

Colloids and Surface Phenomena

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* Colloidal Systems -

True solution -

In true solution, the solute particles are dispersed in the solvent as single molecules or ions.

diameter of solute particles - 1\AA to 10\AA

Ex. Sugar or salt in water.

Suspension -

In suspension, the dispersed solute particles are aggregates of millions of molecules.

diameter of solute particles - 2000\AA or more

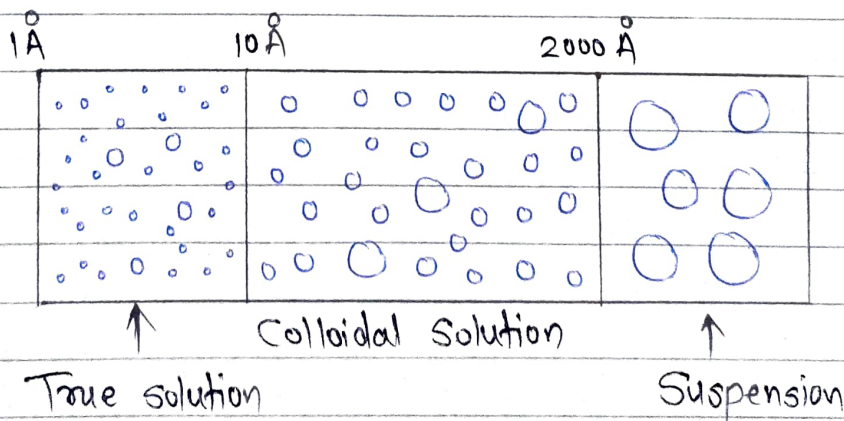
Ex. Sand in water.

Colloidal solution -

The colloidal solutions are intermediate between true solutions and suspensions.

diameter of solute particles - 10\AA to 2000\AA

Ex. fog, ice-cream, butter, soap bubbles



Colloidal system is made up of two phases

1. Dispersed phase
2. Dispersion medium

1] Dispersed phase -

Dispersed phase includes substance distributed as the colloidal particles.

2] Dispersion medium -

Dispersion medium is the continuous phase in which the colloidal particles are dispersed.

There are 8 types of colloidal systems.

Type Name.	Dispersed phase	Dispersion medium	Examples
Foam	Gas	Liquid	whipped cream
Solid foam	Gas	Solid	pumice stone
Aerosol	Liquid	Gas	mist, clouds
Emulsion	Liquid	Liquid	milk, hair cream
Solid emulsion (gel)	Liquid	Solid	butter, cheese
Smoke	Solid	Gas	dust, soot in air
Sol	Solid	Liquid	paint, ink
Solid sol	Solid	Solid	alloys

* Sols -

Dispersed phase - solid

Dispersed medium - Liquid.

The colloidal system which consist of a solid substance dispersed in a liquid is called sol.

If dispersed medium is water, colloidal solution is called Hydrosols or Aquasols.

If dispersion medium is alcohol or benzene, the sols are referred to as Alcosols and Benzosols respectively.

Two types of sols -

1. Lyophilic sols
2. Lyophobic sols.

1] Lyophilic sols -

(Solvent-loving sols)

Sols in which dispersed phase exhibits a definite affinity for the medium or the solvent

Ex. Dispersion of starch, gum and protein in water

2] Lyophobic sols -

(Solvent-hating sols)

Sols in which dispersed phase has no attraction for the medium or the solvent.

Ex. Dispersion of gold, iron hydroxide and sulphur in water.

Lyophilic Sols

1. Prepared by direct mixing with dispersion medium.

2. No charge on particles.

3. Particles are solvated.

4. Precipitated by high concentration of electrolyte.

5. Reversible.

6. Do not exhibit Tyndall effect.

Lyophobic Sols

1. Not prepared by direct mixing.

2. Positive or negative charge.

3. No solvation of particles.

4. Precipitated by low concentration of electrolyte.

5. Irreversible.

6. Exhibit Tyndall effect.

* Properties of Sols -

I] Heterogenous Character -

Colloidal systems are heterogenous in nature. They consist of two phases - the dispersed phase and dispersion medium.

2] Diffusibility -

The colloidal particles constituting dispersed phase do not readily diffuse through any fine membranes.

3] Filterability -

The colloidal particles readily pass through ordinary filter papers. This is because ordinary filter paper has pores bigger than colloidal dimensions.

4] Visibility -

It is not possible to see colloidal particles even with the help of a most powerful microscope. For ex. A gold sol appears to be as clear as a true solution of a gold chloride.

5] Colligative Properties -

The magnitude of osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point, depends upon the number of solute particles present in a given mass of the solvent.

6] Optical Properties

* Coagulation -

The phenomenon of changing colloidal state to a suspended state is known as coagulation, flocculation or precipitation of colloidal solutions.

In case of lyophobic colloids, the stability is due to the electrical charge present on colloidal particles whereas the stability of lyophilic colloids depends upon both the electrical charge & solvation.

In lyophobic sol, the charge on all the colloidal particles is of the same sign. The repulsive force due to same charge prevent the particles from approaching sufficiently close to one another and to coagulate. Removal of this electrical charge may easily bring about coagulation.

In case of lyophilic sol, solvation plays a important role. Since the colloidal particles are enclosed in a solvent cage, this cage serves as a barrier which prevents particles from coalescing to form aggregates. Thus, in case of lyophilic colloids, charge removal may not necessarily result in coagulation. Hence, lyophilic sols are not easily coagulated.

Following methods generally bring about coagulation -

① By action of electrolytes -

Traces of electrolytes are essential for the stability

of sols. But presence of large amount of electrolytes cause their coagulation. The colloidal particles take up ions carrying charge opposite to that present on them. As a result of which the charge is neutralized or reduced which results in coagulation.

The minimum concentration of an electrolyte required to cause coagulation of a sol is called its flocculation value.

② By mutual action of sols-

When two sols carrying opposite charges are mixed together in suitable proportions, mutual precipitation occurs.

③ By persistent dialysis-

Traces of electrolytes are associated with colloidal systems are essential for their stability. If the sols are subjected to prolonged dialysis, these traces of electrolytes are passed out and colloids become unstable which leads to coagulation.

④ Coagulation by mechanical means-

Violent stirring of a sol may coagulate it.

* Electrical phenomena at interfaces including electrokinetic effects

Electrical Properties.

The most important property of lyophobic colloidal dispersions is that the particles carry electric charge.

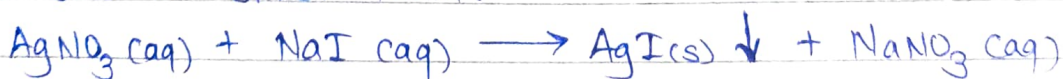
All the particles in a given colloidal system carry the same charge and the dispersion medium has an opposite and equal charge.

The charge on the colloidal particles is due to preferential adsorption of either positive or negative ions on their surface.

If the particles have a preference to adsorb positive ions, they acquire a positive charge and if they prefer to adsorb negative ions, they acquire a negative charge.

* The ion which is more nearly related chemically to the colloidal particle is preferentially adsorbed by it.

For ex. Formation of positively as well as negatively charged sols of silver iodide.



Case I -

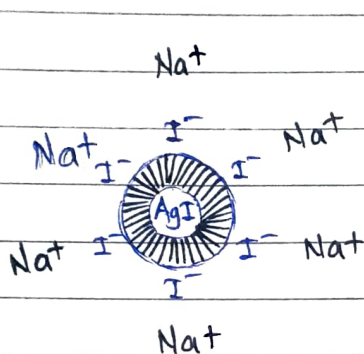
If a dilute solution of AgNO_3 is added to a slight excess of a dilute solution of AgI , a negatively charged sol of AgI is formed.

This is due to adsorption of iodide ions. The counter ion (Na^+) is directed towards liquid phase.

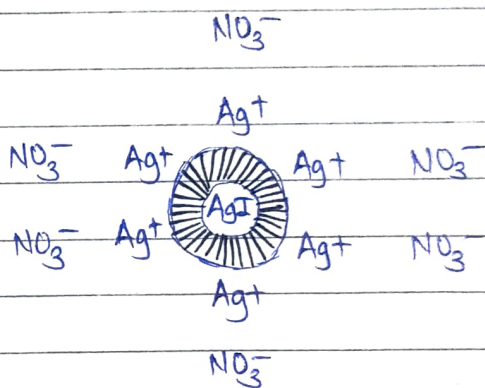
Case II -

If a dilute solution of NaI is added to a slight excess of dilute solution of AgNO_3 , a positively charged sol of AgI is formed.

This is due to adsorption of silver ions. The counter ion (NO_3^-) is directed towards liquid phase.



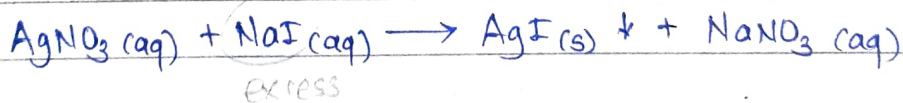
(Case I)



(Case II)

Electrical Double layer-

Consider once again the formation of silver iodide sol from double decomposition reaction.



Suppose electrolyte used in excess is sodium iodide. This results in negatively charged sol of silver iodide.

Hence, surface of AgI particles becomes negatively charged and it attracts the positive ions (Na^+) and repels the negative ions (NO_3^-).

As a result, the positive Na^+ ions tend to form a compact layer in the vicinity of I^- ion layer. This is called Stern layer.

The ions present in stern layer are called counter ions. The diffuse layer between stern layer and the electrically neutral part of the system is called as Gouy-Chapman layer.

The system as a whole is electrically neutral.

The presence of charge gives rise to potential at the surface of particle. The region in which the influence of the charge is appreciable is known as electrical double layer.

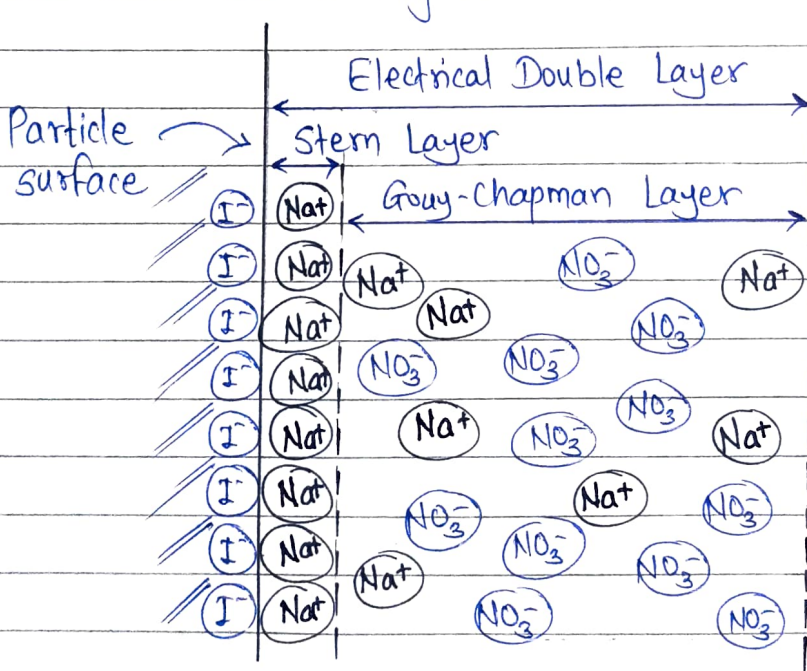


fig. Electrical Double Layer in Colloidal Systems.

Electrokinetic Effects.

The relative movement of the dispersed phase and the dispersion medium with respect to each other are accompanied by certain electrical phenomena, which are referred to as electrokinetic effects.

There are 4 types of electrokinetic effects.

i) Electro-osmosis -

The phenomenon of migration of the dispersion medium with respect to dispersed phase (which is held stationary) in presence of electric field is known as electro-osmosis.

This phenomena was observed by Reuss (1808) using a clay diaphragm.

ii) Electrophoresis -

The phenomenon of the migration of the dispersed particles with respect to dispersion medium (stationary) in presence of electric field is known as electrophoresis.

Electrophoresis was also discovered by Reuss using clay particles suspended in water.

iii) Streaming Potential -

If a liquid is forced through any capillary or porous diaphragm, a difference of potential, known as streaming potential is set up between the two electrodes.

It is the inverse of electro-osmosis.

iv) Sedimentation Potential -

If the particles of a colloidal solution are made to move through a column of stationary dispersion medium, a difference of potential is set up between the two electrodes.

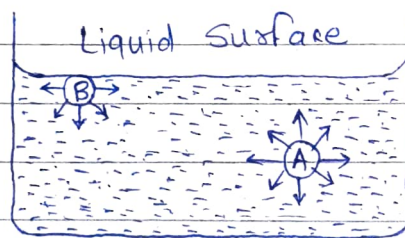
This effect is known as Dorn effect.

The potential developed in Dorn effect is known as sedimentation potential.

It is the inverse of electrophoresis.

Surface Tension.

The phenomenon of surface tension is observed due to presence of intermolecular forces of attraction.



Consider a molecule A, in the bulk of liquid which is attracted equally in all directions by surrounding molecules. Hence, there is no resultant attractive force on molecule A.

Now consider a molecule B, on the surface of liquid. The downward attractive forces are greater than the upward forces because there are more molecules of liquid below than in the air above the surface.

Consequently, the surface molecule is attracted inwards into the bulk of liquid which reduces the surface to a minimum.

It is well known that forces of attraction tend to decrease the energy of system.

Here, attractive forces are more predominant in the bulk of liquid than at the surface. Hence, molecules at surface possess greater energy and molecules in the bulk possess lower energy.

This excess energy of surface molecules tends to move from higher energy state to lower energy state.

i.e. surface molecules move to the bulk of liquid. As a result of this, the surface contracts and behaves as if it is a stretched membrane or is under tension.

The force which is responsible to contract the surface of liquid is called as surface tension.

Mathematically, surface tension is defined as force in Newtons acting at right angles to the surface of a liquid 1 meter in length.

It is represented by γ and expressed in N.m^{-1} or dynes.cm^{-1}

Surface Active Agents (Surfactants)

Substances that lowers the surface tension of water are called as surface active agents or surfactants.

Surfactants are classified into following three types:

1. Cationic Surface Active Agents -

Those substances which dissociate in water to give positively charged ions are called as cationic surface active agents.

ex. cetyl trimethyl ammonium chloride, $C_{16}H_{33}(CH_3)_3N^+Cl^-$
octadecyl ammonium chloride, $C_{18}H_{37}NH_3^+Cl^-$
cetyl pyridinium chloride, $C_{16}H_{33}-\text{C}_6\text{H}_5-N^+Cl^-$

2. Anionic Surface Active Agents -

Anionic surfactants are sodium salts of higher fatty acids

ex. sodium palmitate $C_{15}H_{31}COONa$
sodium stearate $C_{17}H_{35}COONa$
sodium oleate $C_{17}H_{33}COONa$

3. Non- ionogenic Surface Active Agents -

Those substances whose molecules cannot undergo dissociation are called non-ionogenic surfactants. When an alcohol having high molar mass reacts with several molecules of ethylene oxide, a non-ionogenic surfactant is obtained.



Micelles

The micelles or ionic micelles are the clusters or aggregates formed in solution by colloidal electrolytes

Colloidal electrolytes are substances whose molecules aggregate or join up spontaneously in a given solvent to form particles of colloidal size.

Micelles are characterised by the aggregation number i.e. the number of molecules in a micelle and the micellar mass i.e. the sum of the molecular mass of the molecules forming a micelle.

A micelle is a cluster or aggregate of surfactant molecule dispersed in liquid. The process of formation of a micelle is known as micellization.

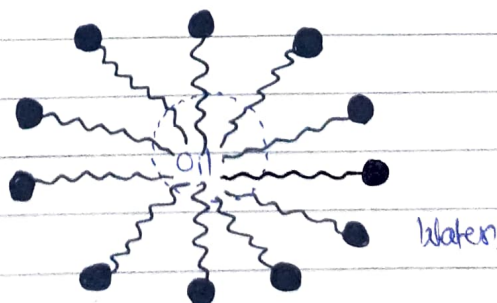
(surfactant)

philic
hydrophilic region
Ionic / Polar head

phobic
hydrophobic region
Non-polar tail

In a micelle, the hydrophobic tail is directed interior in order to minimize their contact with water.

And hydrophilic head remain on the outer surface in order to maximize their contact with water.



Ex. Oil in water micelle.

fig. Micelle formation.

Reverse Micelles.

In an aqueous solution (ex. oil in water), head of surfactant point towards outer surface and the tail (which is hydrophobic) points towards the centre which forms the core of micelle.

In a non-polar medium (ex. water in oil), the micelle is turned inside out. Such a micelle is known as reverse micelle.

In reverse micelle head of surfactant molecule is now point inwards to form core of micelle and the tail points outwards.

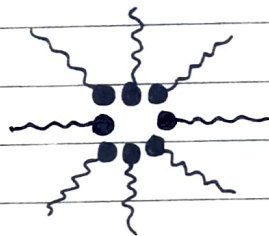


fig. Reverse Micelle formation

Mechanism of Micellization.

Ex. Soap

Soap consist of sodium or potassium salt of higher fatty acids are represented as
$$R\text{COO}^- - \text{Na}^+$$

When soap is dissolved in water, it dissociates as $R\text{COO}^-$ and Na^+ ions.

$R\text{COO}^-$ contains non polar tail which is hydrophobic and polar head which is hydrophilic in nature

The COO^- group is hydrophilic and present in water as tail. The R (hydrocarbon chain) is hydrophobic and stay away from water as head.

At low concentration, surfactant molecules ^(ions) remain on the surface of water. But at CMC (Critical micelle concentration) all surfactant molecules comes inside the bulk and their heads points outwards and tail points towards centre of sphere.

This aggregation forms the ionic micelles

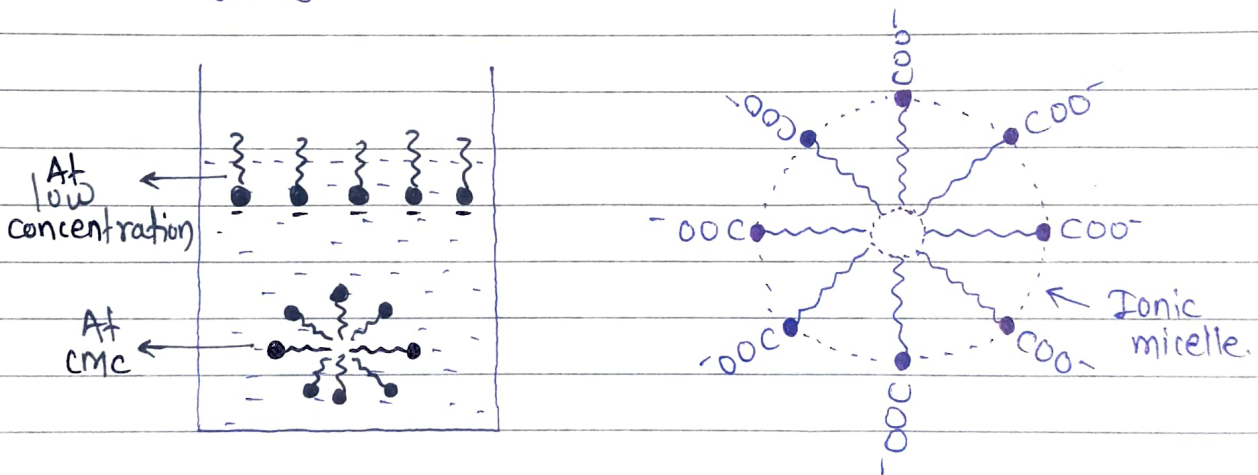


fig. Formation of Micellization.

magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range.

Thermodynamic Approach to CMC. Several equations relating the CMC to its various determining factors have been derived from theoretical considerations by Hobbs, Shinoda and Molyneux. These equations are based on the fact that for non-ionics, the CMC is related to the free energy change ΔG_{mic} associated with the aggregation of the individual surfactant molecules to form micelles by the expression

$$\Delta G_{mic} = 2.303RT \log x_{CMC} \quad \dots(17)$$

Here x_{CMC} is the mole fraction of the surfactant in the liquid phase at the CMC. In aqueous solutions where the CMC is generally $< 10^{-1}$ M, $x_{CMC} = CMC/c$ and

$$\Delta G_{mic} = 2.303RT (\log CMC - \log c) \quad \dots(18)$$

or

$$\log CMC = \frac{\Delta G_{mic}}{2.303RT} + \log c \quad \dots(19)$$

where c is the molar concentration of water (55.6 mol dm^{-3} at 25°C).

ΔG_{mic} can be broken into contributions from the component parts of the surfactant molecule, $\text{CH}_3(\text{CH}_2)_m\text{W}$, where W is the hydrophilic group, as follows :

$$\Delta G_{mic} = \Delta G_{mic}(\text{CH}_3) + m\Delta G_{mic}(\text{CH}_2) + \Delta G_{mic}(-\text{W}) \quad \dots(20)$$

Studies on the solubility of alkanes in water indicate that $\Delta G_{mic}(\text{CH}_3)$ does not change with increase in the length of the alkyl chain and can be represented by $\Delta G_{mic}(\text{CH}_3) = \Delta G_{mic}(\text{CH}_2) + k$ where k is a constant. Thus,

$$\log CMC = \frac{\Delta G_{mic}(-\text{W}) + k}{2.303RT} + \log c + \left[\frac{\Delta G_{mic}(\text{CH}_2)}{2.303RT} \right] N \quad \dots(21)$$

where $N (= m+1)$ is the total number of carbon atoms in the hydrophobic group.

Assuming that the contribution of the hydrophilic head group $\Delta G(-\text{W})$ and the fraction of counter ions bound to the micelle, α , do not change with increase in the length of the hydrophobic group for any homologous series of surfactants, the relation between CMC and the number of carbon atoms in the hydrophobic group can be written in the form

$$\log CMC = A - BN \quad \dots(\text{Eq. 16})$$

where

$$A = \frac{\Delta G_{mic}(-\text{W}) + k}{2.303RT} + \log c \quad \dots(22)$$

and

$$B = \frac{-\Delta G_{mic}(\text{CH}_2)}{2.303RT} \quad \dots(23)$$

Thus, A and B are constants which reflect the free energy changes involved in transferring the hydrophilic group and a methylene unit of the hydrophobic group, respectively, from an aqueous environment to the micelle. This accounts for both the forms of the empirical relations between the CMC and the number of carbon atoms in the hydrophobic group (Eqs. 16 and 19) and the relatively small variation of B in different homologous series of ionic surfactants.

We also see from Eqs. 16 and 23 that the free energy change $\Delta G(\text{CH}_2)$ involved in the transfer of a methylene unit of the hydrophobic group from an aqueous environment to the interior of the micelle is negative, thus, favouring micellization which accounts for the fact that the CMC decreases with increase in the length of the hydrophobic group. From Eq. 22, we can see that the free energy

change involved in the transfer of the hydrophilic group from an aqueous environment to the exterior of the micelle is positive and, therefore, opposes micellization.

Thermodynamics of Micellization

We find from the previous discussion that a clear understanding of the process of micellization is necessary for rational explanation of the effects of structural and environmental factors on the value of the CMC and for predicting the effects on it of new structural and environmental variations. The determination of thermodynamic parameters of micellization, viz., ΔG_{mic}^0 , ΔH_{mic}^0 and ΔS_{mic}^0 has played an important role in developing such an understanding.

The standard free energy of micellization ΔG_{mic}^0 may be calculated by choosing a hypothetical state at unit mole fraction x , for the standard initial state of the non-micellar surfactant species but with the individual ions or molecules behaving as at infinite dilution and for the standard final state, the micelle itself. For non-ionic surfactants, the standard free energy of micellization is given by

$$\Delta G_{mic}^0 = RT \ln x_{CMC} \quad \dots(24)$$

When CMC is 10^{-2} M or less, this can be approximated as

$$\Delta G_{mic}^0 = 2.303 RT \log (CMC/c) \quad \dots(25)$$

where the CMC is expressed in molar units and c is the number of moles of water per litre of water at temperature T . For ionic surfactants of 1:1 electrolyte type AB, where A is the surfactant ion and B the counter ion,

$$\Delta G_{mic}^0 = 2.303 RT [\log CMC/c + \log \gamma_A + K_g(\log c_B/c + \log \gamma_B)] \quad \dots(26)$$

where the activity coefficients γ_A and γ_B can be evaluated by the Debye-Hückel limiting law (DHLL). Often, the activity coefficients are neglected and the expression is used in the form

$$\Delta G_{mic}^0 = 2.303 RT [\log(CMC/c) + K_g(\log c_B/c)] \quad \dots(27)$$

where c_B is the total molar concentration of the counter ion.

K_g can be evaluated by determining the value of CMC in aqueous solutions containing different amounts of 1:1 electrolyte, MB. From Eq. 27,

$$\log (CMC/c) = -K_g \log (c_B/c) + \Delta G_{mic}^0/2.303RT \quad \dots(28)$$

If we assume that ΔG_{mic}^0 does not change significantly with change in the concentration c_B of the counter ion, then K_g can be evaluated from the negative slope of the log-log plot of (CMC/c) versus (c_B/c) .

Since
$$\Delta G_{mic}^0 = \Delta H_{mic}^0 - T\Delta S_{mic}^0 \quad \dots(29)$$

$$\therefore d(\Delta G_{mic}^0)/dT = -\Delta S_{mic}^0 \quad \dots(30)$$

if ΔH_{mic}^0 is constant over the temperature range investigated.

Alternatively,

$$T^2 d(\Delta G_{mic}^0/T)/dT = -\Delta H_{mic}^0 \quad \dots(31)$$

if ΔS_{mic}^0 is constant over the temperature range investigated.

Values of ΔH_{mic} can also be determined calorimetrically. The data available (mainly for aqueous systems) indicate that the negative values of ΔG_{mic}^0 are due mainly to the large positive values of ΔS_{mic}^0 . ΔS_{mic}^0 , ΔH_{mic}^0 is often positive and, even when negative, is much smaller than the value of $T\Delta S_{mic}^0$. Therefore, the micellization process is governed primarily by the entropy gain associated with it and

the driving force for the process is the tendency of the lyophobic group of the surfactant to transfer from the solvent environment to the interior of the micelle.

The large entropy increase on micellization in aqueous medium has been explained in two ways :
 1. Change in the structure of the water molecules surrounding the hydrocarbon chains in aqueous medium resulting in an increase in the entropy of the system when the hydrocarbon chains are removed from the aqueous medium to the interior of the micelle—'hydrophobic bonding'.
 2. Increased freedom of the hydrophobic chain in the non-polar interior of the micelle compared to the aqueous environment. Any structural or environmental factors that may affect solvent-lyophobic group interactions or interactions between the lyophobic groups in the interior of the micelle will, therefore, affect ΔG_{mic}° and consequently the value of the CMC.

SOLUBILIZATION

A very important property of surfactants that is directly related to micelle formation is **solubilization**. Solubilization plays a very important role in industrial and biological processes. McBain and Hutchinson defined **solubilization** as 'a particular mode of bringing into solution substances that are otherwise insoluble in a given medium, involving the previous presence of a colloidal solution whose particles take up and incorporate within or upon themselves the otherwise insoluble material.' This definition is too narrow. A broad definition of solubilization is as follows : "**Solubilization** is the preparation of a thermodynamically stable isotropic solution of a substance normally insoluble or very slightly soluble in a given solvent by the introduction of an additional amphiphilic component or components."

In other words, solubilization may be defined as spontaneous dissolving of a substance (solid, liquid or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution. Fig. 14 shown a plot of amount of material solubilized as a function of the concentration of the surfactant in the bulk phase.

Several applications, for example, the dissolution of drugs in aqueous solutions and their transport through the body, the preparation of agricultural chemical solutions and the recovery of oil, etc., depend upon solubilization by suitable surfactants. Also, studies of the physical chemistry of bile acids and bile salts, on the one hand and their physiological function as solubilizers, on the other hand, make it clear that the behaviour of bile salts *in vitro* and their function *in vivo* are closely related.

Solubilization in aqueous media is of major practical importance in areas such as detergency where solubilization is believed to be one of the major mechanisms involved in (1) the removal of oily soil; (2) in micellar catalysis of organic reactions; (3) in emulsion polymerization where it appears to be an important factor in the initiation step; (4) in the separation of materials for manufacturing or analytical purposes; (5) in the formulation of products containing water-insoluble ingredients where it can replace the use of organic solvents or co-solvents and (6) in enhanced oil recovery where solubilization produces ultra low interfacial tension required for mobilization of the oil. Solubilization in non-aqueous media is of major importance in dry cleaning. The solubilization of materials in biological systems sheds light on the mechanisms of interaction of drugs and other pharmaceutical materials with lipid bilayers and membranes.

Solubilization is distinguished from emulsification (the dispersion of one liquid phase in another) by the fact that in solubilization, the solubilized material (the solubilize) is in the same phase as the solubilizing solution and the system is consequently thermodynamically stable.

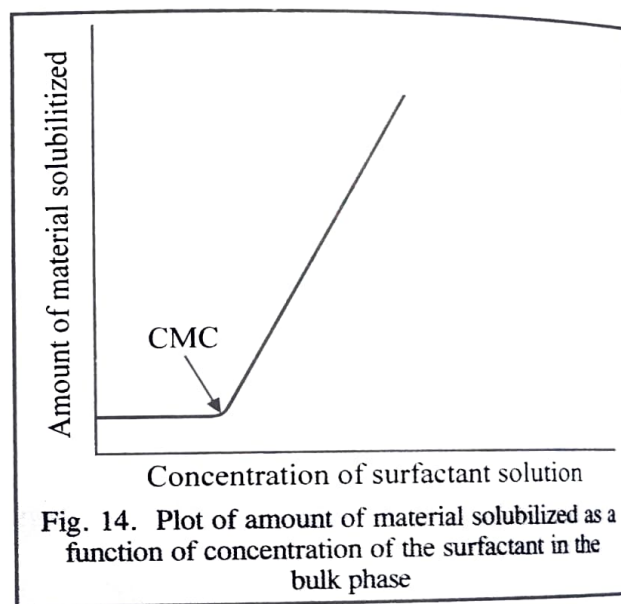
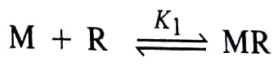


Fig. 14. Plot of amount of material solubilized as a function of concentration of the surfactant in the bulk phase

Location of Solubilizates in Micelles

The position of solubilizates in micelles as well as in living membranes, provides very important information concerning the physico-chemical properties and physiological functions of both the solubilizate and the micelle or the membrane. This property can be investigated using probe molecules, the molecular spectrum of which indicates the surrounding conditions. The absorption spectrum of a molecule depends on the dielectric constant (relative permittivity) of the medium surrounding the molecule. The dielectric constant of a micelle ranges from 2 for the liquid hydrocarbons in the inner core to 80 for the water of the outer micellar surface. The following generally accepted rules for solubilizate position are derived from several works : (1) Non-polar aliphatic hydrocarbons locate in an inner hydrophobic micellar core. (2) Semipolar and polar compounds such as alcohols, acids and amines locate at the so-called palisade layer of the micelle with the polar group at the micellar surface and the non-polar hydrocarbon groups in the micellar core. (3) Aromatic hydrocarbons such as benzene, toluene, and naphthalene sit in the micellar core and at the micellar surface.

Research work done in the 1980s on micelle formation and solubilization has treated micelles as a separate phase. With regard to solubilization, in particular, an increased pressure within the micelle, in accordance with Laplace's law, is generally invoked to explain a diminished transfer of free energy per methylene group from the aqueous medium into the micellar interior compared with the free energy transfer from an aqueous medium into the bulk liquid hydrocarbon. The decreased free energy transfer per methylene group associated with micelle formation has also been attributed to partial crystallization of the alkyl chain in the interior of the micelle, caused by the same Laplace-induced pressure increase. An interfacial tension exists at the boundary between two bulk phases. Therefore, a pressure increase can occur only when micelles are in a separate phase. If interfacial tension exists within the micelle, a difference would be observed in the association constant (K_1) between solubilizate (R) and a vacant micelle (M), depending on whether the solubilization site lies inside or outside the plane of interfacial tension :



This difference might be seen by using solubilization molecules with hydrophobic alkyl chains of varying lengths as probes, since the alkyl chain is believed to be located partly inside and partly outside the micellar plane of tension. Fig. 15 shows the change in the solubilization constant observed in 4-n-alkylbenzoic acid and dodecyl-sulphonic acid micelles when alkyl chains of varying lengths are used. The alkyl chains of the solubilizates range in length from C_0 to C_8 where the C_8 chain is almost as long as the surfactant molecule. Therefore, if a plane of tension is located inside the micelle, the alkyl chains

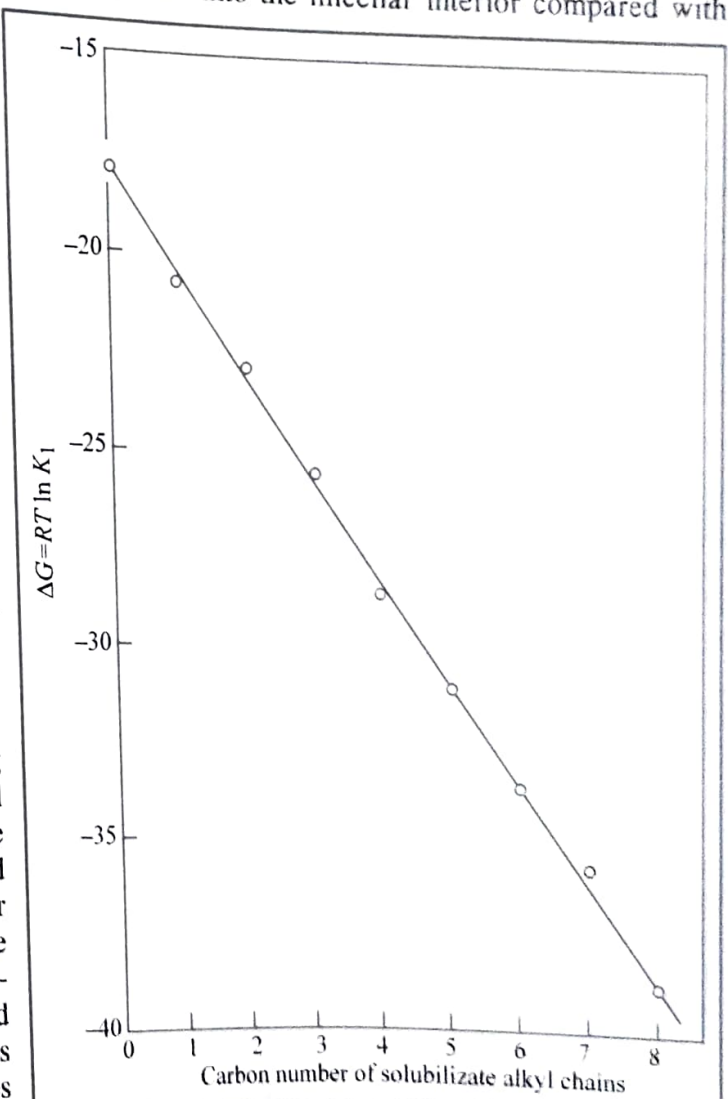


Fig. 15. Standard free energy change for the association constant between solubilizate and micelles plotted against carbon number of the solubilizate alkyl chain. The solubilizate is 4-n-alkylbenzoic acid and the micelle is made of dodecylsulphonic acid.

Critical Micelle Concentration (CMC)

Surfactants are amphiphilic molecules that have hydrophilic and hydrophobic parts.

When surfactants are added to water, they orient themselves at the air-water interface so that the hydrophilic part is in water and hydrophobic part is in air.

At some point, the surface becomes saturated with surfactant molecules and formation of micelles starts. This point is defined as CMC.

Defination -

In colloidal and surface chemistry, the CMC is defined as the lowest conc. of surfactants above which micelles form and all additional surfactants added to the system will form micelles.

OR

CMC is the point at which surfactant molecule aggregate together in a liquid to form a group / cluster known as micelle.

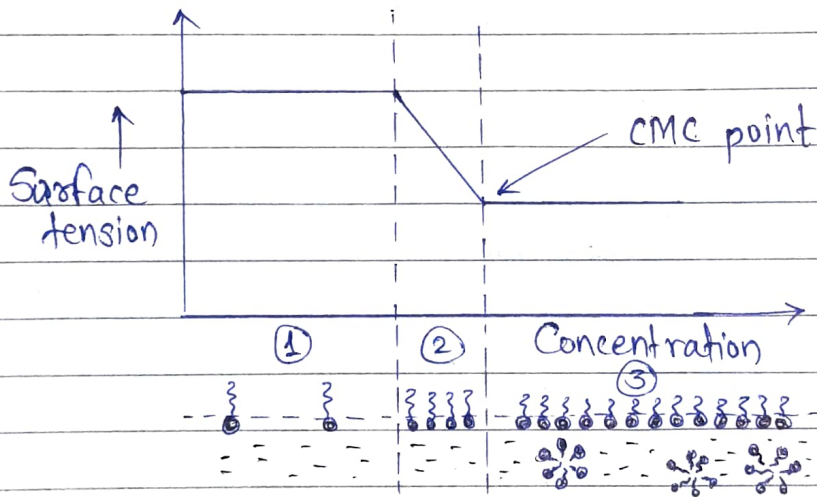
- CMC is an important characteristic of a surfactant.
- Before CMC, surface tension changes strongly with the conc. of the surfactant.
- After CMC, the surface tension remains relatively constant or changes with a lower slope.
- Micelles only form above critical micelle temperature known as Kraft temperature.

Determination of CMC.

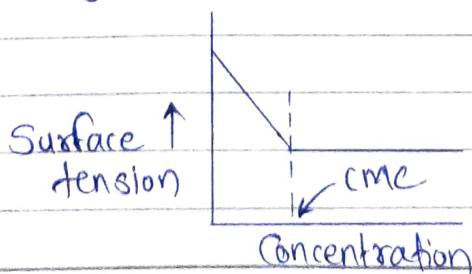
Micelles are formed at a critical micelle concentration which is detected as an inflection point in physical property which is plotted as a function of conc.

1. Surface tension
2. Conductivity
3. Osmotic pressure

1. Surface Tension.



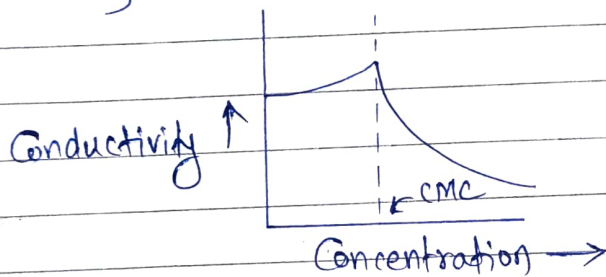
- ① At very low concentrations of surfactants only slight change in surface tension is detected.
- ② Additional surfactant decreases surface tension
- ③ Surface becomes fully loaded, there is no further change in surface tension.



2. Conductometric method.

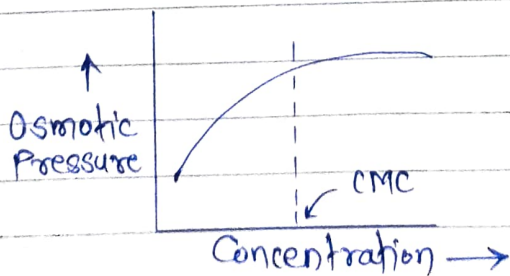
Below the CMC, the addition of surfactant to an aqueous solution causes an increase in the number of charge carriers and consequently an increase in the conductivity.

Above the CMC, further addition of surfactant increases the micelles concentration while the monomer concentration remain approximately constant and conductivity decreases.



3. Osmotic Pressure

Osmotic pressure is a colligative property so it is depend on the number of particle. So as increase in a concentration the osmotic pressure increases.



Factors affecting CMC

1. Structure of Hydrophobic Group -

Hydrophobic group contains hydrocarbon chain.

The larger the size of micelle, lower is the CMC.

The CMC decreases as the number of carbon atoms or hydrocarbon chain increases.

Addition of one methylene group - generally halves the value of CMC.

CMC decreases if carbon chain is branched.

CMC decreases if carbon chain is saturated.

CMC increases if carbon chain is unsaturated.

2. Structure of Hydrophilic Group -

More hydrophilic group in surfactant - High CMC value.

Ionic surfactant - Higher CMC.

Non-ionic surfactant - lower CMC value.

Zwitter ionic surfactant - lower than ionic surfactant.

3. Addition of Electrolyte -

Addition of electrolyte - lowers the CMC.

Generally the value of CMC decreases due to decrease in a thickness of the ionic atmosphere surrounding the ionic head group because of the presence of extra additional electrolyte.

4. Effect of Temperature.

Temperature increases - CMC decreases.

5. Addition of Organic Materials.

A complex change is observed on CMC on addition of a organic molecule.

Class I materials :

includes polar organic molecules like alcohol or amides.
These organic molecules reduces CMC value.

Class II materials :

include urea, formamide.
These organic molecules increases the CMC value.

6. Role of Degree of Binding of Counter ion to the micelle.

Increase in the degree of binding of counter ion decreases the CMC of the surfactant.