V.N. Karazin Kharkiv National University

Medical Chemistry

Module 2. Lecture 9

Physicochemical fundamentals of colloidal systems. The colloid stability

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Lecture topics

- √ The colloidal state
- √ Classification of colloidal systems
- √ Preparation of colloidal systems
- √ Tyndall effect
- √ The structure of colloidal particles
- √ Purification of colloidal systems
- √ Hemodialysis or kidney dialysis
- √ The colloid stability
- √ Coagulation of lyophobic colloidal systems
- √ Coagulation threshold
- √ Schultze-Hardy rule
- √ Kinetic and aggregate stabilities of colloidal systems
- √ Protective action
- √ Flocculation
- √ Introduction to blood coagulation

The colloidal state

Colloidal systems or colloids (from Greek word 'κωλλα', meaning 'glue') are a specific state of matter endowed with certain characteristic properties.

It is not a given class of substances, for instance, salt (potassium chloride, KCl) forms a colloidal solution in benzene (C_6H_6), but forms a true solution in water.

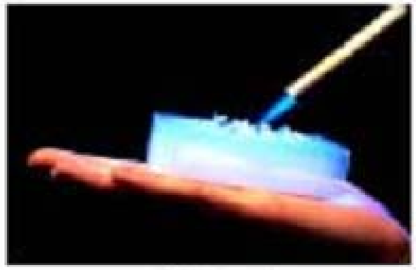
Examples of colloidal systems from daily life

Foams

Milk

Fog, smoke

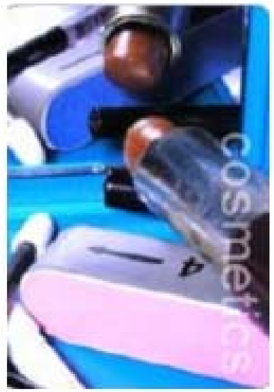
Detergents



Aerogel

Blood

Paints



Cosmetics

The colloidal state

***The first important characteristic* of the colloidal state** is **the presence of particles** which are larger than molecules, but not large enough to be seen in microscope. The size of particles in the colloidal state is from 10^{-9} to 10^{-7} meter, although those limits are far from rigid.

***The second essential property*:** *the colloidal solutions consist of two or more phases*. The two phases may be distinguished by the terms:

dispersed phase (for the phase forming the particles) and

dispersion medium or *continuous phase* for the medium in which the particles are distributed (or dispersed).

Classification of colloidal systems

All colloidal systems may be classified in the following manner.

1. Classification in accordance with *aggregative state of dispersed phase* and *dispersion medium* (see Table below). The medium may be solid, liquid or gaseous; similarly the dispersed phase may be solid, liquid or gaseous, thus leading to a number of possible types of colloidal systems.

If the dispersed phase and medium are nonmixable liquids the result is an ***emulsion.***

Table. Examples of commonly encountered colloidal systems

System	Type	Dispersed phase	Continuous phase or dispersion medium
Fog, mist	Liquid aerosol	Liquid	Gas
Smoke	Solid aerosol	Solid	Gas
Shave cream	Foam	Gas	Liquid
Styrofoam	Solid foam	Gas	Solid
Milk	Direct emulsion	Liquid (fat)	Liquid (water)
Butter	Reverse emulsion	Liquid (water)	Liquid (fat)
Paint	Dispersion	Solid	Liquid
Suspension	Dispersion	Solid	Liquid
Sol	Dispersion	Solid	Liquid
Opal	Dispersion	Solid	Solid
Jello	Gel	Macromolecules	Liquid
Liquid soaps and detergents	Micellar solution	Micelles (aggregates) of detergent molecules	Liquid

Classification of colloidal systems

2. Classification in accordance with *interaction between dispersed phase and dispersion medium.* This classification is used only for colloidal solution with *a liquid dispersion medium*. Sols may be divided into ***lyophobic*** and ***lyophilic*** or *hydrophobic* and *hydrophilic*, if dispersion medium **is aqueous**.

Lyophobic sols are relatively unstable (particles aggregate and sediment); have low affinity for the solvent; addition of electrolytes causes coagulation and precipitation. *Typical examples of lyophobic sols* are sols of metals, sulfur, sulfides, silver halides, and also inks, paints.

Lyophilic sols have strong affinity between dispersed phase and dispersion medium and are stable (particles stay separate). *Typical examples of lyophilic sols* are surfactant solutions at defined concentration and sols of proteins.

Classification of colloidal systems

3. Classification in accordance with the *size of particles of dispersed phase*. If diameter of particles is more than 10^{-4} meter, it is ***heterogeneous systems***; if diameter of particles lies in the range from 10^{-5} to 10^{-7} meter, it is ***microheterogeneous systems***; if diameter of particles less than 10^{-7} meter, but more than 10^{-9} meter it is ***'true' colloidal systems or ultramicroheterogeneous systems.***

4. Classification in accordance with the *shape of particles of dispersed phase*. For example, shape can be spherical, cylindrical, cubic, needle-like, etc.

Preparation of colloidal systems

<u>Lyophilic systems</u> may be prepared when substances with high molecular weight are warmed with a suitable dispersion medium. For example, gelatin and starch in water, rubber in benzene.

<u>Lyophobic systems</u> *may be prepared* by special methods:

(1) *<u>condensation methods</u>*

or

(2) *<u>dispersion methods</u>*.

Preparation of colloidal systems

***<u>Condensation methods</u>* <u>are:</u>**

(1) ***<u>physical condensation</u>*** *<u>is based on physical processes</u>*, such as solvent replacement or vapor condensation (for example, the fog formation);

(2) ***<u>chemical condensation</u>*** is based *<u>on different chemical reactions</u>*, hydrolysis, ion-exchange reactions, oxidation-reduction, etc. For example, hydrolysis of ferric chloride $FeCl_3$:

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3HCl,$$

by adding boiling water dropwise to a solution of ferric chloride one obtains the dark brown sol of ferric hydroxide.

A common feature of both classes of condensation method is that formation of <u>the colloidal particles in the new phase occurs at strong supersaturation</u>.

Preparation of colloidal systems

Dispersion methods. In these methods the starting material consists of the substance in the massive form; by means of suitable devices **it is disintegrated into particles of colloidal dimensions**. Colloidal mill or electrical disintegration (a direct current electrical arc) are used. For example, when a coffee is milled in a grinder, ultrasonic destruction of kidney stones, and etc.

Peptization is the direct disintegration or dispersion of the coagulation products of a sol into particles of colloidal size by an added *peptizing agent*.

For example, a deposit of ferric hydroxide can be peptized by treatment with very small quantities of ferric chloride solution after preliminarily removing of the coagulating substances. In this case peptization is due to adsorption of Fe^{3+} ions which again stabilize the particles.

Tyndal effect

Presence of colloidal particles can be made evident ***by optical means***.

If a strong beam of light is passed through a colloidal solution, ***colloidal particles will scatter the light***.

True solutions are optically clear, *but colloidal solutions scatter light*, producing *so-called the* ***Tyndall effect***.

The path of the light through the sol, which is rendered visible as a result of the scattering, is called the ***Tyndal beam***.

The structure of colloidal particles

Necessary conditions for the stability of lyophobic sols are:

√ the particles must be very small (offsets sedimentation);

√ must carry electrical charges (hinder coagulation);

√ must form solvate shells (hinder coagulation).

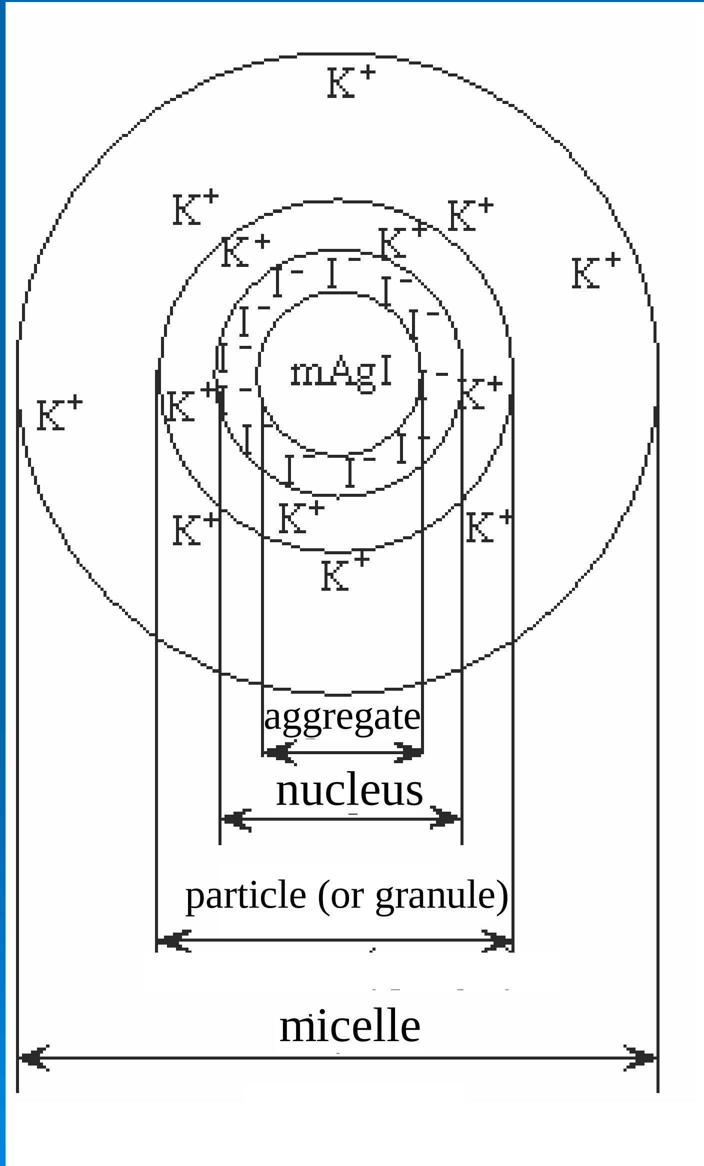
Electrical charges appear on the colloidal particles as a result of adsorption processes, when the particles preferentially adsorb ions of a given species from the solution, depending on the nature of the colloidal and experimental conditions.

The structure of colloidal particles

The particles of a colloid preferentially adsorb ions of a certain species from the electrolyte solution.

The entire part, consisting of ***the particles*** of the dispersed phase with the ***adsorbed ions (potential-determining ions)*** and ***counter-ions of Stern layer (ions of opposite charge)*** partially bound to them, migrates through the solution as a single unit so-called ***particle or granule***.

The counter-ions in the surrounding solution experience an attraction to the charged particles. Those nearest to it are more strongly attracted and become bound to the particle. The entire unit with the ***counter-ions of diffuse layer*** is called ***a micelle***.



The structure of colloidal particles

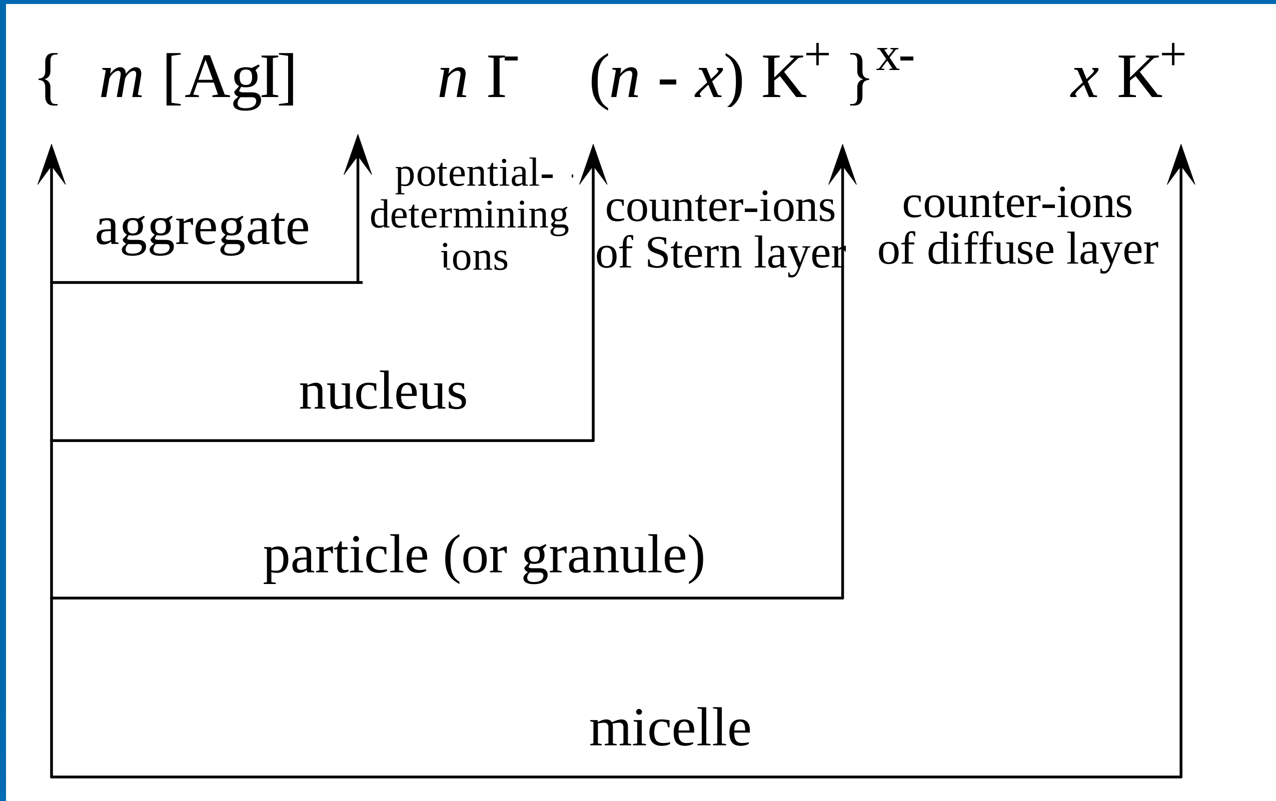


Figure. Structure of silver iodide micelle with negatively charged particles

Purification of colloidal systems

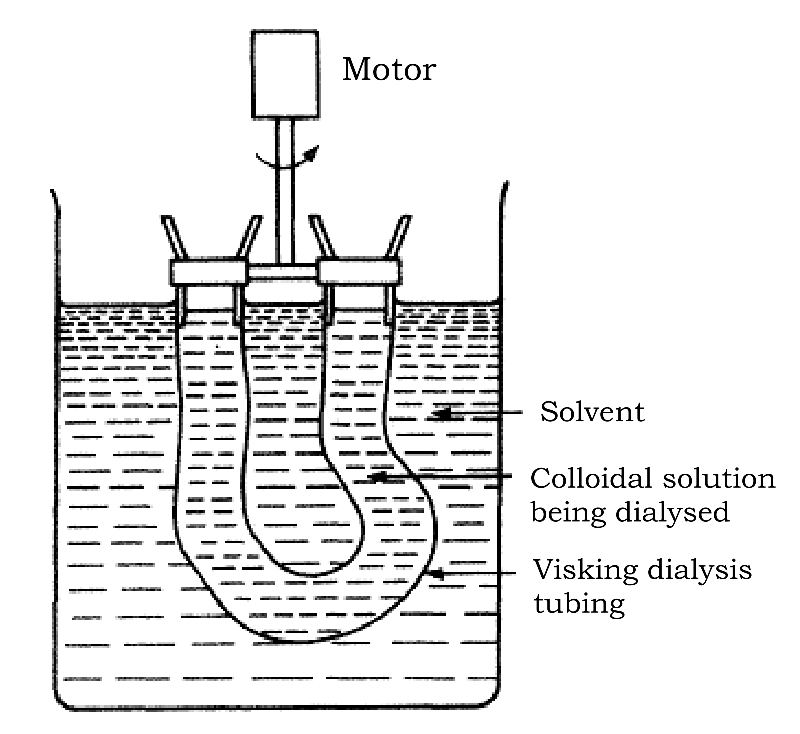
Dialysis

The use of membranes for separating particles of colloidal dimensions is termed ***dialysis***.

The most commonly used membranes are prepared from regenerated cellulose products such as collodion (a partially evaporated solution of cellulose nitrate in alcohol plus ether), cellophane and visking (a type of seamless cellulose tubing used as a membrane in dialysis and as an edible casing for sausages).

Dialysis is particularly useful for removing small dissolved molecules from colloidal solutions or dispersions. The process is hastened by stirring so as to maintain a high concentration gradient of diffusible molecules across the membrane and by renewing the outer liquid from time to time (see Figure below).

Purification of colloidal systems



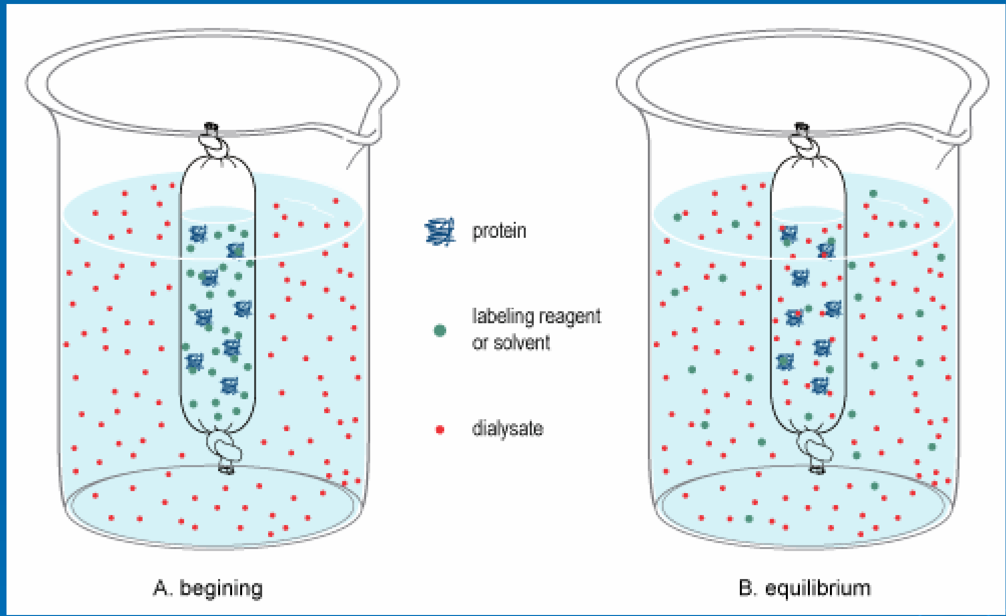


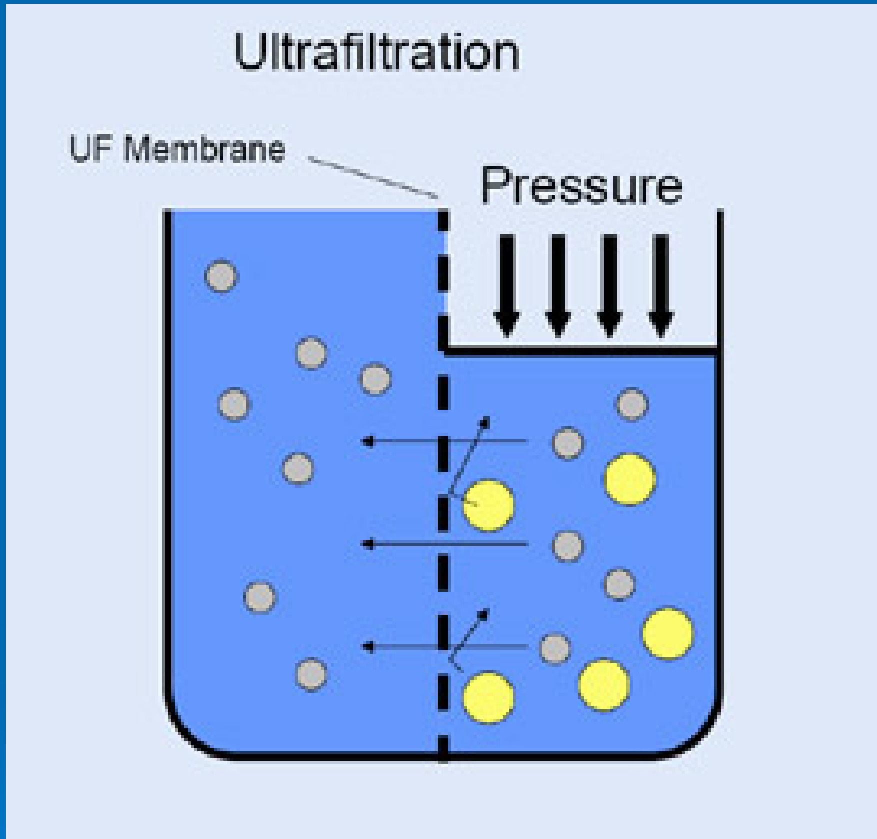
Figure. A simple dialysis set-up

Purification of colloidal systems

Ultrafiltration is the application of pressure or suction to force the solvent and small particles across a membrane while the larger particles are retained.

The membrane is normally supported between fine wire screens or deposited in a highly porous support such as a sintered glass disc.

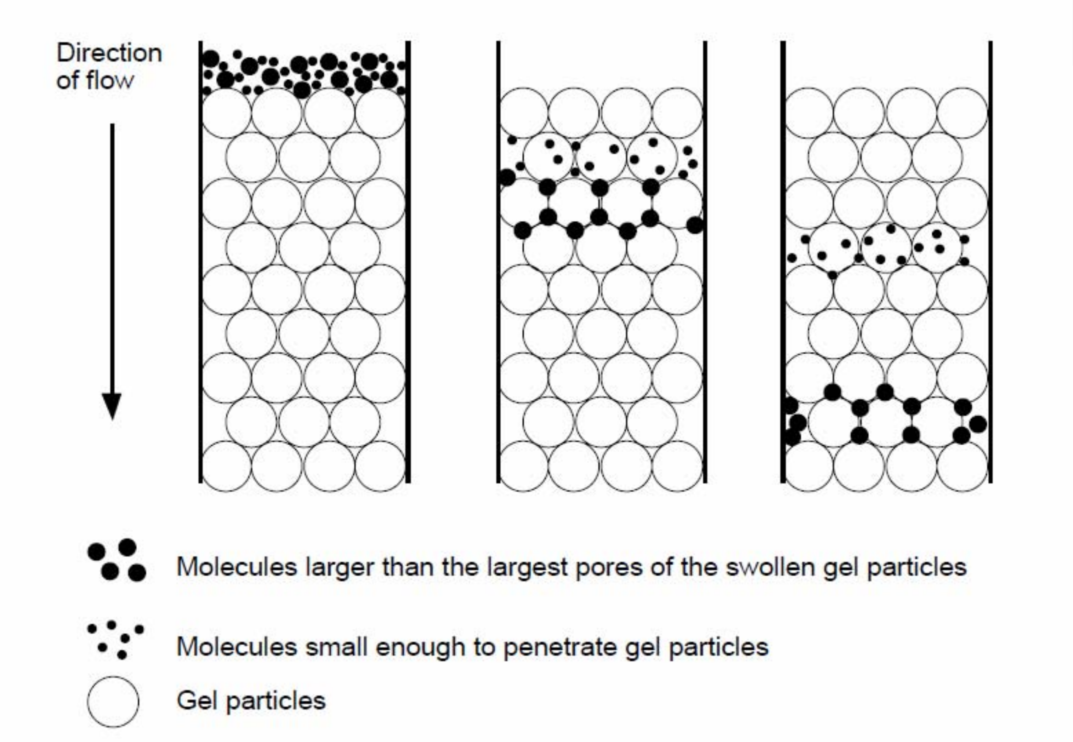
An important application of ultrafiltration is the so-called *reverse osmosis method of water desalination*.



Purification of colloidal systems

Another most valuable development of the <u>ultrafiltration principle</u> is the technique of <u>*gel permeation chromatography*</u> <u>for the separation of the components of a polymeric sample and determination of the relative molecular mass distribution</u>.

The usual experimental arrangement involves the application of a pressure to force polymer solution through a chromatographic column filled with porous beads.



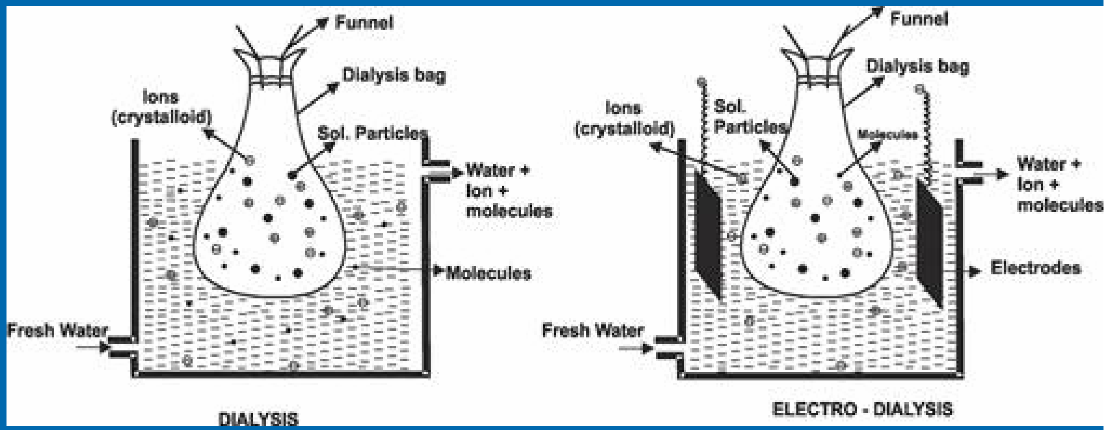
<u>**The larger polymer molecules tend not to enter the pores**</u> of the beads and so pass through the column relatively quickly, whereas <u>**the smaller polymer molecules tend to diffuse**</u> through the pore structure of the beads and so take longer to pass through the column.

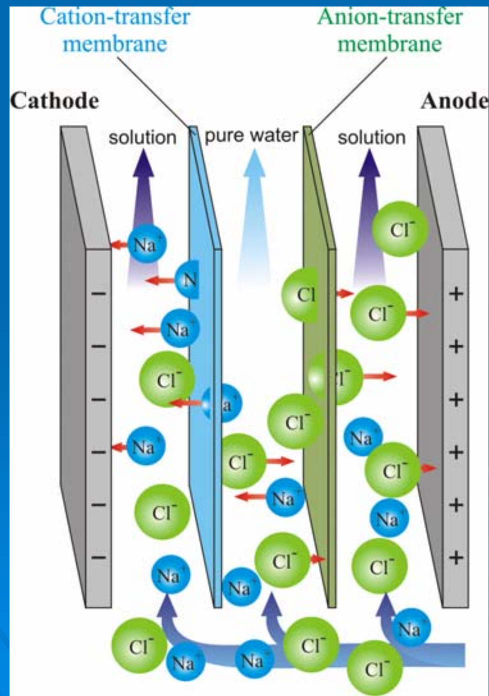
Purification of colloidal systems

A further modification of dialysis is the technique of *electrodialysis*, as illustrated in Figure.

The applied potential between the metal screens supporting the membranes speeds up the migration of small ions to the membrane surface prior to their diffusion to the outer liquid.

The accompanying concentration of charged colloidal particles at one side and, if they sediment significantly, at the bottom of the middle compartment is termed ***electrodecantation***.





Hemodialysis or kidney dialysis

<u>Hemodialysis</u> or **<u>kidney dialysis</u>** is a process of purifying the blood of a person whose kidneys are not working normally.

This type of dialysis achieves the extracorporeal removal of waste products such as creatinine and urea and free water from the blood when the kidneys are in a state of renal failure.

The principle of hemodialysis is the same as other methods of dialysis; it involves diffusion of solutes across a semipermeable membrane (see Figure).

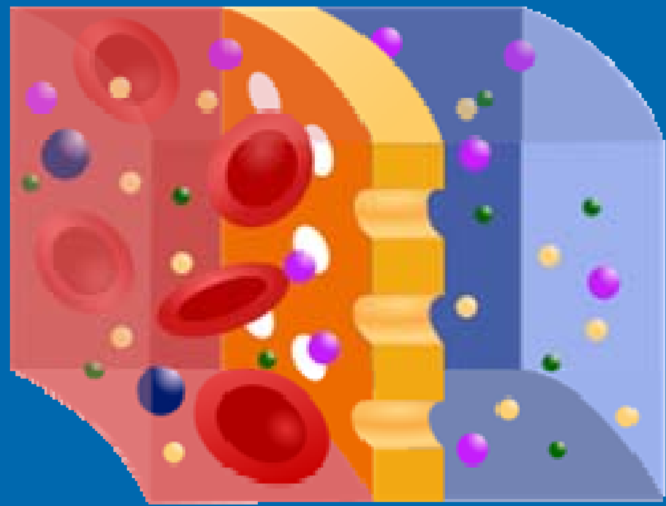


Figure. Semipermeable membrane

Hemodialysis or kidney dialysis

Hemodialysis utilizes counter current flow, where the dialysate is flowing in the opposite direction to blood flow in the extracorporeal circuit. Counter-current flow maintains the concentration gradient across the membrane at a maximum and increases the efficiency of the dialysis.

Fluid removal (ultrafiltration) is achieved by altering the hydrostatic pressure of the dialysate compartment, causing free water and some dissolved solutes to move across the membrane along a created pressure gradient.

The dialysis solution that is used may be a sterilized solution of mineral ions. Urea and other waste products, potassium, and phosphate diffuse into the dialysis solution. However, concentrations of sodium and chloride are similar to those of normal plasma to prevent loss. Sodium bicarbonate is added in a higher concentration than plasma to correct blood acidity. A small amount of glucose is also commonly used.

Hemodialysis or kidney dialysis

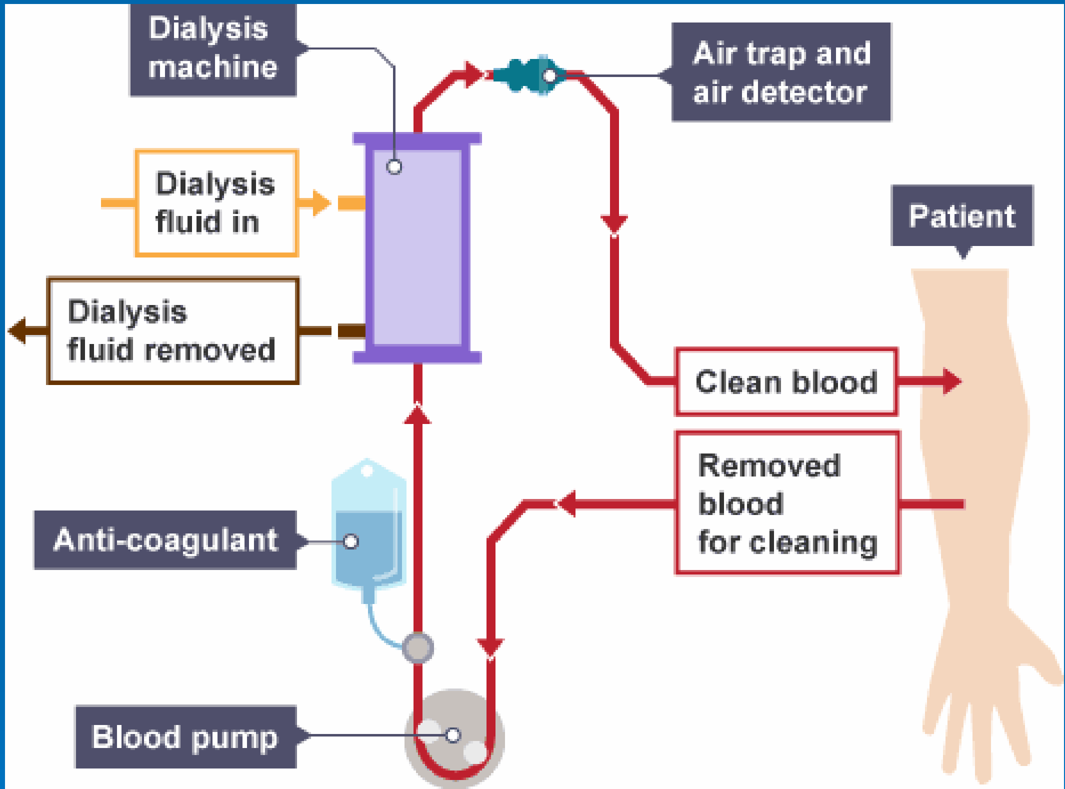


Figure. Principle of hemodialysis

Figure. Hemodialysis machine

Coagulation

Coagulation is the process in which colloidal particles come together to aggregate and form a **visible precipitate or *coagulum***. ***Coagulum*** is an aggregate of colloidal particles having a relatively tight, dense structure formed as a result of the inability of the colloidal system to maintain its dispersed state. Such aggregates are normally formed irreversibly; that is, they cannot be returned to the colloidal state without significant input of work.

stable $Fe(OH)_3$ sol

Sol undergoes coagulation upon the addition of $Al_2(SO_4)_3$ solution

Coagulation threshold

One of the most important ways of the coagulation of lyophobic sols is ***the addition of an electrolyte***.

A certain minimum value of electrolyte concentration in the 1 liter of sol at which coagulation begins is called ***coagulation threshold***, *γ*, *or* ***critical coagulation concentration (ccc)***: $\gamma = n / V$, mol/l

where *n* – electrolyte moles number where coagulation is observed; *V* – total volume of solution.

Investigations of the coagulation process of lyophobic sols by electrolytes have led to the formation of the so-called ***Schultze-Hardy rule*** (H. Schultze, 1882; W.B. Hardy, 1900):

Schultze-Hardy rule

(1) Coagulation of the sol is caused by the ions carrying ***the charge opposite*** to that of sol particles.

(2) Coagulating power of ions causing coagulation is ***directly proportional to the valence of these ions***.

For example, to coagulate **negative particles of sol of As_2S_3**, the coagulation power of different cations has been found to decrease in the order as:

$Al^{3+} > Mg^{2+} > Na^{+}$.

Similarly, to coagulate **positive particles of sol such as $Fe(OH)_3$**, the coagulating power of different anions has been found to decrease in the order:

$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$.

Schultze-Hardy rule

According to the theory of coagulation of hydrophobic sol by the electrolytes the coagulation threshold varies as the inverse ***sixth power*** of the valence of ions causing coagulation:

$$\gamma = \frac{\text{const}}{z^6}$$

For monovalent ions, the effectiveness for coagulating negatively charged colloids has the order:

$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$,

while for divalent cations the order is:

$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

At increasing of the concentration of added electrolyte to the sol *the diffuse layer of electrical double layer is compressed and zeta potential is decreased.* This effect leads to instability of colloidal system and to coagulation process.

Stability of colloidal systems

Colloidal systems differ widely ***with respect to stability***. Some of them can be preserved unchanged for long periods of time; others are comparatively unstable being more sensitive to various influences.

There are two kinds of processes which lead to the disintegration of colloidal systems and which under certain conditions can take place spontaneously. These are *sedimentation processes* and *coagulation processes*. ***Kinetic and aggregate stabilities*** characterize colloidal systems stability with respect to sedimentation process and the changing in particle size (coagulation).

Stability of colloidal systems

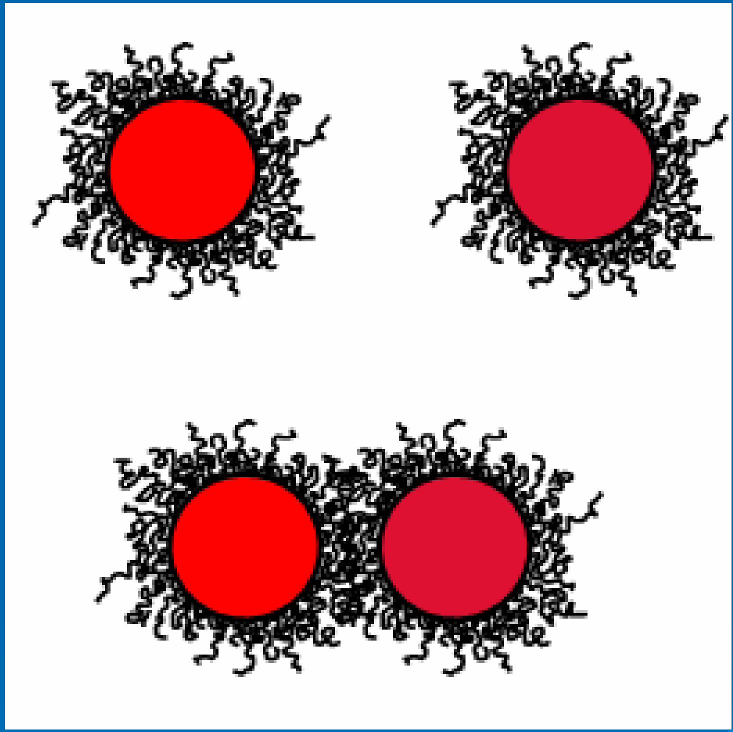
Kinetic stability is determined by two conflicting processes: sedimentation of the particles and their thermal motion.

The *aggregate stability* is a measure of the ability of a colloidal system to preserve its degree of dispersion. It is due to the fact that the particles of the dispersed phase are electrically charged and are surrounded by a solvate (hydrate) shell.

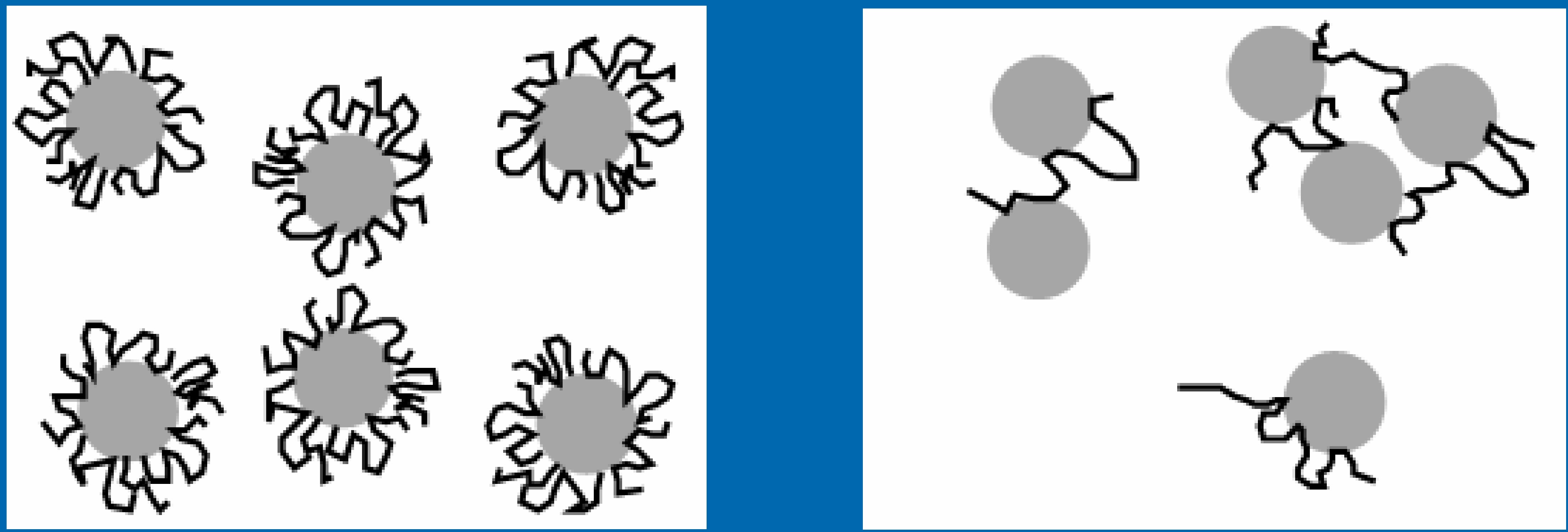
Protective action

The addition of a lyophilic substance (protein, surfactant, starch, gelatin, etc.) to a lyophobic sol frequently renders the latter less sensitive ***to the precipitating effect of electrolytes***.

This is an illustration of the phenomenon of ***protective action***: macromolecules of lyophilic substances are adsorbed onto the colloidal particles of lyophobic sol and provide *steric* or *entropic stabilization*.



Protective action



(**a**) (**b**)

Figure. Sterically stabilized systems: a given adsorbed macromolecule is associated with one particle – <u>a protective action (**a**)</u>. <u>Process of flocculation (**b**)</u>

Flocculation

In colloidal systems containing ***a low concentration of lyophilic substances***, macromolecules can become adsorbed onto two or more particles leading to phenomenon, termed ***flocculation*** (see Figure above).

Flocculation is the process of *flocs* forming.

Flocs are an aggregate of individual colloidal particles associated by lyophilic substance to a coagulum but generally having a rather loose, open structure.

Flocs may sometimes be formed reversibly and returned to the dispersed state with minimal energy input.

Protective action

The relative protective effects of different substances can be expressed quantitatively in terms of what is known as the ***gold number***. This is defined as the dry weight in milligrams of protective material which when added to 10 ml of a standard gold sol is just sufficient to prevent color change from red to blue on the addition of 1 ml of a 10 per cent solution of sodium chloride.

The color change referred to is due to coagulation of the particles, and hence the gold number is a measure of the **quantity of protective colloid which just fails to prevent precipitation by the electrolyte** (sodium chloride).

That ***the smaller the gold number the greater the protective action of the given substance.*** Gelatin has a very small gold number, and hence is a very good protective substance; egg albumin and gum arabic are less effective, while potato starch has relatively little protective action.

Introduction to blood coagulation

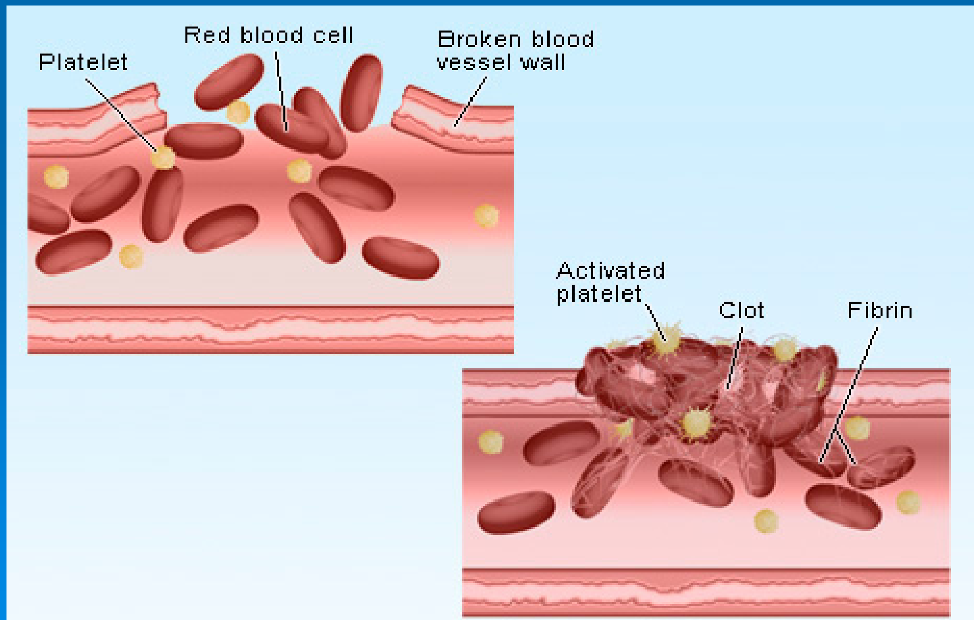
The ability of the body to control the flow of blood following vascular injury is paramount to continued survival. The process of blood clotting and then the subsequent dissolution of the clot, following repair of the injured tissue, is termed *hemostasis*. *Hemostasis, composed of four major events that occur in a set order following the loss of vascular integrity*:

1. The initial phase of the process is vascular constriction. This limits the flow of blood to the area of injury.

2. Next, platelets become activated by thrombin and aggregate at the site of injury, forming a temporary, loose platelet plug. The protein fibrinogen is primarily responsible for stimulating platelet clumping. Platelets clump by binding to collagen that becomes exposed following rupture of the endothelial lining of vessels. In addition to induced secretion, activated platelets change their shape to accommodate the formation of the plug.

Introduction to blood coagulation

3. To insure stability of the initially loose platelet plug, a fibrin mesh (also called the clot) forms and entraps the plug. If the plug contains only platelets it is termed a white thrombus; if red blood cells are present it is called a red thrombus.
4. Finally, the clot must be dissolved in order to normal blood flow to resume following tissue repair. The dissolution of the clot occurs through the action of plasmin.



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