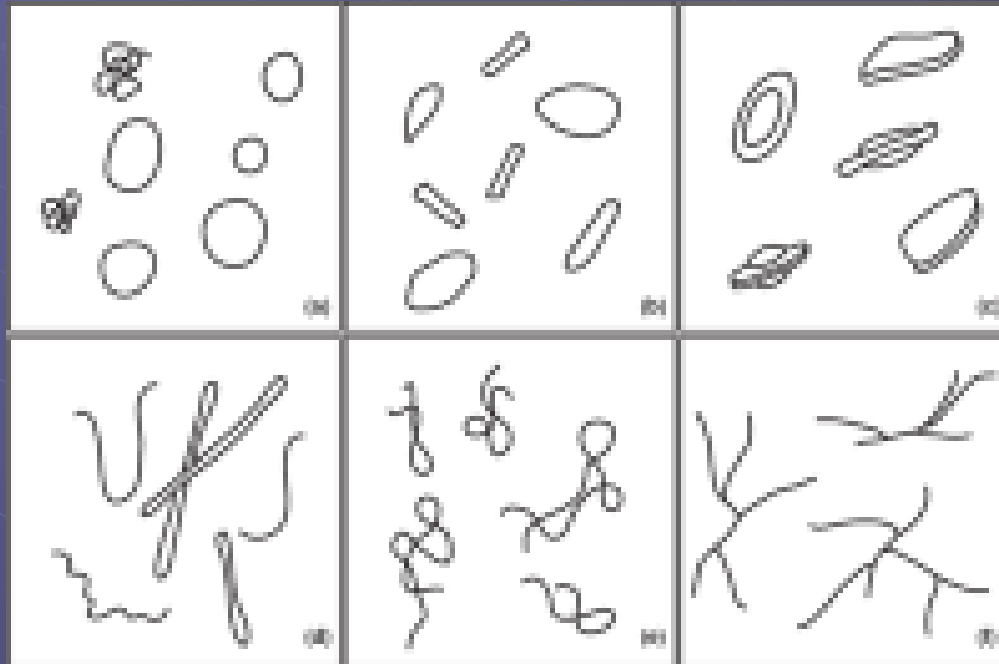


Colloids

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- important for understanding of the theory and technology of dispersed systems
- Important in dialysis, ultrafiltration...
- Some representative shapes of spherocolloids and fibrous colloids:



- flow, sedimentation, and osmotic pressure are affected by changes in the shape
- particle shape may also influence pharmacological action

Class	Particle Size*	Characteristics of System	Examples
Molecular dispersion	Less than 1 nm	Invisible in electron microscope Pass through ultrafilter and semipermeable membrane Undergo rapid diffusion	Oxygen molecules, ordinary ions, glucose...
Colloidal dispersion	From 1 nm to 0.5 μm	Not resolved by ordinary microscope (detected under ultramicroscope) Visible in electron microscope Pass through filter paper Do not pass semipermeable membrane Diffuse very slowly	Colloidal silver sols, natural and synthetic polymers, cheese, butter, jelly, paint, milk, shaving cream...
Coarse dispersion	Greater than 0.5 μm	Visible under microscope Do not pass through normal filter paper Do not dialyze through semipermeable membrane Do not diffuse	Grains of sand, most pharmaceutical emulsions and suspensions, red blood cells...

* 1 nm (nanometer) = 10^{-9} m; 1 μm (micrometer) = 10^{-6} m.

1. Lyophilic Colloids

- *Lyophilic* (solvent-loving) colloids = systems containing colloidal particles that interact to an appreciable extent with the dispersion medium
- usually **obtained** simply **by dissolving** the material in the solvent
- **properties** - **due to the attraction** between the dispersed phase and the dispersion medium - **solvation** (attachment)
- **hydrophilic colloids** - the dispersion medium is **water** - **hydration**
- Most lyophilic colloids: organic molecules:
 - Eg: gelatin, acacia, insulin, albumin – in water,
 - rubber, and polystyrene - in nonaqueous, organic solvents (in water - *lipophilic* colloids – depends on dispersion medium)

2. Lyophobic Colloids

- materials that have **little attraction, if any**, for the dispersion medium
- **lyophobic (solvent-hating) colloids** - their properties differ from those of the lyophilic colloids
- generally **inorganic particles** dispersed **in water** (eg. gold, silver, sulfur, arsenous sulfide, and silver iodide)
- necessary to use **special methods to prepare** lyophobic colloids:
 - a) **dispersion methods** - coarse particles are reduced by eg. ultrasonic generators
 - b) **condensation methods** - materials of subcolloidal dimensions are caused to aggregate into particles within the colloidal size range by the production of an electric arc within a liquid - metal of the electrodes is dispersed as vapor, which condenses to form colloidal particles

2. Lyophobic Colloids

- **required conditions for the formation** - a high degree of initial **supersaturation** followed by the formation and growth of nuclei
- **Supersaturation** - by change in solvent or reduction in temperature – eg. sulfur dissolved in alcohol and the concentrated solution is then poured into an excess of water

3. Association Colloids

- *Association* (or *amphiphilic*) *colloids* - *surface-active agents* characterized by having two distinct regions of opposing solution affinities within the same molecule or ion
- **at low concentrations** the amphiphiles exist separately and are of such a size as to be **subcolloidal**
- as the **concentration is increased** - aggregation occurs - aggregates containing 50 or more monomers are called **micelles** (have colloidal size)
- **critical micelle concentration(CMC)**: the concentration of monomer at which micelles form
- **aggregation number of the micelle**: the number of monomers that aggregate to form a micelle

3. Association Colloids

- Above the CMC, the surface tension remains essentially constant, showing that the interface is saturated by monomers and micelle formation has taken place in the bulk phase
- Amphiphiles may be:
 - Anionic
 - Cationic
 - Nonionic
 - Ampholytic (zwitterionic)

Comparison of viscosity of colloidal sols

Lyophilic	Association	Lyophobic
<p>Viscosity is increased greatly by the presence of the dispersed phase;</p> <p>at sufficiently high concentrations, the sol may become a gel;</p> <p>viscosity and gel formation are related to solvation effects and to the shape of the molecules, which are usually highly asymmetric</p>	<p>Viscosity increases as the concentration of the amphiphile increases, as micelles increase in number and become asymmetric</p>	<p>Viscosity is not greatly increased by the presence of lyophobic colloidal particles, which tend to be unsolvated and symmetric</p>

Comparison of stability of colloidal sols

Lyophilic	Association	Lyophobic
<p>Dispersions are stable generally in the presence of electrolytes; they may be salted out by high concentrations of very soluble electrolytes; effect is due primarily to desolvation of lyophilic molecules</p>	<p>In aqueous solutions, the critical micelle concentration is reduced by the addition of electrolytes; salting out may occur at higher salt concentrations</p>	<p>Dispersions are unstable in the presence of even small concentrations of electrolytes; effect is due to neutralization of the charge on the particles; lyophilic colloids exert a protective effect</p>

Sensitization and Protective Colloidal Action

- the addition of a **small amount of hydrophilic or hydrophobic colloid to a hydrophobic colloid** of opposite charge tends to **sensitize** or even **coagulate** the particles
- the addition of **large amounts of the hydrophilic colloid stabilizes** the system - the hydrophile being adsorbed on the hydrophobic particles - *protection by a protective colloid.*
- the protective property is expressed in terms of the **gold number**
 - the gold number is the minimum weight in milligrams of the protective colloid (dry weight of dispersed phase) required to prevent a color change from red to violet in 10 mL of a gold sol on the addition of 1 mL of a 10% solution of sodium chloride

Optical Properties of Colloids

- **The Faraday–Tyndall Effect**

- = when a strong beam of light is passed through a colloidal sol, a visible cone, resulting from the scattering of light by the colloidal particles, is formed.

- particles can be observed and counted by ultramicroscope

- **Light scattering**

- depends on the Faraday–Tyndall effect

- widely used **for determining the molecular weight, shape and size** of colloids

- **described in terms of the turbidity** - the fractional decrease in intensity due to scattering as the incident light passes through 1 cm of solution

Kinetic Properties of Colloids

- The **motion** of particles may be:
 - **induced thermally** - Brownian movement, diffusion, osmosis
 - **induced gravitationally** – sedimentation
 - **applied externally** – viscosity
- **Brownian Motion**
 - the **random movement** of colloidal particles
 - resulting from the **bombardment** of the particles **by the molecules of the dispersion medium**
 - the velocity **increases with decreasing particle size**
 - **increasing the viscosity** of the medium - **decreases** and finally stops

Kinetic Properties of Colloids

- **Diffusion**

- **spontaneously** from a region of higher concentration to one of lower concentration
- direct **result of Brownian movement**
- according to Fick's laws

- the ***Stokes–Einstein*** equation:
$$D = \frac{R.T}{6.\pi.\eta.r.N}$$

- where D is the diffusion coefficient,
- R is the molar gas constant,
- T is the absolute temperature,
- η is the viscosity of the solvent,
- r is the radius of the spherical particle,
- N is Avogadro's number

Kinetic Properties of Colloids

- **Diffusion**

- the *Stokes–Einstein* equation:
$$D = \frac{R.T}{6.\pi.\eta.r.N}$$

- three main rules of diffusion:

1. the **velocity** of the molecules **increases** with decreasing **particle size**
2. the **velocity** of the molecules **increases** with increasing **temperature**
3. the **velocity** of the molecules **decreases** with increasing **viscosity of the medium**

Kinetic Properties of Colloids

- **Osmotic Pressure**

- dilute spherocolloids - the *van't Hoff equation*: $\pi = c \cdot R \cdot T$

- where c is molar concentration of solute

- to calculate the molecular weight of a spherocolloids in a dilute solution: $\pi = c_g / M \cdot R \cdot T$

- where c_g is the grams of solute per liter of solution and M is the molecular weight

- for linear solvated lyophilic molecules:

- $\pi = c_g \cdot R \cdot T \cdot \left(\frac{1}{M} + B \cdot c_g \right)$

- where B is a constant for any particular solvent/solute system and depends on the degree of interaction between the solvent and the solute molecules (their asymmetry)

Kinetic Properties of Colloids

• Sedimentation

- the velocity of sedimentation of spherical particles is given

by *Stokes's law*:
$$v = \frac{2.r^2.(\rho-\rho_0).g}{9.\eta_0}$$

- where g is the acceleration due to gravity, ρ is density in a medium of density ρ_0 and a η_0 is viscosity

• Viscosity

- *Poiseuille's law* for a liquid flowing through a capillary tube:

$$\eta = \frac{\pi.r^4.t.\Delta P}{8.l.V}$$

- where r is the radius of the inside of the capillary, t is the time of flow, ΔP is the pressure head under which the liquid flows, l is the length of the capillary, and V is the volume of liquid flowing

Electrical Properties of Colloids

- **Electrokinetic Phenomena**

- *Electrophoresis*

- the movement of a charged particle through a liquid under the influence of an applied potential difference

- *Electroosmosis*

- opposite in principle to electrophoresis
- liquid moves through a plug or a membrane across which a potential is applied
- the solid is immobile (e.g., by forming a capillary or making the particles into a porous plug) the liquid moves relative to the charged surface

Electrical Properties of Colloids

- **Donnan Membrane Equilibrium**

Outside (o)	Inside (i)
	R^-
Na^+	Na^+
Cl^-	Cl^-

- in which R^- is the nondiffusible colloidal anion and the vertical line separating the various species represents the semipermeable membrane
- the volumes of solution on the two sides of the membrane are considered to be equal
- after equilibrium:
 - $[Na^+]_o \cdot [Cl^-]_o = [Na^+]_i \cdot [Cl^-]_i$
 - Outside: $[Na^+]_o = [Cl^-]_o$
 - Inside: $[Na^+]_i = [R^-]_i + [Cl^-]_i$

Electrical Properties of Colloids

- **Donnan Membrane Equilibrium**

- after substitution:

- $[Cl^-]_o^2 = ([R^-]_i + [Cl^-]_i) \cdot [Cl^-]_i = [Cl^-]_i^2 \cdot \left(1 + \frac{[R^-]_i}{[Cl^-]_i}\right)$

- *Donnan membrane equilibrium:*

- $\frac{[Cl^-]_o}{[Cl^-]_i} = \sqrt{1 + \frac{[R^-]_i}{[Cl^-]_i}}$

- the ratio of concentrations of the diffusible anion outside and inside the membrane at equilibrium
- a **negatively charged polyelectrolyte** inside a semipermeable sac would **influence the equilibrium concentration ratio** of a diffusible anion
- it tends to drive the **ion of like charge out through the membrane.**

Colloid-Based Delivery Systems for Therapeutics

Typical Mean Particle Diameter	Delivery System Type	Representative Systems of Each Type	Characteristic Applications
0.5–20 μm	Microspheres, hydrogels	Alginate, gelatin, chitosan, polymeric microspheres, synthetic, biodegradable, polymeric hydrogels	Sustained release of therapeutics, scaffolds for cell delivery in tissue engineering
0.2–5 μm	Microparticles	Polystyrene, poly(lactide) microspheres	Targeted delivery of therapeutics
0.15–2 μm	Emulsions, microemulsions	Oil-in-water, water-in-oil, lipid emulsions, oil-in-water microemulsions	Controlled and targeted delivery of therapeutics
30–1000 nm	Liposomes	Phospholipid and polymer-based bilayer vesicles	Targeted delivery of therapeutics
3–80 nm	Micelles	Natural and synthetic surfactant micelles	Targeted delivery of therapeutics
2–100 nm	Nanoparticles	Lipid, polymer, inorganic nanoparticles	Targeted delivery of therapeutics, in vivo navigational devices