SURFACE CHEMISTRY

COLLOIDS SOLUTION AND CLASSIFICATION OF COLLOIDS

COLLOIDAL SOLUTION: -

They considered as a heterogeneous system consisting of the following three essential components:

1. A dispersed phase:

It is also known as discontinuous or inner phase. It consists of discrete particles significantly larger than ordinary molecules and in this small particle of solute is diffused in solvent.

2. A dispersion medium or continuous phase or the outer phase:

It is the medium in which dispersed phase is present. This consists of continuously interlinked molecules.

3. A stabilizing agent:

This is a substance which tends to keep the colloidal particles apart. Some colloids are selfstabilizers.

Dispersed phase + Dispersion medium = Dispersion system (Colloidal solution)

Each of the two phases constituting a colloidal system may be a gas, a liquid or a solid. For example, in milk, the fat globules are dispersed in water. Hence fat globules form a dispersed phase and water is the dispersion medium.

Sol: If dispersion of a solid in a liquid, solid or gaseous medium, the resulting solution is called sol.

1. **Colloidal Solution:**

If dispersion of a solid (dispersed phase) in a liquid (dispersion medium), the resulting solution is called colloidal solution. Solid aerosol: The dispersion of a solid (dispersed phase) in a gas(dispersion medium).

2. Liquid aerosol:

If the dispersed phase is a liquid and the dispersion medium is a gas, the resulting sol is called a liquid aerosol.

3. Emulsion:

When a liquid is dispersed in another liquid the resulting system is called an emulsion.

Gel: If colloidal system becomes fairly rigid, it is termed as a gel.

Types of colloidal solution: -

Classification of colloids:

There are a number of bases for the classification of colloids.

1. Depending upon the nature of the dispersed phase and that of dispersion medium the colloidal solutions are divided into the following eight categories:

S. No.	Dispersed	Dispersion	Name	Examples
	phase	medium		
1	Solid	Solid	Solid sol	Colored, glass,
				gems, alloys
2	Solid	Liquid	Sol	Paints, ink, white
				of egg mud
3	Solid	Gas	Aero sol	Smoke dust
4	Liquid	Solid	Gel	Curds pudding
				chasse jelly
5	Liquid	Liquid	Emulsion	Milk, cream,
				butter, oil in
				water,
6	Liquid	Gas	Liquid Aerosol	Clouds mist fog
				water in air
7	Gas	Solid	Solid Form	Cake, bread lava,
				stone
8	Gas	Liquid	Form	Soap, lather,
				whipped, cream

Since the two gases are completely miscible with each other, they always form a true solution.

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2. Depending upon the appearance of colloids:

On this basis colloids are divided into the following two main categories.

a. Sol:

When a colloidal solution appears as fluids, it is termed as sol. Sols are named after dispersion medium. For example, when dispersion medium is water, they are called hydrosols when the dispersion medium is alcohol, they are called alcohols and so on.

b. Gels:

When a colloid has a solid-like appearance, it is termed as gel. The rigidity of gel varies from substance to substance.

3. Depending upon the interaction of the two phases.

According to Perrin and Freundlich, colloids may be classified into lyophobic and lyophilic.

a. Lyophobic or solvent-hating:

When the dispersed phase has less affinity for the dispersion medium, the colloids are termed as lyophobic. But when the dispersion medium is water, they are given the name hydrophobic. Substances like metals, etc. which have particles of size bigger than the colloidal particles or NaCl which has particles of size smaller than the colloidal size, fall in this category. Such substances are brought into colloidal state with difficulty.

b. Lyophilic or solvent loving:

When dispersed phase has a greater affinity for the dispersion medium, the colloids are termed as lyophilic and when the dispersion medium is water, they are given the name hydrophilic. They are also called natural colloids, substances like proteins, starch and rubber etc. are grouped under this category.

4. Depending upon the electrical charge on the dispersed phase:

On this basis the colloids may be divided into:

a. Positive Colloids:

The dispersed phase carries the positive charge. The particles of $Fe(OH)_3$ sol in water are positively charged. Examples of this type are also methylene blue and TiO_2 sols.

b. Negative Colloids:

This dispersed phase carries the negative charge. For example, the particles of As_2S_3 sol in water are negatively charged. The other examples are copper or gold sol and certain dye-stuffs like eosin, Congo red etc.

5. Depending on the structure of colloid particles:

According to Lumiere and others, colloids can also be classified into molecular and micellar colloids. The particles of molecular colloids are single macromolecules and their structure is similar to that of small molecules. The particles of micellar colloids are aggregates of many molecules or groups of atoms which are held together by cohesive or van der Waal's forces. The examples of molecular colloids are albumin, silicons, rubber etc. while that of micellar colloids or sulphur, gold, soap detergents etc.

a. Multimolecular colloids:

The multimolecular colloidal particles consists of aggregate of atoms of small molecules with diameter less than 10^{-9} m or 1 nm. For example, a sol. of gold contains particles of various sizes having several atoms. A sol. of sulphur consists of particles containing a thousand or so S₂ molecules. These particles are hold together by vandal Waal's forces. These are usually lyophobic sols.

b. Macromolecular colloids:

The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varying from thousand to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polystyrene, Dacron, synthetic rubber, plastics, etc. The size of these molecules is comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resembles true solutions in some respect.

c. The associated colloids or miscellas:

These colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called miscellas. Soap and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions.

RCOONa \rightarrow RCOO⁻ + Na⁺

Sod. Stearate soap ($R = C_{17}H_{35}$)

The long-chain RCOO- ions associate or aggregate at higher concentrations and form miscellas and behave as colloids. They may contain 100 or more molecules.

Sodium stearate $C_{17}H_{35}COONa$ is an example of an associated colloid. In what it gives Na⁺ and state, $C_{17}H_{35}COO^-$ ions. These ions associate to form miscellas of colloidal size.

Emulsion and gels: -

Emulsion

An emulsion can be defined as a colloid consisting of two or more non-homogenous type of liquids wherein one of the liquid contains the dispersion of the different form of liquids.

Properties Of Emulsions

- Emulsions contain both a continuous and the dispersed with the boundary coming between the phases that are called "interface".
- Emulsions have a cloudy appearance due to many phase interfaces scattering light passing through the emulsions.
- Emulsions appear in white colour when the light is dispersed in equal proportions.
- If the emulsion is dilute, then higher-frequency and the low-wavelength type of light will be scattered in more fractions, and this kind of emulsion will appear in blue in colour. This is also referred to as the Tyndall effect.

Types of Emulsion

Emulsions can be classified on the basis of the properties of the dispersed phase and the dispersion medium.

1. Oil in water (O/W):

In this type of emulsion, the oil will be the dispersed phase and water will be the dispersion medium. The best example for o/w emulsion is milk. In milk, the fat globules (which act as the dispersed phase) are suspended in water (which acts as the dispersion medium).

2. Water in oil (w/o):

In this type, water will be the dispersed phase and oil will be the dispersion medium. Margarine (a spread used for flavoring, baking and working) is an example of water in oil emulsion.

Methods to Identify the Type of Emulsions

1. Dilution test

On adding water to an o/w emulsion, it will still remain stable as water is the dispersion medium, but on adding oil it will get destabilized as oil & water are immiscible. Similarly, w/o emulsion can be diluted with oil & would still be stable, but would get destabilized on the addition of water.

2. Conductivity test

In this test the emulsion is kept between 2 electrodes and a bulb is connected in the circuit as shown in the diagram. An o/w emulsion will conduct electricity as water conducts electricity, but a w/o will not conduct electricity.



3. Dye test

In this, a water-soluble dye is added to the emulsion. If it is an o/w emulsion, the dispersion medium appears red and the dispersed phase colourless and vice-versa.

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Separation of Emulsions

The different methods by which emulsions can be separated into its constituent liquids include;

- **1.** Heating
- **2.** Centrifuging
- 3. Freezing, etc

Applications and Uses of Emulsion

Emulsions are very much famous in various fields of science. It is utilized in the tanning and dyeing industries, used in the manufacturing process of plastics and synthetic rubber.

- > Usually used in cosmetics, pharmaceuticals, personal hygiene.
- Microemulsions are used to deliver vaccines to kill various microbes.
- > It is used in chemical synthesis mainly in the manufacture of polymer dispersions.
- It is used in firefighting.
- Nano emulsions such as soybean oil are used to kill microbes.
- Mayonnaise is an oil in water emulsion with egg yolk or sodium stearoyl lactylate.

GELS: -

A gel is a colloidal system in which a liquid is dispersed in a solid. The lyophilic sols may be coagulated to give a semi solid jelly like mass which encloses all the liquid present in the sol.

The process of gel formation is called gelation and the colloidal system formed is called gel.

The Common examples of gel are: gum Arabic, gelatin, processed cheese, silicic acid, ferric hydroxide, etc.

Gels may be classified into two types:

- 1. Elastic gels
- 2. Non-elastic gels

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1. Elastic gels

These are the gels which possess the property of elasticity. They readily change their shape on applying force and return to original shape when the applied force is removed. They change to solid mass on dehydration which can again be converted into gel by addition of water followed by heating and cooling. When these gels are placed in contact with water, they absorb water and swell. This property is called Imbibition.

Examples are gelatin, agar, starch etc.

2. Non-elastic Gels

These are the gels which are rigid and do not have the property of elasticity. They change into solid mass on dehydration which becomes rigid and cannot be converted into original form by heating with water.

They do not show the phenomenon of imbibition.

For example: silica gel.

Lyophilic and lyophobic sols and on the basis of type of dispersed phase: -

In general lyophilic sols are more stable than lyophobic sols. The additional stability is due to the presence of an envelop of the solvent (say water) around the colloidal particle. The process is known as hydration. To coagulate a hydrophilic sol we have to add a dehydrating agent in addition to an electrolyte. Main points of differences between the two types are given in the table:

Preparation of sols

Preparation of lyophilic sols

Many organic substances like gelatin, starch, agar, egg albumin, glycogen etc. dissolve readily in water either in cold or on warming to give colloidal solutions directly. These are the lyophilic colloids. For example, sols of egg albumin or glycogen can be prepared by dissolving 1-2 g of the finely ground substance in 100 mL of distilled water and then allowing it to stand for two hours after constant stirring. After two hours, the solutions are filtered. Gelatin may be regarded as a typical lyophilic linear colloid. If two grams of gelatin are placed in distilled water and kept there for several hours, it

has been observed that unlike egg albumin and glycogen, gelatin does not dissolve in cold water although it does swell. The swellen gelatin may be dissolved by heating with water at 80- 90°C. If two grams of gelatin are dissolved in 400 mL of distilled water, a clear sol. is obtained on cooling.

Preparation of lyophobic sols: Such sols can be prepared by the two general ways.

- **1.** By dispersion of coarse particles (Dispersion method). Here we start with bigger particles and break them down to the colloidal size.
- **2.** By inducing molecular particles to form large aggregates (condensation method). Here we start with particles of molecular dimensions and condense them to the colloidal dimensions.

S. No.	Property	Lyophilic	Lyophobic
		(Intrinsic sol.)	(extrinsic sol.)
1	Preparation	They are easy to	They are difficult to
		prepare. Only contact	prepare. Special
		with the dispersion	methods are used.
		medium is needed to	Addition of stabilizers
		stabilize them	is essential for their
			stability.
2	Size of particles	The particles are just	The particles are
		bigger molecules	aggregates of
			thousands of
			molecules.
3	Nature	Reversible; once	Irreversible, once
		precipitated casily	precipitated does not
		pass back into the	easily pass into
		colloidal state by	colloidal state
		contact with	
		dispersion medium	

4	Conductivity	With lyophilic salts	Owing to their
		high conductivities	sensitivity in
		can generally be	electrolytes the
		measured	conductivity of
			lyophobic sol can
			rarely be measured
			over a considerable
			range of concentration
5	Tyndall effect	Less distinct	More distinct
6	Viscosity	Higher than that of	Almost same as that of
		water	water
7	Surface Tension	Lower than that of	Almost same as that of
		water	water
8	Hydration	Particles are heavily	Particles are poorly
		hydrated	hydrated
9	Stability	Very stable,	Less stable,
		coagulated with	coagulated easily
		difficulty	
10	Charge	Depends on the pH of	Have characteristic
		the medium. It can be	charge (Positive or
		even zero.	negative)
11	Concentration of the	Higher concentrations	Only low
	dispersed phase	of dispersed phase are	concentrations of the
		possible	dispersed phase are
			possible
12	Examples	Albumin, Glycogen,	Au, Ag, some
		Rubber, Silicic acid etc.	emulsions etc.

Critical micelle concentration: -

Critical micelle concentration (cmc):

In very dilute solutions, sodium and potassium oleate and other similar substances, remain as individual molecules ionizing into positive and negative ions. According to Davies and Bury the concentration at which micelle becomes appreciable, is termed as critical micelle concentration. At this concentration there is an abrupt change in the properties, it decreases with the increase of temperature. Every colloidal electrolyte has a definite value of CMC.

Type of ionic micelles:

McBain suggested the presence of more than one type of ionic micelles in a given solution of a colloidal electrolyte. Some of them are described below:



1. Lamellar micelle:

In consists of double leaflet of soap molecules placed end to end and side by side. X-ray study has revealed the existence of other kind of micelle in which molecules are laid end to end, side by side, as in lamellar micelle. The difference from each other and are separated by layer of water, depending upon concentration. Hoffman's investigation has shown that the molecules in the micelle are rotated at an angle of 55°. According to Stuff the molecules are closely packed side by side in an irregular manner as in a liquid crystal.

2. Spherical micelle:

According to Hartley ionic micelles can be spherical. Although this consent is employed but is open to criticism.

3. Ellipsoidal or cylindrical micelle:

Kelvins has suggested that the micelle may also be an elongated ellipsoidal or of cylindrical model.

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Properties of colloidal solutions: -

1. Colligative Properties: -

The values of colligative properties (osmotic pressure, lowering in vapor pressure, depression in freezing point, elevation in boiling point) are of small order as compared to values shown by true solution at same concentration.

2. Tyndall effect: -

It is may be defending as the scattering of the light by the colloidal particles present in the colloidal solution.

3. Colour: -

The colour of the colloidal solution depends on the wavelength of the light scatter by the dispersed particles. The wavelength of light further depends on the size and nature of the particles.

4. Brownian Movement: -

It may be defined as continuous zigzag movement of the colloidal particles in a colloidal solution is known as Brownian movement.

5. Charge as colloidal particles: -

Charge as colloidal particles always carry is electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either +ve or -ve.

Example: -

- (a) +ve charged solution: -Hemoglobin
 Hydrated Metallic oxides
 E.g. AS₂S₃.xH₂O
- (b) -ve charged solution: -Metals E.g. Cu, Ag, Au

Metallic sulphides

E.g. AS_2S_3 , Sb_2S_3 , CdS solutions.

6. Electrophoresis: -

The movement of colloidal particles under the influence of an electric field is called electrophoresis. –ve charged particles move towards the cathode and +ve charged particles moves towards anode.



Electrical double layer :-

The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying +ve or -ve charges respectively. The charges layer attracts counter ions from the medium which forms a second layer. Thus, an electrical double layer is formed on the surface of the particles i.e., one due to absorbed ions and the other due to oppositely charged ions forming a diffused layer. This layer consists of ion of both the signs, but its net charge is equal and opposite to those absorbed by the colloidal particles. The existence of charges of opposite signs on the fixed and diffused parts of the double layer creates a potential between these layers. This potential difference between the fixed charge layer and diffused layer of opposite change is called electrolkinetic potential or zeta potential.

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Hardy Schulze rule :-

(a) Hardy- Schulze Law :

According to them, the greater the valency of the active ion, greater is the power to cause coagulation. Active ion is responsible for coagulation.

Thus, in the case of positively charged sol the coagulation power of anions is in the order of

 $[Fe(CN)_4]^{-4} > [PO_4]^{3-} > [SO_4]^{-2} > [Cl]^{-1}$

In the case of negatively charged sols, the coagulation power is in order of

 $Al^{+++} > Ba^{++} > Na^{+}$

The coagulation values of NaCl, $BaCl_2$ and $La(NO_3)_3$ for silver sol are 30, 0.5 and 0.003 millimoles/liter. The reciprocal of coagulation value is regarded as the coagulating power or flocculating power i.e.

 $\frac{1}{30}:\frac{1}{0.5}:\frac{1}{0.003}$ i.e., 1:60:1000

Coagulation sols of Lophius: -

Coagulation or flocculation

The colloidal sols are stable by the presence of electric charges on the colloidal particles. Because of the electric repulsion the particles do not come close to one another and coalesce. The removal of charge by any means will lead to the aggregation of particles and hence precipitation immediately. The process by means of which the particles of the dispersed phase in a sol are precipitated is known as coagulation or flocculation.

Electric charges on lyophobic particles can be removed by the application of an electric field as is used in electrophoresis. But a common method of producing precipitation is by the addition of electrolytes. The precipitate after being coagulated is known as coagulum.

Methods for coagulating a sol

There are several methods employed for coagulating a sol. Some of them are noted below:

1. By the addition of electrolytes:

In this method large number of electrolytes are added to the sols which cause precipitation. This is due to the fact the colloidal particles take up the ion whose charges are opposite to that on colloidal particles. With the result that the charge on colloidal particles is neutralized and coagulation takes place. In case of arsenious sulphide sol (negatively charged) coagulation

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takes place by adding BaCl₂. It is due to the fact that negatively charged particles of the arsenious sulphide sol take up barium ions, resulting neutralization of the charge on the colloidal particles and hence lowering the stability of the sol.

It has been observed that generally the greater the valency of the added ion, the greater is its power to cause coagulation. An ion having an opposite charge to that of the particles of the sol is responsible for coagulation. This ion is generally called as active ion. For example calcium chloride is approximately 100 times more active than NaCl in the coagulation of a silver sol. The particles of a silver sol are stabilized by negative charges and for the coagulation the valency of the cation is effective. Similarly for the coagulation of positive sols the valency of the anion is decisive. Further, the precipitating power of an electrolyte increases very rapidly with increase in the valency of the cation or anion, the ratios being approximately 1 : 40 : 90 for the ferric hydroxide sol and 1 : 70 : 500 for the arsenious sulphide sol.

Thus in the coagulation of ferric hydroxide sol, the coagulating power increases in the order of $Cl^- > SOO_{4^-} -> PO_{4^-} -- Fe(CN)_{6^-} ---, while in the coagulation of arsenious sulphide sol, the coagulating power increases in the order of Na⁺ > Ba⁺⁺, Al⁺⁺⁺. This importance of valency was first recognized by Schulze (1882) and more data were obtained latter by Linder, Picton, Hardy and Freundlich. The coagulation values of NaCl, BaCl₂ and La(NO₃)₃, for the silver sol prepared by reduction of silver carbonate with tannin are 30, 0.5 and 0.003 milli/mol per/liter respectively. The coagulation or flocculation power can then be expressed as the reciprocal of these flocculation values i.e.$

$$\frac{1}{30}:\frac{1}{0.5}:\frac{1}{0.003}$$

i.e. NaCl: BaCl₂: La(NO₃)₃ as 0.033: 2: 33.3 or 1.60: 10000

2. Physical methods :

The coagulation of some sols can be carried out by (a) mechanical treatment, (b) heating or cooling, (c) irradiation, (d) vigorous shaking, (e) treatment with electric current, etc.

3. By continuous dialysis :

We know that traces of electrolytes are present in the colloidal system which are necessary for the stability. If the sol is subjected to continuous dialyzer the colloidal system becomes unstable.

4. Salting out :

Coagulation of lyophilic sol can be made by the addition of sufficient high concentrations of certain ions. Thus salting out of lyophilic colloids is due to the tendency of ions to become solvated, causing the removal of adsorbed water from the dispersed particles.

5. By hydrated ions:

Since ions can also differ in the degree of hydration or solvation, this factor also plays an important role in the precipitation of sols.

6. By removal of electric charge:

Removal of electric charge on lyophobic particles by means of the application of electric field results precipitation. This is accomplished by electrophoresis.

	Arsenious sullied sol		Ferric hydroxide sol	
S. No.	Electrolyte	Coagulation value miles mole/Liter	Electrolyte	Coagulation value miles mole/Liter
1	NaCI	52	КСІ	132
2	KCI	51	K ₂ CrO ₃	0.225
3	BaCI ₂	0.69	K ₂ SO ₄	0.21
4	MgSO ₄	0.22	K ₃ Fe(CN) ₆	0.096
5	AICI ₃	0.093	K ₄ Fe(CN) ₆	0.085

Applications of colloids: -

A colloid is a heterogeneous mixture in which the minute particles of one substance are dispersed in another substance, called the dispersion medium.

Properties of colloids

- Colloids show the following properties
- > It is a heterogeneous mixture.
- The size of colloidal particles is very small. Their particle size ranges between 1-1000 nanometers.

- It shows the Tyndall effect. It means it scatters the beam of light and shows its path through itself.
- They don't settle down when left undisturbed for some time. It means colloidal solutions are quite stable.
- > They cannot be separated by the filtration process.
- > They can be separated by centrifugation.
- Colloidal particles show Brownian movement.

Applications of Colloids

- Colloids have various applications in many fields. Some uses of colloids are listed below –
- Colloids are used in the foods and food industries at a large level. Many foods which we consume are actually colloidal in nature. Such as milk, cheese etc.
- Colloids have various applications in the medicinal field as well. Many medicines which we use are in the form of emulsions. Antibiotics such as penicillin and streptomycin are given in the form of colloidal solutions so that they can be absorbed by the human body easily.
- Colloids are used in water purification.
- Sewage water contains impurities like dirt, stool, urine etc. which are dispersed in water. Thus, it forms a colloidal system. These can be removed by electrophoresis.
- Smoke is also a colloidal system of carbon particles in the air. This can also be purified by electrophoresis.
- These are used in artificial rain as well.
- Rubber is obtained by a colloidal solution called latex through coagulation.
- Treatment of the skin of animals to get leather is called tanning. In the process of tanning, colloids are used.
- Micelles formed in the cleansing action of soaps are colloids.
- Colloids are used in the form of smoke in smoke screens to hide some things in the military.

- The blue color of the sky is due to a colloidal property shown by the sky. Dust particles dispersed in the air scatter sunlight.
- Many nanomaterials are prepared by colloids.
- > These are used in metallurgy during froth floatation.
- > These are used in the treatment of hypovolemic patients.
- A silver colloid is used as a germicidal agent.
- Many colloids are used as anticancer drugs, such as copper colloids.
- Colloids are used in the preparation of anti-syphilis antibodies.
- Proteins are colloids and are used in various ways.
- These are used for targeted drug delivery.
- > These are used as cosmetic ingredients for many cosmetic products.
- These are used as fungicides and pesticides.
- > These are used in plastic surgery of many body parts.
- These are used in dentistry.
- > These are used in wound dressing materials as well.