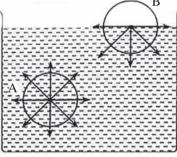
11. Adsorption and Colloids



11.1 Introduction: When a metal spoon is dipped in milk and taken out, you will notice that a film of milk particles cover the spoon surface. If a cold water bottle is taken out from the refrigerater and kept on a table for a while, water vapour is seen to condense on the outer surface of the bottle, forming droplets or a film. Here the milk particles or the water molecules from the air get adsorbed on the surface of the spoon and the bottle. Surfaces of all the objects around us are exposed to the atmosphere. Water molecules as well as other gas molecules such as N2, O2, from the air form an invisible multi molecular film on these objects. This is known as the phenomenon of adsorption.



- A Bulk molecule
- B Surface molecule

Fig 11.1 Unbalanced forces

11.2. Adsorption:

11.2.1 Unblanced forces: Consider a surface of liquid or solid. The molecular forces at the surface of a liquid are unbalanced or in unsaturation state. In solids, the ions or molecules at the surface of a crystal do not have their forces satisfied by the close contact with other particles.

Because of the unsaturation solid and liquid surfaces tend to attract gases or dissolved substances with which they come in close contact. Thus the substance accumulates on the surface of solid or liquid.



11.2.2 Why does adsorption occur?

The adsorption phenomenon is caused by London dispersion forces or van der Waals forces. These are short range and additive. The adsorption force is the sum of all interactions between all the atoms. The pulling interactions cause the surface of a liquid to tighten like an elastic film. A measure of the elastic force at the surface of a liquid is called surface tension. (Refer to Chapter 10).

The surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area. There is a tendency to have minimum surface tension that is, decrease of free energy, which leads to adsorption. Terms involved in adsorption:

Adsorbent: The material or substance present in the bulk, on the surface of which adsorption takes place is called adsorbent.

Adsorbate: The substance getting absorbed on the the adsorbent is called as adsorbate.

11.2.3 Examples of Absorption: You know that when cotton is dipped in water, cotton becomes wet with water which is due to absorption.

Some more examples of adsorption:

- i. Adsorption of gases like hydrogen, oxygen, by finely divided metals, namely, platinum, palladium, copper, nickel, etc.
- ii. Adsorption of gases like nitrogen, carbondioxide, by activated charcoal.
- iii. Removal of colouring matter like an organic dye, for example methylene blue. When charcoal is added to methylene blue solution and shaken, it becomes colourless after some time, as dye molecules accumulate on the surface of charcoal. Table 11.1 shows comparison between adsorption and absorption.

11.2.4 Desorption: The process of removal of an adsorbed substance from a surface on which it was adsorbed is called desorption.

Table 11.1: Comparison between Adsorption and Absorption

| Adsorption | Absorption | |
|---|--|--|
| 1. Adsorbed matter is concentrated only at the surface and does not penetrate through the surface to the bulk of adsorbent. Adsorption is a surface phenomenon. | Absorbed matter is uniformly distributed inside as well as on the surface of the bulk of substance. Absorption is a bulk phenomenon. | |
| 2. Concentration of the adsorbate is high only at the surface of the adsorbent. | Concentration of the absorbate is uniform throughout the bulk of the absorbent. | |
| 3. It is dependent on temperature and pressure. | It is independent of temperature and pressure. | |
| 4. It is accompanied by evolution of heat known as heat of adsorption. | It is not accompanied by evolution or absorption of heat. | |
| 5. It depends on surface area | It is independent of surface area. | |
| 6. Example: Adsorption of a gas or liquid like acetic acid by activated charcoal | Example: Absorption of water by cotton. Absorption of ink by blotting paper. | |



Try this

Dip a chalk in ink. What do you observe?

11.2.5 Sorption: When a chalk is dipped in ink, ink molecules are adsorbed at the surface of chalk and the surface becomes coloured, while the solvent of the ink goes deeper into the chalk due to absorption. When, both adsorption and absorption occur simultaneously it is known as sorption.

11.3 Types of adsorption: There are mainly two types of adsorption phenomenon depending on nature of forces involved.

11.3.1 Physical Adsorption or physisorption:

When the adsorbent such as gas molecules are accumulated at the surface of a solid on account of weak van der Waals forces, the adsorption is termed as physical adsorption or physisorption.

The van der Waals forces, are similar to forces causing condensation of gas into liquid. Thus, heat is released in physisorption. The heat released during physisorption is of the same order of magnitude as heat of condensation. Due to weak nature of van der Waals forces, physisorption is also weak in nature. The adsorbed gas forms several layers of molecules at high pressures. The extent of adsorption is large at low temperatures. The equilibrium is attained rapidly. The physisorption is readily reversed by lowering of pressure of gas or by raising temperature.

11.3.2 Chemical Adsorption **Chemisorption**: Chemisorption was first investigated in 1916 by American Chemist, Irving Langmuir (1881-1957). When the gas molecules accumulate on the surface of a solid or adsorbate by means of chemical bonds, be it covalent or ionic, the adsorption is called chemical adsorption (or chemisorption). Chemisorption is specific in Chemisorption involving the gas-solid as the adsorbate and adsorbent, is usually exothermic. It means that heat is released during this process. (Exception: the adsorption of hydrogen on glass is endothermic: heat is absorbed during the process. This is due to dissociation of hydrogen.) The heat evolved in chemisorption per mole of adsorbate is nearly the same order of magnitude as that accompaning chemical bonding. Chemisorption involves a large energy of activation and referred as activated adsorption. Chemisorption increases with increase in temperature in the beginning, as more number of molecules can have activation But after certain temperature chemisoption decreases with increase in temperature, as the chemical bonds break.

Sometimes at low temperature, physisorption occurs which passes into chemisorption as the temperature is raised. Besides, chemisorption is dependent on surface area of the adsorbent (See Table 11.2).

Table 11.2: Comparison of physisorption and chemisorption

| Physisorption | Chemisorption |
|--|--|
| 1. The forces operating are weak van der Waals | 1. The forces operating are chemical nature |
| forces. | (covalent or ionic bonds). |
| 2. Not specific in nature. All gases adsorb on | 2. Highly specific and occurs only when chemical |
| all solids. For example, all gases adsorb on | bond formation is possible between adsorbent |
| charcoal. | and adsorbate. For example, adsorption of |
| | oxygen on tungsten, hydrogen on nickel, etc. |
| 3. The heat of adsorption is low and lies in the | 3. Higher heat of adsorption and lies in the range |
| range 20 - 40 kJ mol ⁻¹ | 40 - 200 kJ mol ⁻¹ |
| 4. Occurs at low temperature and | 4. Favoured at high temperature, the extent of |
| decreases with an increase of temperature. | chemical adsorption is lowered at very high |
| | temperature, due to bond breaking. |
| 5. For example : at low temperature N_2 gas is | 5. For example N ₂ gas chemically adsorbed on |
| physically adsorbed on iron. | iron at high temperature forms a layer of iron |
| | nitride, which desorbs at very high temperature. |
| 6. Reversible. | 6. Irreversible. |
| 7. Physisorbed layer may be multimolecular layer, of | 7. Chemisorption forms monomolecular layer of |
| adsorbed particles under high pressure. | adsorbed particles. |

- **11.4 Factors affecting adsorption of gases on solids :** All solids adsorb gases to some extent. The extent of adsorption depends upon a number of factors discussed in this section.
- 1. Nature of adsorbate (gas): The amount of gas adsorbed by a solid depends on the nature of the gas. Gases having high critical temperature liquify easily and can readily be adsorbed. (Refer to chapter 10). The gases such as SO_2 , Cl_2 , NH_3 which are easily liquifiable are adsorbed to a large extend compared to N_2 , O_2 , H_2 etc, which are difficult to liquify.

Table 11.3 : Critical temperature of gases and volume adsorbed

| | , oranic was or sea | | |
|-----------------|---------------------------|-------------------------------------|--|
| Gas | Critical temperature/K | Volume adsorbed/ cm ³ | |
| N_2 | 126 | 08 | |
| HCl | 324 | 72 | |
| NH ₃ | 406 | 181 | |
| Cl ₂ | 417 | 235 | |
| SO ₂ | 430 | 380 | |

2. Nature of adsorbent: Substances which provide large surface area for a given mass are effective as adsorbents and adsorb appreciable volumes of gases. Silica gel, charcoal are effective adsorbents due to their porous nature.

- **3. Surface area of adsorbent :** Adsorption is a surface phenomenon. Hence, the extent of adsorption increases with increase in surface area of adsorbent. Finely divided substances, rough surfaces, colloidal substances are good adsorbents as they provide larger surface area for a given mass.
- **4. Temperature :** Adsorption is an exothermic process. According to Le-Chatelier's principle (Chapter 12), it is favoured at low temperature. The amount of gas adsorbed is, thus, inversely proportional to temperature.

Figure 11.2 shows plots of volume of N₂ adsorbed per unit mass of adsorbent against the pressure of a gas at different temperatures. As temperature increases from 193 K to 273 K at a constant pressure 'P' the amount of gas adsorbed decrease.

5. Pressure of gas : At any temperature, the extent of gas adsorbed increases with an increase of pressure. The extent of adsorption is directly proportional to pressure of the gas. At high pressures extent of adsorption becomes independent of the pressure. The surface of adsorbent is, then, almost fully covered by adsorbed gaseous molecules.

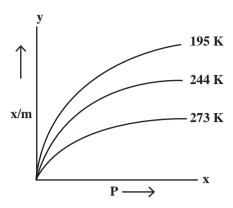


Fig 11.2 Variation of adsorption with temperature and pressure

11.5 Adsorption Isotherm: The relationship between the amount of a substance adsorbed per unit mass of adsorbent and the equilibrium pressure (in case of gas) or concentration (in case of solution) at a given constant temperature is called an adsorption isotherm. Various adsorption isotherms are known.

Freundlich adsorption isotherm : Freundlich proposed an empirical equation for adsorption of a gas on solid.

$$\frac{x}{m} = k P^{1/n}$$
 (n>1) (11.1)

Where x = mass of the gas adsorbed

m = mass of the adsorbent at presure P $\frac{x}{m} = \text{mass of gas adsorbed per unit mass of adsorbent}$

P = equilibrium pressure.

k and n are constants which depend on the nature of adsorbate, adsorbent and temperature.

Graphical Representation of Freundlich equation.

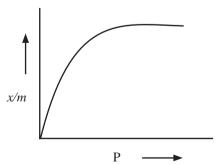


Fig 11.3 Adsorption isotherm

In case of solution, P in the Eq. (11.1) is replaced by the concentration and thus

$$\frac{x}{m} = kC^{1/n}$$
 (11.2)

After taking logarithm of the above Eq. 11.2

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$
(11.3)

Plotting $\log \frac{x}{m}$ against $\log C$ or $\log P$, a straight line is obtained which is shown in Fig.11.4.

The slope of the straight line gives $\frac{1}{n}$. While intercept on y-axis gives log k. The factor $\frac{1}{n}$ ranges from 0 to 1. Equation (11.3) holds good over limited range of pressures.

When $\frac{1}{n} \to 0$, $\frac{x}{m} \to \text{constant}$, the adsorption, then, is independent of pressure.

adsorption, then, is independent of pressure. When $\frac{1}{n} = 1$, $\frac{x}{m} = kP$. i.e. $\frac{x}{m} \propto P$ the adsorption varies directly with pressure. The experimental isotherms as in Fig. 11.3 tend to saturate at the high pressure.

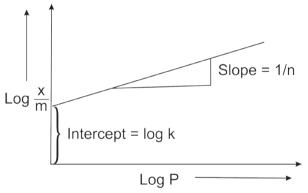


Fig. 11.4: Freundlich isotherm

11.6 Applications of Adsorption:

The adsorption finds large number of applications as illustrated here.

i. Catalysis: Heterogeneous catalysis: The solid catalysts are used in many industrial manufacturing processes. For example, iron is used as the catalyst in manufacturing of ammonia; platinum in manufacturing of sulphuric acid, H₂SO₄ (by contanct process). In hydrogenation of oils, finely divided nickel is employed as catalyst.

- **ii. Gas masks:** It is a device which consists of activated charcoal or mixture of adsorbents. It is used for breathing in coal mines to avoid inhaling of the poisonous gases.
- **iii. Control of humidity :** Silica and alumina gels are good adsorbents of moisture.
- iv. Production of high vacuum: Lowering of temperature at a given pressure, increases the rate of adsorption of gases on charcoal powder. By using this principle, high vacuum can be attained by adsorption. A vessel evacuated by vacuum pump is connected to another vessel containing coconut charcoal cooled by liquid air. The charcoal adsorbs the remaining traces of air or moisture to create a high vacuum.
- v. Adsorption Indicators: The adsorption is used to detect the end point of precipitation titrations. Dyes such as eosin, fluorescein are used as indicators. For example, A solution of sodium chloride containing a small amount of fluorescein is titrated against silver nitrate solution.

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$
White ppt

When chloride ions are over, fluorescein is adsorbed on white silver chloride precipitate and red colour is developed. Thus colour change from pale yellow to reddish pink is observed at the end point.

- vi. Separation of inert gases: In a mixture of noble gases, different gases adsorb to different extent. Due to selective adsorption principle, gases can be separated on coconut charcoal.
- vii. Froth floatation process: A low grade sulfide ore is concentrated by separating it from silica and other earthy matter using pine oil as frothing agent. Hydrophobic pine oil preferentially wets (adsorbs on) sulfide ore which is taken up in the froth.
- viii. Chromatographic analysis: It is based on selective adsorption of ions from solution using powdered adsorbents such as silica or alumina gel. It has several

industrial and analytical applications. Other applications include surface area determination, purification of water, etc.

11.7 Catalysis: Catalysts are of importance in chemical industry and in living organisms. A large number of the chemicals manufactured in industries make use of catalysts to obtain specific products, The use of catalyst lowers the reaction temperature, and energy costs significantly.

A catalyst thus can be defined as a substance which when added to a reacting system increases the rate of a reaction without itself undergoing any permanent chemical change. Catalysis is of two types, namely homogeneous an heterogeneous catalysis.

11.7.1 Homogeneous Catalysis: When the reactants and the catalyst are in the same phase, it is said to be homogenous catalysis.

Examples of homogeneous catalysis:

- i. Iodide ion (I^{Θ}) finds use as homogeneous catalyst in decomposition of aqueous hydrogen peroxide (Both I^{Θ} and H_2O_2 are present in the same aqueous phase)
- ii. Oxidation of sulfur dioxide to sulfur trioxide with dioxygen (O₂) in the presence of nitire oxide as catalyst (lead chamber process).

$$2 SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2 SO_3(g)$$

iii. Hydrolysis of sugar is catalysed by H^{\oplus} ion furnished by sulphuric acid.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H_2SO_4}$$
Sucrose solution
 $C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$
Glucose

Fructose

All reactants and catalyst are in same solution phase.

- iv. Enzyme catalysis is also an important type of homogeneous catalysis.
- **11.7.2 Heterogeneous Catalysis:** When the reactant and catalyst are in different phase, it is said to be heterogeneous catalysis.

The heterogeneous catalyst is generally a solid and the reactants may either be gases

or liquids. The solid catalyst is added to the reaction mixture. It does not dissolve in the reacting system. The reaction accurs on surface of solid catalyst.

Examples of heterogeneous catalysis:

i. Dinitrogen (N₂) and dihydrogen (H₂) combine to form ammonia in Haber process in presence of finely divided iron along with K₂O and Al₂O₃.

$$N_2(g) + 3 H_2(g) \xrightarrow{Fe(s)} 2 NH_3(g)$$

Here Al_2O_3 and K_2O are promoters of the Fe catalyst. Al_2O_3 is added to prevent the fusion of Fe particles. K_2O causes chemisorption of nitrogen atoms. Molybdynum is also used as promoter.

ii. Hydrogenation reaction of vegetable oils to produce solid fat is used in food industry. The reaction is catalysed by finely divided metals like Ni, Pd or Pt. Vegetable oil contains one or more carbon carbon double bonds (C = C) in its structure. On hydrogenation a solid product (which contains only carbon carbon single bonds) is formed. It is called *vanaspati ghee*.

Vegetable oil
$$(l) + H_2(g) \xrightarrow{\text{Ni (s)}}$$

$$(C = C) \qquad \text{Vegetable ghee(s)}$$

$$(C - C)$$

iii. Another important application of heterogenous catalysts is in automobile catalytic converters. In automobile exhaust, large number of air pollutants such as carbon monoxide, nitric oxide, etc. are present. The catalytic converter transforms the air pollutants into carbon dioxide, water, nitrogen and oxygen. The catalyst is poisoned by the adsorption of Pb (lead). The automobiles with catalytic converter require unleaded petrol.

11.7.3 Inhibitors : Inhibitors are substances those decrease rate of chemical reaction. Examples,

i. Chlorofom was once used as anaesthetic. It forms poisonous substance, carbonyl chloride by air oxidation.

$$4 \text{ CHCl}_3(l) + 3 \text{ O}_2(g) \rightarrow 4 \text{ COCl}_2(g) + 2 \text{ H}_2\text{O}(l) + 2 \text{ Cl}_2(g)$$

When 2% ethanol is added to chloroform, the formation of COCl₂ is suppressed. Ethanol acts as an inhibitor and retards the above reaction.

ii. Hydrogen peroxide decomposes as,

$$2 \text{ H}_2\text{O}_2(l) \rightarrow 2 \text{ H}_2\text{O}(l) + \text{O}_2(g)$$

The reaction is inhibited by addition of dilute acid or glycerol acting as inhibitor.

11.8 Adsorption Theory of Heterogeneous catalysis: The catalytic action occurs on the surface of a catalyst. The mechanism involves five steps.

- Diffusion of reactants toward the surface of the catalyst.
- ii. Adsorption of reactant molecules on the surface of the catalyst.
- Occurrence of chemical reaction on the catalyst surface and formation of an intermediate.
- iv. Formation of products.
- Desorption of reaction products from the catalyst surface. Products leave catalyst surface.

The steps involved can be shown as : Diffusion \rightarrow Adsorption \rightarrow intermediate formation

Desorption ← Product formation

Fresh reactant molecules can replace the products to start the cycle again as in step (i). This explains why catalyst remains unchanged in mass and chemical composition at the end of the reaction.

11.8.1 Important features of solid catalysts:

a. Catalytic activity: The activity of a catalyst depends on the strength of chemisorption. If large number of reactant molecules (gas or liquid) are strongly adsorbed on the surface of solid catalyst, the catalyst is said to be active. However, the adsorption of reactant molecules on the surface, that is, the bond formed between adsorbate and adsorbent surface should not be very strong so that they are not immobilized.

It has been found that d-block metals such as Fe, V and Cr tend to be strongly active toward O_2 , C_2H_2 , C_2H_4 , CO, H_2 , CO_2 , N_2 etc; Mn and Cu are unable to adsorb N_2 and CO_2 . The metals Mg and Li adsorb O_2 selectively.

b. Catalytic selectivity : Some solid catalysts are selective in their action. The same gaseous reactants produce different products when different catalysts are used.

For example,

- i. The gaseous ethylene and O₂ react to produce different products with different catalysts.
- $\begin{array}{c} \text{a. C}_2\text{H}_4(g) + \text{O}_2(g) & \xrightarrow{\text{Pd/Al}_2\text{O}_3} \text{2 CH}_3\text{CHO (g)} \\ \text{(ethylene)} & \text{(acetaldehyde)} \\ \text{b. 2 C}_2\text{H}_4(g) + \text{O}_2(g) & \xrightarrow{\text{Ag/Al}_2\text{O}_3} \text{2 CH}_2 & \text{CH}_2 \\ \text{(ethylene)} & \text{(ethylene oxide)} \end{array}$
- ii. The gaseous carbon monoxide and $\rm H_2$ produce different products by using different catalysts.

a. CO (g) + 3
$$H_2(g)$$
 \longrightarrow $CH_4(g) + H_2O(g)$
b. CO (g) + 2 $H_2(g)$ \longrightarrow $Cu/ZnO-Cr_2O_3$ \longrightarrow $CH_3OH(g)$

c. Shape selective catalysis by zeolites:

Zeolites are alumino silicates with three-dimensional network of silicates. Some silicon atoms in this network are replaced by aluminium atoms giving Al-O-Si frame work. This results in microporous structure. The reactions in zeolites are dependent on the size and shape of reactant or products and also on pores and cavities of zeolites. Zeolites, therefore, are shape selective catalysts.

In petroleum industry, zeolite catalyst ZSM-5 converts alcohols directly to gasoline (pertol) by dehydration which gives a mixture of hydrocarbons.

11.9 Colloids: A number of substances we use in our day to day life are colloids. For example, milk, butter, jelly, whipped cream, mayonnaise. Colloid chemistry is the chemistry of everyday life. Knowledge of colloid chemistry is essential for understanding about many useful materials like cement, bricks, pottery, porcelain, glass, enamels; oils, lacquers; rubber, celluloid and other plastics, leather, paper, textiles, filaments, crayons, inks, road construction material etc. In many daily processes like cooking, washing, dyeing, painting, ore floatation, water purification, sewage disposal, smoke prevention, photography, pharmacy, use of colloids is important.

Colloids are heterogeneous mixtures. The component of colloid present in the largest proportion is called **dispersion medium** and the other components are called **dispersed phase**. The particles of the dispersed phase are larger than the size of a molecule and smaller than particles which we can see with naked eye.

Observe the formation of solution of salt and water. Salt dissolves completely in water and forms homegeneous system. On the other hand ground coffee or tea leaves with milk form suspension. Between the two extremes of solution and suspension, we observe a large group of systems called colloidal dispersions or simply colloids.

The essential difference between a solution and a colloid is particle size. **Solutions** contain solute particles with diameter in the range 0.1 to 2 nm, the size of typical ion or small molecule. Solutions are **transparent** and may be coloured and do not separate on standing. On the other hand, **colloids** such as milk, fog contain particles of dispersed phase with diameters in the range at 2 to 500 nm. They are **transluent** to light and do not separate on standing.

- **11.9.1 : Exaples of colloids :** Some examples of phenomenon observed in our daily life, which are understood in terms of colloids are as follows :
- **i. Blue colour of the sky:** The sky appears blue to us because minute dust particles along with minute water droplets dispersed in air scatter blue light which reaches our eyes.
- **ii. Blood:** It is a colloidal dispersion of plasma proteins and antibodies in water. (At the same time blood is also a suspension of blood cells and platelets in water.)
- **iii. Soils :** Fertile soils are colloidal in nature where humus acts as a protective colloid. Soil adsorbs moisture and nourishing materials due to its colloidal nature.

Table 11.4 : Types of colloids based on physical state

| Dispersed phase | Dispersion medium | Type of colloid | Examples |
|-----------------|----------------------|-----------------|---|
| solid | solid | solid sol | coloured glasses, gem stones, porcelain, paper |
| solid | liquid | sols and gels | paints, cell fluids, gelatin, muddy water, starch solution. |
| solid | gas | aerosol | smoke, dust |
| liquid | solid | gel | cheese, butter, jellies |
| liquid | liquid | emulsion | milk, hair cream |
| liquid | gas | aerosol | fog, mist, cloud, hair sprays, insecticide sprays. |
| gas | solid | solid sol | pumice stone, foam rubber, plaster |
| gas | liquid | foam | froth, whipped cream, soap lather |

Table 11.5: Distinction between Lyophilic and Lyophobic colloids

| Lyophilic colloids | Lyophobic colloids |
|--|--|
| 1. Formed easily by direct mixing. | Formed only by special methods. |
| 2. Reversible. | Irreversible. |
| 3. The particles are not easily visible even under ultramicroscope. | The particles are easily detected under ultramicroscope. |
| 4. These are self stabilized. | These are unstable and hence require traces of stabilizers. |
| 5. Addition of large amount of electrolytes causes precipitation/coagulation. | Addition of small amount of electrolytes causes precipitation/ coagulation. |
| 6. Viscosity of dispersed phase much higher than that of the dispersion medium. | Viscosity of dispersed phase is nearly the same as the dispersion medium. |
| 7. Surface tension of dispersed phase is lower than dispersion medium. | Surface tension of dispersed phase is nearly the same as the dispersion medium. |

- iv. Fog, mist and rain: Mist is caused by small droplets of water dispersed in air. Fog is formed whenever there is temperature difference between ground and air. A large portion of air containing dust particles gets cooled below its dew point, the moisture from the air condenses on the surface of these particles which form fine droplets, which are colloid particles and float in air as fog or mist.
- **11.9.2 Classification of colloids :** Colloids are classified in three different ways.
- **a.** Classification of colloids based on physical state: Table 11.4 illustrates the types of colloids in accordance with the physical states of dispersed phase and dispersion medium.
- **b.** Classification of colloids based on interaction or affinity of phases: On the basis of interaction or affinity of phases, a colloidal solution is classified as lyophilic and lyophobic. If water is dispersion medium, the

terms hydrophilic and hydrophobic are used.

- i. Lyophilic colloids: Lyo means liquid and philic means loving. A colloidal solution in which the particles of dispersed phase have a great affinity for the dispersion medium are lyophilic colloids. If the lyophilic sol is evaporated, the dispersed phase separates. But if it is remixed with the medium, the sol can be formed again. That is why such sols are called reversible sols. They are stable and difficult to coagulate.
- **ii. Lyophobic colloids:** Colloidal solution in which the particles of the dispersed phase have no affinity for the dispersion medium are lyophobic colloids. Phobic means fearing, hence liquid hating. The common examples are Ag, Au, hydroxides like Al(OH)₃, Fe(OH)₃, metal sulfides. Once precipitated/coagulated they have little tendency or no tendency to revert back to colloidal state.

Table 11.5 shows comparison of lyophilic and lyophobic colloids.

- **c.** Classification of colloids based on molecular size: Colloids are classified into three types in accordance with size of their molecules.
- i. Multimolecular Colloids: The individual particles consist of an aggregate of atoms or small molecules with size less than 10^3 pm. For examples: Gold sol consists of particles of various sizes having several gold atoms. Colloidal solution in which particles are held together with van der Waals force of attraction is called multimolecular colloid. For Example, $S_{\rm g}$ sulfur molecules.
- **ii. Macromolecular colloids:** The molecules of the dispersed phase are sufficiently large in size (macro) to be of colloidal dimensions. Examples are starch, cellulose, proteins, polythene, nylon, plastics.
- **iii.** Associated colloids or micelles: The substances behave as normal electrolytes at low concentration and associated in higher concentration forming a colloidal solution. The associated particles are called Micelles. For example, soap, detergent. Soap molecule

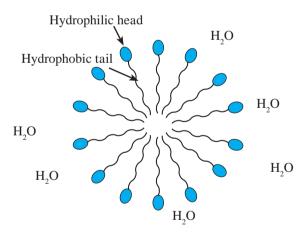


Fig. 11.5 : Soap micelle in water

has a long hydrophobic hydrocarbon chain, called **tail**, attached to hydrophilic ionic group (carboxylate), called **head**. In water the soap molecules arrange themselves to form spherical particles that are called **micelles**. (Fig. 11.5) In each micelle the hydrophobic

tails of soap molecules point to the centre and the hydrophilic heads lie on the surface of the sphere. As a result of this, soap dispersion in water is stable.

- **11.9.3 Preparation of Colloids :** A few important methods for the preparation of colloids are as follows :
- **a.** Chemical methods: By double decomposition, oxidation, reduction or hydrolysis. Molecules of water insoluble products of these reaction aggregate together and form sols.

$$SO_2 + 2H_2S \xrightarrow{Oxidation} 3S \downarrow + 2H_2O$$
 $2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{Reduction} 2Au \downarrow + 3HCOOH + 6HCl$

$$FeCl_3 + 3H_2O \xrightarrow{Hydrolysis} Fe(OH)_3 \downarrow + 3HCl$$

b. Electrical disintegration by Bredig's Arc method: This process involves vaporization as well as condenstion. Colloidal sols of metals such as gold, silver, platinum can be prepared by this method.

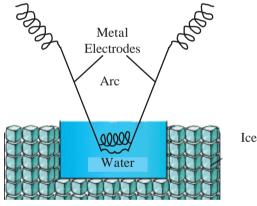


Fig. 11.6: Bredig's arc method

In this method, electric arc is struck between electrodes of metal immersed in the dispersion medium. The intense heat produced vapourises the metal which then condenses to form particles of colloidal sol.

c. Peptization: During peptization a precipitate is converted into colloidal sol by shaking with dispersion medium in the presence of a small amount of an electrolyte. The electrolyte used, is known as peptizing agent.

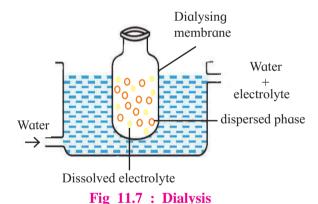
During the process, the precipitate adsorbs one of the ions of the electrolyte on its surface, positive or negative charge is developed on the precipitate which finally breaks up into small particles of colloidal size.

11.9.4 Purification of colloidal solution: Colloidal solution generally contains excessive amount of electrolytes and some other soluble impurities. A small quantity of an electrolyte is necessary for the stability of colloidal solution. A large quantity of electrolyte may result in coagulation. It is also necessary to reduce

"The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution."

soluble impurities.

Purification of colloidal solution can be carried out using dialysis by the following method.



Dialysis: "It is a process of removing a dissolved substance from a colloidal solution by diffusion through a suitable membrane.

The apparatus used is dialyser. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing. The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.

11.9.5 Properties of colloidal dispersions:

Various properties exhibited by colloidal dispersions are described below.

a. General properties.

- Colloidal system is heterogeneous and consists of two phases, dispersed phase and dispersion medium.
- ii. The dispersed phase particles pass slowly through parchment paper or animal membrane, but readily pass through ordinary filter paper.
- iii. The particles usually are not detectable by powerful microscope.

b. Optical property:

Tyndall effect: Tyndall observed that when light passes through true solution the path of light through it cannot be detected.

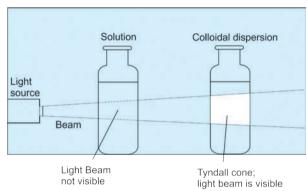


Fig. 11.8 :Tyndall effect

However, if the light passes through a colloidal dispersion, the particles scatter some light in all directions and the path of the light through colloidal dispersion becomes visible to observer standing at right angles to its path.

"The phenomenon of scattering of light by colloidal particles and making path of light visible through the dispersion is referred as Tyndall effect".

"The bright cone of the light is called Tyndall cone". Tyndall effect is observed only when the following conditions are satisfied.

- i. The diameter of the dispersed particles is not much smaller than the wavelength of light used.
- ii. The refractive indices of dispersed phase and dispersion medium differ largely.

Importance of Tyndall effect:

 It is useful in determining number of particles in colloidal system and the particle size therein. ii. It is used to distinguish between colloidal dispersion and true solution.

c. Colour:

- i Colour of colloidal solution depends on the wavelength of light scattered by dispersed particles.
 - The colour of colloidal dispersion also changes with the manner in which the observer receives the light. For example: Mixture of a few drops of milk and large amount of water appears blue when viewed by the scattered light and red when viewed by transmitted light. (Refer to 7th std science book of Balbharati.)
- ii. It also depends on size of colloidol particles For example, finest gold sol is red in colour whereas with increase in size it appears purple.
- **d. Kinetic Property:** The colloidal or microscopic particles undergo ceaseless random zig-zag motion in all directions in a fluid. This motion of dispersed phase particles is called Brownian motion. British botanist, Robert Brown, observed such motion of pollen grains under a microscope. The random motion was explained by Albert Einstein in 1905.

Fig. 11.9: Brownian motion

Cause of Brownian motion:

- i. Constant collision of particles of dispersed phase with the fast moving molecules of dispersion medium (fluid).
- ii. Due to this, the dispersed phase particles acquire kinetic energy from the molecules of the dispersion medium. This kinetic energy brings forth Brownian motion.

e. Electrical Properties:

i. Charge on colloidal particles: Colloidal particles carry an electric charge. The nature of this charge is the same on all particles for a given colloidal solution which can be either

positive or negative. Some common sols with the nature of charge on the particles are listed in Table 11.6.

Table 11.6: Charge on dispersed particles

| Positively charged sols | Negatively charged sols |
|--|---|
| 1. Hydrated metallic oxides Al ₂ O ₃ . x H ₂ O, CrO ₃ . x H ₂ O, Fe ₂ O ₃ . x H ₂ O. | Metals, Cu, Ag, Au Sols metallic sulphides As ₂ S ₃ , Sb ₂ S ₃ , Cds |
| 2. Basic dye stuff, methylene blue sols | Acid dye stuff, eosin, congo red sol |
| 3. Haemoglobin (blood) | Sols of starch, gum |
| 4. Oxides : TiO ₂ sol | Gelatin, clay, gum sols |

ii. Electrophoresis : Electrophoresis set up is shown in Fig. 11.10.

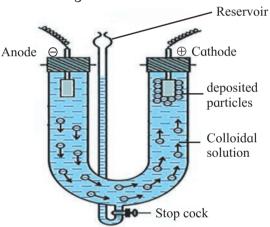


Fig. 11.10: Electrophoresis

Figure shows U tube set up in which two platinum electrodes are dipped in a collodial solution. When electric potential is applied across two electrodes, collodial particles move towards one or other electrode.

"The movement of colloidal particles under an applied electric potential is called electrophoresis."

Positively charged particles move towards cathode while negatively charged particles migrate to anode and get deposited on the respective electrode.

iii. Electroosmosis: Movement of dispersed particles can be prevented by suitable means, such as use of membrane. Then it is observed that the dispersion medium begins to move in an electric field. This is termed as electroosmosis.

Applications of electrophoresis:

- i. On the basis of direction of movement of the colloidal particles under the influence of electric field, it is possible to know the sign of charge on the particles.
- ii. It is also used to measure the rate of migration of sol particles.
- iii. Mixture of colloidal paticles can be separated by electrophoresis since different colloidal particles in mixture migrate with different rates.
- **f. Coagulation:** 'The precipitation of colloids by removal of charge associated with colloidal particles is called coagulation.'

The charge on the colloidal particles is due to the preferential adsorption of ions on their surface. For precipitation of lyophobic colloids removal of charge is required. A situation with lyophilic colloids is a little different. The lyophilic particles first attract the molecules of dispersion medium and form a layer of medium surrounding the particles, which may adsorb the ions. Hence for the precipitation of lyophilic colloids, removal of charge on layer of medium is necessary.

- **11.9.6 Methods to effect coagulation :** A coagulation of the lyophobic sols can be carried out in the following ways.
- **i.** By electrophoresis: The colloidal particles move towards oppositely charged electrodes, get discharged and precipitate.
- **ii.** By mixing two oppositely charged sols: Oppositely charged sols when mixed in almost equal proportions neutralize their charges and get precipitated.
- Example Mixing of hydrated ferric oxide (positive sol) and arsenious sulfide (negative sol) brings them in the precipitated forms. This type of coagulation is called mutual coagulation.
- **iii.** By boiling: When a sol is boiled, the adsorbed layer is disturbed as a result of increased collisions with molecules in dispersion medium. This reduces charge on the particles and subsequently settling down as a precipitate.

- **iv.** By persistent dialysis: On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely. The colloids then become unstable and finally precipitate.
- **v.** By addition of electrolytes: When excess of an electroylte is added, the colloidal particles are precipitated.

Hardy-Schulze rule : Generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as Hardy - Schulze rule. In the coagulation of negative sol, the flocculating power follows the order: $Al^{\oplus 3} > Ba^{\oplus 2} > Na^{\oplus}$

Similarly, coagulation of positive sol, reveal: $[Fe(CN)_6]^{4\Theta} > PO_4^{3\Theta} > SO_4^{2\Theta} > Cl^{\Theta}$ **11.9.7 Emulsions:** A colloidal system in which one liquid is dispersed in another immiscible liquid is called an emulsion. There are liquid-liquid colloidal system in which both liquids are completely or partially immiscible.

Types of emulsions:

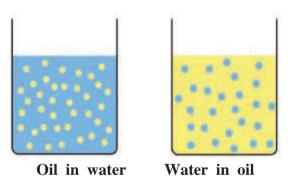


Fig. 11.11: Emulsions

- There are two types of emulsions (Fig. 11.15). **i. Emulsion of oil in water (o/w type) :** An emulsion in which dispersed phase is oil and dispersion medium is water is called emulsion of oil in water. For example : milk, vanishing cream, paint etc. Milk consists of particles of fat dispersed in water.
- ii. Emulsion of water in oil (w/o type): An emulsion in which dispersed phase is water and dispersion medium is oil is called emulsion of water in oil. For example, codliver oil consists of particles of water dispersed in oil. Some other examples of this type include butter, cream, etc.

Table 11.7 describes difference between the two types of emulsion.

Table 11.7: Distinction between oil in water and water in oil emulsions

| Oil in water | Water in oil |
|--|--|
| * | Water is dispersed phase and oil is the dispersion medium. |
| | If oil is added, it will be miscible with the emulsion. |
| | |
| 4. Water is continuous phase. | Oil is continuous phase. |
| 5. Basic metal sulfates, water soluble alkali metal soaps are used as emulsifiers. | such as those of Zn, Al, Fe, alkaline earth |

Properties of Emulsion:

- 1. Emulsion can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed forms a separate layer.
- 2. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes.
- 3. Emulsions show Brownian movement and Tyndall effect.
- 4. The two liquids in emulsions can be separated by heating, freezing or centrifuging etc.
- 11.9.8 Applications of colloids : Colloids find appplications in industry and in daily life. Following are some examples.
- i. Electrical precipitation of smoke: Smoke is colloidal solution of solid particles of carbon, arsenic compound, dust etc. in air. When smoke is allowed to pass through chamber containing plates having charged

smoke particles they lose their charge and get precipitated.

The particles settle down on the floor of the chamber. The precipitator is called Cottrell precipitator.

- ii. Purification of drinking water: Water obtained from natural sources contains colloidal impurities. By addition of alum to such water, colloidal impurities get coagulated and settled down. This makes water potable.
- iii. Medicines: Usually medicines are colloidal in nature. Colloidal medicines are more effective owing to large surface area to volume ratio of a colloidal particle, and easy assimilation.

Argyrol is a silver sol used as an eye lotion. Milk of magnesia, an emulsion is used in stomach disorders.

- iv. Rubber Industry: Rubber is obtained by coagulation of latex.
- v. Cleansing action of soaps and detergents
- vi. Photographic plates, films, and industrial products like paints, inks, synthetic plastics, rubber, graphite lubricants, cement etc. are colloids.

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- 1. Brownian motion https://myoutube.com>watch
- 2. Collect information about Surface Chemstry.
- 3. Collect information about Adsorption.
- 4. Collect information about Brownian Motion



Activity:

Calculate surface area to volume ratio of spherical particle. See how the ratio increases with the raduction of radius of the particle. Plot the ratio against the radius.



1. Choose the correct option.

- A. The size of colloidal particles lies between
 - a. 10⁻¹⁰ m and 10⁻⁹ m
 - b. 10⁻⁹ m and 10⁻⁶ m
 - c. 10⁻⁶ m and 10⁻⁴ m
 - d. 10^{-5} m and 10^{-2} m
- B. Gum in water is an example of
 - a. true solution
- b. suspension
- c. lyophilic sol
- d. lyophobic sol
- C. In Haber process of production of ammonia K₂O is used as
 - a. catalyst
- b. inhibitor
- c. promotor
- d. adsorbate
- D. Fruit Jam is an example of
 - a. sol
- b. gel
- c. emulsion
- d. true solution

2. Answer in one sentence:

- A. Name type of adsorption in which vander Waals focres are present.
- B. Name type of adsorption in which compound is formed.
- C. Write an equation for Freundlich adsorption isotherm.

3. Answer the following questions:

- A. Define the terms:
 - a. Inhibition
 - b. Electrophoresis
 - c. Catalysis.
- B. Define adsorption. Why students can read black board written by chalks?
- C. Write characteristics of adsorption.
- D. Distinguish between Lyophobic and Lyophilic sols.
- E. Identify dispersed phase and dispersion medium in the following colloidal dispersions.
 - a. milk
- b. blood
- c. printing ink
- d. fog
- F. Write notes on:
 - a. Tyndall effect
 - b. Brownian motion
 - c. Types of emulsion
 - d. Hardy-Schulze rule

- G. Explain Electrophoresis in brief with the help of diagram. What are its applications?
- H. Explain why finely divided substance is more effective as adsorbent?
- I. What is the adsorption Isotherm?
- J. Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless. Explain.
- K. What happens when a beam of light is passed through a colloidal sol?
- L. Mention factors affecting adsorption of gas on solids.
- M. Give four uses of adsorption.
- N. Explain Bredig's arc method.
- O. Explain the term emulsions and types of emulsions.

4. Explain the following:

- A. A finely divided substance is more effective as adsorbent.
- B. Freundlich adsorption isotherm, with the help of a graph.

5. Distinguish between the following:

- A. Adsorption and absorption. Give one example.
- B. Physisorption and chemisorption. Give one example.
- 6. Adsorption is surface phenomenon. Explain.

7. Explain how the adsorption of gas on solid varies with

- a. nature of adsorbate and adsorbent
- b. surface area of adsorbent
- 8. Explain two applications of adsorption.
- 9. Explain micelle formation in soap solution.

10. Draw labelled diagrams of the following:

- a. Tyndall effect
- b. Dialysis
- c. Bredig's arc method
- d. Soap micelle



Collect the information about methods to study surface chemistry.