Surface chemistry:-

Surface chemistry is a branch of physical chemistry which deals with the study of phenomenon occuring at interfaces.

→ Interfaces play important role in catalysis, colloid formation, chromatography etc.

Colloidal solutions

In 1861, Thomas graham noted that crystalline substances like sugar, glucose, Urea and NaCl when dissolved in H_2O can pass through a semipermeable membrane. He also observed that the particles of glue, gelatin do not pass through semipermeable membrane. He called the first substance as **crystalloid** & the other **colloid**

Crystalloids

The substances whose solution readily diffuse through a parchment membrane. e.g sugars.

salts. acids and base

colloids The substance whose solution diffused at very slow rate through a parchment membrane e g glue, gelatin, gum Arabic

colloidal system Finely divided particles of any substance with diameters lying b/w 10A° – 2000A° dispered in any medium constitute a colloidal system. it is hetergenous system consisting of 2 phases.

Dispered phase Discontinuous phase of colloidal system.

Dispersion medium The continuous phase of colloidal system

1A°	10A° (1nm)	1000A° (100nm)	10,000A°
True soln	colloidal soln	suspension	

Properties of True solns, colloidal state & suspensions.

Sr No	Property	True soln	Colloidal state	Suspension
1.	Nature	Homogeneous	Heterogeneous	Hetro"

Sr. No	Property	True soln	Colloidal state	Suspension
2	particle size	Less than 1nm i.e 10^{-7} cm or 10 A°	1 to 100 nm or 1×10^{-7} – 1×10^{-5} cm 10 – 1000 A°	More than 100 nm or more than 1×10^{-5} cm or 1000 A°
3	Effect of gravity	No effect, particles do not settle	"	Particle settle on standing
4-	Filterability	pass unchanged through filter paper as well as animal or vegetable membranes	" " but not through An " "	Do not pass through Animal & vegetable membrane
5-	Diffusion	Rapidly	Rapidly	Don't diffuse
6 -	Visibility	particles completely invisible & do not scatter lig.	invisible but scatter lig	visible & scatter lig
7 -	Appearance	Clear & Transparent	Clear & Transparent	opaque
8 -	colligative properties	Affect colligative properties	Don't affect	Don't affect
9 -	Tyndall effect	Don't exhibit	Exhibit	don't
10 -	coagulation	They can be coagulated by adding suitable electrolyte	They can be coagulated by adding suitable electrolyte	NOT coagulated.

Classification of colloids

a) Based upon Apparance

A colloidal system in which the dispersion medium is L | g is sol They are **hydrosols** or **Aquasols** if dispersion is H_2O

When dispersion meduim is alcohol or benzene they are called **Alcosols** or **benzosol**

→ colloidal systems in which the dispersion medium is gas are called **Aerosols**

→ colloidal systems in which dispersion medium is solid are called **gels e.g cheese**

b) Based upon charge

They are positively charged on -vetively charged based upon charge on dispered phase

For e.g Metal OH are +vetively charged while metal sulphides are -vetively charged.

+vetively charged sols	-vetively charged sols.
Hb, Basic dyes such as methylene blue, $Fe(OH)_3$, $Al(OH)_3$	Metals such as Pt, Au, Ag. Metal sulphides As_2S_3. Starch, clay, silicic Acid. ~~Acid dyes such as eosin~~

c) Based on Interaction or Affinity of phase.

Lyophilic sols/colloids (suspensoids) The colloidal system in which particles of dispered phase have great affinity for dispersion medium.

e.g. gum, gelatin, starch, rubber protein.

Lyophobic (Emulsoid) colloidal systems in which particles of dispered phase have no affinity for dispersion medium **Example** metals & their insoluble compounds like sulphides & oxides.

Sr.No	property	Lyophilic Sols	Lyophobic sols
1.	Nature	Reversible	Irreversible
2	preparation	Shaking or warming substance with dispersion medium Not require electrolyte for stabilization.	Difficult to prepare, stabilizer is essential
3	Stability	stable Not coagulated by electrolytes	unstable coagulated on addition of electrolytes

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4	charge	particles carry no or little charge depending on pH of medium.	colligative particles have characteristic charge
5	Viscosity	Much higher than that of medium.	Viscosity same as that of medium.
6	Surface Tension	Higher than that of medium	same as that of medium
7-	Solvation	Heavily solvated	Not solvated
8-	Visibility	can't be seen under ultramicroscope	seen under ultramicroscope.
9-	Tyndall effect	Less distinct	More distinct
10 -	Colligative property	↑ osmotic P, ↑ depression of F.P & lowering of v.p	low O.P low depression of FP & lowering of v.p.
11-	Action of electrolyte	Large amount of electrolyte to cause coagulation	small amount " "
12.	Conductivity	high	Due to sensitivity in electrolyte, conductivity rarely measure
13	e.g	organic substances Starch, gums, proteins, gelatin	Inorganic Metal sols, S^{-2} and oxides

Based on molecular size

Multimolecular colloids.

→ They consist of small molecules with diameters less than 10^{-9} m or 1nm e.g solution of gold contains particles of sizes having several atoms

→ Solution of sulphur consists of particles containing thousand or so S_8 molecules

→ They are lyophobic sols.
They are held by van der wall forces

Macromolecular colloids

→ They are large molecules
→ High molecular wt thousands - millions
Generally polymer
→ starch, cellulose & proteins
→ size is comparable to colloidal particles & hence known as macromolecular colloids.

Association colloid / Micelles

colloids which behave as normal electrolytes at low con, but exhibit colloidal properties at High conc due to formation of aggregated particles called miscelles are referred to. **Associated colloids**

The Micelles are formed by association of dispered particles above certain conc. & certain min conc is required for process of aggregation to take place

Minimum conc required for micelle formation is called **critical Micelle conc (CMC)** and its value depends upon nature of dispered phase. **e.g**

For soaps CMC is **10^{-3} mol L^{-1}** Micelles may contain 100 molecules or more.

The formation of a micelle take place at temp called **Kraft Temp (T_k)** and conc. **(CMC)**

Preparation of Lyophilic sols.

Substances which are intrinsic colloids such as gelatin, rubber are converted into colloidal soln when warmed with H_2O or some other solvent. They are called lyophilic sols. They are converted to colloidal solutions by.

Dispersion methods
condensation "

Dispersion methods These involve breaking of bigger particles to the size of colloidal particles by

→ Mechanical dispersion method.
→ Electro disintegration method. **(Bredig's Arc Method).**
→ peptization.

Mechanical dispersion method.

The particles of substance to be dispered are agitated with dispersion medium i.e H_2O

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or some other liq to get a suspension which can pass through colloidal mill e.g colloids of paint, varnish etc

Electro-Disintegration method (Bredig's Arc method)

Colloidal soln of metal like Ag, Cu, silver, pt etc are obtained by this method.

→ It involved dipping of metals whose colloidal soln is to be prepared into cold H_2O having KOH (stabilizer).

Peptization

It involves conversion of fresh precipitates to colloidal soln & electrolyte added is peptizing agent or dispersing agent.

Example

Fresh ppt of CdS, HgS are peptized by H_2S.

Fresh ppt of stannic acid is peptized by HCl or NH_3

Peptization may carried out by
ⓐ Dispersion medium ⓑ Washing a ppt
ⓒ electrolyte

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Condensation methods

These include

(a) Chemical methods

(b) Physical methods.

Chemical Methods.

1. By Double decomposition

A colloidal soln of (As_2O_3).

As_2S_3 is obtained by passing H_2S gas through cold dil soln of As_2O_3

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

when dil soln of $FeCl_3$ is mixed with $K_4[Fe(CN)_6]$ a soln of prussian blue is formed.

$$3K_4[Fe(CN)_6] + FeCl_3 \rightarrow Fe_4[Fe(CN)_6] + 12KCl$$

→ By Hydrolysis

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

deep red colloidal soln

→ By oxidation

$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + S$$

colloidal soln

By reduction:

$2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + 2Au$
purple.

Physical methods

By exchange of solvent.

Substances like S, resin, phenolphthalein which r soluble in alcohol or organic solvent form colloids when their soln are poured in H_2O in which they are less soluble

Colloidal soln formed are less stable.

By passing vapour of substance into solvent.

Colloidal soln of S & Hg in H_2O prepared by passing vapours of substance in cold H_2O contain Ammonium nitrate as stabilizer

By excess cooling.

Colloidal soln of ice in organic solvent like ether or

Chloroform is obtained by freezing a solution of H_2O in the solvent.

Purification of colloidal solutions

ⓐ **Dialysis** The process of removing a dissolved substance from colloidal soln by means of diffusion through a suitable membrane

Apparatus known as dialyser.

Parchment paper or animal membrane is used.

ⓑ **Electrodialysis** The process of dialysis can be accelerated by applying electric field.

→ By this method we can't remove impurities of non-electrolytes

ⓒ **ultrafiltration** The process of sepearating colloidal particles from solvent & solute present by specially prepared filters permeable to all substances except colloidal particles use ultrafilter papers like cellophane membranes.

Properties of colloidal solutions

(a) Physical properties
(b) Mechanical "
(c) optical "
(d) Electrical "
(e) colligative "

Physical properties

→ **Heterogeneity**

colloidal soln are heterogeneous in nature consist of two phases dispered phase & dispersion medium dialysis and ultrafilteration clearly indicate heterogeneous character of colloidal system.

→ **Filterability**

colloidal particles pass through filter paper.

→ **Non-setting Nature**

colloidal soln are stable as the remain suspended in dispersion medium. There is no effect of gravity on colloidal particles

→ colour.

The colour of colloidal soln is not always same as colour of substance in bulk. The colour of colloidal soln depend on following factors

→ size & shape of colloidal particles
→ λ of source of li8
→ Method of preparation
→ Nature
→ The way an observer receives li8 ie whether by reflection or transmission.

Finest gold is red in colour. As particle size ↑ it becomes purple. Due to this fact, gold sol is also called as **purple of cassius**.

Dilute milk give bluish tinge in reflected li8, whereas reddish tinge in transmitted li8

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Stability:- colloidal soln are quite stable

Mechanical properties

Brownian Movement

colloidal particles show a ceaseless random & swarming zigzag motion

Sedimentation The heavier sol particles tend to settle down very slowly under the influence of gravity

Diffusion The colloidal particles have a tendency to diffuse from high conc — low conc. How rate of diffusion of colloidal particles is less than that of true solutions

Optical properties (Tyndall effect)

When a strong & converging beam of li8 is passed through a colloidal soln, its path becomes visible when viewed at rt angle to beam of light.

The effect was used by **Zsigmondy** and **siedentopf** in devising ultramicroscope.

It is due to scattering of light by colloidal particles.

e.g sky looks blue, dust particles can seen in light coming from ventilator in a dark room, tail of comet.

Conditions needed for Tyndall effect

→ The diameter of dispered particles is not much smaller than λ of light used.

→ The refractive indices of the dispered phase & dispersion medium must differ largely in magnitude.

Electrical properties

Electrophoresis:- It is a movement of electrically charged colloidal particles under the influence of applied electrical field

Electro-osmosis:- This process is just the reverse of electrophoresis. In this process, liquid moves through a fixed porous material.

Sedimentation potential or Dorn effect.

The word sedimentation means settling down. The phenomenon can be observed if the particles are forced to move in a resting liquid. This can be done by gravitational force. The potential so produced is known as sedimentation potential & effect is known as "Dorn effect".

This process is just the reverse of electrophoresis

Streaming potential:-

In the phenomenon of electro-osmosis if water is forced through the tube in which the process take place there will be current production and potential is produced that is proportional to pressure. The potential so developed is called streaming potential

Other definitions of Electrophoresis or cataphoresis

It is the phenomenon involving migration of colloidal particles under the influence of electric field towards oppositely charged electrode.

It is useful in deciding charge present on colloidal particles.

Electro-Osmosis It involves migration of dispersion medium and not the colloidal particles under influence of electric field. It is useful in removal of H_2O from peat in drying dye in dewatering moist clay.

colligative properties:-

colloidal solutions too exhibit colligative properties such as osmotic pressure, depression in F.P & elevation in B.P

→ The effect of colloidal particle on colligative properties except osmotic pressure is very small due to large size of colloidal particles

coagulation / flocculation.

The colloidal sols are stable due to presence of electric charges on collidal particles. Because of the electrical repulsion, the particles do not come close to one another to form ppts

The removal of charge by any means will lead to the aggregation of particles for ppt is known as coagulation and the minimum amount of electrolyte required to cause ppt of one litre of colloidal soln is called coagulation value or flocculation value of electrolyte for sol.

The reciprocal of coagulation value is regarded as coagulating power.

Hardy - Scnylz Rules

"Higher the valency of active electrolyte ion, the more is its power to precipitate the sol"

The coagulation power of cations for negatively charged colloids is $Si^{+4} > Al^{+3} > Mg^{+2} > Na^{+}$

The coagulation power of anion for +vetively charged sol $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

Protection

Protection involve protection of lyophobic colloid from coagulation by using lyophilic colloid which is called lyophilic colloid and expressed in terms of gold no.

Gold Number

It is the no of miligrams of protective colloid needed to prevent coagulation of standard 10ml gold sol when 1ml of 10% soln of NaCl is added to it

Note:- smaller the gold no greater will be the protection power.

Examples

→ Gelatin is added in preparation of ice-cream to protect colloid particles from coagulation

→ Protargols & argyrols are used in eye drops.

Macromolecules

They include gels &, e.g. emulsions. The dimensions of macromolecule lie in the range of 10-1000 A°.

They also show a weak tyndall effect.

They don't show electrophoresis as they don't carry electrical charge.

Emulsions:-

Liq in Liq colloidal system.

"Colloidal solutions in which both dispered phase and dispersion medium are liquid".

Types:-

Oil in water emulsion
water in oil "

O/W

Those emulsions in which oil is dispered phase and H_2O is dispersion medium.

W/O

Those emulsion in which oil is dispersion medium & water is dispersed phase.

Emulsification

The process of emulsion production is known as emulsification

Distinction b/w O/W & W/O emulsions

Dye Test :-

If the emulsion is heated with the oil soluble dye and emulsion gains colour of dye then it is W/O emulsion. If it does not catch colour of dye then it will be O/W

Conductance method :-

Add a small amount of electrolyte in emulsion. If conductance ↑, the emulsion is O/W & if there is no change in conductance it is W/O.

Dilution method.

As a general rule, an emulsion can be diluted with dispersion medium while the addition of dispersed phase form a seperate layer. Thus, if an emulsion can be diluted with oil it is w/o type

Emulsifying Agent.-

substance that lower interfacial tension b/w oil & water and thus help in the intermixing of two liquids

Factors for stability of emulsion

→ Thickness of protective film.
→ Compactness of the " "
→ Electrical charge on droplet
→ Viscosity of dispersion medium
→ ρ difference b/w two liquids

Demulsification

The process of breaking

emulsion to yield constituent liquids

Techniques

→ Heating → centrifuging
→ Adding small amount of electrolyte

Gels & Jellies

Jellie is a common name for gel and they are semi-rigid sols consisting of 2 components one is solid & othe is liquid

Elastic	Non-elastic
→ Change to solid mass on dehydration which can be changed back to orginal form with H_2O	→ They change to solid mass on dehydration which cannot changed back to original form with H_2O.
→ They absorb H_2O when placed in with simultaneous swelling. This phenomenon is called imbibition e.g gelatin, agar, starch, jams, jellies	→ They do not exhibit imbibition e.g silica gel

on

Sol ⇌ gel (Thixotropy)
↓
imp in paints

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Some important things

Electrical double layer:-

The surface of colloidal particle acquires a +ve charge by selective adsorption of a layer of +ve ions around it. This layer attracts counter ions from medium which form a second layer of -ve charge. The combination of 2 layer of +ve & -ve charge around sol particle is called.

Helmholtz double layer

→ a **compact layer** of +ve & -ve charge which are fixed firmly on particle surface.

→ a **diffused layer** of counter ions diffused into the medium containing +ve ions

Adsorption

The phenomenon of high conc of molecular species at the surface than in the bulk of solid or liquid. Forces involved are van der waal's forces

Adsorbate

The substance that concentrates at the surface.

Adsorbent is the solid or liquid at whose surface the conc occurs.

Adsorption

phenomenon of uniform distribution of substance throughout the body of solid or liquid

sorption

Adsorption + Absorption

Characteristics of Adsorption

→ surface phenomenon.

→ spontaneous process

ountries

→ It is accompanied by evolution of heat.

→ Heat evolved on adsorption of 1 mole of gas "is called molar heat of adsorption"

→ It is accompanied by decrease in enthalpy $\Delta H = -ve$

→ " " decrease in entropy $T\Delta G = -ve$

Physical Adsorption

Also called van der walls' adsorption involves weak forces, physical in nature, with small heat of adsorption

Chemical Adsorption

Forces of attraction b/w adsorbate and adsorbent are strong and chemical bonds.

Property	Physical	chemical
Forces	van der walls	Chemical bonds
Temp	at low temp	At ↑ temp
layer	multimolecular	monomolecular

Pressure	increase with ↑ p.	↓ with p
Liquification	related to liquefication of gases	Not related
Enthalpy	20-40 KJ/mol	40-400 KJ/mol
Activation energy	low	high
Reversibility	reversible	irreversible
Specificity	Not specific	very specific

Factors Affecting Adsorption

→ Nature of gas
→ Nature of adsorbent
→ Effect of pressure
→ temperature
→ surface Area ↑ Adsorption ↑
→ Heat of Adsorption

Freundlich Adsorption isotherm

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$