Colloids

• Three primary types of mixtures - a solution, colloid and suspension.



- A colloid is a solution Particle remain evenly distributed throughout the solution.
- *Colloidal dispersions* substances remain dispersed and do not settle.
- The substance being dispersed the *dispersed phase*,
- The substance in which it is dispersed the *continuous phase* or *dispersion medium*.

Particles in a colloid are larger than most simple molecules and scatter light (Tyndall effect).





Preparation of Colloidal Systems

A colloidal system can be produced by distributing particles throughout a dispersion medium.

• *Dispersion methods*: by breaking down larger particles.

For example, paint pigments are produced by dispersing large particles by grinding in special mills.

• *Condensation methods*: growth from smaller units, such as molecules or ions.

For example, clouds form when water molecules condense and form very small droplets.

Classification of Colloids

Based on the Nature of Interaction Between Dispersed Phase and Dispersion Medium

Hydrophilic colloids:

- These are water-loving colloids.
- The colloid particles are attracted to the water.
- They are also known as reversible sols.
- Examples include Agar, gelatin, pectin, etc.

Hydrophobic colloids:

- □ These are the opposite in nature to hydrophilic colloids.
- □ The colloid particles are repelled by water.
- □ They are also called irreversible sols.
- Examples include Gold sols, clay particles, etc



Based on Type of Particles of Dispersed Phase

Multimolecular Colloids:

- Formed as a result of the aggregation of a large number of atoms or small molecules (*having diameters of less than 1 nm*) of the dispersed media.
- The dispersed particles are held together by Van der Val forces

Example: Gold sol, Sulphur sol.

Macromolecular Colloids:

- Colloids formed from macromolecules.
- Macromolecular colloids consist of high molecular mass.
- Lyophilic colloids are macromolecular in nature.

Examples: starch, proteins, gelatin, cellulose, nucleic acids, polyethylene, polypropylene, etc.

Associated Colloids (Micelles):

- Certain colloids behave as strong electrolytes at lower concentrations but exhibit colloidal properties at higher concentrations.
- The colloids that form micelles are known as associated colloids.

Depending Upon the State of Dispersed and Dispersion Medium

Disperse Phase	Dispersion Medium	Туре	Example
Gas	Liquid	Foam	Shaving Cream
Gas	Solid	Solid Foam	Foam rubber
Liquid	Gas	Aerosol	Fog, mist, clouds
Liquid	Liquid	Emulsion	Hair, cream, milk
Liquid	Solid	Solid Emulsion (gel)	Butter, Cheese
Solid	Gas	Smoke	Dust
Solid	Liquid	Sol	Ink, paint
Solid	Solid	Solid Sol	Alloys, ruby glass

CHARGE ON COLLOIDAL PARTICLES

- The colloidal particles carry a charge.
- The presence of similar charge on particles is responsible for the stability of the system.
- The origin of the charge on the sol particles in most cases is due to the preferential adsorption of either positive or negative ions on their surface.
- Depending upon the nature of charge on the particles of the dispersed phase, the colloidal solutions are classified into *positively charged and negatively charged colloids*.
- Metallic hydroxides (Bi, Pb and Fe) are electropositive colloids while metallic sulphides are electronegative colloids.







The sol particles acquire electrical charge in any one or more of the following ways.

DUE TO THE DISSOCIATION OF THE SURFACE MOLECULES

- Some colloidal particles develop electrical charge due to the dissociation / ionisation of the surface molecules.
- The charge on the colloidal particles is balanced by the oppositely charged ions in the sol.
- For example, an aqueous solution of soap (*sodium palmitate*) which dissociates into ions. The cations (Na⁺) pass into the solution while the anions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains.





(2) DUE TO FRICTIONAL ELECTRIFICATION

• The frictional electrification due to the rubbing of the dispersed phase particles with that of dispersion medium results in some charge on the colloidal particles.

(3) DUE TO SELECTIVE ADSORPTION OF IONS

• The particles constituting the dispersed phase adsorb only those ions preferentially which are common with their own lattice ions



when a small quantity of potassium iodide solution is added to a large quantity of silver nitrate solution ; the colloidal silver iodide particles adsorb Ag^+ ions from the solution to become positively charged.

when a small quantity of silver nitrate solution is added to a large quantity of potassium iodide solution, the colloidal particles of silver iodide adsorb I⁻ from the solution to become negatively charged.



Electrical Double Layer

- The electrical properties of a colloid can be well understood by the concept of electrical double layer.
- The colloidal particles acquire charge by the preferential adsorption of ions from solutions. These ions adsorbed on the surface of the colloidal particle and forms a rigid layer are called *potential-determining ions*.
- The potential determining ions attracts oppositely charged ions from solution called the *counter-ions*. The counter-ions form a compact layer above the rigid layer and the layer of counter-ions is known as *Stern layer*.
- The influence of the surface charge diminishes after a certain distance in the solution and the region acquires electrical neutrality. The diffuse layer between the Stern layer and the electrically neutral part of the system is known as the *Gouy-Chapmann* layer.
- The region in which the surface charge has an influence is known as the *electrical double laver*.





The thickness of the electrical double layer is given by:

$$r_D = \left(\frac{\varepsilon_r RT}{2\rho F^2 I}\right)^{\frac{1}{2}}$$

- ε is the dielectric constant,
- ρ is the density,
- *I* is the ionic strength of the solution.
- The thickness of the electrical double layer is of the order of 1 1000 nm.
- It decreases with the ionic strength of counter ions.



Zeta Potential (ζ)

- The Zeta potential of the particles is the electric potential at the boundary of the double layer on the particle surface.
- The stability of the colloidal systems depend on the zeta potential.
- If ζ is very small the resultant potential energy is negative so that Van der Waal's attraction predominates over the electrostatic repulsion and the sol coagulates rapidly.

The Zeta Potential (ζ) is given by the equation

 $\zeta = \frac{4\pi\eta\mu}{\varepsilon}$

 μ is the mobility of colloidal particles; η is the viscosity and ε is the dielectric constant



DLVO Theory

- The **DLVO** theory (*named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodoor Overbeek*) explains the stability of colloids and describes the force between charged surfaces interacting through a liquid medium.
- It combines the effects of the van der Waals attraction and the electrostatic repulsion due to the double layer of counterions.
- In DLVO theory, the zeta potential is used to explain that as two particles approach one another their ionic atmospheres begin to overlap and a repulsion force is developed.
- The total potential energy is described as the sum of the attraction potential and the repulsion potential.
- When two particles approach each other, electrostatic repulsion increases and the interference between their electrical double layers increases.



The potential energy due to repulsion of double layers on particles of radius 'a':

 r_D



is a constant;

is the zeta potential;

is the separation of the centres of particles;

is the separation of the surfaces of the two particles and

is the thickness of the electrical double layer.

The potential arising from the attractive interaction:

 $V_a = -\frac{B}{S}$ Where, 'B' is another constant

- The combination of the two forces results in a deep attractive well, which is referred to as the *primary minimum*.
- At larger distances, the energy profile goes through a maximum energy barrier, and subsequently passes through a shallow minimum, which is referred to as the *secondary minimum*.

Observations from the Potential Energy Curve:

- The primary minimum indicates that the aggregated state is of the lowest-energy condition and this is where we would expect the particles to reside.
- The primary maximum acts as an activation barrier that must be exceeded for aggregation to occur. As two particles come closer, they must collide with sufficient energy to overcome the barrier provided by primary maximum.
- The secondary minimum could be seen as a flocculated state but the particles still have to cross the energy barrier to come into close contact at the minimum energy state.



Coagulation of Colloids

- Coagulation is the destabilization of colloids by neutralizing the electric charge of the dispersed phase particles, which results in aggregation of the colloidal particles.
- Aggregation is a formation of groups of particles (aggregates) bonded to each other by van der Waals or other intermolecular forces.
- Aggregation usually refers to solid particles. If a coagulation of a liquid or gaseous dispersed phase occurs the term coalescence instead of aggregation is used.
- Coalescence is characterized by disappearance of the boundary between the particles resulting in the reduction of the interfacial area.





Methods used for the destabilization of the colloidal particles by neutralization

Addition of an electrolyte to the colloid:

The colloidal particles are neutralized by the oppositely charged electrolyte ions. The destabilization of

a lyophobic colloid occurs at the electrolyte concentrations exceeding the value of the **critical coagulation** concentration

• Addition of another colloid, particles of which are charged oppositely to the particles of the first colloid:

The oppositely charged particles of the colloids attract each other and neutralize the electric charge

• Introduction of electrodes connected to a DC power supply.

The electric circuit provides the charges for neutralizing the colloidal particles.

• <u>MICELLES</u>

- Micelles are lipid molecules that arrange themselves in a spherical form in aqueous solutions.
- The formation of a **micelle** is a response to the amphipathic nature of fatty acids, meaning that they contain both hydrophilic regions (polar head groups) as well as hydrophobic regions (the long hydrophobic chain).
- Or it is an aggregate of surfactant molecules dispersed in a liquid colloid.





Formation of Micelles:

- Micelles form when the polar head and the non-polar tails arrange in a special way.
- They are usually driven to arrange either with the polar heads out (*oil in water*) or with the polar head in (*water in oil*).
- Micelles only form when the concentration of surfactant is greater than the *critical micelle concentration* (CMC).
- The surfactant is any surface active material that can part the surface upon entering. The CMC is the concentration above surfactant when micelles will form spontaneously. The higher the concentration, the more micelles there are.
- Micelle formation also depend on the *Krafft temperature*. This temperature is when surfactants will form micelles.

- If the temperature is below the Krafft temperature, then there is no spontaneous formation of micelles.
- As the temperature increases, the surfactant will turn into a soluble form and be able to form micelles from a crystalline state.
- The hydrophobic effect is also a driving force that needs to be taken into account.
- This effect is characterized by the fact that like to form intermolecular aggregates in aqueous substances and in intramolecular molecules.
- Micelle formation is described by thermodynamics, driven by entropy and enthalpy.
- The CMC (critical micelle concentration) is the concentration of a surfactant in a bulk phase, above which aggregates of tenside molecules, so-called micelles, start to form. The CMC is an important characteristic for surfactants.

- A micelle is a colloid formed by a surfactant in equilibrium with the molecules or with the ions that contribute at micelle formation.
- Micelles can be thought of as a sheet folded back onto itself. Which way it folds depends on the surrounding medium. In an aqueous medium, a micelle has the hydrophobic chains on the inside with the polar heads on the outside. However, if the solvent is organic, then the components of the micelle are reversed—hence the name **reverse micelle**.
- The polar heads are interior, and the hydrophobic chains are exterior.



- The CMC is an important characteristic of a surfactant.
- Before reaching the CMC, the surface tension changes strongly with the concentration of the surfactant.
- After reaching the CMC, the surface tension remains relatively constant or changes with a lower slope.
- The value of the CMC for a given dispersant in a given medium depends on temperature, pressure, and (sometimes strongly) on the presence and concentration of other surface

active substances and electrolytes.

• Micelles only form above critical micelle temperature.



Thermodynamic Approach to Critical Micelle Concentration

The free energy change associated with the aggregation of individual surfactant molecules to form micelles (ΔG_{mic}) is related to the critical micelle concentration as:

$$\Delta G_{mic} = 2.303 RT \log x_{CMC}$$

When the CMC is very small the above equation can be approximated as

$$\Delta G_{mic} = 2.303 RT \log \frac{CMC}{c}$$
 where, c is the concentration of solvent.

 ΔG_{mic} can be broken into contributions from the component parts of the surfactant molecule, generally represented as CH₃-(CH₂)_m-W. Here W is the hydrophilic group.

 $\Delta G_{mic} = \Delta G_{mic}(CH_3) + m\Delta G_{mic}(CH_2) + \Delta G_{mic}(W)$

The study on solubility of alkanes in water indicate that $\Delta G_{mic}(CH_3)$ does not change with increase in length of the alkyl chain and can be represented by:

 $\Delta G_{mic}(CH_3) = \Delta G_{mic}(CH_2) + k \qquad \text{where, } k \text{ is a constant}$

Hence, we have

$$\Delta G_{mic}(CH_2) + k + m\Delta G_{mic}(CH_2) + \Delta G_{mic}(W) = 2.303RT \log \frac{CMC}{c}$$

Or,
$$\log CMC = \frac{\Delta G_{mic}(W) + k}{2.303RT} + \log c + \left[\frac{\Delta G_{mic}(CH_2)}{2.303RT}\right]N$$

Where, N = m+1, the total number of carbon atoms in the hydrophobic group.

The above equation can be written in the form:

 $\log CMC = A - BN$ Where, $A = \frac{\Delta G_{mic}(W) + k}{2.303RT} + \log c$ and $B = -\left[\frac{\Delta G_{mic}(CH_2)}{2.303RT}\right]N$ Constants A and B reflect the free energy changes involved in transferring the hydrophilic group and a methylene unit of the hydrophobic respectively from an aqueous environment to the micelle.

Significance of the equation:

- The equation is a relationship between CMC and the number of carbon atoms in hydrophobic group.
- Micellisation is favoured when $\Delta G_{mic}(CH_2)$ involved in the transfer of a methylene unit of the hydrophobic group from the aqueous environment to the micelle is negative. Consequently the CMC decreases with increase in the length of the hydrophobic group.
- Free energy change involved in the transfer of the hydrophilic group from the aqueous environment to the exterior of the micelle is positive and therefore opposes micellisation.

Structure of Micelles

- The structure of micelles is determined by an equilibrium between the repulsive forces among hydrophilic groups and the short-range attractive forces among hydrophobic groups.
- These forces are due to the chemical structure of the surfactant molecule.
- Hence the shape and size of a micelle can be regarded as a property of its monomer molecule.
- Observations by different scientists revealed different shapes for micelles.



• It is also observed that, for ionic micelles, as the concentration of the surfactant particle is increased, the shape of the ionic micelles changes in the sequence:

spherical – cylindrical – hexagonal – lamellar

The shape of the micelles can be obtained by determining three parameters:

- The hydrocarbon volume (V),
- The critical chain length (l_c) and
- The optimum head group area (a_0) .

The hydrocarbon volume (V)

The critical chain length (l_c)

The optimum head group area (a_0)



- : The effective volume occupied by the tail of the molecule.
- : The length of the hydrocarbon chain when it is fully extended.
- : The area occupied by the head groups.





Critical packing parameter can be determined by : $CPP = V/l_c a_0$

Spherical Micelles:

 $R \leq l_c$

i.e.

The volume and surface area of a spherical micelle can be related to the aggregation number (N), The hydrocarbon volume (V) and the optimum head group area (a_0) .

Volume of the micelle = $\frac{4\pi R^3}{3} = NV$ Surface area of the micelle = $4\pi R^2 = Na_0$ $R = \frac{3V}{a_0}$

For spheres to form the radius of the micelle (R) must be less than the critical chain length (l_c)

or,
$$\frac{3V}{a_0} \le l_c$$
 or, $\frac{V}{l_c a_0} \le \frac{1}{3}$

Cylindrical Micelles:

The volume and surface area of a cylindrical micelle can be related to the aggregation number (N), the hydrocarbon volume (V) and the optimum head group area (a_0).

Volume of the micelle = $\pi R^2 l = NV$ and Surface area of the micelle = $2\pi R l = Na_0$

From the above equations we obtain: $R = \frac{2V}{a_0}$

For cylindrical micelles to form the radius of the micelle (R) must be less than the critical chain length (l_c)

i.e.
$$R \le l_c$$
 or, $\frac{2V}{a_0} \le l_c$ or, $\frac{1}{3} < \frac{V}{l_c a_0} \le \frac{1}{2}$



Bi-Layer Micelles:

The volume and surface area of a cylindrical micelle can be related to the aggregation number (N), the hydrocarbon volume (V) and the optimum head group area (a_0) .

Volume of the micelle = $A \times 2R = NV$ and Surface area of the micelle = $2A = Na_0$

From the above equations we obtain: $R = \frac{V}{a_0}$

For bilayers to form the radius of the micelle (R) must be less than the critical chain length (l_c)

i.e.
$$R \le l_c$$
 or, $\frac{V}{a_0} \le l_c$ or, $\frac{1}{2} < \frac{V}{l_c a_0} \le 1$



Ionic Micelles

Ionic micelles are formed by ionic surfactant molecules.

Ionic surfactant molecules have an ionic head part and a hydrocarbon tail.

For *e.g.*, the surfactant molecule sodium oleate, $C_{17}H_{33}COO^-Na^+$.

The polar head group $-COO^-Na^+$ tends to go into aqueous solution while the hydrophobic part tend to align away from solution.

As the concentration of sodium oleate is increased, the hydrocarbon part forms an aggregate and forms

micelle. The resultant micelle is that of an anion.

