

Physical Chemistry

Surface Chemistry and Colloids

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Introduction

Colloidal systems consist of finely divided particles of any substance dispersed in any medium. Ink, milky dispersion of sulphur, clays and humus, shaving cream, glue and blood serum are all examples of colloids. The dispersed entities are molecules or aggregates of molecules. Generally, these are smaller than coarse, filterable particles but larger than atoms and small molecules. The colloidal particles have dimensions in the range 0.000001–0.0005 nm i.e.

$$1 \text{ m}\mu - 500 \text{ m}\mu \text{ or } 10 - 5000 \text{ \AA}$$

Colloidal particles are invisible under ordinary microscopes and pass through the pores of ordinary filter paper. The dispersed phase can be liquid, solid or gas. For example: Emulsions are composed of liquid particles dispersed in another liquid. Foams contain bubbles of gas in liquid or solid. The degree of dispersion is a quantity varying reciprocally with size of the particles. Emulsions have low degree of dispersion and this means that the droplets are relatively coarse.

Definition of Colloids: A colloidal system is defined as a two phase heterogeneous system in which one phase is dispersed in a fine state of sub-division into another phase called dispersion medium as such i.e. dispersed phase + dispersion medium = Colloidal System.

Table 1 gives some characteristic properties of colloids as compared to “coarse dispersions” and “true solutions”. Table 2 represent some selected Inorganic and Organic Colloids. Table 3 gives the types of colloidal solutions.

Table 1 Characteristics of True Solutions, Colloidal Solutions and suspensions

	True solutions (Molecular Solutions)	Colloidal Solutions Colloidal Dispersion	Suspensions (Coarse Dispersion)
1.	The particle size are in the order of 1 m or 10Å	The particle sizes lie in the range of 1 mm– 200 mm i.e. 10Å–2000Å	The particle sizes are grater than 200 mm or 2000Å
2.	Particles are invisible under the electron microscope	Particles are invisible even under the most powerful microscope but its scattering effect can be observed in ultra microscope.	Particles are visible to the naked eye or at least through a microscope.
3	Particles diffuse readily through parchment membrane	Colloidal particles do not diffuse through parchment membrane	Particles do not diffuse
4	Particles readily pass through ordinary filter paper as well as through parchment membrane	Particles pass through filter paper	Particles do not diffuse through filter paper or parchment membrane
5	No scattering occurs	Particles scatter light. This scattering of light is called Tyndall effect	They do not show Tyndall effect

Table 2 Inorganic and Organic Colloids

Inorganic Colloids	Organic Colloids
(a) Metals such as Au, Ag sols	(a) Homopolar sols (rubber in benzene)
(b) Certain nonmetals sol.	(b) Hydroxy sols (Starch, glycogen in water)
(c) Sulphur sol. Graphite sol	(c) Heteropolar sols (proteins, soaps in water)
(d) Oxide and hydroxide sols (Ferric hydroxide sols)	
(e) Insoluble metal salts (AgBr, BaSO ₄ , AS ₂ S ₃ sols)	

Other kinds of colloids are (a) Natural Colloids and (b) Synthetic Colloids.

Table 3 Types of colloidal solutions

Dispersed phase	Dispersion medium	Colloidal system	Examples
Solid	Solid	Solids sols	Minerals, gem stones, glass, alloys. Paints, gold
Solid	Liquid	Sols	sol, muddy water, starch in water, proteins in water, gelatin in water, cell fluids.
Solid	Gas	Aerosols of solids	Smoke, dust storm.
Liquid	Solid	Gels	Butter, jellies, boot polish, cheese, jams.
Liquid	Liquid	Emulsion	Milk, medicines, shampoo, creams, emulsified oils
Liquid	Gas	Aerosols of liquids	Fog, mist, clouds, insecticide sprays pumice stone, foam rubber
Gas	Solid	Solid foam	Soda water, whipped cream, froth, soap lather etc.
Gas	Liquid	Foam, Froth	

Note: The gas in gas mixtures are always true solutions.

Colloidal systems in which a solid is dispersed in a liquid are frequently referred to as colloidal solutions or simply sols and depending upon the nature of the dispersion medium, colloidal solutions are sometimes given specific names. For example,

Dispersion medium	Name of colloidal solution
Water	Hydrosol
Alcohol	Alcosol
Benzene	Benzosol

(i). Classification Based on Affinity of Dispersed Phase for Dispersion Medium (Lyophilic and Lyophobic Colloids): Depending upon the nature of interactions between dispersed phase

and dispersion medium, colloidal solution can be classified as lyophilic (liquid-loving) and lyophobic (liquid-hating).

(a) Lyophilic colloids: *These are the colloidal solutions in which the particles of the dispersed phase have great affinity (love) for the dispersion medium.* In case water acts as the dispersed phase, the lyophilic colloid is called hydrophilic colloid. These are generally stable due to the strong attractive forces operating between the two phases. These are *reversible* in nature. On evaporating the sol, the dispersed phase obtained can be easily reconverted into the solution by simply agitating it with the dispersion medium. Gums, gelatine and starch form lyophilic (hydrophilic) sols.

(b) Lyophobic sols: *These are the colloidal solutions in which particles of the dispersed phase have no affinity for the dispersion medium.* Such solutions are relatively less stable and are not easily prepared. These can be easily precipitated by heating the sol or on adding small amount of electrolyte to it. *These are irreversible.* The solid obtained by precipitation cannot be reconverted into colloidal solution by simply shaking it with the dispersion medium. Colloidal solutions of gold, silver, $\text{Fe}(\text{OH})_3$, As_2S_3 etc. are lyophobic. Lyophobic sols need stabilising agents for their preservation.

Some important points of distinction between lyophilic and lyophobic colloids are given in Table 4.

Table 4 Distinction between Lyophilic and Lyophobic sols

	Property	Lyophilic	Lyophobic sols
1.	Preparation	Can be easily prepared by direct mixing.	Prepared only by special methods.
2.	<i>Nature</i>	Reversible	Irreversible
3.	Size of particles	Comparable size as true molecules.	Particles constitute aggregates of molecules.
4.	<i>Stabilisation</i>	Self stabilised.	Less stable and require traces of stabilisers.
5.	<i>Visibility</i>	Particles are not visible even under ultra-microscope.	Particles are visible under ultramicroscope.
6.	<i>Viscosity</i>	Viscosity is much higher than that of dispersion medium.	Same viscosity as of dispersion medium.
7.	<i>Surface tension</i>	It is less than that of dispersion medium.	Same surface tension as of dispersion medium.
8.	<i>Action of electric field</i>	Particles may move towards anode or cathode or may not move at all.	Particles may move towards cathode or anode depending upon the charge.

9.	Action of electrolyte	For coagulation of sol, large amounts of electrolytes are required.	For coagulation, small amounts of electrolytes are required.
10.	Tyndall effect	It does not exhibit Tyndall effect.	Exhibits Tyndall effect.
11.	Colligative properties	Have high values of colligative properties, such as osmotic pressure, elevation in b.pt., depression in f.pt. etc.	These show high osmotic pressure, less elevation in b.pt and low depression in f.pt.
12.	Charge	Little or no charge on particles	Particles carry positive or negative charge
13.	Solvation	Particles generally solvated	No solvation of particles.

(ii) Classification based upon molecular size: Depending upon the molecular size, colloids are of three types:

(a) Multimolecular colloids: These are the sols in which the particles of dispersed phase consist of aggregate of large number of atoms or small molecules having molecular size less than 1 nm ($1\text{ nm} = 10^{-9}\text{ m}$) and the aggregate has dimensions of colloidal size. In these colloids, the particles are held together by van der Waal's forces. Some examples of such colloids are (i) Sols of gold atoms (ii) Platinum of (iii) Sulphur sol. Sulphur sol consists of particles containing a thousand or more S_8 molecules.

(b) Macromolecular colloids: In this type of colloids, individual molecules have very large size, which is of colloidal dimensions. The macromolecules constituting the dispersed phase are generally polymers having very high molecular weights. Naturally occurring macromolecules are proteins, enzymes, gelatin, starch, cellulose, etc. Artificial macromolecules are polythene, polystyrene, nylon etc. Since the particle size in case of macromolecules is comparable to those of colloids, solutions of macromolecular substances are **macromolecular colloidal solutions**. Dispersions of macromolecules are quite stable and resemble true solutions in many respects. Thus, common examples of macromolecular colloids are (i) Proteins (ii) Starch (iii) Cellulose (iv) Plastics (v) Enzymes.

(c) Associated Colloids or Micelles: These are the substances which behave as normal electrolytes at low concentrations but as colloids at higher concentrations. It is because these form aggregated (associated) particles called **micelles** at higher concentration. The micelle formation takes place only above a particular concentration called **critical micelle concentration (CMC)** and above a particular temperature called **Kraft temperature (T_k)**. On dilution, these colloids again behave as electrolytes. These colloids have lyophilic as well as lyophobic parts. Micelles may contain as many as 100 molecules are more. Common examples of this type are surface active agents such as soaps and synthetic detergents. For soaps, the CMC is 10^{-4} to $10^{-4}\text{ mol L}^{-1}$.

Mechanism of Micelle Formation: Let us illustrate the micelle formation by taking the example of soap solutions. Soap is a sodium salt of higher fatty acids and may be represented as $\text{RCOO}^- \text{Na}^+$. Sodium stearate, $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^- \text{Na}^+$ is a common example of soaps. On dissolving in water, soap molecules dissociate to form RCOO^- and Na^+ ions. RCOO^- consists of two parts i.e. non-polar long hydrocarbon (R) chain, which is hydrophobic (water repelling) and the polar

COO⁻ group, which is hydrophilic (water loving). Due to their dual nature, i.e. water hating and water loving, association colloids are called **amphiphilic**. The hydrophilic part is **head** of the species and the hydrophobic part is called **tail** of species. In solution, the tail of the anion (RCOO⁻) tries to keep itself dry (being water hating) so it tends to orient away from water while its head interacts with water (being water loving). Above the CMC, RCOO⁻ ions form an oily aggregate with hydrocarbon chains (represented by wavy lines) pointing towards the centre and the COO⁻ part (represented by solid circle) outwards as shown in Figure 1. An aggregate thus formed is known as **ionic micelle**. These micelles contain large number of molecules.

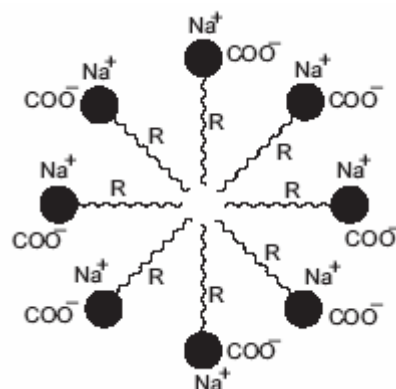


Fig. 1 Aggregation of RCOO⁻ ions to form anionic micells.

In a micellar system of sodium dodecyl sulphate (SDS) and water, a micelle is an aggregation of 80 SDS molecules and CMC is $8.1 \times 10^{-3} \text{ mol L}^{-1}$.

Stability of micelles: It may be attributed to the existence of protective film at the surface of colloidal particles. In absence of this protection, the colloidal particles would attract each other over great distance, join together and would coalesce into a single aggregate.

The cleansing action of soaps and detergents is based upon their ability to form micelles. For fear of water, the tail of soap molecule gets attached into grease oil (Figure 2) while the head of soap molecule gets buried in water leading to the formation of micellar system. Thus a negatively charged shell is formed which repels a possible attack from another similar particle and protects the oil globules from growing into bigger aggregates. Hence, a stable emulsion is formed which can be easily washed away with water and the dirt sticking to the grease is removed.

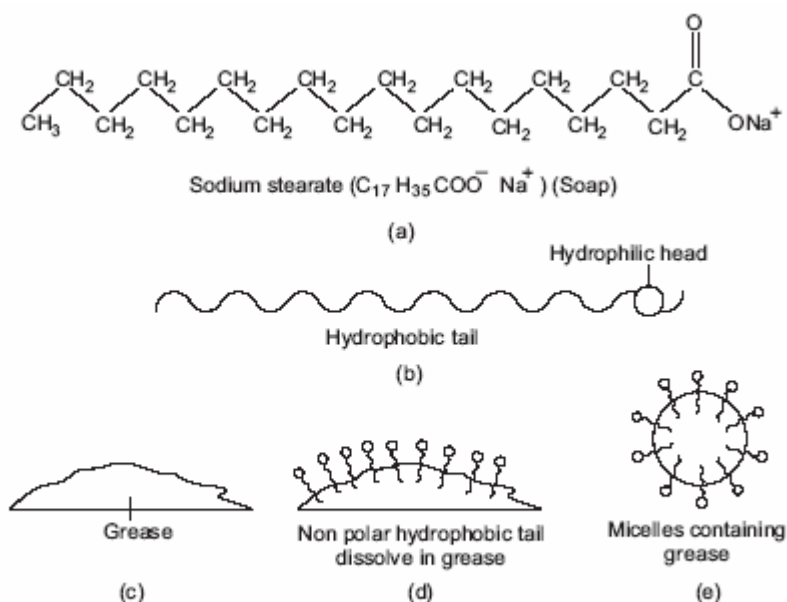


Fig. 2 Cleansing action of soap

Comparison of some important characteristics of multimolecular, macromolecular and associated colloids.

	Multimolecular colloids	Macromolecular colloids	Associated colloids
1.	They consist of aggregates of a large number of atoms or molecules with diameter less than 1 nm e.g. sols of gold, sulphur etc.	The particles of dispersed phase themselves are of large size e.g. polymers like nylon, starch, protein, rubber etc.	Behave as normal electrolytes at low concentrations and as colloids at higher concentrations due to the aggregation of a large number of ions in concentrated solutions.
2.	Their molecular masses are not very high.	They have high molecular masses.	Their molecular masses are generally high.
3.	The atoms or molecules in them are held by weak van der Waals's forces.	The van der Waal's forces holding the particles are comparatively stronger due to the presence of long chain.	The van der Waal's forces depend upon the concentration. Higher the concentration, greater are the van der Waal's forces.
4.	They are usually lyophilic in nature	They are usually lyophobic in nature.	Their molecules contain both lyophilic and lyophobic groups.

Preparation of Colloidal Solutions

(a) Preparation of Lyophilic Sols: Hydrophilic colloids such as starch, gum, gelatin, etc. form colloidal solution when warmed or left in contact with water for a long time. The particles are already of colloidal size and they are readily dispersed in water forming colloidal solution. Sols of water insoluble high molecular weight compounds may similarly be obtained by their dispersal in suitable liquids.

(b) Preparation of Lyophobic Sols: Lyophobic sols cannot be prepared by direct mixing of dispersed phase and the dispersion medium. These are prepared by using special techniques. The methods employed for the preparation of lyophobic colloids fall into two categories:

(i) Dispersion methods in which larger macro-sized particles are broken down to colloidal size.

(ii) Condensation methods in which particles of colloidal size are produced by aggregation of single ions or molecules.

A. Dispersion Methods

1. Bredig's Electric Arc Method: This method is employed to prepare sols of metals such as copper, silver, gold or platinum. The two electrodes used in this method are made of the metal whose sol is to be prepared. The electrodes are immersed in dispersion medium such as water (Figure 3). The dispersion medium is cooled by immersing the container in an ice bath and a trace of alkali is added. An arc is struck between the metal electrodes held close together. The tremendous heat generated by the spark across the electrodes vapourises some of the metal and the vapour condenses immediately in the dispersion medium to give colloidal solution. The trace of added alkali helps to stabilise the sol.

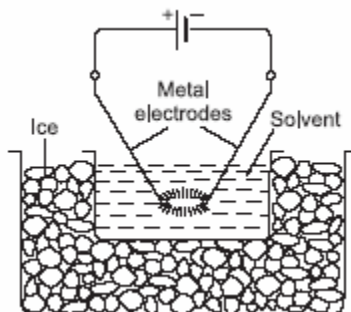


Fig. 3 Electrodispersion Process

2. Mechanical Dispersion: It is done with the help of a colloid mill. The mill consists of two steel discs with a small gap between them. The discs rotate in opposite direction at high speed. The substance whose sol is to be prepared is first ground as finely as possible and then shaken with the dispersion medium to get a suspension. The suspension is now added to the colloid mill (Figure 4). The speed of the rotating discs is adjusted so that the particles of the suspension are broken to produce the particles of colloidal size.

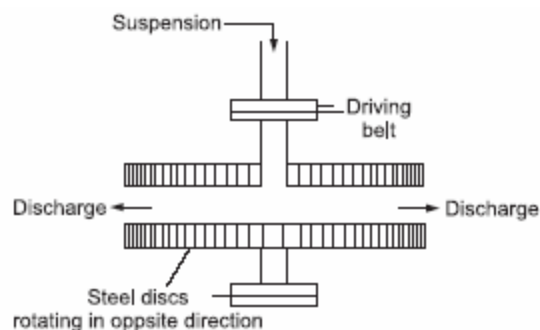


Fig. 4 Colloid mill

3. Ultrasonic Dispersion: Sound waves having frequency more than that of the audible sound are called ultrasonic waves. These waves can produce particles of colloidal size from coarse suspension. This method is used to prepare a sol of mercury in water.

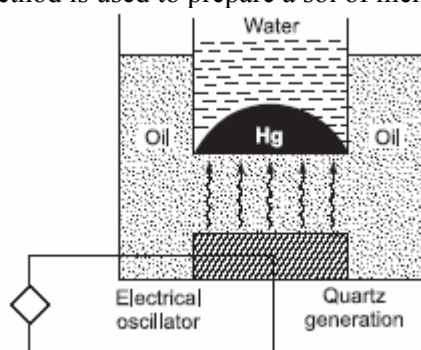


Fig. 5 Ultrasonic dispersion Process

The ultrasonic waves produced from a quartz generator (Figure 5) propagate through the oil and strike the beaker containing mercury under water. The ultrasonic waves transfer their energy to the atoms of mercury. Mercury gets vapourised and the vapours disperse in water producing colloidal solution. This is the latest method for the preparation of metal sols from their coarse suspension.

4. Peptization: The process, which involves the conversion of freshly prepared precipitate into colloidal solution by the addition of a suitable electrolyte is called peptization. The electrolyte added is called peptizing agent or dispersion agent. For example, if freshly prepared ferric hydroxide precipitate is treated with a small quantity of FeCl_3 (electrolyte) solution, a dark reddish brown colloidal solution of Fe(OH)_3 is formed. Here FeCl_3 is a peptizing agent. This process is reverse of coagulation. Similarly, a colloidal solution of Al(OH)_3 is obtained when freshly precipitated Al(OH)_3 is treated with a small quantity of dilute HCl (acid added being insufficient to convert hydroxide completely into chloride)

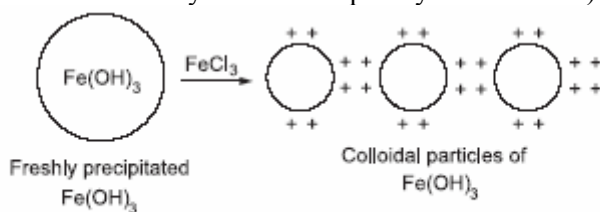


Fig. 6 Peptization

Cause of peptization: The peptizing action is due to the preferential adsorption of one of the ions of the electrolyte, which then gives to the colloidal particle a positive or negative charge. For example $\text{Fe}(\text{OH})_3$ adsorbs Fe^{3+} ions from FeCl_3 (peptizing agent) and thereby gets a positive charge on the surface. Particles carrying similar charges get separated, yielding smaller sized colloidal particles of the type $\text{Fe}(\text{OH})_3\text{Fe}^{3+}$ (Figure 6). Similarly, As_2S_3 precipitate obtained by passing H_2S through arsenious oxide solution is peptized on treatment with excess H_2S and yield a negatively charged sol. of $[\text{As}_2\text{S}_3]\text{S}^{2-}$.

B. Condensation or Aggregation Methods

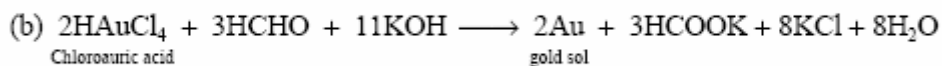
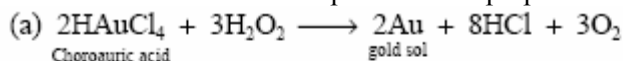
1. Lowering of solubility by exchange of solvent: In this method, a substance is dissolved in a solvent and then the solution is added to another solvent in which it is less soluble. For example if an alcoholic solution (true solution) of sulphur is added in excess of water, a colloidal solution of sulphur results. Sulphur is insoluble in water.

2. Passing vapours of an element into a liquid: When the vapours of an element are passed through a liquid, condensation takes place to give a colloidal solution. For example, colloidal solution of mercury can be obtained by passing the vapours of mercury into cold water containing suitable stabilising agents such as ammonium salts or citrates. Sulphur sol can also be prepared by using a similar procedure.

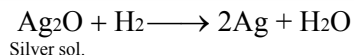
3. Excessive cooling: The method can be used to get colloidal solution of ice in an organic solvent like chloroform or ether. A solution of water in the required solvent is frozen. The molecules of water, which can no longer be held in the solution, get together to form particles of colloidal size.

4. Preparation of colloidal sol by chemical methods:

(1) Reduction Method: Gold or Silver sols are prepared by reduction of the corresponding salts. In this method pure sols are prepared. The following reactions take place:



(c) Reduction of Ag_2O by hydrogen.

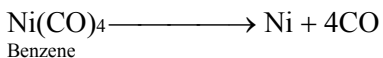


(2) Oxidation Method: Sulphur sol is prepared by the oxidation of H_2S by SO_2 .

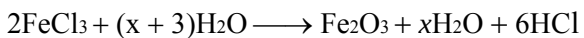


Sols of halides of silver, lead and mercury are obtained by oxidation of the corresponding metal sols with chlorine, bromine or iodine until the characteristic colour of the metal sol is destroyed. To stabilise the sol, some stabilising agent is to be added.

Dissociation: Thermal dissociation of nickel tetracarbonyl in benzene gives nickel benzosol.

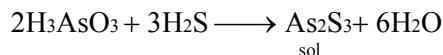


Hydrolysis Method: This method is most frequently used for preparing the common hydrous oxide sols. Ferric oxide sol is prepared by adding concentrated solution of ferric chloride slowly to the boiling water according to the equation.

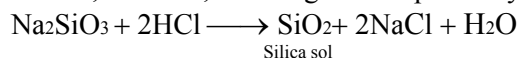


Similarly we can prepare the hydrous oxide sol of Fe, Cr, Al, Cu, Pb, Sn etc.

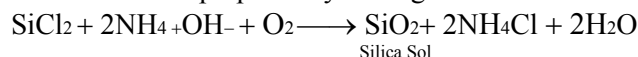
Double Decomposition Method: As_2S_3 sol is usually prepared by the reaction between hydrogen sulphide and arsenious acid:



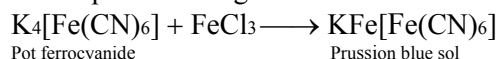
Colloidal silica, stannic oxide and tungstic oxide is prepared by adding HCl to solutions of sodium silicate, stannate, and tungstate respectively e.g.



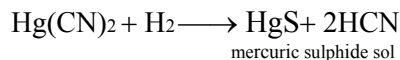
Similar sols can also be prepared by adding ammonia solution to their respective chlorides. e.g.



Sols of prussian blue is prepared by the reaction between potassium ferrocyanide and ferric chloride in the presence of gelatin.



Organosol of HgS is prepared by the reaction of H_2S with $\text{Hg}(\text{CN})_2$ in methanol, ethanol, *n*-propanol or in acetone.



Purification of Colloidal Solutions

Colloidal solutions obtained by chemical methods contain appreciable amounts of electrolytes. To obtain pure sol, it is necessary to remove those electrolytes which tend to coagulate the colloidal particles. The methods employed for this purpose are:

1. Dialysis
2. Electro dialysis
3. Ultra filtration

1. Dialysis: We know that the particles of the colloidal solution cannot pass through the parchment paper, cellophane or animal membrane while those of the pure solution can easily pass through them. It is due to the difference in their particle size. *The process of separating a crystalloid from a colloid by diffusion through a parchment paper or animal membrane is called dialysis. The apparatus which is employed to effect such separation is called **Dialyser**.*

Dialyser used by Graham is known as **Graham's dialyser**. It consists of a hollow cylinder open at both ends. One end of this cylinder is closed by a membrane. A bag made of animal membrane can also be used in place of hollow cylinder (Figure 7). Impure colloidal sol is placed in the dialyser, which is then suspended in a large vessel containing distilled water. The pores of the membrane permit the ions and small molecules to pass through but not the large colloidal particles. By using a continuous flow of fresh water, the concentration of the electrolyte in the

outside vessel is maintained at a negligible level. Thus diffusion of the ions into pure water takes place at a reasonable rate. In this way, practically all the electrolyte present in the sol can be removed easily. Dialysis can be used to remove HCl from ferric hydroxide sol.

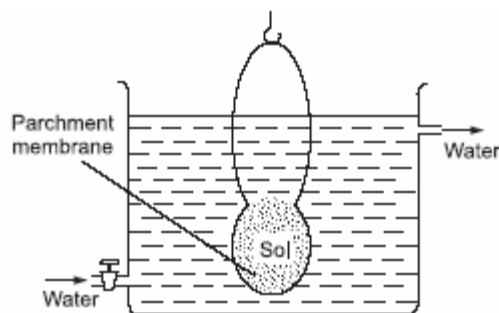


Fig. 7 Dialysis of a sol

2. Electrodialysis: Dialysis is a slow process. To hasten the process, dialysis is carried out under the influence of an electric field. The cations and anions of the electrolyte will be attracted towards the oppositely charged electrodes (Figure 8).

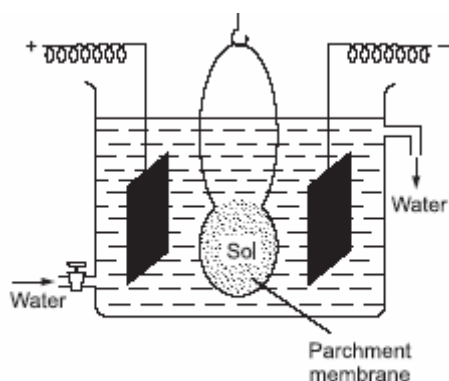


Fig. 8 Electrodialysis

Limitation: Electrodialysis is not suitable for the removal of non-electrolyte impurities such as sugar and urea.

3. Ultra filtration: The separation of crystalloids from colloidal system can also be carried out by ultra-filtration. Ordinarily the filter papers have pores larger than one micron (10^{-6} m). Thus, the colloidal particles can pass through these filter papers along with ions or molecules. *The pores of the filter paper can be made smaller by soaking it in a solution of gelatin or a colloidal and then in turn hardening them by soaking in formaldehyde.* As a result the pores of the filter paper become smaller and the colloidal particles cannot pass through them. Filter papers thus prepared are known as **ultra-filters**. The process of separating colloids from crystalloids by using ultra-filters is called ultra-filtration. By soaking filter papers in solutions of colloid of different concentrations, a series of graded filter papers can be prepared. Even the finest paper will allow the passage of crystalloids through them. Ultra-filters permit the separation of colloidal particles of different sizes from one another.

Properties of Sols

1. Heterogeneity: A colloidal solution is heterogeneous in nature and consists of two phase i.e., the colloidal particles (dispersed phase) and the dispersion medium. Since the colloidal particles are small in size, a sol appears to be homogeneous to the naked eye. However, their heterogeneous nature can be confirmed by seeing under electron microscope.

2. Filterability: Ordinary filter papers have large pore size. Therefore, colloidal particles can pass through them. However, they cannot pass through animal and vegetable membranes and ultra filter papers. This idea tells the basis of separation of colloidal particles from those of crystalloids.

3. Stable nature: Colloidal solutions are quite stable and the colloidal particles do not settle at the bottom. This is because of the constant motion of colloidal particles.

4. Colligative properties: As the colloidal particles are the aggregates of simple molecules, the number of particles per litre of the sol is relatively much smaller than in a true solution. Hence the values of the colligative properties such as elevation in boiling point, depression in freezing point and lowering of vapour pressure are much smaller as compared to true solutions. However, the osmotic pressure of colloidal solutions, though smaller than true solutions is measurable and gives information regarding the number of particles present in one kg of the dispersion medium. Osmotic pressure values thus can be used for the calculation of molecular weights of polymers like proteins.

Optical Properties of Colloids

Light Scattering

When a beam of light is directed at a colloidal solution or dispersion, some of the light is absorbed (colour is produced when light of certain wavelengths is selectively absorbed), some is scattered and the remainder is transmitted undisturbed through the sample. Light scattering results from the electric field associated with the incident light including periodic oscillations of the electron clouds of the atoms of the material in question—these then act as secondary sources and radiate scattered light.

The Tyndall effect-turbidity

All colloidal solutions are capable of scattering light (Tyndall effect) to some extent. The noticeable turbidity associated with many colloidal dispersions is a consequence of intense light scattering. A beam of sunlight is often visible from the side because of light scattered by dust particles. Solutions of certain macromolecular materials may appear to be clear but in fact they are slightly turbid because of weak light scattering. Only a perfectly homogeneous system would not scatter light; therefore, even pure liquids and dust-free gases are very slightly turbid. The turbidity of a material is defined by the expression

$$\frac{I_t}{I_0} = \exp [-\tau l]$$

where I_0 is the intensity of the incident light beam, I_t is the intensity of the transmitted light beam, l is the length of the sample and τ is the turbidity.

There is a wide variation of the intensity of Tyndall cone for colloidal particles. Greater the difference between the refractive index of the dispersed phase and dispersing medium, more intense the cone is. When the difference between the two phases is almost the same, the Tyndall cone will be very faint or entirely absent. This is why lyophobic sols give more clearer cone than lyophilic systems. The Tyndall cone can be observed through ultra microscope as shown below (Figure 9).

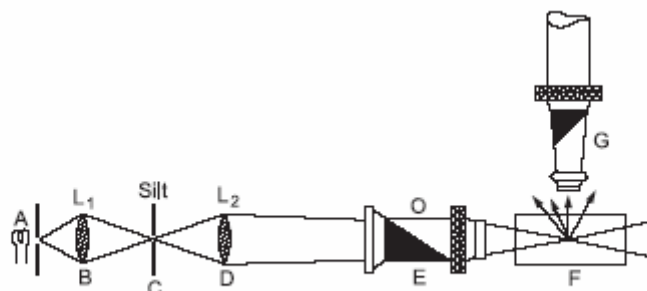


Fig. 9 Tyndall effect

A is an arc light whose beams are condensed by a lens B. This condensed beam passes through a slit C placed near the point of convergence to make the beam narrow to the desired extent. The beam is then passed through another converging lens D in front of which is placed an objective lens O/E whose function is to reduce the image of the slit. The beam is focused by the lens D into the objective lens E before entering cell F. The light scattered by the colloidal particle (kept in F) is observed by a microscope G at an angle of 90° with the direction of the beam. The whole thing is so adjusted that a sharp Tyndall cone is produced inside F immediately below the microscope objective. The colloidal particles will appear as pin points twinkling and moving against the dark background of the dispersion medium. An ultra microscope can resolve particles as small as $3 \text{ m}\mu$ ($3 \times 10^{-7} \text{ cm}$).

Particle size: The size of the colloidal particle in sol may be calculated by counting the volume in a given number by means of ultra-microscope and analyzing for the concentration of dispersed phase. If n be the number of particles per mL of sol, m be the total amount of dispersed phase per mL and d be the density of dispersed phase then the volume of a single particle is

$$V = \frac{m}{nd}$$

Assuming that particles are cubes i.e. $V = l^3$ (l = length of one side or a cube)

$$\text{or, } l^3 = \frac{m}{nd} \quad \therefore l = \left(\frac{m}{nd} \right)^{1/3}$$

Alternatively if we assume that particles are spherical then

$$V = \frac{4}{3} \pi r^3 \quad (r = \text{radius of particle})$$

$$\text{or, } \frac{4}{3} \pi r^3 = \frac{m}{nd} \quad \therefore r = \left(\frac{3m}{4\pi nd} \right)^{1/3}$$

$\therefore$ The radius of particle can be calculated.

Measurement of Scattered light

As we shall see, the intensity, polarisation and angular distribution of the light scattered from a colloidal system depends on the size and shape of the scattering particles, the interactions between them, and the difference between the refractive indices of the particles and the dispersion medium. Light-scattering measurements are, therefore, of great value for estimating particle size, shape and interactions, and have found wide application in the study of colloidal dispersion, association colloids, and solutions of natural and synthetic macromolecules.

Light scattering offers the following advantage over some of the alternative techniques of particle-size analysis:

- (1) It is absolute and no calibration is required.
- (2) Measurements are made almost instantaneously, which makes it suitable for rate studies.
- (3) There is no significant perturbation of the system.
- (4) The number of particles involved is very large, which permits representative sampling of polydispersed samples.

The intensity of the light scattered by colloidal solutions or dispersions of low turbidity is measured directly. A detecting photocell is mounted on a rotating arm to permit measurement of the light scattered at several angles, and fitted with a polaroid for observing the polarisation of the scattered light (see Figure 10). Weakening of the scattered beam itself as it passes through the slightly turbid sample can be neglected, and its intensity can be compared with that of the transmitted beam.

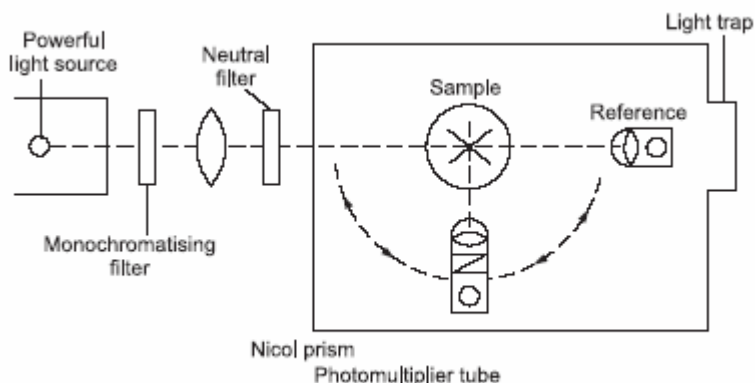


Fig. 10 Measurement of scattered light

Although simple in principle, light-scattering measurements present a number of experimental difficulties, the most notable being the necessity to free the sample from impurities such as dust, the relatively large particles of which would scatter light strongly and introduce serious errors.

Light-scattering theory

It is convenient to divide the scattering of light by independent particles into three classes:

- (1) Rayleigh scattering (where the scattering particles are small enough to act as point sources of scattered light).
- (2) Debye scattering (where the particles are relatively large, but the difference between their refractive index and that of the dispersion medium is small).

(3) Mie scattering (where the particles are relatively large and have a refractive index significantly different from that of the dispersion medium).

Kinetic Properties of Colloids

Brownian motion and translational diffusion

Brownian motion: A fundamental consequence of the kinetic theory is that, in the absence of external forces, all suspended particles, regardless of their size, have the same average translational kinetic energy. The average translational kinetic energy for any particle is $\frac{3}{2}kT$ or $\frac{1}{2}kT$ along a given axis—i.e. $\frac{1}{2}m(dx/dt)^2 = \frac{1}{2}kT$, etc.; in other words, the average particle velocity increases with decreasing particle mass.

The motion of individual particles is continually changing direction as a result of random collisions with the molecules of the suspended medium, other particles and the walls of the containing vessel. Each particle pursues a complicated and irregular zig-zag path. When the particles are large enough for observation, this random motion is referred to as *Brownian motion*, after the botanist who first observed this phenomenon with pollen grains suspended in water. The smaller the particles, the more evident is Brownian motion.

Treating Brownian motion as a three-dimensional ‘random walk’, the mean Brownian displacement $\bar{x}$ of a particle from its original position along a given axis after a time t is given by Einstein’s equation.

$$\bar{x} = (2Dt)^{\frac{1}{2}} \quad \dots (1)$$

where D is the diffusion coefficient.

The theory of random motion helps towards understanding the behaviour of linear high polymers in solution. The various segments of a flexible linear polymer molecule are subjected to independent thermal agitation, and so the molecule as a whole will take up a continually changing and somewhat random configuration. The average distance between the ends of a completely flexible and random chain made up of n segments each of length $l(n)^{\frac{1}{2}}$ (cf. Einstein’s equation above). This average end-to-end distance becomes $l(n)^{\frac{1}{2}}$ if an angle of $109^\circ 28'$ (the tetrahedral angle) between adjacent segments is specified.

The diffusion coefficient of a suspended material is related to the frictional coefficient of the particles by Einstein’s law of diffusion:

$$Df = kT \quad \dots (2)$$

Therefore, for spherical particles,

$$D = \frac{kT}{6\pi\eta a} = \frac{RT}{6\pi\eta a N_A} \quad \dots (3)$$

where N_A is Avogadro constant, and

$$\bar{x} = \left(\frac{RTt}{3\pi\eta a N_A} \right)^{1/2} \quad \dots (4)$$

Translational diffusion

Diffusion is the tendency for molecules to migrate from a region of high concentration to a region of lower concentration and is a direct result of Brownian motion. Fick's first law of diffusion (analogous with the equation of heat conduction) states that the mass of substance dm diffusing in the x direction in a time dt across an area A is proportional to the concentration gradient dc/dx at the plane in question:

$$dm = -DA \frac{dc}{dx} dt \quad \dots (5)$$

(The minus sign denotes that diffusion takes place in the direction of decreasing concentration.)

The rate of change of concentration at any given point is given by an exactly equivalent expression, Fick's second law:

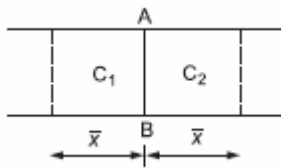
$$\frac{dc}{dt} = -D \frac{d^2c}{dx^2} \quad \dots (6)$$

The proportionality factor D is called the diffusion coefficient. It is not strictly a constant, since it is slightly concentration-dependent.

Equations (1) and (2) can be derived using equation (5), as follows.

Brownian displacement equation (1) i.e. $\bar{x} = (2Dt)^{1/2}$

Consider a plane AB passing through a dispersion and separating regions of concentration c_1 and c_2 , where $c_1 > c_2$. Let the average Brownian displacement of a given particle perpendicular to AB be $\bar{x}$ in time t . For each particle, this displacement has equal probability of being 'left to right' or 'right to left'.



The net mass of particles displaced from left to right across unit area of AB in time t is, therefore, given by

$$m = \frac{(c_1 - c_2)\bar{x}}{2} = \frac{(c_1 - c_2)\bar{x}^2}{2\bar{x}}$$

$$\text{If } \bar{x} \text{ is small, } \frac{c_1 - c_2}{\bar{x}} = -\frac{dc}{dx}$$

Therefore,

$$m = -\frac{1}{2} \frac{dc}{dx} \bar{x}^2 \quad \dots (7)$$

From equation(5)

$$m = -D \frac{dc}{dx} t \quad \dots (8)$$

Therefore, combining equations (7) and (8),

$$\bar{x} = (2Dt)^{1/2} \quad \dots (1)$$

Diffusion equation (2)

The work done in moving a particle through a distance dx against a frictional resistance to motion $f(dx/dt)$ can be equated with the resulting change in chemical potential given by the expression

$$d\mu = kT d \ln c \quad \text{i.e.} \quad f \cdot \left(\frac{dx}{dt} \right) dx = kT d \ln c$$

therefore,

$$\frac{dx}{dt} = \frac{kT}{f} \frac{d \ln c}{dx} = \frac{kT}{fc} \frac{dc}{dx} \quad \dots (9)$$

Since

$$-\frac{dm}{dt} = Ac \frac{dx}{dt}$$

then combining this expression with equation (9) gives

$$c \frac{dx}{dt} = D \frac{dc}{dx} \quad \dots (10)$$

Therefore, combining equations (9) and (10), we get

$$Df = kT \quad \dots (11)$$

For a system containing spherical particles, $D = RT/6\pi\eta aN_A$ i.e. $D \propto 1/m^{1/3}$, where m is the particle mass. For systems containing asymmetric particles, D is correspondingly smaller. Since $D = kT/f$, the ratio D/D_0 (where D is the experimental diffusion coefficient and D_0 is the diffusion coefficient of a system containing the equivalent unsolvated spheres) is equal to the reciprocal of the frictional ratio f/f_0 .

Kinetic Property of Colloids (Brownian Movement)

Brownian Movement: The English botanist Rober Brown observed that pollen grains dispersed in water executed a ceaseless random motion, this perpetual zig-zag motion of the colloidal particles (Figure 11) is called Brownian motion after the name of discoverer.

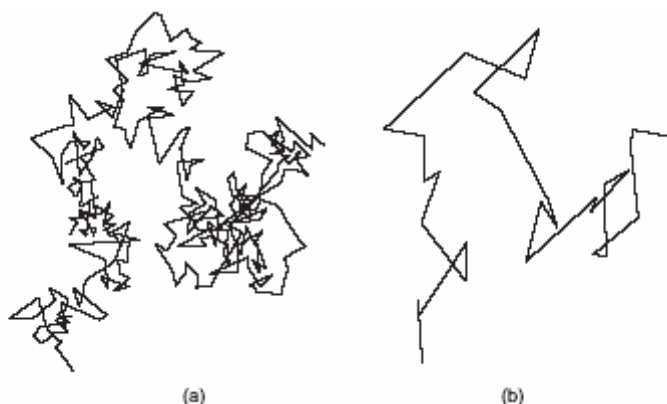


Fig. 11 (a) An observed Brownian motion path of a gamboge particle, (b) the same path, but with only every tenth position shown and connected by straight lines.

The Brownian movement is not caused by external influences such as vibration, convection current or effect of light nor does it originate from gravitational, magnetic, electrical or surface tension forces. This rapid motion is caused by bombardment of colloidal particles suspended in the medium.

Electrical Properties of Colloids (Electrophoresis)

There are two kinds of electrical properties encountered in colloid chemistry. See table 6.

Table 6 Electrical properties

Name	Phenomenon	Produced by
(1) Electrophoresis	Movement of sol particles with respect to the liquid	Applied EMF
(2) Electro-osmosis	Movement of liquid with respect to particles fixed in a porous diaphragm	Applied EMF

The colloidal particle of a sol usually carry either positive or negative charge. Sols, which carry positive charge are called positive sols. Examples of such types of sol are $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, TiO_2 and basic dye stuffs. Correspondingly sols, which carry negative charge, are called **negative sols**. Examples of such types of sols are metal sols such as Ag, Cu, Au, Pt etc., metal sulphides (As_2S_3 , Sb_2S_3 , CdS etc.), gums, starch soap solution and some acid dyestuffs.

Definition

The migration of electrically charged colloidal particles under an applied electric potential is called electrophoresis.

When a sol is placed in an electric field, colloidal particles move towards either cathode or anode depending upon the charge on them. ***This migration of colloidal particles under the influence of an electric field towards an electrode is called electrophoresis.*** If the movement of colloidal particles is towards the cathode, it is called **cataphoresis**. By observing the direction of motion of sol particles under the influence of electric field, we can determine whether they carry positive or negative charge. The phenomenon of electrophoresis can be demonstrated by using an apparatus

shown in figure 12. The apparatus consists of a U-tube provided with two platinum electrodes and a stopcock through which it is connected to a funnel shaped reservoir. A small amount of water is first placed in the U-tube and a reasonable quantity of the sol is taken in the reservoir. The stopcock is then slightly opened and the reservoir is gradually raised so as to introduce the sol in the U-tube gently. The water is displaced upwards producing a sharp boundary. When an electric current of 50–200 volts is passed by connecting the electrodes to the terminals of a battery, the colloidal particles move towards the electrodes. The movement of the colloidal particles can be followed by observing the position of the boundaries by means of a naked eye or a lens. When the particles are negatively charged (as in the case of arsenous sulphide sol), the boundary on the cathode side is seen to move down and that on anode side to move up showing that the particles move towards the anode. Thus, by noting the direction of motion of the particles in an electric field, it is possible to determine the sign of the charge on the colloidal particles.

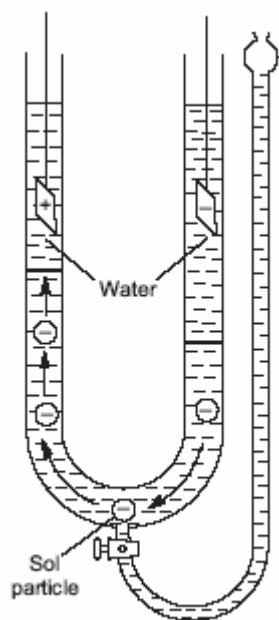


Fig. 12 Electrophoresis

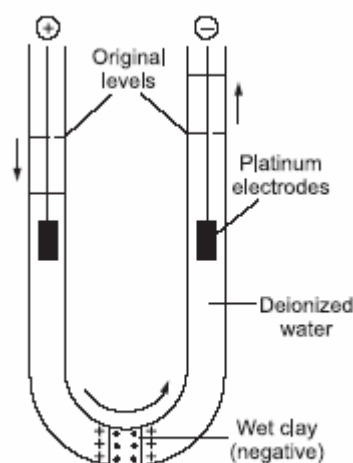


Fig. 13 Illustration of Electro-osmosis

Applications: The process can be utilised in determining the charge on colloidal particles. It finds application in removing carbon from smoke, dirt from sewage and in electro deposition of rubber.

(b) Electro-osmosis: Colloidal particles carry either positive or negative charge and the sol as a whole is electrically neutral. Therefore, the dispersion medium carries an equal but opposite charge to that of the colloidal particles. Thus the dispersion medium will move in opposite direction to the dispersed phase under the influence of an electric field. When the dispersed phase is kept stationary, the dispersion medium is actually found to move towards one or the other electrode. *The movement of the dispersion medium under the influence of an electric field is called electro-osmosis.*

The phenomenon of electro-osmosis can be demonstrated with the help of an apparatus shown in figure 13. The apparatus consists of a U-tube fitted with a plug of wet clay (a negative sol). The two limbs of the tube are filled with water to the same level. The platinum electrodes are immersed in water. When a potential difference is applied across the electrodes, the dispersion medium is seen to move towards the negative electrode. This shows that the charge on the

medium is positive. Similarly, for a positively charged colloid, electro-osmosis will take place in the reverse direction.

Application: Electro-osmosis can be used in dewatering of most clay, drying of dye pastes and the removal of water from peat.

The origin of charge can be explained on the basis of the following:

(i) Due to frictional electrification: It is believed that the frictional electrification caused by the mutual rubbing of the colloidal particles with molecules of the dispersion medium results in some charge on the colloidal particles.

(ii) Electron capture: Electron capture by colloidal particles from air and during electro-dispersion in Bredig's arc method may also result in some charge on colloidal particles.

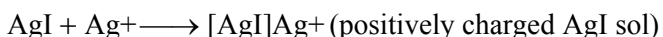
(iii) Preferential adsorption of ions from solutions: It has been found that sols are often associated with small quantities of electrolytes. If the electrolyte (ions) is completely removed from the colloidal solution by repeated dialysis or ultra filtration, the sol becomes unstable. Thus, it is believed that the charge on the colloidal particles is due to the preferential adsorption of either positive or negative ions on their surface. If the positive ions get adsorbed then the sol particles acquire a positive charge. The positive charge on $\text{Fe}(\text{OH})_3$ colloidal particles is due to the preferential adsorption of Fe^{3+} ions on the surface of the particles. The Fe^{3+} ions get produced by the ionisation of ferric chloride. The negative charge on arsenous sulphide sol is due to the preferential adsorption of sulphide ions on the surface of colloidal particles. The sulphide ions are available from the ionisation of hydrogen sulphide. Metal sols are usually prepared by Bredig's arc method. The negative charge on the metal sol is due to the preferential adsorption of hydroxyl ions furnished by the traces of alkali added.

It is important to note that the ion which is more closely related chemically to the colloidal particle is preferentially adsorbed by it. Clearly, in ferric hydroxide sol, Fe^{3+} ion (and not Cl^- ion from FeCl_3) is preferred. In arsenous sulphide, sulphide ion (and not H^+ ion from H_2S) is preferred. Sometimes it is possible to have positively as well as negatively charged sol of the same substance. For example,

(i) When a dilute solution of silver nitrate is added to a slight excess of dilute solution of potassium iodide, a negatively charged sol of silver iodide is formed. It is due to the adsorption of iodide ions (I^-) from the dispersion medium on the precipitate of silver iodide (AgI).



(ii) When a dilute solution of potassium iodide is added to a slight excess of a dilute solution of silver nitrate, a positive charged sol of silver iodide is formed. It is due to the adsorption of Ag^+ ions from the dispersion medium on the precipitate of silver iodide (AgI).



Similarly, when FeCl_3 is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of Fe^{3+} ions. On the other hand, a negatively charged sol is due to adsorption of OH^- ions is obtained when ferric chloride is added to NaOH .



(iii) **Colloidal particles may also acquire charge by the direct ionisation** of the material constituting the particles. An acidic dyestuff furnishes H^+ ions leaving an equivalent amount of negative charge on the particles. Similarly, a basic dyestuff ionises to give hydroxyl ions in solution. Thus, an equivalent amount of positive charge is left on the particles.

(iv) **Dissociation of the molecular electrolytes adsorbed on the surface of particles.** In certain cases, charge on colloidal particles arises from the dissociation of molecules of electrolytes adsorbed on the surface of colloidal particles. For example, H_2S molecules get adsorbed on colloidal particles of metal sulphide during precipitation. Due to dissociation of H_2S , H^+ ions are lost thereby imparting negative charge to colloidal particles. Origin of Charge on Colloidal Particles

The colloidal system is always conducting to the some extent. The colloids have excess or deficiency of electrons. These ions are attached to the particle. The electrostatic forces cannot be responsible for the attachment of these charges to the particle. Hence other forces—covalent bonding, van der Waal's forces or highly localized electrostatic forces are responsible for charges of colloidal particles.

Proteins are formed by long chains of amino acids joined by peptide linkages. Some of the amino acids carry an additional carboxyl or amino group and these may remain free exposed to the solvent. Thus they can form COO^- and NH_4^+ ions, which are covalently attached to the particle. Near neutrality, both NH_4^+ and COO^- groups are present in almost equal number and this is known as **isoelectric point** and net-charge at this point is zero and this corresponding pH is called as isoelectric pH. This corresponds to the presence of equal amounts of oppositely charged groups on the particle. Such a neutral structure of charged particle is called dipolar ion or "zwitterion".

Many porous solids contain building block of acidic or basic groups. Examples include some naturally occurring silicates, zeolite and many synthetic materials. These compounds contain cross-linked long chains, an insoluble network structure. These compounds may contain weakly acidic carboxyl groups or strongly acidic sulphonic acid groups or weakly basic amino groups or strongly basic quaternary ammonium groups. Because of the insoluble nature, these solids are widely used to remove other ions from solutions and are called ion exchangers.

In these two cases, the charge-giving ions are clearly held by covalent bonds.

Gold sol adsorbs strongly the chloride ions forming $AuCl_4^-$ by surface reaction and thus acquire a negative charge by chemisorption.

The water-oil adsorbs ions with long hydrophobic tails, such as fatty acids, long chain sulfonates or sulphates etc. Thus, droplets of emulsions acquire a charge by adsorption of such ions upon their surface (fig. 14) which is governed purely by van der Waals forces.

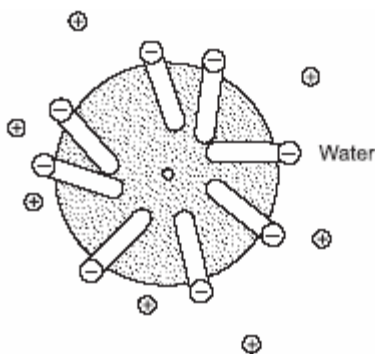


Fig. 14 An oil droplet can acquire a charge by adsorption of amphipathic ions through van der Waal's forces

AgI is an insoluble salt and its solubility product is 10^{-17} . Since the size of iodide ions is greater than that of silver ion, so the iodide ion is more polarized. When the concentrations of the two ions in solution are equal the Ag^+ ions escape more rapidly and the particle is charged negatively. To keep the Ag^+I^- neutral, it is not until the Ag^+ ion concentration is increased above 10^{-6} and I^- ion concentration is decreased to 10^{-11} . At higher concentration of Ag^+ ion and lower concentration of I^- ion, it becomes positively charged (Figure 15).

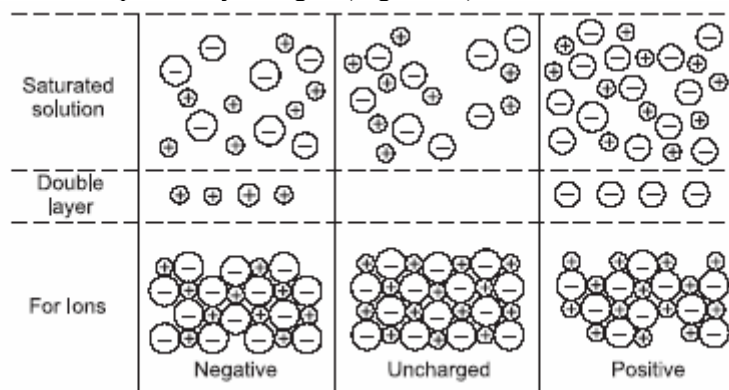


Fig. 15 Schematic presentation of the variation of charge on a AgI particle with the concentration of potential-determining ions in the saturated solution. The concentrations of the + and – ions in solution change from left to right while their product remains constant. Note that ions are missing from the lattice of the charged particles

Table 7 Charge of particle of various colloids

Positively Charge Colloids	Negatively Charge Colloids
Ferric hydroxide, aluminium hydroxide, chromium hydroxide, thorium dioxide, zirconium dioxide, methylene blue, and other basic dyes, basic proteins.	Gold, silver, platinum, sulphur, selenium carbon, As_2S_3 , Sb_2S_3 , Pb, Cu, stannic acid, silicic acid, V_2S_5 , congo red and other acid dyes, Albumins, casein, gums, resins, viruses and microbes

The same specificity of charge (Table 7) is observed also with some lyophilic sols. For positively charge colloids such as proteins the charge on the colloidal particle depends on the pH of the solution. Above a certain pH, characteristic for each sol, colloidal particles are negatively charged, while below this pH, they have a positive value. The *isoelectric point* of a colloiddally dispersed material is the pH value of the dispersion medium at which the dispersed phase does

not migrate in an electric field. At isoelectric point the colloidal particles are uncharged (Figure 16).

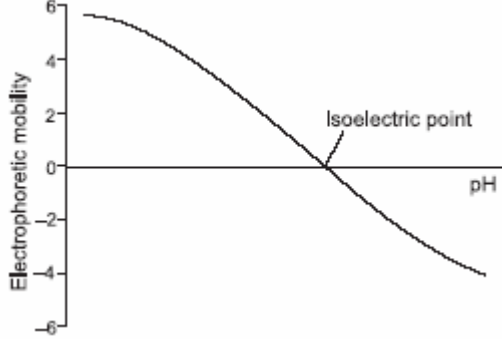


Fig. 16 Determination of the isoelectric point of a protein by plotting its electrophoretic mobility as a function of pH. At lower pH values than the isoelectric point, the protein moves toward the cathode. At higher pH values the protein moves toward the anode

The electrophoresis is similar to sedimentation, for both cases solute molecules move under the influence of an external field. The electrophoresis depends mainly on the charge of colloidal particle and not on the molar mass of solute. Electrophoresis is a useful technique for separating proteins in a mixture.

Calculation of Electrophoretic Mobility

An electric field E , is applied to the solution. The force acting on the charged particle is eZE , where e is the electronic charge, Z is the number of charges on the molecules. After the field is turned on for a very short period, a steady state is reached. The electrostatic force is balanced by the frictional force f , exerted by the solvent medium. The ions are now moving at the constant velocity v at equilibrium

$$eZE = f \cdot v = 6\pi\eta r v$$

Hence $v = \frac{eZE}{f}$

f

The electrophoretic mobility, u is the velocity per unit electric field, i.e.

$$u = \frac{v}{E} = \frac{Ze}{f} = \frac{Ze}{6\pi\eta r}$$

Dimension of u is $m^2V^{-1}s^{-1}$

$$\therefore u \propto e \propto \frac{1}{r} \propto \frac{1}{n}$$

Assuming the ions to be spherical, here we neglect the influence of ionic atmosphere on the movement of ions. By this method, we can separate the mixture of macromolecules.

The theory of Electrical Double Layer: The electrical properties of colloids can be understood by postulating that an electrical double layer of opposite charges exists at a solid-liquid interface i.e. at the separation between a solid and a liquid.

This theory was initiated by Helmholtz and later modified by Guoy, Stern and others. According to modern concept, when a solid is present in contact with a liquid, double layers of ions appear at

the surface of separation. One part of double layer is fixed on the surface of the solid. It is called **fixed part** of double layer. This part either consists of positive ions or negative ions (Figure 17).

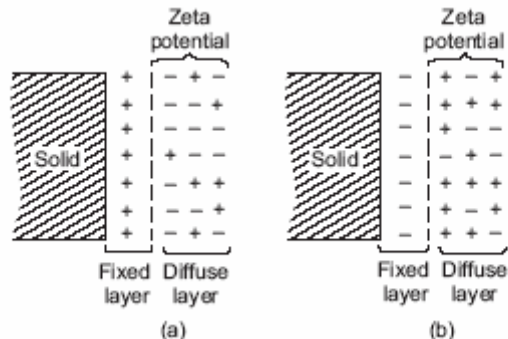


Fig. 17 The electrical double layer

The second part of the double layer consists of mobile or diffuse layer of ions which extend into the liquid phase. This layer contains positive and negative ions but the net charge is equal and opposite to that on the fixed part of the double layer. In Figure 17 (a), the fixed part carries positive charge while in Figure 17 (b), the fixed part carries negative charge. In each case the net charge on mobile layer is equal and opposite to that on the fixed layer. This theory can be safely applied to colloidal systems. The ions, which get preferentially adsorbed on the colloidal particles, are held in the fixed part of double layer. These ions give the characteristic charge to the colloidal particles. On the other hand, the ions with opposite charge are present in the mobile portion of double layer and give opposite charge to this layer.

The presence of oppositely charged ions on the fixed and mobile portion of the double layer leads to the appearance of a difference of potential between the two layers as shown in Figure 17 (a), and (b). This difference of potential between the two layers is called **zeta potential or electrokinetic potential**.

Now the value of zeta potential, can be calculated by using equation $\xi = 4\pi kv/ID$

From above discussion, it is clear that in a colloidal solution, the solid particles carry one kind of charge while the liquid medium carries charge which is opposite to that of the solid particles. Using water as dispersion medium, the charge on colloidal particles of some common sols has been given in table.

Positively charged sols	Negatively charged sols
Hydrated metal oxides or Metal hydroxides e.g. Oxides, e.g. Ca(OH)_2 , Fe(OH)_3 , Al(OH)_3 , Cr(OH)_3 . Oxides, e.g. TiO_2 Basic dyes e.g. Methylene blue, Haemoglobin	Metals e.g. Cu, Ag, Au, Pt. Sulphides e.g. As_2S_3 , CdS, Sb_2S_3 , etc. Acidic dyes e.g. eosin, congo red. Gums, starch, soap solution, clay, silicic acid.

8. Coagulation or Precipitation: Colloidal particles in a sol carry the same charge. Being similarly charged, they repel each other. The repulsive forces between the similarly charged particles do not allow them to come closer. Hence, they remain scattered or suspended throughout

the dispersion medium. However, if the charges are removed by some means, the colloidal particles come together to form bigger aggregates and settle down under the influence of gravity. *This process by which the colloidal particles come closer and result in the precipitation of the colloidal solution is called coagulation.*

The coagulation or precipitation of a sol can be brought about in four different ways as follows:

- (i) By addition of electrolytes
- (ii) By mixing two oppositely charged sols
- (iii) By boiling
- (iv) By electrophoresis
- (v) By persistent dialysis

(i) By addition of electrolytes: When electrolyte is added to a sol, the charged colloidal particles adsorb the oppositely charged ions produced by the dissociation of electrolyte. In this way, the charge on the colloidal particles is neutralized and the resulting neutral particles come together to form bigger aggregates and thus get precipitated. For example, when sodium chloride is added to the negatively charged sol of As_2S_3 , arsenous sulphide settles down in the form of yellow precipitate. On adding NaCl , the Na^+ ions neutralise the negative charge on the colloidal particles. After losing the charge, the particles come together to form bigger aggregates which finally settle down as yellow precipitate.

Regarding coagulation, the following points must be kept in mind:

(a) Addition of electrolyte brings about coagulation of colloidal solution. For example, ***bleeding is stopped*** by the application of alum (electrolyte). This is because blood is coagulated by alum and thus blood vessel gets sealed.

(b) *The ion, which is effective in causing coagulation of a solution, is the one whose charge is of opposite sign to that of the colloidal particles.*

For example, in the precipitation of positively charged $\text{Fe}(\text{OH})_3$ solution, it is the anion which is of importance. It does not matter greatly what the cation is?

(c) The coagulating capacity of various electrolytes is different and depends upon the following:

(i) *Valency of the ion.* The precipitating effect increases with increase in the valency of ion.

(ii) It also depends on the nature of the colloidal sol. *Lyophobic colloidal sols are easily coagulated while lyophilic sols like gelatine, starch, etc. are coagulated with difficulty and with large excess of electrolyte.*

Coagulation or flocculation value: *The minimum amount of an electrolyte required to cause precipitation of one litre of a colloidal solution is called flocculation value or coagulation value of electrolyte for the sol.* It is generally expressed in millimols per litre. The reciprocal value is called flocculating or coagulation power.

The flocculating power of some ions are given in Table 8.

Table 8 Flocculation values (in millimetre per litre)

Arsenous Sulphide (–) Sol			Ferric hydroxide (+) Sol		
Electrolyte	Active ion (cation)	Flocculating value	Electrolyte	Active ion (anion)	Flocculating value
NaCl	Na ⁺	58	KCl	Cl [–]	10.3
KCl	K ⁺	50	MgSO ₄	SO ₄ ^{2–}	0.2
MgSO ₄	Mg ²⁺	0.81	K ₂ Cr ₂ O ₇	Cr ₂ O ₇ ^{2–}	0.19
CaCl ₂	Ca ²⁺	0.65	Na ₂ C ₂ O ₄	C ₂ O ₄ ^{2–}	0.238
AlCl ₃	Al ³⁺	0.093	K ₃ [Fe(CN) ₆]	[Fe(CN) ₆] ^{3–}	0.096

(ii) Mutual Coagulation: When two colloidal sols of opposite charges are mixed, the charge of one is neutralised by the charge of the other and aggregation of the particles and precipitation of colloids takes place. The process is called **mutual coagulation**. In order to bring about mutual coagulation, the two colloids must be mixed in proper proportions. For example, when Fe(OH)₃ and As₂S₃ are mixed in proper proportion, these get precipitated.

(iii) By boiling: Lyophobic sols can also be coagulated by boiling. This is because at higher temperatures, the colloidal particles collide together more frequently and vigorously so that they coalesce to finally form precipitate. For example, egg albumin, a hydrophobic colloid is coagulated by hot water or hot oil in the poaching or frying of eggs.

(iv) By electrophoresis: Under the influence of electric field, the colloidal particles move towards the oppositely charged electrodes. If the process is carried out for a long time, the colloidal particles come in contact with the electrode and lose their charge. Consequently, they get precipitated.

(v) By persistent dialysis: The stability of colloidal sols is due to the presence of a small amount of electrolyte. If the electrolyte is completely removed by persistent dialysis, the particles left will get coagulated.

9. Stability of Sols: Hydrophobic sols are stabilised by the presence of like charges on colloidal particles. Due to the presence of like charges, colloidal particles repel each other and move away from each other and thus do not coalesce to form bigger aggregates. However, the coagulation begins immediately on the removal of the charge.

Stability of lyophilic colloids is for two reasons. Their particles possess a charge and in addition they are heavily solvated and the solvent layer surrounding them prevents them to come into intimate contact with each other. Hence their coagulation is prevented. For example, when sodium chloride is added to a gold sol, it gets precipitated. However, when sodium chloride is added to a colloidal solution of gelatin, its particles are not precipitated. This is because the water layer around gelatin particles does not allow the Na⁺ ions to penetrate and destroy the charge on gelatine particles (Figure 18).

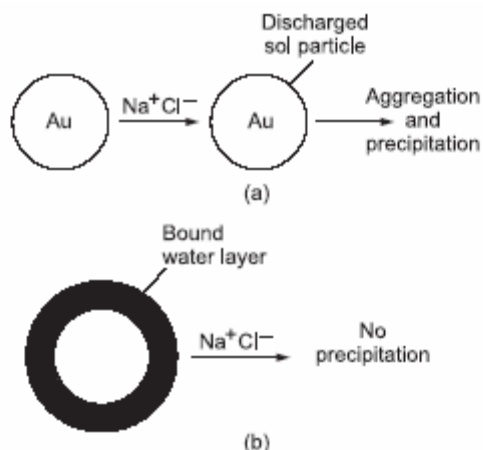


Fig. 18 Illustration of greater stability of gelatin sol (lyophilic) as compared to gold sol (lyophobic)

Thus gelatin sol is not precipitated. This indicates that *lyophilic sols are more stable than lyophobic sols*. To coagulate lyophilic sols, it is necessary to remove charge as well as the solvent layer. This is indicated by the fact that after the addition of an electrolyte if we also add a dehydrating agent, the coagulation sets in at once due to the removal of water layer. Thus the stability of the colloidal solutions is mainly due to three reasons:

- (i) *Brownian motion*
- (ii) *Presence of similar charge on colloidal particles.*
- (iii) *Solvation of colloidal particles.*

10. Protective action of sols: Lyophobic sols such as those of gold and silver, etc. are readily precipitated by the addition of small amounts of electrolytes. However, their coagulation can be prevented by the previous addition of some stable lyophilic colloid like gelatin, albumin, etc. For example, if a little gelatin (hydrophilic colloid) is added to a gold sol (hydrophobic sol), the latter is not readily precipitated by the addition of sodium chloride. *The property of the lyophilic colloids to prevent the precipitation of lyophobic colloids by electrolytes is called protection. The lyophilic sol used to prevent the precipitation of a lyophobic sol is called **protective colloid**.*

The protective action of lyophilic colloids is based on the fact that the particles of the hydrophobic sol adsorb the particles of the lyophilic sol which form a protective coating around the lyophobic sol particles. The hydrophobic sol, therefore, behaves as a hydrophilic colloid and is not readily precipitated on the addition of an electrolyte.

Gold number: The protective power of different lyophilic sols is different. The protective action of different colloids is expressed in terms of **gold number** introduced by Zsigmondy. It is defined as:

The number of milligrams of a hydrophilic colloid which just prevents the precipitation of 10 mL of a gold sol on the addition of 1 mL of ten per cent sodium chloride solution.

The onset of precipitation of gold sol is indicated by change in colour from **red to blue**. Thus gold number is a measure of the quantity of protective colloid which just fails to prevent the coagulation of the sol by the electrolyte. It is obvious, therefore, that smaller the gold number,

greater is the protective power of the given protective colloid. The gold numbers of a few protective colloids are as follows:

Table 9

Substance	Gold number	Substance	Gold number
Gelatine	0.005–0.01	Gum Arabic	0.15–0.25
Haemoglobin	0.03–0.07	Dextrin	6–20
Albumin	0.1–0.2	Potato Starch	20–25
Sodium Oleate	0.4–1.0	Casein	0.01

Experimental Procedure to find Gold Number

The procedure is as follows:

After determining the approximate concentration of protecting colloids required, 0.01, 0.1, 1.0 mL proportion of sol are put into the beakers and 10 mL of gold sol is added to each. After shaking for three minutes, 1 mL of 10% NaCl is added to each. If the colour changes in first beaker but not in others, then gold number lies between 0.01 mL and 0.1 mL of protecting colloid. By repeating concentrations between these limit more exact values are obtained. The gold number found in this way by Zsigmondy and Gortner for several hydrophilic colloids are given in Table 9.

Stability of Colloids

The lyophobic sols are stabilized by electric double layer interactions. Solvation always has good influence on their stability.

Critical Coagulation concentrations – Schulze-Hardy rule

When an electrolyte is added to a lyophobic colloids, the effective ion causes a compression of the diffuse parts of the double layer around the particle. Electro kinetic potential goes down the critical value resulting in a reduction in repulsive interaction between particles and coagulation takes place.

The critical coagulation concentration (c.c.c.) of an indifferent (inert) electrolyte (Table 10).

Table 10 Critical Coagulation Concentrations in millimoles per dm³ for Hydrophobic Sols

As ₂ S ₃ (–ve sol)		AgI (–ve Sol)		Al ₂ O ₃ (+ve Sol)	
LiCl	58	LiNO ₃	165	NaCl	43.5
NaCl	51	NaNO ₃	140	KCl	46.0
KCl	49.5	KNO ₃	136	KNO ₃	60.0
KNO ₃	50	RbNO ₃	126		

K Ac	110	AgNO ₃	0.01		
CaCl ₂	0.65	Ca(NO ₃) ₂	2.40	K ₂ SO ₄	0.30
MgCl ₂	0.72	Mg(NO ₃) ₂	2.60	K ₂ Cr ₂ O ₇	0.63
MgSO ₄	0.81	Rb(NO ₃) ₂	2.43	K ₂ Ox	0.69
AlCl ₃	0.093	Al(NO ₃) ₃	0.067	K ₃ [Fe(CN) ₆]	0.08
102Al ₂ (SO ₄) ₃	0.096	La(NO ₃) ₃	0.069		
Al(NO ₃) ₃	0.095	Ce(NO ₃) ₃	0.069		

In contrast, it is practically independent of specific character of the various ions, the charge number of co-ions and the concentration of the sol and is moderately dependent on the nature of the sol. These generalizations are illustrated in the following table and are known as the Schulze-Hardy rule.

The Schulze-Hardy Rule

This rule of coagulation states that (1) The effective ions in the preparation of sol by electrolytes is the ion opposite in sign to the charge on the colloidal particles and (2) the precipitating power of the effective ion increases greatly with increasing valence of the ion. The effective ion is sometimes referred to as the precipitating ion of an electrolyte, whereas the ion having the same sign of charge as the particle is called **stabilizing ion**.

Table 11 Precipitation Value (x) of Salts for Copper Ferrocyanide Sol

(A) Salts with cations of varying valence		(B) Potassium Salt	
Salt	x(millimoles/L)	Salt	x(millimoles/L)
KCl	35.6	KNO ₃	28.7
NaCl	92.5	KBr	27.5
Ba(C ₂ H ₃ O ₂) ₂	0.445	K ₂ SO ₄	47.5
BaCl ₂	0.458	K ₂ HPO ₄	47.4
SrCl ₂	0.588	K ₂ CrO ₄	80.0
MgSO ₄	0.760	K ₂ C ₄ H ₄ O ₆	95.0
Al ₂ (SO ₄) ₃	0.58	K ₂ C ₂ O ₄	170.0
La(NO ₃) ₃	0.034	K ₃ Fe(CN) ₆	205.0
Th(NO ₃) ₄	0.038	K ₄ Fe(CN) ₆	260.0

Table 12 Precipitation Value (x) of Salts for Copper Ferrocyanide Sol

(A) Salts with cations of varying valence		(B) Potassium Salt	
Salt	x(millimoles/L)	Salt	x(millimoles/L)
Ferrocyanide	0.067	Bromate	31.3
Ferricyanide	0.096	Thiocyanate	46.9
Dichromate	0.188	Chloride	103.1
Tartarate	0.200	Chlorate	115.6
Sulphate	0.219	Nitrate	131.2
Oxalate	0.238	Bromide	137.5
Chromate	0.325	Iodide	153.6
Iodate	0.900	Formate	172.5

Referring to the tables 11 and 12 it is seen that the effect of cations predominates with the negative sols, and of anions, with positive sol. Moreover, if one disregards the univalent organic ions, the salts with precipitating ions of same valence fall in fairly well-defined groups, the precipitating power of which is in the order: quadrivalent > trivalent > bivalent > univalent. If the lowering of the ξ -potential (zeta potential) results wholly or in part from adsorption of the ion of an electrolyte with the sign of charge opposite to that on the sol, the Schulze-Hardy rule states that the adsorption of precipitating ions is in the order: quadrivalent > trivalent > bivalent > univalent. In actual experiments, it is found that ions of the same valence do not behave alike; this is especially true for the univalent ions. Moreover, the behaviour of alkaloid and dye anions follow no rule with reference to valence. The Schulze-Hardy rule must, therefore, be regarded merely as a useful first approximation.

According to Schulze-Hardy Rule *higher the valency of the flocculating ion added, the greater is its power to cause coagulation. Thus, for precipitating an As_2S_3 sol (negative), the precipitating power of positively charged ions is in the order:*



Use of the potash alum in the purification of water is based on the strong power of Al^{3+} ions to coagulate negatively charged colloidal impurities present in natural water.

Similarly, in the coagulation of the positively charged ferric hydroxide sol, the flocculating power decreases in the order $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$. It may be noted that the rule is only approximate and several departures are known.

Generally, the precipitating power of a trivalent ion is nearly 500 to 1000 times as high as that of the monovalent ion. The precipitating power of a bivalent ion is about 100–500 times as high as that of univalent ion.

Various attempts made to explain the valency rule have met with limited success. Whetham applied the theory of probabilities and concluded that the molecular precipitation concentrations will be:

$$\frac{1}{C_1} : \frac{1}{C_2} : \frac{1}{C_3} \dots = 1 : x : x^2$$

Where C_1 , C_2 and C_3 are the precipitation values of electrolytes with univalent, bivalent and trivalent precipitating ions, and x is a constant. Freundlich assumed that in precipitation of sols by electrolytes, equivalent amounts of ions of varying valence are adsorbed from equimolar solutions. If this were true, the following relationship should hold:

$$\frac{1}{C_1} : \frac{1}{C_2} : \frac{1}{C_3} \dots = 1 : 2^n : 3^n$$

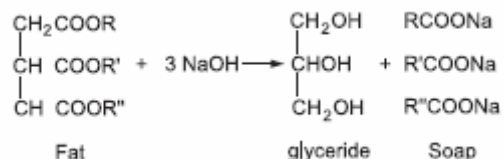
where C 's have the same significance as before, and n is a constant. In most cases the above formulas fit the experimental data so roughly that they are of questionable use. From the consideration of a theory of the interaction of the double layers on hydrophobic salt particles, Verwey concludes that, for monovalent, divalent and trivalent ions, the precipitation concentrations should be in ratio

$$1 : \left(\frac{1}{2}\right)^6 : \left(\frac{1}{3}\right)^6 = 100 : 16 : 0.13$$

Detergency

Detergency is the theory and practice of dirt removal from solid surface by chemical means. It accounts for the bulk of all surfactant usage.

Soap consists of sodium or potassium salts of various long-chain fatty acids and is manufactured by the saponification of glyceride oils and fats with NaOH or KOH, giving glycerol as a by-products.



The potassium soaps are softer and more soluble in water than the corresponding sodium soaps. Soaps from unsaturated fatty acids are softer than those from saturated fatty acids.

Soap is an excellent detergent but suffers from two main drawbacks (a) it does not function very well in acid solutions because of formation of insoluble fatty acid and (b) it forms insoluble precipitates and forms a scum with the Ca^{2+} and Mg^{2+} ions in hard water. Additives such as sodium carbonate, phosphates etc. help to offset these effects.

Mechanisms of Detergency

A satisfactory detergent must possess the following properties.

(1) Good wetting characteristics in order that the detergent may come into intimate contact with the surface to be cleaned.

(2) Ability to solubilise or remove dirt and to prevent it from being redeposited on the cleaned surface or from forming a serum.

Removal of Dirt from a Solid Surface by Detergent

The mechanism for the removal of dirt is

- (a) The surface are covered with greasy dirt
- (b) Water itself fails to dislodge the dirt mainly because of its high surface tension and insufficient wetting action.
- (c) Detergent is added to the water. The hydrophobic parts of the detergent molecules line up both on the dirt and on the solid surface, thus reducing the adhesion of the dirt to the solid. The dirt may now be dislodged by mechanical action.
- (d) Dirt is held suspended in the solution because the detergent molecules form an adsorbed layer on the cleaned surface and around the dirt particles.

The most successful detergents are those forming micelles, which are directly involved in detergent action. The detergent action depends upon the concentration of unassociated surfactant. Therefore, the molecular properties of surfactants associated with good detergent action can lead to micelle formation.

Gels

Lyophilic colloids that is normally stable but may be induced to coagulate partially under certain conditions (e.g. lowering the temperature). This produces a pseudo-solid or easily deformable jelly-like mass enclosing the entire amount of the liquid within itself. Such a product is called a gel, in which entrapping particles endorse the whole dispersing medium. Gel is a liquid-solid system in which a liquid is dispersed in a solid.

Gels may be further subdivided into elastic gels (e.g. gelatin) and rigid gels/inelastic gels (e.g. silica gel). They are distinguished from each other by the process of dehydration and rehydration.

Elastic Gels: An elastic gel is obtained by cooling a lyophilic colloid, such as gelatin or agar solution prepared by warming these substance with water. Starch gelatin, agar-agar and pectin sols belong to this class. Solutions of soap also belong to elastic gels. The elastic gels are reversible. In these cases, dehydration and rehydration on exposure to water vapour are most reversible, even then the process is carried out more than one.

Inelastic gels: The best known example of inelastic gel is silicic acid or silica gel. This is prepared by the addition of hydrochloric acid to sodium silicate at an appropriate concentration. The system sets to gel almost immediately. In some cases the setting may be delayed. Other examples are $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, and $\text{Cr}(\text{OH})_3$. The inelastic gels are irreversible. If silica gel is dehydrated, addition of water will not reset it into the gel.

Among the lyophilic sols the well known gels are gelatin, agar-agar, gum arabic, mastic and gamboge sol, etc. Amongst the **lyophobic sols**, the well known gels are silicic acid, ferric hydroxide, ferric phosphate sols. The sols should be in sufficiently high concentration to facilitate

the gelation process. Both gels and gelation are very important in medicine and biology because the plants and animals are composed of naturally occurring gels. Gelatin made up of macromolecular solutions have got great importance in technological field. In food and technological field industries make use of gelatin.

Preparation of Gels

Gels may be prepared by the following process.

(1) Cooling of sols at Moderate Concentration: Agar-agar, gelatin gels are made by cooling their sols having moderate concentrations prepared in hot water. As we know that hydrophilic sols are extensively hydrated, when cooled, the hydrated particles agglomerate together to form larger aggregates and finally led to form a semi-solid network structure of gel.

(2) Double-Decomposition: Hydrophobic gel such as silicic acids (commonly known as silica gel) and aluminium hydroxide (commonly known as alumina gel) are prepared by double-decomposition method) HCl is added to sodium silicate solution. As a result, a highly hydrated silicic acid gets precipitated. When this is allowed to stand to set, it forms a gel.

By similar method alumina gel is prepared by adding NaOH on AlCl_3 solution. A highly hydrated salt is obtained. On standing for few minutes, it changes to gel.

(3) Change of solvents: Certain hydrophobic gels are prepared by this method. When ethanol is added instantly to a solution of calcium acetate of high concentrations, the salts separates out to form a colloidal solution. On standing the solution undergoes gelation and finally form a semi-rigid gel of CaAc_2 .

The principal difference between elastic and inelastic gels consist in their behaviour upon dehydration and rehydration. Partial dehydration of an elastic gel (e.g., gelatin) leads to an elastic solid from which the elastic gel may be produced again by addition of water. An inelastic gel becomes glassy, falls to powder and loses its elasticity when dried. The essential difference between them is attributed to the rigidity of the walls of the capillaries formed when the inelastic gels are dehydrated. With elastic gels the walls are flexible. Silica gel when dehydrated forms a honeycomb structure with the capillaries so that it is a valuable absorbing agent.

An elastic gel after it has taken up the maximum amount of a liquid from the vapour state can still take up more liquid when actually placed in contact with it. In this process the gel swells and the phenomenon is known as the **swelling** or **imbibition of gels**. The swelling is influenced by electrolytes or ions. The iodide and thiocyanate ions have been observed to be the most effective in this respect. Inelastic gels seldom show the phenomenon of swelling, and although they can take up large amount of water. They do not show any volume change, probably due to the rigidity of the capillary walls. With elastic gels the imbibition or absorption of liquid is selective while in an inelastic gel it is a general phenomenon. Thus gelatin can take up water but not alcohol, while an inelastic gel can take up any liquid by which it is wetted.

The most interesting property for both the elastic and inelastic gels is **shrinkage in volume** when allowed to stand. This phenomena is known as **syneresis**. At isoelectric point maximum syneresis is observed for protein. Syneresis decreases when pH decreased from the isoelectronic point (pI value).

It is believed that the setting of gels is caused by formation of a structure into which the whole of the liquid is taken up. This is true for both elastic and inelastic gels. Usually the setting takes place by cooling specially in the case of elastic gels. But the setting may also take place isothermally. This isothermal sol-gel transformation is known as **thixotropy**. Thus a bentonite sol at the ordinary temperature kept in a test tube in about a minute time sets to a gel and does not flow out of the tube even though carefully inverted. A mild jerk given to the test tube however, destroys the gel structure resulting in the transformation to a sol and becoming mobile again. If the test tube at the time of imparting the jerk is held near the ear, a faint clicking sound may be heard, which evidently indicates the collapse of the structure. It is natural with thixotropic substances that they have high viscosity when they are in the gel state and do not yield to small shearing stress. When the stress is increased there is a certain value when the structure collapses or yields and the system flows. This value of the shearing stress is known as the yield value. Other examples of thixotropic substances are (1) ordinary tooth pastes kept in tubes. They usually do not come out at low pressures but once they come out at a high pressure, it is easy to make them flow even by quite small pressure. (2) Quicksand is another example. When undisturbed they form a set gel. If any animal treads over this, the gel is disturbed and turns into sol and the animal sinks gradually. In course of sinking the animal naturally struggles to get out and this renders the situation worse because the more it is disturbed the less viscous it becomes and the animal hopelessly sinks inside. The phenomenon of thixotropy is of great importance in the drilling of deep oil wells. If the drilling operation has to be stopped for a while the rock chips in the soil would settle to the bottom and form a compact mass round the drill bit so that it is sometimes impossible to move the drill when operation are to be resumed again. Accordingly a “drilling fluid” is usually injected into the well during the drilling operation to carry rock chips to the surface. If the drilling is suspended the drilling fluid solidifies to a gel and the rock chips remain held up in the gel. Bentonite suspensions are commonly used as the drilling fluid.

A few thixotropic systems solidify rapidly if a slow circular to-and-from motion is given to the sol. This phenomenon has been termed **rheopexy**. According to Freundlich the particles in such systems are rod-like or plate-like structure and the slow circular motion serves to impart an orientation to the particles so that the particles being parallel to one another and solidification is facilitated. Such sols usually takes long time to set to a gel if left to themselves and becomes converted into a gel under strong agitation. It is only by mild circular agitation that they set.

Emulsions

Emulsion is a colloid in which a liquid phase (small droplets with a diameter range 10^{-7} – 10^{-9} m) is dispersed or suspended in a liquid medium. Emulsions are classified as lyophobic (solvent-repelling and are generally unstable) or lyophilic (solvent attracting and are generally stable).

Stable emulsions are formed when a very small amount of oil dispersed in large amount of water. The stability of emulsion is due to electrical potential on the colloidal droplets, as they developed electric field toward electricity like hydrophobic sols.

The colloids are also classified as suspensions and emulsions. By suspension we mean colloids in which the dispersed phase is a solid and it is dispersed in a liquid medium but in emulsions, a liquid is dispersed in another liquid. A suspension may be lyophobic or lyophilic but emulsions are in most cases lyophobic and require the addition of some protective agents for their stability.

Types of Emulsion: There are two types of emulsion: (Fig. 19)

- (a) Oil-in-water (O/W) type
- (b) Water-in-oil (W/O) type

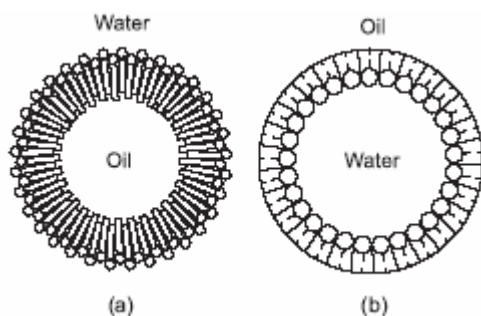


Fig. 19 Diagram of molecular orientation of the stabilizing molecules in oil-in-water and water-in-oil emulsions

Determination of type of Emulsion

In the “oil-in-water” type emulsion it is not necessary that oil should actually be dispersed in water. Any liquid immiscible in water (like nitrobenzene), when dispersed in water is an “oil-in-water” emulsion. The simplest method to distinguish between two types of emulsions is to place a small quantity of the emulsion under the microscope and stir it with one drop of oil or water. If the emulsion be of the oil-in-water type the oil will not mix with the emulsion but water will readily mix with it. Just opposite effect will be observed when the emulsion is of water-in-oil type.

In a nutshell, the type of emulsion is determined from the properties of external phase. An oil-in-water emulsion is freely miscible with water, whereas a water-in-oil emulsion will float on water.

A dye which is oil-soluble but not water-soluble behaves differently when it comes in contact with the two types of emulsion. If the emulsion is of water-in-oil type, the dye dissolves uniformly and develops colour. If the emulsion is of oil-in-water type, they will not mix with emulsion and solution remains colourless. The conductivity of oil-in-water emulsion is high whereas for water-in-oil emulsion it is low. This difference in conductivity is used to distinguish between the two types of emulsion.

Preparation of Emulsion

There are two general methods for the preparation of emulsion:

1. In American method, the gum is first peptized in water and then mixed in a mortar with oil. The oil is added slowly at a time to get emulsion.
2. In continental method the solid gum is first ground with oil followed by the addition of enough water at a time to get an emulsion. To stabilize the emulsion, some emulsifying agent (emulsifier) is added. The emulsifying agent is distributed uniformly around the droplets.

Types of Emulsion Formed

When an oil-water mixture is shaken vigorously in the presence of an emulsifier, they form simultaneously oil droplets in water and water droplets in oil. Both these types of droplets have a strong tendency to coalesce. The types of emulsion formed depend upon two factors.

- (1) the nature of the emulsifier

(2) the relative rate of coalescence of the two types of droplets.

(1) Nature of the emulsifier: Bancroft's Rule: Hydrophilic emulsifier dissolves better in water than in oil, hence these emulsifiers promote the formation of an O/W emulsion. Hydrophobic emulsifiers dissolve better in oils than in water, hence these emulsifiers favours the formation of a W/O emulsion. This is known as **Bancroft's rule**.

A numerical scale was developed by Griffin called hydrophilic-lipophilic balance (HLB). This scale indicate the effectiveness of a particular surfactant to produce a particular type of emulsion. This scale extends from 0 to 30 (See Fig. 20).

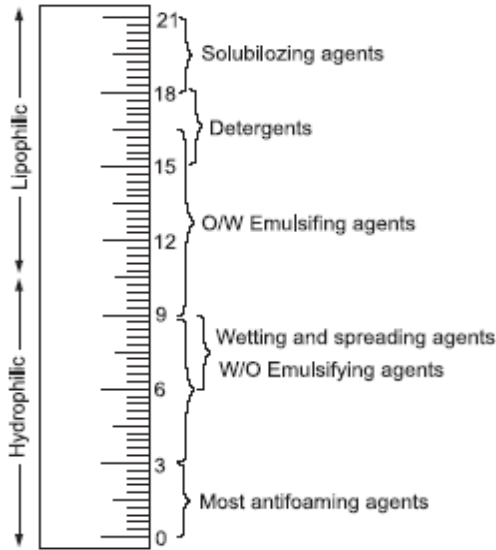


Fig. 18 The HLB scale

If the HLB number of a surfactant lies in the range of 3–6 a W/O emulsion is formed. If it lies in the range of 8–13, an O/W emulsion is formed.

(2) Relative Rates of Coalescence of Droplets: The rate R_1 at the oil droplets coalesce when dispersed in water, is given by the Arrhenius equation.

$$R_1 = A_1 \exp(-E_1/RT) \dots (1)$$

where A_1 is the frequency factor of collision, which is a function of oil-water phase volume divided by the viscosity of the water phase and E_1 is the energy barrier that has to be overcome before coalescence can take place. The energy of a system depends on various factors such as the electrical potential of the oil droplets, the fraction of the surface covered by the emulsifier, etc.

Similarly, the rate R_2 at which the water droplets dispersed in oil coalesce is given by the equation $R_2 = A_2 \exp(-E_2/RT) \dots (2)$

where A_2 is the collision factor which is a function of water-oil phase volume ratio devised by the viscosity of the oil phase and E_2 is the energy factor analogous to E_1 . The factors R_1 and R_2 depend upon the types of emulsion formed. If $R_2 > R_1$ an O/W emulsion is formed, and if $R_2 < R_1$ a W/O emulsion is formed.

Reversal of Emulsion

An oil-in-water emulsion is stabilized by emulsifying agent (solid-soap) is charged into an water-in-oil emulsion by the addition of suitable amount of a bi or trivalent metallic salt. If sufficient amount of CaCl_2 is added to oil-in-water emulsion which gives equivalent amount of sodium and calcium soap, under these conditions the emulsion breaks and produces water-in-oil emulsion and these can be checked by conductivity measurement as mentioned in earlier section.

Breaking of Emulsions

There are two general methods available for breaking the emulsions.

(a) Destruction of the emulsifier and (b) Cracking of the emulsifying film.

(a) Destruction of the emulsifier: The main aim is to destroy the emulsifying agent. The breaking is done by adding some chemical that reacts with it. Addition of acid breaks the emulsion and then stabilised by sodium oleate, since the acid reacts with sodium oleate and changes to oleic acid which has no emulsifying action. Similarly emulsion stabilised by sodium oleate is broken by the addition of a suitable amount of alkaline metal salt. These converts soap of sodium salt to soap of bivalent salt, which is hostile to sodium salt and make the emulsion unstable.

(b) Cracking of emulsifying film: The various processes involved are—

- (1) Addition of an emulsifier, which has ability to form emulsion of opposite type
- (2) Agitating with an excess of the dispersed phase
- (3) Salting out by an excess of salt which dehydrates the swollen film
- (4) Freezing
- (5) Jarring
- (6) High grade filtration
- (7) Centrifuging
- (8) Electrophoresis with a high voltage
- (9) Centrifuging
- (10) Addition of salts with multivalent ions opposite in sign of charge to the drops
- (11) Heating

Inhibition

The rate of growth of colloidal particles depends upon the surface phase reaction and heat of formation. On the surface the rate of growth of crystallization for glycerol is 0.002 cm/sec, whereas for phosphorous the rate of growth is 100 cm/sec. The growth rate depends on proper orientation of molecule.

In general the rate of growth tends to increase with increasing super saturation and decrease with increasing viscosity and loss of mobility of the molecule in liquid. Decreasing the temperature and increasing the supersaturation, the viscosity of liquid increases and growth will become easier.

The growth of colloid may be **retarded** by the presence of impurities which are adsorbed on the surface and prevent the incorporation of additional molecules. Thus the dry quinoline yellow is

adsorbed by potassium sulphate and concentration “as low as 0.16% virtually prevents the growth of its crystals (Fig. 21) Unequal adsorption on different faces of a crystal may lead to unequal reduction of their growth rates and subsequent development of unequal crystal faces (Fig. 22). Thus ordinary salt in the presence of urea forms octahedral crystals instead of the unusual cubic ones.

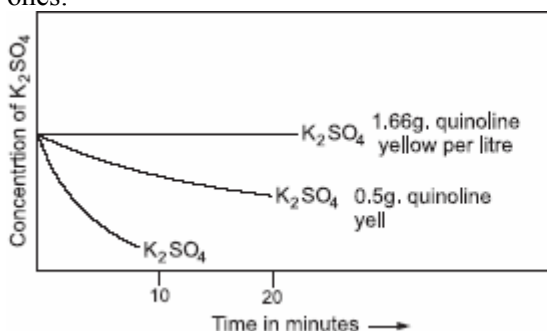


Fig. 21 The effect of an adsorbic impurity on the rate of crystallization

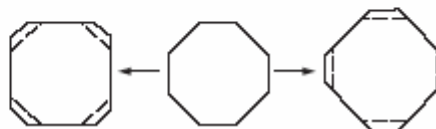


Fig. 22 It is the slowest growing faces of a crystal which develop most fully whereas the fastest growing ones disappear

We have seen that the gold sols are prepared by the reduction of chloroauric acid with hydrogen peroxide/formaldehyde/hydroxyl amine. The progress of reduction in this system can be measured by the increase in electrical conductivity, while the disappearance of the faintly yellow gold complex and the appearance of the intense red colloidal gold can be observed visually. If no nuclei are added, the conductivity of the system changes as shown by solid line (Fig. 21). There is a fast increase in conductivity (A—B) and decrease in yellow colour, showing that part of the gold is rapidly reduced. Then both processes slow down and the system changes, to point C. Then a high degree of supersaturation has been rapidly reached and the reaction slowed down. There after, the reaction proceeds to completion (C—D'). This is called rapid growth of nuclei. By adding external nuclei at any point, the supersaturation can be immediately relieved. Figure 23 shows for nuclei added before the beginning of reduction (B'—D'') or in the middle of the slow state (CD''—D'').

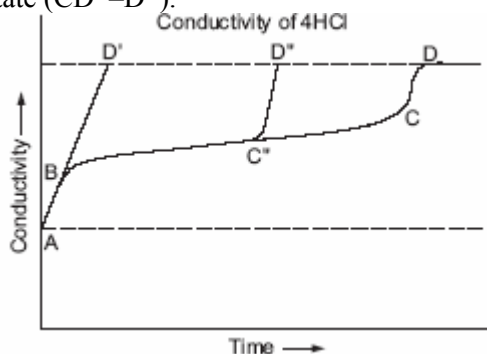


Fig. 23 Nucleation in the formation of a gold sol. Conductivity measures the formation of elemental gold. Curve ABCD in the absence of external nuclei; ABD, with nuclei present from the beginning; ABC''D'' with nuclei added at C''.

Surface-Active Agents

Classification

Surface-active agents, or surfactants, owe their name to their interesting behaviour at surfaces and interfaces. They are positively adsorbed at interfaces between phases, and the adsorption of surfactant lowers the interfacial tension between the phases. Because of their ability to lower interfacial tension, surfactants are used as emulsifiers, detergents, dispersing agents, foaming agents, wetting agents, penetrating agents, and so forth.

Many types of substances act as surfactants, but all share the property of amphipathy: the molecule is composed of a nonpolar hydrophobic portion and a polar hydrophilic portion, and is therefore, partly hydrophilic and partly hydrophobic. Surfactants may be referred to as either *amphiphilic* or *amphipathic*; the terms are synonymous. The polar, hydrophilic part of the molecule is called the *hydrophilic* or *lipophobic* group. Often the hydrophilic part of the molecule is simply called the *head* and the *hydrophobic* part—usually including an elongated alkyl substituent—is called the *tail*. The presence of a hydrophilic group makes surfactants slightly soluble in aqueous media, and is central to the physicochemical properties of aqueous surfactant solutions.

Surfactants are classified on the basis of the charge carried by the polar head group as anionic, cationic, nonionic, or amphoteric. Tables show the chemical structures of typical examples of these classes. Lecithin, cephalin, and the bile acids are usually classified as biosurfactants. The bile acids and their conjugates have different properties in solution from surfactants with a long alkyl chain.

Chemical Structure of Hydrophilic Groups for Anionic Amphiphiles

Chemical structure ^a	Name
$R-(COO^-)_n M^{n+}$	Carboxylate
$R-COO^- M^{2+}$ $ $ SO_3^-	Sulfocarboxylate
$R-COO^- M^{(n+1)+}$ $ $ OPO_3H_{3-n}	Phosphonocarboxylate
$R-CON(CH_3)CH_2COO^- M^+$	Sarcoside
$R-OSO_3^- M^+$	Sulfate
$R-(OCH_2CH_2)_n-OSO_3^- M^+$	Polyoxyethylene
$R-SO_3^- M^+$	Sulfonate
$R-(OCH_2CH_2)_n-SO_3^- M^+$	Polyoxyethylene sulfonate
$R-\underset{\substack{ \\ CH_2OH}}{CH}-SO_3^- M^+$	1-Hydroxyl-2-sulfonate
$R-\text{C}_6\text{H}_4-SO_3^- M^+$	Benzene sulfonate
$R-\text{C}_{10}\text{H}_7-SO_3^- M^+$	Naphthalene sulfonate
$R-OPO_3H_{3-n} M^{n+}$	Phosphate

^aR—: long hydrophobic tail.

Hydrophile- Lipophile Balance

The term *hydrophile-lipophile balance* (HLB), first suggested by Clayton, refers to the balance in size and strength between the hydrophilic and hydrophobic parts of a surfactant molecule. Griffin later developed the concept of the HLB for emulsifiers on the basis of their aqueous solubility. The HLB value is an empirical number assigned to nonionic surfactants on the basis of a wide variety of emulsion experiments carried out on surfactants at the Atlas Powder Company.

Chemical Structure of Hydrophilic Groups for Cationic Amphiphiles

Chemical structure ^a	Name
$\begin{array}{c} \text{R}_1 \\ \\ \text{R}-\text{N}^+-\text{R}_2\text{X}^- \\ \\ \text{R}_3 \end{array}$	Ammonium
$\begin{array}{c} \text{R}-\text{S}^+-\text{R}_1\text{X}^- \\ \\ \text{R}_2 \end{array}$	Sulfonium
$\begin{array}{c} \text{R}_1 \\ \\ \text{R}-\text{P}^+-\text{R}_2\text{X}^- \\ \\ \text{R}_3 \end{array}$	Phosphonium
$\text{R}-\text{N}^+ \text{ (in a pyridine ring) } \text{X}^-$	Pyridinium
$\text{R}-\text{N}^+ \text{ (in a quinoline ring) } \text{X}^-$	Quinolinium
$\text{R}-\text{N}^+ \text{ (in a phenyl ring) } - \text{C}_6\text{H}_4 - \text{N}^+ \text{ (in a phenyl ring) } - \text{R}_1 \quad \text{X}^{2-}$	Viologen

^aR—: long hydrophobic tail; R₁ —; R₂ —; hydrogen or short alkyl chain

These HLB values range from 1 to 40, the low numbers generally indicating solubility in oil and the high numbers indicating solubility in water. Nevertheless, emulsifiers with the same HLB value may differ in solubility. An emulsifier has two different actions: it promotes the formation of an emulsion, and also determines whether an *oil/water* (O/W) or a *water/oil* (W/O) emulsion will be formed. The second action is closely connected with the HLB value. On the basis of systematic emulsion experiments, Griffin found that the HLB values of mixture of two or more emulsifiers are additive: the HLB value of the mixture is equal to the sum of the HLB values of the constituents multiplied by their weight fractions in the mixture $x_i w_i$:

$$\text{HLB} = \sum_i x_i w_i (\text{HLB})_i$$

Importance and Application of Colloids

The colloids have great application in day-to-day life as well as in industry, agriculture, medicine and biological sciences. Some of its applications are given below:

(1) Purification of water: Sometimes it is noticed that there is some turbidity in water. This is due to the presence of some negatively charged colloidal particles in the form of fine clay. The addition of potash alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$) (which furnishes Al^{3+}) coagulates the clay particles. Finally the clay— Al^{3+} substance settles down at the bottom and leaves water in a clear state.

Chemical Structure of Hydrophilic Groups for Nonionic Amphiphiles

Chemical structure ^a	Name
$R-OCH_2CH_2)_n-OH$	Polyoxyethylene alcohol
$R-(OCH_2CH_2CH_2)_n-OH$	Polypyrpropylene alcohol
$R-COO-(CH_2CH_2O)_n-H$	Polyoxyethylene ester
$R-COO-\underset{\begin{array}{c} \\ OH \end{array}}{CH}-CH_2OH$	Glycerol monoester
$R-COO-CH_2-\underset{\begin{array}{c} \\ CH_2OH \end{array}}{\overset{\begin{array}{c} CH_2OH \\ \end{array}}{C}}-CH_2OH$	Pentaerythritol monoester
$R-COO-CH_2-\underset{\begin{array}{c} \\ HO-CH \end{array}}{\overset{\begin{array}{c} CH \\ \end{array}}{O}}-\underset{\begin{array}{c} \\ CH-OH \end{array}}{\overset{\begin{array}{c} CH_2 \\ \end{array}}{O}}-CH_2OH$	Sorbitan monoester
$R-(CH_2CH_2O)_n$	Crown ether
$R-\underset{\begin{array}{c} \\ O \end{array}}{S}-R_1$	Sulfoxide
$R-\underset{\begin{array}{c} \\ O \end{array}}{S}-(CH_2)_n-OH$	Sulfinyl alkanol
$R-S-(CH_2CH_2O)_n-H$	Polyoxyethylene thioether
$R-\underset{\begin{array}{c} \\ R_2 \end{array}}{\overset{\begin{array}{c} R_1 \\ \end{array}}{N}} \rightarrow O$	Amine oxide
$R-(CH_2CH_2NH)_n$	Azacrown
$R-\underset{\begin{array}{c} \\ R_2 \end{array}}{\overset{\begin{array}{c} R_1 \\ \end{array}}{P}} \rightarrow O$	Phosphine oxide
$R-CO-\underset{\begin{array}{c} \\ CH_2 \end{array}}{\overset{\begin{array}{c} CH_3 \\ \end{array}}{N}}-CH_2-\underset{\begin{array}{c} \\ OH \end{array}}{\overset{\begin{array}{c} OH \\ \end{array}}{CH}}-\underset{\begin{array}{c} \\ OH \end{array}}{\overset{\begin{array}{c} OH \\ \end{array}}{CH}}-\underset{\begin{array}{c} \\ OH \end{array}}{\overset{\begin{array}{c} OH \\ \end{array}}{CH}}-CH_2OH$	N-Methylglucamine

^aR—: long hydrophobic tail; R_1-R_2 —: hydrogen or short alkyl chain.

Chemical Structure of Hydrophilic Groups for Amphoteric Amphiphiles

Chemical structure ^a	Name
$\begin{array}{c} \text{R}_1 \\ \\ \text{R}-\text{CH}-\text{N}^+-\text{R}_2 \\ \quad \\ \text{COO}^- \quad \text{R}_3 \end{array}$	C betaine
$\begin{array}{c} \text{R}_1 \\ \\ \text{R}-\text{N}^+-\text{CH}_2\text{COO}^- \\ \\ \text{R}_2 \end{array}$	N betaine
$\begin{array}{c} \text{CH}_2\text{COOH} \\ \\ \text{R}-\text{N}^+-\text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{COO}^- \end{array}$	Triglycine
$\begin{array}{c} \text{R}_1 \\ \\ \text{R}-\text{N}^+-\text{CH}_2\text{CH}_2\text{SO}_3^- \\ \\ \text{R}_2 \end{array}$	N, N-Dialkyl taurine
$\begin{array}{c} \text{O}^- \\ \\ \text{R} \cdots \text{O}-\text{P}-\text{O}-\text{CH}_2\text{CH}_2-\text{N}^+(\text{CH}_3)_3 \\ \\ \text{O} \end{array}$	Phosphatidylcholine

^aR—: long hydrophobic tail; R₁—, R₂—, R₃—: hydrogen or short alkyl chain. Taken from Moroi's book. Micelles

(2) Foods articles: Most of our foods are colloidal in nature. For example, milk is an emulsion having fat disposed in water. To preserve the smoothness of ice cream some gelatin is added as a protective agent. Whipped cream fruits, jellies, gels, fruit juice, eggs, salads are substances having colloidal nature.

(3) Rubber industry: Using the process of electrophoresis the deposit on the wires or handles of various tools. The article to be rubber-plated is made the anode. The rubber particles migrate in an electric field towards the anode and get deposited on it. This process is known as insulation.

(4) Sewage disposal: The sewage water consists of dirt, mud, and many unwanted particles etc. having the colloidal dimension which carry electric charge and they do not settled down easily. On creating electric field in the sewage tank, those particles migrate to the oppositely charged electrodes, get neutralized and finally settle down at the bottom.

(5) Formation of deltas: The deltas are formed at the mouth of the rivers by the precipitation of the charged clay particles.

(6) Artificial rain: Clouds are charged particles of water dispersed in air. Rain is caused by the aggregation of these particles. Artificial rains are possible by throwing electrified sound from aero planes, which convert water to rainfall.

(7) Chrome-tanning: The Chrome-tanning of leather is done by the penetration of positively charged particles of hydrated chromic oxide into leather. The rate of penetration may be increased by the process of electrophoresis.

(8) Industrial applications: The industry manufactures pairs, soaps, varnishes, gums, glues, many adhesives, enamels, celluloses, rayon, nylon 66, terylene, textiles, leather, papers, opaque glass of high quality, etc all of them are colloidal in nature. Many industrial processes such as dying, tanning, lubrication, polymerisations etc are colloidal in nature. So colloids have great role to play in industry.

(9) Smoke Screens: The smoke screens are used in warfare for the purpose of concealment and camouflage. The smoke screens consist of very fine particles of titanium oxide in air and are ejected from the aeroplanes. The titanium oxide colloid is heavy and form heavy smoke screen like curtain of dazzling whiteness.

(10) Blue Colour of the Sky: Colloidal dust particles along with water suspended in air scatter blue light which reaches our eyes and sky appears blue to us.

(11) Curdling of milk: The sugar present in milk produces lactic acid on fermentation. Ions produced by acid, destroy the charge on the colloidal particles present in milk, which then coagulate and separate as curd.

(12) Tail of the comets: When the comet flies with very high speed, it leaves behind a tail of tiny solid particles suspended in air. These particles scatter light forming Tyndall's cone, which looks like tail of the comet.

(13) Photographic plates and films: The photographic plates and films are obtained by coating an emulsion of the light sensitive AgBr in gelatin over glass plates or celluloid films.

(14) Coagulation of Blood: Bleeding caused by razor shaving can be stopped by rubbing alum (containing Al^{3+}) against the cut which coagulates the blood and seals the blood vessels.

(15) Industrial Products: Paints, rubber, inks, graphite lubricants, cement, etc. are all colloidal solution.

Exercises

I. Subjective Questions

- What do you understand by colloidal solution. Mention the types of colloidal system.
 - Define lyophobic and lyophilic colloids. How they differ from each other. Give examples of lyophobic and lyophilic colloid.
- Discuss the various methods of preparation of colloidal solution. How the colloidal sols are purified?
 - Give the important properties of Colloidal Solution.
- Discuss critically:
 - Sols
 - Peptization
 - Brownian movement
 - Tyndall phenomena
 - Electrophoresis
 - Coagulation
 - Gold number
 - Schulze-Hardy rule
 - Gels
 - Isoelectric point
 - Protective action and gold number
 - Inhibition
- What are emulsions? How they are classified? How they are prepared?
 - How emulsions are destroyed?
- What is Schulze-Hardy rule? How this rule predict the coagulation of sols?
 - Give various applications of colloidal phenomena.
- Classify the following on the basis of colloidal system:
 - Milk
 - Flesh
 - Paints
 - Ceramics
 - Whipped cream
 - Insecticide spray
 - Gems
 - Ink
 - Shaving lather
- Describe briefly a preparation method for each of the following sols:
 - Ferric hydroxide sol
 - Arsenious sulphide sol
 - Gold Sol.
 - gelatine jelly
 - oil emulsion
- Make a comparative table for the properties of (i) lyophobic and (ii) lyophilic colloids with respect to stability, electric charge and other physical properties, comparison and method of preparation.

II. Account for the following.

- Why organic reducing agents such as tannin give stabler and finer gold sol than inorganic reducing agents?
- Why river mouths have to be periodically dredged to keep it navigable?
- The formation of delta at the mouth of river.
- Why oil spill from petroleum tanker is considered as an ecological menance.
- Why vinyl plastic emulsion paints for walls are much more durable than simple colour wash or line wash?

6. Alum is used in town water supply.
7. A cone appears when a beam of light passes through gold sol.
8. The colour of sky appeared blue.
9. A sulphur sol is coagulated by adding a little electrolyte whereas a gelatine sol remain unaffected.
10. Activated charcoal is used to recover volatile solvents.
11. Hydrrous oxide of Fe, Cr, Al are positively charge sols.

III. Fill in the blanks.

1. The range of colloidal particle lie between
2. A freshly prepared $\text{Fe}(\text{OH})_3$ precipitate is peptized by adding FeCl_3 solution. The charge on the colloidal particles is due to preferential adsorption of
3. Peptization involvesof colloidal aggregates.
4. The coagulating power of an effective ion carrying charge opposite to the sol particles is given by
5. Micelles are
6. During adsorption
7. Gold number is an index for
8. Micelle systems are used in
9. At low pressure, the fraction of surface covered follows
10. Fog is a colloidal solution ofparticles dispersed in

IV. Multiple Choice Questions (More than one option may be correct).

1. The size of the colloidal particle is of the order of
(a) 10^2 m (b) $100 \text{ m}\mu$ (c) $1 \text{ m}\mu$ (d) wavelength of light
2. The surface area of colloid is about
(a) 6 cm^2 (b) $6 \times 10^6 \text{ cm}^2$ (c) $6 \times 10^2 \text{ m}^2$ (d) 600 cm^2
3. Fog is an example of
(a) Liquid dispersed in gas (b) Solid dispersed in gas
(c) Gas dispersed in liquid (d) Gas dispersed in liquid
4. Polymer composites belong to
(a) gas dispersed in gas (b) solid dispersed in solid

(c) liquid dispersed in liquid (d) gas dispersed in liquid

5. A colloidal solution in which a solid is dispersed in a liquid is called?

(a) Gel (b) Emulsion (c) Sol (d) coagulation

6. Lyophilic sols are more stable than lyophobic sols because

(a) The colloidal particles have positive charge (b) The colloidal particles have no charge
(c) The colloidal particles are solvated (d) Large size of their particles

7. Which of the following is the property of hydrophilic sols

(a) High concentration of dispersed phase can be easily attained
(b) Coagulation is reversible
(c) Viscosity and surface tension are about the same as water
(d) The charge of colloidal particles depends on the pH of the medium and it may be positive, negative or zero

8. The purification of colloidal solution is called

(a) Electrodialysis (b) Peptization (c) Pyrolysis (d) Coagulation

9. Which of the following factors give rise to colloidal properties

(a) High ratio of electrical charge to the mass (b) High ratio of surface area to the volume
(c) High charge density (d) Large size

10. Which of the following is irreversible colloid?

(a) Clay (b) Pt (c) $\text{Fe}(\text{OH})_3$ (d) None of these

11. Which of the following is not a colloid

(a) Milk (b) Egg (c) Glue (d) Chlorophyll

12. Which of the following is hydrophilic colloids?

(a) Gelatin (b) Starch (c) Clay (d) all of these

13. Colloidal solutions are prepared by the method of

(a) oxidation (b) reduction (c) hydrolysis (d) double decomposition

14. Brownian movement is due to

(a) external influence of dispersed phase
(b) gravitational and electrical field
(c) bombardment of the dispersed particles by the molecules of dispersion particles
(d) attraction and repulsion between charges on the colloidal particles

15. Which of the following is true for Brownian movement?

(a) particle size larger than 4μ diameter do not exhibit Brownian movement
(b) velocity of Brownian movement cannot be measured with any degree of accuracy
(c) Zig-zag motion of suspended particle
(d) Brownian movement is accelerated by light

16. Which of the following is true for Tyndal effect?

(a) The scattering and polarizing of light by small suspended particles is called Tyndall effect
(b) Tyndall effect of colloidal particles is due to dispersion of light
(c) Tyndall beam is observed by ultra microscope

(d) Tyndall effect is due to refraction of light

17. Which of the following are true for electrophoresis

- (a) Colloids are charged particles and migrate toward the electrode when electric field is applied
- (b) In electrophoresis, sol migrates to the anode or cathode depending on the sign of positively or negatively charged colloidal particles.
- (c) Electrophoresis is useful to find the charge of sol
- (d) Electrophoresis is an optical phenomena

18. Which of the following is the positively charged sol

- (a) Methylene blue (b) Hydrated oxide of Al
- (b) Dyes (d) Sn

19. Negatively charged sol is

- (a) metals (b) oxides (c) gums (d) starch

20. Gold number is associated with protective actions of

- (a) lyophobic colloids only (b) lyophilic colloids only
- (c) both lyophobic and lyophilic colloids (d) None of these

21. On adding 2 mL solution of 5% NaCl to 10 mL of gold sol in the presence of 0.025 g of starch the

coagulation is just prevented. Starch has the gold number of

- (a) 0.25 (b) 2.5 (c) 25.0 (d) 0.025

22. Gold number is minimum for

- (a) Gelatin (b) Casein (c) Gum Arabic (d) Potato starch

23. Which of the following statement is incorrect?

- (a) Higher the gold number of a lyophilic substance better is its protective action
- (b) Lower the gold number of a lyophilic substance better is its protective action
- (c) The Bredig arc method is usually suitable for preparing sols of metals
- (d) All of these

24. The arsenious sol is negatively charged. The maximum power of precipitating it is in

- (a) Na_2SO_4 (b) Na_3PO_4
- (c) AlCl_3 (d) MgNO_3

25. Which of the following has minimum flocculating power?

- (a) Sn^{2+} (b) Sn^{4+}
- (c) Al^{3+} (d) K

26. In the coagulation of positively charged colloidal solution which of the following has maximum

coagulating power?

- (a) CO_3^{2-} (b) $[\text{FeCN}_6]^{4-}$ (c) PO_4^{3-} (d) Al^{3+}

27. In the coagulation of positively charged $\text{Fe}(\text{OH})_3$ which of the following has the minimum coagulating power?

- (a) HCOONa (b) $\text{Na}_2\text{C}_2\text{O}_4$
- (c) $\text{K}_3[\text{FeCN}_6]$ (d) $\text{K}_4[\text{FeCN}_6]$

28. Schulze-Hardy rule states that

- (a) larger the size of the coagulating ion greater its coagulating power
- (b) sol must have zero gold number
- (c) precipitating ion must be of oppositely charge sol
- (d) all of these

29. Indicate the correct statement

- (a) Gel is a system which constituting the liquid as a dispersed phase and solid as a dispersion medium
- (b) Gels are less viscous substance
- (c) Gelatinous precipitates are the examples of gels
- (d) Gels are continuous three dimensional network having sponge-like structure

30. Gelatin is mostly used in making ice cream in order to

- (a) prevent the formation of colloid
- (b) to stabilize the colloid and prevent crystallization
- (c) form gel
- (d) produce smell in ice cream

31. Butter is a colloid, which is formed when

- (a) Fat is dispersed in water (b) Fat is dispersed in gel
- (c) Water is dispersed in fat (d) All of the above

32. Emulsions are

- (a) Drops of one liquid dispersed in the bulk of a second liquid
- (b) Stable when some emulsifying agent are added
- (c) Stable due to electrical potential on the colloidal droplets
- (d) Solid dispersed in liquid

33. Indicate the correct statement:

- (a) Emulsions are prepared by shaking two liquid components say oil and water and adding some emulsifying agent
- (b) Oil-in-Water emulsions are formed when the emulsifying agent at the interface is chiefly in the water phase
- (c) Water-in-Oil emulsions are formed when the emulsifying agent at the interface is chiefly in the oil phase
- (d) Gels and sols mixed together to give emulsion.

34. An emulsifier is a substance which

- (a) Stabilizes the emulsion (b) helps in coagulation
- (c) helps in breaking emulsion (d) homogenises the emulsions

35. Which of the following is an emulsifier?

- (a) Oil (b) Water (c) Milk (d) Soap

36. Emulsion can be destroyed by

- (a) Addition of an emulsifier which tends to form an emulsions of opposite type
- (b) Freezing
- (c) Electrophoresis with a high potential
- (d) Centrifuging

37. FeCl_3 is used to stop bleeding because
 (a) Fe^{3+} ion coagulates the blood which is a negatively charged sol.
 (b) Fe^{3+} ion coagulates the blood which is a positively charged sol.
 (c) Cl^- ion coagulates the blood which is a positively charged sol
 (d) Cl^- ion coagulates the blood which is a negatively charged sol
38. The blue colour of water in the sea is due to
 (a) Absorption of other colours except blue by water molecules
 (b) Scattering of blue light by water molecules
 (c) Refraction of blue light by water molecules
 (d) Reflection of blue sky by sea water
39. Blue colour of the sky and red colour of the sunsets are due to
 (a) Scattering of light from particles of dust in the atmosphere
 (b) Scattering of light from the sun
 (c) Scattering of light due to ozone layer
 (d) all of these
40. Applications of colloids are
 (a) Formation of deltas at the mouth of rivers (b) Colour of living things
 (c) Soaps and synthetic detergents (d) Ceramics and paper industry

Exercises

Fill in the Blanks

1. 0.5μ to $1\text{ m}\mu$ 2. Fe_2O_3 3. disintegration 4. Schulze-Hardy law
 5. associated colloids 6. ΔH $T\Delta S$ is negative 7. Protective power of lyophilic colloids
 8. detergents and petroleum recovery 9. first order reaction 10. liquid, gas

MCQ

1. c 2. b, c 3. a 4. b, d 5. c 6. c
 7. c 8. a 9. b 10. a, b, c 11. d 12. a, b
 13. a, b, c, d 14. c 15. a, b, c 16. a 17. a, b, c 18. a, b
 19. a, c, d 20. b 21. c 22. a 23. a 24. c
 25. d 26. b 27. a 28. a, c 29. a, c, d 30. b
 31. a 32. a, b, c 34. a 35. d 36. a, b, c, d 37. a
 38. b 39. a 40. a, b, c, d

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