

## surface chemistry

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### ADSORPTION

- **Adsorption** is the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid, resulting in a higher concentration of molecules on the surface.
- *Adsorption* is a surface phenomenon.
- The substance being adsorbed is called *adsorbate* and the substance on whose surface it is being adsorbed is called the *adsorbent*.
- Surface area of adsorbate per unit mass of adsorbent is known as specific surface area.
- **Sorption** is a term used when both absorption and adsorption occur simultaneously.
- **Desorption** is the reverse of adsorption, i.e. the removal of the adsorbed substance from the surface of the adsorbent.
- **Occlusion** is a term used for adsorption of gases on a metal surface.
- Adsorption occurs on the surface of solids due to the presence of unbalanced forces, believed to have developed either during crystallisation of solids or due to the presence of unpaired electrons in *d*-orbitals.
- Adsorption is specific and selective in nature.
- Adsorption is accompanied by decrease in free energy, i.e.  $\Delta G = -ve$ . When  $\Delta G = 0$ , adsorption equilibrium is established.
- Adsorption is a spontaneous process. According to Gibbs' Helmholtz equation:  $\Delta G = \Delta H - T\Delta S$   
 $\Delta G = -ve$ ;  $\Delta H = -ve$ ;  $\Delta S = -ve$  (because adhering of gas molecules to a surface, lowers randomness).
- Enthalpy of adsorption is the enthalpy change accompanying the adsorption of 1 mole of adsorbate on the adsorbent surface.
- Adsorption isotherm is a graph between amount of adsorption and gas pressure keeping the temperature constant.
- Adsorption isobar is the graph drawn between quantities adsorbed under a constant gas pressure at definite temperatures.
- Adsorption isostere is the plot of temperature versus pressure for a given amount of adsorption.

- Physical Adsorption or Physisorption is the process in which the adsorbate particles are held on the surface of adsorbent by weak van der Waal's forces.
- Chemical Adsorption or Chemisorption is the process in which the adsorbate molecules are held by the adsorbent by chemical forces.

	Physical Adsorption	Chemical Adsorption
1.	Molecules are attracted to the surface by van der Waal's forces.	Molecules are held to the surface by chemical bonds.
2.	Heat of adsorption is low (20-40 kJ mol <sup>-1</sup> ).	Heat of adsorption is high (40-400 kJ mol <sup>-1</sup> ).
3.	Process is reversible it decreases with temperature.	Process is irreversible first increases, then decreases with temperature.
4.	Non-specific in nature.	Specific in nature.
5.	Forms multi-molecular layer on surface.	Forms unimolecular layer.

- Positive adsorption occurs when concentration of adsorbate is more on surface of the adsorbent than in the bulk.
- Negative adsorption occurs when concentration of adsorbate on the surface of adsorbent is less than that in the bulk.

### Factors affecting adsorption of gases on solids

- Nature of Adsorbent:** Transition metals act as good adsorbents for gases due to vacant or half-filled *d*-orbitals and high charge-size ratio.
- Surface Area of Adsorbent:** Highly porous substances like silica gel, Fuller's earth, charcoal are very good adsorbents since they have larger surface areas.
- Nature of Adsorbate:** Easily liquefiable gases like NH<sub>3</sub>, HCl, CO<sub>2</sub> etc. are adsorbed to a much greater extent than permanent gases like N<sub>2</sub>, H<sub>2</sub> etc.
- Pressure:** At constant temperature, if pressure is increased, adsorption increases. The increase is much greater if temperature is low.
- Temperature:** Adsorption is an exothermic process having an equilibrium:  
 Gas (Adsorbate) + Solid (Adsorbent)  $\rightleftharpoons$  Gas adsorbed + heat  
 Increase in temperature decreases adsorption.
- Activation of solid Adsorbent:** It is done by subdividing the solid into smaller particles or by passing super heated steam to increase its adsorbing power.

### Adsorption Isotherms

- The variation of the amount of the gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve, which is termed as adsorption isotherm at the particular temperature.
- Freundlich (1909) gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

$$\frac{x}{m} = k \cdot P^{1/n} \quad \dots(i)$$

where 'x' is the mass of the gas adsorbed on a mass 'm' of the adsorbent at a pressure *P*. *k* and *n* are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P \quad \dots(ii)$$

- Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor  $1/n$  can have values between 0 and 1. Thus equation (i) holds good over a limited range of pressure
- The factor  $1/n$  can have values between 0 and 1.  
when  $1/n = 0$ ,  $x/m = \text{constant}$  which shows that adsorption is independent of pressure.  
when  $1/n = 1$ ,  $x/m = kP$ . The adsorption varies directly with pressure.

- **Limitations of Freundlich adsorption isotherm:**

- At higher pressures, it shows deviation.
- The values of constants  $k$  and  $n$  change with temperature.
- It is empirical one and has no theoretical basis.

- According to Langmuir (1916)

- The layer of the gas adsorbed on the solid adsorbent is one molecule thick.
- The adsorbed layer is uniform all over the adsorbent.
- There is no interaction between the adjacent adsorbed molecules.

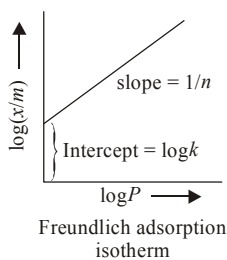
- If  $\theta$  is the fraction of the total surface covered by the adsorbed molecules, the fraction of the naked area is  $(1 - \theta)$ . The rate of adsorption ( $R_a$ ) is proportional to the available naked surface  $(1 - \theta)$  and the pressure ( $P$ ) of the gas.

Langmuir adsorption isotherm can be derived and represented in short as follows:

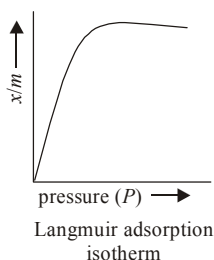
$$\frac{x}{m} = \frac{aP}{1 + bP}$$

where  $a$  and  $b$  are constants.  $x/m$  and  $P$  are the terms similar to those expressed in Freundlich isotherm.

(a) At low pressure,  $\frac{x}{m} = aP$



(b) At high pressure,  $\frac{x}{m} = \frac{a}{b}$



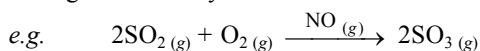
- **Temperature:** Adsorption is an exothermic process having an equilibrium:  

$$\text{Gas (Adsorbate)} + \text{Solid (Adsorbent)} \rightleftharpoons \text{Gas adsorbed} + \text{heat}$$
 Increase in temperature decreases adsorption.
- Gas masks used by miners contain activated charcoal to adsorb poisonous gases like  $\text{CH}_4$ ,  $\text{CO}$  etc.
- Industrial wastes and toxic chemicals are removed by treating water with an adsorbent.
- Chromatographic technique of separation and purification is based on adsorption.
- In sugar industry to decolourise the crude sugar and ion-exchange resins to purify water.

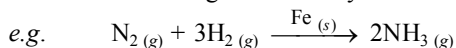
- Cleansing action of soaps and detergents, concentration of ores like froth floatation process are all based on adsorption.
- Used in dehumidifiers and deodourisers, in catalytic reactions and formation of stable emulsions.
- Adsorption of reactants on the solid surface of the catalysts affects the rate of reaction between the reactants. The reaction proceeds more rapidly after adsorption.
- Different adsorbates are adsorbed to different extent on the same adsorbent under similar conditions of temperature and pressure.
- If a mixture of gases (or vapours) is allowed to come in contact with a particular adsorbent, the more strongly adsorbable adsorbate is adsorbed to a greater extent, irrespective of its amount present in the mixture.
- Generally, higher the critical temperature of a gas greater is the amount of that gas adsorbed.

## CATALYST

- Catalyst is a substance which changes the speed of a reaction, and usually, can be recovered completely at the end of a reaction. However it may take part in a reaction -consumed in one step and regenerated in another.
- If the reaction mixture and the catalyst form a single phase, then it is known as homogeneous catalysis.

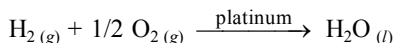


- The catalyst process in which the reaction mixture and the catalyst are in different phases is known as heterogeneous catalysis.



- Activity of a catalyst refers to the ability of a catalyst to accelerate chemical reaction.

e.g. Pt acts as a catalyst in the reaction



- Selectivity of a catalyst refers to the ability of a catalyst to direct reaction to yield a particular product (excluding others), e.g. *n*-heptane selectively gives toluene in presence of platinum as catalyst.
- The catalysis that depends upon the pore-structure of the catalyst and molecular sizes of reactants and product molecules is called *shape selective catalysis*. e.g. zeolites are shape selective catalysts due to their honey-comb structure. ZSM-5 is used for converting methanol to gasoline.
- Zeolites are micro-porous aluminosilicates of the general formula  $M_{x/n}[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot m\text{H}_2\text{O}$ . The pore size of the zeolites generally vary between 260 pm and 740 pm.

	Process	Catalyst
1.	Haber's process for the manufacture of ammonia $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightleftharpoons 2\text{NH}_3 (\text{g})$	Finely divided iron Molybdenum as promoter. Conditions: 200 atmo-spheric pressure and 450-500°C temperature
2.	Ostwald's process for the manufacture of nitric acid $4\text{NH}_3 (\text{g}) + 5\text{O}_2 (\text{g}) \rightarrow 4\text{NO} (\text{g}) + 6\text{H}_2\text{O} (\text{g})$ $2\text{NO} (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{NO}_2 (\text{g})$ $4\text{NO}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l}) + \text{O}_2 (\text{g}) \rightarrow 4\text{HNO}_3 (\text{l})$	Platinised asbestos Temperature 300°C
3.	Lead chamber process for the manufacture of sulphuric acid $2\text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightleftharpoons 2\text{SO}_3 (\text{g})$ $\text{SO}_3 (\text{g}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2\text{SO}_4 (\text{l})$	Nitric oxide
4.	Contact process for the manufacture of sulphuric acid $2\text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightleftharpoons 2\text{SO}_3 (\text{g})$ $\text{SO}_3 (\text{g}) + \text{H}_2\text{SO}_4 (\text{l}) \rightarrow \text{H}_2\text{S}_2\text{O}_7 (\text{l})$ $\text{H}_2\text{S}_2\text{O}_7 (\text{l}) + \text{H}_2\text{O} (\text{l}) \rightarrow 2\text{H}_2\text{SO}_4 (\text{l})$	Platinised asbestos or vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) Temperature 400 - 450°C
5.	Deacon's process for the manufacture of chlorine. $4\text{HCl} (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{H}_2\text{O} (\text{l}) + 2\text{Cl}_2 (\text{g})$	Cupric chloride ( $\text{CuCl}_2$ ) Temperature 500°C
6.	Manufacture of ethyl alcohol from starch (a) Starch $\xrightarrow{\text{diastase}}$ maltose (b) Maltose $\xrightarrow{\text{maltase}}$ glucose $\xrightarrow{\text{zymase}}$ alcohol	Germinated barley (diastase enzyme) Temperature 50-60°C Yeast (maltase and zymase enzyme) Temperature 25-30°C.

- Enzymes are complex nitrogenous compounds which are produced by living plants and animals.

#### Some enzymatic reactions

	Enzyme	Source	Enzymatic reaction
1.	Invertase	Yeast	Sucrose $\rightarrow$ glucose and fructose
2.	Zymase	Yeast	Glucose $\rightarrow$ ethyl alcohol and carbon dioxide
3.	Diastase	Malt	Starch $\rightarrow$ maltose
4.	Maltase	Yeast	Maltose $\rightarrow$ glucose
5.	Urease	Soyabean	Urea $\rightarrow$ ammonia and carbon dioxide.

### COLLOIDAL STATE

- The study for this state of matter was initiated by Thomas Graham in 1861.

- Substances whose solutions could pass through filter paper and animal membrane, having higher rate of diffusion are called *crystalloids*.
- Substances whose solutions can pass through filter paper and not animal membrane, also, having slower rate of diffusion are called *colloids*.
- Mixtures of substances in water, which can neither pass through filter paper nor animal membrane are called *suspensions*.

Suspension	Colloid	Solution
size $> 10^{-5}$ cm or $10^3 \text{ \AA}$ or $100 \text{ }\mu\text{m}$	$10^{-7}$ cm to $10^{-5}$ cm or $10 \text{ \AA}$ to $10^3 \text{ \AA}$ or $100 \text{ }\mu\text{m}$	$< 10^{-7}$ cm or $0 \text{ \AA}$ or $1 \text{ }\mu\text{m}$
Visible with naked eye	Visible with ultra-microscope	Not visible with any of optical means
Does not diffuse Settles under gravity	Diffuses very slowly Does not settle but it may settle under centrifuge	Diffuses rapidly Does not settle
Heterogeneous	Heterogeneous	Homogeneous
Opaque	Generally clear	Clear

Internal phase or Dispersed phase	External phase or Dispersion medium	Colloidal name	Examples
S	S	Solid sols	Alloys, ruby glass, gems or precious stones, marbles, optical and vision glasses.
	L	Sols	Muddy water, gold sol, protein, starch, agar, gelatin in water.
	G	Aerosols of solids	Smoke, storm.
L	S	Gels	Cheese, jams, jellies, curd, plants, fruits, vegetables, cementation, butter.
	L	Emulsions	Milk, blood, cosmetic products e.g. shampoo, creams, emulsified oils polish and medicines.
	G	Aerosols of liquids	Fog, clouds, mist.
G	S	Solid foams	Pumice stone, styrene foam, foam rubber, porous pot, rubber pillows and mattresses.
	L	Foam or froths	Froths, soap suds, air bubble.
	G	Homogeneous system	—

- True solutions are homogeneous while suspensions are heterogeneous systems. The colloidal state is regarded as intermediate between the two.

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- We can say that the colloidal state is a heterogeneous dispersion of solute particles of size ranging between  $10 \text{ \AA}$  to  $10^3 \text{ \AA}$  ( $10^{-7} \text{ cm}$  to  $10^{-5} \text{ cm}$ ) into a solvent.
  - Colloid is a heterogeneous state with at least two phases. The phase which is dispersed in the other (medium) is called *dispersed phase* (DP) or *internal phase*, or *discontinuous phase*.
  - The phase or medium in which the dispersion is made is called the *dispersion medium* (DM) or *external phase*, or *continuous phase*.
  - Colloids refer to substances in the intermediate state between true solution and suspension.
  - Particle size varies between  $10 \text{ \AA}$  to  $1000 \text{ \AA}$  or  $1 \text{ nm}$  to  $100 \text{ nm}$ .
  - Particles can only be seen in an ultra-microscope when they scatter light.
  - Colloidal particles do not settle under force of gravity even on keeping for long, but may settle under centrifuge.
  - Particles always carry a charge, either positive or negative.
  - **Types of colloidal systems**
    - Two gases cannot form a colloidal system as they diffuse and form a homogeneous mixture.
    - Colloidal systems which have a fluid like appearance are called *sols*. Depending on the nature of dispersion medium the colloids (sols) are given special names:  
 Water – hydrosols or aquasols                      Alcohol – alcosols  
 Benzene – benzosols                                  Gases – aerosols
    - **Lyophilic colloids** or **sols** are those in which the particles have a great affinity for the DM and readily form a colloid. They are also called *intrinsic colloids*.
    - **Lyophobic colloids** or **sols** are those in which the particles have very little or no affinity for the DM. Their sols are prepared by indirect methods and are also called *extrinsic colloids*.
  - **Differences between lyophilic and lyophobic sols are given in the table:**

Property	Lyophilic sols	Lyophobic sols
1. Nature	DP has more affinity for DM, if DM is water then hydrophilic	Less affinity, if DM is water; hydrophobic
2. Preparation	As soon as DP comes in contact with DM, sols are formed	Special methods are required
3. Concentration of sol	More concentration of DP in sol	Less concentration of DP in sol
4. Stability	More stable	Less stable
5. Size of sol particle	Small	Large
6. Viscosity	More viscous than DM	Same as of DM
7. Surface tension	Much less than DM	Same as of DM
8. Reversibility	Reversible with temperature	Irreversible
9. Charge	The charge on sol particles depends upon pH of medium.	Independent of pH
10. Tyndall effect	Less scattering	More scattering
11. Solvation	Higher degree of solvation	Lower degree of solvation

- Some substances on warming with suitable liquid pass into colloidal solution readily. These are called **intrinsic colloids**. e.g. gum-arabic, glue, starch, gelatin etc. The colloidal solution of such substances are lyophilic sols.
- Substances which do not pass into colloidal solution even on heating are called **extrinsic colloids**. e.g. silver, gold sol.
- **Multimolecular colloids** refer to those colloidal systems in which the dispersed phase is constituted by large aggregates of atoms or molecules with diameters less than 1 nm which are formed as a result of aggregating properties of the dispersing particles. e.g. gold sol, hydrated ferric oxide sol etc.
- **Macromolecular colloids** refer to those colloidal systems in which dispersed phase is constituted by large molecules which are called macromolecules (usually polymers). e.g. starch, cellulose, rubber etc.
- Lyophilic sols are prepared directly by mixing the substance with the dispersion medium.
- Lyophobic sols are prepared indirectly by any of the following methods:
- **Dispersion or Disintegration methods**
  - Electro-dispersion by *Bredig's arc* method is used to prepare sols of metals like Ag, Cu, Au, Pt etc. A direct current is passed through electrodes of the metal, the electric arc vapourizes the metal and vapours condense in the medium to form a sol.
  - **Peptization** involves the conversion of a freshly prepared precipitate into colloidal size particles by shaking with a suitable electrolyte, e.g. freshly prepared  $\text{Fe}(\text{OH})_3$  is treated with  $\text{FeCl}_3$  or  $\text{AgI}$  with  $\text{AgNO}_3$  etc. The electrolyte used is called a peptizing agent. Peptization is generally carried out by following methods:
    - (i) **By electrolytes:** Freshly formed precipitates can usually be peptized by electrolytes providing ions common with the precipitates. e.g.  $\text{AgCl}$  by  $\text{AgNO}_3$ ,  $\text{Fe}(\text{OH})_3$  by  $\text{FeCl}_3$ . In this case peptization is due to the preferential adsorption of one type of ions (common ions) furnished by the electrolyte added.
    - (ii) **By adding another colloid:** Peptization of lamp black is carried out by adding gums. Lamp black peptized this way is used under the name 'Indian ink'.
    - (iii) **By washing a precipitate:** If precipitates of  $\text{CuS}$ ,  $\text{BaSO}_4$  or Prussian blue are washed continuously with water, a stage is reached in each case when the wash water begins to take precipitate also through the filter paper.
- **Condensation or Aggregation methods:** These methods involve the joining together of smaller particles to form colloidal size particles.
- Chemical methods involve different chemical reactions yielding a sol, e.g.
 

*Double decomposition:*  $\text{As}_2\text{O}_{3(aq)} + 3\text{H}_2\text{S}_{(aq)} \rightarrow \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$

sol

*Reduction:*  $2\text{AuCl}_{3(aq)} + 3\text{SnCl}_{2(aq)} \rightarrow 2\text{Au} + 3\text{SnCl}_4$

sol

*Oxidation:*  $\text{Br}_{2(aq)} + \text{H}_2\text{S}_{(aq)} \rightarrow \text{S} + 2\text{HBr}$

sol

*Hydrolysis :*  $\text{FeCl}_{3(aq)} + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 3\text{HCl}$



- Exchange of solvent is the method used to prepare sols of substances less soluble in water, e.g. water is added to a solution of sulphur or phosphorus in alcohol to yield a sol.
- By change of state of a substance, e.g. mercury or sulphur are vapourized and the vapours passed in cold water containing a stabilizing agent (ammonium salt).
- By controlled condensation of certain insoluble substances in presence of a protective colloid, e.g. carbon sol is prepared in presence of gum arabic, or Prussian blue sol is obtained in presence of starch.
- **Dialysis** is the separation of ions or particles of crystalloids from colloids by passing them through a parchment paper or animal membrane.
- **Electrodialysis** is a fast method as ionic impurities are removed under the influence of electric field.
- **Ultra filtration** is the process of separating colloidal particles from the solvent and other solute particles using specially prepared filters or filter papers.
- **Ultra centrifugation** involves placing of a colloidal sol in a high speed centrifuge when colloidal particles settle down and can be separated to form a purified sol.
- **Physical Properties:**
  - Heterogeneous in nature.
  - Diffusion through parchment membrane is slow.
  - Pass through normal filter papers.
  - Sol particles do not settle down due to gravity.
  - Viscosity and surface tension of lyophobic colloids are almost similar to those of pure solvent but, for lyophilic colloids viscosity is higher and surface tension is lower than that of solvent.
- **Colligative Properties** like osmotic pressure, elevation in boiling point or depression in freezing pt., lowering of vapour pressure etc. are much lesser than true solutions due to number of particles being relatively lower.
- **Optical Properties** : All colloidal particles are capable of scattering light in all directions, giving rise to a bright glowing cone when seen sideways, this is known as *Tyndall effect*. Scattering of light depends on the wavelength of light used, size of particles and difference in refractive indices ( $\Delta\mu$ ) of DP and DM.
- **Kinetic Properties** : Brownian motion or irregular chaotic motion is observed in sol particles upto particle size of 0.5 microns. This motion depends on temperature and offers an explanation for the stability of colloids.
- **Electrical Properties** : The dispersed phase particles carry either +ve or –ve charge and dispersion medium has an equal and opposite charge. The particles repel one another and hence do not coagulate, thus making the colloid stable.
- Cataphoresis or Electrophoresis is the movement of colloidal particles either towards cathode or anode, depending on their charge, under the influence of an electric field.
- Electro-Osmosis is the movement of only the molecules of dispersion medium towards oppositely charged electrode under the influence of electric field, whereas the colloidal particles are not allowed to move.

- Coagulation or flocculation is the process of bringing colloidal particles closer so that they aggregate to form larger particles that precipitate and settle down or float on the surface. It is usually done by addition of an electrolyte.
  - *Hardy-Schulze rule* states that “greater is the valency of the oppositely charged ion of electrolyte being added, faster is the coagulation”, e.g. for a negatively charged sol, the order is:  $\text{Al}^{3+} > \text{Ba}^{2+} > \text{K}^+$ , for a positively charged sol the order is:  $\text{Fe}(\text{CN})_6^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$ .
  - *Coagulating power* is the minimum amount of electrolyte required to coagulate a definite amount of sol.
- **Protection of colloids**
  - Lyophilic sols are more stable than lyophobic sols hence they are used as *protective colloids* to increase the stability of lyophobic sols, e.g. addition of gums, gelatin etc. to certain metal sols.
  - Protective action of lyophilic sols is explained due to formation of a thin layer around the lyophobic sol particles, thus preventing them from coming closer.
  - Gold number is a term used to compare protective action of different lyophilic colloids.
  - Gold number of a lyophilic sol is the minimum amount of it in milligram, which prevents the coagulation of 10 ml gold sol against 1 ml of 10% NaCl solution.
  - Higher the gold number, lesser is the protective power.
  - Examples:

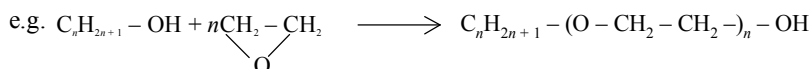
Sol	Gold number
Gelatin	0.005-0.01
Casein	0.01-0.02
Gum-arabic	0.15-0.25
Potato Starch	20-25

- **Emulsion** is a colloidal system involving one liquid dispersed in another, provided both are immiscible.
- Emulsifiers or emulsifying agents are substances which help in making the emulsions stable, e.g. soaps, agar, gum etc.
- Examples: milk, butter, milk cream, cold cream, vanishing cream, etc. There are many drugs and medicines which are also in the form of emulsions e.g. various ointments, cod liver oil etc.
- **Oil in water emulsions (O in W)** are those in which oil is the dispersed phase and water is the dispersion medium e.g. milk.
- **Water in oil emulsions (W/O)** are those in which water is the dispersed phase and oil is the dispersion medium, e.g. butter, cream etc.
- The process of breaking an emulsion to yield the constituent liquids is known as *demulsification*.
- **Gels** are colloidal systems where liquids are the dispersed phase and solids act as dispersion medium, e.g. curd, cheese etc. Liquid rich systems are called *jellies*.
- Gelling agent is added to stabilize a gel, e.g. gelatin.
- Elastic gels are reversible and can be changed back to original form even after dehydration, e.g. gelatin, agar-agar etc. swell up after absorbing water (imbibition).

- Non-elastic gels are irreversible and change into a powder on dehydration which does not absorb water, e.g. silicic acid.
- *Syneresis* or weeping of gels is the loss of water (liquid) without disturbing the gel structure.
- Some gels (e.g. gelatin) liquify on shaking in a sol. The sol on standing again changes into a gel. This property is known as **thixotropy**.
- **Surfactants** are substances which possess surface activity, i.e. lower the surface tension or increase surface area.
- Surfactants get preferentially adsorbed at the air-water, oil water and solid-water interfaces, forming an oriented mono layer.
- The hydrophilic groups point towards the aqueous phase and the hydrocarbon chains (hydrophobic) point towards air or the oil phase.

- **Types of surfactants**

- Anionic surfactants* : Soaps and detergents
- Cationic surfactants* : Quarternary ammonium salts of long chain tertiary amines form detergents which are cationic surfactants. e.g. octadecyl ammonium chloride,  $C_{18}H_{37}N^+H_3Cl^-$ ; cetyl tri-methyl ammonium chloride,  $C_{16}H_{33}(CH_3)_3N^+Cl^-$ .
- Non-inorganic surfactants* : This type of surfactants are formed when alcohols react with epoxides.



- **Micelles** are an aggregation of ions or molecules from a sol and are sub-microscopic, e.g. soaps and detergents.
- The minimum concentration of the surfactant at which micelle formation starts is called, *Critical Micelle Concentration*, (CMC).
- Lesser the CMC of surfactant, more is its surface activity and cleaning action (for detergents).
- Shapes of micelles change with change in concentration, e.g. at high concentrations, rod-shaped micelles are formed while spherical micelles are formed near CMC.
- The importance of micelles and their use is based on the fact that their hydrophobic interior can dissolve fat or oil etc. While the water soluble part, makes a hydrophilic surface around this interior, rendering the entire micelle water soluble.
- **Aqua-dag** is a colloidal solution of graphite in water.
- **Oil-dag** is a colloidal solution of graphite in oil.
- **Saturation state** is the state of the system when extent of adsorption becomes constant ( $x/m$  value does not change) and does not change with pressure.
- Macromolecules are themselves composed of giant molecules and dissolve in a solvent to yield colloidal solutions directly.
- The dimensions of the macromolecules fall in a range between  $10 \text{ \AA}$  and  $10,000 \text{ \AA}$ .
- Number of average molecular weight is defined as :

$$\bar{M}_n = \frac{\text{total weight, } W}{\text{total number of particles}} = \frac{\sum n_i M_i}{\sum n_i}$$

where  $n_i M_i$  stands for the weight of macromolecules numbering  $n_i$  and having molecular weight  $M_i$ .

- Weight average molecular weight is defined as

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + \dots}{m_1 + m_2 + \dots} = \frac{\sum m_i M_i}{\sum m_i}$$

where  $m_1, m_2$  etc. represents mass of macromolecules having molecular weights  $M_1, M_2$  etc.

- The **deltas** at the mouths of great rivers are formed by the precipitation of the charged clay particles carried in suspension in the river water, by the action of salts present in sea-water.
- The **chrome tanning of leather** is brought about by the penetration of positively charged particles of hydrated chromic oxide into the leather.

*End*