Chapter-VI
Colloidal State

Contents:

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6.1Introduction:

A) Crystalline substances: Solution of Sugar, urea, common salt passes through membrane but others like gelatin, glue did not. Solutions of sugar, urea and common salt seen clear like water but of gelatin glue thicker than water and not clear.

B) Graham's statement: 1861 (Founder of colloidal state)

Materials like sugars, urea be called as crystalloids and gelatin, glue be called as collides. This is due to particle size. Any substance can be convertible to collide.

C) Characteristics of solution:

- Solutions contain small particles (ions or molecules).
- Solutions are transparent
- Solutions do not separate
- Solutions cannot be filtered.
- Solutions do not scatter light.(Tyandell effect)
- Solute particles dispersed in solvent as single molecules or ions.
- Particle size (diameter) of Solutions 10^{-7} to 10^{-8}cm
- Examples Salt, sugar, oxalic acid Solutions etc.

D) Characteristics of suspension:

- Suspension have very large particles.10^{-2} to 10-7cm
- Suspension settle out and can be filtered
- Suspension must be stirred to stay suspended
- In Suspension, Insoluble particles remains suspended in liquid or gas
- Examples. Coffee/tea with milk, blood platelets, muddy water, Calamine lotion, oil, vinegar dressing, milo drink etc.

A colloid is one of the three primary types of mixtures, with the other two being a solution and suspension. A colloid is a solution that has particles ranging between 1 and 1000 nanometers (10^{-9} meters) in diameter, yet is still able to remain evenly distributed throughout the solution. These are also known as colloidal dispersions because the substances remain dispersed and do not settle to the bottom of the container. In colloids, one substance is evenly dispersed in another. The substance being dispersed is referred to as being in the dispersed phase, while the substance in which it is dispersed is in the continuous phase.

6.2 Definition of colloids: Colloids (also known as colloidal solutions or colloidal systems) are mixtures in which microscopically dispersed insoluble particles of one substance are suspended in another substance.

A) Characteristics of colloids:

- Colloids have medium size particles.10^{-4} to 10^{-7} cm. that is Intermediate between the true solution and suspension.
- Colloids cannot be filtered.
- Colloids can be separated by semipermeable membranes.
- Colloids scatter light (Tyndall effect-in which the path of a beam of light through the colloid is visible due to scatter light).
- Colloids usually corpuscular (Grain like) but may be rod, disc shaped, thin films or long filament
- Ex…Fog, Whipped cream, Milk, Cheese, Blood plasma, Pearls etc.

B) Differentiation between True Solution, Colloids and Suspension. (Table-6.1)

Sr. No	Property	True solution	Colloids	Suspension
01	Particle size	1 Å – 10 Å	10 Å – 1000 Å	More than 1000 Å
02	Appearance	Clear	Generally clear	Opaque
03	Nature	Homogeneous	Heterogeneous	Heterogeneous
04	Separation by filtration	Not possible	Not possible	Possible

05	Separation by cellophane paper	Not possible	Possible	Possible
06	Visibility	Not visible under microscope	Visible under ultra-microscope	Visible to naked eye
07	Brownian motion	Not observable	Occurs	May occur
08	Sedimentation	Do not settle	Do not settle	Settle on standing
09	Diffusion	Diffuse quickly	Diffuse slowly	Unable to diffuse
10	Filterability	Pass easily through animal membrane and filter paper	Pass through filter paper but not through animal membrane	Unable to pass through animal membrane and filter paper

C) Components of colloids:

1) A dispersed phase- substance distributed as colloidal particles.

2) Dispersed medium- medium in which the colloidal particles are dispersed.

Ex. As_2S_3(Arsenic sulphide) is dispersed phase and water as dispersion medium.

3) Stabilizing agent (adding agent) - agent added in colloidal solution for to keep colloidal particles in a pair.

Dispersed phase + Dispersion medium $\longrightarrow$ Dispersion system (colloidal solution)

6.3 Classification of colloids: (Table-6.2)

Sr. No.	Dispersed phase	Dispersion medium	Type/ Name	Examples
01	Gas	Liquid	Foam	Shaving cream, soap lather, whipped cream, froth on beer
02	Gas	Solid	Solid soal	Cake, foam rubber, bread, lava, pumice stone
03	Liquid	Gas	Aerosol	Fog, mist, cloud, smoke, dust, Insecticide sprays
04	Liquid	Liquid	Emulsion	Milk, oil in water, hair cream, butter
05	Liquid	Solid	Gel	Cheese, jellies, curds, pudding
06	Solid	Gas	Smoke	Dust, soot in air, smoke

07	Solid	Liquid	Sol	Paint, ink, white of egg, mud, cell fluid
08	Solid	solid	Solid sol	Ruby glass, gem stones, coloured glass, alloys

6.4 Solids in liquids (Sols):

Sols are colloidal solutions in which solid is dispersed in liquid. |

1.When water is dispersion medium-----called as hydrosol or **aquasol.**

2. When medium is alcohol……..called as **alcosols.**

3. When benzene is medium…..called as **benzosols.**

A)There are two types of Sol: (depends on interaction of two phases).

1) Lyophilic sols (solvent loving):

- In this type of sols the particles in a lyophilic system have a great affinity for the solvent.
- They readily solvated (combined chemically or physically, with the solvent) and dispersed, even at high concentrations.
- Due to high degree of solvation it has high viscosity and surface tension is lower than the medium.
- In this type the dispersed phase does not precipitate easily.
- In these sols, process of precipitation called coagulation. Stabilized agents are added to prevent coagulation…
- These sols are quite stable as the solute particle surrounded by two stability factors: a- negative or positive charge and b- layer of solvent
- Ex. sols of gum, gelatin, starch, proteins and certain polymers (rubber) in organic solvents.

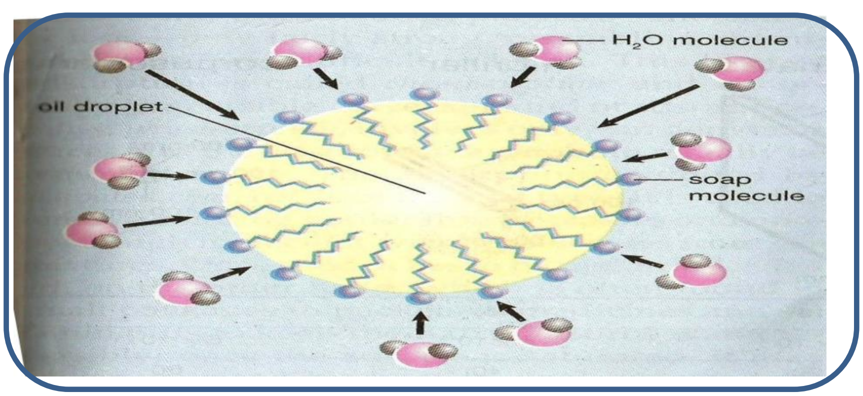
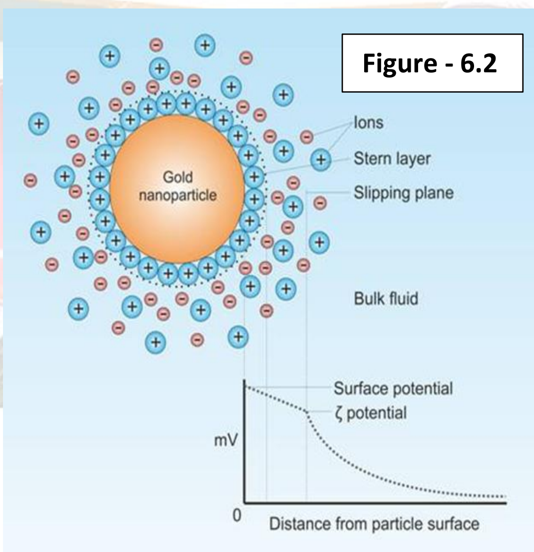


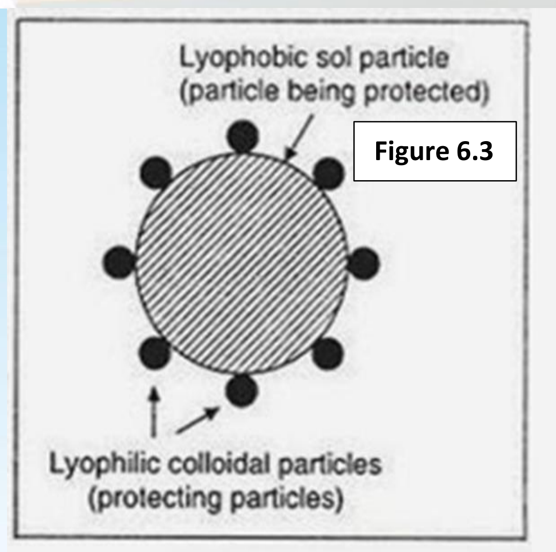
Figure: 6.1

2) Lyophobic sols (solvent repelling) (solvent hating):

- In these types of sols the particles resist solvation and dispersion in the solvent.
- They are slight interaction between suspended particles and medium.
- The concentration of sol particles is usually relatively low.
- Lyophobic sols are less viscid.
- These sols/colloids are easily precipitated on the addition of small amounts of electrolytes, by heating or by shaking
- They are less stable as the particles surrounded only with a layer of + or -.
- If once lyophobic sols they precipitated, it is not easy to reconstitute the sol by simple mixing with the dispersion medium. Hence, these sols are called irreversible sols.
- Ex… sols of metals and their insoluble compounds like sulphides and oxides.

  1) Gold in water (As_2S_3) 2) Iron (II) hydroxide and sulphur in water.





6.4.1 Properties of Colloids:-

1) Physical property: Lyophilic and lyophobic sols (earlier discussed)

2) Colligative property: (V.P., elevation in B.P., lowering of freezing pt., osmotic pressure)

These are very much smaller than that of true solution.(Except effect in osmatic press.) **3) Optical property:** (Tyndall effect Colloidal particles scatter light. Discovered by Tyndall (1820-1893) known as Tyndall effect.

Examples of Tyndall effect:

1. Head light of car on dusty road.

2. Light beam of film projector in smoke filled theatre

3. Light beam coming through roof in a dust filled huts

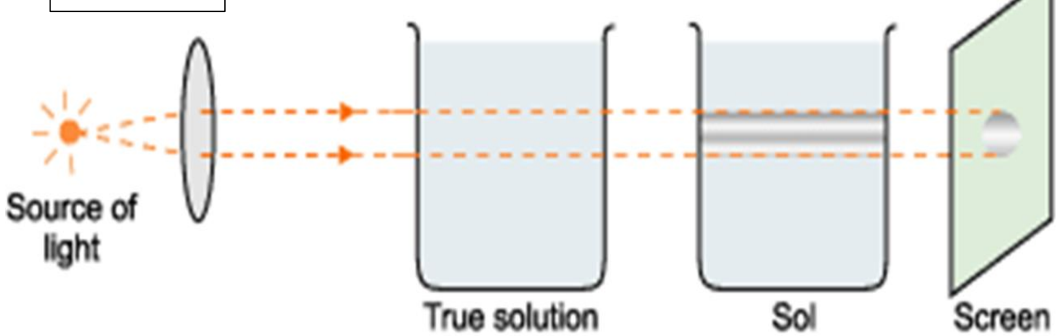
A) Description of Tyndall effect: When a strong beam of light passed through a sol and is viewed at right angles, the path of light shows up as a heavy beam or cone. The scattering of light as it is called as illuminates the path of the beam in the colloidal dispersion.(Shining a beam of light through a colloid)

The cone formed by scattering of light by sol particles is often called as Tyndall beam or Tyndall cone.

B) Characteristics of Tyndall effect:

1. It is a positive sign to detect colloidal particles.
2. True solution never shows this effect due to too much smaller ions, can’t scatter light.
3. Intensity of scattered light depends on the difference between the R.I. of phase and medium.
4. Extent of scattering depends on the size of solute, in very dilute soln.it is small.
5. In this effects no difference between the wavelength of incident and scattered light.
6. In case of Lyophobic collides the R.I.is appreciable, Tyndall effect is well defined.
7. In case of Lyophilic collides there is high solvation and R.I. diff.is small hence shows weak Tyndall effect.

Figure: 6.4



C) Conditions for Tyndall effect:

1) Wavelength of light not larger than diameter of size of particle of phase.
2) R.I. of phase and medium should have considerable difference.

Figure: 6.5

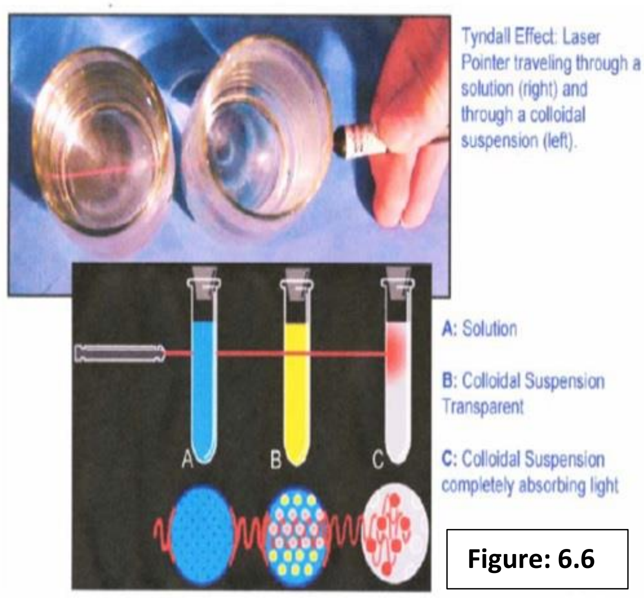


Figure: 6.6

4) Kinetic properties of sol: Robert Brown (Botanist) 1827

A) Diffusion: Colloidal particle diffuse much more slowly than solutes in true solutions.

B) Brownian motion: Robert Brown showed that pollen grains when suspended in water show continuous rapid and random motion in all directions. (Zigzag motion in straight line path seen under ultra-microscope).

- The constant pushing of colloidal particles by the molecules of the medium does not permit to settle.
- The Zigzag movement of colloidal particles continuously and randomly.
- Brownian motion arises due to the uneven distribution of the collision between colloid particle and the solvent molecule.
- Brownian motion was more rapid for smaller particles.
- Brownian motion increases with decrease in viscosity of the medium.

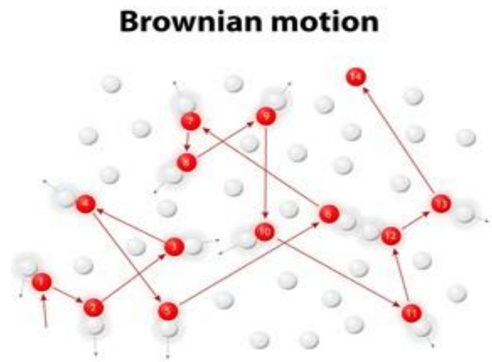


Figure: 6.7

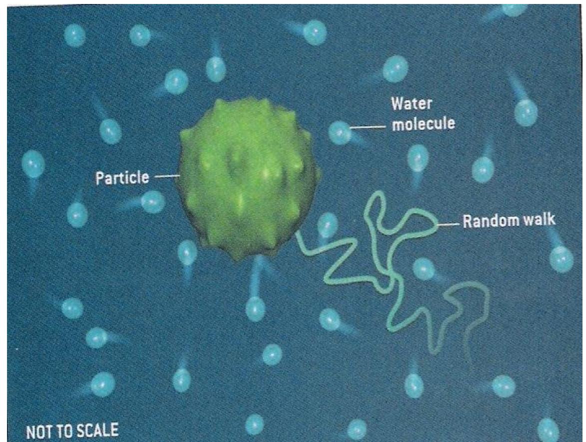


Figure: 6.8

Examples of Brownian motion:

1) Glittering, tumbling motion of small dust particles

2) Pollen grains in water

3) Tea diffusing in water

4) Ink drops added in water

5) Burning incense stick (Agarbatti) in air

6) Milk fat jiggles in water

7) Heavy drunker walking randomly

C) Sedimentation: Sedimentation, or clarification, is the processes of letting suspended material settle by gravity.

Sedimentation is the tendency for particles in suspension to settle out of the fluid in which they are entrained and come to rest against a barrier. This is due to their motion through the fluid in response to the forces acting on them: these forces can be due to gravity, centrifugal acceleration, or electromagnetism.

Under influence of gravity on prolonged standing colloids gets settles very slowly hence from that we can calculate dimensions and masses of particles by knowing density and viscosity of phase and medium and time of sedimentation.

At small particle size (less than 0.5 um) Brownian motion is significant and ends to prevent sedimentation due to gravity and promote mixing. So Sedimentation can be carried out by ultracentrifugation (high speed centrifuge machine) which creates high centrifugal force so promote sedimentation in a measurable manner.

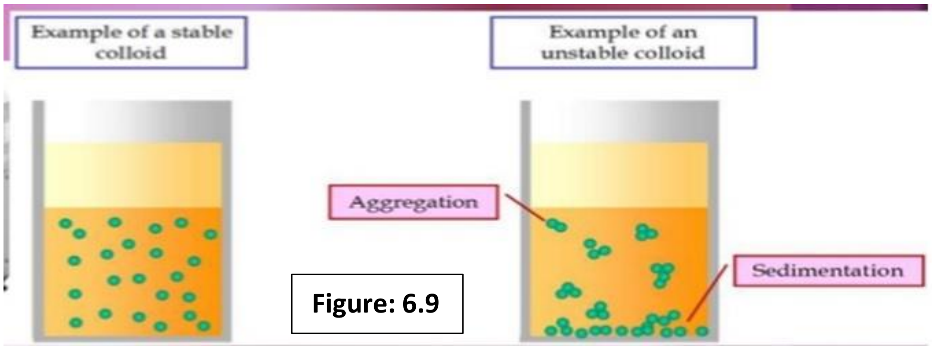


Figure: 6.9

05) Electrical properties: As colloidal particles carries an electric charge, when they placed in electric field, certain effects are observes….which are known as **electro kinetic effects.**

There are of four types of electro kinetic effects.

5.1) Electrophresis or cataphoresis.

5.2) Electrosmosis or Electro endosmosis.

5.3) Streaming potential

5.4) Sedimentation potential or Dorn effect

5.1 Electrophoresis or cataphoresis:

Electrophoresis refers to the motion of charged particles related to the fluid under the influence of an applied electric field. If an electric potential is applied to a colloid, the charged colloidal particles move toward the oppositely charged electrode.

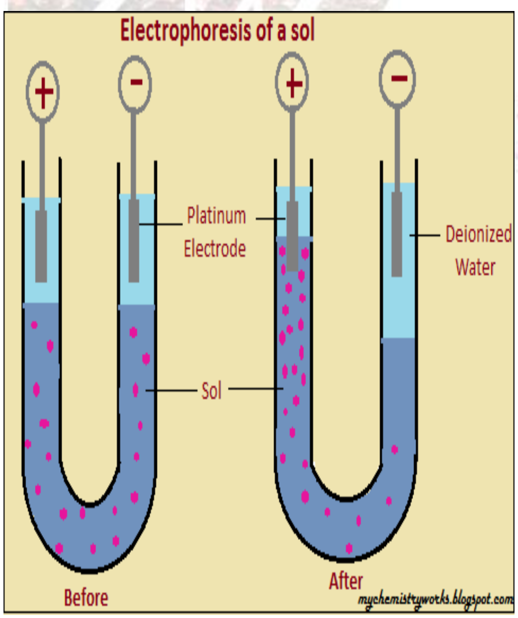


Figure: 6.10

Applications:

1. Rate of migration of colloids under influence of electric field.
2. Method is used for preparative separations of colloids.
3. It is used to detect charge of colloids
4. Used to separate proteins, DNA, RNA, polysaccharides
5. Useful for coagulation of carbon from colloidal smoke of industry chimney and removed on cathode.
6. Useful in electroplating of rubber on metal surfaces.
7. Used in Paintings of metal parts of cars from colloidal pigments.

5.2) Electrosmosis:

- It is the opposite in principal to that of electrophoresis.
- It is migration of ions in a solvent through the capillaries of membrane under the influence of an applied electric field.
- When electrodes are placed across clay mass and a direct current is applied, water in the clay pore space is transported to the cathodically charged electrode by electro-osmosis.
- Electro-osmotic transport of water through clay is a result of diffuse double layer cations in the clay pores being attracted to a negatively charged electrode or cathode. As these cations move toward the cathode, they bring with them water molecules that clump around the cations as a consequence of their dipolar nature.

5.3) Diffusion: It is tendency for molecules to migrate from a region of high concentration to a region of lower concentration and is a direct result of Brownian motions. Colloids show diffusion property.

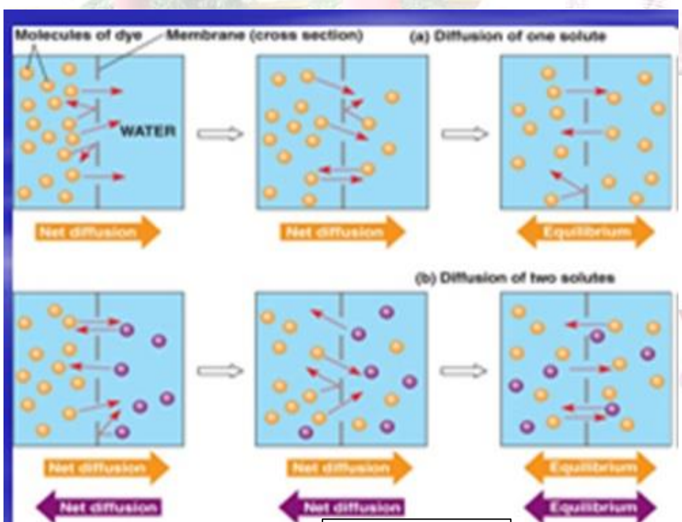


Figure: 6.11

Applications:

1. Diffusion technique is used to prepare pure colloids.
2. This technique is used in drying of peat and clay.
3. Useful In the tanning of hides.
4. Useful in manufacture of gelation for photographic emulsions and high grade glue.

6.4.2 Stability of colloids:

<u>A) Stability of lyophobic sols:</u>

Stability due to presence of electric charge on it to precipitate a colloidal solution or sol , the particles must coalesce so as to form aggregates. Such type of agglomeration is avoided by presence of electric charges of same sign.

For e.g. AgBr sol (if there is presence of excess of $AgNO_3$) contains positively charged Br particles, on account of adsorption of Ag+ ions on the surface of particles. **B) Stability of lyophilic sols:** Stability due to electric charges of same sign. **Solvation:** It is tendency to bind with solvent…. The layers of molecules of solvent forms and envelop which prevents aggregation. Lyophobic colloids readily coagulated by removing the electric charge while lyophilic colloids, the charge removal may decrease stability but does not lead to coagulation.

C) Isoelectric Point of colloids: The concentration at which the colloidal particles have no charge.(The concentration of H^+ can be increased by addition of acid and OH^- by addition of NaOH.

Hardy's opinion is that, at isoelectric point colloidal particles are electrophoretically inert. Most of the colloids coagulate at this point, if they don't, they are least stable, and they can be readily coagulated with alcohol.

Eg….Gelatin has isoelectric pt.at P_H 4.7 indicates it has no motion at this P_H at a P_H below 4.7 it moves towards the cathode…..while at P_H above moves towards the anode.

6.4.3 Hardy-Schulze law:

- Due to repulsive force lyophobic sols do not allow them to settle. They would be settling if the charge is removed.
- Hardy Schulze rule states that **the amount of electrolyte required for the coagulation of a definite amount of a colloidal solution is dependent on the valence of the coagulating ion**.
- Hardy and Schulze observed that greater the valence of the flocculating ion or coagulating ion, the greater is its power to coagulate. **OR**
- In other words we may say that, **Greater is the valences of the oppositely charged ion of the electrolyte being added, the faster is the coagulation**.
- That is greater the charge, greater the coagulating capacity.
- The idea behind this is the attractive electrostatic forces between ions of opposite charges.

- **Examples:** precipitation of As_2S_3 (negative surface) the precipitating power as an order….$Al^{+3} > Ba^{+2} > Na^+$; similarly precipitation of Fe(OH)3 sol (negative surface) the precipitation power of anions is in order $[Fe(CN)_6]^{3-} > SO_4^{-2} > Cl^-$

6.4.4 Protective action: Process of addition of lyophilic sols by which the lyophobic sols are protected from precipitation on adding an electrolyte is known as protection.

The lyophilic colloid added as the protective colloid and lyophobic sols achieve extra stability…**This may be due to:**

The hydrophile (hydrophilic) is adsorbed as a monomolecular layer on the hydrophobic particles. For eg. Hydrophilic colloids such as gelatin, starch etc. act as protective colloids for the gold sol and prevents their precipitation by addition of limited amount of NaCl.
Eg.1) Soluble $Ca_3(PO_4)_2$ are held as colloids in blood due to protective action of protein in blood.
2) To prevent clogging in pen; superior pen inks contains some protective colloids.
3) Protargol and Argyrol powders are protected forms of the colloidal silver.

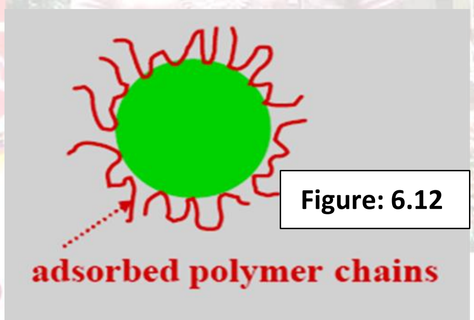


Figure: 6.12

6.5 Liquid in liquid (Emulsions): An emulsion is a colloidal system of two immiscible liquids one of which is dispersed throughout the other in small droplets. Thus we can have an emulsion of oil in water by shaking vigorously few drops of oil in excess water. Similarly, an emulsion of water in oil can be obtained by taking few drops of water in oil.

6.5.1 Types of emulsions:

1. **Oil in water (O/W):** Oil is dispersed in water medium. Example: Milk emulsion.
2. **Water in Oil (W/O):** Water is dispersed in oil. Example: Cod liver oil.

Term oil is used to designate any liquid which is immiscible with water and capable of forming an emulsion with water. Emulsion particles can be observes by microscope or sometimes magnifying lens, due to diameter of droplets are in range of 0.1 micron and having small stability.

A) Experimental methods for identification of emulsions:

01) Conductivity method

02) Fluorescence method or dilution method

B) Emulsifiers: colloidal emulsions can be prepared when two immiscible liquids such are oil and water are shaken together vigorously. But the emulsions thus prepared are not stable and tend to separate on standing. **In order to get stable emulsion small quantity of third substance is added** called an **emulsifying agent or emulsifier**.

C) Role of emulsifier: It reduces the surface tension of one of the liquids.

Examples: 1) Emulsifiers such as Soaps or detergents are used to reduce the surface tension.
2) While Gelatin, egg albumin, gum that is lyophilic colloids can used which forms protective coating around small drops.

6.5.2 Preparation of emulsions:

1. By shaking or stirring the two phases. That is dispersion phase and medium in presence of liquid emulsifier.
2. By adding a solution in excess to another solvent, which quickly dissolves the solvent of the added solution but keeps liquid solute dissolved.
3. Emulsions can also prepared by using ultrasonic waves.

6.6 Liquid in Solid (Gels): A colloidal solution in which liquid is dispersed in solid is called as Gel.

Lyophilic sols like gelatin or agar –agar when treated with sufficient quantity of water produce a sol. When these sols are cooled, the whole mass sets to a homogeneous semisolid and elastic mass.

In a process of gel formation, the sol particles come together and forms bigger aggregates which finally grow so large that they touch each other. These aggregate continue to grow and form a continuous network of bigger particles. Liquid droplets get caught in this network, so in gel the solid mass is continuous while liquid is discontinuous. Thus the structure of gel is similar to honeycomb.

Examples: 1) When alcohol is added to saturated solution of calcium carbonate in water initially produces a colloid which coagulates to a semisolid mass of $CaCo_3$ in which alcohol is trapped. This gel of alcohol in $CaCO_3$called solid alcohol, is used as solid fuel in picnic stoves, military camp,etc.
2) Silicic acid gel in water, sodium oleate gel in water or gelatin in water, curdled milk, piece of meat(complex gel).

6.6.1 Types or classification of gels:

1. On the basis of dispersion medium: If medium is benzene then sols called benzogel and if the medium is alcohol called as alcogel similarly if water then called as hydrogel.

2) On the basis of particle size: A) Colloidal gel: In the sols size of gel is bog size and B) Coarse Gels: In this type there is small size of gel is observed.

3) On basis of chemical Composition: A) Inorganic gels B) Organic gels

4) On the basis of their property: A) Rigid gel B) Elastic gels C) Non elastic gellies D) Thixo-tropic gel

5) Elastic or reversible gels: These are semisolid and somewhat elastic in nature**.** In this type substance is mixed with warm water properly and then cooled till it sets after dehydration it converts into elastic semisolid form. This may be regenerated by adding water. Example: Gelatin and agar-agar.

6) Non elastic or irreversible gels: When dry solid mixed with water and further dried then loses their acidity and becomes glassy, thus rigidity increases with time. There is no deformation on applying force. Example: Silica gel, Ferric oxide gel.

6.6.2 Methods of preparation of gels: 1.By coagulation or decrease in solubility: Many colloids transformed into gel by this method. This transformation is characterized by,

A) Shape of particle. B) Concentration of sol C) degree of solvation.
Eg.1) Sol of pectin sets on addition of alcohol or sugar.

2) Sol of Al/Fe hydroxide sets on addition of aluminum salt and ammonium hydroxide.
2) By chemical reaction: A) When Barium thiocyanate mixed with manganeous sulphate produces barium sulphate gel. B) When Aluminum salt solution combined with ammonium hydroxide gives aluminum Hydroxide Gel. C) Silica gel, a non-elastic gels obtained by mixing solutions of sodium silicate and HCl of appropriate concentrations.

$$Na_2SiO_3 + 2HCl \longrightarrow \underset{\text{Silica acid Gel}}{H_2SiO_3} + NaCl$$

3) By cooling colloidal solution: When Agar-agar, gelatin, soap etc. when heated in hot solvent they are soluble when they cooled they forms a gel. Formation of gelation sol depends on Temperature of gelation, time of gelation, viscosity of medium and minimum concentration of colloid.
4) By exchange of solvents: Exchange of solvent in which the sol is insoluble. Example: Calcium acetate gel, pure alcohol can be added to aq. Solution of calcium acetate, thus whole calcium acetate goes to alcohol which then sets in the form of a gel having the liquid.

6.6.3 Properties of Gels: 1) Electrical conductivity: (Kistler 1931): There is no change of electrical conductivity when sol converts into a gel. It is simply the change of state during this conversion.
2) Optical properties:1) Gels shows double refraction due to some property starts in gels or formed due to internal tension.2) Gels shows property of polarized light….thus we can measure R.I. of different gelatin gels.

3) Elastic properties: Gels shows compressibility, flexibility & tensile strength etc… properties.
4) Swelling or imbibition of gels: Hydrophilic or plastic gels having property of adsorbing definite amount of water or other liquid causes increase in volume of gels…it depends on A)Temperature of system B) P_H of solution C) nature of gel

5) Syneresis: Continuous liberation of liquid from a gel called as syneresis. Elastic and non-elastic gels both shrink when they kept standing. **Example:** 1) perspiring of cheese 2) suitable electrolyte added in silicic acid sol to form jelly and shrinks in size. Syneresis is reversal of swelling; it depends on temperature, pressure of electrolyte, medium and state of gel. It is important phenomenon in biological problems.

6.7 General applications of colloids:

- Colloid plays vital role in our daily life. Human body itself as a colloid.
- Protoplasm, the building material of plant cells and animal tissues and blood flows through our veins are colloidal in nature.
- Fats pass through our intestines in the form of emulsion.
- **Foods:** Milk is emulsions of butter fat in water protected by a protein.
- Fruit jellies, whipped cream.
- Ice-cream is dispersion of ice in cream.
- Bread is dispersion of air in baked dough.
- **Medicines:** Many colloidal solutions used in medicine as they are easily assimilated into body.
- Cod liver oil, shark liver oils are emulsions.
- Argyrols an eye lotion is colloidal soln. of silver protected by gelatin.
- Colloidal gold used in tuberculosis.
- Milk of magnesia is a popular emulsion.
- Many ointments are emulsions.
- Sulphur colloids are sprayed on plants to kill germs.
- Smoke is colloidal solution particulate matter from smoke is removed by applying voltage.
- Kidney removes urea and unwanted electrolyte from colloidal blood by dialysis. This is useful for kidney failure patients.
- Muddy water is purified by adding potash alum Al^{+3}.Reaction involves in following way,
  $Al\ (OH)_3 + 4H_2O \longrightarrow Al(OH)_3(H_2O)^{4+}$
- Cleaning action of soap is due to formation of oil in water type emulsions.
- Solid alcohols are used as fuels.
- Bleeding of blood can be stopped by Al^{+3} salts like alum.