# **Unit I**

CHAPTER

# Colloidal Dispersions

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A dispersed system is defined as a system in which one phase, the dispersed phase, is distributed uniformly as particles throughout another phase, called the dispersion medium or continuous phase.

# CLASSIFICATION OF DISPERSED SYSTEMS

Dispersed systems can be classified on the basis of the physical state of two phases, i.e. the dispersed phase and the dispersion medium. Since matter exists as gas, liquid and solid, nine different types of dispersed systems are possible as shown in Table 1.1.

Dispersed systems can also be classified on the basis of the size of dispersed phase as molecular dispersions (true solutions), colloidal dispersions and coarse dispersions.

Table 1.1: Examples of dispersed systems based on physical state			
Dispersion medium	Dispersed phase	Examples	
		Colloidal	Coarse
Gas	Liquid	Fog	Spray
Gas	Solid	Smoke	Dust
Liquid	Gas	Foam (aerosol)	Foam
Liquid	Liquid (immiscible)	Oil globules $<1 \times 10^{-3}$ mm	Emulsions
Liquid	Solid	Colloidal gold in water	Suspension of Kaolin in water
Solid	Gas	Solid foam (aerosol)	Solid foam
Solid	Liquid	Mineral oil in wax	Solid emulsion
Solid	Solid	Colloidal gold in glass	Solid suspension

# COLLOIDAL DISPERSIONS

It is the particle size of the dispersed phase that distinguishes the colloidal dispersions from true solutions as well as the coarse dispersions. Dispersed particles in the colloidal dispersions usually have a particle size ranging from 1 nm to 1 µm. The dispersed particles in the colloidal dispersions however have an enormous area as compared to the surface area of an equal volume of larger particles. This enormous surface area confers many unique properties to colloidal dispersions.

# CLASSIFICATION OF COLLOIDS

Colloidal dispersion can be broadly classified into the following types based on interaction of the particles of the dispersed phase (molecules/ions) with the molecules of the dispersion medium.

## 1. Lyophilic Colloids

Lyo means solvent. Lyophilic colloids may therefore be called solvent loving colloids. The degree of interaction in such types of colloids is appreciable, i.e. the dispersed particle and dispersion medium interact to a great extent. When the dispersion medium in these types of colloids is water, they are known as hydrophilic colloids. Examples of hydrophilic colloids include gelatin, acacia and albumin which form colloidal dispersion in water. Rubber and polystyrene form lyophilic colloids in non-aqueous, organic solvents such as benzene and are therefore also referred to as lipophilic colloids.

Lyophilic colloids are usually thermodynamically stable. These form colloidal dispersions spontaneously on adding to the appropriate dispersion medium. The viscosity of the dispersion medium generally increases greatly on addition of the dispersed phase with the sol turning to a gel at sufficiently high concentration. The dispersions are generally stable even in presence of electrolytes although the dispersed phase can be salted out by high concentrations of very soluble electrolytes.

## 2. Lyophobic Colloids

Lyophobic colloids may also be called solvent hating colloids. In these types of colloids, there is very little attraction between the dispersed particles and the dispersion medium. When the dispersion medium in these types of colloids is water, they are known as

hydrophobic colloids. Examples include colloidal dispersions of gold, silver and sulphur in water.

Lyophobic colloids are generally difficult to prepare and are thermodynamically unstable. The dispersed phase can be easily salted out even in presence of very small concentrations of electrolytes. The viscosity of the dispersion medium does not increase greatly by the presence of lyophobic colloidal particles which tend to remain unsolvated.

#### 3. Association Colloids

These are also known as amphiphilic colloids. Small molecules or ions having both polar and non-polar groups (amphiphiles) exist separately in dilute solutions but associate at the critical micelle concentration (CMC) to form micelle of colloidal dimensions.

Association colloids are thermodynamically stable. In aqueous solutions, the CMC is reduced by the addition of electrolytes. However, salting-out may occur at higher salt concentrations. The viscosity of the dispersion medium generally increases with increase in the concentration of amphiphiles. They are also easy to prepare and form spontaneously once the CMC is exceeded.

# PREPARATION OF COLLOIDS

### 1. Lyophilic Colloids

Because of the affinity of the lyophilic colloids for the dispersion medium, these colloids are relatively easy to form. As there is a considerable interaction between the disperse phase and the dispersion medium, they form spontaneously by placing the colloidal material in contact with the proper solvent. For example, acacia and gelatin disperse easily to form colloidal dispersions when kept in contact with water.

### 2. Hydrophobic Colloids

Since there is a lack of affinity between the molecules of the disperse phase and the dispersion medium, lyophobic colloids are more difficult to prepare. Generally, two methods are used:

- A. Dispersion method: In this method, the coarser particles are broken down into smaller particles of colloidal dimension through suitable means including the following:
  - 1. *Colloid mill:* Coarse materials are sheared between a static cone and a rapidly rotating cone. This method is also suitable for preparation of emulsions which require the use of protective colloid.
  - 2. *Electrical dispersion:* Certain metals may be dispersed by passage of an electric arc between electrodes made up of the metal and immersed in the dispersion medium.
  - 3. *Ultrasonic radiation:* The passage of ultrasonic waves through a dispersion medium produces high frequency oscillations (20,000 to 200,000 cycles per second) resulting in size reduction of coarse particles to colloidal size.
  - 4. *Peptization:* This is a process of converting precipitates of large particle size to colloidal size by means of low concentration of an electrolyte known as the peptizing agent. Certain dispersions of hydrophobic materials require a certain charge for stability. Certain ionic materials get preferentially adsorbed on the surface of a finely divided solid (precipitate) and convert it into a colloidal dispersion.
- B. **Condensation method:** In this method, particles of colloidal dimension are prepared by aggregation of particles of molecular range. This is usually achieved by means of

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a chemical reaction that results in the formation of colloidal dispersions from true solutions. By carefully controlling the conditions, the situation is altered so that particle growth stops at the colloidal state and large size particle formation is avoided. Factors which influence the particle size include the solubility and concentration of the disperse phase, the viscosity of the medium and the temperature. For example, colloidal sulphur is obtained by passing hydrogen sulphide through an aqueous solution of sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

Similarly colloidal dispersions of silver chloride may be obtained by double decomposition of sodium chloride with silver nitrate.

 $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$ 

A change in solvent may also cause the production of colloidal particles through condensation methods. For example, if alcoholic solution of resinous materials is added slowly into water, a colloidal dispersion of resin particles results. Similarly, if a saturated solution of sulphur in acetone is poured slowly into hot water, the acetone vaporizes leaving behind a colloidal dispersion of sulphur in water.

# PURIFICATION OF COLLOIDS

Many methods of preparation of colloids may give product which is a mixture of colloidally dispersed particles and particles in true solution. Purification means removal of such materials from true solution since coarse particles, if present can be easily removed by filtration.

The following techniques are generally applied for purification of colloids:

#### 1. Dialysis

Colloidal particles do not diffuse through membrane of parchment, cellophane, etc. whereas particles of molecular or ionic dimension readily diffuse through such membranes.

Dialysis involves the separation of micro-molecular impurities from colloidal dispersion based on the difference in diffusibility through membrane. In this method, colloidal material containing impurities is put in a cellophane bag, tied and suspended in large volume of water (Fig. 1.1). The small molecules pass through like ions (sodium and chloride), glucose,



Fig. 1.1: Assembly and principle of dialysis

urea, etc., pass through the pores leaving only colloidal particles in the bag. Water may be changed several times.

A certain amount of dilution of colloidal material takes place because water passes through the membrane pores under the influence of the osmotic pressure of colloids. This can however be prevented by applying pressure equal to or greater than the osmotic pressure. This technique is known as dialysis under pressure.

#### 2. Electrodialysis

Ordinarily, dialysis is a relatively slow process and if electrolytes of low molecular weight are present as impurities to be removed, the process can be speeded up by the application of electric potential. This technique is known as electrodialysis. An electrodialyser, as shown in Fig. 1.2 consists of three compartments, two outer compartments and one central compartment. The central compartment is separated from the outer compartments by two dialysing membranes supported by screens. The outer compartments, in which the two electrodes are placed, are filled with water while the colloidal sol is placed in the central compartment. When an electrical potential is applied, the anions move from the sol towards the anode compartment while the cations move towards the cathode compartment. Nonelectrolyte impurities move into either of the two compartments.



Fig. 1.2: Assembly and principle of electrodialyser

Since the colloidal particles also usually carry a charge, they also tend to migrate towards one of the electrodes but are blocked by the membrane. They therefore accumulate near one of the compartments and settle down due to gravitational force. The supernatant liquid can then be changed by decantation and the process is often referred to as electrodecantation.

#### 3. Ultrafiltration

Colloids easily pass through an ordinary filter paper but are retained on nitrocellulose or collodion impregnated filter membranes. Purification of colloids is thus possible by filtering them through membrane filters of very small pore size whereby the small molecules filter through leaving behind the colloidal material on the filter membrane. Since the size of colloidal particles and that of the pores of the filter membrane is very small, the process is referred to as ultrafiltration.

Since the process involves application of high pressure or suction, the membrane filters are generally supported by fine wire screens. In order to avoid the increase in the concentration of colloidal particles and to remove the dissolved impurities completely, the water squeezed out from the sol is replaced continuously or repeatedly with an equal quantity of water. The sol is also stirred continuously in order to maintain a uniform concentration throughout the bulk. Fig 1.3 shows an assembly and principle of *ultrafiltration*.



# PROPERTIES OF COLLOIDS

# A. Particle Size

The particle size of colloids generally varies from 1nm to 1 $\mu$ m. The actual particle size of a colloidal dispersion can be determined by the use of ultramicroscope or by using graded filters during ultrafiltration or by determining the rate of sedimentation in a centrifuge.

## **B.** Optical Properties

## 1. Tyndall Effect

When a narrow beam of light is passed through a colloidal dispersion, the path of the light becomes illuminated and can be observed at right angles under an ultramicroscope. This is the Faraday-Tyndall effect. Lyophobic systems show most intense Tyndall effect and certain lyophilic systems show little or no effect.

## 2. Ultramicroscopy

The colloidal particles are too small to be seen with an optical microscope. However, when a cell containing a colloidal dispersion is viewed through an ultramicroscope against a dark background at right angles to an intense beam of incident light, the particles appear as bright spots against the dark background (Fig. 1.4). The ultramicroscope is used in the technique of microelectrophoresis for measuring the particle charge.



Fig. 1.4: Assembly and principle of an ultramicroscope

#### 3. Electron Microscopy

Ultramicroscopes are sometimes not able to resolve some lyophilic colloids and hence electron microscopes are employed for studying the colloidal dispersions. The electron microscope is useful in getting picture of actual particles and helps in the study of the size, shape and structure of colloidal particles.

#### 4. Light Scattering

When a beam of light is passed through a colloidal dispersion, some of it is absorbed, some is scattered and the remainder is transmitted undisturbed through the sample. The absorbed light is responsible for the highly coloured nature of certain colloids. For example, gold chloride particles absorb light of deep red colour, silver particles absorb brown while silver iodide particles absorb light of yellow colour. The scattered light causes the colloidal dispersion to appear turbid. The turbidity of the colloidal dispersion is given by:

$$I = I_0 \exp^{-1}$$

where,

 $I_{o}$  is the intensity of the incident beam.

*I* is the intensity of transmitted light.

*l* is the length of the sample.

 $\tau$  is the turbidity.

Light scattering measurements are of importance in estimating the particle size, shape and interactions of the dissolved macromolecules. It has also been used for determining the molecular weight of colloidal particles using the following equation:

$$Hc/\tau = 1/M + 2Bc$$

where,

$$Hc/\tau = 1/M + 2Bc$$

 $\tau$  is the turbidity measured at 90° to the incident beam.

*c* is the concentration of the solute in grams/litre.

*M* is the molecular weight.

*B* is an interaction constant related to the non-ideality of the solution

*H* is an optical constant for a particular system.

A plot of  $Hc/\tau$  versus c yields a straight line at low concentration with the slope equal to 2B. The intercept on the  $Hc/\tau$  axis gives the value of 1/M from which molecular weight can be determined.

Light scattering measurements are specially useful for determining the size of association colloids and the number of molecules of the surface active agent forming them and also for studying the nature of proteins and natural and synthetic polymers.

# **C. Kinetic Properties**

#### 1. Brownian Motion

The colloidal particles in dispersion are always in a state of continuous and random motion within the medium due to bombardment by the molecules of the dispersion medium. This random motion which can be observed under an ultramicroscope in the form of an erratic motion is referred to as Brownian motion after Robert Brown who had first observed this phenomenon. The velocity of the particles increases with decreasing particle size. Increasing the viscosity of the medium decreases and finally stops the Brownian movement.

#### 2. Diffusion

Diffusion is a spontaneous process whereby solute molecules move from a region of higher concentration to one of lower concentration until the concentration of the system

becomes uniform throughout. Colloidal particles also exhibit diffusion which in their case is a direct result of Brownian movement. The rate of diffusion is expressed by Fick's first law which is written as:

$$dq/dt = -DS dc/dx$$

where, dq is the amount of material diffusing in time dt across an area S under the influence of a concentration gradient dc/dx. D is the diffusion coefficient and has the dimensions of area per unit time.

It is possible to determine the molecular weight of approximately spherical particles from the diffusion coefficient by substituting the data obtained from diffusion experiments in the following expression:

$$D = \frac{RT}{6\pi r\eta N} \frac{4\pi N}{3Mv}$$

where,

M is the molecular weight.

*v* is the partial specific volume.

 $\boldsymbol{\eta}$  is the viscosity of the solvent.

*R* is the molar gas constant.

*T* is the absolute temperature.

*r* is the radius of spherical particle.

*N* is the Avagadro's number.

#### 3. Osmotic Pressure

Osmotic pressure which is a colligative property depends upon the number of particles in dispersion. In case of associated colloids, each aggregate acts as one particle and osmotic pressure is small. Osmotic pressure can be used to calculate the molecular weight of colloidal material.

$$P = C/M RT$$

where,

*P* is the osmotic pressure.

*C* is the concentration in gram solute per litre solvent.

*M* is the molecular weight.

*R* is the gas constant.

*T* is the temperature in kelvin.

#### 4. Sedimentation

In normal dispersions, the dispersed particles tend to settle under the influence of gravity but in case of colloidal dispersions, the Brownian movement tends to offset this sedimentation but promotes mixing instead. Therefore, stronger force must be applied to bring about sedimentation of colloidal particles. Ultracentrifuge is generally used for bringing about and studying sedimentation in colloidal dispersions.

In an ultracentrifuge, the particles settle according to their molecular weight and hence this is also helpful in determining the molecular weight. The following expression is used for determining the molecular weight:

$$M = \frac{RTS}{D(1 - v\rho_{\rm o})}$$

#### where,

*R* is the gas constant.

*T* is the absolute temperature.

 $\boldsymbol{v}$  is the partial specific volume of the polymer.

 $\rho_{o}$  is the density of the solvent.

S is the Svedberg sedimentation coefficient determined at 20°C.

*D* is the diffusion coefficient obtained by calculation from diffusion data at 20°C.

Ultracentrifugation is helpful in not only determining the molecular weight but also the relative homogeneity of a polymer with respect to molecular weight.

#### 5. Viscosity

The viscosity of colloids depends upon the shape of the colloidal material. Spherical colloidal material yields dispersions of relatively low viscosity. Linear colloids are comparatively more viscous. Viscosity increase is due to solvation effect. When the degree of solvation is more, the dispersion becomes more viscous. If a linear colloid is placed in a solvent for which it has low affinity, the linear particles tend to assume a spherical shape and as a result, the viscosity falls. Therefore, viscosity studies provide a means of detecting changes in the shape of flexible colloidal particles and macromolecules. Viscosity studies also provide a means of determining the molecular weight of colloidal particles.

The Einstein equation provides a quantitative expression for the flow of disperse systems consisting of spherical particles.

Thus,

$$\eta = \eta_0 (1 + 2.5\phi)$$

where,

 $\eta_o$  is the viscosity of the dispersion medium and  $\eta$  is the viscosity of the dispersion when the volume fraction of the colloidal particles present is  $\phi$ .

#### **D. Electrical Properties**

Colloidal particles carry electrical charge of either positive or negative type. Negatively charged colloidal particles include that of kaolin, sulphur and arsenious sulphide while positively charged ones include ferric oxide and other metal hydroxide colloidal dispersions. In certain colloidal dispersions such as that of proteins, the charge on the particles may be positive, negative or neutral depending upon the pH of the medium.

The particles in a colloidal dispersion acquire charges from several sources mainly by ionisation or by adsorption.

#### 1. Electrical Double Layer

Let us consider a solid surface carrying negative charge in contact with an aqueous solution containing positive and negative ions. The negatively charged solid surface will influence the distribution of ions surrounding each of its particles. Thermal motion also has some influence over the distribution of charges. The resultant effect is that each particle is surrounded by an electric double layer.

Consider the colloidal dispersion of silver iodide prepared by chemical reaction.

The colloidal dispersion in water as such will contain  $Ag^+$ ,  $I^-$ ,  $Na^+$ ,  $NO_3^-$  and traces of  $H^+$  and  $OH^-$  ions.

If the reaction is conducted with an excess of sodium iodide, the surface layer of silver iodide contains more I<sup>-</sup> ions than  $Ag^+$  ions while the aqueous solution contains relatively high concentration of Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup>, a lower concentration of I<sup>-</sup> and traces of H<sup>+</sup>, OH<sup>-</sup> and Ag<sup>+</sup> ions.

Since the silver iodide particles contain more of I<sup>-</sup> ions on their surface, each of the silver iodide particles is negatively charged and it attracts positive ions from the solution and repels negative ions. As a result of this, the aqueous solution near the surface of the AgI particles contains a much higher concentration of Na<sup>+</sup> ions (*called counter ions* or *gegenions*) and much lower concentration of NO<sub>3</sub><sup>-</sup> ions than in the bulk of the solution.

The counter ions Na<sup>+</sup> are pulled closer to its surface and these counter ions tend to stick to the surface as closely as possible as the hydration sphere (the solvated layer on the particle) permits. At the same time, thermal motion (of water molecules) tends to disperse the Na<sup>+</sup> ions throughout the solution. As a result, the layer of counter ions surrounding the particle is spread out. The Na<sup>+</sup> concentration is highest in the immediate vicinity of the negative surface forming a compact layer called Stern layer and decreases with distance from the surface throughout a diffuse layer called the *Gouy-Chapman layer*. Thus, the negatively charged surface layer is surrounded by a cloud of Na<sup>+</sup> ions (counter ions) required for electroneutrality. The combination of the two layers of oppositely charged ions constitutes an electric double layer as shown in Fig. 1.5. The thickness of the double layers usually ranges from 10 to 100Å.



Fig. 1.5: Electric double layer at the surface of silver iodide particles

The presence of electrical double layer around each particle in a colloidal dispersion gives rise to electrokinetic effects. They are electrophoresis, electro-osmosis, sedimentation potential, and steaming potential.

#### 2. Electrophoresis

When an electric field is applied to a colloidal dispersion, the particles carrying charge (either negative or positive) move towards the electrode of opposite charge. Negatively charged particles (such as of kaolin and sulphur) move towards anode while positively charged particles (such as ferric hydroxide and other metal hydroxides) move towards cathode. When the particles move, the counter ions within the solvation layer are dragged along with the surface of the hydration shell in the plane of shear and the counter ions in the free or mobile solvent move towards the other electrode. This phenomenon is termed *electrophoresis*.