

5. Copper crystallizes in a f.c.c. lattice with the edge length,  $a=360$  pm. If the density of Cu is  $8.94 \times 10^3 \text{ kg m}^{-3}$ , calculate the Avogadro's number. (Molar mass of copper =  $63.54 \text{ g mol}^{-1}$ ). [Ans.  $6.095 \times 10^{23} \text{ mol}^{-1}$ ]
6. Calculate the lattice energy of cesium iodide which crystallizes in the cesium chloride structure and has an interionic distance of 395 pm. The Madelung constant and the Born exponent for CsI are 1.76 and 12, respectively. [Ans.  $-564.8 \text{ kJ mol}^{-1}$ ]
7. The only metal that crystallizes in a primitive cubic lattice is polonium which has a unit cell side of 334.5 pm. What are the perpendicular distances between planes with Miller indices (110), (111), (210) and (211)? [Ans. 236.5, 193.1, 149.5 and 136.6 pm]
8. Calculate the interplanar spacing ( $d_{hkl}$ ) for a cubic system between the following sets of planes : (a) 110 (b) 111 (c) 222. Assume that  $a$  is the edge length of the unit cell. [Ans. (a)  $d_{110}=a/\sqrt{2}$  (b)  $d_{111}=a/\sqrt{3}$  (c)  $d_{222}=a/2\sqrt{3}$ ]
9. Calculate the angles at which first, second, and third order reflections are obtained from planes 500 pm apart, using X-rays of wave length 100 pm. [Ans.  $5.74^\circ$ ,  $11.54^\circ$ ,  $17.46^\circ$ ]
10. X-rays of wave length 154 pm are diffracted by the 200 plane of AgCl crystal. At what angle would the maximum reflection occur? Given :  $a = 555$  pm. [Ans.  $\theta = 16.1^\circ$ ]
11. A powder pattern of MgO, known to crystallize in the cubic system, shows diffraction lines at  $\sin \theta$  values of 0.1461, 0.1690, 0.2801, 0.2801, 0.2935 and 0.3697. Determine the lattice type of MgO. [Ans. f.c.c.]
12. NaCl has a face-centred cubic lattice? What is the coordination number of (a) the sodium, and (b) the ion? (c) What are the individual lattice structures of sodium and ions in NaCl? (d) What is the number of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in the unit cell of NaCl? [Ans. (a) 6 (b) 6 (c) f.c.c., (d)  $\text{Na}^+=4$ ,  $\text{Cl}^-=4$ ]
13. A compound alloy of gold and copper crystallizes in a cubic lattice in which gold atoms occupy the lattice points at the corners of a cube and the copper atoms occupy the centres of each of the cube faces. What is the formula of the compound? [Ans.  $\text{AuCu}_3$ ]
14. Ag crystallizes in a cubic lattice. The density is  $10.7 \times 10^3 \text{ kg m}^{-3}$ . If the edge length of the unit cell is 406 pm, determine the type of the lattice. [Ans. f.c.c.]
15. Calculate the interplanar spacing ( $d_{hkl}$ ) for a cubic system between the following sets of planes : (a) 110 (b) 111 (c) 222. Assume that  $a$  is the edge length of the unit cell. [Ans. (a)  $d_{110} = a/\sqrt{2}$  (b)  $d_{111} = a/\sqrt{3}$  (c)  $d_{222} = a/2\sqrt{3}$ ]
16. The density of NaCl at  $25^\circ\text{C}$  is  $2.163 \times 10^3 \text{ kg m}^{-3}$ . When X-rays from a palladium target having a wave length of 58.1 pm are used, the 200 reflection of NaCl occurs at an angle of  $5.91^\circ$ . Calculate the number of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in the unit cell. [Ans.  $n = 3.999 \approx 4$ ]

## CHAPTER 32

## THE COLLOIDAL STATE

**The Colloidal Systems.** A colloidal dispersion has traditionally been defined as a suspension of small particles in a continuous medium. Because of their ability to scatter light and their very low osmotic pressure, these particles were recognized to be much larger than simple small molecules such as water, alcohol or benzene and simple salts like NaCl. It was assumed that they were aggregates of many small molecules, held together in a kind of amorphous state quite different from the usual crystalline state of these substances. Today we recognize that many of these "aggregates" are in fact single molecules that have a very high molar mass. The size limits are difficult to specify but if the dispersed particles are between  $1 \mu\text{m}$  and  $1 \text{ nm}$ , we may say that the system is a colloidal dispersion.

There are two classical subdivisions of colloidal systems : (1) *lyophilic* or *solvent-loving* colloids (also called *gels*) and (2) *lyophobic* or *solvent-fearing* colloids (also called *sols*).

The **lyophilic colloids** are invariably polymeric molecules so that the colloidal solution consists of a dispersion of single molecules. The stability of the lyophilic colloid is a consequence of the strong, favourable solvent-solute interactions. Typical lyophilic systems would be proteins (especially gelatin) or starch in water, rubber in benzene and cellulose nitrate or cellulose acetate in acetone. The process of dissolution may be rather slow. The first additions of solvent are slowly absorbed by the solid which swells as a result (this stage is called *imbibition*). Further addition of solvent together with mechanical kneading (as in the case of rubber) slowly distributes the solvent and solute uniformly. In the case of ordinary gelatin, the dissolution process is aided considerably by raising the temperature. As the solution cools, the long and twisted protein molecules get entangled in a network with much open space between the molecules. The presence of the protein induces some structure in the water which is physically trapped in the interstices of the network. The result is a gel. The addition of gross amounts of salts to a hydrophilic gel will ultimately precipitate the protein. However, this is a consequence of competition between the protein and the salt for the solvent, water. Lithium salts are particularly effective because of the large amount of water than can be bound by the lithium-ion. The charge of the ion is not a primary determinant of its effectiveness as a precipitant.

The **lyophobic colloids** are invariably substances that are highly insoluble in the dispersion medium. The lyophobic colloids are usually aggregates of small molecules (or in cases where a molecule is not defined, such as  $\text{AgI}$ , they consist of a large number of units of the formula).

### Preparation of Lyophobic Colloidal Solutions

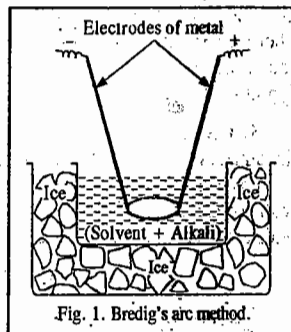
The primary consideration in the preparation of colloidal solutions is that the dispersed particles should be within the size range of  $1 \text{ m}\mu$ – $200 \text{ m}\mu$ . The lyophilic sols can be readily prepared since colloidal materials such as starch, gelatin, acacia, etc., when added to water swell up and spontaneously break into particulates of matter of colloidal range. The lyophobic sols, however, require special techniques for their preparation. The methods consist either in 1. *Breaking down the coarser aggregates into particles of colloidal size* or 2. *Grouping molecules into larger aggregates of colloidal size*. The methods belonging to these two categories are known as **dispersion** and **condensation** methods, respectively.

**A. Dispersion Methods.** 1. **Mechanical Dispersion.** The most obvious method of dispersion

consists in breaking down the coarser solid particles by mechanical grinding. This is done in the so-called 'colloid mill' which generally consists of two metal discs held at a very small distance apart from one another which are capable of revolving at a high speed (of the order of 7000 rpm) in opposite direction. The material to be ground is fed in between the two discs in the form of a wet slurry. The particles get broken to colloidal dimensions by the operating shearing force. However, it is doubtful if this method produces particles uniformly of colloidal dimensions.

Some sols can alternatively be prepared by mechanical dispersion in a high intensity ultrasonic generators operating at a frequency of 20 kHz (not audible to human ear) and above. This technique is effective only if the substance being dispersed is of low mechanical strength such as sulphur, graphite, resins and gypsum. Ultrasonic vibrations are usually obtained by piezoelectric oscillations which convert electric vibrations of high frequency into mechanical vibrations. Ultrasonic waves of vibrations of 1 MHz frequency are obtained from quartz oscillators whereas those having vibrations of 50 kHz frequency are obtained from magnetostriction oscillators whose working component is a ferromagnetic rod. Ultrasonic vibrations cause local, rapidly alternating contractions and expansions of the solid substance resulting in the formation of minute cavities which disappear immediately under the action of external pressure thereby destroying the solid and converting it into a colloidal dispersion.

**2. Electrical Dispersion.** In this method an arc is struck between two electrodes of a metal like platinum, gold, silver or copper, in water containing traces of an alkali, when the metal passes into colloidal solution of a reasonable, though not high concentration (Fig. 1). It is believed that in this method, introduced by G. Bredig in 1898, the metal first changes into vapours (molecular state) on account of the heat of the spark and the vapours then condense in water to give aggregates of colloidal range. The function of the alkali will be explained shortly in this chapter.



T. Svedberg devised a method to obtain organosols of metals and non-metals. In Svedberg's method, the electrodes are usually of iron or aluminium and alternating current (instead of the direct current used in Bredig method) is employed. The material to be dispersed is taken in the form of granules and pasted on the electrodes (immersed in the organic medium) through which the electric arc is passed. Electroputtering occurs as the electric spark gets through the granules of the material pasted on the electrode. Electroputtering technique is used for obtaining organosols of several metals and non-metals.

Organosols of metals are used (i) in the hydrogenation and reduction of organic compounds, (ii) as catalysts for combustion of liquid fuels in rockets, (iii) as fillers of plastics, glues, anticorrosive lacquers and paints and (iv) in medicine.

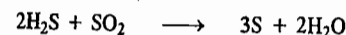
**3. Peptization.** Certain freshly formed precipitates, such as silver chloride, ferric hydroxide, aluminium hydroxide, can be converted into colloidal solutions by the addition of a small amount of a suitable electrolyte. An electrolyte having an ion in common with the material to be dispersed is required for sol formation. The peptization action is due to the preferential adsorption of one of the ions of the electrolyte by the particles of the material. As would be illustrated a little later in this chapter, as a result of the preferential adsorption of the ion which is more closely related chemically to the precipitate, the particles acquire a positive or a negative charge depending upon the charge on the ion adsorbed. Because of the presence of the same type of charge, the particles of the precipitate are pushed apart. The precipitate thus gets dispersed resulting in the formation of a stable sol. Thus, ferric hydroxide sol is obtained when a small quantity of ferric chloride solution is added. The peptization action is due to the preferential adsorption of  $\text{Fe}^{3+}$  ions. Similarly, an aluminium hydroxide sol is obtained when dilute hydrochloric acid is added to freshly precipitated aluminium hydroxide. The ion preferentially adsorbed, viz., the  $\text{Al}^{3+}$  ion, is generated by the action of hydrochloric acid on  $\text{Al}(\text{OH})_3$ .

**B. Condensation Methods.** Colloidal systems can be obtained by various chemical reactions such as double decomposition, oxidation, reduction, hydrolysis, etc. It should be noted that colloidal systems are not always formed in reactions capable of producing sols; they are formed under specific conditions, as for example, at definite concentrations of the initial substances, at a definite temperature and a definite order of their mixing, etc.

**1. Double Decomposition.** A sol of arsenious sulphide is prepared by passing  $\text{H}_2\text{S}$  gas through a dilute solution of arsenious oxide and removing the excess  $\text{H}_2\text{S}$  by boiling.

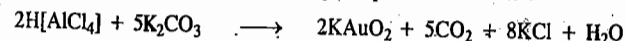


**2. Oxidation.** A colloidal sulphur sol is obtained by the oxidation of an aqueous solution of hydrogen sulphide with air or sulphur dioxide.

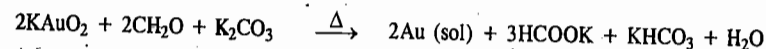


During the oxidation of  $\text{H}_2\text{S}$  to S, complex oxidation reactions occur simultaneously resulting in the formation of polythionic acids. These acids readily get associated with the colloidal particles of sulphur to form bigger colloidal particles called *miscelles* which are thermodynamically more stable than the constituent species. In other words, polythionic acids act as *stabilizers* for the sulphur sol. There is experimental evidence that pentathionic acid,  $\text{H}_2\text{S}_5\text{O}_6$ , formed during the oxidation reaction acts as the stabilizing electrolyte, converting the sulphur colloidal particle into a *miscelle* having the formula:  $(m[\text{S}]n\text{S}_5\text{O}_6^{2-} \cdot 2(n-x)\text{H}^+)2x\text{H}^+$ .

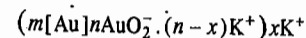
**3. Reduction.** Sols of metals such as silver, copper, gold and platinum are obtained by reducing the aqueous solutions of their salts by non-electrolytes such as formaldehyde, tannin, phenyl hydrazine, carbon monoxide and phosphorus. Zsigmondy prepared the gold hydrosol by reducing potassium aurate with formaldehyde. In this reaction, chloroauric acid,  $\text{H}[\text{AuCl}_4] \cdot 4\text{H}_2\text{O}$ , first formed, is made to react with potassium carbonate in an aqueous solution to yield potassium aurate:



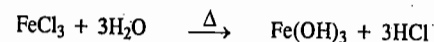
The resulting solution is heated and a dilute solution of formaldehyde is added dropwise when reduction occurs according to the reaction:



Potassium aurate,  $\text{KAuO}_2$ , acts as the stabilizer of the red gold sol obtained. The *miscelle* of the gold sol is represented by the formula:

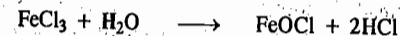


**4. Hydrolysis.** Colloidal sols of heavy metals are obtained by the hydrolysis of the solutions of their salts. Thus, when a small amount of ferric chloride is added to boiling water, a red-brown sol of ferric hydroxide is obtained:



Boiling promotes the reaction because HCl formed is removed along with water vapours from the system.

In this reaction, iron oxychloride,  $\text{FeOCl}$ , formed as a result of incomplete hydrolysis of  $\text{FeCl}_3$ , is believed to act as the stabilizer:



The stabilizer can also be  $\text{FeCl}_3$  or HCl. The stabilising action of  $\text{FeCl}_3$  is evidently due to the  $\text{Fe}^{3+}$  ions which it yields in solution. Evidence in favour of HCl comes from the fact that the surface

of ferric hydroxide sol has a number of hydroxyl groups which are capable of adsorbing the hydrogen ions provided by HCl. Thus, the structure of the  $\text{Fe}(\text{OH})_3$  sol can be expressed by any of the following formulae depending upon which substance acts as a stabilizer :

1.  $(m[\text{Fe}(\text{OH})_3] \cdot n\text{FeO}^+ \cdot (n-x)\text{Cl}^-) \cdot x\text{Cl}^-$
2.  $(m[\text{Fe}(\text{OH})_3] \cdot n\text{Fe}^{3+} \cdot 3(n-x)\text{Cl}^-) \cdot 3x\text{Cl}^-$
3.  $(m[\text{Fe}(\text{OH})_3] \cdot n\text{H}^+ \cdot (n-x)\text{Cl}^-) \cdot x\text{Cl}^-$

5. **Exchange of Solvents.** Sols can also be obtained by exchange of solvents. For instance, when a concentrated solution of sulphur in alcohol is poured in a large amount of boiling water, the alcohol evaporates leaving behind sulphur particles which form nuclei that rapidly grow into a colloidal sol.

**Purification of Colloidal Solutions.** The presence of impurities, particularly the electrolytes, renders the sols unstable. The cause of this instability will be discussed shortly in this chapter. These impurities must be eliminated by suitable means. Two simple methods are generally employed.

1. **Dialysis.** It has already been stated that while particles in true solution can easily diffuse through parchment and other fine membranes, the colloidal particles, being much larger, cannot do so readily. If a mixture, containing colloidal particles as well as particles in true solution, is placed in a parchment bag which is then held in a wider vessel containing pure water, the substances in true solution pass out while the colloids remain in the bag. The distilled water in the wider vessel is renewed frequently.

The process of separating substances in colloidal state from those present in true solution with the help of fine membranes, is known as dialysis and the membrane used for the purpose is known as dialyser.

Ordinarily, the process of dialysis is quite slow but it can be quickened by applying an electric field if the substance in true solution is an electrolyte. The process is then called **electrodialysis**. The mixture is placed between two dialysing membranes while pure water is contained in a compartment on each side. There is one electrode in each compartment by means of which the required voltage is applied. The ions of the electrolyte migrate out to the oppositely charged electrodes while the colloidal particles are held back.

2. **Ultra-filtration.** The separation of solutes from colloidal systems can also be carried out by the process known as **ultra-filtration**. Ordinarily, filter papers have pores larger than  $1 \mu$  (i.e., 1000 m $\mu$ ) so that the colloidal particles which are less than 200 m $\mu$  can readily pass through along with the ions or molecules in solution. But the pores can be made smaller by soaking the filter papers in a solution of gelatin or collodion and subsequently hardening them by soaking in formaldehyde. The pores thus become very small and the colloidal particles may be retained on the treated filter paper. The treated filters are known as **ultra-filters**. This process of separating colloids from solutes is known as **ultra-filtration**. A series of graded ultra-filters can be prepared by soaking filter papers in solutions of collodion of different concentrations. The pores even in the finest ultra-filters will be large enough to permit the passage of ions or molecules in true solution but these will be small enough to withhold the colloidal particles. By using a series of graded ultra-filters, it may be possible to separate colloidal particles of different sizes from one another. The process is very slow and sometimes a small pressure is needed to drive the solute particles through the filters.

### General Properties of Colloidal Systems

1. **Heterogeneous Character.** As already stated, colloidal systems, unlike true solutions, are heterogeneous in character. They consist of two phases : the dispersed phase and dispersion medium.

2. **Diffusibility.** The colloidal particles constituting the dispersed phase do not readily diffuse through parchment or other fine membranes. In fact, it was this property which led Thomas Graham to lay the foundation of colloid science, as already mentioned.

3. **Filterability.** The colloidal particles readily pass through ordinary filter papers along with any dissolved material. This is because even the finest filter paper has pores bigger than the colloidal dimensions.

4. **Visibility.** It is not possible to see colloidal particles even with the help of a most powerful microscope. A gold sol, for instance, appears to be as clear as a true solution of gold chloride in water. The reason of the invisibility of colloidal particles has already been discussed.

Attempts have been made in recent times to use ultraviolet rays or cathode rays for seeing the colloidal particles. But, these rays make no impression on the retina of the eye. However, the images formed by them can be photographed. The **electron microscope**, for instance, makes use of a beam of cathode rays and by combination of special types of lenses, images of colloidal particles can be obtained on photographic plates.

5. **Colligative Properties.** The magnitude of osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point, depend upon the number of solute particles present in a given mass of the solvent. Now, colloidal particles are not simple molecules. These are physical aggregations of molecules. In arsenic sulphide sol, for instance, each particle is composed of about 1000 molecules. Thus, for a given mass of arsenic sulphide, the number of particles in the sol will be only  $\frac{1}{1000}$ th of the number present in true solution. Hence, all colloidal dispersions (unlike true solutions) give very low osmotic pressure and show very small freezing point depression or boiling point elevation.

6. **Optical Properties.** It was observed by Tyndall, in 1869, that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in its path. However, when the same beam of light is passed through a colloidal dispersion, it becomes visible as a bright streak. This phenomenon is known as the **Tyndall effect** and the illuminated path (streak of light) is known as **Tyndall cone** (Fig. 2). This phenomenon is due to the scattering of light from the surface of colloidal particles. In a true solution, there are no particles of sufficiently large diameter to scatter light and hence the beam is invisible.

The visibility of dust particles in a semi-darkened room when a sun beam enters or when light is thrown from a light projector, are familiar examples of Tyndall effect. The dust particles are large enough to scatter light and thus render the path of light visible.

The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and the dispersion medium. In lyophobic sols, this difference is appreciable and, therefore, the Tyndall effect is quite well-defined. In lyophilic sols, the particles are largely solvated. This lowers the difference in the refractive indices of the two phases and hence the Tyndall effect is much weaker. Thus, in the sols of freshly prepared silicic acid, blood serum, albumins, etc., there is little or no Tyndall effect.

The Tyndall effect has been used by Zsigmondy and Siedentopf in devising the **ultra-microscope**. A strong beam of light from an arc lamp or any other source is condensed by a system of lenses and passed through the colloidal solution. The scattered beam (Tyndall beam) is viewed through a microscope placed at right angles to the beam (Fig. 2). In this way, the colloidal

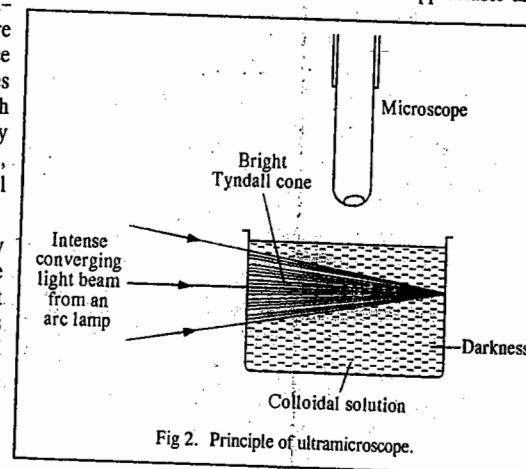


Fig 2. Principle of ultramicroscope.

particles which are too small to be seen under an ordinary microscope, can be detected as spots of light moving irregularly. It may be emphasised that we do not see the actual particles; they are too small to be visible. We see only the light scattered by them. Our eye pictures various spots of light as round or spherical particles.

**7. The Brownian Movement.** Robert Brown, an English botanist, in 1827, observed that pollen grains in aqueous suspensions were in constant motion. Later on when ultra-microscope was invented, it was found that particles of lyophobic sols were also in a state of ceaseless erratic and random motion similar to pollen grains. This kinetic activity of particles suspended in a liquid is called **Brownian movement**. The Brownian movement is due to the bombardment of colloidal particles by molecules of dispersion medium which are in constant motion like molecules in a gas. As a result, the colloidal particles acquire almost the same amount of kinetic energy as possessed by the molecules of the dispersion medium. But, since the colloidal particles are considerably heavier than molecules of the dispersion medium, their movement is considerably slower than that of the molecules of the medium.

The Brownian movement is not observed in ordinary suspensions because the mass of each particle in this case is so large that the bombardment by molecules of the dispersion medium produces little effect on them. Brownian movement offers a visible proof of the random kinetic motion of molecules in a liquid.

### Properties of Hydrophobic Colloidal Systems

#### I. Electrical Properties

**Charge on Colloidal Particles.** The most important property of hydrophobic colloidal dispersions is that the particles carry electric charge. All the particles in a given hydrophobic colloidal system carry the same charge and the dispersion medium has an opposite and equal charge, the system as a whole being electrically neutral. The presence of similar charges on colloidal particles is largely responsible in giving stability to colloidal systems because the mutual forces of repulsion between similarly charged particles prevent them from coalescing and coagulating or aggregating when they come closer to one another. Metallic hydroxides, some metals (such as bismuth, lead, iron), methyl violet and methylene blue, are *electropositive colloids* while metallic sulphides, prussian blue, many metals (such as silver, gold, platinum), silicic acid, tannic acid and mastic are *electronegative colloids*.

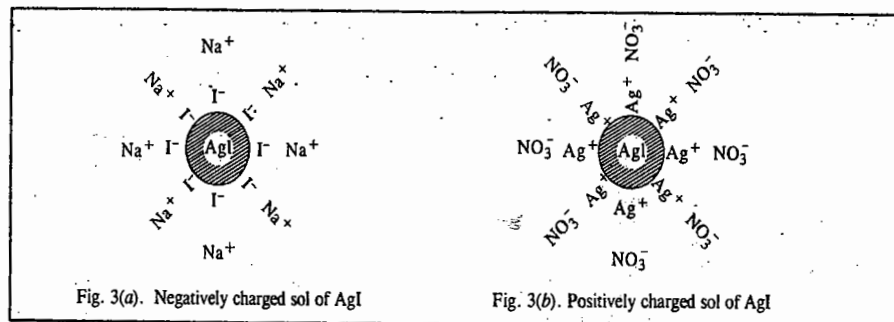
**The Origin of Charge on Colloidal Particles.** The origin of charge on colloidal particles has not been completely understood. However, it has been observed that sols are invariably associated with minute quantities of electrolytes and that if the latter are completely removed by persistent dialysis, the sols become unstable. It is believed, therefore, that 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. According to this view, positive charge on ferric hydroxide sol prepared by hydrolysis of ferric chloride is largely due to preferential adsorption of  $\text{Fe}^{3+}$  ions on the surface of particles of ferric hydroxide. The ferric ions come from ionisation of ferric chloride which is always present in traces in the sol.

Similarly, the negative charge on arsenic sulphide sol is due to preferential adsorption of sulphide ions on the surface of arsenic sulphide particles. The sulphide ions are furnished by ionisation of hydrogen sulphide which is present in traces. Likewise, the negative charge on metal sols prepared by the Bredig's arc method is due to adsorption of hydroxyl ions furnished by traces of the alkali added. It should be remembered that the ion which is more nearly related chemically to the colloidal particle is preferentially adsorbed by it. Thus, in ferric hydroxide sol, ferric and not chloride ion is preferred. Similarly, in arsenic sulphide sol, sulphide and not hydrogen ion is preferred.

An interesting case is furnished by stannic oxide sol. If a freshly formed precipitate of stannic oxide is peptised by a small amount of hydrochloric acid, the sol carries a positive charge but if peptised by a small amount of sodium hydroxide, the sol carries a negative charge. In the former case, a small amount

of stannic chloride,  $\text{SnCl}_4$ , is formed and the positively charged  $\text{Sn}^{4+}$  ion is preferred and the sol is positively charged. In the latter case, a small amount of sodium stannate,  $\text{Na}_2\text{SnO}_3$ , is formed and now the negatively charged  $\text{SnO}_3^{2-}$  ion is preferred and accordingly the sol is negatively charged. The chloride and sodium ions, known as counter ions, are directed towards the liquid phase.

Another interesting case is furnished by the formation of positively as well as negatively charged sols of silver iodide. If a dilute solution of silver nitrate is added to a slight excess of a dilute solution of sodium iodide, a negatively charged sol of silver iodide is formed. This is due to the adsorption of iodide ions. The structure of the sol particle is represented as in Fig. 3(a). But, if a dilute solution of sodium iodide is added to a slight excess of dilute solution of silver nitrate, a positively charged sol of silver iodide is formed due to the adsorption of silver ions. The structure of the sol particle is now represented as in Fig. 3(b). However, if silver nitrate and sodium iodide are mixed in equivalent amounts, there is precipitation of silver iodide and no sol is formed. It may be mentioned once again that the ions preferred by colloidal particles are those which are common to them. Thus, in the above example, in the first case, silver iodide prefers iodide ion and not sodium ion. In the second case, it prefers silver ion and not nitrate ion. The counter ion, in each case, is directed towards the liquid phase.

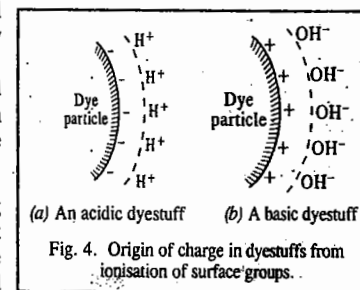
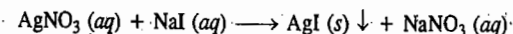


Thus, on the surface of a colloidal particle there is an electrical double layer of opposite charges. The aspect has been discussed in adequate details in the next section.

Another possible way in which colloidal particles may acquire charge is by direct ionisation of the material constituting the particles. This phenomenon is observed mostly in the case of acidic and basic dyestuffs. An acidic dyestuff, for example, ionises yielding hydrogen ions in solution and thereby leaving an equivalent amount of negative charge on the particles. The structure of the colloidal dye particles of the dye may be represented as shown in Fig. 4(a).

A basic dyestuff, on the other hand, ionises yielding hydroxyl ions in solution and thereby leaving an equivalent amount of positive charge on the particles. The structure of the colloidal dye particles in this case may be represented as shown in Fig. 4(b).

**The Electrical Double Layer.** Central to the understanding of the electrical properties of colloids is the concept of electrical double layer. Consider once again the formation of silver iodide sol from the double decomposition reaction





Let us suppose that the electrolyte used in excess is sodium iodide. This would result in preferential adsorption of  $I^-$  ions giving a negatively charged sol of silver iodide, as illustrated above (Fig. 3a).

The ions preferentially adsorbed on the surface of a particle of a colloidal system are called **potential-determining ions**.

The negatively charged surface of AgI particle 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 the potential-determining  $I^-$  ion layer. This is called the **Stern layer** (Fig. 5). The ions present in the Stern layer are called the **counter ions**.

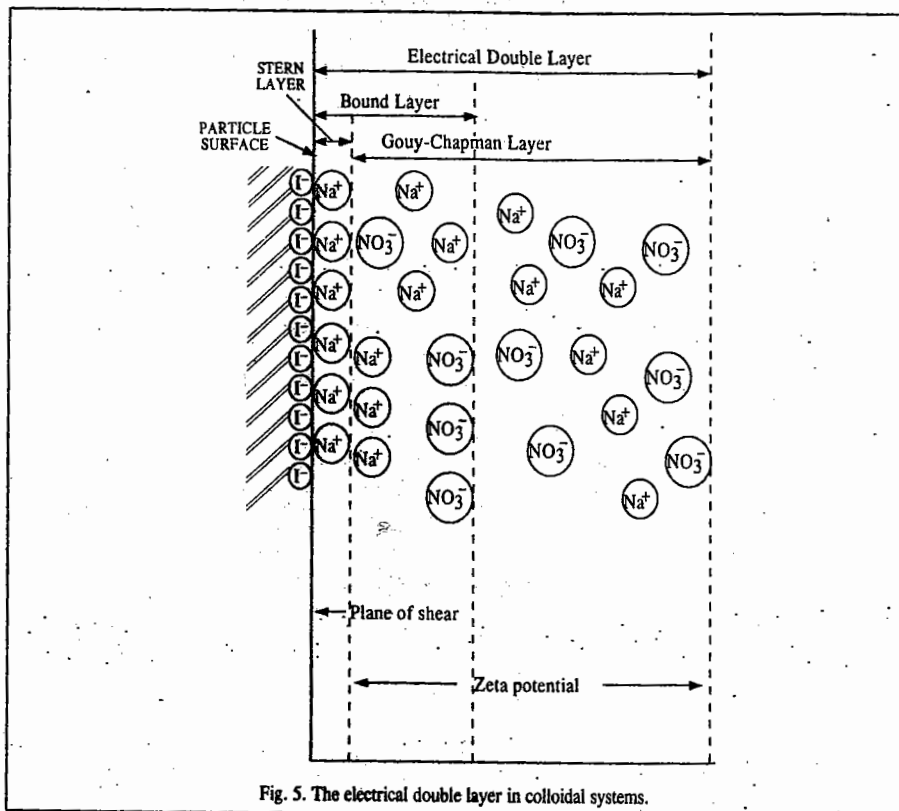


Fig. 5. The electrical double layer in colloidal systems.

The influence of the surface charge decreases with distance and so does the number of ions with the result that at a certain distance from the surface of the particle, the concentration of  $Na^+$  ions equals the concentration of  $NO_3^-$  ions and a state of electroneutrality prevails (Fig. 5). It must be borne in mind that the system as a whole is electrically neutral even though there exist regions of unequal distribution of anions and cations. The diffuse layer between the Stern layer and the electrically neutral part of the system is referred to as the **Gouy-Chapman layer**.

The presence of charge gives rise to potential at the surface of the particle. This potential drops to zero at some distance away from the surface depending upon the concentration of the counter ions in the bulk phase. The region in which the influence of the charge is appreciable is known as the

**electrical double layer.** The double layer consists of two parts : the Stern layer, the thickness of which is of the order of ionic dimensions and the Gouy-Chapman diffuse layer, the thickness of which is given by

$$r_D = \left( \frac{\epsilon_r RT}{2\rho F^2 I} \right)^{1/2} \quad \dots(1)$$

where  $\rho$ ,  $\epsilon_r$  and  $I$  are, respectively, the density, the dielectric constant and the ionic strength of the solution.  $F$  is the Faraday constant. The value of  $r_D$  is of the order of 1-100 nm. It decreases as the ionic strength of the solution increases; more rapidly for counter ions of high valency.

A very important quantity reckoned with in the present context is the so-called **zeta potential** ( $\zeta$ ) defined as the difference in potential between the surface of the tightly bound layer (called the **plane of shear**) and the electroneutral region of the solution. The zeta potential is located at the shear plane. It determines the stability of colloidal systems.

### DLVO Theory of the Stability of Lyophobic Colloids

This theory, involving the concept of zeta potential, was developed by the Russian scientists D. Derjaguin and L.D. Landau, and independently, by the Dutch scientists E. Verwey and J.T.G. Overbeek. According to this theory, there is a balance between the repulsive interactions between the charges of the electrical double layers on neighbouring particles and the attractive van der Waals interactions between the molecules in the particles. The repulsive potential energy of the double layer on particles, each of radius  $a$ , is given by

$$V_{rep} = \frac{Aa^2\zeta^2}{R} e^{-s/r_D}; \quad a \ll r_D \quad \dots(2)$$

where  $A$  is a constant,  $\zeta$  is the zeta potential,  $R$  is the separation of the centres,  $s$  is the separation of the surfaces of the two particles ( $s = R - 2a$  for spherical particles of radius  $a$ ) and  $r_D$  is the thickness of the electrical double layer. Eq. 2 holds for a **thick** double layer ( $a \ll r_D$ ). For a **thin** double layer ( $a \gg r_D$ ),

$$V_{rep} = \frac{Aa\zeta^2}{2} \ln(1 + e^{-s/r_D}); \quad a \gg r_D \quad \dots(3)$$

The potential arising from the attractive interaction is given by

$$V_{att} = -B/s \quad \dots(4)$$

where  $B$  is another constant.

Treating the electrical double layer as a simple electrical condenser, the zeta potential  $\zeta$  is given by the expression,

$$\zeta = 4\pi\eta u/\epsilon_r \quad \dots(5)$$

where  $\eta$  are  $\epsilon_r$  are the viscosity and the dielectric constant, respectively, of the dispersion medium and  $u$  is the mobility of the colloidal particles.

For water as the dispersion medium,  $\zeta$  is found to lie between 0.03 and 0.06 V. The value of  $\zeta$  decreases when an ion of opposite charge to that of the colloidal particle is adsorbed. This reduces the mutual repulsion between the similarly charged colloidal particles. As a result, the colloidal particles easily come closer to one another to coalesce and form bigger aggregates which lie outside the colloidal range. This phenomenon of changing colloidal state to a suspended state is known as **coagulation, flocculation or precipitation** of colloidal solutions.

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

charge and solvation. In order to cause precipitation of the dispersed particles, it is necessary that they coalesce into large aggregates. Since in a lyophobic sol, the charge on all the colloidal particles is of the same sign, the repulsive forces prevent the particles from approaching sufficiently close to one another and to coalesce and coagulate. The magnitude of the repulsive forces depends upon the magnitude of the surface charge and the thickness of the electrical double layer. These factors also determine the value of the zeta potential which actually governs the stability of the colloidal system. If  $\zeta$  is small, the resultant potential energy is negative so that the van der Waals attraction predominates over the electrostatic repulsion and the sol coagulates rapidly.

On the other hand, in the case of lyophilic sols, solvation plays a very important role. Since the colloidal particles are enclosed in a solvent 'cage', the cage serves as a barrier preventing the particles from coalescing to form aggregates. Thus, whereas in the case of lyophobic sols, removal of electrical charge may easily bring about coagulation, in the case of lyophilic colloids, the charge removal may not necessarily result in coagulation though it may decrease the stability of the sol.

When a lyophilic colloid is added to a lyophobic colloid, the latter is rendered less sensitive to the precipitating action of an electrolyte. This is expressed by saying that the *lyophilic colloid protects a lyophobic colloid* from precipitation by the action of electrolytes. That is why substances such as gum acacia, gelatin, tragacanth, etc., are known as protective colloids. They probably function by getting adsorbed on the solid surface in the form of loops wherein water gets trapped. These loops prevent the approach of particles to cause coagulation.

Zsigmondy gave quantitative treatment of the stabilizing action of the protective colloids. He introduced a quantity called the gold number of a protective colloid. The **gold number** is defined as the largest number of milligrams of a protective colloid which, when added to 10 ml of a special standard gold sol, just fails to prevent the colour change from red to blue upon the addition of one ml of 10 percent sodium chloride solution. It must be emphasized that the protective action of a lyophilic sol depends upon several factors such as sol dispersity, the molar mass of the lyophilic sol, the pH of the solution at which the experiment is carried out, and so on.

It is customary to use sols other than gold sols to determine the protective action of a high molar mass colloid. Thus, silver, sulphur, prussian blue, etc., sols have been used and the corresponding 'numbers' determined accordingly (Table 1)

TABLE 1  
Protective Action of High Molar Mass Lyophilic Colloids on Some Hydrophobic Sols

Protective Colloids	Numbers					
	Gold	Silver	Sulphur	Iron oxide	Rubin	Prussian blue
Gelatin	0.01	0.035	0.00012	5	2.5	0.05
Dextrin	20	100	0.125	20	.....	250
Saponin	115	35	0.015	11.5	.....	2.5
Potato starch	20	.....	.....	.....	20	.....
Haemoglobin	0.03-0.07	.....	.....	.....	0.8	.....
Egg albumin	2.5	1.5	0.025	15	2.0	25
Gum arabic	0.5	1.25	0.125	20	.....	5

**Coagulation of Colloidal Sols.** The stability of the colloidal state rests on the existence of charge on the particles. If this charge is destroyed or reduced, the sol is precipitated. The following methods generally bring about coagulation.

1. **By the Action of Electrolytes.** If traces of electrolytes are essential for the stability of sols, the presence of large amounts of electrolytes cause their coagulation. This due to the fact that colloidal

particles take up ions carrying charge opposite to that present on them as a result of which the charge is neutralized or reduced to a certain critical value so that the zeta potential falls below 0.02 V. This results in the reduction of the repulsion between the colloidal particles to such an extent that the sol gets precipitated or coagulated or flocculated. Based on the experiments carried out on coagulation, Hardy and Schulze formulated the following rules :

1. Coagulation is brought about by ions having opposite charge to that of the sol. Accordingly, negative ions cause coagulation of the positively charged sols and positive ions cause coagulation of negatively charged sols. Thus,  $\text{Fe}(\text{OH})_3$  sol, which is positively charged, is coagulated by negative ions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , etc. Similarly,  $\text{As}_2\text{S}_3$  sol, which is negatively charged, is coagulated by positive ions such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ , etc.

2. The efficacy of an ion to cause coagulation depends upon its valency. Thus, the efficacy of  $\text{Al}^{3+} >> \text{Mg}^{2+} > \text{Na}^+$  and that of  $[\text{Fe}(\text{CN})_6]^{4-} >>> \text{PO}_4^{3-} >> \text{SO}_4^{2-} > \text{Cl}^-$ .

Quantitatively, the efficacy varies directly as the square of the valency of the ion. Thus a  $\text{Mg}^{2+}$  ion is 4 times more effective and an  $\text{Al}^{3+}$  ion is 9 times more effective than a  $\text{Na}^+$  ion in flocculating a negatively charged sol.

3. The minimum concentration of an electrolyte required to cause coagulation or flocculation of a sol is called its **flocculation value**. This is usually expressed in terms of millimoles per litre of the electrolyte. The flocculation values of a few electrolytes for arsenic sulphide and ferric hydroxide sols are given in Table 2.

TABLE 2  
Flocculation Values of Different Electrolytes

Arsenic Sulphide Sol			Ferric Hydroxide Sol		
Electrolyte	Cation Valency	Flocc. Value (millimoles per litre)	Electrolyte	Anion Valency	Flocc. Value (millimoles per litre)
NaCl	1	52	HCl	1	132
KCl	1	52	KBr	1	138
HCl	1	30	$\text{KNO}_3$	1	132
$\text{K}_2\text{SO}_4$	1	64	$\text{KBrO}_3$	1	31
$\text{MgSO}_4$	2	0.72	$\text{K}_2\text{CrO}_4$	2	0.315
$\text{CaCl}_2$	2	0.69	$\text{K}_2\text{SO}_4$	2	0.210
$\text{ZnCl}_2$	2	0.68	$\text{K}_2\text{C}_2\text{O}_4$	2	0.238
$\text{AlCl}_3$	3	0.093	$\text{K}_3[\text{Fe}(\text{CN})_6]$	3	0.096

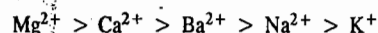
We find significant departures from the Hardy-Schulze rules in this Table. For example, the flocculation value of HCl for  $\text{As}_2\text{S}_3$  sol and that of  $\text{KBrO}_3$  for  $\text{Fe}(\text{OH})_3$  sol are relatively low. This can be attributed to strong adsorption of  $\text{H}^+$  ions in the first case and that of  $\text{BrO}_3^-$  ions in the second case.

Even more striking departures are known. For instance, the flocculation values of potassium citrate, potassium acetate and potassium formate for arsenic sulphide sol are known to be 270, 115 and 85 millimoles per litre. Since potassium ion which is effective in the present case is common, one would have expected the flocculation value of each electrolyte to be about the same. The marked discrepancy in the flocculation values shows that the ion carrying the same charge as the colloidal particles is also effective in some way in determining the flocculation value of an electrolyte. It has been established by experiment that citrate, acetate and formate ions in the above electrolytes are also adsorbed to different extents on the surface of arsenic sulphide particles thus raising the negative zeta potential of the particles to different extents. Hence, different concentrations of potassium ions

are needed to bring about neutralisation or reduction of the negative charge on the arsenic sulphide sol particles in order to cause their flocculation.

Generally, hydrophobic sols are coagulated by electrolytes at 0.0001–0.1 M concentrations. The coagulation is *irreversible* so that the removal of the coagulating electrolyte does not allow the coagulum to be redispersed. Lyophilic sols, on the other hand, are not easily coagulated. They require much higher concentrations (usually of the order of 1M) of the electrolyte for precipitation. The coagulation of lyophilic sols by the addition of electrolytes is not due to the neutralization of charge on the particles. The electrolyte binds part of the water thereby getting hydrated. As a result, the polymer molecules in the hydrophilic sol get dehydrated. The dehydration leads to coagulation.

Various ions are arranged in increasing order of their efficacy for coagulating a lyophobic sol in the form of a series, as shown below :



This series is known as **lyotropic series** or **Hofmeister series**.

**2. By the Mutual Action of Sols.** When two sols carrying opposite charges are mixed together in suitable proportions, mutual precipitation occurs. For example, when negatively charged arsenic sulphide sol is added to positively charged ferric hydroxide sol in suitable proportions, precipitation of both the sols takes place simultaneously.

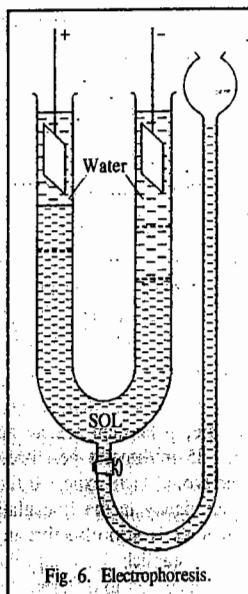
**3. By Persistent Dialysis.** It has been reported earlier that traces of electrolytes are invariably associated with colloidal systems and that this is essential for their stability. If the sols are subjected to prolonged dialysis, these traces of electrolytes also pass out through the dialyser and the colloids become unstable.

**4. Coagulation by Mechanical Means.** Violent stirring of a sol may coagulate it. Also, sols may coagulate due to the vibratory action caused by ultrasound. Vibratory coagulation is used in technological processes relating to the manufacture of pastes and other similar materials.

## II. Electrokinetic Properties

Since the solid particles and the liquid medium carry opposite charges, it is obvious that when an electric field is applied, the particles and the liquid will migrate in opposite directions. When experiments are so arranged that the particles can move but not the medium, we have the phenomenon of **electrophoresis**. If, on the other hand, the experiments are designed in such a way that the medium can move but not the particles, we come across the phenomenon of **electro-osmosis**. Both these phenomena are discussed below.

**Electrophoresis.** The electrophoretic effect can be studied by the simple apparatus shown in Fig. 6. It consists of a U-tube provided with a stop-cock through which it is connected to a funnel-shaped reservoir. A small amount of water is first placed in the U-tube and a reasonable quantity of the sol is taken in the reservoir. The stop-cock is then slightly opened and the reservoir gradually raised so as to introduce the sol into the U-tube gently. The water is displaced upwards producing a sharp boundary in each arm. A voltage of 50 to 200 Volts is then applied by means of the platinum electrodes which are immersed in water layer only. The movement of the particles can readily be followed by observing



the position of the boundary by means of naked eye or a lens or a cathetometer. When the particles are *negatively charged* (as in the case of arsenic sulphide sol), the boundary on the negative electrode side is seen to move down and that on the positive electrode side to move up, showing that *the particles move towards the positive electrode*. Thus, by noting the direction of motion of the particles in the electric field, it is possible to determine the *sign of the charge* carried by the particles. It is also possible by this technique to determine the rate at which colloidal particles migrate in an electric field. This rate is expressed in terms of electrophoretic mobility of colloidal particles.

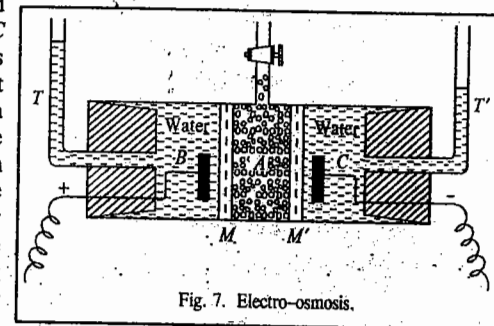
The **electrophoretic mobility** of colloidal particles is defined as the distance travelled by them in one second under a potential gradient of one volt per centimetre. It has been found that the electrophoretic mobilities of colloidal particles are of the same order as those of ions under similar conditions, that is, of the order of  $(10 - 60) \times 10^{-5}$  cm/sec/volt/cm.

Since different colloidal materials have different mobilities, it is possible to separate them from one another from their mixtures. This method has been used for the fractionation of proteins, polysaccharides, nucleic acids and other complex substances.

**Electro-osmosis.** When electrophoresis of dispersed particles in a colloidal system is prevented by some suitable means, it is observed that *the dispersion medium itself begins to move in an electric field*. This phenomenon is known as **electro-osmosis**.

A simple apparatus for studying electro-osmosis is shown in Fig. 7. The colloidal system is placed in the central compartment A which is separated from the compartments B and C filled with water by the dialysing membranes M and M'.

The water in the compartments B and C also extends to the side tubes T and T', as shown. The membranes prevent the movement of the colloidal particles. Therefore, when a potential difference is applied across the electrodes held close to the membranes in the compartments B and C, as shown, the water begins to move. If the particles carry positive charge, the water will carry negative charge. Therefore, it would start moving towards the anode and hence the level of water in the side tube T would be seen to rise. If, on the other hand, the particles carry negative charge, the water, which now carries positive charge, will start moving towards the cathode and the level of water in the side tube T' would start rising.



**Determination of Size of Colloidal Particles.** There are a number of methods for the determination of size of colloidal particles. Some of these are given below.

**1. By Using Ultrafilters.** An approximate idea about the size of particles in a colloidal system can be obtained by the use of ultrafilters. These are prepared by impregnating filter papers with collodion or gelatin which are subsequently hardened by immersing in formaldehyde. The pores can be made small enough to retain particles of colloidal dimensions. The size of the pores depends upon the particular filter paper employed and the concentration of the collodion or gelatin solution used for impregnating it. It is thus possible to obtain a series of graded ultrafilters by means of which a colloidal solution may be separated into fractions containing particles of different sizes. An approximate estimate of the size of particles can be obtained from a knowledge of the dimensions of the pores of the ultrafilters. The latter parameter is determined from the pressure required to force air or water through the pores. The results obtained by this method are only approximate because pore size is by

no means the only factor which determines whether a given particle will pass through an ultrafilter or not.

**2. From Brownian Movement.** Colloidal particles suspended in a liquid medium are subjected to Brownian movement. They also tend to settle down due to gravitation. Under the influence of both these effects, the particles distribute themselves in a vertical column in accordance with the equation

$$(RT/N_A) \ln (n_1/n_2) = (4/3)\pi r^3(h_2 - h_1)(\rho - \rho') \quad \dots(6)$$

Since the number of particles  $n_1$  and  $n_2$  at two depths  $h_1$  and  $h_2$  of the vertical column can be counted with the help of an ultra-microscope and densities of the particles and of the liquid medium,  $\rho$  and  $\rho'$ , can be determined by the usual methods, the radius of the particles,  $r$ , can be easily calculated. Brownian motion of colloidal systems was investigated by the French physicist Jean Perrin (1870-1942) to determine the Avogadro's number. Perrin was awarded the 1926 Physics Nobel prize for his work on the discontinuous structure of matter and especially for his discovery of the sedimentation equilibrium.

**3. From Scattering of Light.** Zsigmondy used the ultra-microscope for determining the size of the particles of colloidal dimensions. As already mentioned, each spot of light viewed in ultra-microscope corresponds to a particle. The number of particles in a given volume of a solution, therefore, can be counted. The observation is repeated several times and an average is taken. The length and breadth of the field of vision are measured with the help of an eye-piece micrometer. The depth is determined by rotating the slit through  $90^\circ$ . From these dimensions, the exact volume of the solution containing the observed number of particles can be obtained. From this, the number of particles  $n$ , contained per unit volume of the solution can be determined.

Next, a known volume of the colloidal solution is evaporated to dryness. From the mass of the residue, the mass of colloidal particles per unit volume can easily be obtained. Let this be  $m$ . Now two assumptions are made. Firstly, the particles are spherical. Secondly, the density  $\rho$  of the colloidal particles is the same as that of the material in the bulk state. The volume of colloidal phase is  $m/\rho$  and, therefore,

$$m/\rho = (4/3)\pi r^3 \times n \quad \text{or} \quad r = (3m/4\pi\rho n)^{1/3} \quad \dots(7)$$

Richard Zsigmondy (1865-1929), the German chemist, was the recipient of the 1925 Chemistry Nobel Prize for demonstration of the heterogeneous nature of colloidal solutions.

#### SURFACTANTS (SURFACE-ACTIVE AGENTS)

Surface-active agents or surfactants, derive their name from their behaviour at surfaces and interfaces. They are positively adsorbed at interfaces between two phases and the adsorption of surfactant lowers the interfacial tension between the two phases. Because of their ability to lower interfacial tension, surfactants are used as emulsifiers, detergents, dispersing agents, foaming agents, wetting agents, penetrating agents, and so forth. The surfactants are frequently referred to as **amphiphiles**. Many types of substances act as surfactants but they all share the property of **amphipathy**. The molecule is composed of a non-polar hydrophobic portion and a polar hydrophilic portion and is, therefore, partly hydrophilic and partly hydrophobic. The property to partly have both these characters is known as amphipathy. Surfactants may be referred to as either *amphiphilic* or *amphipathic*; the terms are synonymous. The polar, hydrophilic part of the molecule is called the *hydrophilic* or *lipophilic group* and the non-polar, hydrophobic part is called the *hydrophobic* or *lipophilic group*. Often the hydrophilic part of the molecule is simply called the *head* and the hydrophobic part (usually including an elongated alkyl substituent) is called the *tail*. The presence of a hydrophilic group makes surfactants somewhat soluble in aqueous media. This is central to the physicochemical properties of aqueous surfactant solutions.

Surfactants can be classified on the basis of the charge carried by the polar head group as *anionic*, *cationic*, *non-ionic* or *amphoteric*. Tables 3 to 6 show the chemical structures of typical examples of these classes.

TABLE 3

Chemical Structures of Hydrophilic Groups for Anionic Amphiphiles

Chemical Structure <sup>a</sup>	Name
$R-(COO^-)_n M^{n+}$	Carboxylate
$R-COO-M^{2+}$ $SO_3^-$	Sulphocarboxylate
$R-COO-M^{(n+1)+}$ $OPO_3H_{3-n}$	Phosphonocarboxylate
$R-OSO_3^- M^+$	Sulphate
$R-(OCH_2CH_2)_n-OSO_3^- M^+$	Polyoxyethylene sulfate
$R-SO_3^- M^+$	Sulphonate
$R-(OCH_2CH_2)_n-SO_3^- M^+$	Polyoxyethylene sulfonate
$R-\text{C}_6\text{H}_4-SO_3^- M^+$	Benzene sulphonate
$R-\text{C}_{10}\text{H}_7-SO_3^- M^+$	Naphthalene sulphonate
$R-OPO_3H_{3-n} M^{n+}$	Phosphate

<sup>a</sup> R stands for long hydrophobic tail.

TABLE 4

Chemical Structures of Hydrophilic Groups for Cationic Amphiphiles

Chemical structure <sup>*</sup>	Name	Chemical structure <sup>*</sup>	Name
$R-\overset{+}{N}(R_1)(R_2)R_3 X^-$	Ammonium	$R-\overset{+}{N}(\text{C}_5\text{H}_4)-X^-$	Pyridinium
$R-\overset{+}{S}(R_1)(R_2)R_3 X^-$	Sulphonium	$R-\overset{+}{N}(\text{C}_{10}\text{H}_7)-X^-$	Quinolinium
$R-\overset{+}{P}(R_1)(R_2)R_3 X^-$	Phosphonium		

<sup>\*</sup> R stands for long hydrophobic tail;  $R_1$ ,  $R_2$  and  $R_3$  stand for hydrogen or a short alkyl chain.



TABLE 5

Chemical Structure of Hydrophilic Groups for Non-ionic Amphiphiles

Chemical structure *	Name	Chemical structure *	Name
$R-(OCH_2CH_2)_n-OH$	Polyoxyethylene alcohol	$R-(OCH_2CH_2CH_2)_n-OH$	Polyoxypropylene alcohol
$R-COO-(CH_2CH_2O)_n-R_1$	Polyoxyethylene ester	$R-(CH_2CH_2O)_n$	Crown ether
$R-S-R_1$ ↓ O	Sulphoxide	$R-S-(CH_2)_n-OH$ ↓ O	Sulphinyl alcohol
$R-S-(CH_2CH_2O)_n$	Polyoxypropylene thioether	$R-\overset{R_1}{N} \rightarrow O$ ↓ $R_2$	Amine oxide
$R-(CH_2CH_2NH)_n$	Azacrown	$R-\overset{R_1}{P} \rightarrow O$ ↓ $R_2$	Phosphine oxide

\* R stands for long hydrophobic tail;  $R_1$  and  $R_2$  stand for a short alkyl chain.

TABLE 6

Chemical Structure of Hydrophilic Groups for Amphoteric Amphiphiles (Zwitter Ions)

Chemical structure *	Name	Chemical structure *	Name
$R-\overset{R_1}{CH}-\overset{+}{N}(R_2)R_3$ ↓ COO <sup>-</sup>	C betaine	$R-\overset{CH_2COOH}{N}-CH_2COOH$ ↓ $CH_2COO^-$	Triglycine
$R-\overset{R_1}{N}^+-CH_2COO^-$ ↓ $R_2$	N betaine		

\* R stands for long hydrophobic tail;  $R_1$ ,  $R_2$  and  $R_3$  stand for short alkyl chains.

### Hydrophile-Lipophile Balance (HLB)

This term, first suggested by Clayton, refers to the balance in size and strength between the hydrophilic and hydrophobic parts of a surfactant molecule. Griffin later developed the concept of the HLB for emulsifiers on the basis of their aqueous solubility. The HLB value is an empirical number assigned to non-ionic surfactants on the basis of a wide variety of experiments carried out on surfactants. The HLB values range from 1 to 40, the low numbers generally indicating solubility in oil and the high numbers indicating solubility in water. Nevertheless, emulsifiers with the same HLB value may differ in solubility. An emulsifier has two different actions: it promotes the formation of an emulsion and it determines whether an oil/water (O/W) or a water/oil (W/O) emulsion will be formed. The second action is closely connected with the HLB value.

On the basis of systematic experiments, Griffin found that the HLB values of mixtures of two or more emulsifiers are additive. The HLB value of a mixture is equal to the sum of the HLB values of the constituents multiplied by their mass fractions in the mixture  $x_i^m$ :

$$HLB = \sum x_i^m (HLB)_i \quad \dots(8)$$

Griffin also listed several estimated HLB values for emulsifiers which had been determined and correlated by an extensive series of emulsifier blending tests (Table 5). Using these values and Eq. 9, we can determine an HLB value for any surfactant by blending it with a surfactant of known HLB value.

For most polyhydric alcohols, fatty acid and esters, approximate HLB values may be obtained using the following equation:

$$HLB = 20 (1 - S/A) \quad \dots(9)$$

where  $S$  is the saponification number of the ester and  $A$  is the acid number of the acid. This equation can be written as

$$HLB = 20 (1 - M_h/M_m) \quad \dots(10)$$

where  $M_h$  is the mass of the hydrophobic group and  $M_m$  is the molar mass of the emulsifier.

HLB values for the various types of emulsifiers are shown below in parenthesis:

- (a) Anionic: (i) Tea oleate (12); (ii) Sodium oleate (18).
- (b) Cationic: (i) Atlas G-251 (25-35).
- (c) Non-ionic: (i) Oleic acid (~1); (ii) Span 85 (1.8); (iii) Span 80 (4.3); (iv) Span 60 (4.7); (v) Tween 20 (16.7).

Davies suggested assigning an HLB contribution group number to each functional group in a molecule after studying the relative coalescence rates of stabilized oil droplets in water and water droplets in oil. The Davies equation which is applicable to ionic as well as non-ionic surfactants is

$$HLB = \Sigma (\text{hydrophilic group number}) - \Sigma (\text{hydrophobic group number}) + 7 \quad \dots(11)$$

Table 7 lists the HLB group numbers of some common functional groups.

TABLE 7

HLB Group Numbers for Various Hydrophilic and Hydrophobic Groups

Hydrophilic	Group number	Hydrophobic	Group number
$-SO_3Na$	38.7	$=CH-$	0.475
$-CO_2Na$	19.1	$-CH_2-$	0.475
$-SO_3Na$	11.0	$-CH_3$	0.475
N (tertiary amine)	9.4		
Ester (free)	2.4	$-CF_2-$	0.870
$-CO_2H$	2.1		
$-OH$ (free)	1.9		
$-O-$	1.3		

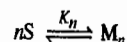
### MICELLE FORMATION

An important property of amphiphilic molecules is their capacity to aggregate in solutions. The aggregation process depends on the amphiphilic species and the condition of the system in which they are dissolved. The abrupt change in many physicochemical properties seen in aqueous solutions of amphiphilic molecules or surfactants with long hydrophobic chains when a specific concentration is exceeded is attributed to the formation of oriented colloidal aggregates. The narrow concentration range over which these changes occur is called the critical micelle concentration (CMC) and the molecular aggregates that are formed above the CMC are known as micelles. The difference between micellar colloids and other colloids is that micellar colloids are in dynamic equilibrium with monomers in the solution. Micellar colloids represent dynamic association-dissociation equilibria. However, the theoretical treatment of micelles depends on whether the micelle is regarded as a chemical species or as a separate phase. The mass action model, which has been used ever since the discovery of micelles, takes the former point of view whereas the phase separation model regards micelles as a separate

phase. To apply the mass action model strictly, one must know every association constant over the whole stepwise association from monomer to micelle, a requirement almost impossible to meet experimentally. Therefore, this model has the disadvantage that either monodispersity of the micelle aggregation number must be employed or numerical values of each association constant have to be assumed. The phase separation model, on the other hand, is based on the assumption that the activity of a surfactant molecule and/or the surface tension of a surfactant solution remain constant over the CMC. In practice, however, neither quantity remains constant; so this model is also not strictly correct.

The variety of the theories on micelle formation results from the versatile properties of micelles. Thus, although a micelle may not have such a large aggregation number that it can be regarded as a phase in the usual sense, it will still have properties similar to those of a phase. At the same time, each micelle contains too many aggregated monomer molecules to be regarded as a chemical species, even a bulky chemical species.

It is thus instructive to consider the micellar solution system from the viewpoint of the phase rule. Fig. 8 illustrates the changes in solubility and CMC of sodium tetradecyl sulphonate with temperature. If the micelle is regarded as a phase, three phases (intermicellar bulk phase, surfactant solid phase and micellar phase) coexist along the solubility curve above  $T_k$ , called the Krafft point and Gibbs's phase rule  $F = C - P + 2$  (where  $F$ ,  $C$  and  $P$  are the number of degrees of freedom, number of components and the number of phases, respectively) gives only one degree of freedom since the number of components is two (solvent water and surfactant). In other words, according to this model, the solubility cannot change with temperature at constant pressure because the solubility is determined only by the pressure. On the other hand, if the mass action model is applied to micelle formation, the solubility problem can be solved in a way consistent with the phase rule. In addition, increase in the solubility observed above the point of micellization can be elucidated by the following semiquantitative discussion. Let us consider a simple association equilibrium between surfactant monomers ( $S$ ) and micelles ( $M_n$ ) of aggregation number  $n$ :



The micellization constant  $K_n$  is, therefore, written as

$$K_n = [M_n] / [S]^n \quad \dots(12)$$

The equivalent concentration of surfactant ( $C_t$ ) used for micelles then becomes:

$$C_t - [S] = nK_n [S]^n \quad \dots(13)$$

The ratio of the equivalent concentration at  $T$  to that at  $T_k$  is given by

$$\frac{[C_t(T) - [S(T)]]}{[C_t(T_k) - [S(T_k)]]} = \frac{[S(T)]}{[S(T_k)]^n} \quad \dots(14)$$

where  $K_n$  is assumed constant because of the very small temperature range. The heat of dissolution obtained from the solubility change with temperature is about  $100 \text{ kJ mol}^{-1}$  for many ionic surfactants.

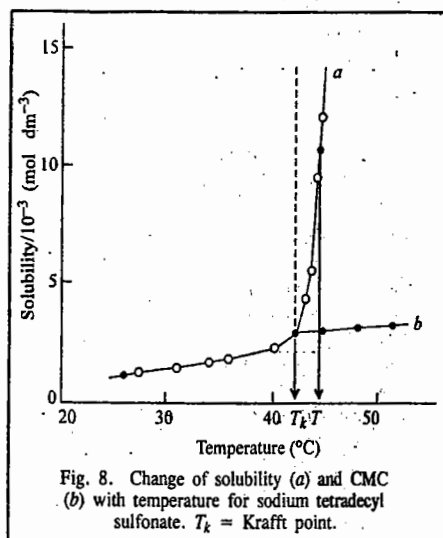


Fig. 8. Change of solubility (a) and CMC (b) with temperature for sodium tetradecyl sulfonate.  $T_k$  = Krafft point.

Hence the solubility change with temperature may be expressed roughly as:

$$\frac{[S(T_k + \Delta T)]}{[S(T_k)]} = 1 + 0.13 \times \Delta T \quad \dots(15)$$

For  $\Delta T = 0.2^\circ\text{C}$ , the above ratios become 2.8 and 13.8 for  $n=50$  and  $n=100$ , respectively.

It is evident that a small temperature increase brings about a large increase in solubility and that the micelle aggregation number  $n$  has a strong influence (Fig. 9). As is clear from the above discussion, the abrupt increase in the total solubility above  $T_k$  is due not to an increase in the solubility of the monomeric surfactant but rather to an increasing number of micelles. In addition, the treatment of micelles as a separate phase has turned out to be incorrect whereas the mass action model is consistent not only with the phase rule but also with the solubility increase.

### Shape and Structure of Micelles

Ever since McBain proposed the presence of molecular aggregates in soap solutions on the basis of the unusual changes in electrical conductivity observed with changing soap concentration, the structure of micelles has been a matter of discussion. Hartley proposed that micelles are spherical with the charged groups situated at the micellar surface (Fig. 10c) whereas McBain suggested that lamellar (Fig. 10a) and spherical forms coexist. X-ray studies by Harkins suggested the sandwich or lamellar model. Later, Debye and Anacker proposed that micelles are rod-shaped rather than spherical or disc-like (Fig. 10b). The cross-section of such a rod would be circular with the polar heads of the micelle lying on the periphery and the hydrocarbon tails filling the interior. The ends of the rod would almost certainly have to be rounded and polar. In 1956, Hartley's spherical micelle model was established by Reich from the viewpoint of entropy, and the spherical form is now generally accepted as approximating the actual structure (Fig. 10c). The formation of micelles by ionic surfactants is ascribed to a balance between hydrocarbon chain attraction and ionic repulsion. The net charge on micelles is less than the degree of micellar aggregation, indicating that a large fraction of counter ions remains associated with the micelle; these counter ions form the Stern layer (cf. Fig. 5) at the micellar surface. For non-ionic surfactants, however, the hydrocarbon chain attraction is opposed by the requirements of hydrophilic groups for hydration and space. Therefore, the micellar structure is determined by an equilibrium between the repulsive forces among hydrophilic groups and the short-range

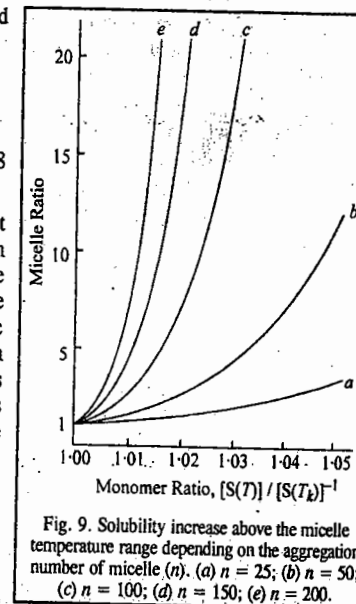


Fig. 9. Solubility increase above the micelle temperature range depending on the aggregation number of micelle ( $n$ ). (a)  $n = 25$ ; (b)  $n = 50$ ; (c)  $n = 100$ ; (d)  $n = 150$ ; (e)  $n = 200$ .

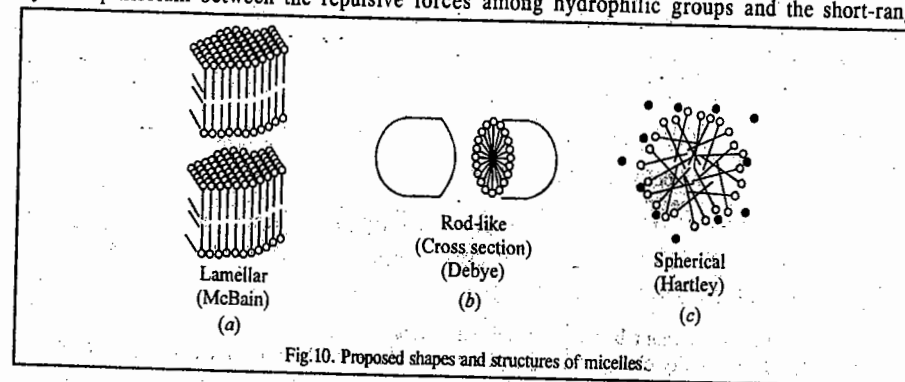


Fig. 10. Proposed shapes and structures of micelles.

attractive forces among hydrophobic groups. In other words, the chemical structure of a given surfactant determines the size and shape of its micelles.

The shape and structure of micelles have been elucidated with the help of techniques such as NMR, ESR, neutron scattering, etc. Neutron scattering experiments on sodium dodecyl sulphate and other ionic micelles support the basic Hartley model of a spherical micelle. However, as the ion concentration is increased, the shape of ionic micelles changes in the sequence: spherical  $\rightarrow$  cylindrical/hexagonal  $\rightarrow$  lamellar (Fig. 11). For non-ionic micelles, on the other hand, the shape seems to change from spherical directly to lamellar with increasing concentration.

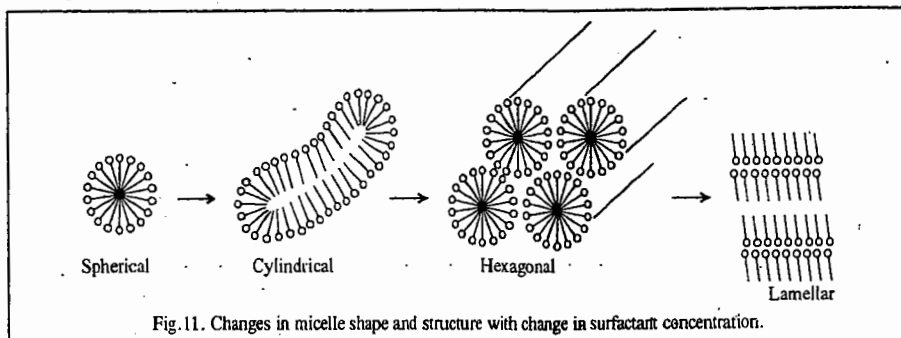


Fig. 11. Changes in micelle shape and structure with change in surfactant concentration.

The shape of the micelle produced in aqueous media is of importance in determining various properties of the surfactant solution, such as its viscosity and its capacity to solubilize water-insoluble materials. The major types of micelles appear to be (1) relatively small, spherical structures (aggregation number  $< 100$ ), (2) elongated cylindrical, rodlike micelles with hemispherical ends (prolate ellipsoids), (3) large, flat lamellar micelles (disc-like extended oblate spheroids) and (4) vesicles — more or less spherical structures consisting of lamellar micelles arranged in one or more concentric spheres.

In aqueous media, the surfactant molecules are oriented, in all these structures, with their polar heads toward the aqueous phase and their hydrophobic groups away from it. In vesicles, there will also be an aqueous phase in the interior of the structure. In ionic micelles, the interfacial region between the aqueous solution and the micelle contains the ionic head groups and the Stern layer portion of the electrical double layer contains more than half of the counter ions associated with the micelle and water. The remaining counter ions are contained in the Gouy-Chapman portion of the double layer that extends further into the aqueous phase. For polyoxyethylenated non-ionics, the structure is essentially the same except that the outer region contains no counter ions but includes coils of hydrated polyoxyethylene chains. The interior region of the micelle, containing the hydrophobic groups, is of the radius approximately equal to the length of the fully extended hydrophobic chain. The aqueous phase is believed to penetrate into the micelle beyond the hydrophobic head group and the first few methylene groups of the hydrophobic chain adjacent to the hydrophobic head are often concentrated in the hydration sphere. It is, therefore, useful to divide the interior region into an outer core that may be penetrated by water and an inner core from which water is excluded. In non-polar media, the structure of the micelle is similar but reversed, with the hydrophilic heads comprising the interior region surrounded by an outer region containing the hydrophobic groups and non-polar solvent. Dipole-dipole interactions hold the hydrophilic heads together in the core. Changes in temperature, concentration of surfactant, additives in the liquid phase and structural groups in the surfactant may all cause change in the size, shape and aggregation number of the micelle, with the structure varying from spherical through rod or disc-like to lamellar in shape.

#### Micellar Aggregation Numbers

Micellar aggregation numbers have classically been determined by light-scattering and from sedimentation rates in the ultracentrifuge. Currently, NMR, Small Angle Neutron Scattering (SANS) and freezing point and vapour pressure methods are being used. A convenient method using fluorescent

probes has also been used to calculate aggregation numbers of several different types of surfactants. Micelle aggregation numbers range from less than 100 for ionic surfactants to several hundred for non-ionic surfactants.

From geometric considerations, the aggregation numbers of micelles in aqueous media should increase rapidly with increase in the length of the hydrophobic group  $l_c$  of the surfactant molecule and decrease with increase in the cross-sectional area of the hydrophilic group  $a_0$  or the volume of the micelle in aqueous media, the surface area,  $n \times a_0 = 4\pi(l_c + \Delta)^2$  or  $n = 4\pi(l_c + \Delta)^2/a_0$ , where  $\Delta$  is the added length of the radius of the sphere due to the hydrophilic group. Similarly, the volume of the hydrophobic core  $n \times V_h = (4/3)\pi(l_c)^3$  or  $n = (4/3)\pi(l_c)^3/V_h$ .

#### Critical Micelle Concentration (CMC)

When molar conductance of an anionic surfactant of the type  $\text{Na}^+\text{R}^-$  in water is plotted against the square root of the molarity of the solution, the curve obtained, instead of being the smoothly decreasing curve characteristic of ionic electrolytes of this type, has a sharp break in it, at low concentrations (Fig. 12). This sharp break in the curve accompanied by reduction in the conductance of the solution, indicating a sharp increase in the mass per unit charge of the material in solution, is interpreted as evidence for the formation of micelles at that point. The concentration at which this phenomenon occurs is called the critical micelle concentration (CMC). Similar breaks in almost every measurable physical property that depends on size or number of particles in solution are shown by all types of surfactants—non-ionic, anionic, cationic and zwitter ionic in aqueous media. Changes in some physical properties in the neighbourhood of the CMC are shown in Figure. 13.

We can determine the value of the CMC by using any of these physical properties, but most commonly the breaks in the molar conductance, surface tension, light scattering or refractive index versus concentration curves have been used for this purpose. Critical micelle concentrations have also very frequently been determined from the change in the spectral characteristics of some dyestuff added to the surfactant solution when the CMC of the latter is reached. However, this method is open to the serious objection that the presence of the dyestuff may affect the value of the CMC.

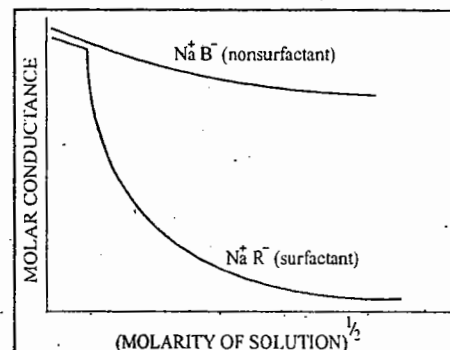


Fig. 12. Plot of equivalent conductance versus  $\sqrt{\text{normality of solution}}$  for an aqueous solution of a surfactant of the type  $\text{Na}^+\text{R}^-$ .

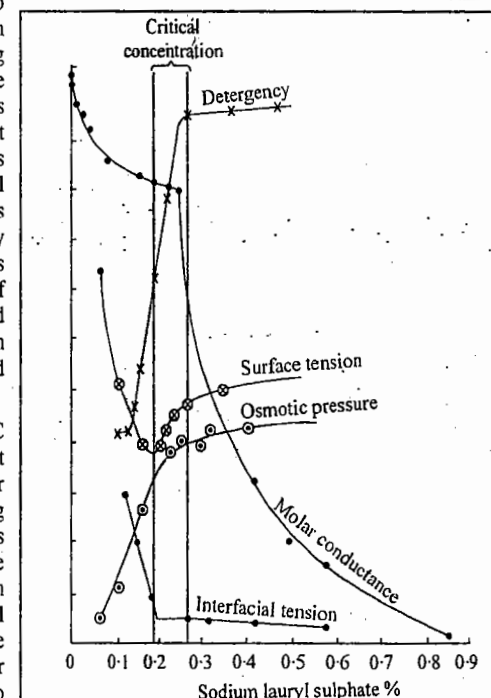


Fig. 13. Changes in some physical properties of an aqueous solution of sodium lauryl sulphate in the neighbourhood of the critical micelle concentration.

### Factors Affecting Critical Micelle Concentration in Aqueous Media

Several factors such as the structure of the surfactant, concentration of electrolyte, addition of organics, presence of a second liquid phase and temperature affect the CMC in aqueous media. These are discussed below.

#### 1. Structure of the Surfactant

**Role of the Hydrophobic Group.** In aqueous medium, the CMC decreases as the number of carbon atoms in the hydrophobic group increases to about 16 and a general rule for ionic surfactants is that the CMC is halved by the addition of one methylene group to a straight-chain hydrophobic group attached to a single terminal hydrophilic group. For non-ionics and zwitter ionics, the decrease with increase in the hydrophobic group is somewhat larger, an increase by two methylene units decreasing the CMC to about one-tenth its previous value (compared to one-quarter in ionics). A phenyl group that is part of a hydrophobic group with terminal hydrophilic group is equivalent to about three and a half methylene groups. When the number of carbon atoms in a straight-chain hydrophobic group exceeds 16, however, the CMC no longer decreases so rapidly with increase in the length of the chain and when the chain exceeds 18 carbons it may remain substantially unchanged with further increase in the chain length. This may be due to the coiling of these long chains in water.

When the hydrophobic group is branched, the carbon atoms on the branches appear to have about one-half the effect of carbon atoms on a straight chain. When carbon-carbon double bonds are present in the hydrophobic chain, the CMC is generally higher than that of the corresponding saturated compound, with the *cis* isomer generally having a higher CMC than the *trans* isomer. This may be the result of a steric factor in micelle formation. Surfactants with either bulky hydrophobic or bulky hydrophilic groups have larger CMC values than those with similar but less bulky groups.

**Role of the hydrophilic group.** In aqueous medium, ionic surfactants have much higher CMCs than non-ionic surfactants containing equivalent hydrophobic groups. The 12-carbon straight chain ionics have CMCs of approximately  $1 \times 10^{-2}$  M, whereas non-ionics with the same hydrophobic group have CMCs of approximately  $1 \times 10^{-4}$  M. Zwitter ionics appear to have slightly smaller CMCs than ionics with the same number of carbon atoms in the hydrophobic groups. As expected, surfactants containing more than one hydrophilic group in the molecule show larger CMCs than those with one hydrophilic group and the equivalent hydrophobic group.

**Role of the degree of binding of the counter ion to the micelle.** The critical micelle concentration in aqueous solution reflects the degree of binding of the counter ion to the micelle. Increased binding of the counter ion, in aqueous systems, causes a decrease in the CMC of the surfactant. It may, however, be mentioned that CMC is not a measure of the degree of binding of the counter ion to the micelle, when different types of surfactants are compared. The degree of binding of the counter ion to the micelle also depends on the surface charge density of the micelle. The greater the surface charge density, *i.e.*, the smaller the surface area per head group, the greater is the degree of binding of the counter ion.

For homologous straight chain ionic surfactants (soaps, alkane sulphonates, alkyl sulphates, alkylammonium chlorides) in aqueous medium, a relation between the CMC and the number of carbon atoms *N* in the hydrophobic chain is found to be given by

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

where *A* is a constant for a particular ionic head at the given temperature and *B* is a constant  $\approx 0.3$  ( $= \log 2$ ) at 35°C.

#### 2. Concentration of Electrolyte

It is found experimentally that for the first two classes of surfactants, the effect of the concentration of electrolyte is given by

$$\log \text{CMC} = -a \log c_i + b$$

where *a* and *b* are constants for a given ionic head at a particular temperature and *c<sub>i</sub>* is the molar concentration of the counter ion. The decrease in the CMC in these cases is due mainly to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte and the consequent decreased electrical repulsion between them in the micelle. For non-ionics and zwitter ionics the above relation does not hold.

#### 3. Addition of Organic Materials

Small amounts of organic materials may produce marked changes in the CMC in aqueous media. A knowledge of the effects of organic materials on the CMC of surfactants is, therefore, of great importance, both for theoretical and practical purposes. To understand the effects produced, it is necessary to distinguish between two classes of organic materials that markedly affect the critical micelle concentrations of aqueous solutions surfactants: Class I materials that affect the CMC by being incorporated in the micelle and Class II materials that change the CMC by modifying solvent micelle or solvent surfactant interactions.

**Class I Materials.** Materials in Class I are generally polar organic compounds such as alcohols and amides. They affect the CMC at much lower liquid phase concentrations than those in Class II. Water-soluble compounds in this class may operate as members of Class I at low bulk phase concentrations and as members of Class II at high bulk phase concentrations. Members of Class I reduce the CMC. Shorter-chain members of this class are probably adsorbed mainly in the outer portion of the micelle close to the water-micelle 'interface'. The longer-chain members are probably adsorbed mainly in the outer portion of the core, between the surfactant molecules. Adsorption of the additives in this manner decreases the work required for micellization in the case of ionic surfactants by decreasing the mutual repulsion of the ionic heads in the micelle.

**Class II Materials.** Members of Class II change the CMC but at bulk phase concentration which are usually considerably higher than those at which Class I members are effective. The members of this class change the CMC by modifying the interaction of water with the surfactant molecule or with the micelle, by modifying the structure of the water, its dielectric constant or its solubility parameter (cohesive energy density). Members of this class include urea, formamide, *N*-methylacetamide, guanidinium salts, short-chain alcohols, water-soluble esters, dioxane, ethylene glycol and other polyhydric alcohols such as fructose and xylose.

Urea, formamide and guanidinium salts are believed to increase the CMC of surfactants in aqueous solution because of their tendency to distort the structure of water. This may increase the degree of hydration of the hydrophilic group and since hydration of the hydrophilic group opposes micellization, this causes an increase in the CMC.

#### 4. The Presence of Second Liquid Phase

The CMC of a surfactant in aqueous phase is changed very little by the presence of a second liquid phase in which the surfactant does not dissolve appreciably and which, in turn, either does not dissolve appreciably in the aqueous phase or is solubilized only in the inner core of the micelles (*e.g.*, saturated aliphatic hydrocarbons). When the hydrocarbon is a short-chain unsaturated hydrocarbon or an aromatic hydrocarbon, the CMC is significantly less than that in air, with the more polar hydrocarbon causing a larger decrease. This is presumably because some of the second liquid phase adsorbs on the outer portion of the surfactant micelle and acts as a Class I material.

#### 5. Temperature

The effect of temperature on the CMC of surfactants in aqueous medium is complex, the value first decreases with increase in temperature to a certain minimum and then increases with further increase in temperature. Temperature increase causes decreased hydration of the hydrophilic group which favours micellization. However, temperature increase also produces distortion in the structure of water surrounding the hydrophobic group, an effect that disfavors micellization. The relative



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  $\Delta G_{\text{mic}}$  associated with the aggregation of the individual surfactant molecules to form micelles by the expression

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

Here  $x_{\text{CMC}}$  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,  $x_{\text{CMC}} = \text{CMC}/c$  and

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

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

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

$\Delta G_{\text{mic}}$  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:

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

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

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

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,  $\alpha$ , 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

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

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

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

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.,  $\Delta G_{\text{mic}}^0$ ,  $\Delta H_{\text{mic}}^0$  and  $\Delta S_{\text{mic}}^0$  has played an important role in developing such an understanding.

The standard free energy of micellization  $\Delta G_{\text{mic}}^0$  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

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

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

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

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,

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

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

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

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,

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

If we assume that  $\Delta G_{\text{mic}}^0$  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  $(\text{CMC}/c)$  versus  $(c_B/c)$ .

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

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

if  $\Delta H_{\text{mic}}^0$  is constant over the temperature range investigated.

Alternatively,

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

if  $\Delta S_{\text{mic}}^0$  is constant over the temperature range investigated.

Values of  $\Delta H_{\text{mic}}^0$  can also be determined calorimetrically. The data available (mainly for aqueous systems) indicate that the negative values of  $\Delta G_{\text{mic}}^0$  are due mainly to the large positive values of  $\Delta S_{\text{mic}}^0$ ,  $\Delta H_{\text{mic}}^0$  is often positive and, even when negative, is much smaller than the value of  $T\Delta S_{\text{mic}}^0$ . 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  $\Delta G_{mic}^0$  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.

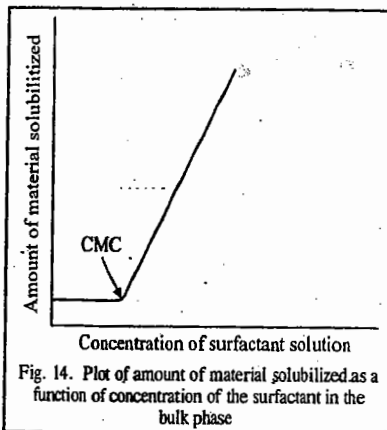
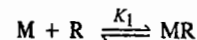


Fig. 14. Plot of amount of material solubilized as a function of concentration of the surfactant in the bulk phase

### Location of Solubilizes in Micelles

The position of solubilizes in micelles as well as in living membranes, provides very important information concerning the physico-chemical properties and physiological functions of both the solubilize 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 solubilize 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 solubilize (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 solubilizes 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

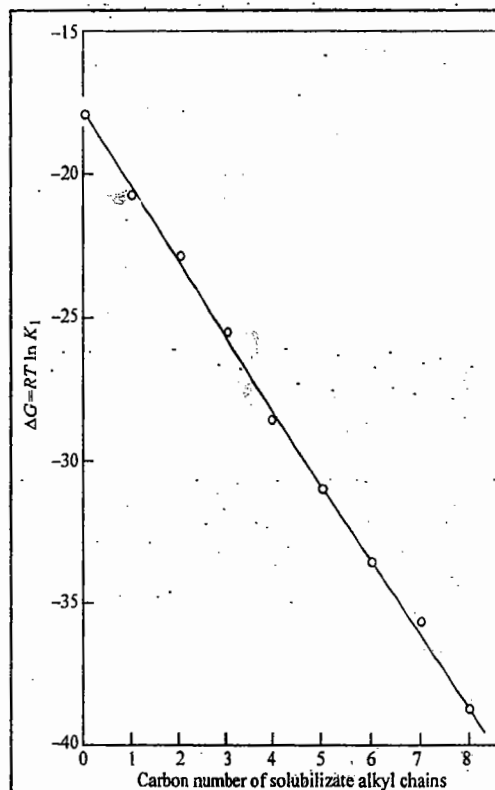


Fig. 15. Standard free energy change for the association constant between solubilize and micelles plotted against carbon number of the solubilize alkyl chain. The solubilize is 4-n-alkylbenzoic acid and the micelle is made of dodecylsulphonic acid.

long enough to penetrate the micelle core would encounter an increased Laplace pressure and the plot in Fig. 15 should become less steep above a certain carbon number. The experimental data did not show this effect indicating that probably there is no plane of interfacial tension in the micelle.

### The Phase Rule of Solubilization

Research on solubilization has used the phase-separation model of the micelle. Accordingly, solubilization has been treated as partitioning of solubilize molecules between a micellar phase and the intermicellar bulk phase. Some published work has also been based on the mass-action approach. Here we shall examine solubilization in terms of the Gibbs phase rule.

If the micelles are regarded as a separate phase, then adding an excess solubilize means there are three phases (the third is the intermicellar bulk phase). The total number of components is three (solvent, surfactant and solubilize). Thus, the presence of three phases makes the system bivariate. This would mean that surfactant concentration would be constant at constant temperature and pressure. But, in practice, the maximum additive concentration (MAC) changes with total surfactant concentration. Even if we assume that the increase in the MAC with surfactant concentration above the CMC is due to an increase in the total micellar phase, the concentration of solubilize in the micellar phase should still remain constant because the concentration is an intensive property of the system and is, therefore, homogeneous throughout the micellar phase.

If, on the other hand, the micelles are regarded as a separate phase and the system does not contain an excess solubilize phase, there are three degrees of freedom. The surfactant concentration is then a unique variable that determines every intensive property of the system at constant temperature and pressure. In other words, the solubilize monomer concentration in the intermicellar bulk phase (and, therefore, also in the micellar phase) is set automatically by the surfactant concentration, irrespective of the total solubilize concentration in the system. This is not only totally incorrect in theory but is contrary to the experimental evidence that the concentration of solubilizes is determined only by the amount added to the system.

### MICELLAR CATALYSIS

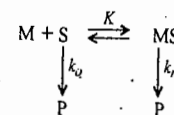
Micelles in aqueous media have either a polar region or a region of high charge density, accompanied by an electrostatic potential of up to a few hundred millivolts at the micellar surface and a non-polar hydrophobic region in the micelle core. The kinetics of micellar reactions are governed by electrostatic and hydrophobic interactions between micelles and reactants, transition state complexes and products. If any of the reaction species interacts with micelles, then the presence of micelles will affect the reaction rate. Micelle-catalyzed reactions are somewhat similar to enzyme-catalyzed reactions. The proper choice of surfactant brings about a rate increase of up to 1000-fold. The diameter of micelles is 30–50 Å, similar in size to globular enzymes. Micelle-catalyzed reactions can be treated in a manner analogous to the reaction scheme for enzymatic catalysis.

However, the analogy between the high reactivity of an enzyme-substrate complex and the reactivity of substrates bound to micelles is not entirely satisfactory. In a substrate-enzyme complex the reactants are fixed in position, whereas reactants incorporated into a micelle are free to move about in the micellar region. Furthermore, reactants distribute into micelles according to their solubilities and not according to the stoichiometry of the reaction. The solubilization of reactants and their distribution among micelles play the most important role in micelle-catalyzed reactions. In addition, the rate enhancement generally increases with increasing hydrophobicity of reactants and amphiphiles, which is not always the case for enzymatic reactions. These differences are mainly due to the fact that micelles do not maintain a definite configuration but are in dynamic association-dissociation equilibrium with monomeric surfactants in the bulk phase, changing their size and shape at rates involving milliseconds and microseconds.

The incorporation of reagents into micelles often alters the CMC of the surfactant. Therefore, the CMC must be determined for each reaction system in order to correctly interpret the results.

The effect of micelles on organic reactions can be attributed to both electrostatic and hydrophobic interactions. Electrostatic interaction may affect the rate of a reaction either by its effect on the transition state of the reaction or by its effect on the concentration of reactant in the vicinity of the reaction site. Thus, a cationic micelle with its multiplicity of positively charged hydrophilic heads may catalyze the reaction between a nucleophilic anion and a neutral substrate by delocalizing the negative charge developing in the transition state of this reaction, thereby decreasing the energy of activation of the reaction. It may also catalyze the reaction by increasing the concentration of nucleophilic anion at the micelle-water interface close to the reactive site of the substrate. For catalysis to occur, it is necessary (1) that the substrate be solubilized by the micelle and (2) that the locus of solubilization be such that the reactive site of the substrate is accessible to the attacking reagent. It is here that hydrophobic interactions become important because they determine the extent and the locus of solubilization in the micelle.

In the simplest case, where we assume that the surfactant does not complex with (*i.e.*, solubilize) the substrate *S*, except when the former is in the form of micelles *M* and that complexing between the substrate and the micelle is in a 1:1 stoichiometric ratio, we can symbolize the formation of a reaction product *P* as



where  $k_0$  is the rate constant for the reaction of the substrate in the bulk phase and  $k_m$  is the rate constant for the reaction of the substrate in the micelle. The overall rate constant for the reaction  $k_p$  is then given by the expression

$$k_p = k_0[f_0] + k_m[f_m] \quad \dots(32)$$

where  $f_0$  is the fraction of the uncomplexed substrate and  $f_m$  is the fraction of the complexed substrate. The equilibrium constant  $K$  for the interaction between substrate and micelle, usually called the binding constant, is then given by the relation

$$K = \frac{[f_m]}{[M][f_0]} \quad \dots(33)$$

from which

$$k_p = k_0[f_0] + k_m K[M][f_0] = (k_0 + k_m K[M])f_0 \quad \dots(34)$$

Since  $f_0 + f_m = 1$ ,

$$K = \frac{[f_m]}{[M][f_0]} = \frac{[1 - f_0]}{[M][f_0]} \quad \dots(35)$$

and

$$f_0 = \frac{1}{1 + K[M]} \quad \dots(36)$$

Hence,

$$k_p = \frac{k_0 + k_m K[M]}{1 + K[M]} \quad \dots(37)$$

If we assume that  $[M]$  is given by the expression

$$[M] = \frac{(c - \text{CMC})}{N} \quad \dots(38)$$

where  $c$  is the total concentration of surfactant and  $N$  is the aggregation number in its micelles, then the expression for the overall rate constant becomes

$$\frac{1}{k_0 - k_p} = \frac{1}{k_0 - k_m} + \left( \frac{1}{k_0 - k_m} \right) \left[ \frac{N}{K(c - \text{CMC})} \right] \quad \dots(39)$$

Since the overall rate constant for the reaction  $k_p$  and the rate constant for the reaction in the absence of micelles  $k_0$  are readily obtained from kinetic data, a plot of  $1/(k_0 - k_p)$  versus  $[1/c - \text{CMC}]$ , which should be a straight line with slope  $= N/K(k_0 - k_m)$  and intercept  $= 1/(k_0 - k_m)$ , allows the calculation of  $k_m$ , the rate constant for the substrate complexed with the micelles and  $K$ , the binding constant of the substrate to the micelle.

Since surfactant concentrations are usually below  $10^{-1} \text{ M}$ , there will generally be little enhancement of the rate of reaction in the presence of micelles unless the product  $k_m K$  is  $10^2$  or more. Since the binding constant  $K$  depends on the extent of hydrophobic bonding between surfactant and substrate, it can be expected that  $K$  will increase with increase in the chain length of both the surfactant and the substrate. However, if the length of the hydrophobic group of the substrate is too long, it may be solubilized so deeply in the micelle that access to its reactive site by a reagent in an aqueous solution phase is hindered. In that case, solubilization will inhibit, rather than catalyze, the reaction.

### EMULSIFICATION BY SURFACTANTS

Emulsification—the formation of emulsions from two immiscible liquid phases—is probably the most versatile property of surface-active agents for practical applications. Paints, polishes, pesticides, metal cutting oils, margarine, ice cream, cosmetics, metal cleaners and textile processing oils are all emulsions and are used in emulsified form. An emulsion is a significantly stable suspension of particles of a liquid of certain size in another immiscible liquid. The term *significantly stable* means relative to the intended use and may range from a few minutes to a few years. At the present time, investigators in this field distinguish between three different types of emulsions based upon the size of the dispersed particles: (1) **macroemulsions**, the most well known type, opaque emulsions with particles  $> 400 \text{ nm}$ , easily visible under a microscope; (2) **microemulsions**, transparent dispersions with particles  $< 100 \text{ nm}$  in size that have been intensively studied during the 1970s because of their use in enhanced oil recovery; (3) **miniemulsions**, a type that is blue-white with particle sizes between the first two types ( $100\text{--}400 \text{ nm}$ ). Recently, **multiple emulsions** in which the dispersed particles are themselves emulsions, have been the subject of considerable investigation.

Two immiscible, pure liquids cannot form an emulsion. For a suspension of one liquid in another to be stable enough to be classified as an emulsion, a third component must be present to *stabilize the system*. The third component is called the **emulsifying agent** (or **emulsifier**) and it is usually a surface-active agent, although not necessarily of the type that is usually considered a surface-active agent (finely divided solids, for example, may act as emulsifying agents).

Macroemulsions and microemulsions have been discussed below in some details.

#### Macroemulsions

Macroemulsions are of two types based on the nature of the dispersed phase: oil-in-water (*O/W*) and water-in-oil (*W/O*). The oil-in-water type emulsion is a dispersion of a water-immiscible liquid or solution, always called the "oil" (*O*), regardless of its nature in an aqueous phase (*W*). The oil is, in this case, the 'discontinuous' (inner) phase; the aqueous phase is the 'continuous' (outer) phase. The water-in-oil type emulsion is a dispersion of water or an aqueous solution (*W*) in a water-immiscible liquid (*O*). The type of emulsion formed by water and oil depends primarily on the nature of the emulsifying agent and to a minor extent, on the process used in preparing the emulsion and the relative proportions of oil and water present. In general, *O/W* emulsions are produced by emulsifying agents that are more soluble in water than in the oil phase whereas *W/O* emulsions are produced by emulsifying agents that are more soluble in the oil than in water. This is known as the **Bancroft rule**. *O/W* and *W/O* emulsions are not in thermodynamic equilibrium with each other; one type is usually inherently more stable than the other for a particular emulsifying agent at a given concentration under a given set of conditions. However, the one type of emulsion can be converted to the other by changing conditions. This is called **inversion of the emulsion**.

These two types of macroemulsions are easily distinguished: 1. A macroemulsion can readily be diluted with more of the outer phase but not as easily with the inner phase. Consequently while *O/W* emulsions disperse readily in water, *W/O* emulsions do not. But they do disperse readily in oil. This method works best on dilute emulsions. 2. *O/W* emulsions have electrical conductivities similar to that of the water phase; *W/O* emulsions do not conduct current significantly. 3. *W/O* emulsions will be coloured by oil-soluble dyes whereas *O/W* emulsions show the colour faintly, if at all, but will be coloured by water-soluble dyes. 4. If the two phases have different refractive indices, microscopic examination of the droplets will determine their nature. A droplet, on focusing upward, will appear brighter if its refractive index is greater than that of the continuous phase and darker if its refractive index is less than that of the continuous phase. This clearly identifies the substance in the droplet if one knows the relative refractive indices of the two phases. 5. In filter paper tests, a drop of an *O/W* emulsion produces an immediate wide, moist area; a drop of *W/O* emulsion does not. If the filter paper is first impregnated with a 20% cobaltous chloride solution and dried before the test, the area around the drop immediately turns pink if the emulsion is *O/W* and remains blue (shows no colour change) if it is *W/O*.

There are a number of similarities between macroemulsions and foams: 1. They both consist of a dispersion of an immiscible state of matter in a liquid phase. Foams are dispersions of a gas in a liquid; emulsions are dispersions of a liquid in a second immiscible liquid. 2. The interfacial tension  $\gamma_i$  at the relevant interface is always greater than zero and since there is a marked increase in interfacial area  $\Delta A$  during the process (of emulsification or foaming), the minimum work involved is the product of the interfacial tension and the increase in interfacial area ( $w_{\text{min}} = \Delta A \times \gamma_i$ ). (3) The system will spontaneously revert to two bulk phases unless there is an interfacial film present that produces steric and/or electrical barriers to coalescence of the dispersed phase.

On the other hand, there are a number of significant differences between macroemulsions and foams: 1. The surfactants in the interfacial film of a foam cannot dissolve in the dispersed (gas) phase, while in a macroemulsion the solubility of the surfactants in the liquid being dispersed is a major factor determining the stability of the emulsion. 2. In macroemulsions, both *O* and *W* can serve as the continuous phase, i.e., both *O/W* and *W/O* emulsions are commonly encountered while in foams, only the liquid acts as the continuous phase.

**Formation of Macroemulsions.** In the formation of macroemulsions, one of the two immiscible liquids is broken up into particles that are dispersed in the second liquid. Since the interfacial tension between two immiscible pure liquids is always greater than zero, the dispersion of the inner liquid, which produces a tremendous increase in the area of the interface between them, results in a correspondingly large increase in the interfacial free energy of the system. The emulsion produced is consequently highly unstable thermodynamically, relative to the two bulk phases separated by a minimum surface area. It is for this reason that two immiscible liquids when pure, cannot form an emulsion. The function of the emulsifying agent is to stabilize this basically unstable system for a sufficient time so that it can perform some function. The emulsifying agent does this job by getting adsorbed at the liquid-liquid interface as an oriented interfacial film. The oriented film performs two functions: (1) It reduces the interfacial tension between the two liquids and hence reduces the thermodynamic instability of the system which results from the increase in the interfacial area between the two phases. (2) It decreases the rate of coalescence of the dispersed liquid particles by forming mechanical, steric and/or electrical barriers around them. The steric and electrical barriers inhibit the close approach of one particle to another. The mechanical barrier increases the resistance of the dispersed particles to mechanical shock and prevents them from coalescing when they do collide. In the formation of macroemulsions, the reduction of interfacial tension reduces the amount of mechanical work required to break the inner phase into dispersed particles.

**Factors Determining Stability of Emulsions.** The term *stability*, when applied to emulsions used for practical applications, usually refers to the resistance of emulsions to the coalescence of



their dispersed droplets. The rate of coalescence of the droplets in an emulsion is stated to be the only quantitative measure of emulsion stability. It can be measured by counting the number of droplets per unit volume of the emulsion as a function of time in a haemocytometer cell under a microscope. The rate at which the droplets of a macroemulsion coalesce to form larger droplets and eventually 'break' the emulsion, has been found to depend on the following factors:

1. **Physical nature of the interfacial film.** The droplets of dispersed liquid in an emulsion are in constant motion and, therefore, there are frequent collisions between them. If, on collision, the interfacial film surrounding the two colliding droplets in a macroemulsion ruptures, the two droplets will coalesce to form a larger one, since this results in a decrease in the free energy of the system. If this process continues, the dispersed phase will separate from the emulsion, and it will 'break'. The mechanical strength of the interfacial film is, therefore, one of the prime factors determining macroemulsion stability. Liquid-crystal formation can also stabilize the emulsion. By accumulating at the interface surrounding the dispersed particles, liquid crystals surround the particles with a high viscosity region that resists the coalescence of individual droplets.

2. **Existence of an electrical or steric barrier to coalescence of the dispersed droplets.** The presence of a charge on the dispersed droplets constitutes an electrical barrier to the close approach of two particles to each other. This is believed to be a significant factor only in *O/W* emulsions. In *O/W* emulsions, the source of the charge on the dispersed droplets is the adsorbed layer of surfactant with its hydrophilic end oriented toward the water phase. In emulsions stabilized by ionic surfactants, the sign of the charge on the dispersed droplets is always that of the amphipathic ion. In emulsions stabilized by non-ionic surfactants, the charge on the dispersed phase may arise either from adsorption of ions from the aqueous phase or from frictional contact between droplets and the aqueous phase. In the latter case, the phase with the higher dielectric constant is charged positively. In *W/O* emulsions, there is very little charge, if any, on the dispersed particles and experimental data indicate no correlation between stability and any charge present.

3. **Viscosity of the continuous phase.** An increase in the viscosity  $\eta$  of the continuous phase reduces the diffusion coefficient  $D$  of the droplets, since for spherical droplets of radius  $a$ ,

$$D = \frac{kT}{6\pi\eta a} \quad \dots(38)$$

As the diffusion coefficient is reduced, the frequency of collision of the droplets and their rate of coalescence are reduced. The viscosity of the external phase is increased as the number of suspended particles increases. This is one of the reasons that many emulsions are more stable in concentrated form than when diluted. The viscosity of the external phase in emulsions is often increased by the addition of special ingredients for this purpose, such as natural and synthetic 'thickening' agents.

4. **Size distribution of droplets.** A factor influencing the rate of coalescence of the droplets is the size distribution. The smaller the range of sizes, the more stable the emulsion. Since larger particles have less interfacial surface per unit volume than smaller droplets in macroemulsions, they are thermodynamically more stable than the smaller droplets and tend to grow at the expense of the smaller ones.

5. **Phase volume ratio.** As the volume of the dispersed phase in a macroemulsion increases, the interfacial film expands further and further to surround the droplets of dispersed material and the basic instability of the system increases. As the volume of the dispersed phase increases beyond that of the continuous phase, the type of emulsion (*O/W*) or (*W/O*) becomes basically more and more unstable relative to the other type of emulsion, since the area of the interface that is now enclosing the dispersed phase is larger than that which would be needed to enclose the continuous phase. It often happens, therefore, that the emulsion inverts as more and more of the dispersed phase is added, unless the emulsifying agent is so unbalanced as to be capable of forming only one type of emulsion.

6. **Temperature.** A change in temperature causes changes in the interfacial tension between the two phases, in the nature and viscosity of the interfacial film, in the relative solubility of the emulsifying agent in the two phases, in the vapour pressures and viscosities of the liquid phases, and in the thermal agitation of the dispersed particles. Therefore, temperature changes usually cause considerable changes in the stability of emulsions; they may invert the emulsion or cause it to break. Emulsifying agents are usually most effective when near the point of minimum solubility in the solvent in which they are dissolved since at that point they are most surface active.

#### Inversion of Macroemulsions

Macroemulsions may be changed from *W/O* or *O/W* and vice versa by varying the emulsification conditions. Thus: 1. The addition of water to the oil plus emulsifier produces *W/O* emulsion whereas the addition of oil to the same emulsifier plus water produces an *O/W* emulsion. 2. If the emulsifier is rendered more oil-soluble, it tends to produce a *W/O* emulsion and if it is rendered more water-soluble it tends to produce an *O/W* emulsion. 3. Increasing the ratio of oil to water tends to produce a *W/O* emulsion and vice versa. 4. As the temperature of an *O/W* emulsion stabilized with a polyoxyethylenated non-ionic surfactant is increased, the surfactant becomes more hydrophobic and the emulsion may invert to *W/O*.

#### Microemulsions

Although microemulsions have been produced commercially since the 1930s, their importance has become significant only since the 1970s, mainly as a result of the intense interest generated in them by laboratory and field tests that showed that they could increase the recovery of petroleum from reservoir rock. This is due to the ultra low interfacial tensions attained at the microemulsion-petroleum interface, a pre-requisite for the displacement of the residual petroleum in the capillaries of the rock. There has also been considerable recent interest in microemulsions of fluorocarbons as a result of the exceptionally high solubility of oxygen in these systems and their consequent use as oxygen carriers in cases of circulatory disfunction.

Microemulsions are transparent dispersions containing two immiscible liquids with particles of 10–100 nm diameter that are generally obtained upon mixing the ingredients gently. Macroemulsions, on the other hand, need intense agitation for their formation. Like macroemulsions, the microemulsions may be oil-in-water (*O/W*) or water-in-oil (*W/O*) type. Certain aspects of microemulsions remain controversial, such as the nature of the interface between the dispersed particles, the nature of the continuous phase and whether they contain one type of dispersed particles or micelles or more.

Whether one considers a microemulsion to be a solution of micelles, swollen by solubilized second liquid, in one liquid or a dispersion of tiny droplets of one liquid in a second liquid, the interfacial tension of the microemulsion against both these liquids must be close to zero. In the first case, the system is one-phase and, therefore, has no interface against either liquid as long as the micelles are capable of solubilizing more of the second liquid. In the second case, the interfacial area is so large that an exceedingly low interfacial tension must be present to permit formation of the microemulsion with so little work. In addition, the interfacial region must be highly flexible, either to permit the large curvature required to surround exceedingly small particles or to allow the easy transition from oil-continuous to water-continuous structure that is characteristic of microemulsions.

It is generally accepted that the clear, fluid (surfactant) phase between a non-polar phase (*O*) and an aqueous phase (*W*) in a three-phase system is a microemulsion. If the concentration of surfactant is increased, the middle phase incorporates both the *O* and *W* phases into a single (microemulsion) phase.

Microemulsions are generally prepared with more than one surfactant or with a mixture of a surfactant and a co-surfactant (e.g., a polar compound of intermediate chain length). The combination is usually required to provide the proper balance between hydrophilic and lipophilic properties for the required oil and water phases under the conditions of use. This balance can be determined experimentally by mixing the oil and water phases in the desired proportions with appropriate surfactant-co-surfactant

combination. It is advisable to use graduated vessels for this purpose so that the volumes of the phases can be measured. If a three-phase system is finally obtained instead of a one-phase microemulsion, the concentration of surfactant-co-surfactant mixture can be increased until both water and oil phases disappear by solubilization into the surfactant phase.

### Theories of Emulsions

The theories to decide the type of emulsion formed can be classified into : Qualitative theories and 2. Quantitative theories.

**1. Qualitative Theories.** All the theories which attempt to explain the formation of *O/W* and *W/O* emulsions are based on the empirical Bancroft rule. It is believed by some researchers that the interfacial region produced by the adsorption and orientation of the surface-active molecules at the liquid-liquid interface can have different interfacial tensions on each of its two sides; that is, the interfacial tension between the hydrophilic ends of the surfactant molecules and the water-phase molecules is different from the interfacial tension between the hydrophobic ends of the surfactant and the oil phase molecules. In the formation of emulsion, this interfacial tension would tend to curve so as to shorten the area of that side which has greater interfacial tension thus minimizing the interfacial free energy. A preferentially oil-soluble emulsifying agent would, of course, produce a lower interfacial tension at the oil interface, yielding a *W/O* emulsion; a preferentially water-soluble emulsifying agent would produce a lower interfacial tension at the water interface, yielding an *O/W* emulsion.

According to Schulmann (1954), however, the formation of the two types of emulsions can be explained on the basis of the difference in the contact angles at the oil-water-emulsifier boundary (Fig. 16): If, at the contact between oil, water and emulsifier, the oil contact angle (the contact angle, measured in the oil phase) is less than  $90^\circ$ , then the oil surface is concave toward the water producing a *W/O* emulsion. On the other hand, if at the same oil-water-emulsifier contact, the water contact angle is less than  $90^\circ$ , then the water surface is concave toward the oil, producing an *O/W* emulsion.

It may, however, be noted that if the oil contact angle is  $< 90^\circ$ , then  $\gamma_{OE} < \gamma_{WE}$  (i.e., the emulsifier is more hydrophobic than hydrophilic). If the water contact angle is  $< 90^\circ$ , then  $\gamma_{WE} < \gamma_{OE}$  and the emulsifying agent is more hydrophilic than hydrophobic. Thus, emulsifying agents with mainly hydrophilic character produce *O/W* emulsions whereas those with mainly hydrophobic character produce *W/O* emulsions.

**2. Quantitative Theory.** Davies (1957) developed a quantitative theory relating the type of emulsion formed to the kinetics of coalescence of the two types of droplets present : oil droplets and water droplets. According to this theory, the type of emulsion formed when oil and water are agitated together in the presence of an emulsifying agent is due to the relative rates of the two competing processes, viz., coalescence of oil droplets and coalescence of water droplets. Agitation is presumed to break simultaneously both the oil and water phases into droplets, with the emulsifying agent being adsorbed at the interface around these droplets. The phase that becomes the continuous one is that which has the faster rate of coalescence. If the rate of coalescence of the water droplets is much greater than that of the oil droplets, then an *O/W* emulsion is formed. If the rate of coalescence of the oil droplets is much greater than that of the water droplets, then a *W/O* emulsion is formed. When the rates of coalescence of the two phases are similar, then the phase of larger volume becomes the outer phase.

In general, hydrophilic groups in the interfacial film constitute a barrier to the coalescence of oil droplets whereas hydrophobic groups in the interfacial film constitute a barrier to the coalescence of water droplets. Hence, an interfacial film that is predominantly hydrophilic tends to form *O/W* emulsions whereas one that is predominantly hydrophobic tends to produce *W/O* emulsions.

### The Selection of Surfactants as Emulsifying Agents (Emulsifiers)

**1. The HLB Method.** The most frequently used method is known as the HLB (hydrophile-

lipophile balance) method. In this method (Griffin, 1949), a number (between 0 and 40) indicative of emulsification behavior and related to the balance between the hydrophilic and lipophilic (hydrophobic) portions of the molecule has been assigned to many commercial emulsifying agents. In addition, a similar range of numbers has been assigned to various substances that are frequently emulsified, such as oils, lanolin, paraffin wax, xylene, carbon tetrachloride, and so on. These numbers are generally based on the emulsification experience, rather than on structural considerations. Then an emulsifying agent—or better still, a combination of emulsifying agents—is selected whose HLB number is approximately the same as that of the ingredients to be emulsified. As expected from the definition of the HLB value, materials with high HLB values are *O/W* emulsifiers and materials with low HLB value are *W/O* emulsifiers. An HLB value of 3–6 is the recommended range for *W/O* emulsification while an HLB value of 8–18 is recommended for *O/W* emulsification.

It has been pointed out (Shinoda, 1968) that a single surfactant can produce either an *O/W* or a *W/O* emulsion, depending on the temperature at which the emulsion is prepared. At high oil concentrations, it depends on the ratio of surfactant to oil.

**2. The PIT Method.** An *O/W* emulsion made with a non-ionic surfactant may invert to a *W/O* emulsion when the temperature is raised; a *W/O* emulsion may invert to an *O/W* emulsion when the temperature is lowered. The temperature at which inversion occurs is known as the phase inversion temperature or PIT and is the temperature at which the hydrophilic and lipophilic tendencies of the surfactant (or surfactant-co-surfactant mixture) 'balance' in that particular system of *O* and *W* phases. For optimum stability, the Japanese pioneers in emulsion science—Shinoda and Saito—have suggested 'emulsification by the PIT method' in which the emulsion is prepared at a temperature  $2-4^\circ\text{C}$  below the PIT and then cooled down to the storage temperature (for *O/W* emulsion). This is because an emulsion prepared near the PIT has a very fine average particle size but is not very stable to coalescence. Cooling it down to a temperature considerably below the PIT increases its stability without significantly increasing its average particle size.

### GELS

Several lyophilic sols and a few lyophobic sols as well, when coagulated under certain conditions, change into a semi-rigid mass, enclosing the entire amount of the liquid within itself. Such a product is called a gel. The process of transformation of a sol into a gel is known as gelation.

Gel represents a liquid-solid system, i.e., a liquid dispersed in a solid. Amongst lyophilic sols, the examples are : gelatin, agar-agar, gum arabic, mastic and gamboge sols, etc. Amongst lyophobic sols, the examples are : silicic acid, ferric hydroxide, ferric phosphate sols, etc. The sols should be of sufficiently high concentration to facilitate the gelation process. Gels and gelation are very important in medicine and biology because plants and animals are primarily composed of gels. The gelation of macromolecular solutions is of great importance in technology. The formation of a glue layer in pastings, the gelation of pyroxlin and the production of artificial fibres are all gelation processes. Several processes in food and bread-baking industries make use of gelation. Clear raw hide which does not have a hair cover and from which leather is obtained is a gel.

**Preparation of Gels.** Gels may be prepared by any one of the following methods.

**1. Cooling of Sols of Moderate Concentrations.** Gels of gelatin and agar-agar, etc., are obtained by cooling their sols of moderate concentrations prepared in hot water. As has been mentioned earlier, the particles of hydrophilic sols are extensively hydrated. When cooled, the hydrated particles agglomerate together to form larger aggregates which ultimately form a semi-solid network entrapping the entire liquid within itself. The product is a semi-rigid gel structure.

**2. Double Decomposition.** The hydrophobic gels like silicic acid, aluminium hydroxide (commonly known as silica gel and alumina gel) are prepared by this method. By adding hydrochloric acid to an aqueous solution of sodium silicate, highly hydrated silicic acid gets precipitated. This when allowed to stand sets into a gel.

Similarly, by mixing solutions of sodium hydroxide and aluminium chloride of suitable concentration, a highly hydrated precipitate of aluminium hydroxide is obtained. On standing it changes into a gel.

**3. Change of Solvents.** This method is also used for preparing some of the hydrophobic gels. To take an example, when ethanol is added rapidly to a solution of calcium acetate of fair concentration, the salt separates out to give a colloidal solution. When allowed to stand, it undergoes gelation. The ultimate product is a semi-rigid gel of calcium acetate. The entire liquid is entrapped within.

**Elastic and Non-elastic Gels.** Gels are divided into two categories depending upon their properties. These are : elastic gels and non-elastic gels. The two varieties are distinguished chiefly by their behaviour on dehydration and rehydration. Elastic gels are reversible. When partially dehydrated, they change into a solid mass which, however, changes back into the original form on simple addition of water followed by slight warming, if necessary. Non-elastic gels, on the contrary, are irreversible. When dehydrated they become glassy or change into a powder which on addition of water and followed by warming does not change back into the original gel.

Gelatin, agar-agar and starch are examples of elastic gels. In these cases, dehydration and rehydration on exposure to water vapour are almost reversible even when the cycle is carried out more than once.

Silica, alumina and ferric oxide gels are examples of non-elastic gels. Thus, if silica gel is dehydrated, addition of water will not reset it into the form of a gel.

There is another point of difference between elastic and non-elastic gels. While elastic gels can imbibe water when placed in it and undergo swelling, non-elastic gels are incapable of doing so. This phenomenon is known as **imbibition** or **swelling**.

Another characteristic property possessed both by elastic and non-elastic gels is to undergo *shrinkage in volume* when allowed to stand. This phenomenon is called **syneresis**. Application of external pressure to a gel enhances syneresis. For amphoteric proteins, maximum syneresis is observed at the isoelectric point since the molecules then have equal number of opposite charges and this favours the shrinkage of the molecular framework of a gel. Syneresis decreases as the pH of the medium declines from the isoelectric point because the molecular chains acquire a charge of the same sign. The chains unfold and repel one another.

Some of the gels, particularly gelatin (reversible gel) and silica (irreversible gel), liquefy on shaking, changing into the corresponding sol. The sol on standing reverts back to the gel. This phenomenon of reversible sol-gel transformation is generally referred to as **thixotropy**.

#### Importance and Application of Colloids

Colloids play a very important role in everyday life as well as in industry, agriculture, medicine and biology. The following discussion, therefore, will be of interest.

**1. Foods.** Many of our foods are colloidal in nature. For example, milk is an emulsion of fat dispersed in water. It is stabilised by casein which itself is a lyophilic colloid and, being a protein, is a nutrient of great value. Gelatin is added to ice cream as a protective agent so as to preserve its 'smoothness'. Whipped cream, fruit jellies, salad dressings, eggs and a host of other materials used as food, are colloidal in nature.

**2. Medicines.** A number of medicinal and pharmaceutical preparations are emulsions, i.e., colloidal in nature. It is believed that in this form they can be more effective and are easily assimilated. Colloidal calcium and gold, for instance, are administered by injections to raise the vitality of the human system.

**3. Industrial goods.** Soap, the index of modern civilization, is a colloidal electrolyte. The same is true of a series of newer detergents and wetting agents that have been produced in recent years. Paints, varnishes, enamels, celluloses, resins, gums, glues and other adhesives; rayon, nylon, terylene,

textiles, leather, paper, etc., are all colloidal in nature. Latex, from which rubber is obtained, is suspension of negatively charged colloidal particles of rubber. Industrial processes such as tanning, dyeing, lubrication, etc., are of colloidal nature. This list is by no means exhaustive and can be extended further.

**4. Rubber-plating.** The negatively charged particles of rubber (latex) are made to deposit on to wires or handles of various tools (in order to insulate them) by electrophoresis. The article to be rubber-plated is made the anode. The rubber particles migrate in an electric field towards the anode and get deposited on it.

**5. Chrome-tanning.** The chrome-tanning of leather is brought about by the penetration of positively charged particles of hydrated chromic oxide into the leather. The rate of penetration can be increased by applying an electric field, i.e., by the process of electrophoresis.

**6. Cottrell precipitator.** Smokes and dusts are a nuisance and create health problems in industrial areas. Actually these are dispersions of electrically charged colloidal particles in air. The removal of these particles from air involves the principle of electrophoresis. The air from a furnace or an industrial plant carrying these particles is passed between metal electrodes maintained at a high difference of potential (about 50,000 volts). The particles are discharged and deposited as precipitates on the oppositely charged electrodes from which they can be scrapped mechanically.

**7. Sewage disposal.** Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry electric charge and, therefore, do not settle down easily. On creating an electric field in the sewage tank, these particles migrate to the oppositely charged electrodes, get neutralised and settle down at the bottom. It will be seen that here, too, the electrophoretic property of colloids has been made use of.

**8. Clarification of water.** Sometimes slight turbidity is noticed in water. This is due to the presence of negatively charged particles of very fine clay. The addition of potash alum or aluminium sulphate furnishes the trivalent aluminium ions ( $Al^{3+}$ ) which cause the coagulation of the clay particles, which, therefore, settle down leaving water in clear state.

**9. Detergent action of soap.** Most of the dirt or dust sticks on to grease or some oily material which somehow gathers on cloth. As grease is not readily wetted by water, it is difficult to clean the garment by water alone. The addition of soap lowers the interfacial tension between water and grease and this causes the emulsification of grease in water. The mechanical action, such as rubbing, etc., releases the dirt.

**10. Artificial rain.** Clouds consist of charged particles of water dispersed in air. Rain is caused by the aggregation of these minute particles. Some workers have succeeded in causing such aggregation by artificial means such as by throwing electrified sand from aeroplanes.

**11. Formation of deltas.** The deltas at the mouths of great rivers are formed by the precipitation of the charged clay particles, carried as suspension in the river water, by the action of salts present in sea water.

**12. Smoke screens.** Smoke screens are used in warfare for the purpose of concealment and camouflage. Smoke screens generally consist of very fine particles of titanium oxide dispersed in air and are ejected from aeroplanes. As titanium oxide is very heavy, the smoke screen drops down rapidly as a curtain of dazzling whiteness.

It is worth mentioning that since 1950, colloid science has generated a number of important fields such as the study of polymers, semiconductors, liquid crystals, membranes and vesicles. Micellar aggregates have served as an important bridge between microscopic and macroscopic chemical species in the development of new technologies. The importance of colloid science is now fully recognized. It is the basic foundation of almost all fields of solution science.

## I. Review Questions

1. Carefully distinguish between a molecular solution, a colloidal dispersion and a coarse dispersion.
2. Explain the use of (a) dialysis (b) electro-dialysis and (c) ultrafiltration in the purification of colloidal solutions.
3. Discuss the electrical properties of colloidal solutions and explain the action of electrolytes on them.
4. Discuss the origin of charge on colloidal particles. What is meant by electrical double layer? What is DLVO theory?
5. What are protective colloids? Explain how a lyophilic colloid can stabilise a lyophobic colloid.
6. Describe various methods for the determination of the size of colloidal particles.
7. What are colloidal miscelles? Discuss the structure of miscelles in polar and non-polar media.
8. What does HLB stand for? What is its significance?
9. Define critical micelle concentration. Show graphically how the physical properties of solutions of surfactants such as molar conductance, surface tension, osmotic pressure change at the critical micelle concentration.
10. How is CMC related to free energy change, enthalpy change and entropy change accompanying the process of micelle formation?
11. State and explain the Laplace's law. Discuss solubilization from the point of view of the phase rule.
12. Compare and contrast micellar catalysis from enzyme catalysis.
13. What are emulsions? Discuss the methods used in finding the type of an emulsion. How are emulsions prepared?
14. What are gels? How would you distinguish between elastic and non-elastic gels.

CHAPTER  
33

## SURFACE CHEMISTRY

## ADSORPTION BY SOLIDS

Surface chemistry research is an interdisciplinary area on the frontiers of physical chemistry, chemical physics, materials science and nanoscience. Its impact on industrial processes and technology has grown over the years and will continue to grow in future. Residual unbalanced forces exist on the surface of a solid. As a result of these residual forces, the surface of a solid has a tendency to attract and retain molecules of other species with which it is brought into contact. As these molecules remain only at the surface, their concentration is more at the surface than in the bulk of the solid. The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as **adsorption**. Solids, when finely divided, have a large surface area and, therefore, show this property to a large extent. The solid that takes up a gas or vapour or a solute from a solution, is called the **adsorbent** while the gas or vapour or the solute, which is held to the surface of the solid, is called the **adsorbate**. Colloids, on account of their extremely small dimensions, possess enormous surface area per unit mass and are, therefore, good adsorbents. The examples are charcoal, silica gel, alumina gel, clay, etc.

**Adsorption** is to be carefully distinguished from **absorption**. The latter term implies that a substance is uniformly distributed throughout the body of a solid or a liquid. Thus, while water vapours are absorbed by anhydrous calcium chloride, these are adsorbed by silica gel. Similarly, while ammonia is absorbed in water, it is adsorbed by charcoal. When a hot crucible is cooled in atmosphere, a film of moisture collects at its surface. This is a case of adsorption of water vapour on the material of the crucible. Charcoal when mixed with a coloured solution of sugar, adsorbs the colouring matter and is used as a decoloriser. McBain suggested the use of the term **sorption** to describe a process in which both absorption and adsorption take place simultaneously.

Adsorption is not necessarily a physical phenomenon always. It may as well be a chemical process involving chemical interaction between the surface atoms of the adsorbent and the atoms of the adsorbate. This type of adsorption is known as **chemisorption**. For example, oxygen is chemisorbed by carbon and hydrogen is chemisorbed by nickel under suitable conditions. In each case, a stable surface compound, frequently referred to as **surface complex**, results.

Chemisorption differs from physical adsorption (or physisorption) in the following respects:

1. Physical adsorption occurs appreciably only at very low temperatures falling below the boiling point of the adsorbate. Chemisorption can occur at all temperatures.
2. The magnitude of chemisorption increases with rise in temperature. This is just as the magnitude of a chemical reaction in a given time increases with rise in temperature. Physisorption, on the other hand, decreases with rise in temperature.
3. The heat evolved in chemisorption is very high, varying generally between 40–400 kJ mol<sup>-1</sup>, as in many chemical reactions. The heat evolved in physisorption, on the other hand, is quite low, varying generally between 4–40 kJ mol<sup>-1</sup>.