Physical Pharmacy I
2nd stage
College of Pharmacy

lec: 8 -Colloidal Dispersions

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Colloidal Dispersions

Dispersed Systems

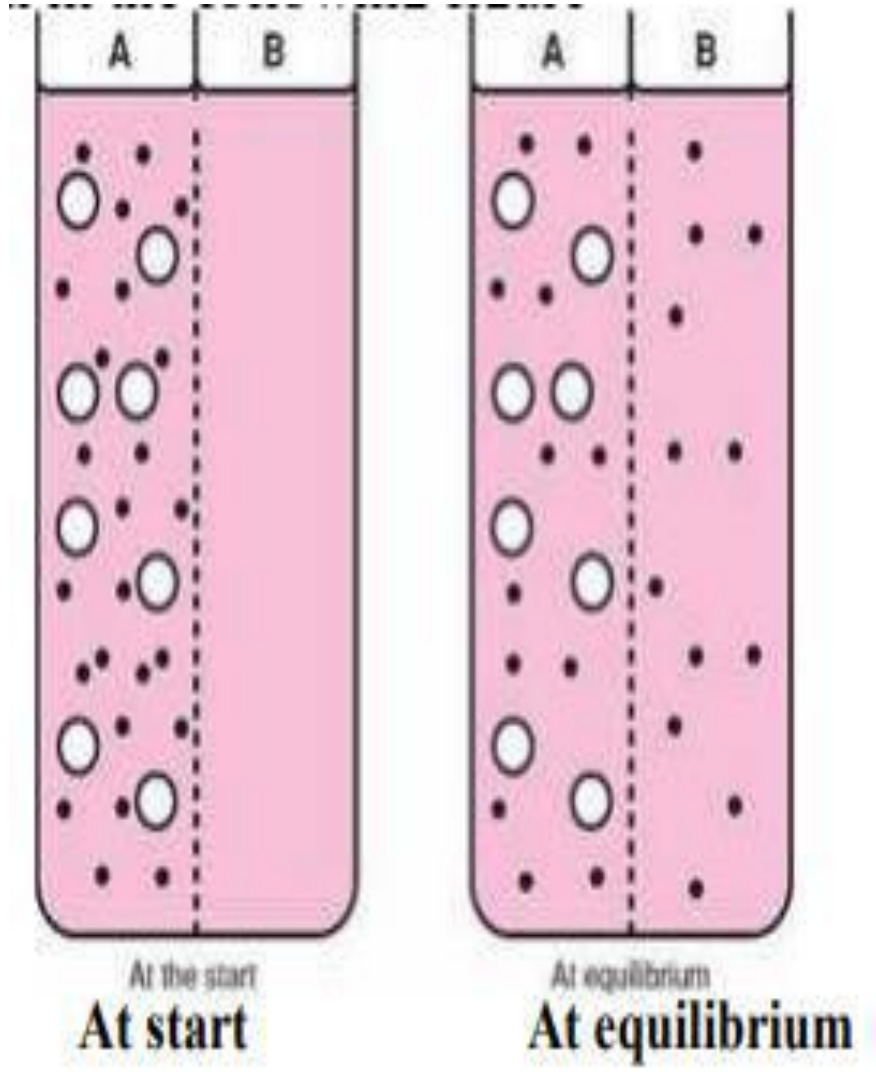
- **Dispersed systems** consist of particulate matter, known as the dispersed phase, distributed throughout a continuous or dispersion medium.
- The dispersed material may range in size from particles of atomic and molecular dimensions to particles whose size is measured in millimeters.
- Based on the size of the dispersed phase, three types of dispersed systems are generally considered:
  - (a) molecular dispersions
  - (b) colloidal dispersions
  - (c) coarse dispersions.
- The size ranges assigned to these classes, together with some of the associated characteristics, are shown in the accompanying table

Classification of Dispersed Systems Based on Particle Size

Class	Particle Size	Characteristics of System	Examples
Molecular Dispersion	Less than 1 nm	1. Invisible in electron microscope 2. Pass through ultrafilter and semipermeable membrane 3. Undergo rapid diffusion	Oxygen molecules, ions, glucose
Colloidal Dispersion	1 nm – 0.5 µm	1. Not resolved by ordinary microscope; visible in electron microscope 2. Pass through filter paper 3. Do not pass semipermeable membrane 4. Diffuse very slowly	Colloidal silver sols, polymers, cheese, butter, jelly, paint, milk, shaving cream
Coarse Dispersion	Greater than 0.5 µm	1. Visible under microscope 2. Do not pass filter paper 3. Do not pass semipermeable membrane 4. Do not diffuse	Grains of sand, emulsions, suspensions, red blood cells

Diffusion through a semipermeable membrane

- Because the size of colloidal particles, they can be separated from molecular particles by the use of semipermeable membrane.
- This technique is known as **Dialysis.** As shown in the following figure
- Conditions on the two sides, A and B, of the membrane are shown at the start and at equilibrium.
  - The **open circles** are the colloidal particles that are too large to pass through the membrane.
  - The **solid dots** are the electrolyte particles that pass through the pores of the membrane.
- Dialysis occurs in vivo. Thus, ions and small molecules pass readily from the blood, through a natural semipermeable membrane, to the tissue fluids; the colloidal components of the blood remain within the capillary system.
- The principle of dialysis is utilized in the artificial kidney, which removes low–molecular-weight impurities from the body by passage through a semipermeable membrane



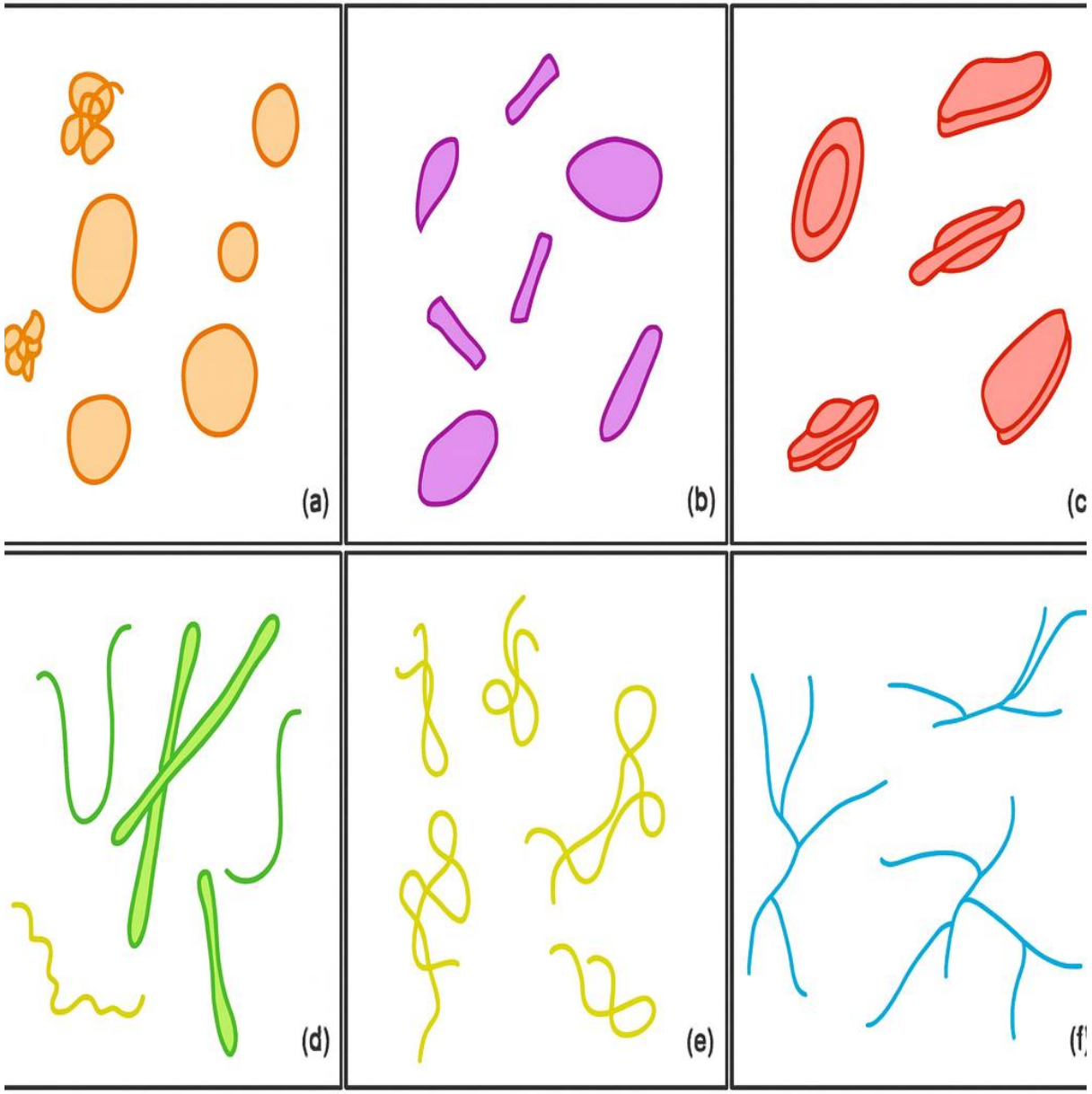
Types of Colloidal Dispersions*
(According to the type of dispersed phase and dispersion medium)

Dispersed Phase	Dispersion Medium	Colloid Type	Examples
Solid	Solid	Solid sol	Pearls, opals
Liquid	Solid	Solid emulsion	Cheese, butter
Gas	Solid	Solid foam	Pumice, marshmallow
Solid	Liquid	Sol, gel	Jelly, paint
Liquid	Liquid	Emulsion	Milk, mayonnaise
Gas	Liquid	Foam	Whipped cream, shaving cream
Solid	Gas	Solid aerosols	Smoke, dust
Liquid	Gas	Liquid aerosols	Clouds, mist, fog

Types of Colloidal Dispersion

(According to the shape of dispersed particles)

- The shape adopted by particles in dispersion is important because the more extended the particle, the greater is its specific surface and the greater is the opportunity for attractive forces to develop between the particles of the dispersed phase and the dispersion medium. Some representative shapes of spherocolloids and fibrous colloids are shown in Figure below
- Some shapes that can be assumed by colloidal particles:
  a. spheres and globules
  b. short rods and prolate ellipsoids
  c. oblate ellipsoids and flakes
  d. long rods and threads
  e. loosely coiled threads
  f. branched threads.



Types of Colloidal Systems
(According to the interaction between the dispersed phase and dispersion medium)
Lyophilic Colloids

- Systems containing colloidal particles that interact to an appreciable extent with the dispersion medium are referred to as **lyophilic** (solvent-loving) **colloids**. Owing to their affinity for the dispersion medium, such materials form colloidal dispersions, or sols, with relative ease.
- Thus, lyophilic colloidal sols are usually obtained simply by dissolving the material in the solvent being used.
- For example, the dissolution of acacia or gelatin in water leads to the formation of a sol. The various properties of this class of colloids are due to the attraction between the dispersed phase and the dispersion medium, which leads to **solvation (** the attachment of solvent molecules to the molecules of the dispersed phase). In the case of hydrophilic colloids, in which water is the dispersion medium, this is term is known as hydration .
- ((One of the most important property of lyophilic colloid is the presence of solvent sheath))
- Most lyophilic colloids are organic molecules, for example, gelatin, acacia, insulin, albumin, rubber, and polystyrene. Of these, the first four produce lyophilic colloids in aqueous dispersion media (hydrophilic sols). Rubber and polystyrene form lyophilic colloids in nonaqueous, organic solvents. These materials accordingly are referred to as **lipophilic colloids**.
- These examples illustrate the important point that the term *lyophilic has meaning only when applied to the material dispersed in a specific dispersion medium*. **A material that forms a lyophilic colloidal system in one liquid (e.g., water) may not do so in another liquid (e.g., benzene).**

Types of Colloidal Systems
(According to the interaction between the dispersed phase and dispersion medium)

Lyophobic Colloids

- The second class of colloids is composed of materials that have little attraction, if any, for the dispersion medium.
- These are the **lyophobic (solvent-hating) colloids** and, so, their properties differ from those of the lyophilic colloids. This is primarily due to the absence of a solvent sheath around the particle.
- Lyophobic colloids are generally composed of **inorganic particles dispersed in water**.
- Examples of such materials are *gold, silver, sulfur, arsenous sulfide, and silver iodide.*
- In contrast to lyophilic colloids, it is necessary to use special methods to prepare lyophobic colloids.

Types of Colloidal Systems
(According to the interaction between the dispersed phase and dispersion medium)

Association Colloid

- Association or amphiphilic colloids form the third group in this classification.
- They are certain organic molecules or ions, termed amphiphiles or surface-active agents, are characterized by having *two distinct regions of opposing solution affinities within the same molecule or ion.*
- When present in a liquid medium at low concentrations, the amphiphiles exist separately and are of such a size as to be subcolloidal.
- As the concentration is increased, aggregation occurs over a narrow concentration range.
- These aggregates, which may contain 50 or more monomers, are called **micelles**.
- **Because the diameter of each micelle is of the order of 50 Å, micelles lie within the size range of colloidal particles , such compounds are called association colloidal**.

Lyophilic	Lyophobic	Association (Amphiphilic)
Dispersed phase consists generally of large organic molecules lying within colloidal size range	Dispersed phase ordinarily consists of inorganic particles, such as gold or silver	Dispersed phase consists of aggregates (micelles) of small organic molecules or ions whose size individually is below the colloidal range
Molecules of dispersed phase are solvated; they are associated with the molecules comprising the dispersion medium	Little if any interaction occurs between particles and dispersion medium (no solvation)	Hydrophilic or lipophilic portion of the molecule is solvated, depending on whether the dispersion medium is aqueous or nonaqueous
Molecules disperse spontaneously to form colloidal solution	Material does not disperse spontaneously; special procedures must be adopted to produce colloidal dispersion	Colloidal aggregates are formed spontaneously when the concentration of amphiphile exceeds the critical micelle concentration
Viscosity of the dispersion medium is increased greatly by dispersed phase; at high concentration sol may become gel; viscosity relates to solvation and molecular asymmetry	Viscosity is not greatly increased by lyophobic particles, which tend to be unsolvated and symmetric	Viscosity increases as amphiphile concentration increases because micelles increase in number and become asymmetric
Dispersions are stable generally in presence of electrolytes; may be **salted out** by high concentrations of soluble electrolytes due to desolvation	Lyophobic dispersions are unstable with small electrolyte concentrations; effect due to charge neutralization; lyophilic colloids exert protective effect	In aqueous solutions, the CMC is reduced by electrolytes; **salting out** may occur at higher salt concentrations

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.
- This is the Faraday–Tyndall effect.
- The ultramicroscope, developed by Zsigmondy, allows one to examine the light points responsible for the Tyndall cone.
- An intense light beam is passed through the sol against a dark background at right angles to the plane of observation, and, although the particles cannot be seen directly, the bright spots corresponding to particles can be observed and counted.

Kinetic Properties of Colloids

- There are several properties of colloidal systems that relate to the motion of particles with respect to the dispersion medium. The motion may be:-
  1. **Thermally induced**
  2. **Gravitationally induced**
  3. **Applied externally**
  4. **Electrically induced motion**

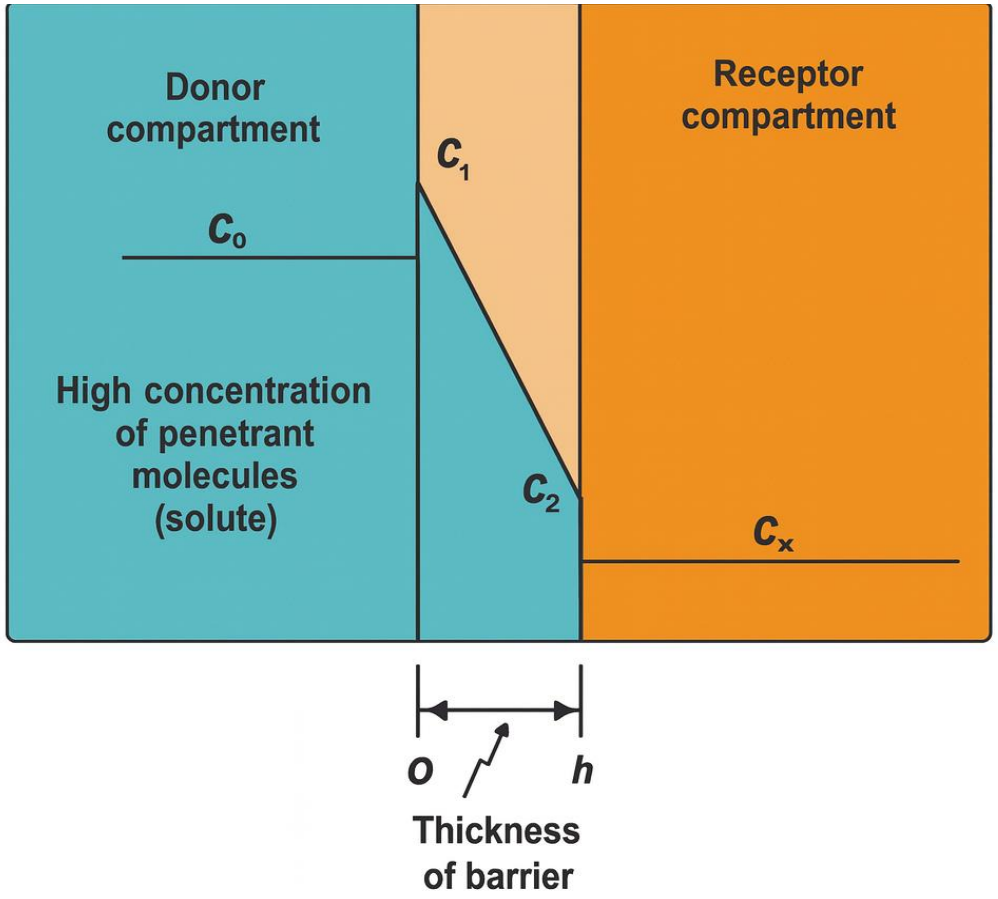
Thermally induced (increased by increasing temp)

- **Brownian motion**
  - **Brownian motion** describes the random movement of colloidal particles. The erratic motion, resulting from the bombardment of the particles by the molecules of the dispersion medium.
  - The motion of the molecules cannot be observed, of course, because the molecules are too small to see.
  - The **velocity** of the particles **increases with decreasing particle size**, while increasing the viscosity of the medium decreases and finally stops the Brownian movement.

Thermally induced (increased by increasing temp)

Diffusion

- Particles diffuse spontaneously from a region of higher concentration to one of lower concentration until the concentration of the system is uniform throughout. Diffusion is a direct result of Brownian movement, therefore (all factors affect Brownian movement will affect diffusion)
- According to **Fick's first law,** the amount (dq) of substance diffusing in time (dt) across a plane of area (S) is directly proportional to the change of concentration, dc, with distance traveled, dx. Fick's law is written as



$$dq = - DS \frac{dc}{dx} dt$$

$$g = - D\ cm^2 \frac{g/cm\ 3}{cm} \sec \rightarrow\rightarrow \quad D = cm^2 / \sec. \quad \textbf{(Units)}$$

- Dc/dx = concentration gradient = **g/cm⁴**
- D = diffusion coefficient = **cm²/s**
- dq = amount of substance diffused = **grams (g)**

- **D** is the **diffusion coefficient**, the amount of material diffusing per unit time across a unit area when **dc/dx**, called the concentration gradient, is unity.
- **D thus has the dimensions of area per unit time.**
- **Negative** sign in the equation, signifies that the diffusion occurs in decreasing concentration of diffusion
- Smaller particles diffuse faster in a given media
  - **Molecular > colloid > coarse**
- **Passive diffusion** caused by a concentration gradient and carried out through Brownian motion
- It is important for the release of drug from topical preparation and in the GIT absorption of drugs

Osmosis

- It is the action in which only the solvent is transferred, while the diffusion involve the passage of solute.
- The osmotic pressure, **π**, of a dilute colloidal solution is described by the van't Hoff equation:

$$\pi = cRT$$

- where c is molar concentration of solute , R, gas constant = 0.082 atm.mole/ L.deg
- This equation can be used to calculate the molecular weight of a colloid in a dilute solution.

Gravitationally induced

Sedimentation

- The **velocity**, v, of sedimentation of spherical particles having a density ρ in a dispersion medium of density ρ_0 and a viscosity η0 is given by **Stokes's law**:

$$V = \frac{2r^2 (\rho - \rho_0) g}{9 \eta 0}$$

r = radius of particle,
ρ = density of particle
ρ_0 = density of the dispersion medium
η_0 = viscosity of the dispersion medium
g = is the acceleration due to gravity

Factors affecting sedimentation

- Particle size (↓ particle size → ↓ sedimentation)
- Viscosity (↑ viscosity → ↓ sedimentation)
- Difference between the densities of the dispersed particles and the dispersion medium (↑ difference → ↑ sedimentation)

- If the particles are subjected only to the force of gravity, then the lower size limit of particles obeying Stokes's equation is about 0.5 μm. This is because Brownian movement becomes significant and tends to offset sedimentation due to gravity and promotes mixing instead.
- Consequently, a stronger force must be applied to bring about the sedimentation of colloidal particles in a quantitative and measurable manner. This is accomplished by use of the ultracentrifuge, which can produce a force one million times that of gravity.

Applied externally

Viscosity

- **Viscosity** is an expression of the resistance to flow of a system under an applied stress. The more viscous a liquid is, the greater is the applied force required to make it flow at a particular rate.
- Viscosity study can give us information about
  - The shape of particles in dispersion
  - The molecular weight of the dispersed phase

The shape of particles in dispersion

- The shapes of particles of the disperse phase affect the viscosity of colloidal dispersions.
- **Spherocolloids** form dispersions of relatively low viscosity, whereas systems containing **linear particles** are more viscous.
- If a linear colloid is placed in a solvent for which it has a low affinity, it tends to "ball up," that is, to assume a spherical shape, and the **viscosity falls**.
- This provides a means of detecting changes in the shape of flexible colloidal particles and macromolecules

Applied externally

The molecular weight of the dispersed phase

- The molecular weight is measured by using viscometer and the molecular weight obtained by this technique is called viscosity average molecular weight .
- The molecular weight of the polymer solution is very high so the viscosity of polymer solution is very high compared to that of pure solvent.
- From the Mark-Houwink equation the relationship between the molecular weight and viscosity is given below

$$[\eta] = KM^{\alpha}$$

Where

[η] is the intrinsic viscosity

M is the molecular weight

K and α are constants for a particular polymer solvent system.

- If we know the k and α values for a given polymer solution, the intrinsic viscosity and molecular weight can be calculated using the above equation.

Electrically induced motion

- It is the movement of charged surface with respect to an adjacent liquid phase.
- One of the most important application for such movement is the electrophoresis.

Electrical properties of colloids

- The properties of colloids that depend on, or are affected by, the presence of a charge on the surface of a particle are discussed under this heading.
- The various ways in which the surfaces of particles dispersed in a liquid medium acquire a charge were outlined in the Interfacial Phenomena chapter.
- Mention was also made of the zeta (electrokinetic) potential and how it is related to the Nernst (electrothermodynamic) potential.
- The potential versus distance diagram for a spherical colloidal particle can be represented as shown in Figure 16–11.
- Such a system can be formed, for example, by adding a dilute solution of potassium iodide to an equimolar solution of silver nitrate.
- A colloidal precipitate of silver iodide particles is produced, and, because the silver ions are in excess and are adsorbed, a positively charged particle is produced.
- If the reverse procedure is adopted, that is, if silver nitrate is added to the potassium iodide solution, iodide ions are adsorbed on the particles as the potential-determining ion and result in the formation of a negatively charged sol.

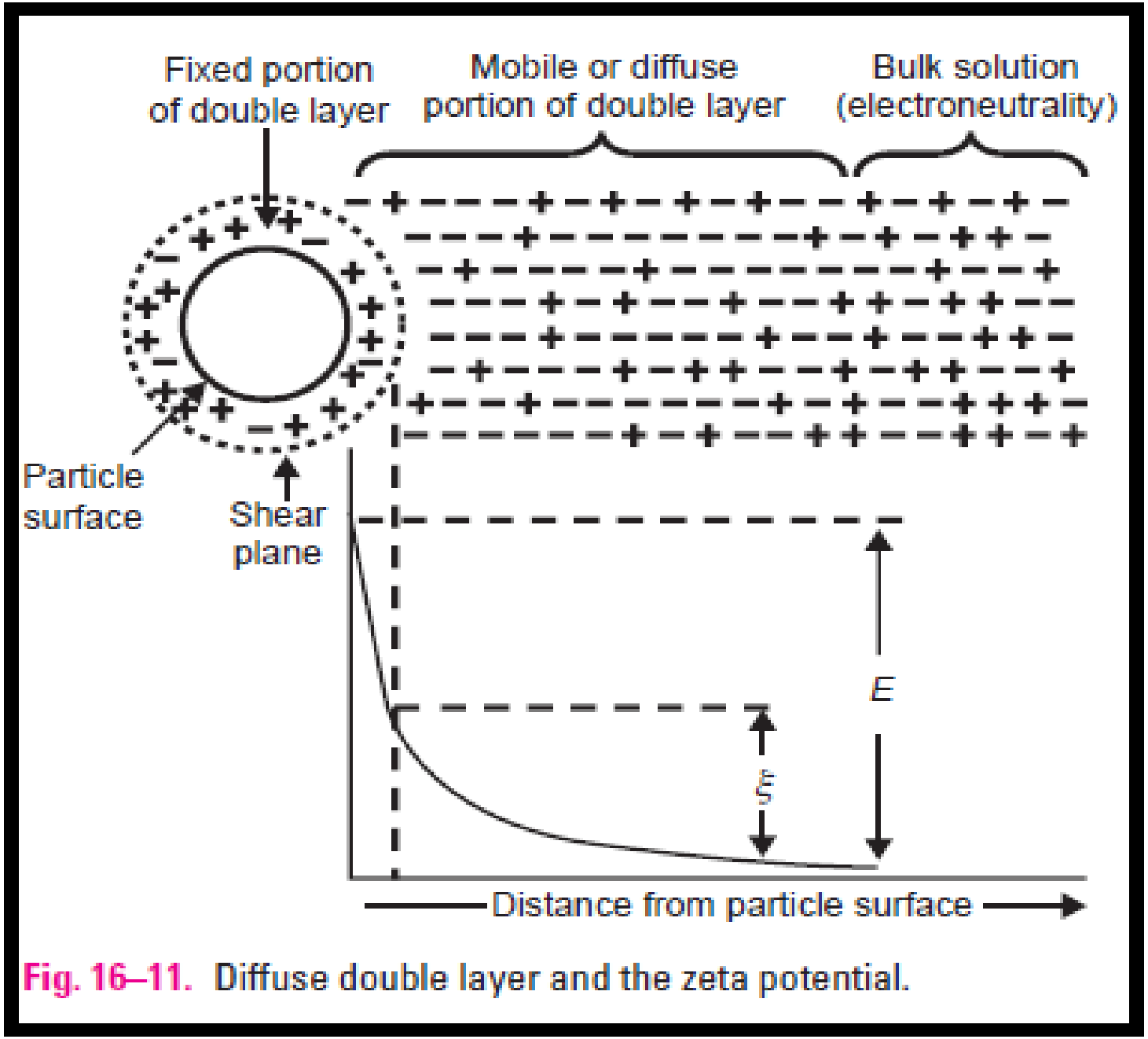


Fig. 16–11. Diffuse double layer and the zeta potential.

Solubilization using colloids

- An important property of association colloids in solution is the ability of the micelles to increase the solubility of materials that are normally insoluble, or only slightly soluble, in the dispersion medium used.
- This phenomenon, known as solubilization. Solubilization has been used with advantage in pharmacy for many years.
- Knowing the location, distribution, and orientation of solubilized drugs in the micelle is important to understanding the kinetic aspect of the solubilization process and the interaction of drugs with the different elements that constitute the micelle.
- These factors may also affect the stability and bioavailability of the drug.
- The location of the molecule undergoing solubilization in a micelle is related to the balance between the polar and nonpolar properties of the molecule.

Pharmaceutical applications of colloids

- Certain medicinals have been found to possess unusual or increased therapeutic properties when formulated in the colloidal state.
- Colloidal silver chloride, silver iodide, and silver protein are effective germicides and do not cause the irritation that is characteristic of ionic silver salts.
- Colloidal copper has been used in the treatment of cancer, colloidal gold as a diagnostic agent for paresis, and colloidal mercury for syphilis.
- Many natural and synthetic polymers are important in contemporary pharmaceutical practice.
- Naturally occurring plant macromolecules such as starch and cellulose that are used as pharmaceutical adjuncts are capable of existing in the colloidal state.
- Hydroxyethyl starch is a macromolecule used as a plasma substitute.
- Colloidal electrolytes (surface-active agents) are sometimes used to increase the solubility, stability, and taste of certain compounds in aqueous and oily pharmaceutical preparations.