

Colloids

Originally derived from a GREEK word – **KOLLA** means **GLUE**

Definition:

Colloidal dispersions – *discontinuous particle phase* (dispersed phase) distributed uniformly in a finely divided state in a *continuous phase* (dispersion medium).

Staudinger – particles with 10^3 to 10^9 atoms.

Dimension of disperse phase

1 nm – 1 μ m

Historical data:

Selmi (1845) - described pseudosolution i.e particles that are larger than the usual molecules.
- first to investigate colloidal system systematically e.g. preparation of colloidal sulphur, silver chloride and prussian blue, albumin and starch solutions.

Michael Faraday (1857) - investigation of optical properties of gold sol (*Faraday sols* ~ 3 nm radius). Prepared by reduction of a gold chloride solution with phosphorus.

Thomas Graham (1861) - classical experiment e.g. rate of diffusion from different substances.

Coined the term “Colloid” (glue like) to describe Selmi’s pseudosolution. Displayed a low rate of diffusion and lack of crystallinity therefore the particles must be very large at least 1 nm. On the other hand, failure of the particle to sediment under the influence of gravity explained that the particles have an upper limit of about 1 micron.

Tyndal (1869) - light scattered by colloidal particles is polarised.

Ostwald - *Any dispersed system consists of a homogeneous medium and particles, and both of the medium and the particles can either be solid, liquid, or gaseous.*

Association colloids:

James Mcbain - found that the osmotic pressure of alkali metal fatty acid salt displays a pronounced break in the concentration beyond which the osmotic pressure coefficient remains constant. The aggregate structure he called micelles. G. S. Hartly proposed a spherical structure. William Harkins – cylindrical. Mcbain – flat laminar.

Derjaguin-Landau and Verwey-Overbeek (1945)

– Provide DLVO theory that explains the quantitative relationship between the attractive van der Waals forces (coagulation) and the repulsive electrostatic forces which stabilize the colloidal dispersion.

General description for the size of colloidal particles:

- Smaller than coarse
- Filterable
- Larger than small molecules.
- Can scatter light
- 1 nm – 1000 nm

Colloidal state

Marriage of several disciplines
or
crossed-disciplinary subjects

One substance distributed **uniformly, homogeneously** in one another.

Substance can be

- solid
- liquid
- gas

True solution

made of dissolution of matter.
Typically in molecular dimension.

Colloidal system, solute is considerably larger than the solvent.

Colloidal suspension response to environment

- Thermodynamics
- Temperature
- Pressure
- pH of solution
- Electrolyte

Sizes?

- In micron or submicron
- Larger than the solvent
- May floc to form larger particles
- Larger particle may breakdown into smaller ones.

Industrial and technological significances

- Telecommunication
- Ceramics
- Oil industries.
- Paint industries.

Biological Significances

- Cell and cell adhesion / interaction
- Drug delivery system
- Digestion system
- Synovial fluid (joint lubrication)

Food industries.

- Ice-cream
- Chocolate
- Dough making / Bread
- Confectionaries
- Butter
- Fizzer drinks

Cosmetics and pharmaceutical industries

- Vitamines
- Mineral supplement
- Cream
- shampoos

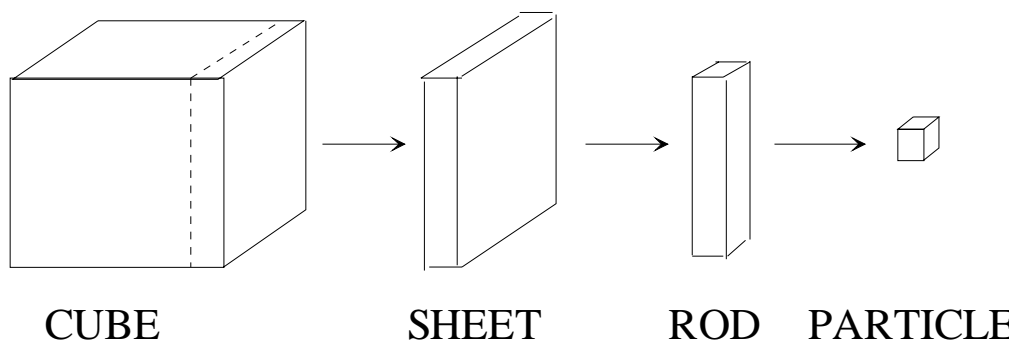
Type of Colloidal Systems

Colloidal suspensions or sols (dispersion of solid in liquid) – in the form of various soups and sauces. Paints, inks clay particles and delta formation. Called lyophobic colloids.

1. Emulsions - dispersion of liquid in liquid such as milk, mayonnaise cosmetics and pharmaceutical, w/o and o/w emulsion.
2. Solid dispersions – solid in solid dispersion such as in some gem stones, concrete, alloy.
3. Aerosols – liquid dispersion in gases such as fog, mist deodorants.
4. Macromolecules – Gels, DNA, protein. Also called lyophilic colloids. Exhibit thermodynamic stability.
5. Association colloids – soap bubbles, foams, biological membrane, micelles, vesicles and liquid crystals.

Colloidal particles are normally associated with providing a large surface area. The colloidal particles size characteristic forms an intrinsic property of a colloidal system. For example, a typical micellar solution containing 0.1 M surfactant has ~ $4 \times 10^4 \text{ m}^2$ of micellar-water interfacial area per liter of solution.

Simple approach to make colloidal particles

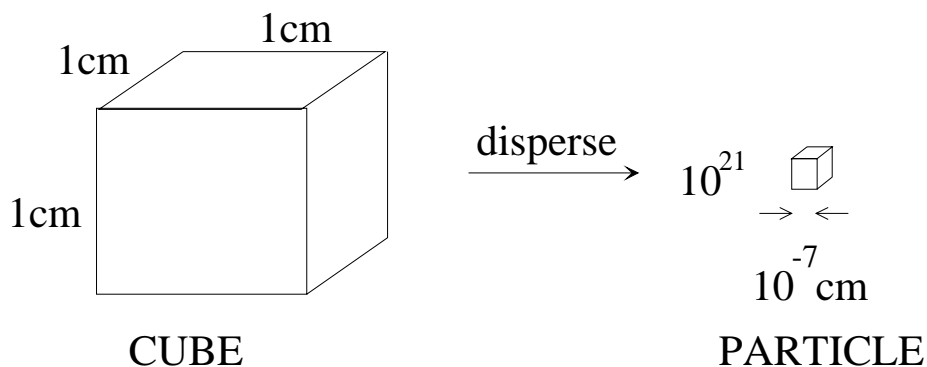


SHEET → e.g. thin film, clay.

ROD → e.g. gels

PARTICLE → e.g. gold sols, micelles.

Say we have a cube with 1×1×1 cm then disperse into 10^{21} small cubic particles.



Now, we start with a cube.

Total volume = 1 cm^3

Then make 10^{21} particles of side 10^{-7} cm .

∴ Area of small particle = no. of faces × area of one face

$$= 6 \times 10^{-14} \text{ cm}^2$$

Total area by these particles = $6 \times 10^{-14} \times 10^{21} \text{ cm}^2$

$$= 6 \times 10^7 \text{ cm}^2$$

Therefore an increase by 10^7

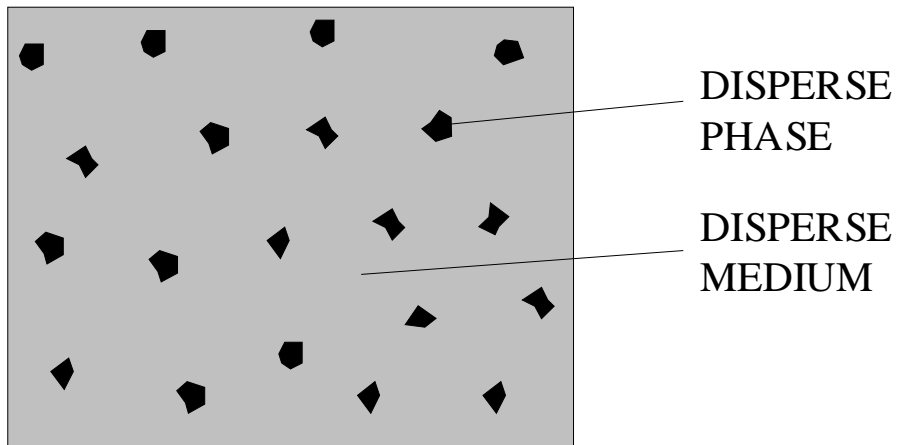
This also tells us that molecules at surface are very important!

- because it may affect the properties of the system.

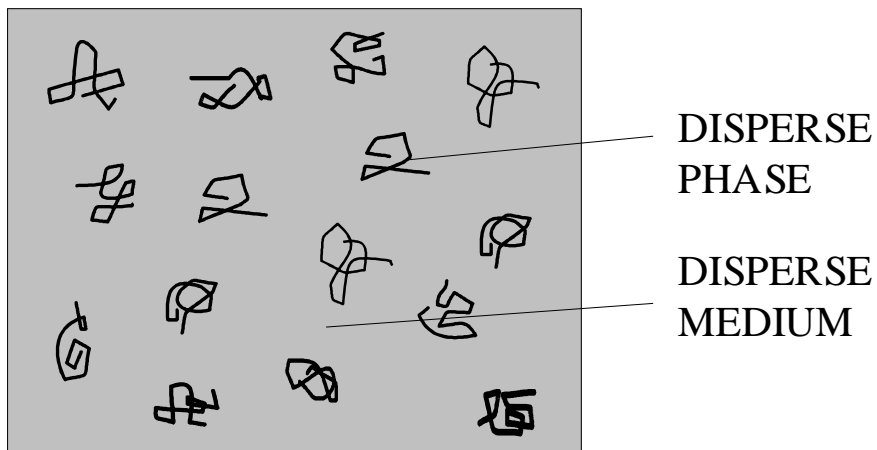
e.g solubility, free energy

LYOPHOBIC AND LYOPHILIC COLLOID

Lyophobic colloid:



Discrete particles of one material suspended in another.
Interface is well defined.



Lyophilic colloid:

Solution of high molecular weight substance (protein, polymer, etc.) in liquid medium. No clear defined interface.

Types of colloidal system:

Name	Disperse phase	Disperse medium	Examples
Colloidal sol	Solid	Liquid	Ink, paint.
<i>Emulsion</i>	Liquid	Liquid	Mayonaise, emulsion, fat digestion, biomembrane.
<i>Foam</i>	Gas	Liquid	Fire extinguisher, vacuoles
<i>Aerosol</i>	Solid	Gas	Smoke, volcanic smoke, pollen.
	Liquid	gas	Fog, mist, hairspray.
<i>Solid dispersion</i>	Solid	Solid	Wood, bone, pearl, opal, composite, alloy, glasses.
<i>Solid emulsion</i>	Liquid	Solid	Bitumin, ice-cream.
<i>Solid foam</i>	Gas	Solid	Styrofoam, zeolites, fruits, bread

Compare with

macromolecular colloids:-

In the case of gel – macromolecules dissolve in solvent e.g water as in GLUE

Association colloids:-

Soaps / detergents dissolve in solvent (water) as in washing-up liquid.

Other definitions

1. *Disperse medium / continuous phase* It refers to the medium. e.g. water, oil, gas, solid etc.
2. *Discontinuous phase* – small particles as colloid.
3. *Monodisperse* – all particles similar size.
4. *Polydisperse* – range of sizes

Lyophilic and lyophobic sols

Lyophobic	Lyophilic
Solvent hating e.g. $\text{AgCl}_{(s)}$ in water	Solvent loving e.g. proteins in aq. Solution, microemulsion droplets
Dispersed by vigorous mechanical agitation or by an external energy	Dispersed by adding a suitable solvent
Technological and agricultural materials.	Biological colloid e.g. protein, polysaccharide
Subjected to van der Waals forces (attractive), thermodynamically unstable	Thermodynamically stable

Very complex phenomena

– cannot be classified accordingly

Preparation of Colloidal suspensions

Dispersion

- Grinder (solid)
- High speed stirring (solid and liquid)
- Sonication

These are essentially mechanical but nonetheless effective.

Condensation methods.

- Dissolution and precipitation
e.g. a)– to precipitate the solid from the solvent by sudden mixing with a second liquid which is immiscible with the first but a non solvent for the solid. – many water insoluble dyes and pigments – pouring their solutions in concentrated H_2SO_4 into large volume of water.

b) - pouring a dissolved wax in ethanol into hot water – opalescent paraffin wax sol.

- Condensation from vapour
e.g. mist – spontaneous condensation of supersaturated vapour as T drops below condensation point.
- Chemical reactions
Producing an insoluble product
e.g. $2\text{Fe}^{3+} + 3\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+$

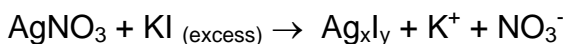
Colloid Stability

Consider LYOPHOBIC sol:

Small solid particles (1-100 nm)

e.g. AgI, CdS, Au

Preparation :



Usually the value of $y > x$

Thus, we have negatively charged sols

Say, typical $x = 100$ and $y = 200$

Hence overall charge = - 100

Definition of colloidal stability

- no change in particle size with time.
- Instability normally will lead to FLOCCULATION

i.e. a process when small particles clump to gether but do not fuse into new particle.

Colloidal Stability

- Particles in a dispersion may adhere together and form aggregates of increasing size which may settle out due to gravity
- An initially formed aggregate is called a FLOC and its formation FLOCCULATION - this process is reversible (DEFLOCCULATION)
- If the aggregate changes to a much denser form it is said to undergo COAGULATION - this process is irreversible
- In the 1940s Derjaguin, Verwey, Landau and Overbeek developed a theory which dealt with colloidal stability DVLO.

DVLO Theory

- It says that the stability of a colloidal system is determined by the sum of the electrical double layer repulsive and van de Waals attractive forces which the particles experience as they approach one another
- The theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together
- But if the particles collide with sufficient energy to overcome that barrier, the attractive force will pull them into contact where they adhere strongly and irreversibly together.

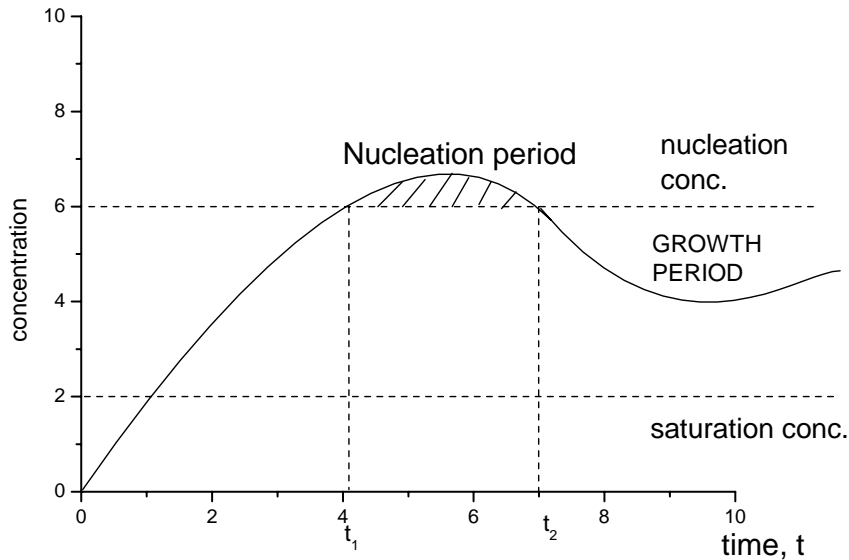
Maintaining Colloidal Stability

For colloidal stability, the repulsive forces between particles must be dominant

There are two fundamental mechanisms that affect colloidal stability:

- Steric repulsion.
- Electrostatic (Charge) repulsion.

Preparation of Mono disperse Colloids



The La Mer diagram formation of nuclei – $t_1 \rightarrow t_2$ allowing for a short period

must allow growth on nuclei $t > t_2$

Increase the concentration of the required material get supersaturation

→ formation of nuclei .Then grow into final particles (t_1-t_2)

Solution concentration thereby reduced!

Growth occurs when concentration maintained between the saturation and nucleation.

e.g : Preparation of metal carbonates.

COAGULATION and FLOCCULATION

No clear distinction between the two processes.

Both involve “aggregation”

i.e the gathering together of suspended particulates to form larger ones.

Principally concerned with lyophobic colloids since their most stable TD state is one where all the particles are condensed!

Attempts for the distinction between these processes.

1) In terms of the resultant of aggregate size

Purchas 1968 , Kirk-Othmer 1980 and Perry & Green 1984.

Coagulation – addition of reagent that cause aggregation of colloidal particles

Flocculation – gentle agitation that promotes collisions between these small aggregates to form “floc”

i.e : large enough to settle

2) Classification on the basis of mechanisms

La Mer & Healy 1963,1966

Widespread acceptance

Akers 1972, O'Melia and Weber 1972, Ubehend 1976

MECHANISM of AGGREGATION

1- Charge neutralization by double-layer compression

reduction of repulsive potential obtained by addition of polyvalent ions of opposite sign to that of the surface charge.

2- Action of material of high molecular weight

e.g polymer ,starch, gelatine – to produce “ Bridging effect “

3- Entrapment of smaller particles

e.g : additional of a hydrolysing metal salt in water treatment of alkalinity – formation of gelatinous ppt of metallic hydroxide may entrap suspended turbid particles.

Coagulation : aggregation process in which member particles are not in direct physical contact but are separated from each other by a thin film – estimated thickness < 0.1 mm.

Flocculation : aggregation process which is characterized by the action of a bonding agent, usually a high MW polymer that physically bridges primary particles together into large units.

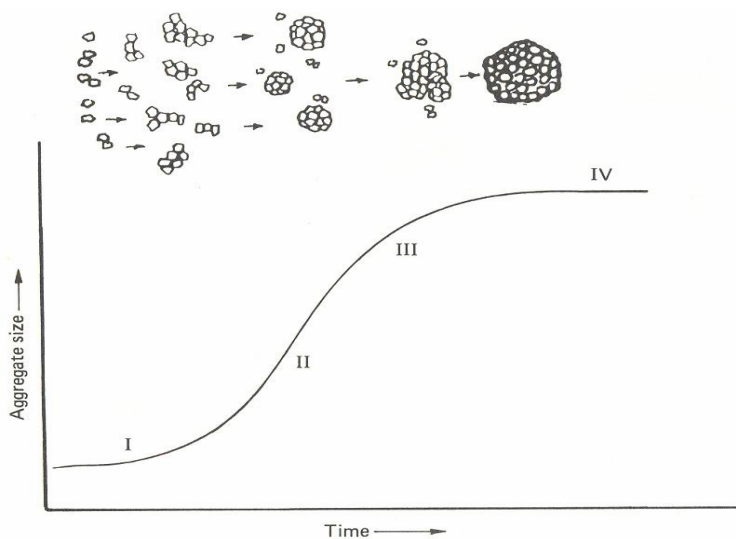


Figure 1.4 Schematic diagram showing the course of aggregation process in a stirred vessel.

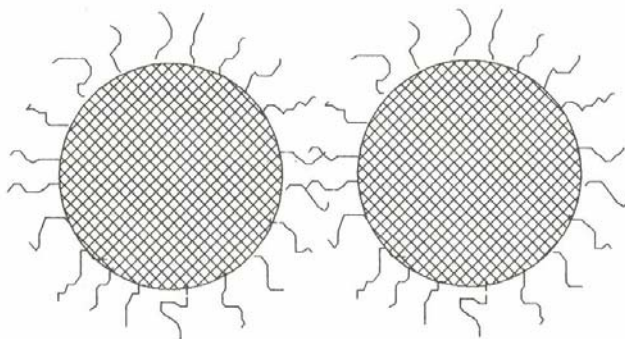


Figure 3.3 Prevention of particle contact by terminally adsorbed polymer chains – steric stabilization.

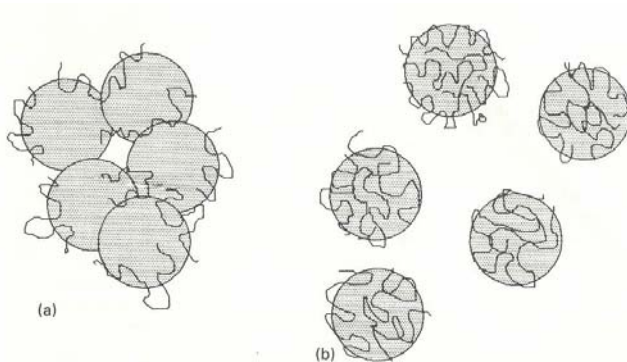


Figure 3.4 Schematic diagram showing (a) bridging flocculation and (b) restabilization by adsorbed polymer.

PARTICLE AGGREGATION

Particles collide and adhere to one another – aggregation

It has been suggested that at least there are 4 stages of aggregation

Stage I >> formation of doublets

a slow process

growth is due to binary collision between primary particles of equal size

Stage II >> growth is rapid

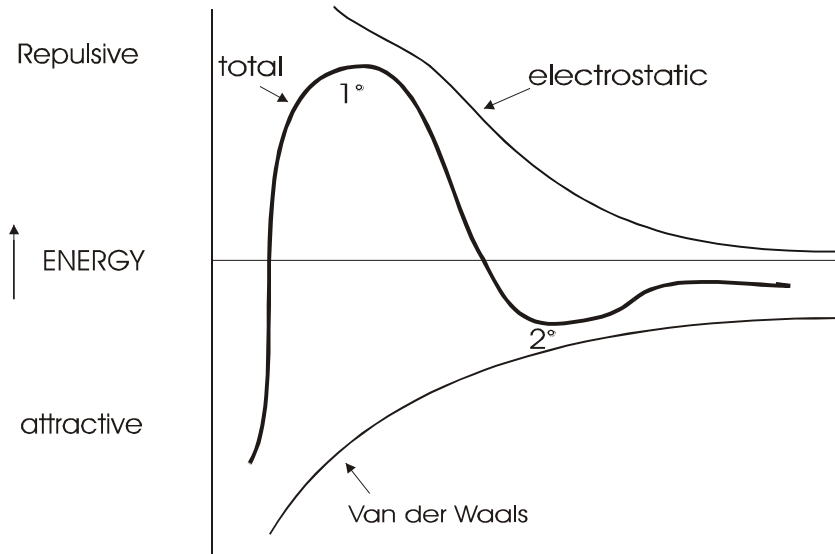
Stage III >> the rate of increase in aggregate size decreases

Stage IV >> stable aggregate size

IDEALISED PAIR POTENTIAL ENERGY DIAGRAM

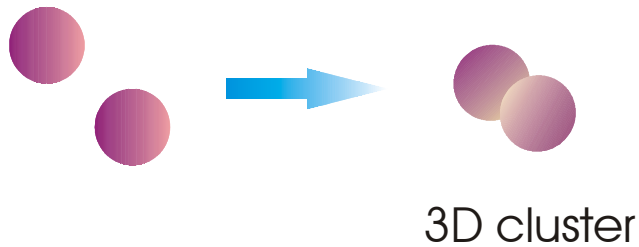
Total free energy of interaction between two colloidal particles – identical

$$\begin{aligned} \Delta G = & \Delta G_{aH} \text{ (van der Waals)} + \Delta G_{rep} \text{ (electrostatic)} \\ & + \Delta G_{rep} \text{ (short range)} + \Delta G_{rep} \text{ (steric)} \\ & + \Delta G \text{ (other effects)} \end{aligned}$$



- 1° Primary maximum (prevents flocculation)
- 2° Secondary minimum (assists flocculation)

Flocculation / aggregation



Reversibility dependent upon mechanism
 Dependent upon balance between a number of forces

Attractive – Van der Waals
 Repulsive – electrostatic

Attractive Force

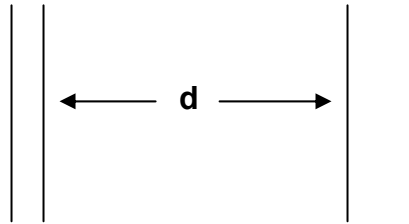
Every atom is a fluctuating dipole
 i.e : electrons surrounding a nucleus do not constitute a spatially and temporally uniform screen
 creates an attraction between atoms
 >> Van der Waals or dispersion energy (*electronic oscillations*)

Approximately additive:

Play an important part in the interaction between particles in colloidal dimension to cause flocculation.

Hamaker (1937)

For the case of parallel flat plates, separated by a distance d , the interaction energy per unit area is



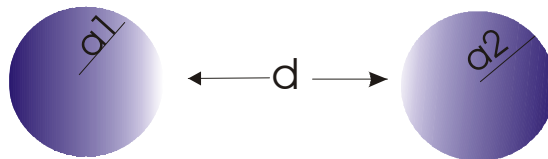
$$E_{aH} = -\frac{A}{12\pi d^2}$$
 where A is the Hamaker constant for the interacting media. A is in the order of $10^{-19} - 10^{-20}$ J. A negative sign indicates an attractive energy.

For a spherical particles with radii a_1 and a_2

$$E_{aH} = -\left(\frac{A}{6d}\right)\left(\frac{a_1 a_2}{a_1 + a_2}\right)$$

For the case of identical spheres in a medium

$$E_{aH} = \frac{Aa}{12d}$$
 Where d is the distance of maximum approach
Holds for $a > d$



Note : for atoms,

$$E_{aH} \propto \frac{1}{d^6}$$

Hamaker constant is also called Van der Waals constant.

E_{aH} is always negative because its value at infinity is zero, decreases as the particles approach each other.

A becomes inaccurate at separations greater than about 10% of the particle radius.

REPULSIVE FORCE

Practically all particles in aqueous suspensions carry a nett surface charge.

- ionization of surface groups
- specific adsorption of ions

Particles can be associated to the surface or attracted to the surface.

The nature of electrical double layer formed can greatly influence the interaction between charged particles.

At Low Ionic Strength ;

The diffuse layer of counterions around the particles extends to a considerable distance when particles approach each other , the DL is less extensive , need to be really close in order to experience the repulsion.

At High Ionic Strength ; (high electrolyte concentration)

DL is less extensive , need to be really close in order to experience the repulsion.

Electrical Potential is now an important quantity when considering particles interaction.

Region? Inner boundary of the DL and just outside the closely associated counterions. i.e : Stern layer

Can be experimentally measured by **Zeta Potential**, ζ for to spherical particles, radii a_1 and a_2 , zeta potential ζ_1 and ζ_2 , the electrical interaction energy.

$$E_{rep} = \frac{64a_1a_2}{a_1+a_2} \epsilon\pi \left(\frac{kt}{zq} \right)^2 r_1 r_2 \exp(-\kappa d)$$

where, ϵ - permittivity of the medium
 z - valency of the ions
 q - elementary charge
 γ_1 - dimensionless function ,

The interaction decreases exponentially with separation distance , with a decay

length. $\frac{1}{\kappa}$.

κ is Debye- Huckel parameter.

$\frac{1}{\kappa} \propto$ ionic strength.

For aqueous electrolyte at 25° C ,

$$\kappa = 2.3 \times 10^9 \left(\sum c_i z_i^2 \right)^{1/2} \text{ units, m}^{-1}$$

Where c_i is molar concentration.

Solution	$1/\kappa$ distance
Water (deionized)	1 μm
1-1 electrolyte	30 nm in 10^{-4} M solution
-same-	3nm in 10^{-2} M solution

NB : The effective thickness of DL

$$\frac{1}{\kappa} = \left[\frac{\epsilon_r \epsilon_0}{4\pi F^2 \sum c_i z_i^2} \right]^{1/2}$$

ϵ_0 = permittivity volume

F = Faraday constant

For identical particles $a_1 = a_2$

$$E_{rep} = 32\pi\epsilon a_1 \left[\frac{kT}{zq} \right]^2 \gamma_1^2 \exp(-\kappa d)$$

for small values of zeta potential

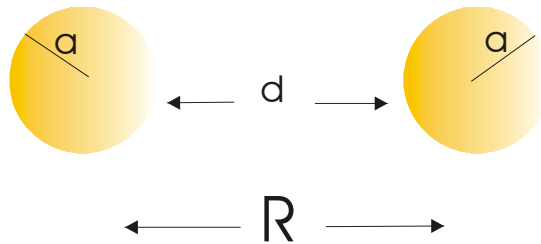
$$E_{rep} = 2\pi\epsilon a_1 \zeta^2 \exp(-\kappa d)$$

Lyklema (1968) – Two Spherical Particles

For small particle, $\frac{a}{1/\kappa} \ll 1$

we have a relatively thick electrical double layer ,

$$E_{rep}^s = \frac{\epsilon a^2 \psi_o^2}{R} \exp(-\kappa d)$$



For large particle , $\frac{a}{(1/\kappa)} \gg 1$

Thus , relatively thin electrical double layer

$$E_{rep}^l = \frac{\epsilon a \psi_o^2}{2} \ln(1 + \exp(-\kappa d))$$

E_{rep} is always +ve , its valuent ∞ is zero and increases as particles approach each other. Added salts cause a decrease in *zeta potential* , reduces the repulsion , increases in κ .

Effect more pronounce with highly charged ions thus multivalent ions are expected to have a greater effect on colloid stability.

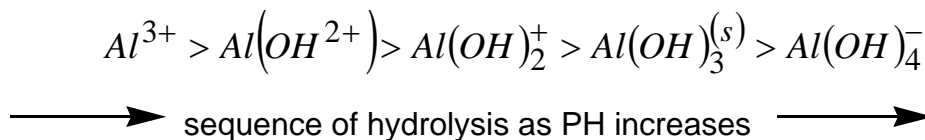
E_{rep} Depends on :

- ❖ Size and shape of the dispersed particles
- ❖ Separations distances
- ❖ Surface potential ψ_o i.e zeta potential
- ❖ ϵ , the dielectric constant of the dispersing liquid.
- ❖ The effective thickness of the electrical double layer

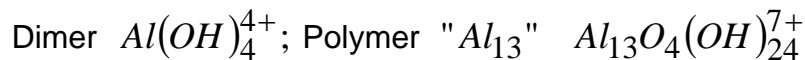
Note:

Examples of most commonly use inorganic flocculants : iron and aluminium compounds.

Their effectiveness could be explained in terms of the highly charge Fe^{3+} and Al^{3+} ions.



The hydrolysis products adsorbed by many particles due to positively charge , can cause charge neutralisation and reversal.



Mechanisms Affecting Dispersion Stability

Steric Stabilization - this involves polymers added to the system adsorbing onto the particle surface and causing repulsion

It is a simple process requiring just the addition of a suitable polymer
However it can be difficult to subsequently flocculate the system if required
The polymer can be expensive and in some cases undesirable (e.g. when a ceramic slip is cast the polymer has to be burnt out causing shrinkage and possible defects).

Mechanisms Affecting Dispersion Stability

Electrostatic or Charge Stabilization - this is the effect on particle interaction due to the distribution of charged species in the system

Stabilization or flocculation of a system may be modified simply by altering the concentration of ions in a system

It is a reversible process

It is potentially inexpensive

Zeta Potential is a very good index of the magnitude of the interaction between colloidal particles and Zeta Potential measurements are used to assess the stability of colloidal systems.