Colloidal state

(1) The foundation of colloidal chemistry was laid down by an English scientist, ***Thomas Graham*****,** in 1861**.** The credit for the various advances in this field goes to eminent scientists like ***Tyndall, Hardy, Zsigmondy, N.R. Dhar, S.S. Bhatnagar and others.***

(2) **Thomas Graham** classified the soluble substances into two categories depending upon the rate of diffusion through animal and vegetable membranes or ***parchment paper.***

(i) ***Crystalloids*****:** They have higher rate of diffusion and diffused from parchment paper.

Examples: All organic acids, bases and salts and organic compounds such as sugar, urea etc.

(ii) ***Colloids*** (*Greek word, kolla, meaning glue-like*)**:** They have slower rate of diffusion and can not diffused from parchment paper.

Examples: Starch, gelatin, gums, silicic acid and hdemoglobin etc.

(3) The above classification was discarded *i.e.,* the terms colloid does not apply to a particular class of substances but is a state of matter like solid, liquid and gas. Any substance can be brought into colloidal state.

(4) The colloidal state depends on the particle size. If is regarded as intermediate state between true solution and suspension.

Table: 14.2 Features of the three types of solutions

Property	**Suspension**	**Colloid solution**	**True solution**
Nature	Heterogeneous	Heterogeneous	Homogeneous
Particle size	> 100 *nm*	1 *nm* – 100 *nm*	< 1 *nm*
Separation by			
(i) Ordinary filtration	Possible	Not possible	Not possible
(ii) Ultra-filtration	Possible	Possible	Not possible
Settling of particles	Settle under gravity	Settle only on centrifugation	Do not settle
Appearance	Opaque	Generally transparent	Transparent
Tyndall effect	Shows	Shows	Does not show
Diffusion of particles	Does not diffuse	Diffuses slowly	Diffuses rapidly
Brownian movement	May show	Shows	Negligible

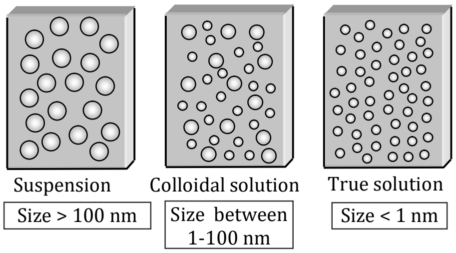


Fig. 14.1 Three types solutions

Phases of colloids and Their classification

(1) **Phases of colloids:** We know that a colloidal solution is of heterogeneous nature. It consists of two phases which are as follows

(i) ***Internal phase or Dispersed phase*** (Discontinuous phase) **:** It is the component present in small proportion and is just like a solute in a solution. For example in the colloidal solution of silver in water (silver acts as a dispersed phase)

(ii) ***External phase or Dispersion medium*** (continuous phase) **:** It is generally component present in excess and is just like a solvent in a solution. For example, in the colloidal solution of silver in water. Water act as a dispersion medium.

(2) **Classification of colloids:** The colloids are classified on the basis of the following criteria

(i) ***Classification based on the physical state of the dispersed phase and dispersion medium*****:** Depending upon the physical state of dispersed phase and dispersion medium whether these are solids, liquids or gases, eight types of colloidal systems are possible.

Table: 14.3 Different types of colloidal systems

Dispersed phase	Dispersion Medium	Colloidal System	Examples
Liquid	Gas	Aerosol of liquids	Fogs, clouds, mists, fine insecticide sprays
Solid	Gas	Aerosol of solids	Smoke, volcanic dust, haze
Gas	Liquid	Foam or froth	Soap lather. Lemonade froth, foam, whipped cream, soda water
Liquid	Liquid	Emulsions	Milk, emulsified oils, medicines
Solid	Liquid	Sols	Most paints, starch in water, proteins, gold sol, arsenic sulphide sol, ink
Gas	Solid	Solid foam	Pumice stone, styrene rubber, foam rubber
Liquid	Solid	Gels	Cheese, butter, boot polish, jelly, curd
Solid	Solid	Solid sols (coloured glass)	Ruby glass, some gem stones and alloys

(ii) ***Classification based on Nature of interaction between dispersed phase and dispersion medium*****:** Depending upon the nature of interactions between dispersed phase and the dispersion medium, the colloidal solutions can be classified into two types as (a) Lyophilic and (b) Lyophobic sols.

(a) *Lyophilic colloids* (water loving) : "The colloidal solutions in which the particles of the dispersed phase have a great affinity for the dispersion medium, are called ***lyophilic collodis."***

(b) *Lyophobic colloids* (water hateing) : *"The colloidal solutions in which* there *is no affinity between particles of the dispersed phase and the dispersion medium are called* ***lyophobic colloids****.*"

Distinction between lyophilic and lyophobic sols

Property	Lyophilic sols (suspensoid)	Lyophobic sols (Emulsoid)
Surface tension	Lower than that of the medium	Same as that of the medium
Viscosity	Much higher than that of the medium	Same as that of the medium
Reversibility	Reversible	Irreversible
Stability	More stable	Less stable
Visibility	Particles can't be detected even under ultramicroscope	Particles can be detected under ultramicroscope.
Migration	Particles may migrate in either direction or do not migrate in an electric field because do not carry any charge.	Particles migrate either towards cathode or anode in an electric field because they carry charge.
Action of electrolyte	Addition of smaller quantity of electrolyte has little effect	Coagulation takes place
Hydration	Extensive hydration takes place	No hydration
Examples	Gum, gelatin, starch, proteins, rubber etc.	Metals like *Ag* and *Au,* hydroxides like $Al(OH)_3$,

		$Fe(OH)_3$ metal sulphides like AS_2S_3 etc.

(iii) ***Classification based on types of particle of dispersed phase*****:** Depending upon the type of the particles of the dispersed phase, the colloids are classified as follows.

(a) ***Multimolecular colloids***

- When on dissolution, atoms or smaller molecules of substances (having diameter less than 1*nm*) aggregate together to form particles of colloidal dimensions, the particles thus formed are called ***multimolecular colloids***.
- In these sols the dispersed phase consists of aggregates of atoms or molecules with molecular size less than 1 *nm.*
- For example, sols of gold atoms and sulphur (S_8) molecules. In these colloids, the particles are held together by ***Vander Waal's forces.*** They have usually ***lyophilic character.***

(b) ***Macromolecular colloids***

- These are the substances having big size molecules (called macromolecules) which on dissolution form size in the colloidal range. Such substances are called ***macromolecular colloids***.
- These macromolecules forming the dispersed phase are generally ***polymers*** having very high molecular masses.
- Naturally occurring macromolecules are starch, cellulose, proteins, enzymes, gelatin etc. Artificial macromolecules are synthetic polymers such as nylon, polythene, plastics, polystyrene etc.
- They have usually ***lyophobic character.***

(c) ***Associated colloids***

- These are the substances which on dissolved in a medium behave as normal electrolytes at low concentration but behave, as colloidal particles at higher concentration due to the formation of aggregated particles. The aggregates particles thus formed are called ***micelles.***
- Their molecules contain both ***lyophilic*** and ***lyophobic*** groups.

Micelles

- Micelles are the cluster or aggregated particles formed by association of colloid in solution.
- The common examples of micelles are ***soaps*** and ***detergents***.
- The formation of micelles takes place above a particular temperature called ***Kraft temperature*** (T_k) and above a particular concentration called ***critical micellization concentration*** (CMC).
- They are capable of forming ions.
- Micelles may contain as many as 100 molecules or more.
- For example sodium stearate $(C_{17}H_{35}COONa)$ is a typical example of such type of molecules.
- When sodium stearate is dissolved in water, it gives Na^+ and $C_{17}H_{35}COO^-$ ions.

$$\underset{\text{Sodium stearate}}{C_{17}H_{35}COONa} \longrightarrow \underset{\text{Stearate ion}}{C_{17}H_{35}COO^-} + Na^+$$

The stearate ions associate to form ***ionic micelles*** of colloidal size.

- It has long hydrocarbon part of $C_{17}H_{35}$ radical. Which is ***lyophobic*** and COO^- part which is ***lyophilic.***
- In the figure, the chain corresponds to stearate ion, $(C_{17}H_{35}COO^-)$. When the concentration of the solution is below from its CMC $(10^{-3}\ mol\ \ L^{-1})$, it behaves as normal electrolyte. But above this concentration it is aggregated to behave as micelles.

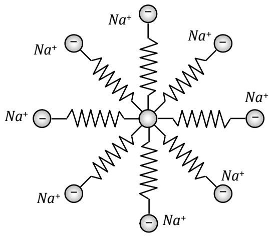


Fig. 14.2 Aggregation of several ions to form ionic micelle

- The main function of a soap is to reduce oily and greasy dirt to colloidal particles (an emulsion). Soap therefore, are known as ***emulsifying agents***.

- Some other examples of micelles are sodium palmitate $(C_{15}H_{31}COONa)$, Sodium lauryl sulphate $[CH_3(CH_2)_{11}SO_3O^-Na^+]$, Cetyl trimethyl ammonium bromide $CH_3(CH_2)_{15}(CH_2)_3N^+Br^-$ etc.

General methods of preparation of colloids

Lyophilic and lyophobic colloidal solutions (or sols) are generally prepared by different types of methods. Some of the common methods are as follows.

(1) **Preparation of Lyophilic colloids**

(i) The lyophilic colloids have strong affinity between particles of dispersed phase and dispersion medium.

(ii) Simply mixing the dispersed phase and dispersion medium under ordinary conditions readily forms these colloidal solutions.

(iii) For example, the substance like gelatin, gum, starch, egg, albumin etc. pass readily into water to give colloidal solution.

(iv) They are reversible in nature become these can be precipitated and directly converted into colloidal state.

(2) **Preparation of Lyophobic colloids**: Lyophobic colloids can be prepared by mainly two types of methods.

(i) ***Condensation method***: In these method, smaller particles of dispersed phase are condensed suitably to be of colloidal size. This is done by the following methods.

(a) *By oxidation*: A colloidal solution of sulphur can be obtained by bubbling oxygen (or any other oxidising agent like HNO_3, Br_2 etc.) through a solution of hydrogen sulphide in water.

$$2H_2S + O_2 \text{ (or any other oxidising agent)} \longrightarrow 2H_2O + 2S$$

(b) *By reduction*: A number of metals such as silver, gold and platinum, have been obtained in colloidal state by treating the aqueous solution of their salts, with a suitable reducing agent such as formaldehyde, phenyl hydrazine, hydrogen peroxide, stannous chloride etc.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + \underset{\text{Gold sol}}{2Au}$$

$$2AuCl_3 + 3HCHO + 3H_2O \longrightarrow \underset{\text{Gold sol}}{2Au} + 3HCOOH + 6HCl$$

The gold sol, thus prepared, has a purple colour and is called purple of cassius.

(c) *By hydrolysis*: Many salt solutions are rapidly hydrolysed by boiling dilute solutions of their salts. For example, ferric hydroxide and aluminium hydroxide sols are obtained by boiling solutions of the corresponding chlorides.

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

Similarly silicic acid sol is obtained by the hydrolysis of sodium silicate.

(d) *By double decomposition*: A sol of arsenic sulphide is obtained by passing hydrogen sulphide through a cold solution of arsenious oxide in water.

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

(e) *By excessive cooling*: A colloidal solution of ice in an organic solvent like ether or chloroform can be prepared by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution, separately combine to form particles of colloidal size.

(f) *By exchange of solvent*: Colloidal solution of certain substances such as sulphur, phosphorus, which are soluble in alcohol but insoluble in water can be prepared by pouring their alcoholic solution in excess of water. For example, alcoholic solution of sulphur on pouring into water gives milky colloidal solution of sulphur.

(g) *By change of physical state*: Sols of substances like mercury and sulphur are prepared by passing their vapour's through a cold water containing a suitable stabilizer such as ammonium salt or citrate.

(ii) ***Dispersion methods***: In these methods, larger particles of a substance (suspensions) are broken into smaller particles. The following methods are employed.

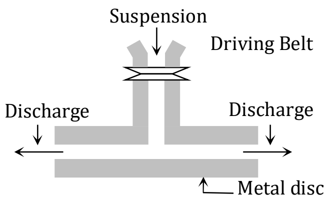


Fig. 14.3 Colloidal mill

(a) ***Mechanical dispersion***

- In this method, the substance is first ground to coarse particles.
- It is then mixed with the dispersion medium to get a suspension.
- The suspension is then grinded in colloidal mill.
- It consists of two metallic discs nearly touching each other and rotating in opposite directions at a very high speed about 7000 revolution per minute.
- The space between the discs of the mill is so adjusted that coarse suspension is subjected to great shearing force giving rise to particles of colloidal size.
- Colloidal solutions of black ink, paints, varnishes, dyes etc. are obtained by this method.

(b) ***By electrical dispersion or Bredig's arc method***

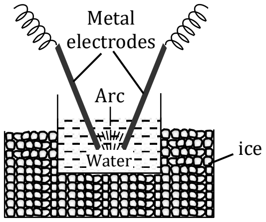


Fig. 14.4 Bredig's arc method

- This method is used to prepare sols of platinum, silver, copper or gold.
- The metal whose sol is to be prepared is made as two electrodes which immerged in dispersion medium such as water etc.
- The dispersion medium is kept cooled by ice.
- An electric arc is struck between the electrodes.
- The tremendous heat generate by this method and give colloidal solution.
- The colloidal solution prepared is stabilised by adding a small amount of KOH to it.

(c) *By peptisation*

- The process of converting a freshly prepared precipitate into colloidal form by the addition of suitable electrolyte is called ***peptisation.***
- The electrolyte is used for this purpose is called ***peptizing agent*** or ***stabilizing agent***.
- Cause of peptisation is the adsorption of the ions of the electrolyte by the particles of the precipitate.
- Important peptizing agents are sugar, gum, gelatin and electrolytes.
- Freshly prepared ferric hydroxide can be converted into colloidal state by shaking it with water containing Fe^{3+} or OH^- ions, viz. $FeCl_3$ or NH_4OH respectively.

$$\underset{\text{Precipitate}}{Fe(OH)_3} + \underset{\text{electrolyte}}{FeCl_3} \longrightarrow \underset{\text{Colloidal sol}}{[Fe(OH)_3Fe]^{3+}} + 3Cl^-$$

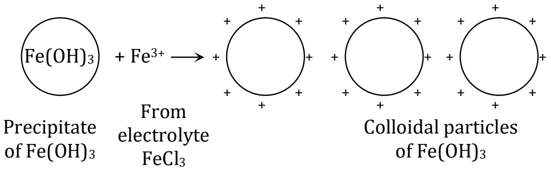


Fig. 14.5 Preparation of colloidal sol by peptisation

- A stable sol of stannic oxide is obtained by adding a small amount of dilute HCl to stannic oxide precipitates.
- Similarly, a colloidal solution of $Al(OH)_3$ and $AgCl$ are obtained by treating the corresponding freshly prepared precipitate with very dilute solution of HCl and $AgNO_3$ or KCl respectively.

Purification of colloidal solution

The following methods are commonly used for the purification of colloidal solutions.

(1) **Dialysis**

(i) The process of separating the particles of colloid from those of crystalloid, by means of diffusion through a suitable membrane is called dialysis.

(ii) It's principle is based upon the fact that colloidal particles can not pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.

(iii) The impurities slowly diffused out of the bag leaving behind pure colloidal solution

(iv) The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag.

(v) Dialysis can be used for removing HCl from the ferric hydroxide sol.

(2) **Electrodialysis**

(i) The ordinary process of dialysis is slow.

(ii) To increase the process of purification, the dialysis is carried out by applying electric field. This process is called ***electrodialysis.***

(iii) The important application of electrodialysis process in the artificial kidney machine used for the purification of blood of the patients whose kidneys have failed to work. The artificial kidney machine works on the principle of ***dialysis.***

(3) **Ultra – filtration**

(i) Sol particles directly pass through ordinary filter paper because their pores are larger (more than 1μ or $1000 m\mu$) than the size of sol particles (less than $200 m\mu$).

(ii) If the pores of the ordinary filter paper are made smaller by soaking the filter paper in a solution of gelatin of colloidion and subsequently hardened by soaking in formaldehyde, the treated filter paper may retain colloidal particles and allow the true solution particles to escape. Such filter paper is known as ***ultra - filter*** and the process of separating colloids by using ultra – filters is known as ***ultra – filtration.***

(4) **Ultra – centrifugation**

(i) The sol particles are prevented from setting out under the action of gravity by kinetic impacts of the molecules of the medium.

(ii) The setting force can be enhanced by using high speed centrifugal machines having 15,000 or more revolutions per minute. Such machines are known as ***ultra–centrifuges***.

Properties of colloidal solutions

The main characteristic properties of colloidal solutions are as follows.

(1) **Physical properties**

(i) ***Heterogeneous nature*:** Colloidal sols are heterogeneous in nature. They consists of two phases; the dispersed phase and the dispersion medium.

(ii) ***Stable nature*:** The colloidal solutions are quite stable. Their particles are in a state of motion and do not settle down at the bottom of the container.

(iii) ***Filterability*:** Colloidal particles are readily passed through the ordinary filter papers. However they can be retained by special filters known as ultrafilters (parchment paper).

(2) **Colligative properties**

(i) Due to formation of associated molecules, observed values of colligative properties like relative decrease in vapour pressure, elevation in boiling point, depression in freezing point, osmotic pressure are smaller than expected.

(ii) For a given colloidal sol the number of particles will be very small as compared to the true solution.

(3) **Mechanical properties**

(i) ***Brownian movement***

(a) ***Robert Brown*****,** a botanist discovered in 1827 that the ***pollen grains*** suspended in water do not remain at rest but move about continuously and randomly in all directions.

(b) Later on, it was observed that the colloidal particles are moving at random in a ***zig – zag*** motion. This type of motion is called ***Brownian movement.***

(c) The molecules of the dispersion medium are constantly colloiding with the particles of the dispersed phase. It was stated by ***Wiener*** in 1863 that *the impacts of the dispersion medium particles are unequal, thus causing a zig-zag motion of the dispersed phase particles.*

(d) The Brownian movement explains the force of gravity acting on colloidal particles. This helps in providing stability to colloidal sols by not allowing them to settle down.

(ii) ***Diffusion*****:** The sol particles diffuse from higher concentration to lower concentration region. However, due to bigger size, they diffuse at a lesser speed.

(iii) ***Sedimentation*****:** The colloidal particles settle down under the influence of gravity at a very slow rate. This phenomenon is used for determining the molecular mass of the macromolecules.

(4) **Optical properties:** ***Tyandall effect***

(i) When light passes through a sol, its path becomes visible because of scattering of light by particles. It is called ***Tyndall effect.*** This phenomenon was studied for the first time by ***Tyndall.*** The illuminated path of the beam is called ***Tyndall cone.***

(ii) The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and the dispersion medium.

(iii) In lyophobic colloids, the difference is appreciable and, therefore, the Tyndall effect is well - defined. But in lyophilic sols, the difference is very small and the Tyndall effect is very weak.

(iv) The Tyndall effect confirms the ***heterogeneous nature of the colloidal solution*****.**

(v) The Tyndall effect has also been observed by an instrument called ***ultra – microscope.***

Some example of Tyndall effect are as follows

(a) *Tail of comets is seen as a* **Tyndall cone due** *to the scattering of light by the tiny solid particles left by the comet in its path.*

(b) *Due to scattering the sky looks blue.*

(c) *The blue colour of water in the sea is due to scattering of blue light by water molecules.*

(d) *Visibility of projector path and circus light.*

(e) *Visibility of sharp ray of sunlight passing through a slit in dark room.*

(5) **Electrical properties**

(i) ***Electrophoresis***

(a) The phenomenon of movement of colloidal particles under an applied electric field is called ***electrophoresis.***

(b) If the particles accumulate near the negative electrode, the charge on the particles is ***positive.***

(c) On the other hand, if the sol particles accumulate near the positive electrode, the charge on the particles is ***negative.***

(d) The apparatus consists of a U-tube with two *Pt*-electrodes in each limb.

(e) When electrophoresis of a sol is carried out with out stirring, the bottom layer gradually becomes more concentrated while the top layer which contain pure and concentrated colloidal solution may be decanted. This is called ***electro decanation*** and is used for the purification as well as for concentrating the sol.

(f) The reverse of electrophoresis is called ***Sedimentation potential or Dorn effect.*** The sedimentation potential is setup when a particle is forced to move in a resting liquid. This phenomenon was discovered by ***Dorn*** and is also called ***Dorn effect.***

(ii) ***Electrical double layer theory***

(a) The electrical properties of colloids can also be explained by electrical double layer theory. According to this theory ***a double layer of ions appear at the surface of solid.***

(b) The ion preferentially adsorbed is held in fixed part and imparts charge to colloidal particles.

(c) The second part consists of a diffuse mobile layer of ions. This second layer consists of both the type of charges. The net charge on the second layer is exactly equal to that on the fixed part.

(d) The existence of opposite sign on fixed and diffuse parts of double layer leads to appearance of a difference of potential, known as ***zeta potential or electrokinetic potential.*** Now when electric field is employed the particles move (electrophoresis)

(iii) ***Electro-osmosis***

(a) In it the movement of the dispersed particles are prevented from moving by ***semipermeable membrane.***

(b) Electro-osmosis is a phenomenon in which dispersion medium is allowed to move under the influence of an electrical field, whereas colloidal particles are not allowed to move.

(c) The existence of electro-osmosis has suggested that when liquid forced through a porous material or a capillary tube, a potential difference is setup between the two sides called as streaming potential. So the reverse of electro-osmosis is called ***streaming potential.***

Origin of the charge on colloidal particles

The origin of the charge on the sol particles in most cases is due to the preferential adsorption of either positive or negative ions on their surface. The sol particles acquire electrical charge in any one or more of the following ways.

(1) **Due to the dissociation of the surface molecules:** Some colloidal particles develope electrical charge due to the dissociation / ionisation of the surface molecules. The charge on the colloidal particles is balanced by the oppositely charged ions in the sol. For example, an aqueous solution of soap (sodium palmitate) which dissociates into ions as,

$$\underset{\text{Sodium palmitate}}{C_{15}H_{31}COONa} \rightleftharpoons C_{15}H_{31}COO^- + Na^+$$

The cations (Na^+) pass into the solution while the anions $(C_{15}H_{31}COO^-)$ have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains.

(2) **Due to frictional electrification**

(i) It is believed that the frictional electrification due to the rubbing of the dispersed phase particles with that of dispersion medium results in some charge on the colloidal particles.

(ii) The dispersion medium must also get some charge, because of the friction. Since it does not carry any charge, the theory does not seem to be correct.

(3) **Due to selective adsorption of ions**

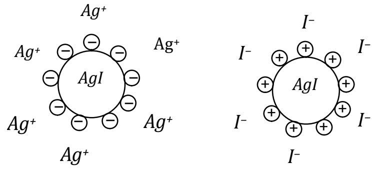
(i) The particles constituting the dispersed phase adsorb only those ions preferentially which are common with their own lattice ions.

(ii) For example, when a small quantity of silver nitrate $(AgNO_3)$ solution is added to a large quantity of potassium iodide (KI) solution, the colloidal particles of silver iodide adsorb I^- from the solution to become ***negatively charged,*** *(at this stage KI is in excess, and I^- being common to AgI)*

$$\underset{\text{(Colloidal particle)}}{AgI} + \underset{\text{(in excess in the medium)}}{I^-} \longrightarrow \underset{\text{(Colloidal particle becomes positively charged)}}{(AgI)I^-}$$

But, when a small quantity of potassium iodide (KI) solution is added to a large quantity of silver nitrate solution $(AgNO_3)$; the colloidal silver iodide particles adsorb Ag^+ from the solution to become ***positively charged,*** *(at this stage $AgNO_3$ is in excess and Ag^+ is common to AgI),*

$$\underset{\text{(Colloidal particle)}}{AgI} + \underset{\text{(in excess in the medium)}}{Ag^+} \longrightarrow \underset{\text{(Colloidal particle becomes positively charged)}}{(AgI)Ag^+}$$



Ag+ ions remain in dispersed medium (Agl, I- Sol)

I- ions remain in dispersion medium (Agl, Ag+ Sol)

Fig. 14.6

(iii) Depending upon the nature of charge on the particles of the dispersed phase, the colloidal solutions are classified into positively charged and negatively charged colloids. Some typical examples are as follows

(a) Negatively charged colloids	**(b) Positively charged colloids**
• Metal sulphides**:** As_2S_3 , CdS	• Metal hydroxides**:** $Al(OH)_3$, $Fe(OH)_3$
• Metal dispersions**:** Ag, Au, Pt	• Metal oxide: TiO_2
• Acid dyes**:** Eosin, congo red	• Basic dyes**:** Methylene blue
• Sols of starch, gums, gold, gelatin etc.	• Haemoglobin
	• Sulphur sol

Stability of sols

Sols are thermodynamically unstable and the dispersed phase (colloidal particles) tend to separate out on long standing due to the ***Vander Waal's attractive forces.*** However, sols tend to exhibit some stability due to

(1) **Stronger repulsive forces between the similarly charged particles**

(2) **Particle-solvent interactions:** Due to strong particle-solvent (dispersion medium) interactions, the colloidal particles get strongly solvated.

Coagulation or Flocculation or Precipitation

"*The phenomenon of the precipitation of a colloidal solution by the addition of the excess of an electrolyte is called **coagulation or flocculation**.*"

The coagulation of the ***lyophobic sols*** can be carried out by following methods.

(1) **By electrophoresis:** In electrophoresis the colloidal particles move towards oppositely charged electrode. When these come in contact with the electrode for long these are discharged and precipitated.

(2) **By mixing two oppositely charged sols :** When oppositely charged sols are mixed in almost equal proportions, their charges are neutralised. Both sols may be partially or completely precipitated as the mixing of ferric hydroxide (+*ve* sol) and arsenious sulphide (–*ve* sol) bring them in precipitated form. This type of coagulation is called ***mutual coagulation** or **meteral coagulation.***

(3) **By boiling :** When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately they settle down to form a precipitate.

(4) **By persistent dialysis :** On prolonged dialysis, the traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable.

(5) **By addition of electrolytes:** The particles of the dispersed phase *i.e.,* colloids bear some charge. When an electrolyte is added to sol, the colloidal particles take up ions carrying opposite charge from the electrolyte. As a result, their charge gets neutralised and this causes the uncharged, particles to come closer and to get coagulated or precipitated. For example, if $BaCl_2$ solution is added to As_2S_3 sol the Ba^{2+} ions are attracted by the negatively charged sol particles and their charge gets neutralised. This lead to coagulation.

(6) **Hardy schulze rule:** The coagulation capacity of different electrolytes is different. It depends upon the valency of the active ion are called flocculating ion, which is the ion carrying charge opposite to the charge on the colloidal particles. "*According to Hardy Schulze rule, greater the valency of the active ion or flocculating ion, greater will be its coagulating power*" thus, Hardy Schulze law state:

(i) *The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.*

(ii) *Coagulating power of an electrolyte is directly proportional to the valency of the active ions (ions causing coagulation).*

For example to coagulate ***negative sol*** of As_2S_3 , the ***coagulation power*** of different cations has been found to ***decrease*** in the order as, $Al^{3+} > Mg^{2+} > Na^+$

Similarly, to coagulate a ***positive sol*** such as $Fe(OH)_3$, the ***coagulating power*** of different anions has been found to ***decrease*** in the order : $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

(7) **Coagulation or flocculation value**

*"The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as **flocculation value**."*

or

*"The number of millimoles of an electrolyte required to bring about the coagulation of one litre of a colloidal solution is called its **flocculation value**."*

$$\text{Coagulation value or flocculating value} \propto \frac{1}{\text{Coagulatin g power}}$$

(8) **Coagulation of lyophilic sols**

(i) There are two factors which are responsible for the stability of lyophilic sols.

(ii) These factors are the charge and solvation of the colloidal particles.

(iii) When these two factors are removed, a lyophilic sol can be coagulated.

(iv) This is done (i) by adding electrolyte (ii) and by adding suitable solvent.

(v) When solvent such as alcohol and acetone are added to hydrophilic sols the dehydration of dispersed phase occurs. Under this condition a small quantity of electrolyte can bring about coagulation.

Protection of colloids and Gold number

- Lyophilic sols are more stable than lyophobic sols.
- Lyophobic sols can be easily coagulated by the addition of small quantity of an electrolyte.
- When a lyophilic sol is added to any lyophobic sol, it becomes less sensitive towards electrolytes. Thus, lyophilic colloids can prevent the coagulation of any lyophobic sol.

"The phenomenon of preventing the coagulation of a lyophobic sol due to the addition of some lyophilic colloid is called sol protection or protection of colloids."

- The protecting power of different protective (lyophilic) colloids is different. The efficiency of any protective colloid is expressed in terms of ***gold number.***

Gold number*: *Zsigmondy introduced a term called ***gold number*** to describe the protective power of different colloids. This is defined as, *"weight of the dried protective agent in milligrams, which when added to 10 ml of a standard gold sol* (0.0053 to 0.0058%) *is just sufficient to prevent a colour change from red to blue on the addition of 1 ml of 10 % sodium chloride solution, is equal to the gold number of that protective colloid."*

Thus, smaller is the gold number, higher is the protective action of the protective agent.

$$\text{Protective power} \propto \frac{1}{\text{Gold number}}$$

Table : 14.4 Gold numbers of some hydrophilic substances

Hydrophilic substance	Gold number	Hydrophilic substance	Gold number
Gelatin	0.005 - 0.01	Sodium oleate	0.4 – 1.0
Sodium caseinate	0.01	Gum tragacanth	2
Hamoglobin	0.03 – 0.07	Potato starch	25
Gum arabic	0.15 – 0.25		

Congo rubin number: *Ostwald* introduced congo rubin number to account for protective nature of colloids. It is defined as "*the amount of protective colloid in milligrams which prevents colour change in 100 ml of 0.01 % congo rubin dye to which 0.16 g equivalent of KCl is added."*

Mechanism of sol protection

(i) The actual mechanism of sol protection is very complex. However it may be due to the adsorption of the protective colloid on the lyophobic sol particles, followed by its solvation. Thus it stabilises the sol *via* ***solvation effects***.

(ii) Solvation effects contribute much towards the stability of lyophilic systems. For example, gelatin has a sufficiently strong affinity for water. It is only because of the solvation effects that even the addition of electrolytes in small amounts does not cause any flocculation of hydrophilic sols. However at higher concentration, precipitation occurs. This phenomenon is called ***salting out.***

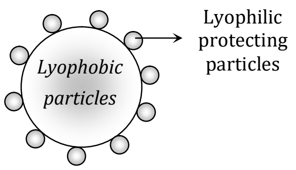


Fig. 14.7 Protection of colloids

(iii) The salting out efficiency of an electrolyte depends upon the tendency of its constituents ions to get hydrated *i.e,* the tendency to squeeze out water initially fied up with the colloidal particle.

(iv) The cations and the anions can be arranged in the decreasing order of the salting out power, such an arrangement is called ***lyotropic series.***

Cations: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^{+} > Na^{+} > K^{+} > NH_4^{+} > Rb^{+} > Cs^{+}$

Anions: $\text{Citrate}^{3-} > SO_4^{2-} > Cl^{-} > NH_3^{-} > I^{-} > CNS^{-}$

Ammonium sulphate, due to its very high solubility in water, is oftenly used for precipitating proteins from aqueous solutions.

(v) The precipitation of lyophilic colloids can also be affected by the addition of organic solvents of non-electrolytes. For example, the addition of acetone or alcohol to aqueous gelatin solution causes precipitation of gelatin. Addition of petroleum ether to a solution of rubber in benzene causes the precipitation of rubber.

Emulsion

"The colloidal systems in which fine droplets of one liquid are dispersed in another liquid are called emulsions the two liquids otherwise being mutually immiscible." **or**

"Emulsion are the colloidal solutions in which both the dispersed phase and the dispersion medium are liquids."

A good example of an emulsion is milk in which fat globules are dispersed in water. The size of the emulsified globules is generally of the order of $10^{-6}\ m$. Emulsion resemble lyophobic sols in some properties.

(1) **Types of Emulsion:** Depending upon the nature of the dispersed phase, the emulsions are classified as;

(i) ***Oil-in-water emulsions (O/W)*** **:** The emulsion in which oil is present as the dispersed phase and water as the dispersion medium ***(continuous phase)*** is called an oil-in-water emulsion. Milk is an example of the oil-in-water type of emulsion. In milk liquid fat globules are dispersed in water. Other examples are, vanishing cream etc.

(ii) ***Water-in-oil emulsion (W/O)*** **:** The emulsion in which water forms the dispersed phase, and the oil acts as the dispersion medium is called a water-in-oil emulsion. These emulsion are also termed ***oil emulsions. Butter*** and ***cold cream*** are typical examples of this types of emulsions. Other examples are cod liver oil etc.

(2) Properties of emulsion

(i) Emulsions show all the characteristic properties of colloidal solution such as Brownian movement, Tyndall effect, electrophoresis etc.

(ii) These are coagulated by the addition of electrolytes containing polyvalent metal ions indicating the negative charge on the globules.

(iii) The size of the dispersed particles in emulsions in larger than those in the sols. It ranges from 1000 Å to 10,000 Å. However, the size is smaller than the particles in suspensioins.

(iv) Emulsions can be converted into two separate liquids by heating, centrifuging, freezing etc. This process is also known as ***demulsification***.

(3) Applications of emulsions

(i) Concentration of ores in metallurgy

(ii) In medicine (Emulsion water-in-oil type)

(iii) Cleansing action of soaps.

(iv) Milk, which is an important constituent of our diet an emulsion of fat in water.

(v) Digestion of fats in intestine is through ***emulsification***.

Gels

(1) "A gel is a colloidal system in which a liquid is dispersed in a solid."

(2) The lyophilic sols may be coagulated to give a semisolid jelly like mass, which encloses all the liquid present in the sol. The process of gel formation is called ***gelation*** and the colloidal system formed called ***gel.***

(3) Some gels are known to liquify on shaking and reset on being allowed to stand. This reversible ***sol-gel transformation*** is called ***thixotropy.***

(4) The common examples of gel are gum arabic, gelatin, processed cheese, silicic acid, ferric hydroxide etc.

(5) Gels may shrink by loosing some liquid help them. This is known as ***synereises or weeping.***

(6) Gels may be classified into two types

(i) ***Elastic gels*** **:** These are the gels which possess the property of elasticity. They readily change their shape on applying force and return to original shape when the applied force is removed. Common examples are gelatin, agar-agar, starch etc.

(ii) ***Non-elastic gels*** **:** These are the gels which are rigid and do not have the property of elasticity. For example, silica gel.

Application of colloids

(1) **Purification of water by alum** (coagulation) **:** Alum which yield Al^{3+} ions, is added to water to coagulate the negatively charged clay particles.

(2) **In rubber and tanning industry** (coagulation and mutual coagulation) **:** Several industrial processes such as rubber plating, chrome tanning, dyeing, lubrication etc are of colloidal nature

(i) In rubber platting, the negatively charged particles of rubber (latex) are made to deposit on the wires or handle of various tools by means of electrophoresis. The article on which rubber is to be deposited is made anode.

(ii) In tanning the positively charged colloidal particles of hides and leather are coagulated by impregnating, them in negatively charged tanning materials (present in the barks of trees). Among the tanning agent chromium salts are most commonly used for the coagulation of the hide material and the process is called ***chrome tanning***.

(3) **Artificial rains:** It is possible to cause artificial rain by throwing the electrified sand or silver iodide from an aeroplane and thus coagulating the mist hanging in air.

(4) **Smoke precipitation** (Coagulation)**:** Smoke is a *negative* sol consisting of carbon particles dispersed in air. Thus, these particles are removed by passing through a chamber provided with highly positively charged metallic knob.

(5) **Formation of deltas** (coagulation)**:** River water consists of negatively charged clay particles of colloidal dimension. When the river falls into the sea, the clay particles are coagulated by the positive Na^{+}, K^{+}, Mg^{2+} ions etc. present in sea water and new lands called deltas are formed.

(6) **Clot formation:** Blood consists of negatively charged colloidal particles (albuminoid substance). The colloidal nature of blood explains why bleeding stops by applying a ferric chloride solution to the wound. Actually ferric chloride solution causes coagulation of blood to form a clot which stops further bleeding.

(7) **Colloidal medicine:** Argyrol and protargyrol are colloidal solution of silver and are used as eye lotions colloidal sulphur is used as disinfectant colloidal gold, calcium and iron are used as tonics.

(8) **Coating of Photographic plates:** These are thin glass plates coated with gelatin containing a fine suspension of silver bromide. The particles of silver bromide are colloidal in nature.