COLLOIDAL SOLUTIONS

COLLOIDS

- Between pure bulk materials and molecularly dispersed solutions lies a wide variety of important systems in which one phase is dispersed in a second, but in units which are much larger than the molecular unit (a classical sol) or in which the molecular size of the dispersed material is significantly greater than that of the solvent or continuous phase (a macromolecular or polymer solution). Such systems are generally defined as colloids, although there may be accepted limitations on the unit size of the dispersed phase, beyond which other terminology may be used.
- Colloidal chemistry studies the properties of the heterogeneous high-dispersed systems, the rules of the processes occurring in them, and the processes proceeding on the high-developed surface.

COLLOIDS

Many properties of colloids differ markedly from those of true solutions:

- – The solute does not diffuse through the semi-penetrable membranes.
- – Diffusion occurs very slowly in them.
- – They give phenomena of the electrophoresis and diffraction of light.
- – Osmotic pressure has a very low and changeable magnitude.
- – They are unstable systems.

COLLOIDS

- Systems in which one substance is uniformly distributed throughout of another one in the form of finely divided particles are called ***disperse systems***.
- They usually consist of two or more phases: the ***dispersed phase***, consisting of the aggregate of dispersed particles and the ***dispersion medium*** (or the continuous phase) surrounding them.
- A great number of molecules form these aggregates.
- All disperse systems are heterogeneous systems with large summary interphase area between particles and medium.

Disperse systems are characterized by two properties: ***degree of dispersion*** and ***specific surface***.

- ***Degree of dispersion*** shows the degree of comminuting of the substance forming the dispersed phase. Its equal the inverse of the particle size: D=1/a.
- ***Specific surface area*** shows the surface of the unit volume or unit mass of material. A system containing very fine particles is called highly disperse with highly specific surface. When particles are not so finely divided, we speak of a coarse dispersion. As the bulk phase is subdivided into finer and finer particles, the relative ratio of surface to bulk molecules will increase until the effect of specific surface properties will begin to become significant, or even dominate the characteristics of a system.

Classification of the disperse systems

1. Depending on the size of disperse phase particles (dispersion degree) the following types are they distinguished:

- Coarse disperse systems with particle size about 100 nm (1 nm = 1x10^{-9}) and more (suspensions, some emulsions, powders).
- Colloid disperse systems with particle size from 1 to 100 nm (colloid solutions).

Classification of the disperse systems

2. Disperse systems can be classified according to the aggregation state of both the dispersion medium and the dispersed phase, either of which can be in the solid, liquid or gaseous state.

- ***When the dispersion medium is a gas, the system is called aerosol.*** Depending on the state of aggregation of the dispersed phase, aerosols are subdivided into smokes (solid dispersed phase) and fogs (liquid dispersed phase).
- ***Disperse systems with liquid dispersion medium are called liosols or just sols***. They are subdivided into foams (with gaseous dispersed phase), emulsions (liquid dispersed phase), suspensions and colloid solutions (solid dispersed phase).
- ***Disperse systems with solid dispersion medium are called solidosols***. They could be with gaseous dispersed phase (solid foams, silicagel, activated coals), with liquid dispersed phase (wetted soil), and with solid dispersed phase (colored glasses, alloys).

Classification of the disperse systems

3. Depending on the character and intensity of dispersed particles interaction with the dispersion medium for liquid-medium systems they are divided into two types:

- ***A lyophilic (solvent attracting) colloids*** is one particles of which have a strong attraction for the molecules of the dispersion medium.
- ***In lyophobic (solvent repelling) colloids*** the particles do not interact so strongly with the molecules of the surrounding medium.

Classification of the disperse systems

4. According to the interaction intensity of dispersed phase particles disperse systems are divided into two types:

- ***Free disperse systems*** in which there is no interaction between dispersed phase particles and the latter can easily be moved through the medium.
- ***Linked disperse systems*** in which the particles are binding to each other, restricting their motion.

Preparation of the disperse systems

With respect to particle size, colloid systems occupy an intermediate position between molecules and macroscopic bulk phases. They can therefore be produced by breaking down large pieces to the size required (***dispersion methods***) or, vice versa, by bringing up the agglomeration (condensation) of molecules, ions or atoms to particles of the required size (***condensation methods***).

Preparation of the disperse systems

Dispersion methods

- A coarse material can be made into a colloid by different type of colloid mills in the presence of a stabilizer. It also could be done by ultrasound or by acting of an electrical force (***electrodispersion***).
- Besides, there is the ***method of peptization***, in which fresh sediment is converted into a colloid solution by adding a special substance (peptizator).
- Colloids can be obtain by ***dilution of certain substances (such as starch, gelatin) in the suitable solvent***. It is reasonable to assume that the work required reducing a given material to colloidal size; higher surface-energy materials require more work input. In addition, the natural tendency of subdivided particles is to reduce the total surface area by some aggregation process. This tendency could be reduced by the introduction of an intervening medium, usually a liquid

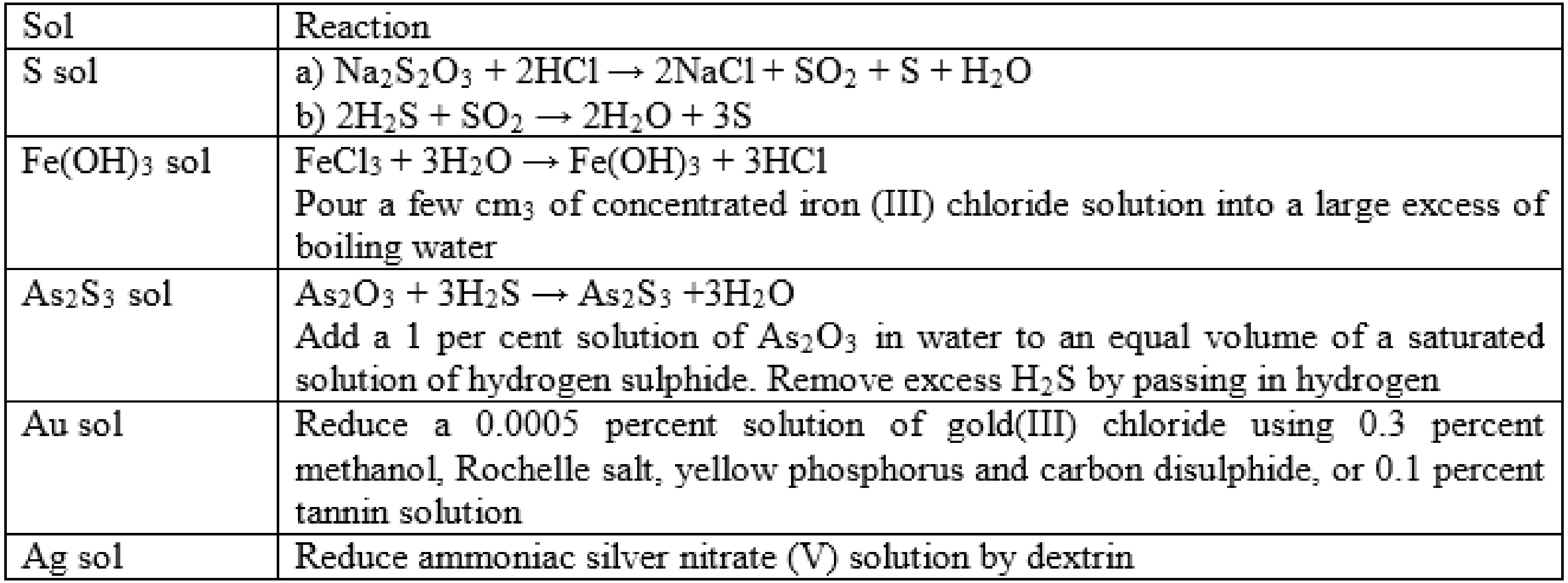
Preparation of the disperse systems

Condensation methods are based on purely ***physical processes***, such as the fast condensation of vapor or on different ***chemical reactions***.

- A common feature of both classes of methods is that the formation or separation of the colloid in the new phase occurs at strong supersaturation, i.e. from a highly supersaturated vapor or a highly supersaturated solution.
- ***In chemical condensation methods***, the colloidal substance is obtained by means of some chemical reactions in which it is separated out in the colloidal state. Such methods are usually based on interactions in solution in which the substance formed is insoluble. Originally formed in the molecular-dispersed state it tends to precipitate from the solution. The conditions of the reaction must be so chosen that aggregation of the molecules into larger particles stop at a certain stage, before coagulation begins. This is usually achieved by taking solutions of sufficiently low concentration (with excess one of them) and slowly mixing them.
- Condensation methods are commonly employed for the production of colloids and aerosols, and less commonly in the production of emulsions.

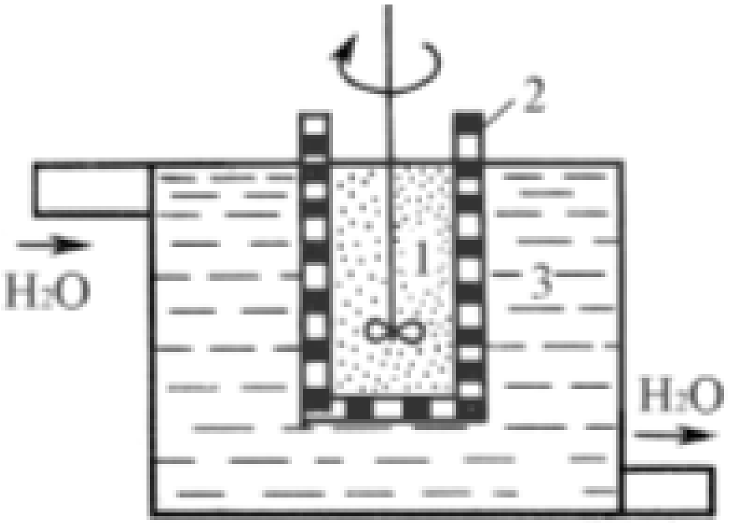
Preparation of the disperse systems

Chemical reactions



Sol	Reaction
S sol	a) $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$ b) $2H_2S + SO_2 \rightarrow 2H_2O + 3S$
$Fe(OH)_3$ sol	$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$ Pour a few cm_3 of concentrated iron (III) chloride solution into a large excess of boiling water
As_2S_3 sol	$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$ Add a 1 per cent solution of As_2O_3 in water to an equal volume of a saturated solution of hydrogen sulphide. Remove excess H_2S by passing in hydrogen
Au sol	Reduce a 0.0005 percent solution of gold(III) chloride using 0.3 percent methanol, Rochelle salt, yellow phosphorus and carbon disulphide, or 0.1 percent tannin solution
Ag sol	Reduce ammoniac silver nitrate (V) solution by dextrin

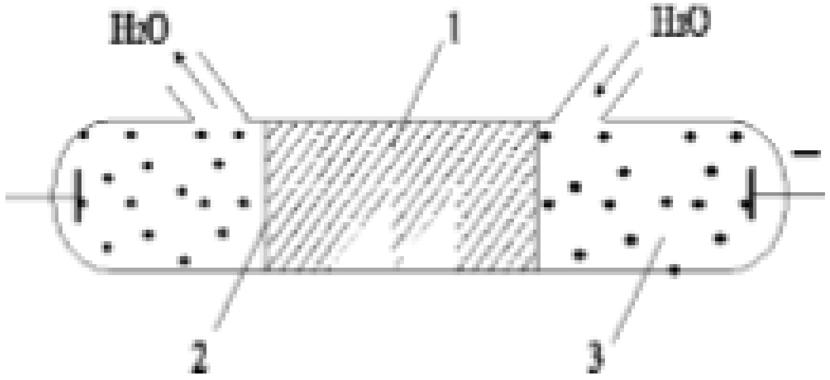
Purification of the disperse systems



Dialysis. In this method the semipermeable membranes are used, which are pervious only for ions and small molecules, but impervious for colloidal particles. Dissolved ions or small molecules move from the region of their higher concentration to a region of lower concentration. For purification the colloid solution containing a crystalloid (electrolytes) it is placed into the bag made of dialyzing (semipermeable) membrane and the bag is immersed into the water. Water continuously circulates around the bag. The molecules and ions move out of the bag into the circulating water where they are removed. Colloid particles cannot cross the membrane and therefore remains in the bag.

Purification of the disperse systems

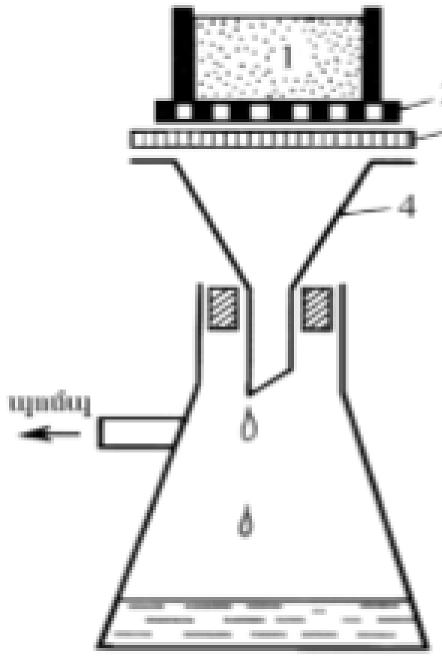
Dialysis can be greatly accelerated by the simultaneous action of an electric current. This technique is called **electrodialysis.** When current is sent through the solution, the electrolytes in it are carried in the form of ions to the corresponding electrodes and carried off by water.



Purification of the disperse systems

Dialysis is often applied in industry and in medicine and biology, especially for analysis and purification of biological liquids. The principal of the dialysis is also used also in the apparatus of the “artificial kidney” whereby separates waste molecules of metabolism such as urea and excess ions from the blood for the people with kidney failure

Purification of the disperse systems



Ultrafiltration. The colloid solution purified by passing through such a filter (3), from which only the molecules and ions of the crystalloid pass through the pores of the filter, while colloid particles are held back by the membrane. The process is hastened by pressure difference on the both sides of the filter.

MOLECULAR – KINETIC PROPERTIES OF COLLOIDS

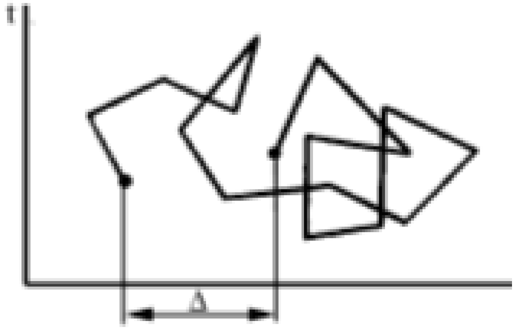
Molecular-kinetic properties of colloids include:

- Brownian motion
- Diffusion,
- Osmotic pressure
- Sedimentation

They subordinate to molecular-kinetic laws of the true solutions, but are expressed much weakly (because of large size of particles).

Brownian motion

This is the term applied to the random motion of particles suspended in a liquid (colloid particles) that is due to the random impacts by the molecules of the surrounding medium (liquid) in their thermal motion. It is called ***<u>Brownian motion</u>*** after its discoverer, the botanist Robert Brown.



Brownian motion

Brownian motion is expressed by average square displacement (Δ^2), which shows projection of the distance between the initial and final positions of the particle in a unit of time on the abscise. Einstein averaged over many colloidal particles and found the equation for Δ^2:

$$\Delta^2 = \frac{RT}{3\pi\eta r N_A} t$$

where **t** is the time of displacement, **R** is the gaseous constant, **T** is the absolute temperature, **η** is the viscosity of the surrounding, **r** is the radius of the particle, $\mathbf{N_A}$ is the number of Avogadro.

Diffusion

The solute always has a tendency to pass from points of higher concentration to the ones of lower concentration. This spontaneous decrease in concentration differences is called ***diffusion***. It is occurred due to the difference of chemical potentials of the substances in different parts of the system caused by Brownian motion. This process is characteristic to both true solutions and colloids, but the diffusion rate is many times less in the latter.

Diffusion

The expression, which relates the flow of material to the concentration gradient, is referred to as ***Fick's first law equation***:

$$\frac{dm}{dt} = -DS\frac{dC}{dx}$$

where dm is the amount of matter passing through a cross section S in a time interval dt when the concentration changes by dC through a distance dx (dC/dx is called concentration gradient).

- ***The proportionality constant D*** is called the diffusion coefficient. It is numerically equal to the quantity of matter that diffuses in unit time (1s) through a cross section of 1 sq cm when the concentration gradient is unity, i.e., when the concentration decreases by one unit per cm of path.
- ***Fick's first law equation describes*** the diffusion process under conditions of steady state; that is, the concentration gradient does not change with time.

Diffusion

Fick's second law equation:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

Fick's second law states that the rate of concentration change in a volume element within the diffusion field is proportional to the rate of change in the concentration gradient at that point in the field, the proportionality "constant" being the diffusion coefficient or diffusivity.

Diffusion

The relationship between the radius (r) of the drug molecule (or other particle) and its diffusion coefficient is given by the ***Stokes-Einstein equation*** as

$$D = \frac{RT}{6\pi\eta r N_A}$$

This relation shows that the rate of diffusion increases in direct proportion to the temperature, and in inverse proportion to the viscosity of the medium and the size of the particles. By means of this relation, it is possible to determine the "molecular weight" of colloid particles from measurements of the rate of diffusion.

Diffusion

- There is a connection between the diffusion coefficient and the average square displacement, which is expressed by equation

$$\Delta 2 = 2Dt$$

- The solution of the diffusion equation can be used to predict the concentration of particles at any location. We can also use them to calculate the net distance through which the particles diffuse in a given time. It is very important also to determine drug diffusion rate through the organism tissues and liquids as well in different diffusion processes in organism.

Osmotic pressure

The ***osmotic pressure*** of colloid solutions as well as true solutions is directly proportional to the number of colloid particles in a unit volume of the solution:

$$\pi = \frac{n}{V}RT$$

- The osmotic pressure of colloid solutions is much lower than that of true solutions.
- The osmotic pressure for the same colloid solution measured in different time under the same conditions has a different value. It is due to the aggregating and disaggregating processes occurred in the colloid solutions, hence the number of the colloid particles changes, so changes the osmotic pressure.
- For these reasons, the measurement of the osmotic pressure is not applied for solute concentration determination in colloid systems.

Sedimentation

If the size and density of particles suspended in a liquid are sufficiently more than those of the liquid they settle under the force of gravity. This process is called ***sedimentation.*** The rate of sedimentation is expressed by ***Stock's equation***:

$$V = \frac{2}{3}\frac{r^2(\rho - \rho_0)g}{\eta}$$

where **r** is the radius of the particle, **ρ** and **ρ_o** are the solution and the solvent densities accordingly, **g** is the acceleration of gravity, **η** is the viscosity of the medium.

Sedimentation

The particles in the colloid solutions are not only under gravitation force, but also under diffusion force. With large particles, the force of gravity is the decisive factors, and such particles eventually, depending on their size, settle on the bottom of the vessel. However, with smaller particles the rate of diffusion is sufficient to prevent their settling. Hence, for small particles equilibrium between gravitation and diffusion force could be states, which is known as ***sedimentation equilibrium***. It is characterized by a gradual decrease in concentration from the bottom of the vessel to the upper layers of the solution. This phenomenon, for example, causes the decrease in atmospheric pressure (i.e., the concentration of molecules of air), with altitude.

OPTICAL PROPERTIES OF COLLOIDS

Optical properties of colloids differ from those of true solutions due to difference in optical densities of particles and medium. It depends on particle amount and size, as well as on the wavelength of the light. To put it more precisely optical properties depend on the ratio of the diameter of the particles of dispersed phase (2r) to the length of the light (λ) passing through dispersed system as well as on the distance between particles.

When the beam of the light passes throughout the colloid solution the following optical phenomena could occur:

- Scattering,
- Absorption,
- Deflection
- Reflection of the light

If $2r \gg \lambda$, the reflection, deflection and absorption of light happen.

OPTICAL PROPERTIES OF COLLOIDS

- If particle size of colloid dispersed system is about or less then λ, the diffraction light scattering takes place. Each colloid particle becomes secondary source of light, causing an ***opalescention***. This is a process, when the colors of sole under the passing light and light passing from a side are different. It has been observed that the path of a beam of light through a perfectly transparent colloidal solution of gold becomes outlined when observed laterally against a dark background. This is known as the ***Tyndall effect*** and is due to the scattering of light by the colloidal particles.
- This phenomenon of light scattering describes by ***Reley's equation***:

$$I = K\frac{\nu V^2}{\lambda^4}$$

where I is the intensity of scattering light, ν is the number of the particles in the unit volume, V is the volume of a particle (its size), λ is the length of falling light wave, and K is the optical coefficient.

OPTICAL PROPERTIES OF COLLOIDS

The ***Tyndall effect***

OPTICAL PROPERTIES OF COLLOIDS

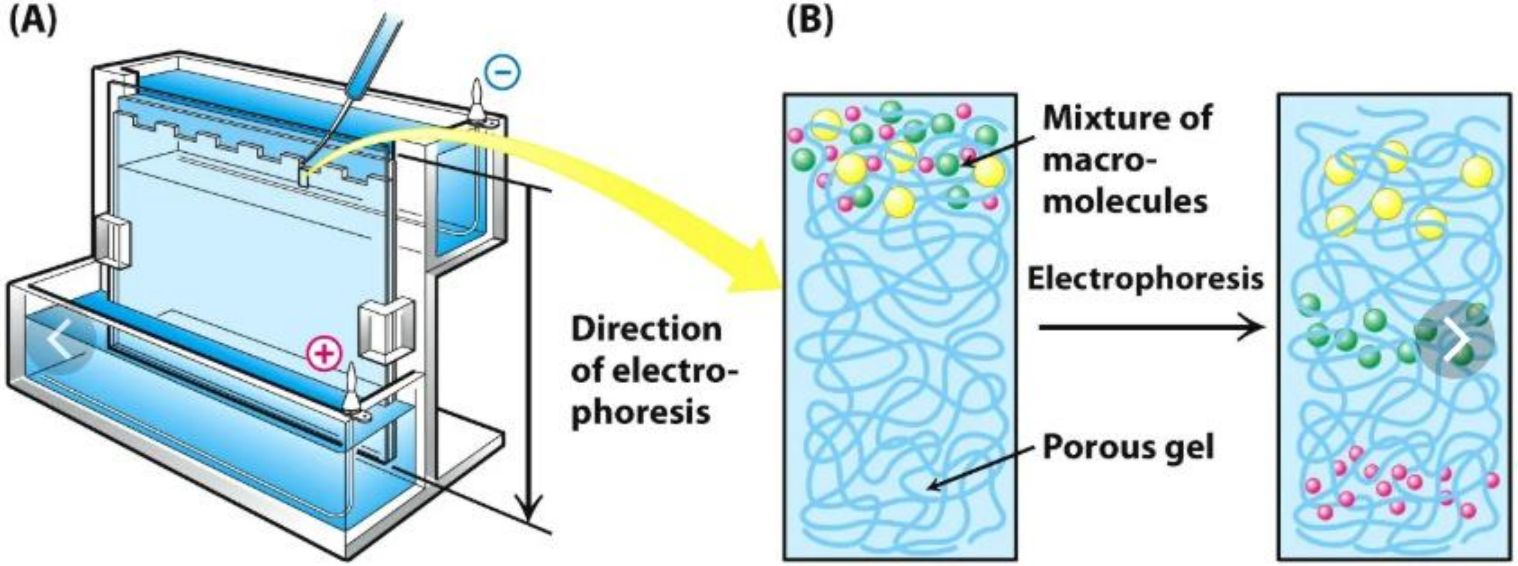
In colloidal systems, besides scattering ***absorption*** of the certain wavelength of white sunlight by colloidal particle might occur. It depends on the nature of particles, their size and shape. ***Light absorption is described by Lambert-Buger equation***:

$$I_n = I_o e^{-kl}$$

where Io is the incident intensity of the light, I – transmitted intensity, l is the thickness of the sample, k is the absorption coefficient. Then by Beer-Lambert was found that k is proportional of the molar concentration: k=εc, where ε is the molar absorption coefficient.

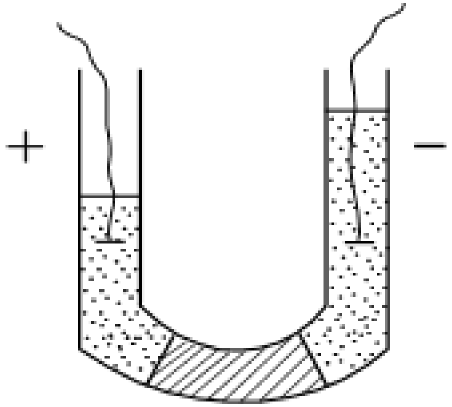
ELECTRICAL PROPERTIES OF COLLOIDS

1. *Electrophoresis* is the movement of a charged interface (usually colloidal particles or macromolecules) with its electrical double layer together relative to a stationary liquid under the influence of an applied electrical field



ELECTRICAL PROPERTIES OF COLLOIDS

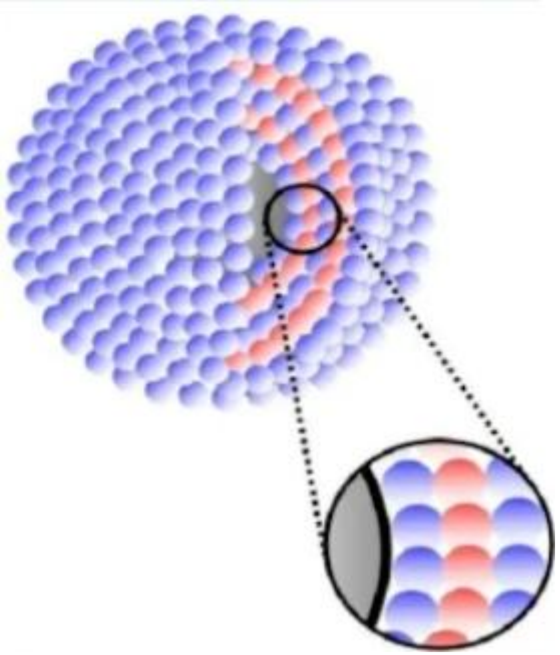
2. Electroosmosis is the movement of a liquid relative to a stationary charged interface under the influence of an applied electrical field. The level of water in cathode part is raised, i.e. the solvent of the colloid solution is moved through the pores of a diaphragm of very fine particles under the influence of an applied potential gradient.



Micellar theory of colloid particle structure

According of this theory colloidal solutions (it relates only to lyophobic sols) consist of the micelles and the intermicellar liquid (solvent with dissolved inorganic species). ***Micelle*** is the colloidal particles with double electrical layer. It has the following structure: the centre of the micelle, nucleus, is the original particle composed of a great number of molecules of a certain species. Then nucleus with adsorption layer is formed granule. In addition, granule with diffusion layer is called micelle.

Micellar theory of colloid particle structure



$$KI + AgNO_3(\text{ex.}) - AgI\downarrow + KNO_3$$

$$mKI + (m + n)AgNO_3 \rightarrow mAgI \cdot nAg^+ + + nNO_3^- + mKNO_3$$

$$\{m[AgI]nAg^+(n - x)NO_3^-\}^{x+}xNO_3^-$$

$$\underbrace{\underbrace{\underbrace{\{m[AgI]}_{\text{aggregate}}\underbrace{nAg^+(n - x)NO_3^-\}^{x+}}_{\text{adsorption layer}}}_{\text{colloid particle}}\underbrace{xNO_3^-}_{\text{diffuse layer}}}_{\text{Micella}}$$

Stability and coagulation of colloids

- ***Stability of colloid systems*** means the stability of their properties for a precise time. It is related to a degree of dispersion and uniform distribution of particles through the solution, i.e., there mustn't be increase in size of particles and sediment formation.
- There are two kinds of processes leads to the disintegration of colloid system and that under certain conditions can take place spontaneously. These are ***sedimentation*** and ***coagulation processes***. In sedimentation processes, the particles of the dispersed phase settle out or rise to the surface of the system, depending on the ratio of the densities of the dispersed particles and the dispersion medium. In coagulation processes, the particles of the dispersed phase adhere to one another increasing in size.

Stability and coagulation of colloids

The ability of dispersed phase to stay equally diffused in dispersed medium is called the ***kinetic stability of the system***. Two conflicting processes determine kinetic stability: ***sedimentation*** and ***thermal motion*** of the particles of the dispersed phase. The particles doing movement tend to spread equality in the whole volume of the system. If the diffusion forces are larger than the gravitation forces of the Earth, the system is kinetically stable. ***Kinetic stability depends*** on the particles size; the smaller particles size, the more stability. The molecules of the dispersion medium continually collide with the dispersed particles, which in view of their small size are thereby kept in a state of suspension.

Stability and coagulation of colloids

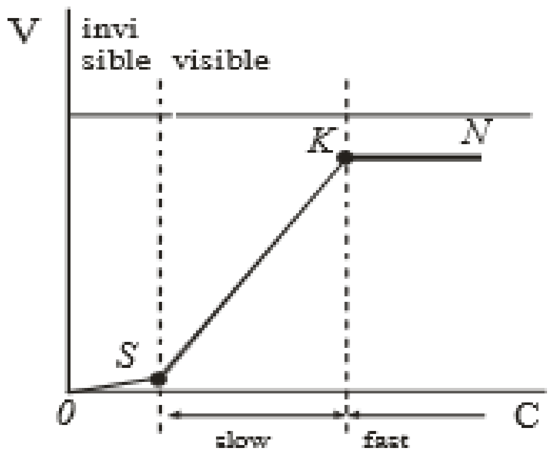
Investigations of the coagulation of lyophobic sols by electrolytes have led to the following conclusions:

- All electrolytes, in sufficient concentration, are capable of coagulating lyophobic sols.
- The coagulating action of an electrolyte is due to the ion whose charge is opposite in sign to that of the colloid particle.
- The effect of coagulation may be visible to the naked eye (apparently by turbidity of a solution) and is known as the stage of visible coagulation.
- Visible coagulation begins when the concentration of the electrolyte (mol electrolyte/dm^3 of sol) exceeds a certain minimum value of the electrolyte, called the coagulation threshold (mol electrolyte/dm^3 of sol). Thus, one may characterize the stability of a charge-stabilized colloidal system by its critical coagulation concentration (ccc), the concentration of electrolyte necessary to bring the system into the regime of rapid coagulation.

Stability and coagulation of colloids

- The effect of coagulation depends on the coagulating ion size and valence. According Schulze-Hardy's rule the larger the valence of the coagulating ion the stronger effect of coagulation and the smaller coagulation threshold. For example, the coagulation effect (coagulation threshold) of ions of different valence K^+, Ba^{2+} and Al^{3+} is accordingly 540:7,4:1.
- For the univalent ions, the coagulation effect is non-equal because of their different size. Thus, the cations of the alkali metals form the series in the order of decreasing coagulating ability: $Cs^+>Rb^+>K^+>Na^+>Li^+$ Such series are called ***lyotropic.***

Stability and coagulation of colloids



Coagulation rate dependence on the amount of an electrolyte. Segment OS corresponds to invisible coagulation. During this period the aggregation of particles takes place and a decrease of the dispersion degree, but there are not any visible changes. This period is called hidden period of coagulation (invisible stage). Point S is the coagulation threshold point, after which the visible coagulation occurs. During the segment OK the rate of the coagulation increases with the electrolyte concentration increasing. Point K is an isoelectric state of the colloid system, when zeta potential is equal to zero. After this point, coagulation occurs independently on the presence of an electrolyte

Stability and coagulation of colloids

There are three types of coagulation could be observed:

- ***Additive coagulation*** occurs when electrolytes are close in nature, such as NaCl and KCl. In this case the coagulation threshold is intermediate in value between the coagulation thresholds of these electrolytes when used separately.
- Much more frequently, the coagulating power of a given electrolyte decreases when it is used with another electrolyte together. This phenomenon is called ***antagonist coagulation***.
- In ***synergist coagulation*** the coagulating power of a given electrolyte increases when another electrolyte is added to it.

Stability and coagulation of colloids

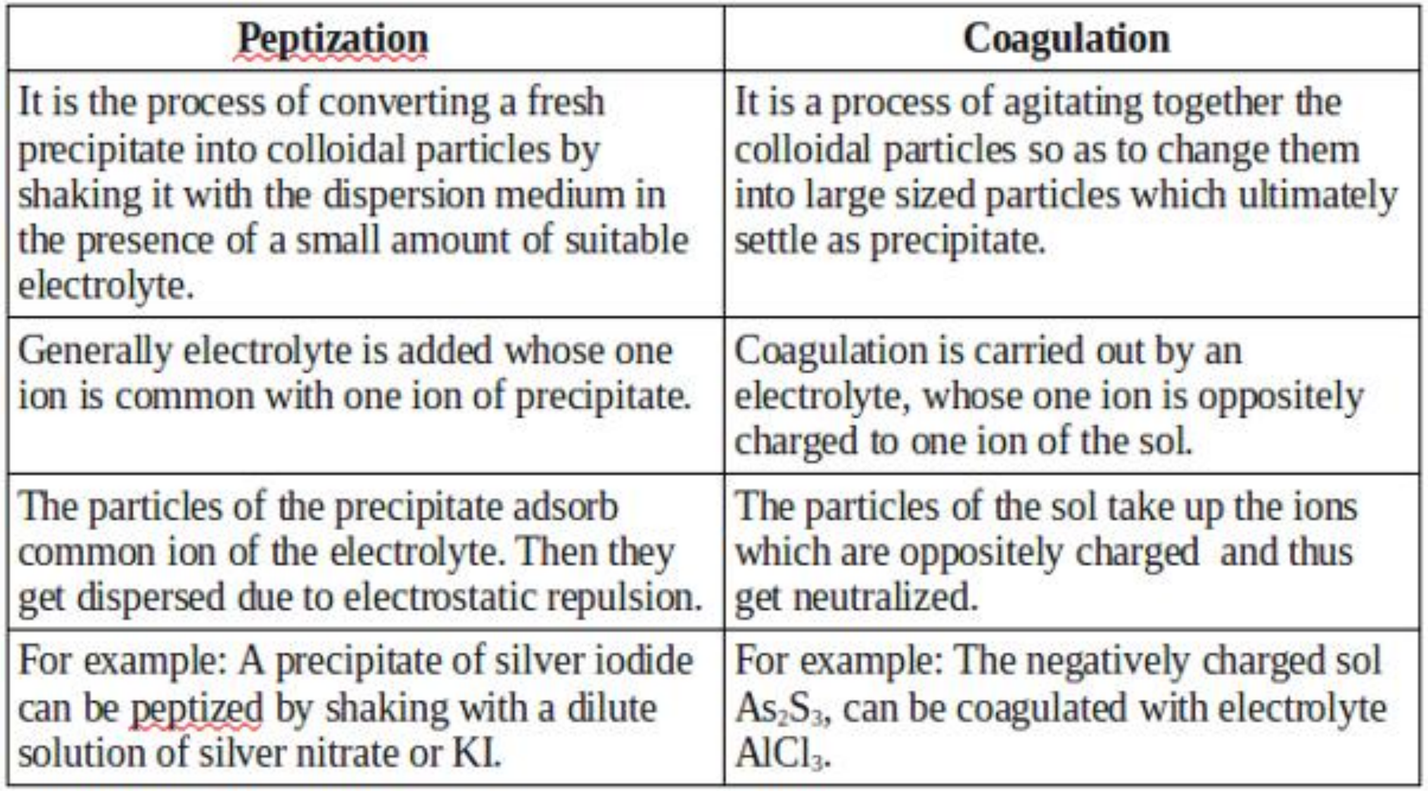
Protection of colloids

- For greater stability of colloids some special substances, which are called ***protective species or stabilizers***, are added to colloids. Usually it is high-molecular compounds (proteins, gelatin, albumin, polysaccharide), which are adsorbed on the surface of the colloid particles forming protective films that stabilizes the interface and cannot be penetrated when two particles touch each other.
- One must be careful in the precise amount of the stabilizer. When a protective species is applied in an amount too small for protection it may, on the contrary, reduce the stability of the sol. This increase in sensitivity of the sol is called ***sensitization***. It occurs as the small amount of the polymer of high molecular weight as stabilizer is insufficient for all particles surfaces adsorption and one molecule of the stabilizer could simultaneously adsorb on a few particles surfaces promoting faster coagulation

Protection of colloids

- ***Peptization (resolution)*** is the disintegration of the coagulation product (fresh-forming sediment) into a sol under the action of compounds called peptisate)rs. Their main function is to decrease significantly the intermolecular adhesion forces.
- Peptization is divided into two groups: ***adsorption*** and ***ablution***.

Peptization and coagulation



Peptization	Coagulation
It is the process of converting a fresh precipitate into colloidal particles by shaking it with the dispersion medium in the presence of a small amount of suitable electrolyte.	It is a process of agitating together the colloidal particles so as to change them into large sized particles which ultimately settle as precipitate.
Generally electrolyte is added whose one ion is common with one ion of precipitate.	Coagulation is carried out by an electrolyte, whose one ion is oppositely charged to one ion of the sol.
The particles of the precipitate adsorb common ion of the electrolyte. Then they get dispersed due to electrostatic repulsion.	The particles of the sol take up the ions which are oppositely charged and thus get neutralized.
For example: A precipitate of silver iodide can be peptized by shaking with a dilute solution of silver nitrate or KI.	For example: The negatively charged sol As_2S_3, can be coagulated with electrolyte $AlCl_3$.