only due to their charge. A small amount of electrolyte added to this sol in this condition produces ready precipitation

13. Protection. The stability of lyophobic sols can be increased by the addition of more stable loyphilic sol like gelation or albumin. These lyophilic substances are absorbed on the surface of lyophobic particles by electrostatic forces or sometimes by chemical interaction, thus converting the lyophobic sol into one with more lyophilic character, and as a result the sols acquire greater resistance to precipitation.

The property of lyophilic sols to prevent the precipitation of a lyophobic sol is called Protection. The lyophilic sol used to protect a lyophobic sol from precipitation is

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commonly called a **protective colloid** . If a little gelation (protective colloid) is added to a gold sol (lyophobic sols); it is no longer precipitated on the addition of NaCl solution .

Gold Number. The lyophilic colloids differ widely in their powers of protection . The protective power of different colloids is measured in terms of , Gold Number; as introduced by zaigmondy. The gold number is defined as the number of milligram of a hydrophilic colloid that will just prevent the precipitation of 10 cm^3 of a gold sol on the addition of 1 cm^3 of 10 per cent sodium chloride solution. The smaller the gold number of a hydrophilic colloid , the greater is its protective power. The gold number of a few lyophilic colloids are given in table 5.5 .

Table .5.5 : Gold Numbers of some hydrophilic colloids .

Lyophilic sol	Gold Number	Lyophilic sol	Gold Number
Gelatin	0.005 – 0.01	Egg albumin	0.08 – 0.1
Casein	0.01 – 0.02	Dextrin	6 – 20
Homoglobin	0.03 – 0.07	Potato starch	20 – 25

5.7 GELS

A jelly like colloidal system in which a liquid is dispersed in a solid medium is called a **gel**. Jelly is the common name for a gel. The process of gel formation is known as **gelation.**

In the course of gel formation the coagulating sol particles first unite to form long thread- like chains, which are then inter-locked to form a rigid frame-work enclosing within it all of the liquid dispersion medium yielding a semisolid mass , which has a gel structure . Thus it is assumed that a gel has a somewhat like honey - comb.

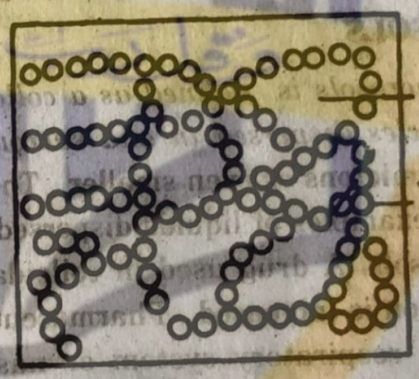

Fig.5.14. The network of the coagulated sole particles enclosing liquid forming a gel.

Types of Gels . Gels may be classified into three types ; depending upon their mechanical properties .

(i) **Elastic Gels** are those which possess the property of elasticity. They change their shape on applying force and return to original shape when the force is removed. Elastic gels are obtained by cooling fairly concentrated lyophilic sols . Gelatin, starch and soaps are examples of substances which form elastic gels.

(ii) **Non Elastic Gels** are those which are rigid. These are prepared by appropriate chemical reactions (by double decomposition or metathesis). Thus silica gel is obtained by the addition of an acid (HCl) to water solution of sodium silicate. The resulting molecules