
Surface Chemistry - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following:

- Explain the Nature of Colloidal State
- Classify Colloids on the Basis of Physical State and Nature of Interaction between Dispersed Phase and Dispersion Medium, and the Type of Particles of Dispersed Phase
- Describe Methods of Preparation and Purification of Colloids
- Understand the Mechanism of Micelle Formation
- Know how the Soaps Clean our Clothings

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- Introduction
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Introduction

Colloids form an intermediate between a true solution and a suspension. Owing to their size, the colloids have unique properties which make them highly adaptable to specific uses and functions, and find special applications in industry as well as in life form. Cosmetics, paints, pharmaceuticals, ceramics, food, plastics and rubber, and biological processes are some of the most significant applications of colloids.

In this module, we will be discussing colloids in terms of their nature, classification preparation and purification. We will also discuss the mechanism of micelle formation and cleaning action of soaps.

Colloids

Activity: Take three glasses of water and add salt, clay and sand to them and stir. Identify the suspension, solution and colloid.

We have learnt in earlier Modules that solutions are homogeneous systems. We also know that sand in water when stirred gives a suspension, which slowly settles down with time. Between the two extremes of suspensions and solutions we come across a large group of systems called colloidal dispersions or simply colloids. A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

Study of colloids began towards the later part of the 19th century. Substances such as NaCl or sugar which formed solutions that could pass through parchment membrane or a filter easily were called crystalloids, whereas substances such as starch in solution could not pass through membrane or filter and were referred to as colloids. However, subsequently it was observed that even NaCl behaved as a colloid in benzene. A detailed investigation revealed that a substance behaves as a crystalloid or colloid depending upon its particle size.

The essential difference between a solution and a colloid is that of particle size. While in a solution, the constituent particles are ions or small molecules, in a colloid, the dispersed phase may consist of particles of a single macromolecule (such as protein or synthetic polymer) or an aggregate of many atoms, ions or molecules. Colloidal particles are larger than simple molecules but small enough to remain suspended. Their range of diameters is between 1 and 1000 nm (10^{-9} to 10^{-6} m).

Colloidal particles have an enormous surface area per unit mass as a result of their small size. Consider a cube with 1 cm side. It has a total surface area of 6 cm². If it were divided equally into 10^{12} cubes, each cube would be the size of a colloidal particles and have a total surface area of 60,000 cm² or 6 m². This enormous surface area leads to some special properties of colloids to be discussed later in this Module (Fig. 1).

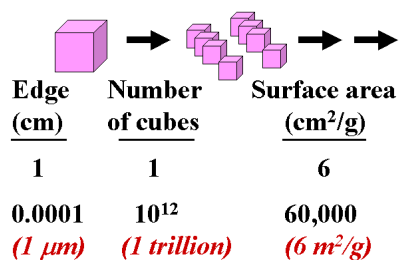


Fig 1: Increase in surface area of colloidal particles

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It is important to bear in mind that a colloid is not a mere substance, but it is the state of the substance, which depends upon its particle size.

Classification of Colloids

Colloids are classified on the basis of the following criteria:

- i. Physical state of dispersed phase and dispersion medium
- ii. Nature of interaction between dispersed phase and dispersion medium
- iii. Type of particles of the dispersed phase.

Classification Based on Physical State of Dispersed Phase and Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table 1.

Table 1: Types of Colloidal Systems

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Many familiar commercial products and natural objects are colloids. For example, whipped cream is a foam, which is a gas dispersed in a liquid. Firefighting foams are also colloidal systems. Most biological fluids are aqueous sols (solids dispersed in water). Within a typical cell, proteins and nucleic acids are colloidal-sized particles dispersed in an aqueous solution of ions and small molecules.

Out of the various types of colloids given in Table 1, the most common are sols (solids in liquids), gels (liquids in solids) and emulsions (liquids in liquids). However, in the present module, we shall take up discussion of the ‘sols’ and ‘emulsions’ only. Further, it may be mentioned that if the dispersion medium is water, the sol is called aquasol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on. If it is benzene the sol is called benzosol. If air is the dispersion medium the sol is called aerosol.

Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, lyophilic (solvent attracting) and lyophobic (solvent repelling). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

- i. **Lyophilic Colloids:** The word ‘lyophilic’ means liquid-loving. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called **lyophilic sols**. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called **reversible sols**. Furthermore, these sols are quite stable and cannot be easily coagulated as discussed later.
- ii. **Lyophobic Colloids:** The word ‘lyophobic’ means liquid-hating. Substances like metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods (as discussed later). Such sols are called **lyophobic sols**. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence, are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these

sols are also called **irreversible sols**. Lyophobic sols need stabilising agents for their preservation.

Classification Based on Type of Particles of the Dispersed Phase: Multimolecular, Macromolecular and Associated Colloids

Depending upon the type of the particles of the dispersed phase, colloids are classified as: multimolecular, macromolecular and associated colloids.

- i. **Multimolecular colloids:** On dissolution, a large number of atoms or smaller molecules of a substance (diameter <1 nm) aggregate together to form species having size in the colloidal range (diameter >1 nm). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many gold atoms. Sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.
- ii. **Macromolecular colloids:** The macromolecules are usually polymers with high molecular masses. Macromolecules in suitable solvents form particles of size in the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many respects. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.
- iii. **Associated colloids (Micelles):** There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called **micelles**. These are also known as **associated colloids**. The formation of micelles takes place only above a particular temperature called **Krafft temperature (T_K)** and above a particular concentration called **critical micelle concentration (CMC)**. On dilution, these colloids revert back to true solutions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is 10^{-4} to 10^{-3} mol L^{-1} . These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

Mechanism of Micelle Formation

Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as $RCOO^-Na^+$ (e.g., sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$, which

is a major component of many bar soaps). When dissolved in water, it dissociates into RCOO^- and Na^+ ions. The RCOO^- ions, however, consist of two parts — a long hydrocarbon chain R (also called non-polar ‘tail’) which is hydrophobic (water repelling), and a polar group COO^- (also called polar-ionic ‘head’), which is hydrophilic (water loving) (Fig. 2).

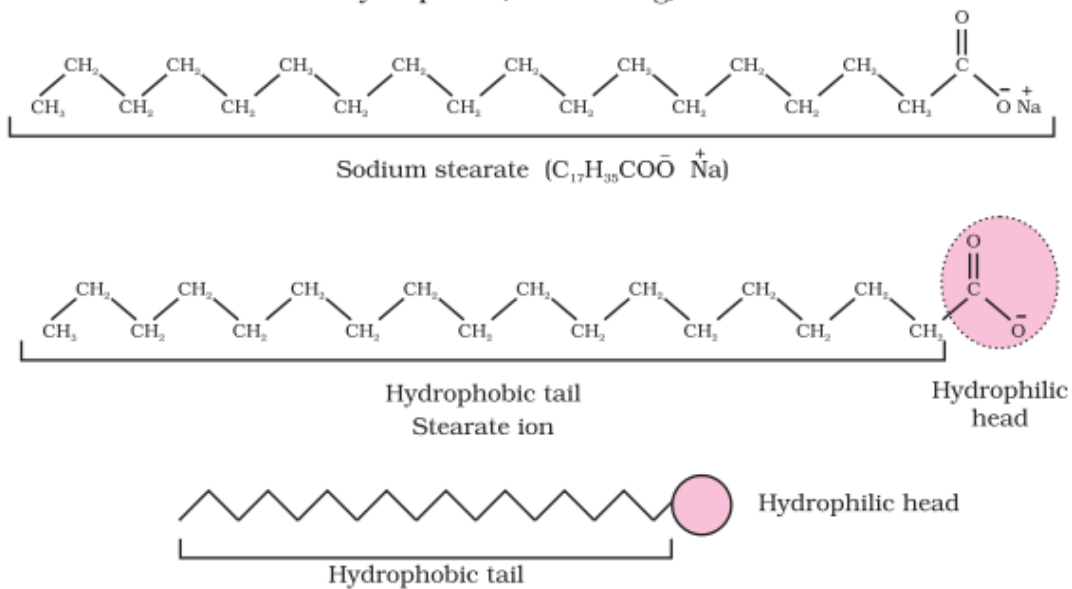


Fig.2: Hydrophobic and hydrophilic parts of stearate ion

The RCOO^- ions are, therefore, present on the surface with their COO^- groups in water and the hydrocarbon chains R staying away from it and remaining at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with COO^- part remaining outward on the surface of the sphere. An aggregate thus formed is known as ‘ionic micelle’. These micelles may contain as many as 100 such ions (Fig. 3).

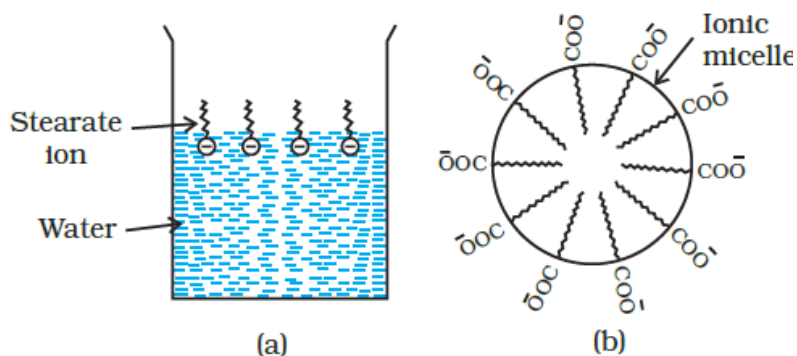


Fig. 3: (a) Arrangement of stearate ions on the surface of water at low concentrations of soap
(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

Similarly, in case of detergents, e.g., sodium lauryl sulphate, $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-\text{Na}^+$, the polar group is $-\text{SO}_4^{2-}$ along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

Cleansing Action of Soaps

It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon – like the central core. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles (Fig. 4). Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

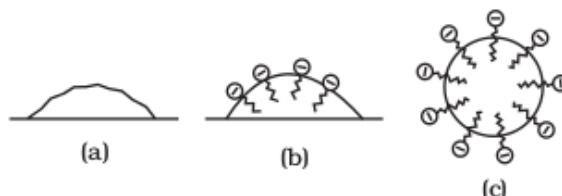


Fig. 4: (a) Grease on cloth (b) Stearate ions arranging around the grease droplet and (c) Grease droplet surrounded by stearate ions (micelle formed)

Preparation of Colloids

Sols of lyophilic and lyophobic colloids are prepared differently. In lyophilic colloids, owing to strong affinity between the particles of dispersed phase and dispersion medium, by merely mixing and shaking the dispersed phase and dispersion medium together form these colloids. Gum, egg albumin, gelatin and starch are substances that form lyophilic colloids with water as dispersion medium.

Lyophobic colloids are prepared by two methods as described below.

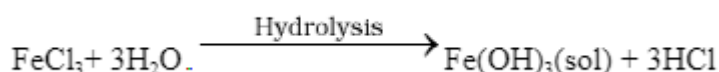
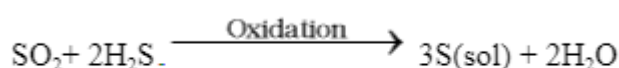
1. Condensation methods.
2. Dispersion methods.

Condensation Methods

In these methods, colloidal size particles are formed by inducing the small atoms or molecules to aggregate together. This is done by using both chemical and physical methods.:

I. Chemical Methods

Colloidal solutions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.



II. Physical methods

1. Exchange of solvent method: For substances like phosphorus, sulphur, their colloidal solutions are prepared by this method. They dissolve in alcohol, but

insoluble in water. Colloidal sols (milky sols) of these substances are prepared by pouring their alcoholic solution into a large quantity of water.

2. Excessive cooling method: A colloidal solution of ice in chloroform or ether is prepared by freezing a solution of water in the solvent. Molecules of water that cannot be held in solution separate out and combine to form particles of colloidal size.

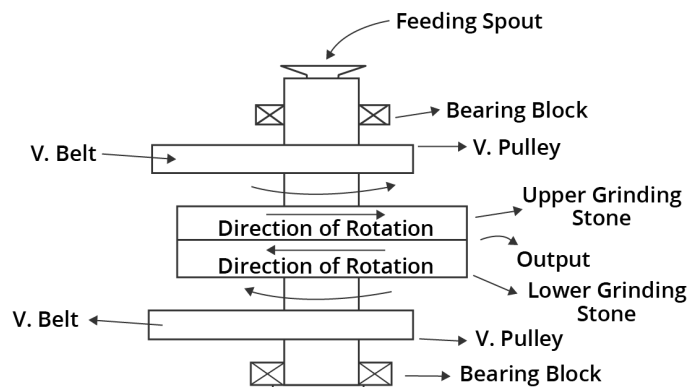
Dispersion Methods

In dispersion methods the large particles of a substance are broken into small particles of colloidal size in a dispersion medium. Suitable stabilizers are used to stabilize these sols. Various dispersion methods are detailed below.

- I. Mechanical dispersion
- II. Electrical disintegration or Bredig's arc method
- III. Peptisation

Mechanical Dispersion

Colloidal solutions of inks, paints and varnishes are prepared by this method. The large sized substances of suspension are broken down to colloidal size by grinding it in a colloidal mill or ball mill or ultrasonic disintegrator. Figure 5 depicts a typical colloidal mill.



Colloidal Mill

Fig.5: Colloidal Mill

Electrical Dispersion (Electrical Disintegration) or Bredig's Arc Method

This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium (Fig. 6). The

intense heat produced vapourises the metal, which then condenses to form particles of colloidal size. Stabilizers in small quantities are used to stabilize the colloidal sol.

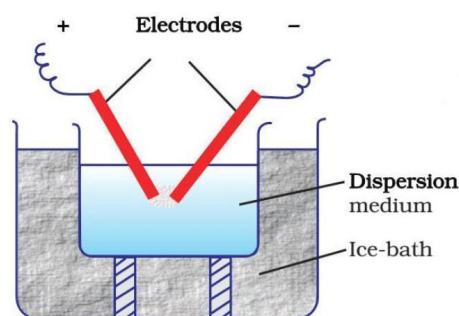


Fig. 6: Bredig's Arc Method

Peptization

Peptization may be defined as the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called **peptizing agent**. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol.

During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates. These repel each other and ultimately lead to the break-up of the precipitate into smaller particles of the size of a colloid.

When a small quantity of ferric chloride (FeCl_3), a peptizing agent in this instance, is added to freshly prepared ferric hydroxide ($\text{Fe}(\text{OH})_3$), ferric hydroxide particles adsorb Fe^{3+} ions and form dark reddish brown coloured ferric hydroxide sol.

Purification of Colloidal Solutions

Colloidal solutions when prepared (as described above) generally contain excessive amount of electrolytes and some other soluble impurities. While the presence of traces of electrolyte is essential for the stability of the colloidal solution, larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods:

- i. **Dialysis:** It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. Since particles (ions or smaller

molecules) in a true solution can pass through animal membrane (bladder) or parchment paper or cellophane sheet but not the colloidal (sol) particles, the membrane can be used for dialysis. The apparatus used for this purpose is called a dialyser. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing (Fig. 7). The molecules and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.

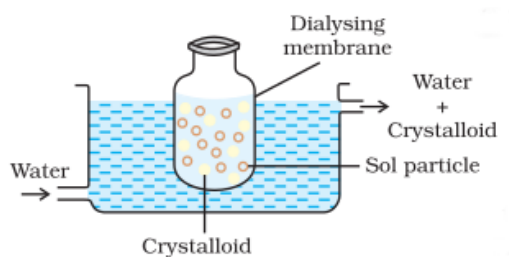


Fig.7: Dialysis

Dialysis plays an important role in purification of blood of patients with kidney failure. The kidneys carry out a critical function of purification of blood by removing waste products like urea and excess electrolytes from the blood. When the kidneys fail to function partially or totally, the purification of blood has to be carried out externally (outside the human body) with the help of an artificial kidney machine, which works on dialysis principle. The blood is passed through the machine where the harmful products are filtered out.

- ii. **Electrodialysis:** Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substances in the impure colloidal solution are electrolytes. The process is then named **electrodialysis**. The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in Fig. 8. The ions present in the colloidal solution migrate out to the oppositely charged electrodes.

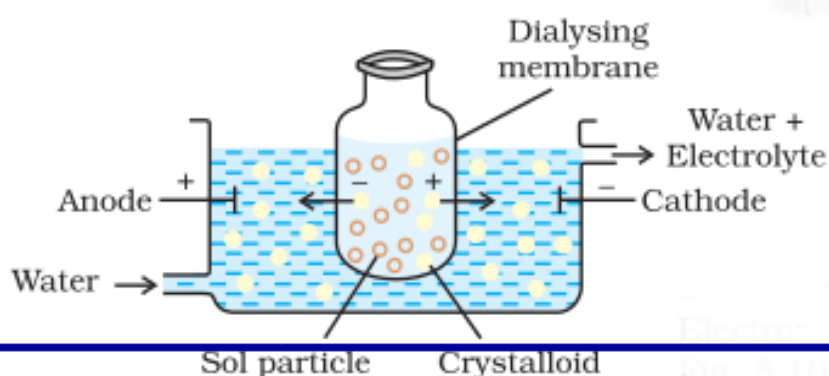


Fig.8: Electrodialysis

- iii. **Ultrafiltration:** Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with a collodion solution to stop the flow of colloidal particles. The usual collodion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultra filter paper may be prepared by soaking the filter paper in a collodion solution, hardening by formaldehyde and then finally drying it. Thus, by using ultra filter paper, the colloidal particles are separated from the rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with a fresh dispersion medium (solvent) to get a pure colloid.

Summary

Colloidal solutions are intermediate between true solutions and suspensions. The size of the colloidal particles range from 1 to 1000 nm. A colloidal system consists of two phases - the dispersed phase and the dispersion medium. Colloidal systems are classified in three ways depending upon (i) physical states of the dispersed phase and dispersion medium (ii) nature of interaction between the dispersed phase and dispersion medium and (iii) nature of particles of dispersed phase. Lyophilic, lyophobic, multimolecular, macromolecular and associated (micelle) colloids are various important colloids. Lyophilic colloids, owing to strong affinity between the particles of dispersed phase and dispersion medium, are formed by merely mixing and shaking the dispersed phase and dispersion medium together. Lyophobic colloids are prepared by condensation and dispersion methods. Bredig's Arc and peptization methods are the important dispersion methods. Dialysis, electrodialysis and ultrafiltration are the methods used for purification of colloids.