

4. Properties of Colloidal Solutions

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Introduction:

Colloid science concerns systems in which one or more of the components has at least one dimension within the nanometre (10^{-9}m) to micrometre (10^{-6}m) range. The adjective 'micro-heterogeneous' provides an appropriate description of most colloidal systems as they consist of a dispersed phase (or discontinuous phase) distributed uniformly in a dispersion medium (or continuous phase). The range of colloidal systems of practical importance and their processes is vast. They have special properties which are of great practical importance, and they were appropriately described by Ostwald as lying in the World of Neglected Dimensions. A full understanding of the properties of colloids calls upon a wide range of physical and chemical ideas, while the multitude of colloidal systems presented to us in nature, and familiar in modern society, exhibit a daunting complexity.

A detailed and fundamental theoretical understanding of colloidal behavior is possible only through a thorough knowledge of broad areas of physics, chemistry, mathematical physics, biological structures, and biological processes. On the experimental side there is an ever-increasing emphasis on the application of modern physical techniques to colloidal problems. Colloid science is truly an interdisciplinary subject.

In this chapters an attempt is made to summarize the basic concepts related to properties of colloidal solutions which can help readers to get an insight of colloid science.

4.1 Nature:

Colloidal solutions are heterogenous and polydispersed in nature. They consist of two phases: Dispersed phase and dispersion medium where the molecules or particles vary in size.

4.2 Particle Shape:

Colloidal particles can be classified according to shape as corpuscular, laminar, spherical, or linear (Figure 4.1). Many colloidal systems contain spherical or nearly spherical particles. Emulsions, latexes, liquid aerosols, etc., contain spherical particles. Certain protein molecules are approximately spherical. The crystallite particles in dispersions such as gold and silver iodide sols are sufficiently symmetrical to behave like spheres. Corpuscular particles which deviate from spherical shape can often be treated theoretically as ellipsoids of revolution. Many proteins approximate this shape. Iron (III) oxide and clay suspensions are examples of systems containing plate-like particles. High-polymeric material usually exists in the form of long thread like straight or branched-chain molecules.

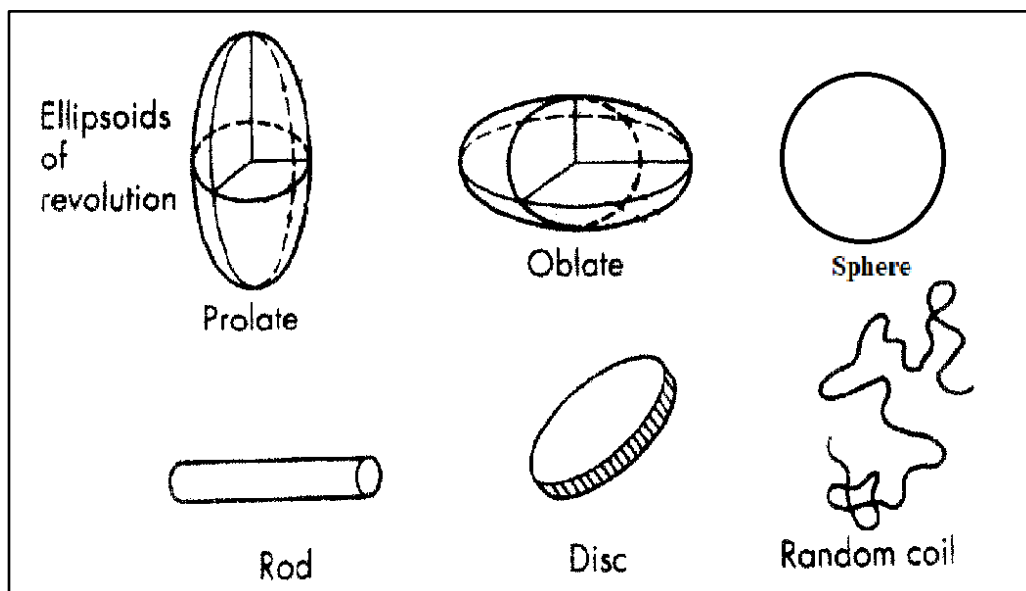


Figure 4.1: Some model representations of colloidal particles.

When particles aggregate together, many different shapes can be formed. These do not necessarily correspond to the shape of the primary particles.

4.3 Filterability:

Colloids can easily pass-through filter papers but can not diffuse through parchment or other fine membranes due to their particle size, which is smaller than pore size of filter paper and larger than pore size of fine membranes.

4.4 Visibility:

Colloidal particles cannot be seen through naked eyes or ordinary microscope due to their exceedingly small size. The shortest wavelength in visible spectra is about 4000 \AA . Hence, we cannot see any object less than $200\mu\text{m}$ and colloidal particles have sizes less than $200\mu\text{m}$.

Recently new techniques like Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and Scanning Transmission Electron Microscope (STEM) are used to determine the size and shape of colloidal particles.

4.5 Kinetic Properties:

In this section we will try to understand the properties of colloidal particles related to their movement. Colloidal particles exhibit movement under different circumstances, it could be random, or it could be due to various factors like gravitational field, electrical environment, concentration gradient, etc. (Figure 4.2).

Random Movement	<ul style="list-style-type: none"> • Brownian Movement
Movement due to Concentration Gradient	<ul style="list-style-type: none"> • Diffusion • Osmosis
Movement due to Electrical Environment	<ul style="list-style-type: none"> • Electrophoresis • Electro-osmosis • Streaming
Movement due to Gravitational Field	<ul style="list-style-type: none"> • Sedimentation • Creaming

Figure 4.2: Kinetic properties of colloidal solutions

Here, we will cover Brownian movement, diffusion, and various osmotic phenomena. Next, we will briefly deal with sedimentation and creaming in a gravitational field. We will discuss electro-kinetic properties like, electrophoresis, electro-osmosis, and streaming potential in detail in a different section.

4.5.1 Brownian Motion:

In 1827, Robert Brown, an English botanist first observed the random stepwise or zig-zag movement of colloidal particles (Figure 4.3). It was later named after him as Brownian motion and provided early evidence for the molecular kinetic theory. It was interpreted as arising from the random bombardment of the molecules of the surrounding dispersion medium on the particles of dispersed phase. Now, the questions that arise here are, what will be the speed of colliding particles, are the collisions occurring at constant speed, what will be the impact of collision on the direction of motion of particle?

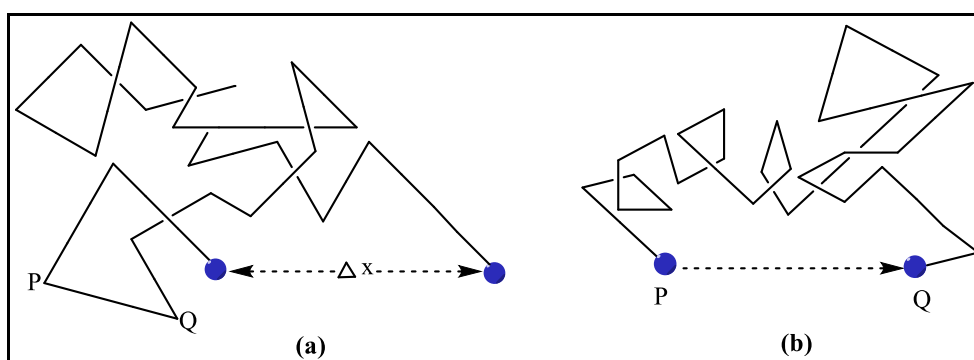


Figure 4.3: Schematic representation of the zig-zag stepwise path executed by a particle doing Brownian motion. (a) After successive time intervals δt , the particle is shown at a

position with the total displacement Δx after a time Δt . **(b)** If δt is longer than the gap between collisions of molecules of the medium with the particle, then each of the steps in (a), e.g., PQ, is itself comprises an array of random substeps executed on a shorter timescale, as represented in (b). The shorter δt will result in more fine-grained representation of the motion.

To answer these questions, one must understand that the molecules of the medium immediately adjacent to the particles can move randomly in any direction and their speeds are distributed according to the Maxwell-Boltzmann law. The impact of the collision on the colloidal particle is determined by the force acting upon its surface and it is proportional to both the velocity of the molecules of dispersion medium and the frequency with which they are colliding with the particles of dispersed phase. The later is proportional to the local density of the molecules within one free path of the surface. Since the local density and molecular velocity in a liquid fluctuates, the force on unit area of particle surface will also fluctuate. At any instant, the particle will feel a net force arising due to the imbalance of forces on various parts of its surface [Figure 4.4(a)]. Thus, the direction and magnitude of the resultant force will vary randomly from instant to instant, resulting in a zig-zag motion of the particle.

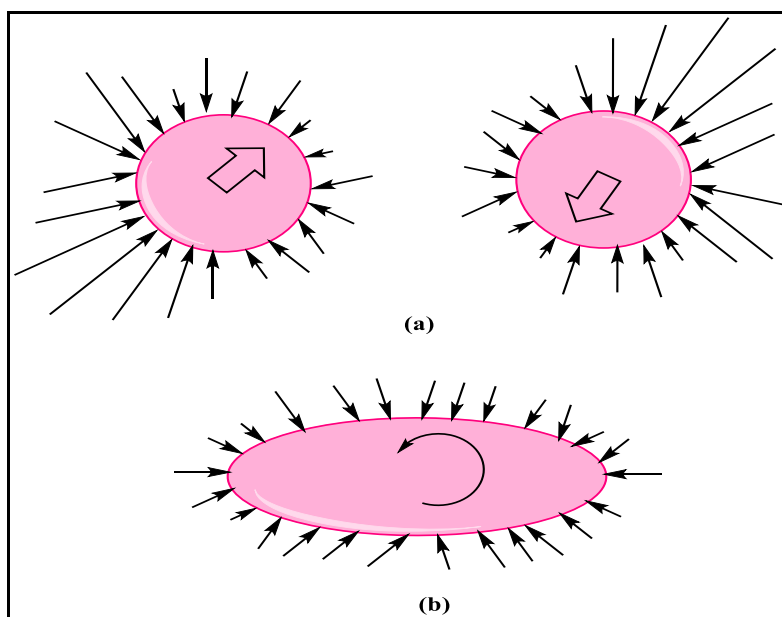


Figure 4.4: **(a)** Resultant force on a particle arising due to the random forces caused by the bombardment of molecules of the dispersion medium; the direction and magnitude of the resultant force vary randomly from instant to instant. **(b)** Rotational Brownian motion of a non-spherical particle.

To understand Brownian motion more clearly one must consider the equation of motion of the particle facing randomly varying instantaneous forces (Langevin, 1908). The resultant motion of this force is opposed by the resistance arising from viscous forces, which is proportional to the velocity of the particle. Solution of this equation leads to an expression for the mean square velocity of a large number of particles.

According to the principle of equipartition of energy, the mean square velocity is equal to $3kT/m$, where m is the mass of the particle. This can lead to the mean Brownian displacement $\overline{\Delta x}$ of a particle from its original position after a time Δt and is given by:

$$\overline{\Delta x^2} = (2kT/B) \Delta t, \quad (1)$$

where B is the viscous friction coefficient. Considering colloidal particles to be spherical we can use Stokes' equation which will relate B to the viscosity of the medium (η) and the radius of the particle (r):

$$B = 6\pi\eta r, \quad (2)$$

hence

$$\overline{\Delta x^2} = (kT/3\pi\eta r) \Delta t, \quad (3)$$

$$\overline{\Delta x} = \{(kT/3\pi\eta r) \Delta t\}^{1/2}, \quad (4)$$

Note that the mass of the particle does not appear openly in equation (3), but the mean square displacement is proportional to the reciprocal of its radius and hence to the reciprocal of the cube root of its volume. This means that the smaller the particle the more extensive the Brownian motion. We also observe the important result from equation (4), that the mean displacement is proportional to the square root of the time.

Now imagine if the particles are non-spherical then what will happen? To answer this one must consider that in this case, firstly, the simple form of Stokes' equation will not be applicable, and secondly, the unsymmetrical forces applied on the particle by molecules of dispersion medium cause the particles to rotate. This phenomenon is called Brownian rotation or rotational diffusion where particles undergo rotational motion rather than translational motion [Figure 4.4(b)].

In conclusion, Brownian motion is a three dimensional 'random walk' taken by the particles due to random collisions with molecules of medium and is consisted of a sequence of steps whose directions being chosen at random without being affected by the direction of the preceding step.

4.5.2 Diffusion:

In colloidal solutions diffusion occurs as a consequence of Brownian motion. Let us consider consider a thin sheet which initially contains c^0 particles in unit volume [Figure 5 (a)] and observe the distribution of these particles after a time Δt . They will have spread out in both directions.

Random walks follow the square root of time (See equation 4) as compared to linear or ballistic walks which directly follow time thus, the chance that a given particle will have reached a distance Δx is proportional to $\Delta t^{1/2}$.

On observing the graph between distance covered Δx and concentration c we will find that the sharp initial concentration peak will spread out into a broad peak, which has the shape of a Gaussian probability curve [Figure 4.5 (b)].

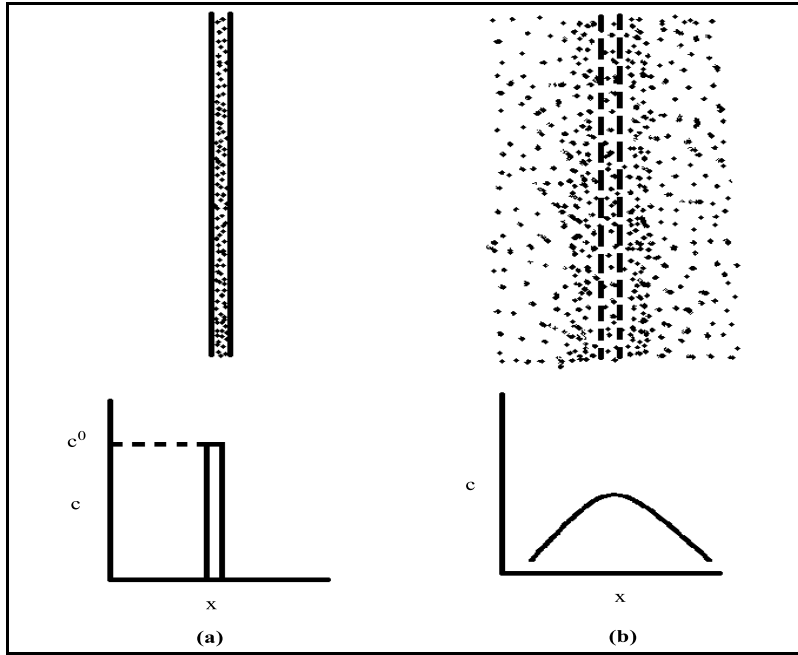


Figure 4.5. Diffusion of particles from a thin sheet at a concentration c^0 (a) at zero time, (b) after a time interval.

Consider a plane AB (Figure 4.6) passing through a dispersion and separating regions of concentration c_1 and c_2 , where $c_1 > c_2$. Let the average Brownian displacement of a given particle perpendicular to AB in time Δt be $\overline{\Delta x}$.

For each particle, this displacement has equal probability of being 'left to right' or 'right to left'. The net mass of particles displaced from left to right across unit area of AB in time Δt is, therefore given by :

$$m = \frac{(c_1 - c_2)\overline{\Delta x}}{2} = \frac{(c_1 - c_2)\overline{\Delta x^2}}{2\overline{\Delta x}} \quad 5$$

If $\overline{\Delta x}$ is small,

$$\frac{(c_1 - c_2)}{\overline{\Delta x}} = -\frac{\partial c}{\partial x} \quad 6$$

Therefore,

$$m = -\frac{1}{2} \frac{\partial c}{\partial x} \overline{\Delta x^2} \quad 7$$

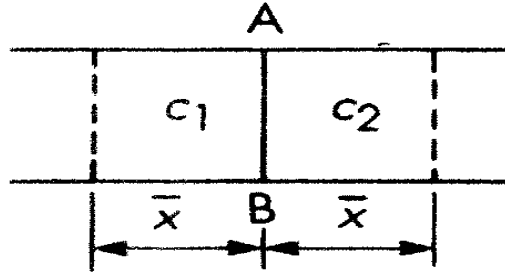


Figure 4.6: Diffusion across the plane AB passing through a dispersion and separating regions of concentration c_1 and c_2 , where $c_1 > c_2$.

Now, as we know that diffusion is the tendency for molecules to migrate from a region of high concentration to a region of lower concentration and is a direct result of Brownian motion. Fick's first law of diffusion states that the mass of substance dm diffusing in the x direction in a time Δt across an area A is proportional to the concentration gradient $\partial c/\partial x$ at the plane in question:

$$dm = -DA \frac{\partial c}{\partial x} dt \quad 8$$

Where D , denotes diffusion constant, it is a constitutive parameter that describes the constitution of the diffusing system. The minus signs in equation 6, 7, and 8 denote that diffusion takes place in the direction of decreasing concentration.

If the diffusion taking place in unit area ($A = 1 \text{ m}^2$) then

$$dm = -D \frac{\partial c}{\partial x} dt$$

$$m = -D \frac{\partial c}{\partial x} t \quad 9$$

On comparing equations 7 and 9 we will get

$$-\frac{1}{2} \frac{\partial c}{\partial x} \overline{\Delta x^2} = -D \frac{\partial c}{\partial x} t$$

$$\overline{\Delta x} = (2Dt)^{\frac{1}{2}} \quad 10$$

The above interpretation of diffusion is based on a molecular model of Brownian motion and follows broadly the arguments of Einstein (1905). On comparing equation 10 with equation 4 we can get the value of diffusion constant D , which agrees with Stokes-Einstein Equation.

$$(2Dt)^{\frac{1}{2}} = \{(kT/3\pi\eta r) \Delta t\}^{1/2}$$

$$D = \frac{kT}{6\pi\eta r} \quad 11$$

4.5.3 Osmosis:

The phenomenon of osmosis is another example in which molecules flow from a location of higher chemical potential to a region of lower potential. In an osmotic experiment a sample of dispersion in compartment II is separated from pure medium in compartment I by a semi-permeable membrane which allows passage of molecules of the medium but is completely impermeable to particles of the suspension (Figure 4.7).

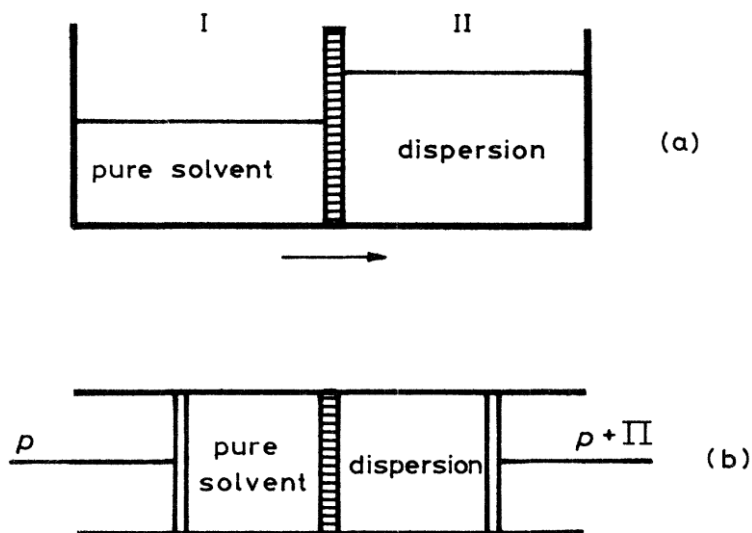


Figure 4.7: Osmosis. (a) Dispersion separated from pure solvent by a semi-permeable membrane. Solvent molecules diffuse into the dispersion. (b) Osmotic equilibrium is set up when an excess pressure Π is applied to the dispersion to stop the flow of solvent through the membrane.

The tendency to equalise chemical potentials (and, hence, concentrations) on either side of the membrane results in a net diffusion of solvent across the membrane. The counter-pressure necessary to balance this osmotic flow is termed the osmotic pressure (Π).

Osmosis can also take place in gels and constitutes an important swelling mechanism. The osmotic pressure Π of a solution is described in general terms by the virial equation:

$$\Pi = cRT \left(\frac{1}{M} + A_2c + A_3c^2 + \dots \right) \quad 12$$

where c is the concentration of the solution (expressed as mass of solute divided by volume of solution), M is the molar mass of the solute, and A_2, A_3 , etc., are constants.

Therefore,

$$M = \frac{RT}{\lim_{c \rightarrow 0} \Pi/c} \quad 13$$

Hence, in principle, the molar mass of the particles can be calculated from measurements of osmotic pressure (Π) as a function of concentration in an extremely dilute suspension. However, in practice, the magnitude of osmotic pressure (Π) is so small for particulate dispersions that osmometry does not provide a useful route to particle size determination. It is nevertheless used for the determination of the molar mass of macromolecules.

A. Donnan Equilibrium:

A somewhat more complex situation arises when osmotic equilibrium is set up between solutions containing both non-diffusible and (inevitably) diffusible ionic species. Gibbs predicted and later Donnan demonstrated that if the non-diffusible ions are located on one side of a semipermeable membrane, the distribution of the diffusible ions become unequal and when equilibrium is attained, the diffusion is greater on the side of the membrane containing the non-diffusible ions. This distribution can be calculated thermodynamically, although a simpler kinetic treatment will suffice. Let us assume a simple example in which equal volumes of solutions of the sodium salt of a protein (PrNa, non-diffusible ionic species) and of sodium chloride (diffusible ionic species) with respective equivalent concentrations a and b are initially separated by a semipermeable membrane, as shown in Figure 4.8.

	(1)	(2)
Initial concentrations	Na ⁺ = a Pr ⁻ = a	Na ⁺ = b Cl ⁻ = b
Equilibrium concentrations	Na ⁺ = $a + x$ Pr ⁻ = a Cl ⁻ = x	Na ⁺ = $b - x$ Cl ⁻ = $b - x$

Figure 4.8: The Donnan membrane equilibrium

To maintain overall electrical neutrality Na⁺ and Cl⁻ ions must diffuse across the membrane in pairs. Now, assume that x amount of Na⁺ and Cl⁻ ions diffused from compartment (2) to (1) till equilibrium is reached. Thus, equilibrium concentrations in compartment (1) will be,

$$\text{Concentration of Na}^+ = a + x$$

$$\text{Concentration of Pr}^- = a$$

$$\text{Concentration of Cl}^- = x$$

And in compartment (2) will be,

$$\text{Concentration of Na}^+ = b - x$$

$$\text{Concentration of Cl}^- = b - x$$

Now, one must keep in mind the rate of diffusion in any particular direction will depend on the probability of an Na⁺ and a Cl⁻ ion arriving at a given point on the membrane surface simultaneously. This probability is proportional to the product of the Na⁺ and Cl⁻ ion concentrations (strictly, activities), so that,

$$\text{rate of diffusion from (1) to (2)} = k(a+x) x$$

$$\text{rate of diffusion from (2) to (1)} = k(b-x)^2$$

At equilibrium, these rates of diffusion are equal i.e.,

$$(a + x) x = (b-x)^2 \quad 14$$

$$x = \frac{b^2}{a+2b} \quad 15$$

At equilibrium, the concentrations of diffusible ions in compartments (1) and (2) are $(a+2x)$ and $2(b-x)$, respectively, so,

$$\begin{aligned} \text{Excess diffusible ion concentration} &= (a+2x) - 2(b-x) \\ &= (a-2b+4x) \quad 16 \end{aligned}$$

Substituting value of x from equation 15 in equation 16,

$$\text{Excess diffusible ion concentration} = a^2/(a+2b) \quad 17$$

Clearly, due to unequal ion transfer a pressure difference will be established and under these circumstances' equilibrium involves not only the establishment of a pressure difference but also an electrical potential difference across the membrane, which is given by,

$$\psi^2 - \psi^1 = \left(\frac{RT}{F}\right) \ln \left(\frac{x_{Na}^1}{x_{Na}^2}\right) = \left(\frac{RT}{F}\right) \ln \left(\frac{x_{Cl}^2}{x_{Cl}^1}\right) \quad 18$$

Where,

ψ^1 = electric potential developed in compartment (1)

ψ^2 = electric potential developed in compartment (2)

$F = \text{Faraday } ((96\,487 \text{ coulombs mol}^{-1}))$

$x^1 = \text{number of diffusible ions in compartment (1)}$

$x^2 = \text{number of diffusible ions in compartment (2)}$

Thus, three effects are observed:

- An osmotic pressure is set up.
- There is a net transfer of salt into the compartment containing the non-diffusible ion. This applies whether this ion is an anion or a cation.
- An electrical potential difference (membrane potential) is set up across the membrane.

4.5.4 Sedimentation and Creaming:

If the particles of a colloidal dispersion have different density from that of the medium then, they will tend to either sink (sediment), if they are denser than the medium, or rise to the surface (cream), if they are less dense due to the gravitational force. In either case a concentration gradient of particles is produced to restore a uniform concentration. Thus, gravitational forces are opposed by diffusion, and a steady state is set up in which the two processes are in balance. We can express the gravitational force as $-(\rho_p - \rho_m)v g$, where ρ_p and ρ_m are the densities of particle and medium, respectively, and v is the volume of a particle. The driving force for diffusion is $(d\mu/dh)$ where $(d\mu/dh)$ represents change in chemical potential with changing height. Hence in the steady state,

$$-(\rho_p - \rho_m)v g = (d\mu/dh) = kT(d\ln c/dh) \quad 19$$

Where, $c = \text{Concentration of the dispersion}$

$$kT d\ln c = -(\rho_p - \rho_m)mg dh \quad 20$$

Integrating this equation between a height h^0 and $h^0 + \Delta h$ we obtain,

$$c/c^0 = \exp[-(\rho_p - \rho_m)v g \Delta h / kT] \quad 21$$

The above argument brings out very clearly the way in which physicochemical equilibrium is achieved by the balance between the effects of potential energy (gravitational energy here) and thermal energy (represented here by diffusion or Brownian motion).

The experimental test of equation 21, and of 3, was first carried out by Perrin (1908) in his classical work on the sedimentation of gamboge particles in the Earth's gravitational field. This relationship is now widely applied in two main areas, first, to determine particle sizes of exceedingly small particles and, secondly, to study both the diffusion and molar mass of macromolecules by increasing the gravitational force using a centrifuge (or ultracentrifuge).

4.6. Electrical Properties:

4.6.1 Charge on Colloids:

When brought in to contact with polar medium, most substances acquire a surface electric charge, may be due to ionisation, ion adsorption, or ion dissolution. This surface charge influences the distribution of nearby ions in the polar medium as counterions (ions of opposite charge) are attracted towards the surface and co-ions (ions of like charge) are repelled away from the surface. Now this, along with the mixing tendency of thermal motion, results in the formation of an electric double layer made up of the charged surface and an excess of counter-ions over co-ions distributed in a diffuse manner in the polar medium. Hence, the theory of the electric double layer gives an insight about distribution of ions and, the magnitude of the electric potentials occurring in the locality of the charged surface. It is important to understand this concept as it provides an understanding of electrokinetic behaviour and stability of charged colloidal systems.

A. Origin of Charge:

The charge on colloidal surface can be acquired either by ionization, adsorption, dissolution, or presence and orientation of dipoles. We will now discuss the detailed account of the origin of charge on colloidal surface.

a. Ionisation:

Several colloidal solutions acquire their charge through the direct ionisation of their surface groups in polar media. Proteins represent a perfect case in this scenario as they gain their charge in aqueous medium due to ionization of carboxyl and amino groups into COO^- and NH_3^+ ions. The ionisation of such colloidal particles and their net molecular charge, depends strongly on the pH of the solution. For example, in acidic medium, a protein molecule will be positively charged while in basic medium it will be negatively charged (Figure 4.9). The pH at which the net charge (and electrophoretic mobility) is zero is called the iso-electric point.

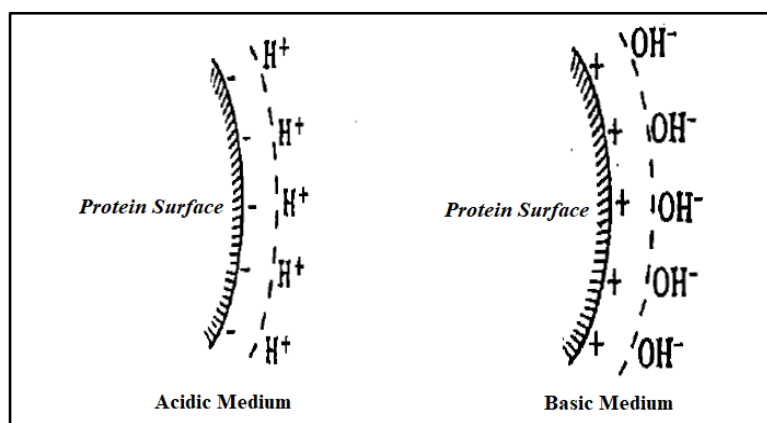


Figure 4.9: Origin of Charge in proteins due to ionization of surface groups.

b. Ion Adsorption:

A net surface charge can also be attained by the unequal adsorption of oppositely charged ions which results in either positive or negative surface excess concentrations. Surfaces which are already charged (e.g., by ionisation) usually show a preferential tendency to adsorb counter-ions, especially those with a high charge number. It is possible that a reversal of charge will be observed because the charge will be determined by adsorbed counter-ions. Interestingly, the surfaces in contact with aqueous media are more often negatively charged than positively charged. This is a consequence of the fact that cations are usually more hydrated than anions and so have the greater tendency to reside in the bulk aqueous medium, whereas the smaller, less hydrated, and more polarising anions have the greater tendency to be specifically adsorbed. Hydrocarbon oil droplets and even air bubbles suspended in water and in most aqueous electrolyte solutions have negative electrophoretic mobilities (i.e., they migrate towards the anode under the influence of an applied electric field). This net negative charge is explained in terms of negative adsorption of ions. Hydrated (e.g., protein and polysaccharide) surfaces adsorb ions less readily than hydrophobic (e.g., lipid) surfaces.

c. Ion Dissolution:

Ionic substances can acquire a surface charge by virtue of unequal dissolution of the oppositely charged ions of which they are composed. For example, silver iodide particles in aqueous suspension are in equilibrium with a saturated solution of which the solubility product, $a_{\text{Ag}^+} a_{\text{I}^-}$, is about 10^{-16} at room temperature. With excess I^- ions, the silver iodide particles are negatively charged; and with sufficient excess Ag^+ ions, they are positively charged (Figure 4.10). The zero point of charge is not at $\text{pAg } 8$ but is displaced to $\text{pAg } 5.5$ ($\text{pI } 10.5$), because the smaller and more mobile Ag^+ ions are held less strongly than the I^- ions in the silver iodide crystal lattice. The silver and iodide ions are referred to as *potential-determining* ions since their concentrations determine the electric potential at the particle surface. Silver iodide sols have been used extensively for testing electric double layer and colloid stability theories.

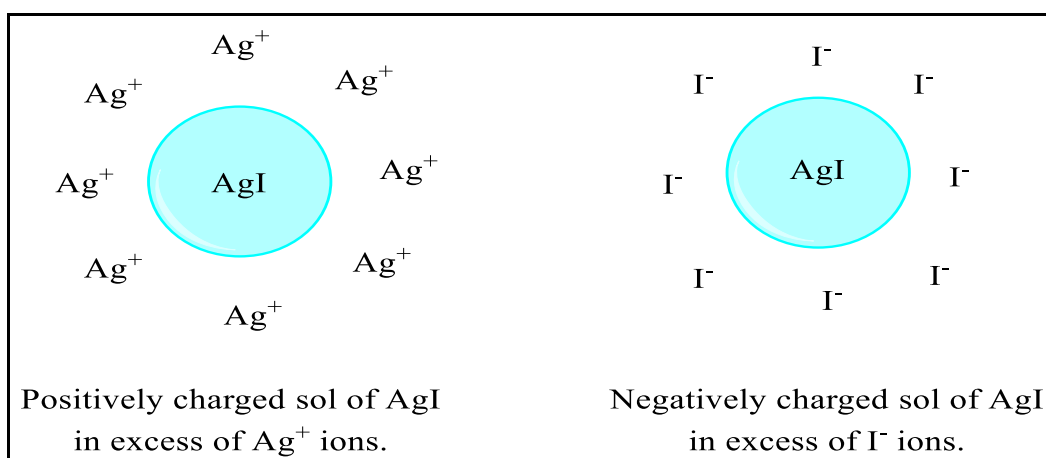


Figure 4.10: Surface charge due to Ion dissolution

d. Adsorption and Orientation of Dipoles

Net surface charge may not be affected by adsorption of dipolar molecules, but the orientation of dipolar molecules layer at the surface may make a significant contribution to the nature of the electric double layer.

4.6.2 Electrical Double Layer:

The electric double layer can be considered as consisting of two regions: 'an inner region which may include adsorbed ions, and a diffuse region in which ions are distributed according to the influence of electrical forces and random thermal motion. The diffuse part of the double layer will be discussed first.

Quantitative treatment of the electric double layer represents an extremely difficult and, in some respects, unresolved problem. The requirement of overall electroneutrality is, for any dividing surface, the charge density (charge per unit area) must be $+\sigma$ and $-\sigma$ on the opposite sides of the surface. Therefore, it dictates, that the magnitude of σ will depend on the location of the surface. Surface location is not a straightforward matter because of the geometric and chemical heterogeneity of the colloidal solutions. It follows, furthermore, that electric double-layer parameters (potentials, surface charge densities, distances) are not agreeable to unambiguous definition. Despite this, various simplifications and approximations were made to develop double-layer theory at a high level of sophistication and usefulness. The simplest quantitative treatment of the diffuse part of the double layer is that due to Gouy (1910) and Chapman (1913), which is based on the following model:

- The surface is assumed to be of infinite extent, flat, and uniformly charged.
- The ions in the diffuse part of the double layer are assumed to be point charges distributed according to the Boltzmann distribution.
- The solvent is assumed to influence the double layer only through its dielectric constant, which is assumed to have the same value throughout the diffuse part.
- A single symmetrical electrolyte of charge number z will be assumed. This assumption facilitates the derivation while losing little owing to the relative unimportance of co-ion charge number.

Let the electric potential be ψ_0 at a flat surface and ψ at a distance x from the surface in the electrolyte solution. Taking the surface to be positively charged (Figure 4.11) and applying the Boltzmann distribution, Poisson's equation, and Debye-Hückel approximation we will finally get,

$$\psi_0 = \sigma_0 / \epsilon \kappa \quad (\text{at low potential}) \quad 22$$

Where,

ψ_0 = Surface Potential

σ_0 = Charge Density

ϵ = Permittivity

κ = Debye's Length (represents distance of ions from charged surface)

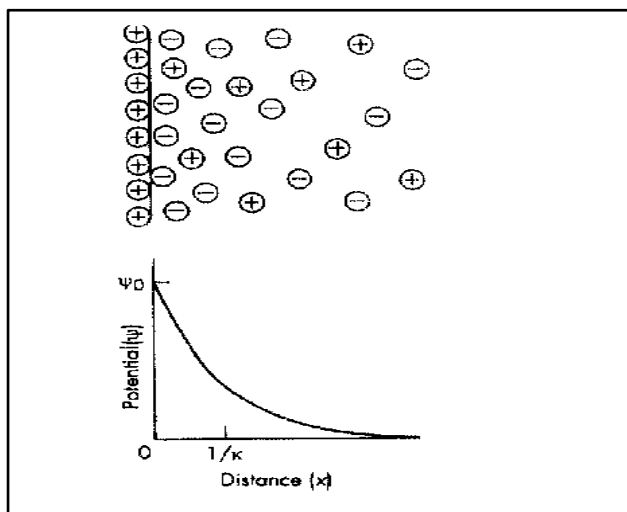


Figure 4.11: Schematic representation of a diffuse electric double layer (Gouy and Chapman model).

Therefore, the surface potential ψ_0 , depends on both the surface charge density σ_0 and (through κ) on the ionic composition of the medium. If the double layer is compressed (i.e., κ increased), then either σ_0 must increase, or ψ_0 must decrease, or both.

The above treatment of the diffuse double layer assumes point charges in the electrolyte medium, however, in many colloidal systems, the double layer is created by the preferential adsorption of potential-determining ions. For example, the potential ψ_0 at the surface of a silver iodide particle depends on the concentration of silver (and iodide) ions in solution. Here, the finite size of the ions will, however, limit the inner boundary of the diffuse part of the double layer since the centre of an ion can only approach the surface to within its hydrated radius without becoming specifically adsorbed. In such cases, unfortunately, the Debye-Hückel approximation is often not applicable.

Stern (1924) proposed a model in which the double layer is divided into two parts separated by a plane (the Stern plane) located at about a hydrated ion radius from the surface and considered the possibility of specific ion adsorption (Figure 4.12). Specifically adsorbed ions are those which are attached (albeit temporarily) to the surface by electrostatic and/or van der Waals forces strongly enough to overcome thermal agitation. The centres of any specifically adsorbed ions are in the Stern layer- i.e., between the surface and the Stern plane. Ions with centres located beyond the Stern plane form the diffuse part of the double layer, for which the Gouy-Chapman treatment outlined before, is applicable.

The potential changes from ψ_0 (the surface or wall potential) to ψ_d (the Stern potential) in the Stern layer, and decays from ψ_d to zero in the diffuse double layer.

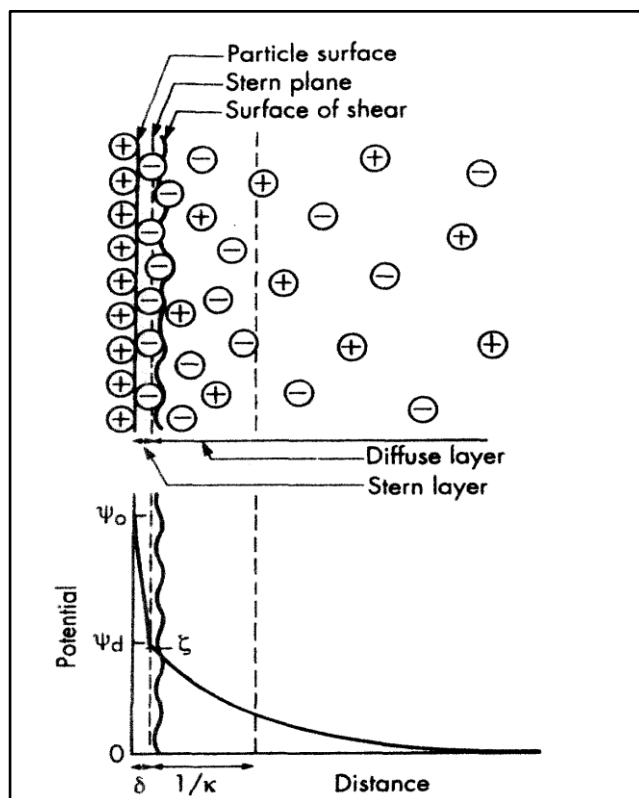


Figure 4.12 Schematic representation of the structure of the electric double layer according to Stern's theory

Estimation of Stern potential (ψ_d) can be done from electrokinetic measurements. Electrokinetic behaviour (discussed in the following sections of this chapter) depends on the potential at the surface of shear (surface of the tightly bound layer) which is located somewhere between the charged surface and the electrolyte solution. This potential of the surface of shear is called the electrokinetic or ζ (zeta) potential. The exact location of the shear plane (which is a region of rapidly changing viscosity) is another unknown feature of the electric double layer. To understand surface of shear one must understand that in addition to ions in the Stern layer, a certain amount of solvent will probably be bound to the charged surface and form a part of the electrokinetic unit. It is, therefore, reasonable to suppose that the shear plane is usually located at a small distance further out from the surface than the Stern plane and that ζ is, in general, marginally smaller in magnitude than ψ_d (see Figures 11). In tests of double-layer theory it is customary to assume ψ_d and ζ as identical, and the bulk of experimental evidence suggests that errors introduced through this assumption are generally small, especially at lyophobic surfaces. Any difference between ψ_d and ζ will clearly be most pronounced at high potentials ($\zeta = 0$ when $\psi_d = 0$), and at high electrolyte concentration (compression of the diffuse part of the double layer will cause more of the potential drop from ψ_d to zero to take place within the shear plane). The adsorption of non-ionic surfactant would result in the surface of shear being located at a relatively large distance from the Stern plane and a zeta potential significantly lower than ψ_d .

4.6.3 Electrokinetic Phenomena:

Electrokinetic is the general description applied to four phenomena (electrophoresis, electro-osmosis, streaming potential, sedimentation potential) which arise when attempts are made to cut off the mobile part of the electric double layer from a charged surface. If an electric field is applied tangentially along a charged surface, a force is exerted on both parts of the electric double layer.

The charged surface (plus attached material) tends to move in the appropriate direction, while the ions in the mobile part of the double layer show a net migration in the opposite direction, carrying solvent along with them, thus causing its flow.

On the contrary, an electric field is created if the charged surface and the diffuse part of the double layer are made to move relative to each other.

Among all the electrokinetic phenomena, electrophoresis has the greatest practical applicability and has been studied extensively in its various forms, whereas electro-osmosis and streaming potential have been studied to a moderate extent and sedimentation potential rarely, owing to experimental difficulties.

A. Electrophoresis:

Electrophoresis can be understood as the movement of a charged surface plus attached material (i.e., dissolved, or suspended material) relative to stationary liquid by an applied electric field.

The electrophoretic effect can be studied by a simple apparatus shown in Figure 4.13. It consists of a U-tube provided with a stopcock through which it is connected to a funnel shaped reservoir. The reservoir is filled with a reasonable quantity of sol and a small amount of water is placed in the U-tube.

Then, the stopcock is slightly opened to gradually raise the reservoir which leads to introduction of the sol into the U-tube. The water is displaced upwards, producing a sharp boundary in each arm. 50 to 200 volts of voltage is then applied using the platinum electrodes, immersed in water layer only.

The movement of the particles can easily be followed by observing the position of the boundary by means of naked eyes or a lens or a cathetometer. When the particles are positively charged, the boundary on the positive electrode side is seen to move down, and that on the negative electrode side to move up, showing that the particles move toward the negative electrode.

Thus, by noting the direction of motion of particles in the electric field it is possible to determine the sign of the charge carried by the particles. Determination of the rate at which colloidal particles migrate in an electric field can also be done using this technique. This rate is expressed in terms of electrophoretic mobility of colloidal particles.

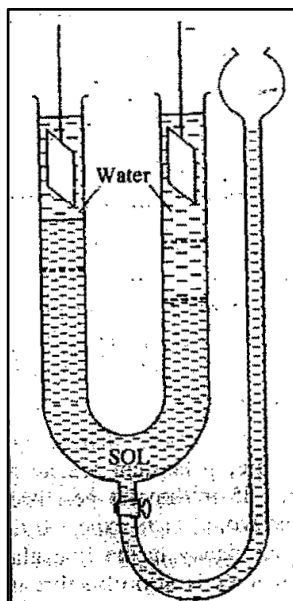


Figure 4.13: Apparatus to study Electrophoresis

The electrophoretic mobility of colloidal particles is defined as the distance travelled by them in one second under a potential gradient of 1 Volt per centimetre. It has been found that the electrophoretic mobility of colloidal particles are of the same order as those of ions under similar conditions, that is, of the order of $(10 - 60) * 10^{-5}$ cm /s/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, polysaccharide, nucleic acids, and other complex substances.

B. Electro-Osmosis:

The movement of dispersion medium relative to a stationary charged surface (e.g., a capillary or porous plug) by an applied electric field (i.e., the complement of electrophoresis) is known as electro-osmosis. The pressure necessary to counterbalance electro-osmotic flow is termed the electro-osmotic pressure.

A simple apparatus for studying electro-osmosis is shown in Figure 4.14. The colloidal system is placed in the central compartment A. Compartment A 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. Now, the movement of colloidal particles is restricted by the membranes, therefore, when a potential difference is applied across the electrodes held close to the membranes in the compartments B and C, the water begins to move. If the particles carry negative charge, the water will carry positive charge, therefore, it will start moving towards the cathode and hence the level of water in the side tube T' would be seen to rise. Similarly, if the particles carry positive charge, the water, which now carries negative charge, will start moving towards the anode and the level of water in the side tube T would start rising.

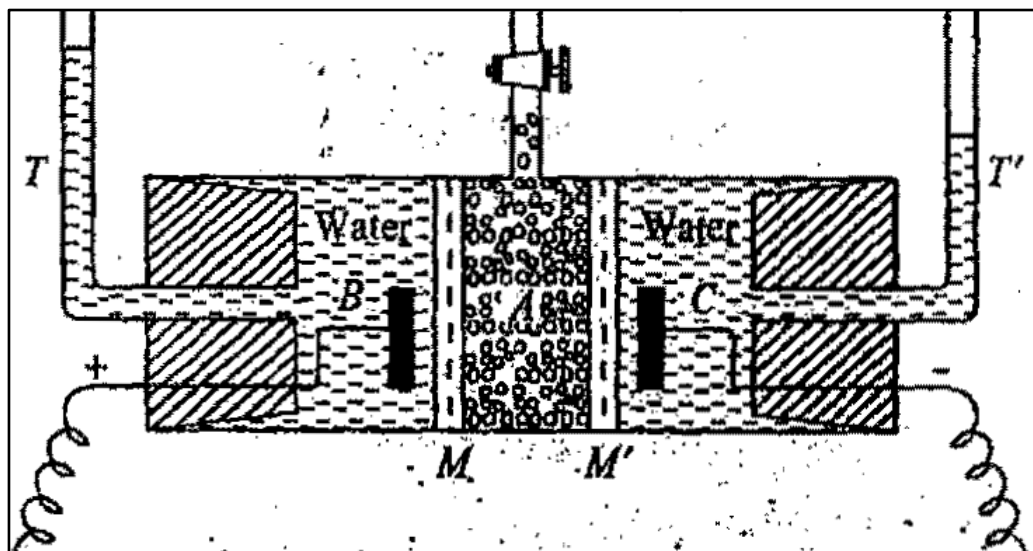


Figure 4.14: Apparatus to study Electro-Osmosis

C. Streaming Potential:

The electric field which is created when liquid is made to flow along a stationary charged surface (i.e., the opposite of electro-osmosis) is called streaming potential.

The development of a streaming potential when an electrolyte is forced through a capillary or porous plug is, in fact, a complex process as charge and mass transfer were occurring simultaneously by several mechanisms.

The liquid in the capillary or plug carries a net charge (that of the mobile part of the electric double layer) and its flow gives rise to a streaming current which consequently generates a potential difference. This potential opposes the mechanical transfer of charge by either back conduction (ion diffusion) or by electro-osmosis (in a much less extent). The transfer of charge due to these two effects is called the leak current, and the measured streaming potential relates to an equilibrium condition when streaming current and leak current cancel each other.

Figure 4.15 depicts a suitable apparatus for studying streaming potentials. A high-resistance voltmeter must be used to minimise current drain. Most of the difficulties associated with streaming potential measurement originate at the electrodes. A superimposed asymmetry potential often develops; however, it can be made to reinforce and oppose the streaming potential by reversing the direction of liquid flow.

The streaming current can be measured if the high-resistance voltmeter is replaced with a microammeter of low resistance compared with that of the plug. An alternating streaming current can be generated by forcing liquid through the plug by means of a reciprocating pump. The main advantage of studying alternating rather than direct streaming currents is that electrode polarisation is far less likely.

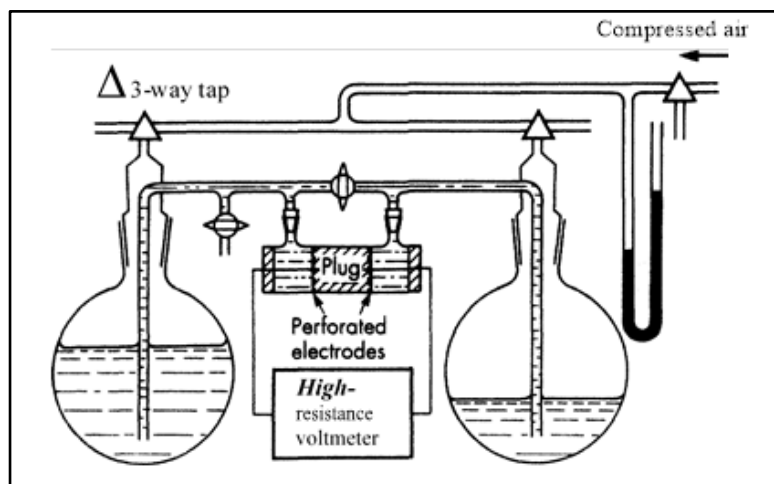


Figure 4.15: A Streaming potential apparatus

D. Sedimentation Potential:

Sedimentation potential can be considered as the opposite of electrophoresis. It can be explained as the phenomena where electric field is created by movement of charged particles relative to stationary medium. Sedimentation potential is studied rarely because of the experimental complexities.

4.6.4 Electrokinetic Theory:

Electrokinetic phenomena are only related to the nature of the mobile part of the electric double layer and may, therefore, be interpreted only in terms of the zeta potential or the charge density at the surface of shear. No direct information is given about the potentials ψ_0 and ψ_d (although, as already discussed, the value of ζ may not differ substantially from that of ψ_d), or about the charge density at the surface of the material in question.

Electrokinetic theory involves both the theory of the electric double layer and that of liquid flow and is quite complicated. In this section the relation between electrokinetically determined quantities (particularly electrophoretic mobility) and the zeta potential will be considered.

For curved surfaces, the shape of the double layer can be described in terms of the dimensionless quantity ' $\kappa\alpha$ ', which is the ratio of radius of curvature to double-layer thickness. When $\kappa\alpha$ is small, a charged particle may be treated as a point charge; when $\kappa\alpha$ is large, the double layer is effectively flat and may be treated as such.

Henry derived a general electrophoretic equation for conducting and non-conducting spheres which takes the form,

$$u_E = \frac{\zeta\epsilon}{1.5\eta} [1 + \lambda F(\kappa\alpha)] \quad 23$$

Where,

u_E = electrophoretic mobility of the particle

ζ = zeta potential

ε = permittivity of the electrolyte medium

η = viscosity of the medium

λ = overall conductivity of the system

Here, $F(\kappa\alpha)$ varies between zero for small values of $\kappa\alpha$ and 1.0 for large values of $\kappa\alpha$ and $\lambda = (k_0 - k_1)/(2k_0 + k_1)$, where k_0 is the conductivity of the bulk electrolyte solution and k_1 is the conductivity of the particles. For small $\kappa\alpha$ the effect of particle conductance is negligible. For large $\kappa\alpha$ the Henry equation predicts that λ should approach -1 and the electrophoretic mobility approach zero as the particle conductivity increases; however, in most practical cases, 'conducting' particles are rapidly polarised by the applied electric field and behave as non-conductors. For non-conducting particles ($\lambda = 1/2$) the Henry equation can be written in the form,

$$u_E = \frac{\zeta\varepsilon}{1.5\eta} f(\kappa\alpha) \quad 24$$

where $f(\kappa\alpha)$ varies between 1.0 for small $\kappa\alpha$ (Hückel equation, $u_E = \frac{\zeta\varepsilon}{1.5\eta}$) and 1.5 for large $\kappa\alpha$ (Smoluchowski equation, $u_E = \frac{\zeta\varepsilon}{\eta}$). Zeta potentials calculated from the Hückel equation (for $\kappa\alpha = 0.5$) and from the Smoluchowski equation (for $\kappa\alpha = 300$) differ by about 1 percent from the corresponding zeta potentials calculated from the Henry equation.

The Henry equation is based on several simplifying assumptions:

- The Debye-Huckel approximation is made.
- The applied electric field and the field of the electric double layer are assumed to be simply superimposed.
- ε and η are assumed to be constant throughout the mobile part of the double layer.

4.7 Stability:

The stability of a colloidal system is described by particles staying suspended in solution and depends on the interaction between the particles. These include van der Waals, and electrostatic interactions as they both contribute to the overall free energy of the system. Ideally, lyophobic sols are stabilised entirely by electric double-layer interactions and, as such, present colloid stability at its simplest whereas the stability of the lyophilic colloids depends upon both the electrical charge and solvation. 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 governs the stability of the colloidal system. If ζ 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 particularly 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.

4.7.1 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 neighboring particles and the attractive van der Waals interactions between the molecules in the particle. The repulsive potential energy of the double layer on particles each of radius r is given by,

$$V_{rep} = \frac{Ar^2\zeta^2}{R} e^{-s/r_D}; \quad r \ll r_D \quad 25$$

Where A is a constant, ζ is the zeta potential, R is the separation of the centers, s is the separation of the surfaces of the two particles ($s = R - 2r$ for spherical particles of radius r) and r_D is the thickness of the electrical double layer. Equation 25 holds for a thick double layer ($r \ll r_D$). For a thin double layer ($r \gg r_D$),

$$V_{rep} = \frac{Ar\zeta^2}{2} \ln(1 + e^{-s/r_D}); \quad r \gg r_D \quad 26$$

The potential arising from the attractive interaction is given by,

$$V_{att} = -B/s \quad 27$$

where B is another constant.

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

$$\zeta = 4\pi\eta u / \epsilon_r \quad 28$$

where η and ϵ_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, ζ , is found to lie between 0.03 and 0.06 V. The value of ζ ; 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 lies outside the colloidal range.

4.7.2 Coagulation of Colloidal Solutions:

A most important physical property of colloidal dispersions is the tendency of the particles to aggregate. This phenomenon of changing colloidal state to a suspended state is known as coagulation, flocculation, or precipitation of colloidal solutions. Encounters between particles dispersed in liquid media occur frequently and the stability of a dispersion is determined by the interaction between the particles during these encounters.

A. Coagulation of Lyophobic Colloids:

Coagulation can occur due to several reasons but in case of lyophobic sols, the most important way of coagulation is by small amounts of added electrolyte. The added electrolyte causes a compression of the diffuse parts of the double layers around the particles and may, in addition, exert a specific effect through ion adsorption into the Stern layer. The sol coagulates when the range of double-layer repulsive interaction is sufficiently reduced to permit particles to approach close enough for van der Waals forces to predominate. The critical coagulation concentration (c.c.c.) or flocculation value of an electrolyte (i.e., the minimum concentration of the electrolyte which is just sufficient to coagulate a lyophobic sol to an arbitrarily defined extent in an arbitrarily chosen time) shows considerable dependence upon the charge number of its ions oppositely charged to the coagulating sol. In contrast, it is practically independent of the specific character of the various ions, the charge number of the co-ions and the concentration of the sol, and only moderately dependent on the nature of the sol. These generalisations are illustrated in Table 1 and are known as the Schulze-Hardy rule. Thus, according to Hardy Schulze rule, greater the valency of the active ion or flocculating ion, greater will be its coagulating power.” In nutshell, Hardy Schulze law states:

- The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.
- Coagulating power of an electrolyte is directly proportional to the valency of the active ions (ions causing coagulation).

For example, to coagulate negative sol of As_2S_3 , the coagulation power of different cations has been found to decrease in the order as, $Al^{3+} > Mg^{2+} > Na^+$ (See Table 4.1)

Similarly, to coagulate a positive sol such as Al_2O_3 , the coagulating power of different anions has been found to decrease in the order as, $[Fe(CN)_6]^{4-} > SO_4^{3-} > Cl^-$ (See Table 4.1)

Such arrangement of ions to represent their coagulating power against oppositely charged sols is known as lyotropic series or Hofmeister series. One must remember, more the coagulating power of the oppositely charged active ion smaller will be its flocculation value.

Table 4.1: Critical coagulation concentrations / Flocculation value (in millimoles per dm³) for lyophobic sols.

<i>As₂S₃ (-ve sol)</i>		<i>AgI (-ve sol)</i>		<i>Al₂O₃ (+ve sol)</i>	
LiCl	58	LiNO ₃	165	NaCl	43.5
NaCl	51	NaNO ₃	140	KCl	46
KCl	49.5	KNO ₃	136	KNO ₃	60
KNO ₃	50	RbNO ₃	126		
K acetate	110	AgNO ₃	0.01)		
CaCl ₂	0.65	Ca(NO ₃) ₂	2.40	K ₂ SO ₄	0.30
MgCl ₂	0.72	Mg(NO ₃) ₂	2.60	K ₂ Cr ₂ O ₇	0.63
MgSO ₄	0.81	Pb(NO ₃) ₂	2.43	K ₂ oxalate	0.69
AlCl ₃	0.093	Al(NO ₃) ₃	0.067	K ₃ [Fe(CN) ₆]	0.08
½Al ₂ (SO ₄) ₃	0.096	La(NO ₃) ₃	0.069		
Al(NO ₃) ₃	0.095	Ce(NO ₃) ₃	0.69		

The other means to attain coagulation of lyophobic colloids are by electrophoresis, by mixing equal quantities of oppositely charged sols (mutual coagulation), by boiling, by persistent dialysis, or by mechanical means like using vibrations, ultrasound, etc.

B. Coagulation of Lyophilic Colloids:

Majorly two factors are responsible for the stability of lyophilic sols: charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. Although, solvation plays more important role in stability of lyophilic colloids. Thus, addition of only small amount of electrolyte is not sufficient to coagulate the lyophilic sols. Unlike lyophobic colloids, they are required in much higher concentration (usually of the order of 1 M) for coagulation. Here, coagulation does not occur due to the neutralization of charge on the particles. The electrolyte binds with water and get hydrated, due to which polymer molecules in the lyophilic sol get dehydrated. This dehydration ultimately leads to coagulation. Similarly when solvent such as alcohol and acetone are added to hydrophilic sols the dehydration of dispersed phase occurs resulting in coagulation.

4.7.3 Protection of Colloids:

Addition of a lyophilic colloid to a lyophobic colloid, leads to the lesser sensitivity of the later towards 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.

Substances such as gum acacia, gelatin, gum tragacanth, etc., are known as protective colloids as they probably get adsorbed on the solid surface in the form of loops wherein water gets trapped. The loops prevent the approach of particles to cause coagulation.

Zsigmondy gave quantitative treatment known as gold number of a protective colloid which represents stabilizing action of the protective colloids. 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 (Table 4.2). 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.

Table 4.2: Gold Number of some hydrophilic substances

Hydrophilic substance	Gold number	Hydrophilic substance	Gold number
Gelatin	0.005 - 0.01	Sodium oleate	0.4 – 1.0
Sodium caseinate	0.01	Gum tragacanth	2
Hamoglobin	0.03 – 0.07	Potato starch	25
Gum arabic	0.15 – 0.25		

Overall, stability of colloids depends upon the long-range van der Waals attractive forces between the particles, as they are the principal cause of aggregation. To counteract these and promote stability, equally long-range repulsive forces are required. Solvation tends to be too short-range; however, the molecular ordering associated with solvation can propagate several molecular diameters into the liquid phase and may exert some influence on stability.

The principal stabilising options are electrostatic (i.e., the overlap of similarly charged electric double layers) and polymeric. Polymeric and/or surfactant additives can influence stability by a variety of mechanisms and the overall situation is often overly complicated.

4.8 Optical Properties:

When a beam of light is directed at a colloidal solution or dispersion, some of the light may be absorbed (colour is produced when light of certain wavelengths is selectively absorbed), some is scattered, and the remainder is transmitted undisturbed through the sample. Light scattering results from the electric field associated with the incident light inducing periodic oscillations of the electron clouds of the atoms of the material in question - these then act as secondary sources and radiate scattered light.

4.8.1 The Tyndall Effect-Turbidity:

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 Tyndall cone (Figure 4.16).

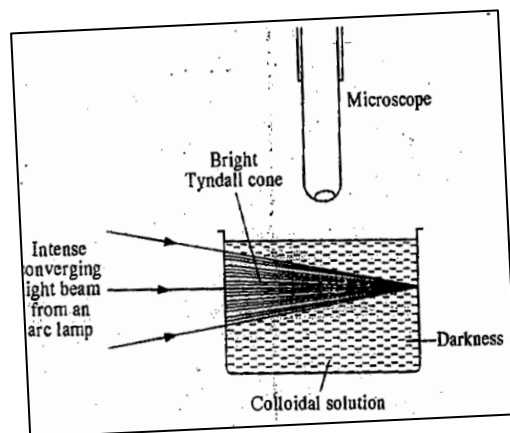


Figure 4.16: Tyndall effect

All materials are capable of scattering light (Tyndall effect) to some extent. The noticeable turbidity associated with many colloidal dispersions is a consequence of intense light scattering. A beam of sunlight is often visible from the side because of light scattered by dust particles. Solutions of certain macromolecular materials may appear to be clear, but in fact they are slightly turbid because of weak light scattering. Only a perfectly homogeneous system would not scatter light; therefore, even pure liquids and dust-free gases are very slightly turbid. The turbidity of a material is defined by the expression,

$$I_t / I_0 = \exp(-\tau l) \quad 29$$

where I_0 is the intensity of the incident light beam, I_t is the intensity of the transmitted light beam, l is the length of the sample and τ is the turbidity.

4.8.2 Measurement of Scattered Light:

As we shall see, the intensity, polarisation and angular distribution of the light scattered from a colloidal system depend on the size and shape of the scattering particles, the interactions between them, and the difference between the refractive indices of the particles and the dispersion medium. Light-scattering measurements are, therefore, of great value for estimating particle size, shape, and interactions, and have found wide application in the study of colloidal dispersions, association colloids, and solutions of natural and synthetic macro-molecules.

Light scattering offers the following advantages over some of the alternative techniques of particle-size analysis:

- Instantaneous measurements which makes it suitable for rate studies.
- No calibration is required as it is absolute.
- The number of particles involved is exceptionally large, which permits representative sampling of polydispersed samples.
- There is no significant perturbation of the system.

The intensity of the light scattered by colloidal solutions or dispersions of low turbidity is measured directly. To measure the light scattering at several angles a detecting photocell is mounted on a rotating arm and fitted with a polaroid for observing the polarisation of the scattered light (see Figure 4.17). Weakening of the scattered beam itself as it passes through the slightly turbid sample can be neglected, and its intensity can be compared with that of the transmitted beam.

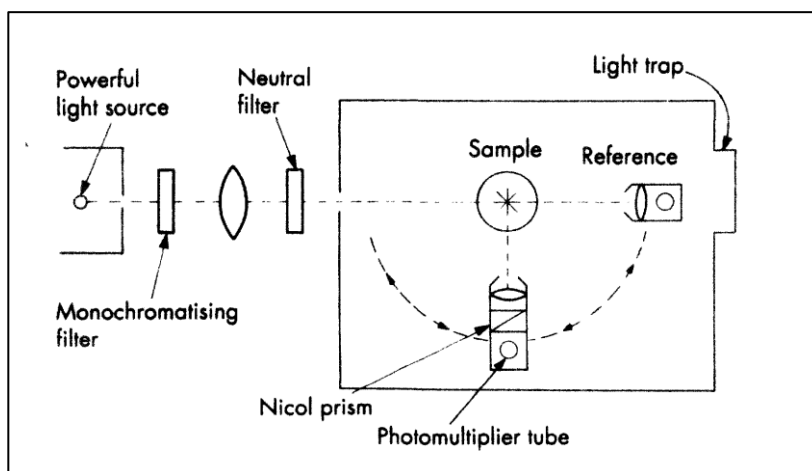


Figure 4.17: Measurement of scattered light

Although simple in principle, light-scattering measurements present several experimental difficulties, the most notable being the necessity to free the sample from impurities such as dust, the relatively large particles of which would scatter light strongly and introduce serious errors.

4.9 Viscosity and Surface Tension:

Lyophilic sols have a higher viscosity and lower surface tension than dispersion medium while lyophobic sols have a nearly same viscosity and surface tension as dispersion medium. This can be understood as lyophilic sols possess higher affinity towards dispersion medium and can be heavily solvated which results in increased viscosity and decreased surface tension than the dispersion medium. On the other hand, lyophobic sols do not possess such affinity for the dispersion medium, and they do not readily solvated. They have much less interaction with dispersion medium due to which their viscosity and surface tension are same as that of dispersion medium.

4.10 Colligative Properties:

Colloidal particles are bigger aggregates. The colligative properties depend on the number of particles. Due to a smaller number of particles compared to true solution, colligative properties are of lower order. Hence the magnitudes of colligative properties, like osmotic pressure, depression in freezing point, and elevation in boiling points are small as compared to the values shown by the true solutions at the same concentration.

4.11 Colour:

Many sols are coloured as they can scatter light rays. Colour of the sol depends upon the wavelength of scattered light by the sol particles, and which again depends upon their size. For example, the colour of silver sol changes from violet to orange red to finally orange yellow as particle size increases (Table 4.3).

Table 4.3: Change in colour of silver sol with increasing particle size.

Colour of Silver sol	Diameter of Colloidal Particles
Violet	15×10^{-8} m
Purple	13×10^{-8} m
Orange Red	9×10^{-8} m
Orange Yellow	6×10^{-8} m

4.12 Bibliography:

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