

# CHAPTER :COLLOIDS

**Subject: Physical Pharmacy**

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## **CHAPTER 05**

# COLLOIDS

The term colloid means glue like substances, kolla-glue and eoids-like

Colloidal system is dispersion where in internal phase dispersed particles are distributed uniformly in a dispersion medium (External/continuous Phase). Particle size-0.5 to 1 micron

In colloidal systems particles pass through filter paper but do not pass through semipermeable membrane diffuse very slowly.

Example: Gelatin Acacia and Rubber

## DEFINITIONS

Colloidal systems encountered in pharmacy include :

- surfactant micelles
- suspensions (may be  $> 1 \mu\text{m}$ )
- emulsions (may be  $> 1 \mu\text{m}$ )
- inhalation aerosols
- suspensions of microorganisms

# CLASSIFICATION OF COLLOIDAL SYSTEMS ACCORDING TO PARTICLE SIZE

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

\* 1 nm (nanometer) =  $10^{-9}$  m; 1  $\mu\text{m}$  (micrometer) =  $10^{-6}$  m.

# TYPES OF COLLOIDS

ON THE BASES OF THE INTERACTION OF THE PARTICLES, MOLECULES OR IONS OF THE DISPERSED PHASE WITH THE MOLECULES OF THE DISPERSION MEDIUM:

1. LYOPHILIC COLLOIDS
2. LYOPHOBIC COLLOIDS
3. ASSOCIATION COLLOIDS

# LYOPHILIC COLLOIDS

In this system dispersed particles have a greater affinity to the dispersion medium (solvent).

The dispersion medium forms a sheath around the colloidal particles and solvates. This makes the dispersion thermodynamically stable.

For this reason, preparation of lyophilic colloids is relatively easy.

**Exp: the dissolution acacia or gelatin in water or celluloid in amyl acetate leads to formation of a solution.**

# LYOPHOBIC COLLOIDS

Colloids is composed of materials that have little attraction (*solvent hating*), is possible between the dispersed phase and dispersion medium.

These are stable because of the presence of a charge on particles.

These are the lyophobic colloids and their properties differ from those of the lyophilic colloids. This is due to primarily the absence of a solvent sheath around the particles

# PREPARATION LYOPHOBIC COLLOIDS

1. *Reduced the particle size of the coarse particles*

2. *Condensation methods*

1. *Dispersion of particles by using high intensity ultrasonic generators at frequencies 20000 cycles/min.*

2. *Production of electric arc within a liquid*

3. *Milling and grinding method*

4. *Super saturation method*

*Example: sulfur is dissolved in alcohol and concentrated solution to transfer to water  
Small nuclei will produced these grow rapidly to form colloidal solution.*



# PREPARATION LYOPHOBIC COLLOIDS

## 5. BY CHEMICAL REACTIONS:

**A. Reduction:** *when metal salts treated with reducing agent (formaldehyde) produced atoms leads to form colloidal aggregates.*

**B. Oxidation:** *the oxidation of hydrogen sulfide produced sulfur atoms leads to form colloidal aggregates.*

**C. Hydrolysis:** *Add excess qty of water to ferric chloride solution hydrolysis produced leads to form red solution hydrated ferric oxide*

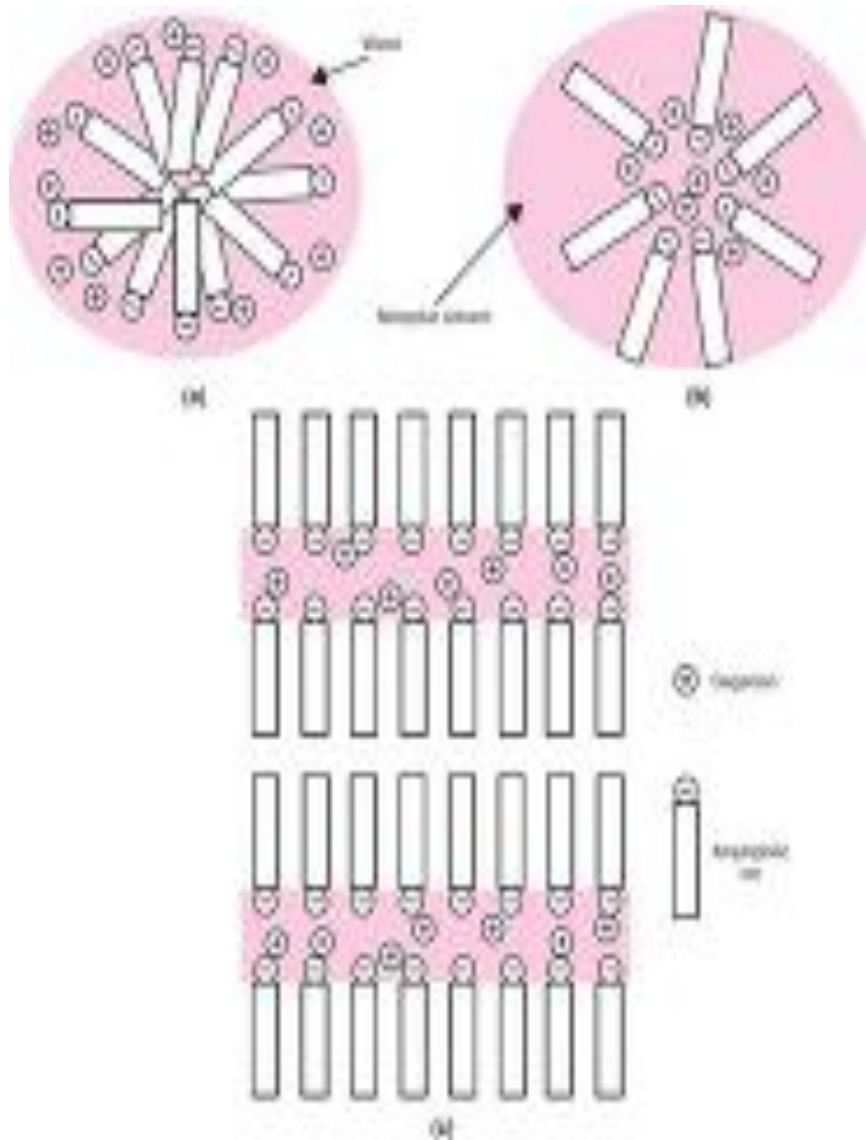
*c. **Hydrolysis:** Add excess Qty of water to ferric chloride solution hydrolysis produced leads to form red solution of hydrated ferric oxide.*

*D. **Double decomposition:** The double decomposition between hydrogen sulfide and arsenous acid leads to produced arsenous sulfide solution.*

# ASSOCIATION COLLOIDS

In this system certain molecules or ions called 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 concentration, are called subcolloids

As the concentration is increased aggregation occurs. These aggregated contains 50 or more monomers, these are micelle. (CMC)



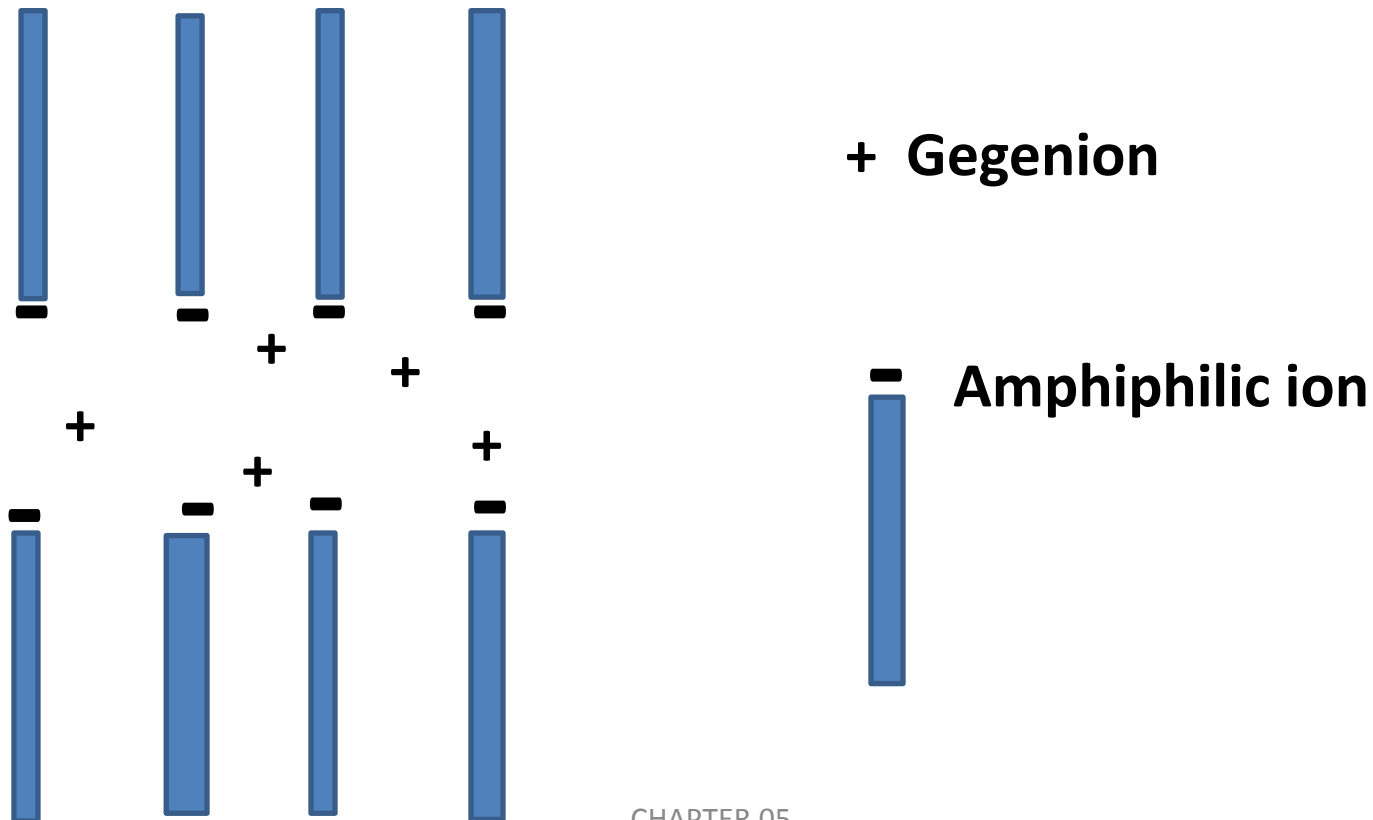
Some probable shapes of micelles: (a) spherical micelle in aqueous media, (b) reversed micelle in nonaqueous media, and (c) lamellar micelle, formed at higher amphiphile concentration, in aqueous media.

# AMPHIPHILES/SURFACE ACTIVE AGENTS

Anionic,  
cationic

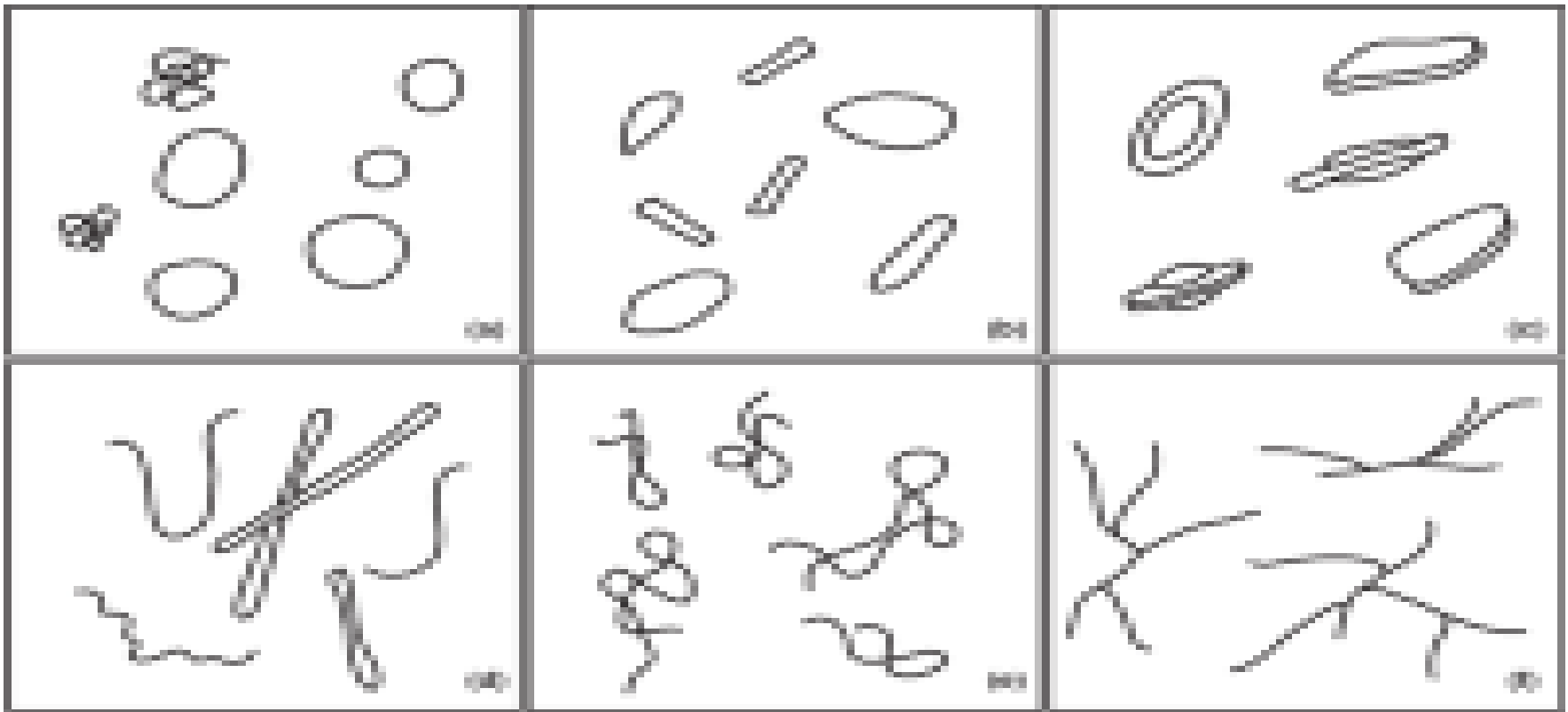
Nonionic

Ampholytic (zwitterionic)



# TYPES OF COLLOIDAL SYSTEMS

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



**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, and (f) branched threads.**

# Hydrophilic colloids

**Starch**  
**Proteins**  
**Milk**



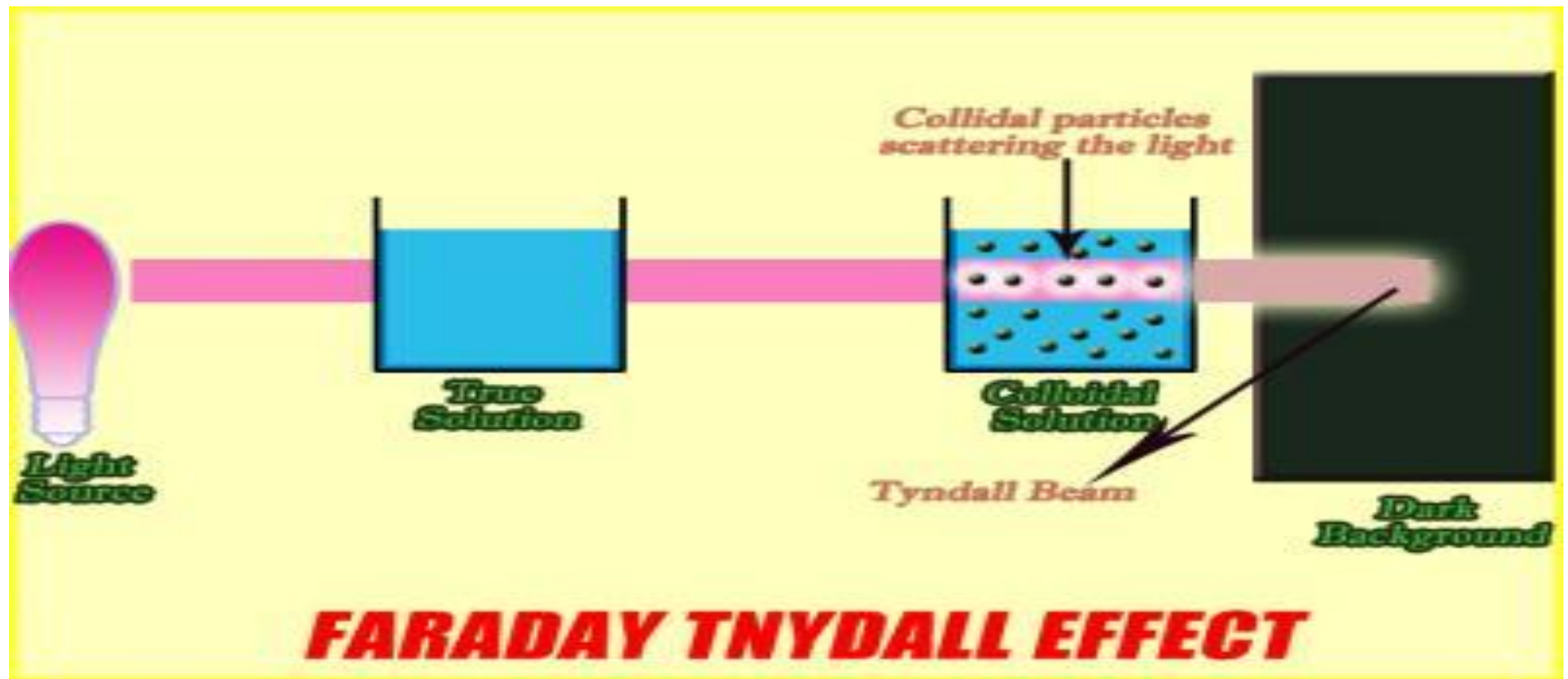


# COMPARISON OF PROPERTIES OF COLLOIDAL SOLUTIONS

LYOPHILIC	LYOPHOBIC	ASSOCIATION (AMPHIPHILIC)
Disperse phase contains large organic molecule lying within colloidal range.	Dispersed phase contains inorganic particles Ex: Gold	Dispersed phase consists of aggregates of small organic molecules or ions whose size is below the colloidal range.
Molecules of the dispersed phase is solvated, i.e. they are associated with the molecules adjust with dispersion medium.	Small interaction (solvation) between particles and dispersion medium.	Hydrophilic or lipophilic portion of the molecule is solvated depends on solvent system.
Dispersion are generally stable in presence of electrolytes	These dispersions are unstable even in small concentration of electrolytes	CMC can be reduced by addition of electrolyte

# OPTICAL PROPERTIES OF COLLOIDS

A strong beam of light passed through colloidal solution a visible cone is formed, resulting from the scattering of light by the colloidal particles, is formed this is the Faraday-Tyndall effect.



# ELECTRON MICROSCOPE

The electron microscope will provide the actual pictures of the colloidal particles in the form of

Shape

Surface area

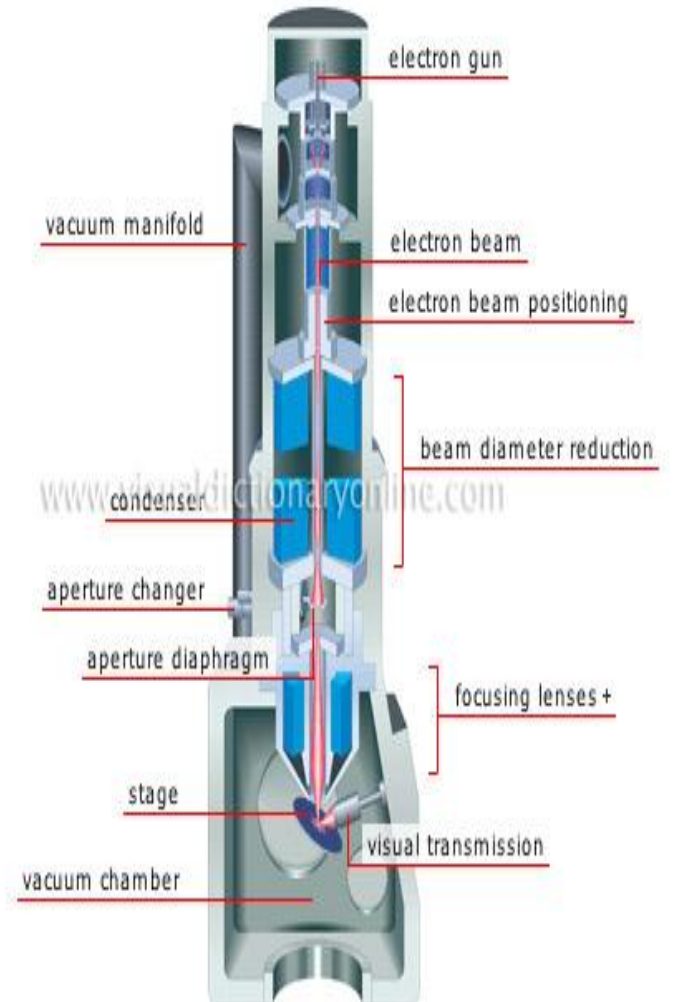
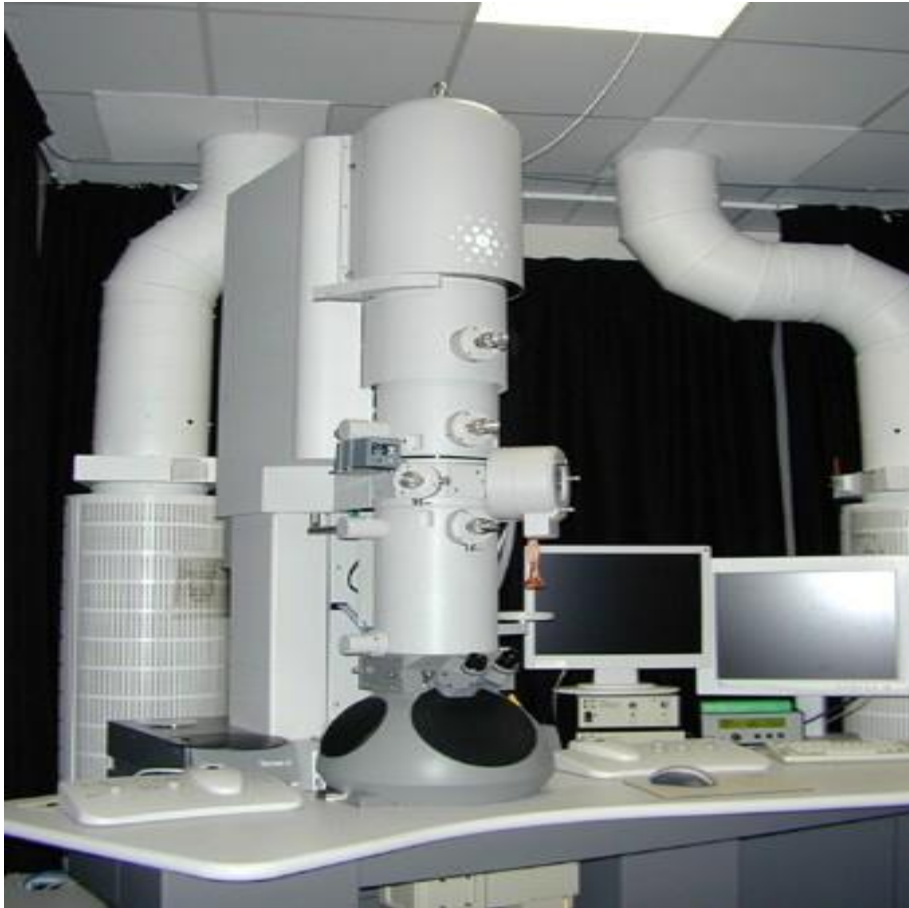
Size

Porosity

Density of the particles

Microscope : visible light as source (20 nm size of the particles can be separated and visible.

Resolving power ( $d$ ): the smallest distance by which two objects are separated and yet remain distinguishable .



# LIGHT SCATTERING

This is based on Faraday-Tyndall effect it is widely used in the determination of

Molecular weight of the colloids

Size and shape of the colloids

Principle: Scattering method: in terms of turbidity,  $\tau$  the frictional decrease in the intensity due to scattering as the incident light passes through 1 cm of solution.

The turbidity can be calculated as follows :

$$\frac{Hc}{\tau} = \frac{l}{M} + 2Bc \quad (16-2)$$

T=turbidity in  $\text{cm}^{-1}$  , c= concentration of the solute in  $\text{gm}/\text{cm}^3$   
at wave length in  $\text{cm}^{-1}$  M=weight of the average molecular weight, in g/mol or Daltons

THE TURBIDITY CAN BE CALCULATED AS FOLLOWS :

$$Hc/\tau = 1/M + 2Bc$$

$\tau$  =turbidity in  $\text{cm}^{-1}$  ,  $c$ = concentration of the solute in  $\text{gm}/\text{cm}^3$   
at wave length in  $\text{cm}^{-1}$   $M$ =weight of the average molecular  
weight, in  $\text{g}/\text{mol}$  or Daltons



## Equations:

$$H.c / T = 1/M + 2BC$$

$$H = 32 \pi^3 n^2 (dn/dc)^2 / 3 \lambda^4 N$$

*T* = Turbidity in  $\text{cm}^{-1}$

*c* = Concentration of solution in  $\text{g}/\text{cm}^3$

*M* = Weight- Average Molecular Weight in  $\text{g}/\text{mole}$  or Daltons

*B* and *H* = Constants for a particular system

*n* = Refractive index of solution

*N* = Avagrado number

$\lambda$  = Wavelength of light

$dn/dc$  = Change in refractive index with concentration (*c*)

## Why sky is blue

The intensity of scattered  $I_s$  light is inversely proportional to the fourth power of wavelength,  $\lambda$  (Rayleigh law)

$$I_s \sim 1/\lambda^4$$

Thus shorter wavelength light is (BLUE) is scattered more intensely than longer wavelength light (YELLOW AND RED), scattered light is mostly blue, where transmitted light has a yellow or reddish.



*ANSWER: 1*

*Due to the constant motion of molecules, the atmosphere is homogenous and constantly forms clusters with high density of air.*

*Answer:2*

*At sunrise and sun set, sunlight has to travel a longer distance through the atmosphere than at noon.*

*Answer:3*

*This is important, because the lower the atmosphere the higher the density of gas molecules.*

*Answer:4*

*Due to this longer distance, the yellow light also scatters*

# KINETICS OF COLLOIDAL PARTICLES

## BROWNIAN MOTION

- ✓ Random motion of colloidal particles.
- ✓ The erratic motion particles size as large as 5 micro meter.
- ✓ Bombardment of particles by the molecules of dispersion medium.
- ✓ The motion of molecules cannot be observed
- ✓ The velocity of the particles increases with decreasing the size
- ✓ If add the viscosity agent BROWNIAN MOTION stops

## DIFFUSION

Particles diffuse spontaneously from a region of higher concentration to one of lower concentration until the concentration of the system is equilibrium.

Diffusion is a direct result of Brownian movement

$$dq = -Ds \frac{dc}{dx} \times dt$$

D= is the diffusion coefficient, the amount of material diffusing per unit time across a unit area when  $\frac{dc}{dx}$ , called the concentration gradient, is unity.

D= is thus dimensions of the area per unit time.

Colloidal molecules diffusion can be analyzed diffusion experiment.

## Sutherland and Einstein

According to them, can able to determine:

**radius of the particle**

**Particle weight or molecular weight of the colloidal solution particles.**

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

$$D = \frac{RT}{6\pi\eta r N} \quad (16-7)$$

**K=Boltzmann constant** , R=molar gas constant , T =absolute temperature,  $\eta$ = viscosity of the solvent , r=radius of the spherical particle and N= Avogadro's number.

**If we want molecular weight:**

$$D = \frac{RT}{6\pi\eta N} \sqrt[3]{\frac{4\pi N}{3M\bar{v}}} \quad (16-8)$$

M=molecular weight

V = is the partial specific volume (approximately equal to the volume in 1cm<sup>3</sup> of 1 gm of solute as obtained from density measurements.

# SEDIMENTATION

The velocity  $v$  of sedimentation of spherical particles having a density  $\rho$  in a medium of density  $\rho_0$  and a viscosity  $\eta_0$  is given by Stokes's Law

$$V = \frac{2r^2 (\rho - \rho_0) g}{9\eta} \quad \text{or} \quad V = \frac{d^2 (\rho - \rho_0) g}{18\eta}$$

- This law obeys only if the particles should be spherical
- Stokes equation about only  $5\mu\text{m}$ .
- Brownian movement becomes active sedimentation will becomes slow due to gravity, promotes mixing.
- A strong force must be applied to bring sedimentation
- Ultracentruge is used for the complete sedimentation
- Ultracentrifuge can produce a force one million times that of gravity

# VISCOSITY

*The viscosity is an expression of the resistance to flow of a system under an applied stress.*

*In this section concerned with the flow properties of dilute colloidal systems.*

- 1. We can determine the molecular weight of the molecules in the dispersed system*
- 2. shape of the particles in solution*

## *Einstein equation for dilute colloidal dispersions*

$$\eta = \eta_0 (1 + 2.5 \phi)$$

*This is based on hydrodynamic theory ,*

$\eta_0$  = viscosity of the dispersion medium

$\eta$  = viscosity of the dispersion when the volume fraction of colloidal particles present is  $\phi$

***WHAT IS VOLUME FRACTION :*** the volume fraction is defined as the volume of the particles divided by the total volume of dispersion



From the above equation we can determine the

Relative viscosity  $\eta_{rel} = \eta/\eta_0 = 2.5\dot{\gamma}$

Specific viscosity  $\eta_{sp} = \eta/\eta_0 - 1 = \eta - \eta_0/\eta_0 = 2.5\dot{\gamma}$

$$\text{or } \eta_{sp}/\dot{\gamma} = 2.5$$

Since volume fraction is directly related to concentration, then the above equation becomes:

$$\eta_{sp}/c = k$$

From this equation we can calculate the approximate molecular weight of the polymers.

# **GENERAL FACTORS AFFECTING THE STABILITY OF COLLOIDS**

- 1. Brownian motion*
- 2. Electrostatic forces of repulsion.*
- 3. Van der Waals forces of attraction.*
- 4. Born forces - short range - repulsion.*
- 5. Steric forces dependent on geometry and conformation at interface - repulsion.*
- 6. Solvation forces due to changes in quantities of adsorbed*
- 7. solvent on approach of neighboring particles  
repulsion*