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Comments: The highlighted and the quoted portions are must read. This portion is totally theory based and only one derivation (Determination of N by Perrin's method) is present.

Reference:

Physical Chemistry: P.C. Rakshit

THE COLLOIDAL STATE

XXV.1. The Colloidal System

The subject of colloidal system had a diffuse beginning. Various stray and independent investigations carried out by Richter, Berzelius, Selmi, Graham and others in the nineteenth century yielded results from which systematisation followed to form, in the early part of the present century, a sort of nucleus around which the science of colloidal system developed and rapidly proliferated.

i) Substances like sand, powdered glass, barium sulphate, etc. when added to water sink to the bottom of the container; others such as naphthalene powder, charcoal, etc. when added remain afloat in water as a distinct phase. This is not only true for water as the medium but for many other solvents as well. On the other hand lumps of sugar or salt in water or naphthalene in benzene form true solutions in which the phase distinctions between the components—solutes and solvents—are obliterated.

Between these extremes of heterogeneous coarse suspensions and homogeneous true solutions, exist systems with properties intermediate between those of the former two. Besides, these systems have sets of properties which can be called as characteristically theirs only. Examples of such systems are provided by suspensions of gum in water, fine suspension of soil in water, suspension of NaCl in alcohol or of arsenious sulphide in water. That these suspensions are really different from true solutions can be shown by allowing them to percolate through parchment or cellophane papers, as Graham did. The true solutions will get through, but these set of suspensions will not; only the continuous medium water or benzene etc. will seep through. But these suspensions pass through ordinary filter paper like true solutions. The solute particles in true solutions are molecularly dispersed ($\sigma = 10^{-8}$ cm approx) and are invisible. In the case of these fine suspensions, the particles are bigger (σ between $10^{-7} \sim 10^{-4}$ cms approx) and can be seen either with the help of a high powered microscope or at least can be indirectly discerned utilising some optical effect (Tyndall effect).

Substances in such a state of subdivision and suspended or dispersed in a continuous medium as to demonstrate the above effects are said to be in the colloidal state. The colloidal system, often called a sol, would thus consist of a dispersed phase (gum etc.) in dispersion medium (water, benzene etc). A rigorous definition of a colloidal system is difficult to lay down, a workable definition can be given in the following words:

“A colloidal system is a two-phase heterogeneous system in which one phase is dispersed in a fine state of subdivision (ranging from 1μ to $50 m\mu$ approx) in another medium termed the continuous or dispersion medium.” In actual instances, the size limits are not rigid and may vary on either side but most systems conform to the above description.

(Although we shall be dealing chiefly with colloidal systems in which the disperse phase is a solid and dispersion medium a liquid, called sols, such as a sol of As_2S_3 in water, the dispersion medium may also be a gas, a liquid or a solid. In foams, we have a gas dispersed in liquid, where as in smokes the disperse phase is a solid in gas medium. In fogs liquid is dispersed in gas medium. When a liquid is dispersed in another liquid, it is often called an emulsion as in milk. Ruby glass or carbon in steel are examples of one solid dispersed in another solid.)

XXV.2. Preparation of Colloidal Systems

The preparation of a sol usually involves three operations:

(i) To obtain the substance directly or indirectly in the desired state of fine division in the dispersion medium;

(ii) To add protective or stabilising agents to maintain the stability of the system. In many instances, however, the protective agents are inherently present in the reagents used in obtaining the finely divided substance in process (i). In other cases, stabilising agents are to be specially added.

(iii) To purify the colloidal system from excess of reagents used or by-products formed by suitable techniques.

There are two general ways (a) *Condensation method* and (b) *Disintegration or dispersion method*, in which a disperse phase can be formed in a medium.

(a) **Condensation Methods.** It is an indirect process for the preparation of a sol. The substance which is to be dispersed is *generated in situ* by some chemical reaction (or sometimes by physical change) under controlled conditions of temperature, concentration, agitation etc. to form insoluble particles of the substance having sizes within the colloidal range. The chemical reactions may be different in different cases, such as oxidation, reduction, hydrolysis, metathesis, etc. Certain specific examples rather than a description in general terms will clarify the procedures.

Gold Sol. A gold sol is conveniently prepared by *reduction* of chlorauric acid say with formate or hydrazine.

Sulphur Sol. Sulphur sols are easily obtained by *oxidation* of H_2S solution by oxygen or SO_2 or some dilute oxyacid and then purified.

When a solution of sulphur in alcohol is poured into water a sulphur sol is formed. The addition of a solution of a substance to a solvent in which the solute is insoluble is often a convenient process of preparing a sol.

Nickel Sol. When a benzene solution of nickel carbonyl is heated, a fine nickel sol is obtained through the *dissociation* process, $Ni(CO)_4 \rightleftharpoons Ni + 4CO$.

Silver iodide Sol. To a suitably dilute solution of KI is added $AgNO_3$ solution in a quantity appreciably less than the stoichiometric requirement. Silver iodide, produced by *metathesis*, has particle sizes in the colloidal domain and the whole system is stabilised by a small amount of iodide ions present in solution. The unwanted excess of all ions are removed during subsequent purification by dialysis as described later.

Similar metathetical processes are employed in many instances, such as in preparation of $BaSO_4$ sol from $Ba(SCN)_2$ and $(NH_4)_2SO_4$; As_2S_3 from As_2O_3 and H_2S ; silicic acid sol from sodium silicate and hydrochloric acid etc.

Ferric oxide Hydrosol. When small quantities of ferric chloride are added intermittently to almost boiling water, ferric hydroxide is formed in colloidal state. Small quantities of ferric ions, and possibly hydrogen ions stabilise the sol. The excess of hydrochloric acid formed is removed during the purification of the sol. Many such oxide hydrosols, such as aluminium oxide, tin oxide, thorium oxide etc. are prepared by similar hydrolysis of their chlorides or nitrates.

(b) **Dispersion Methods.** This technique is a direct method and consists in finely pulverising the substance to be dispersed in the medium which is to constitute the dispersion phase. Sometimes the pulverisation is spontaneously effected; for instance, when gelatine is heated in water with stirring, gelatine sol is produced. Sols of agar, gum-arabic, etc. are obtained in the same fashion and no stabilising agents need be added nor any purification necessary.

In certain instances, pulverisation to the colloidal range is done through electric sparking. For example, dilute sols of gold, silver, platinum, etc. are prepared by bringing close two electrodes of the metal concerned under water so as to permit electric discharge between them. Fine particles of the metal in the colloidal

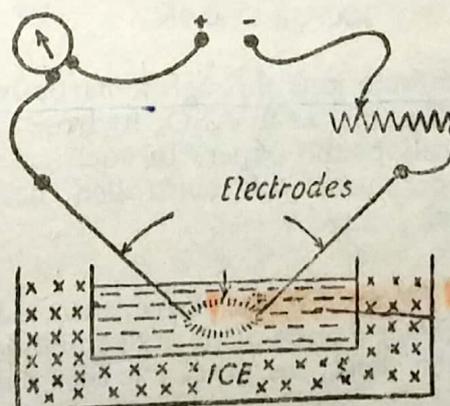


Fig. XXV.1 Bredig's process

range are formed by this process, Bredig's process. Employing the same technique, using alternate current between conducting metal electrodes or between partially conducting electrodes of inorganic compounds dipped under water or organic solvents, different hydrosols or organosols were prepared by Svedberg.

Freshly precipitated substances in some cases can be brought to the colloidal state by shaking with small quantities of suitable reagents or sometimes by continued washing with water alone. Thus freshly precipitated $\text{Fe}(\text{OH})_3$, if shaken with a dilute solution of FeCl_3 , would give rise to ferric oxide sol. This process of dispersing a fine precipitate into colloidal state by adding a little specific electrolyte is called peptisation. Freshly precipitated tungstic oxide or vanadium oxide will turn into a sol on continued shaking or washing with water.)

Dispersion is also sometimes carried out by the use of atomiser as in the dispersion of a liquid in a gas. 'Colloid mills' are also used in mechanically grinding a solid dipped in the dispersion medium.

Purification of Sols. The final stage in sol preparation is its purification. Not all sols, as mentioned earlier, need this purification process. Even for those systems where purification is imperative, it is carried out only to a certain limit as complete purification induces instability of the sol.

The property common to all sols, namely the inability of the disperse phase to percolate through some membranes such as parchment paper, cellophane etc. where as the dispersion medium, free ions, molecules in solution etc. can easily get through, is taken advantage of in purifying a sol. The most commonly employed techniques are dialysis and electro dialysis.

Dialysis. The sol to be purified is taken in a parchment paper or cellophane bag which is kept suspended in a basin containing sufficient amount of water (or the dispersion medium of the sol if it be not water), as in Fig. XXV.1a. The unwanted ions in the sol move out through the cellophane wall while some amount of solvent from outside may enter the bag. From time to time, the solvent in the basin is replaced and the process allowed to continue for several days. To check the extent of purity, small portions of the sol are pipetted out and its electrical conductance is measured. When the conductance reaches a sufficiently low limit as desired by the experimenter, the process is stopped. For reasons to be described later, extreme purification induces instability of the sol. Such a process of separation or removal

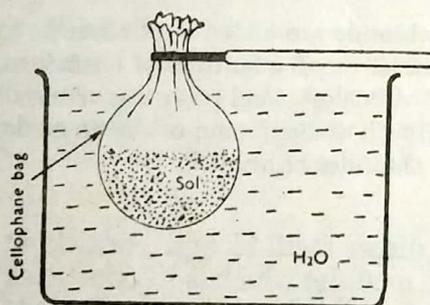


Fig. XXV.1a Dialysis

of soluble ions through a partially permeable membrane is called dialysis. In certain sols, as in Al_2O_3 hydrosol, the disperse phase is too small to be retained by cellophane paper. In such cases, dialysis is carried out at somewhat higher temperatures with controlled heating. The particles thereby grow bigger in sizes.

Electrodialysis. To accelerate the process of purification and also to achieve a greater degree of purity sometimes the dialysis is carried out in a direct current electric field; the process is then called electrodialysis.

A simple electro dialyser consists of three detachable chambers A, B, and C.

The middle chamber B which contains the sol is separated on either side from A and C by partitions of cellophane paper D and E (Fig. XXV.2). The side-chambers A and C are filled with water in which are inserted two Pt-gauze electrodes. A 220-volts direct current field is applied to the system with a carbon-filament bulb in series. On passing electric current, the ionic impurities travel outwards, cations to the negative electrode and anions to the positive. For hastening the process, the water in A and C are drawn out from time to time and replaced afresh. With gradual removal of ions, the resistance increases and the fall in current strength is revealed from the bulb in circuit. The process is stopped when a certain degree of purity is attained.

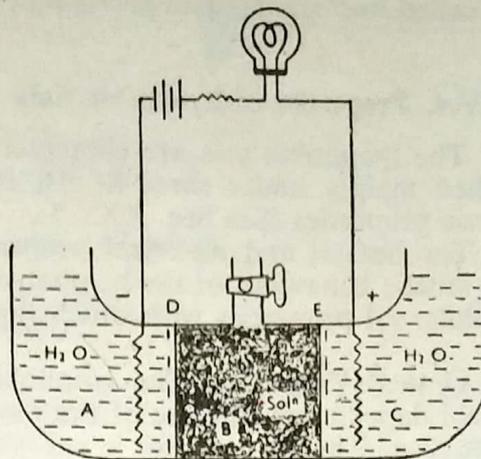


Fig. XXV.2. Electrolysers (diagrammatic)

XXV.3. Classification of Colloid Systems

The colloidal systems are sometimes classified into two broad groups: (1) Reversible sols and (2) Irreversible sols. In the reversible sols, the disperse phase is spontaneously distributed in the surrounding medium due to thermal energy. Such spontaneous dispersion leads to some equilibrium size distribution corresponding to minimum value of thermodynamic potential. The reversible sols are characterised by very low interfacial tension and hence low interfacial energy, 0.01 ergs/cm² approx. Once the disperse phase is thrown out of colloidal state its redispersion is easily achieved.

The 'irreversible sols' are thermodynamically unstable; these have a natural tendency to be thrown out of the dispersion medium from the colloidal state to the macrostate. The concept of their colloidal stability is a kinetic one. It is with considerable difficulty that the substance in such cases are taken into the colloidal state.

But the more common way of classifying the colloids is to divide them into two groups (a) Lyophobic and (b) Lyophilic sols. Lyophobic sols are those which have no spontaneous tendency to pass into the colloidal state and are obtained with difficulty; hence these are irreversible in character, e.g., gold, As₂S₃ etc. Lyophilic sols are quite easily formed by the spontaneous dispersion of a substance in the dispersion medium; these are reversible and even if thrown out of medium, they easily revert back to the colloidal state, e.g., gums, starch etc. There are other properties by which these two groups of sols are distinguished.

(i) Very small amounts of neutral electrolyte solutions ^{NaNO₃ or NaCl} bring about precipitation of the disperse phase in lyophobic sols, but have hardly any effect on the lyophilic ones.

(ii) Lyophobic sol particles carry charges, either positive or negative, and migrate towards the proper electrode when placed in an electrical field. The charges on the lyophilic sol particles are not conspicuous, though truly lyophilic sol particles do move towards one electrode or the other very slowly.

(iii) The viscous properties of the two groups are widely different. Lyophilic sols have very high viscosities whereas the lyophobic ones have viscosity almost equal to that of the dispersion medium. The lyophobic sols can be obtained only in small concentrations but lyophilic ones can be prepared at high concentrations. The disperse phase particles are often highly solvated in lyophilic systems but not so in lyophobic ones.

Sols of AgI, SnO₂, Pt, etc. are all lyophobic in character whereas agaragar, gum arabic, etc. are lyophilic. Examples are also available where the systems

belong to the border line. Ferric hydroxide, chromic hydroxide sols are pronouncedly lyophobic but these also possess a certain amount of lyophilicity. Sols are called *hydrophobic* and *hydrophilic* when the medium is water.

XXV.4. Properties of Lyophobic Sols

The lyophobic sols are characterised by many unique properties which are studied mainly under three heads, optical properties, electrical properties and kinetic properties (See Sec. XXV.7).

The optical and electrical properties of lyophobic sols are taken up here. The kinetic behaviour of the lyophobic systems will be dealt with later along with lyophilic sol properties with which these are similar.

Optical Properties. The lyophobic sols are often coloured. The colour of the sol depends on the size of the particles in suspension and sometimes on the shape also. Thus, a gold sol is red when the particles are extremely fine but the sol is blue when the dispersed particles are bigger. But the most important property of lyophobic sols is the scattering of light by the suspended particles, commonly known as the *Tyndall effect*. Visible light has wave lengths spanning over 350 $m\mu$ and 100 $m\mu$ approximately and these are scattered when they are incident on

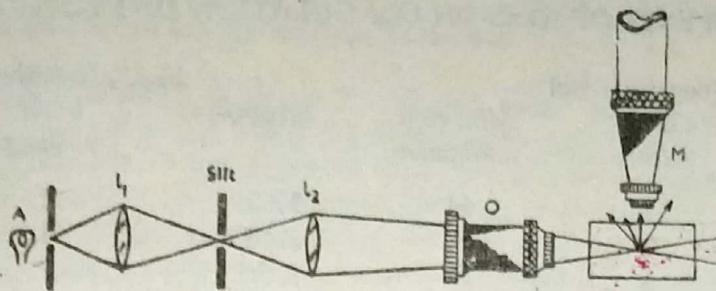


Fig. XXV.3. Ultra-microscope (Zsigmondy)

✓XXV.5. Electrical Properties of Lyophobic sols

The electrical properties of lyophobic sols are studied from their behaviour (a) towards added electrolytes and (b) in applied electric fields. These two are closely interrelated and a proper understanding of their behaviour also leads to an explanation of the fundamental question of the stability of the sols.

(a) Effect of addition of electrolytes to lyophobic sols. It has been stated earlier that while purifying a sol by dialysis the system should not be completely freed from all foreign ions. The presence of small traces of suitable ions is necessary to impart stability to the sol. If the system be divested of all ions, the colloid particles grow bigger and are ultimately thrown out as precipitates. रिश्ता

While small amounts of specific foreign ions are essential, the addition of comparatively larger amounts of a neutral electrolyte proves destructive to the stability of the sol. For example, a small quantity of NaNO_3 solution, when added to, say, 10 c.c. of a dialysed AgI -sol, will cause the colloidal silver iodide particles to precipitate out as a flocculant gelatinous mass, often called coagulum, leaving a clear supernatant liquid. This phenomenon of coagulating the sol particles is known as 'floculation'. If insufficient sodium nitrate be added, either no floculation or partial floculation will occur. Such coagulation is found with other lyophobic sols also.

Experimental observations on the coagulation of various sols with different electrolytes led to two general conclusions:

(i) Ions carrying the charge opposite to that of the colloid particles are effective in inducing coagulation.

(ii) The larger the valency of the coagulating ion, the smaller is the quantity of electrolyte (containing that ion) necessary to flocculate a given amount of sol in a given time.

These generalisations are often mentioned as Hardy-Schulze rule. There may be some exceptions to rule (ii) above where conspicuous adsorbability of the coagulating ion may violate the principle. सूचना

Continuing with our example of silver iodide sol, it can be coagulated by, say, NaNO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Th}(\text{NO}_3)_4$. Silver iodide sol has negatively charged dispersed particles. So the positive ions Na^+ , Ba^{++} etc. are the coagulating ions. This is established from the fact that if NO_3^- ion were responsible for flocculation, then the minimum molar concentrations of the different electrolytes used in equal volumes to coagulate a definite amount of sol completely in just a given time would have been in the ratio 4 : 3 : 2 : 1. But experimentally it is found that the concentrations of ions of higher valency needed is much less than this. Thus if x c.c. of 0.001 M NaNO_3 is required, then x c.c. of $0.0001 \text{ M Ba}(\text{NO}_3)_2$ solution would be quite sufficient for the same coagulation. This proves that oppositely charged ions are responsible for coagulating the dispersed phase and that equicoagulating concentrations of these ions decrease as the valencies increase. On the other hand, if the dispersed particles are positively charged as in ferric oxide sol, the anions would be responsible for coagulation and the equicoagulating concentrations of anions (added in equal volumes) would decrease with increase in their valencies. Some data are quoted below from the literature in respect of As_2S_3 (negative) sol and Fe_2O_3 (positive) sol. 1:1

(b) **Effect of applied electric field on Lyophobic sols.** If two electrodes are inserted in a lyophobic sol (Fig. XXV.4a) the disperse phase migrates slowly either to the cathode or to the anode. This indicates that the colloid particles are charged either positively or negatively. In fact, the flocculation of lyophobic sols by addition of electrolytes also suggested the same. The migration of the colloiddally dispersed particles in electric field is called *electrophoresis* or sometimes, though not happily, *cataphoresis*.

On the other hand, if the sol is enclosed by compact diaphragms, so that the motion of the sol particles be mechanically prevented and the two electrodes are inserted in the dispersion medium outside the diaphragm (Fig. XXV.4b), then the dispersion medium moves through the diaphragm towards one of the electrodes. This relative motion of the dispersion medium in the electric field is known as *electroosmosis* or *endosmosis*.

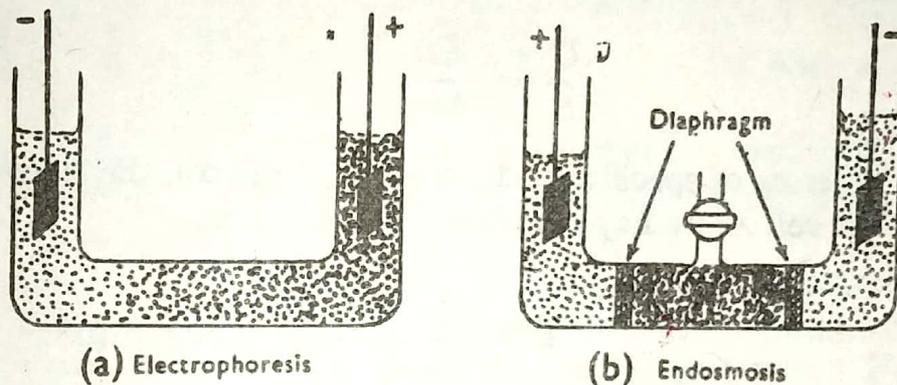


Fig. XXV.4

Both electrophoresis and electroosmosis observed with colloidal systems are just the specific illustrations of the general interface phenomena, namely the electrokinetic effects. These therefore can be explained in terms of the electrical double layer theory as before (section XXI.9 et seq.). In colloidal systems, due to smallness of sizes of sol particles, a very large surface area exists. Because of this, the adsorption is very pronounced and the resultant electrokinetic phenomena are conspicuously displayed. Surrounding the charged sol particles, there exist double layers trailed by diffuse layers with their zeta-potentials. The zeta-potentials play an important role in the stability of colloidal state and it is necessary to determine them. The experimental determination of zeta-potential of sols is done either by electrophoresis or by endosmosis. There are different ways of carrying out the two techniques, we shall discuss here briefly one for each.

II. Streaming potential : In electroosmosis, it is seen that there results a mechanical flow of liquid across a diaphragm or a capillary from an application of an electrical potential. The reverse of this process, called streaming potential, involves a generation of a potential difference between the liquids on either side of a diaphragm or a capillary, when a solvent is forced to flow through the latter by hydrostatic pressure. *Liquid/solvent flows, as a result, Potential generates, no electrode*

III. Electrophoresis : The third type of electrokinetic phenomenon is electrophoresis, also commonly called cataphoresis. Fine grains of solid or liquid or gas held in suspension in a solvent, such as, colloidal particles of clay, emulsion globules or foams, move towards electrodes when an external field is applied. Electrophoresis, thus, constitutes a relative motion of one phase past another phase (viz. dispersion medium) and is, like electroosmosis, a mechanical effect at the expense of an externally applied electrical field.

IV. Sedimentation Potential : The last of these phenomena, and incidentally, also the last one to be discovered, is the sedimentation potential first studied by Dorn. It stands in the same relationship to electrophoresis as does streaming potential to endosmosis. If small grains of an insoluble solid, such as clay particles, are allowed to fall in sufficient number through a long vertical column of dilute solution, an electrical potential difference can be registered between any two points, not in the same horizontal plane, of this column of solution. The points chosen should preferably be far from each other and sufficient number of particles should stream down the solution to cause an effect appreciably enough for experimental discernment.

Different ideas regarding the structure of the double layer at an interface have been put forward. Helmholtz, to whom the original concept of the double layer is due, Gouy and Stern, all held separate views as to its structure. The idea of Stern, mostly accepted nowadays, is briefly described here with qualitative representations in Fig. XXI.11. According to him, in the case of a solid-liquid interface, the charges in the first part of the double layer remain fixed on the solid surface at l_1 ; the solution side of the double layer containing the counter ions can be divided into two parts—a fixed part (l_2) of the counter ions at a distance of a few angstroms from the solid surface and another diffuse portion of counter ions with concentration gradually falling off (Fig. XXI.11a) or rising (Fig. XXI.11b) to that uniform value as prevalent in the bulk, say at l_3 .

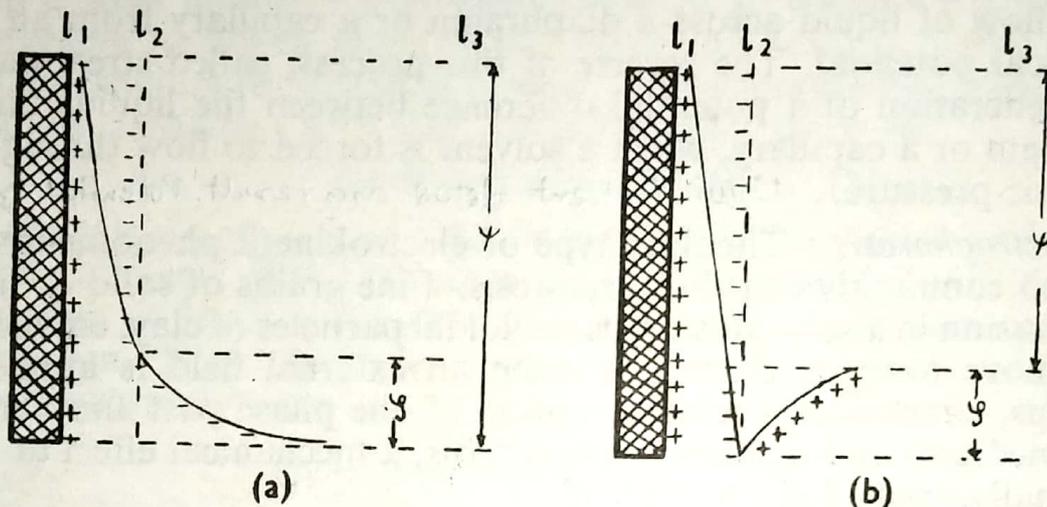


Fig. XXI.11

The ions in the diffuse layer have a limited freedom of movement as compared to that of ions of like charge in the bulk of solution. Under a more or less moderately drastic external condition viz., the impression of an electrical potential difference or the mechanical application of hydrostatic pressure, the ions in the diffuse part of the double layer along with the solvent molecules in the region may be swept away tangentially from their usual place of habitation near the solid surface.

(In the undisturbed conditions, there exists a sharp drop of potential from the solid surface (l_1) to the fixed part (l_2) of the double layer on the solution side. It is then followed by a gradual change in potential across the diffuse part upto the bulk of the solution (Figs. XXI.11). The total potential drop from the solid surface (l_1) to the bulk of the solution is called the double layer potential ψ , while the difference in potential between the fixed part of the double layer (l_2) and the solution bulk (i.e., the potential change across the diffuse portion of the double layer) is termed zeta potential or electrokinetic potential and conventionally represented by the symbol ζ .)

(e) Origin of charge and the mechanism of flocculation: Theories of stability of sols.

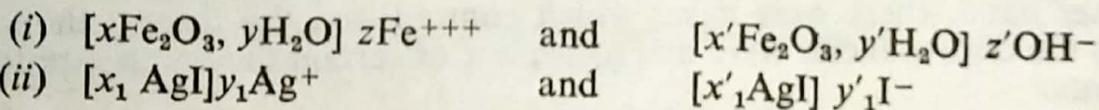
The conspicuous effect of ions of particular charge type on the coagulation of sol and the latter's behaviour in applied electric field are indicative of the presence of charges on the surface of the colloidal units. The way of acquirement of these charges is mainly by adsorption and, sometimes, by self-dissociation. Structurally a colloidal unit may be viewed as an aggregate of thousands or tens of thousands of molecules forming a sort of microcrystal.

These microcrystals have enormous surface area and hence pronounced adsorption characteristics. They adsorb ions, either positive or negative, from the environmental medium in which they are prepared. Often they exhibit a preference for those ions which are common with one of the ions composing the colloidal microcrystal.

Thus, the colloidal particles of Fe_2O_3 sol, in its preparation from hydrolysis of FeCl_3 by hot water, adsorb Fe^{+++} ions and acquire a positive charge. Fe^{+++} ions are common to both microcrystals and medium. But when Fe_2O_3 sol is prepared from FeCl_3 soln with excess of caustic soda solution, the sol particles adsorb OH^- ions and become negatively charged, the hydroxyl ions being common to the medium and the hydrated colloidal particles of Fe_2O_3 .

To cite another common instance, the colloidal silver iodide particles have a negative charge due to adsorption of I^- ions when excess potassium iodide is used in its preparation. But if in its preparation excess AgNO_3 is used, the resulting sol particles carry a positive charge due to adsorption of Ag^+ ions.

The structures of the colloidal units of positively and negatively charged Fe_2O_3 sols, AgI sols, may be expressed as:



The preference for common ion adsorption stems from the fact that these ions easily fit in the lattice of the microcrystals. Other ions of similar charge or more or less of similar dimensions may also be adsorbed to impart charge to the colloidal particles. While in positively charged Al_2O_3 sols Al^{+++} ions (and some H^+ ions) are adsorbed by the colloidal particles, it is the adsorbed AlO_2^- ion which is responsible for the charge in the negative Al_2O_3 sols. Sulphide sols, such as As_2S_3 sol, are generally stabilised by adsorption of HS^- ions. The charges on metal sol particles are attributed to either the adsorption of OH^- ions from water or the dissociation of certain surface complexes formed on the metal bodies by the action of water, e.g., $[a\text{Pt}, b\text{PtO}_2] \text{Pt}(\text{OH})^{--}$.

Mechanism of flocculation. The fact that the colloidal particles are charged and that ions bearing charge opposite to that of the colloidal particles have pronounced flocculating power led to the adoption of the idea in primitive stages that flocculation was caused by direct adsorption of oppositely charged ions on the surface. This adsorption would neutralise the particle charge and thus favour coagulation. This idea, though partially true in a sense in specific cases, was found to be inadequate for many reasons and soon renounced. Since coagulation is related to the question of stability of colloidal system, we may therefore explain it from the theories suggested for stability.

Critical Potential theory for colloid stability. From our concept of electrical double layer at the solid-liquid interface, it is readily understood that each colloidal particle will have a double layer surrounding it. The solution part of this double layer consists of a fixed and a diffuse portion (Sec. XXI.9). The diffuse portion will predominantly contain ions bearing opposite charges. The same is true of the fixed part of the solution side of the double layer. Thus, in negatively charged As_2S_3 sol, each particle carries a number of stabilising HS^- ion on its surface. In the close neighbourhood of this particle, there exists in the solution side one layer of oppositely charged H^+ ions which are more or less fixed and beyond this is the diffuse portion also with H^+ ions predominance. When two such As_2S_3 colloid particles with their accompanying shrouds of diffuse layers approach each other, there is repulsion of similar charges and the particles are prevented from coalescing.

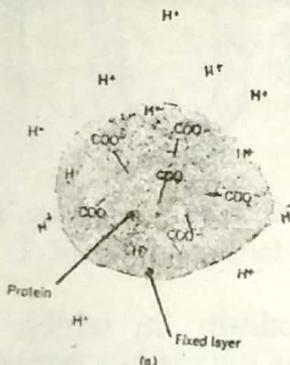


Fig. XXV.7. Colloid particle with fixed and diffuse layers (diagrammatic)

If now an indifferent electrolyte, say BaCl_2 , be added, Ba^{++} ions will be preferentially adsorbed on the fixed part of the solution side of the double layer. The colloidal particle together or with the fixed part of the solution side will now have a resultant surface density (σ) considerably less than before. The consequence will be the release of a number of H^+ ions from the diffuse part of the double layer. These will migrate to the bulk solution effecting a contraction of the value of the zeta-potential. It follows that, after addition of BaCl_2 , two As_2S_3 colloid particles can approach nearer because of contraction of the diffuse layer thickness.

When the contraction of double layer is quite large, there would be a considerable lowering of ζ -potential, the thermal motions then may overcome the electrical effect and cause coagulation.

The measurements of zeta-potentials in many sols indicate that when coagulation starts, the ζ -potential values are lowered down to the range 0.02 to 0.05 volts. Ellis and Powis, from a series of experiments, suggested that for a given sol there is a critical value of ζ -potential at which coagulation commences. This is true irrespective of the nature of the electrolytes used for flocculation. Plenty of instances were found supporting the critical zeta-potential theory of colloidal stability. On the other hand, there were cases which contradicted the theory, though in many cases the discrepancies were due to neglect of certain factors in ζ -potential measurements.

XXV.6. Properties of Lyophilic sols

Certain distinctive features of lyophilic colloidal systems have been mentioned earlier. In general, lyophilic sols show very weak Tyndall scattering and, unlike lyophobic sols, do not coagulate with the addition of small quantities of electrolytes. Considerable quantities of electrolyte solution added to lyophilic systems cause the latter to separate out in clusters of coacervates. Generally it is often called 'salting out'. The ability of different cations or of anions in salting out varies from ion to ion; and the valences of ions concerned also have definite influence in the process of coacervation.

A series, based on experimental observations and called Hofmeister series or lyotropic-series, has been drawn up for anions and for cations demonstrating qualitatively their capacity in salting out the lyophilic micelles. The series are

- (a) for anions: $\text{Ac} > \text{Cl} > \text{NO}_3 > \text{Br} > \text{I} > \text{CNS}$
 (b) for cations: $\text{Th} > \text{Al} > \text{H} > \text{Ba} > \text{Sr} > \text{Ca} > \text{K} > \text{Na} > \text{Li}$ etc.

When two lyophilic systems with opposite charges of the disperse phases are brought together, coacervation occurs. Thus gum and gelatine suspensions having opposite charges when brought together, they are both salted out together in thick micelles. Electrostatic interaction tends to cause coagulation but this is resisted by the elasticity of the water shell surrounding them. The individual charged micelles are held together by electrostatic attraction to form a coacervate.

The principle in *cottrell precipitation* is also similar. Extremely fine dust or solid particles suspended in a gas can be removed by subjecting them to strong electric fields. A high tension current is applied to wires kept hanging in the gas; the suspended solid particles in the gas become charged. These then recede away from the wires and are deposited at the bottom plates having opposite electrical charge. This method has been profitably applied in purifying gases from dusts, in removing dust of cement plants and of gases from smelters etc.

(a) **Viscosity of Lyophilic sols.** A striking difference between lyophobic and lyophilic sols is the high viscosity of the latter. This is due to the extensive solvation of the disperse phase particles which increases the resistance to flow.

the zeta-potentials. It is then expected that in lyophilic sols, the large viscosity values will in general be greatly lowered in presence of small amounts of added electrolyte. This is found to be true for many systems such as sols of starch, gelatine, gum arabic, etc. This pronounced lowering of viscosity in the presence of electrolytes is known as *electroviscous effect*.

(b) **Protective action of lyophilic sols.** When lyophilic sols are added to lyophobic sols, the sensitivity of the latter towards electrolytes depends on how and in what manner the lyophilic sol is added. If a little lyophilic sol is added slowly to a lyophobic system the latter becomes very sensitive to flocculation on addition of electrolytes. If however a comparatively large amount is added to a lyophobic sol quickly, the sol becomes more stable and thus less sensitive towards electrolyte addition. Lyophilic sols thus can play a protective role as **peptisers**.

All lyophilic sols do not afford the same degree of protection to any given lyophobic sol. As a measure of their protective capacities Zsigmondy set up a standard by which protective capacities are expressed in terms of what is called '**Gold numbers**'. (The weight in milligrams of the disperse phase of the lyophilic sol in the dry condition, which ought to be added to a 10 c.c. portion of a standard Gold sol (appr. $5.5 \times 10^{-3}\%$ by wt.) to just prevent its turning from red to blue on the addition of 1 c.c. of a 10% solution of NaCl, is called the 'gold number' of the lyophilic sol.) The change of colour is indicative of the start of flocculation. It is evident that the lower the gold number the greater is the protective action of a lyophilic colloid. Gelatine, salts of protalbic and lysalbic acids obtained from albumen, etc. have low gold numbers and thus high protective capacities. Some of the gold numbers are given here:

TABLE: GOLD NUMBERS OF LYOPHILIC SOLS

Sol	Gelatine	Haemoglobin	Albumin	Gum arabic	Dextrin	Potato starch
Gold number	0.005–0.01	0.03–0.07	0.1–0.2	0.15–0.25	6–20	>25

It is not clearly understood how the lyophilic sol affords protection to lyophobic colloidal particles against flocculation but it is obvious that the particles of the two sols are associated or united in some manner.

XXV.8. Determination of Avogadro's Number from Vertical distribution of Sol particles.

Consider a dilute suspension contained in a tall cylinder. The equilibrium distribution of the sol particles at different heights from the bottom of the container will depend upon the forces acting on the particles. Had the gravity force only been operative, all the sol particles would settle down to the bottom after a time. But the sol particles undergo Brownian motions which have no preference for directions. Take a sol particle at a height h_0 from the bottom and let it undertake certain Brownian displacements in diverse arbitrary directions. The projection of the resultant displacement of the vertical axis will measure the vertical displacement, either upward or downward, of the particle from the reference plane at h_0 . It is evident that in the case of downward displacement it aids the gravity force and in the opposite event, the Brownian displacement acts against gravity settling.

The situation is quite analogous to the distribution of pressure and, hence, of molecules of a gas contained in a tall vertical column. The distribution of the gas molecules at different heights is obtained in the following way:

Let the pressure at height, h_0 (reference plane) = p_0
and the pressure at height, $h_0 + dh_0 = p_0 - dp_0$

The downward thrust of the gas due to the column between h_0 and $h_0 + dh_0$ heights is counterbalanced at equilibrium by the upward thrust (F_0) of the said portion originating from the kinetic motions of the gas molecules.

If σ be the cross-section of the column and ρ_0 the density at height h_0 , then

$$\begin{aligned} \sigma \rho_0 g dh_0 &= F_0 \\ \text{or } \sigma \rho_0 g dh_0 &= -dp_0 \sigma \end{aligned} \quad \dots (A)$$

The upward thrust F_0 is equal to $|dp_0 \sigma|$, the negative sign in (A) is due to the fact that dp_0 denotes increment of pressure.

Again, from kinetic theory.

$$dp_0 = \frac{1}{3} mc^2 dn_0 = \frac{2}{3} \cdot \frac{1}{2} mc^2 \cdot dn_0 \quad \dots (B)$$

where n_0 is the number density of the molecules at height h_0 . Substituting $\frac{1}{2} mc^2$ by $3/2 kT$ per molecule, k being Boltzmann constant, we have

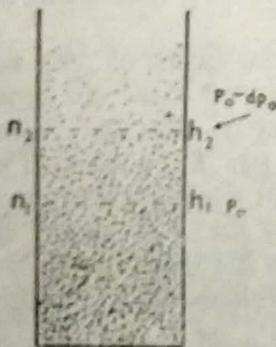
$$dp_0 = kT dn_0$$

On introducing this in equation (A),

$$mn_0 g dh_0 = -kT dn_0 \quad (\because mn_0 = \rho_0)$$

$$\text{or } kT \frac{dn_0}{n_0} = -mg dh_0 \quad \dots (C)$$

Integrating (C) over a height h_1 to h_2 with the corresponding number densities n_1 and n_2 , we have (Fig. XXV.8),



$$kT \ln \frac{n_1}{n_2} = mg (h_2 - h_1) = mg \Delta h$$

$$\text{Since } k = R/N_0, \quad \frac{RT}{N_0} \ln \frac{n_1}{n_2} = mg \Delta h$$

$$\text{i.e., Avogadro's number, } N_0 = \frac{RT \ln n_1/n_2}{mg \Delta h} \quad \dots (D)$$

Fig. XXV.8
Vertical distribution
of particles

This relation (D) valid for distribution of molecules in a gas will also hold good for equilibrium distribution of sol particles in suspension. For a homogeneous suspension

with spherical sol particles of radius r and with effective density $(d-d_0)$, since the particles are suspended in a medium of density d_0 , equation (D) may be written as,

$$N_0 = \frac{RT \ln n_1/n_2}{\frac{4}{3}\pi r^3 (d-d_0) g \Delta h} \dots \text{(XXV.1)}$$

The determination of N_0 , therefore, demands the experimental measurements of the following quantities:

- (a) n_1 and n_2 or n_1/n_2 at heights h_1 and h_2 ,
- (b) $(d-d_0)$, the effective density of the sol particles,
- (c) the radius r of the sol particles.

In a series of painstaking and laborious investigations Perrin and, afterwards, other investigators determined the quantities involved in equation (XXV.1) and evaluated N_0 . The methods followed for such determinations are very briefly narrated below. The experiments were made with a dilute and as far as possible homogeneous suspension of gamboge. The sol was allowed to stand in a cylinder to attain distribution equilibrium.

XXV.15. Association Colloids

There are instances where in a solution, with increase in concentration, the solute molecules or their ions come together to aggregate spontaneously to form thermodynamically stable bigger particles of colloidal dimensions. These are called *association colloids* and these usually incorporate into the aggregate appreciable quantity of solvent molecules. The association colloids cannot be regarded as macromolecules as the latter are individual molecules of giant size in solution. They also differ from lyophobic colloids which are thermodynamically unstable. The term '*micelles*' is almost universally employed for the clusters or aggregates formed in solution by association colloids. Although there are some examples of micelle formation from neutral or nonionic molecules, such as polyethylene oxide, but mostly micellizations occur from the large ions of molecules in solution. Usually such molecules have a lyophobic group and a lyophilic group. A typical example

of association colloid is that of sodium oleate, $[C_{17}H_{33}]COO^-Na^+$. The long hydrocarbon part $C_{17}H_{33}$ is the lyophobic portion which tries to recede away from the solvent water. But the 'head' $COONa$ is the ionisable lyophilic group which tends to go into water resulting into ions. When the concentration is quite low say less than $3 \times 10^{-3} M$, we have a simple solution of sodium oleate. But as the concentration is increased, the lyophobic hydrocarbon parts receding away from the solvent approach each other and form a cluster as in Fig. XXV.12. The micelle formed is therefore one of anions. The micelle may contain a hundred or more oleate ions clumped together. It is more or less spherical, the hydrocarbon ends are in the interior and $-COO^-$ groups projecting outward, in contact with the solvent. It is thus a colloid particle with charges on the surface to which oppositely charged Na^+ ions would be attracted forming double layers. The name 'colloidal electrolyte' is also often used for such suspensions. Similar micellization with anionic groups are found in other soaps,

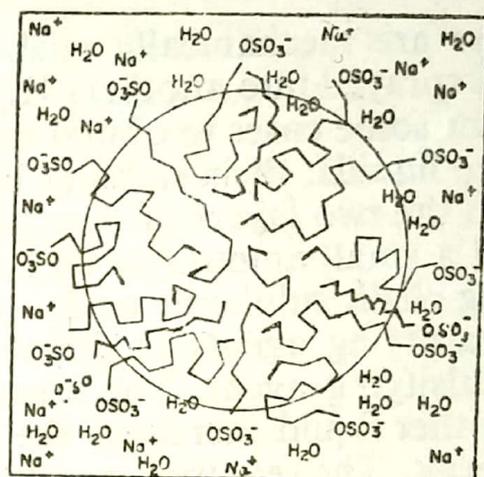


Fig. XXV.12. Micelle formation (diagrammatic)

sulphonates, some dyes etc. Micellization with cations are also known as in amine salts such as in CTAB (cetyltrimethyl ammonium bromide), $(C_{16}H_{33})(CH_3)_3N^+Br^-$. In very dilute solutions, potassium oleate and similar other substances, which later on micellize, remain as individual molecules ionising into positive and negative ions. Micellization occurs when a particular concentration is reached at a given temperature. The initial concentration at which micellization begins is designated as the *critical micellization concentration*, abbreviated as 'cmc'. Every association colloid has a definite cmc at a given temperature. Increase of temperature lowers the cmc. The change from ions to micelles is reversible. Hence, by diluting an association colloid, it is possible to revert to the original simple solution.

Starting with a very dilute solution if the concentration is gradually increased, the properties of the solution such as equivalent conductance, surface tension, osmotic coefficient change regularly and smoothly just as with solutions of strong electrolytes. But after reaching a certain concentration, i.e., the cmc, these properties undergo an abrupt change. This is obviously due to the start of the micelle formation. In fact, these properties are observed and plotted against some function of concentration, say \sqrt{m} . From the sudden break of the curve, as shown in Fig. XXV.13, the critical micellization concentration would be known.

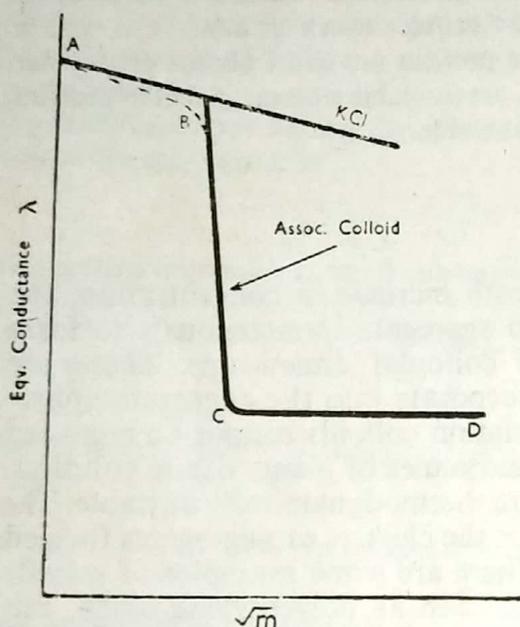


Fig. XXV.13. Eqv. conductance of association colloid vs. \sqrt{m}

The study of association colloids has become of great importance in recent years as many of these function as excellent detergents and emulsifying agents. These colloids also play a very important part in solubilization of solvent repellant substances by accommodating the latter inside the micelle clusters. Water insoluble dyes are solubilized in soap solutions and subsequently deposited uniformly on fabrics (McBain).

XXV.16. Emulsions

An emulsion is obtained when fine droplets of a liquid are dispersed in another liquid immiscible with it. Milk is a naturally occurring emulsion in which fine globules of fat are dispersed in water. The sizes of the droplets are approximately in the region of 1μ in diameter. Emulsions are often prepared by vigorously shaking together the two liquids, or sometimes these are mechanically mixed in homogenizers in which one liquid is atomised and sprayed into another. High frequency ultrasonic waves have also been employed in some cases to obtain emulsions. When the emulsions are formed from two pure liquids, their stability is poor and on standing for some time these separate into the two layers of pure liquids. To prepare stable emulsions, it is necessary to add a small amount of an *emulsifying agent*. Soaps of different types, detergents, long chain sulphonic acids, lyophilic colloids such as gelatine, albumin, etc. act as emulsifying agents in different cases. In milk, the protein casein serves as the emulsifying agent. The creation of a large number of droplets of a liquid into another liquid increases the surface area and hence requires large amount of energy. The required energy would be less if the surface tension is decreased. The function of the emulsifying agents is to diminish the surface tension.

Emulsions are broadly classified into two types: (i) oil in water type in which the disperse phase is the oil in medium water and (ii) water in oil type in which water droplets are dispersed in oil. Here the term 'oil' is synonymous with any liquid immiscible with water. The type of emulsion produced depends upon the nature of the emulsifying agent used. Thus, when sodium oleate is used as an emulsifier, an oil in water emulsion is formed. But if a soap with a bivalent cation

is employed, say calcium oleate, a water in oil type emulsion is obtained. If to an oil in water emulsion stabilised by sodium oleate, a calcium or magnesium salt is added, the emulsion tends to be unstable at a particular concentration ratio of $\text{Na}^+ : \text{Ca}^{++}$. If the concentration of Ca^{++} be quickly increased, the inversion of the type of emulsion occurs and water-in-oil emulsion is produced.