ZETA SIZER

Lecture by

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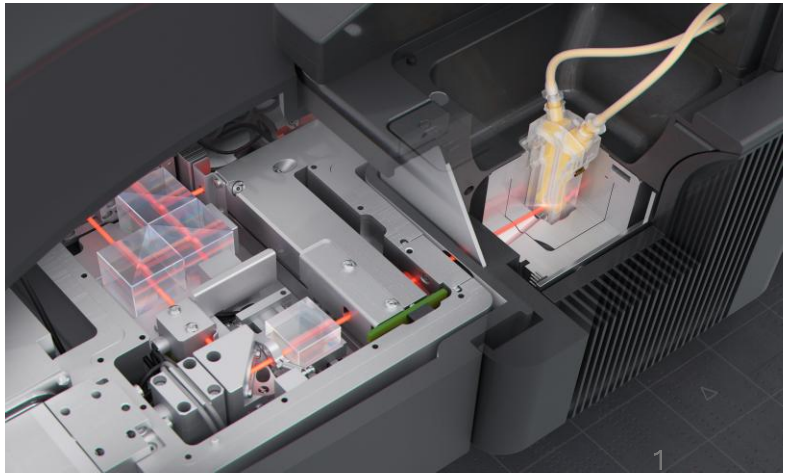

Introduction to zeta potential

- **Zeta potential** is a **physical property** which is exhibited by any particle in suspension, macromolecule or material surface.

Uses of Zeta potential:

1. **Optimize the formulations of suspensions, emulsions and protein solutions.**
2. **Predict interactions with surfaces.**
3. **Optimize the formation of films and coatings.**
4. **Reduce time needed to produce trial formulations.**
5. **Aid in predicting long-term stability.**

- This introduction concentrates on the **zeta potential** of **colloidal systems**, with a density low enough such that if they **remain dispersed**, **sedimentation is negligible**.

Colloid Science

- **'Colloidal system'**: composed of solids, liquids and gases dispersed in another (aerosols, emulsions, colloidal suspensions and association colloids).
- **The particles in a dispersion may adhere to one another and form aggregates so increasing size, then settle out under the influence of gravity.**
- An initially formed aggregate is called a floc and the process of its formation **flocculation**. **The floc may or may not sediment or phase separate.**

- **Coagulation: If the aggregate changes to a much denser form.**

An **aggregate usually separates out** either by **sedimentation** (if it is denser than the medium) or by **creaming** (if it less dense than the medium).

Usually, coagulation is irreversible whereas flocculation can be reversed by the process of deflocculation. Figure 1 schematically represents some of these processes.

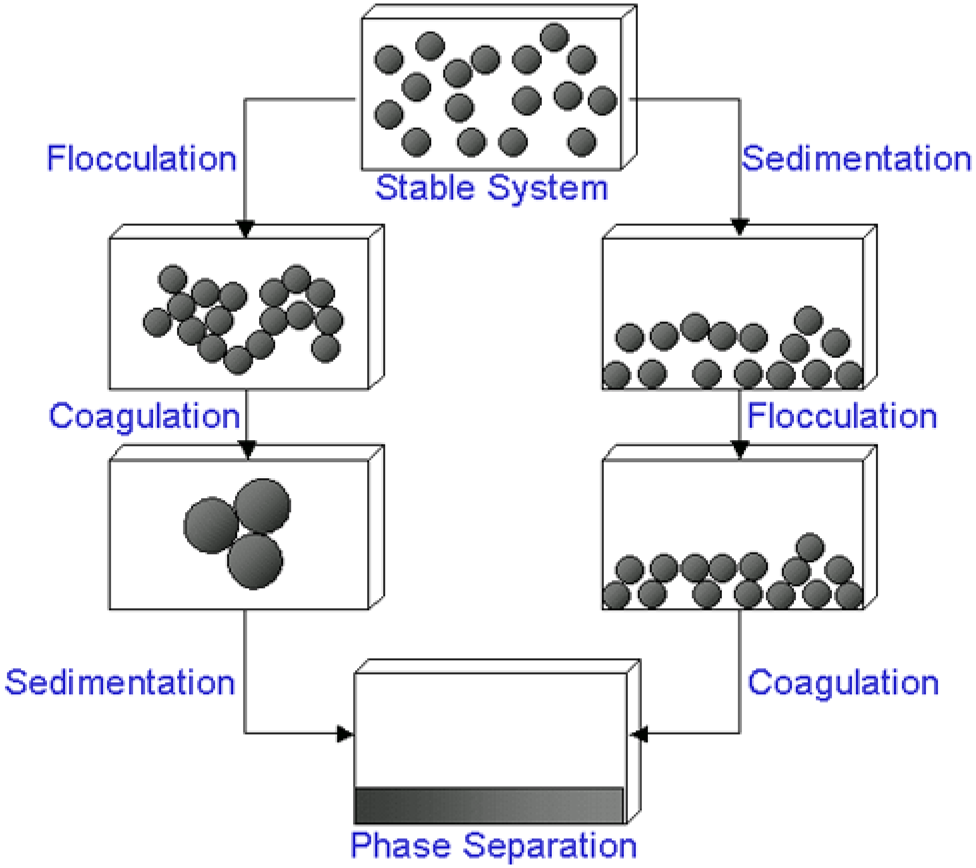

Figure 1: Schematic diagram showing various mechanisms where stability may be lost in a colloidal dispersion

Colloidal Stability and DVLO Theory

DVLO theory dealt with stability of colloidal systems (**suggests that stability of a particle in solution is dependent upon its total potential energy function V_T**).

$$V_T = V_A + V_R + V_S$$

V_S is the potential energy due to the solvent (marginal contribution to the total potential energy over nanometers of separation).

Much more important is the **balance between V_A and V_R, these are the attractive and repulsive contributions**.

$$V_A = -A/(12\,\pi\, D^2)$$

Where A is the Hamaker constant and **D** is the particle separation. The repulsive potential V_R is a far more complex function.

$$V_R = 2\,\pi\,\varepsilon\, a\, \zeta^2 \exp(-\kappa D)$$

where **a** is the particle radius, **π** is the solvent permeability, **κ** is a function of the ionic composition and **ζ** is the zeta potential.

- DVLO theory suggests that the stability of a colloidal system is determined by the sum of these van der Waals attractive ($\boldsymbol{V_A}$) and electrical double layer repulsive ($\boldsymbol{V_R}$) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing.

- Figure 2a shows the separate forces as a dotted line, and the sum of these forces as the solid line.
- This sum has a peak, and the **theory proposes that particles that are initially separated are prevented from approaching each other because of the repulsive force.**

- **Exception:** particles are forced with sufficient energy to overcome that barrier (by increasing temperature)

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Attractive force will pull them into contact (adhere strongly) and **irreversibly together**.

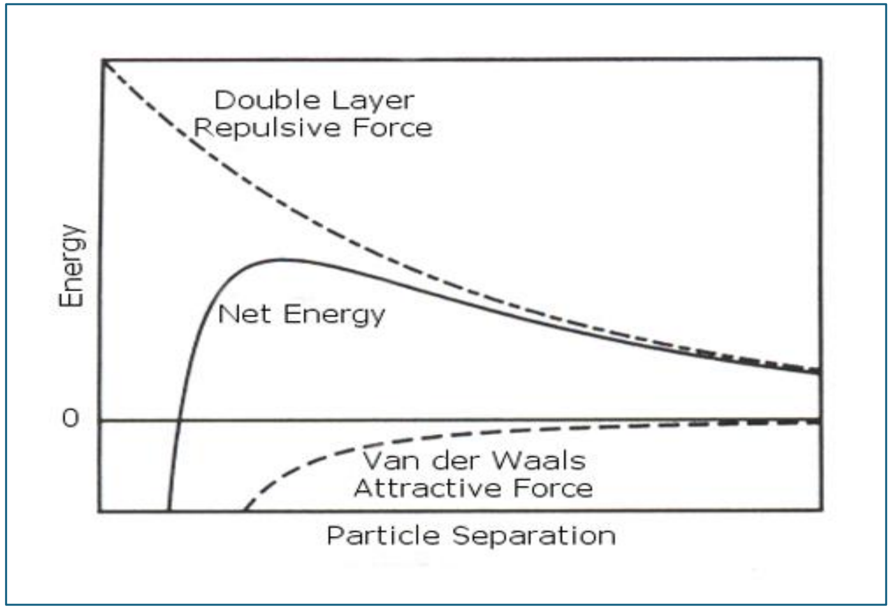
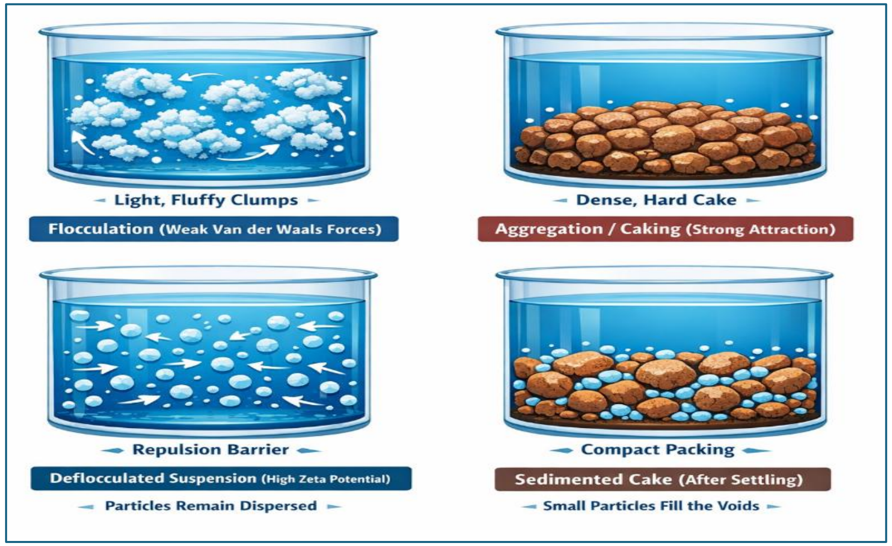


Figure 2(a): Schematic diagram of the variation of free energy with particle separation according to DVLO theory.



Note:

1. if the particles have a sufficiently high repulsion, the dispersion will resist flocculation, and the colloidal system will be stable.
2. if a repulsion mechanism does not exist then flocculation or coagulation will eventually take place.

- If **zeta potential is reduced** (e.g. in high salt concentrations= cohesion H_20 mol.), a "secondary minimum" being created, where a weaker and reversible adhesion between particles exists (figure 2 (b)).

These weak flocs are sufficiently stable not to be broken up by Brownian motion but may disperse under an externally applied force such as vigorous agitation.

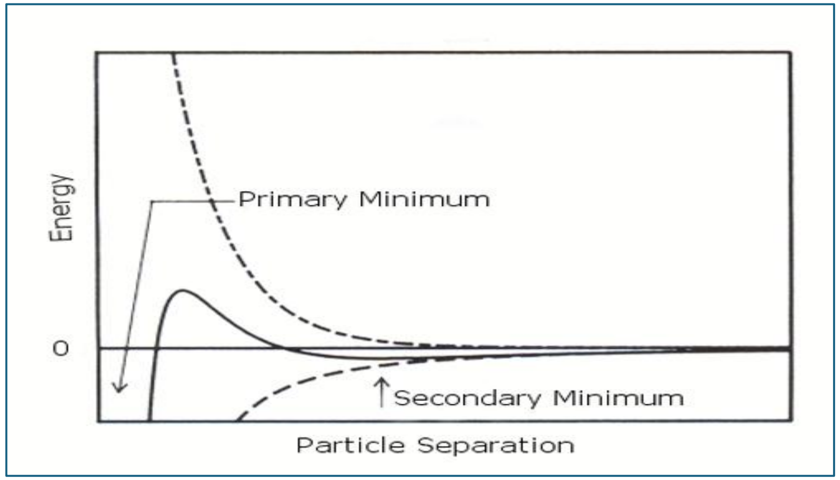


Figure 2(b): Schematic diagram of the variation of free energy with particle separation at higher salt concentrations showing the possibility of a secondary minimum.

- **How can colloidal stability be achieved?**

Two fundamental mechanisms that affect dispersion stability (figure 3).

1. **Steric repulsion:**

This involves polymers added to the system adsorbing onto the particle surface and preventing the particle surfaces coming into close contact.

- If enough polymer adsorbs, the **thickness of the coating will be sufficient to keep particles separated by steric repulsions between the polymer layers**, and at those separations the van der Waals forces are too weak to cause the particles to adhere.

2. **Electrostatic or charge stabilization:**

This is the effect on particle interaction due to the distribution of charged species in the system.

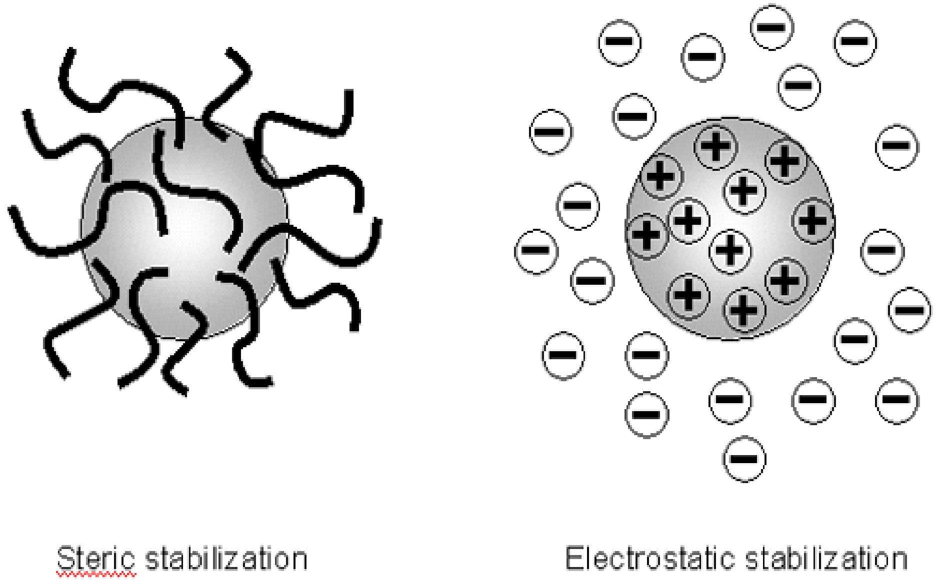


Figure 3: Steric and electrostatic stabilization mechanisms of colloidal dispersions

Each mechanism has its benefits for particular systems:

- **Steric stabilization** (simple, requiring addition of a suitable polymer)

Disadvantages: difficult to subsequently flocculate the system if this is required, the polymer expensive and in some cases the polymer is undesirable .

e.g. when a ceramic slip is cast and sintered, the polymer has to be 'burnt out'. This causes shrinkage and can lead to defects.

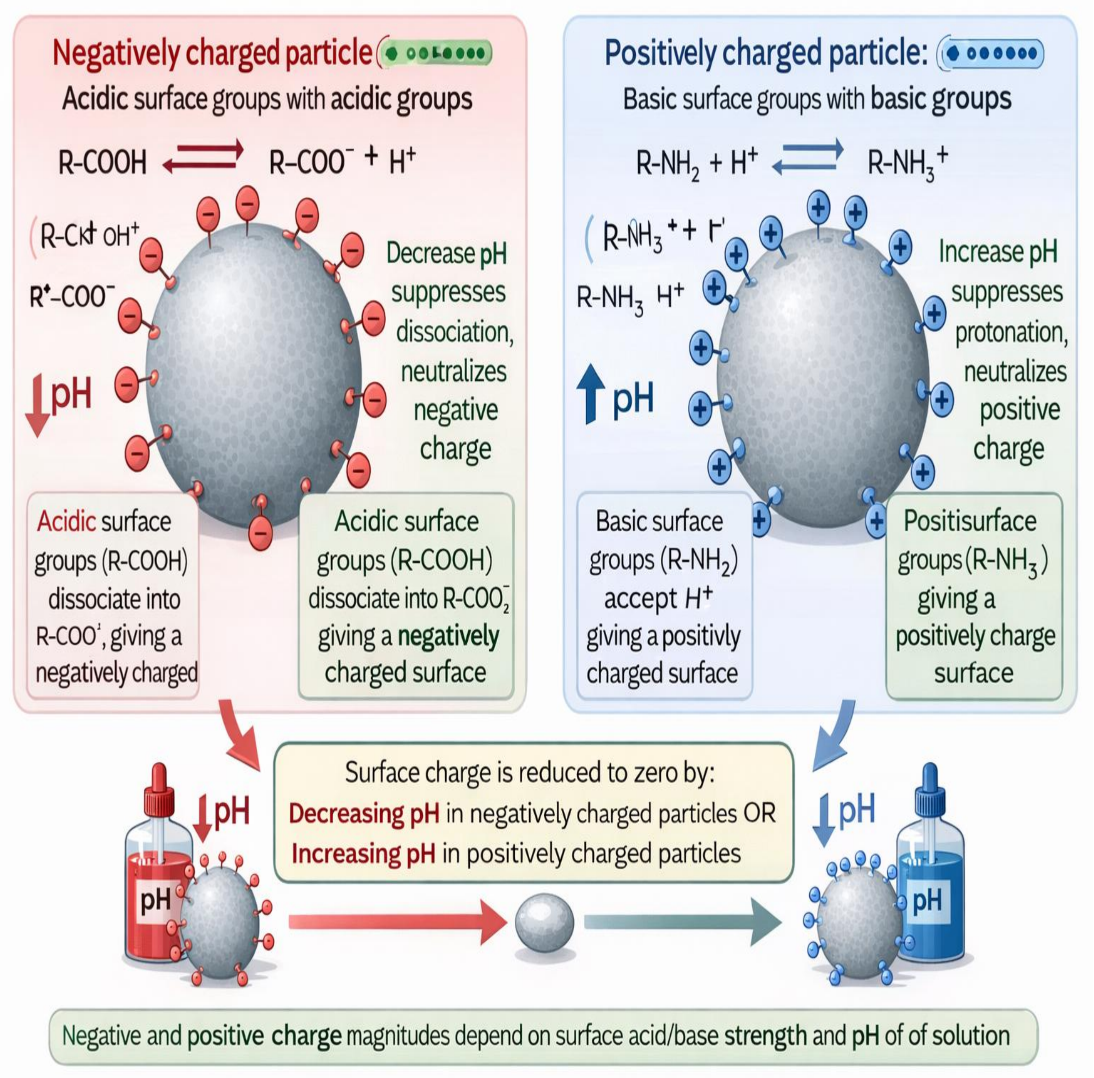
- **Electrostatic or charge stabilization** (stabilizing or flocculating a system by simply altering the concentration of ions in the system) (reversible and inexpensive).

Origins of Surface Charge

Most colloidal dispersions in aqueous media carry an electric charge. There are many origins of this surface charge depending upon (nature of the particle and its surrounding medium), the most important mechanisms:

A. Ionization of Surface Groups

1. Dissociation of acidic groups on the surface of a particle will give a negatively charged surface. While basic surface will take on a positive charge (figure 4). **In both cases, the magnitude of the surface charge depends on (acidic or basic strengths of the surface groups and on the pH of the solution).**



2. The surface charge can be reduced to zero by suppressing the surface ionization by decreasing the pH in negatively charged particles (figure 4(a)) or by increasing the pH in positively charged particles (figure 4(b)).

Clarification:

•For **negatively charged particles** with surface **carboxyl (-COOH)** or **hydroxyl (-OH)** groups:

- These groups ionize and release H^+, making the surface **negatively charged**.
- **Lowering the pH** (making the solution more acidic) **suppresses ionization** (more H^+ in solution pushes equilibrium back toward the neutral form), reducing the negative charge so reach to zero.

•For **positively charged particles**, with **amine ($-NH_2$)** groups:

- These groups can **accept protons** to become **$-NH_3^+$**, giving a **positive surface charge**.
- **Raising the pH** (making the solution more basic) **removes protons**, reducing the positive charge so reaches to zero.

This is how surface charge approaches **zero**—called the **isoelectric point**.

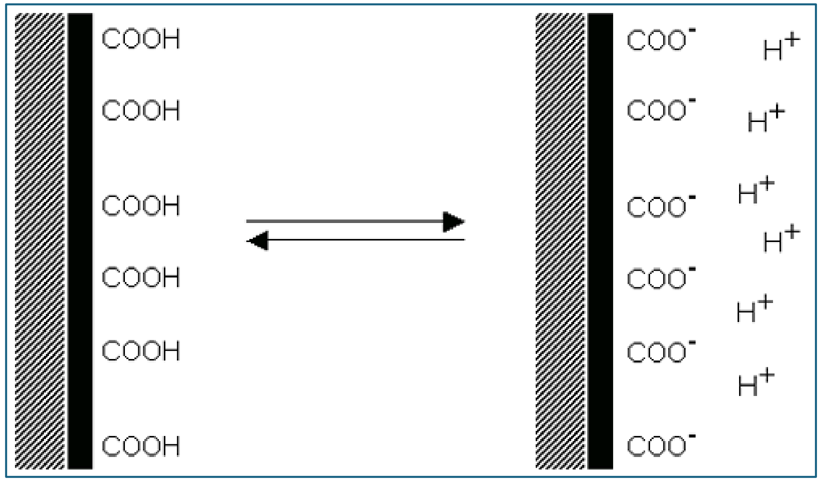


Figure 4(a): Origin of surface charge by ionization of acidic groups to give a negatively charged surface

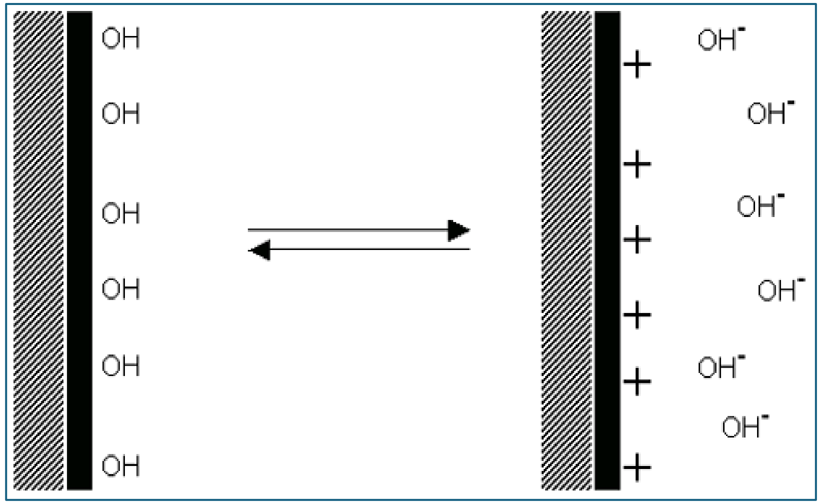


Figure 4(b): Origin of surface charge by ionization of basic groups to give a positively charged surface

B. Differential loss of ions from the crystal lattice

As an example, consider a **crystal of silver iodide placed in water.** Solution of ions occurs.

a) If equal amounts of Ag^+ and I^- ions were to dissolve; the surface would be uncharged.

b) In fact, silver ions dissolve preferentially, leaving a negatively charged surface (figure 5).

c) If Ag^+ ions are now added the charge falls to zero.

d) Further addition leads to a positively charged surface.

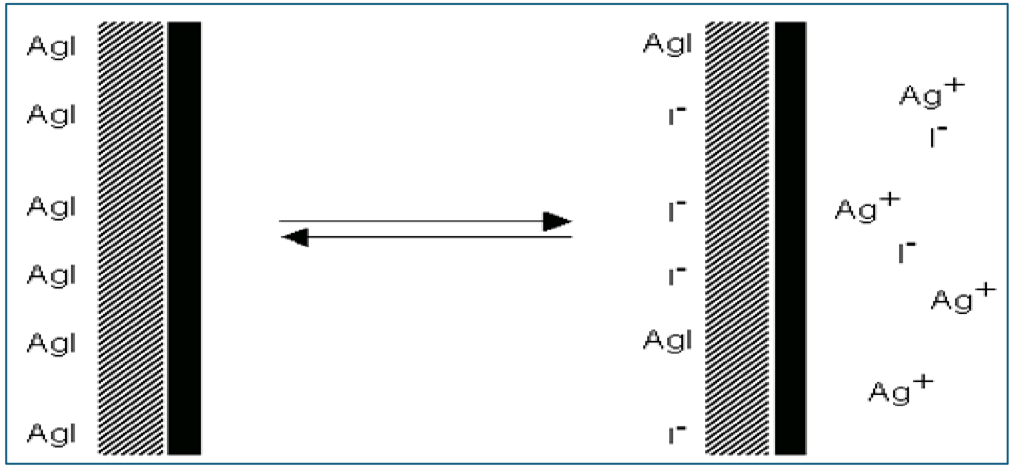
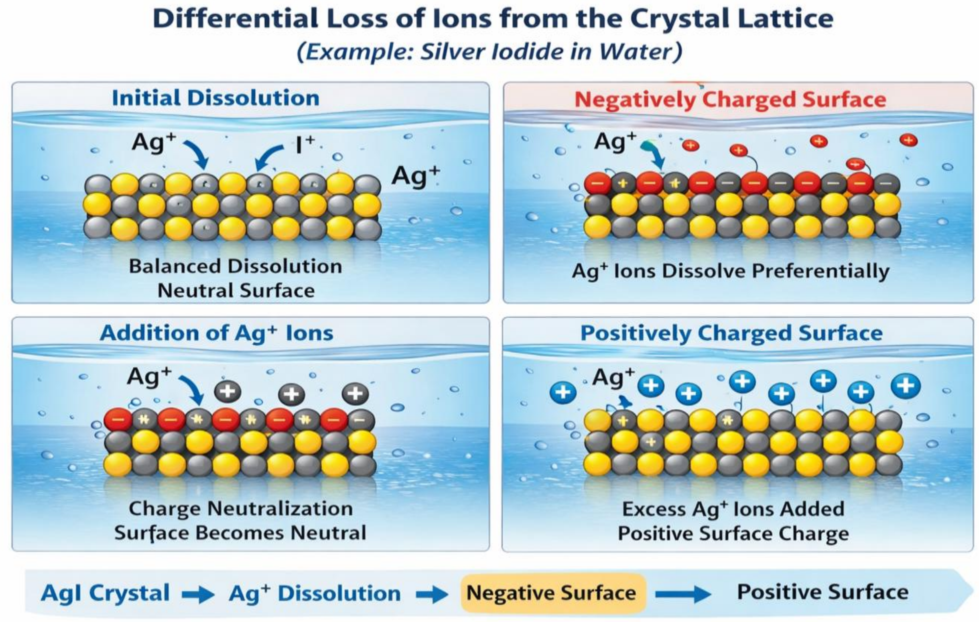


Figure 5: Origin of surface charge by differential solution of silver ions from a AgI surface



C. Adsorption of charged species (ions and ionic surfactants)

- Surfactant ions may be specifically adsorbed on the surface of a particle, leading, in the case of cationic surfactants, to a positively charged surface (figure 6(a)) and, in the case of anionic surfactants, to a negatively charged surface (figure 6(b)) = to keep repulsion and maintain stability

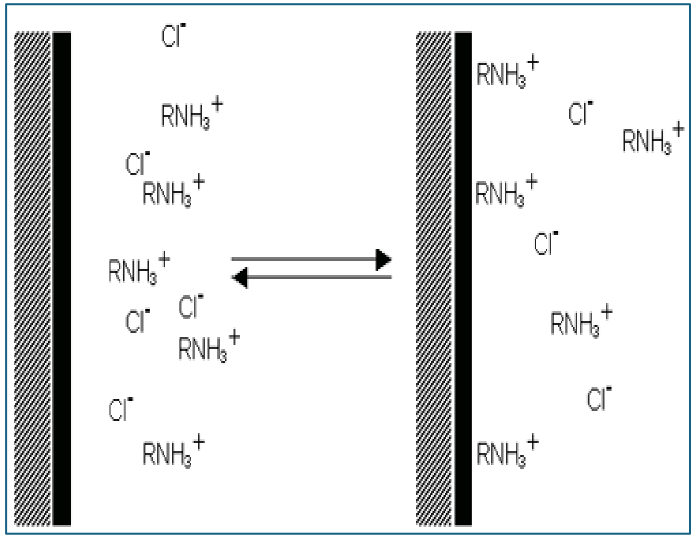


Figure 6(a): Origin of surface charge by specific adsorption of a cationic surfactant. R = hydrocarbon chain

Cetyltrimethylammonium bromide (CTAB) adsorbs onto **Silicon dioxide (SiO_2),** it generally **increases the positive surface charge** of the particles.

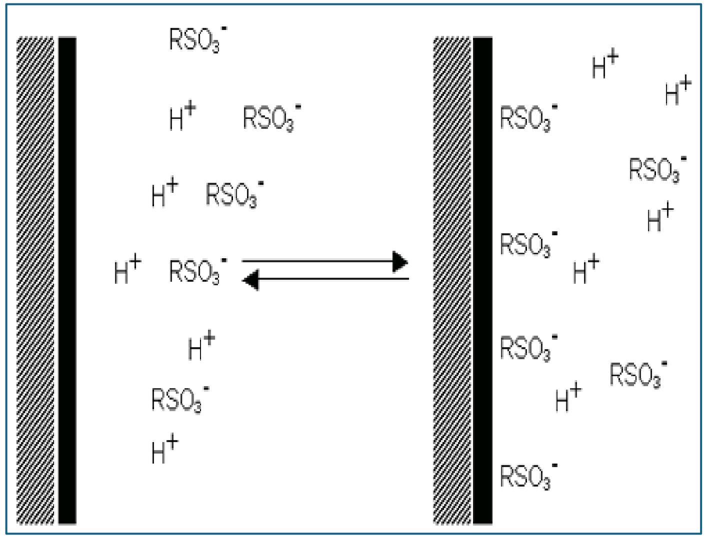
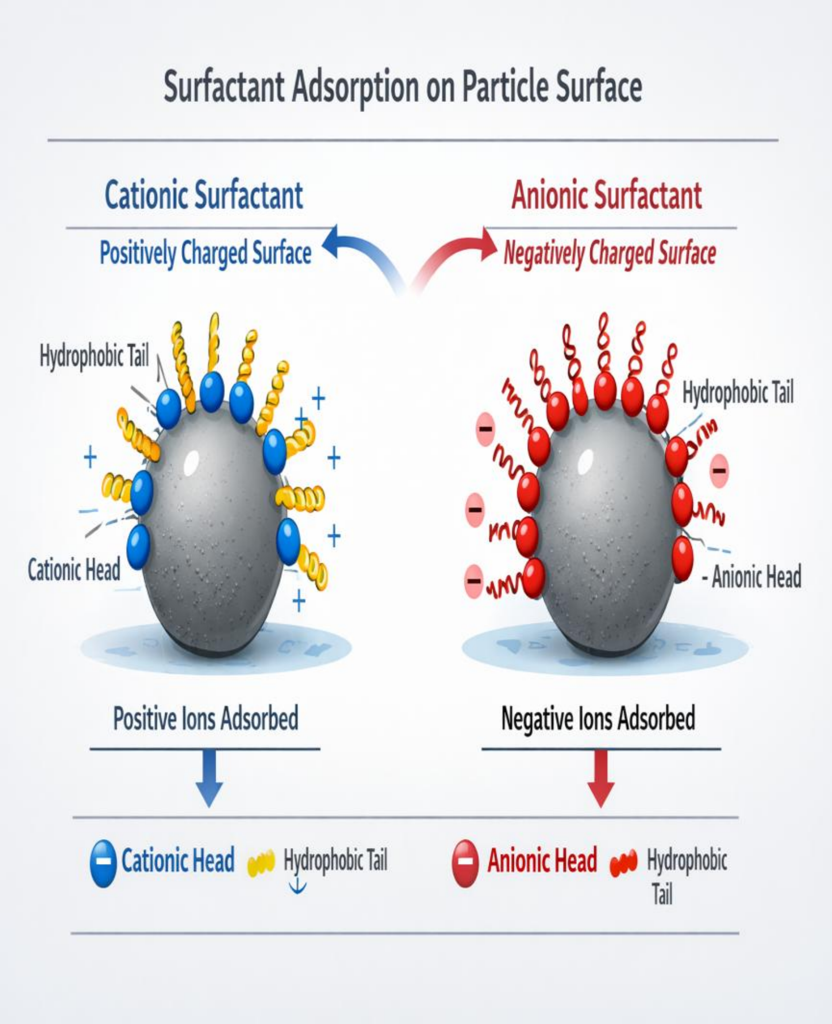


Figure 6(b): Origin of surface charge by specific adsorption of an anonic surfactant. R = hydrocarbon chain

Sodium dodecyl sulfate (SDS) adsorbs on **oxide particles** (such as alumina, iron oxide, or titania), it generally **increases the negative surface charge** of the particles.



Zeta Potential

The Electrical Double Layer

The development of a net charge at the particle surface affects the **distribution of ions in the surrounding interfacial region**, resulting in an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface. Thus, an electrical double layer exists round each particle.

- The liquid layer surrounding the particle exists as two parts:

a) an inner region (Stern layer) where the ions are strongly bound

b) an outer region (diffuse) where they are less firmly associated. Within the diffuse layer there is a **(notional boundary)** inside which the ions and particles form a stable entity **(+ve and –ve equal so neutrality reach)**.

c) When a **particle moves (e.g. due to gravity), ions within the boundary move it.** Those ions beyond the boundary stay with the bulk dispersant. The potential at this boundary (surface of hydrodynamic shear) is the zeta potential (figure 7).

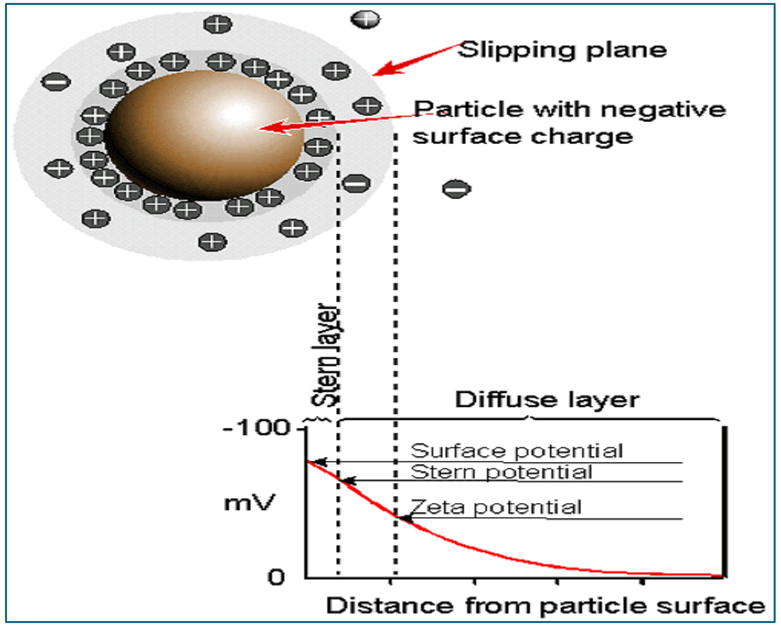


Figure 7: Schematic representation of zeta potential

The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system.

- If all particles in suspension have a large negative or positive zeta potential (**repel each other**).

Stable (particles with zeta potentials more positive than +30 mV or more negative than -30 mV).

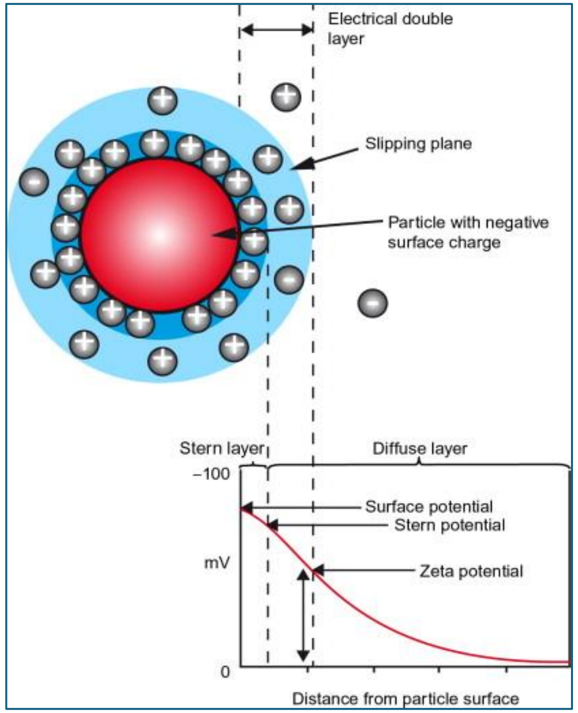
If the particles have:

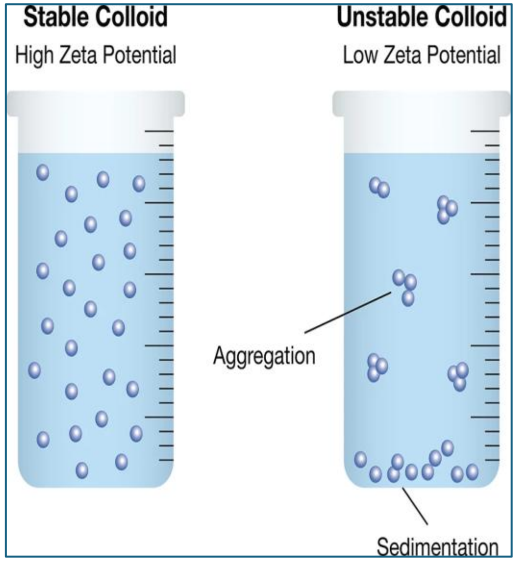
- low zeta potential values (**no force to prevent the particles coming together and flocculating**).
- if particles have a density greater than the dispersant, even though they are dispersed, **they will eventually sediment forming a close packed bed (i.e. a hard cake).**

Zeta potential depends on:

a) Nature of the dispersant

b) The surface.





Factors Affecting Zeta Potential

(1) pH

In aqueous media, the pH of the sample is one of the most important factors that affects its zeta potential.

- **A particle in suspension with a negative zeta potential.** A typical plot of zeta potential versus pH is shown in figure 8.

a) If more alkali is added, then the particles tend to acquire **more negative charge (greater than pH 7.5).**

b) If acid is added, then a point will be reached where the **charge will be neutralized.**

c) Further addition of acid cause a build up of **positive charge if the ions are specifically adsorbed (pH values less than 4).**

- In this case a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. The **point where the plot passes through zero zeta potential (pH 5.5)** is called the **isoelectric point** (point where aggregation is most and colloidal system is least stable).
- Problems with dispersion stability would be expected at pH values between 4 and 7.5 as the zeta potential values are between +30 and -30 mV.

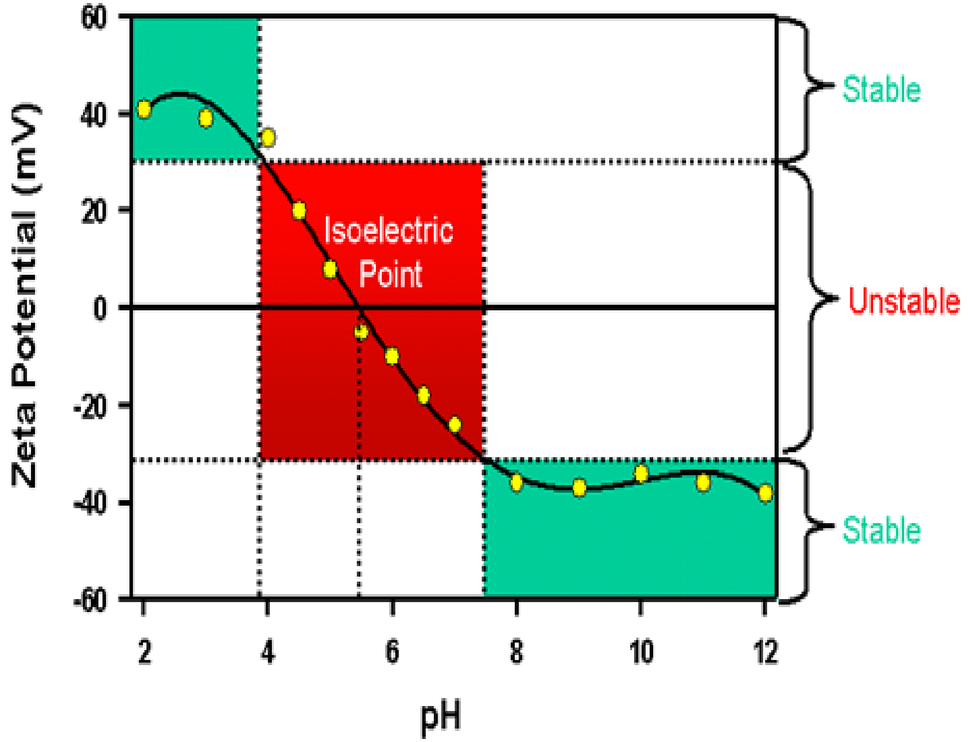


Figure 8: Typical plot of zeta potential versus pH showing the position of the isoelectric point and the pH values in the green sectors where the dispersion would be expected to be stable

(2) Conductivity

The thickness of the double layer (κ-1) depends upon:

1. **Concentration of ions in solution** (calculated from the ionic strength of the medium).

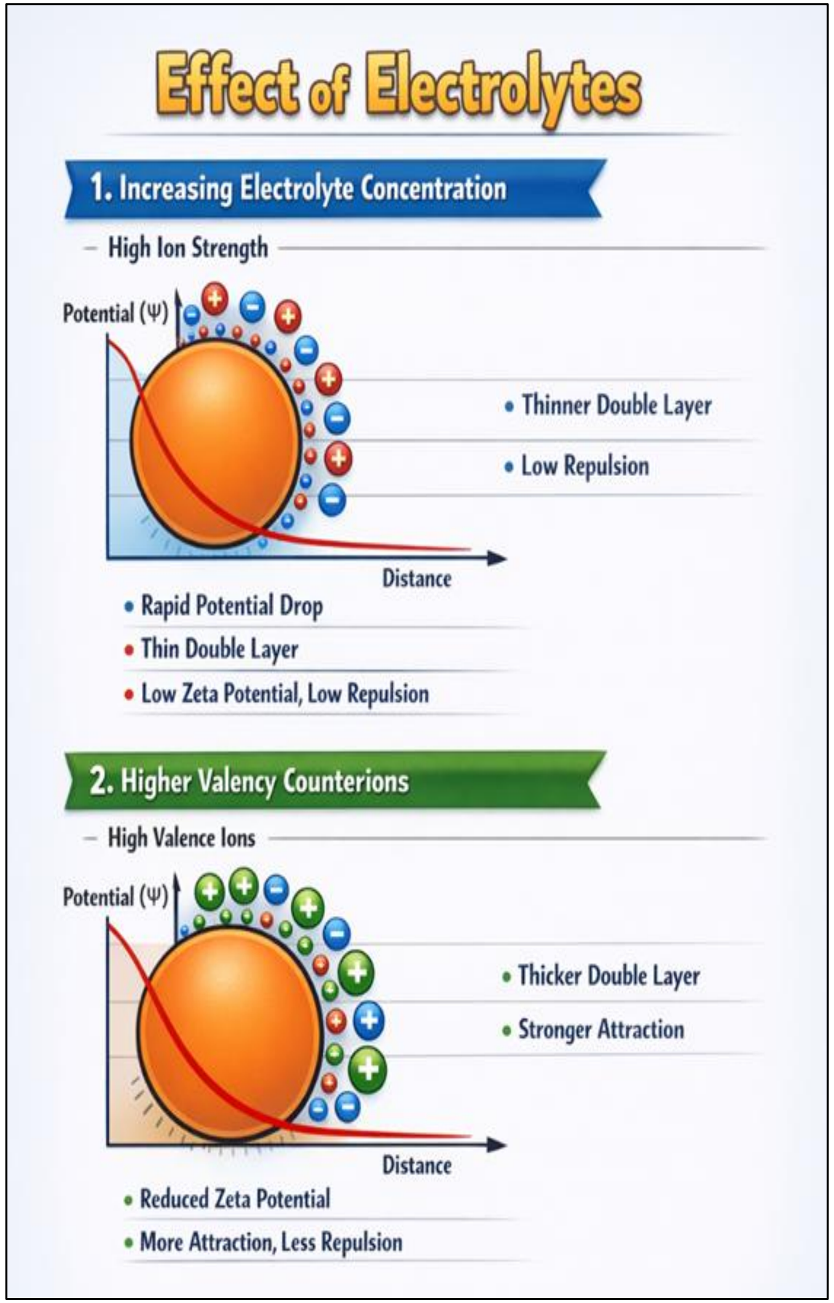
The higher the ionic strength, the more compressed the double layer becomes (low repulsion, low zeta potential).

2. **The valency of the ions.**

A trivalent ion (Al^{3+}) will compress the double layer to a greater extent in comparison with a monovalent ion such as Na^{+}.

- **Inorganic ions can interact with charged surfaces in one of two distinct ways:**

i. **Non- specific ion adsorption where they have no effect on the isoelectric point [Ions are attracted to the surface due to electrostatic forces, but they do not form strong chemical bonds** (ions reside in the diffuse layer and not alter the ionization state of surface groups) e.g. Na^{+} loosely associating with a negatively charged silica surface].



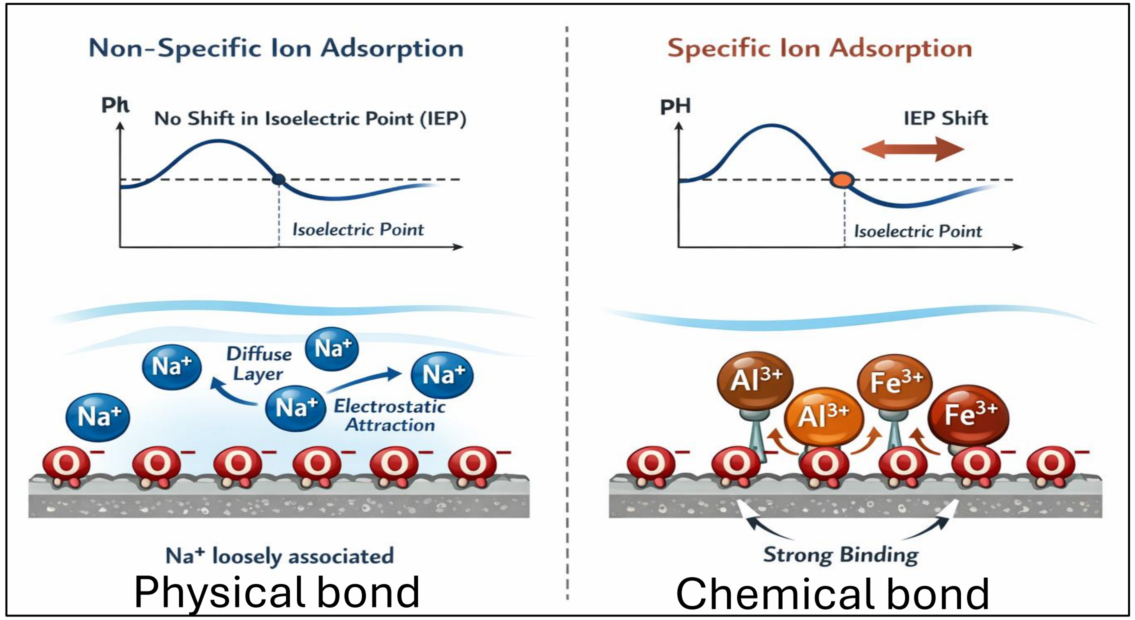
ii. Specific ion adsorption, lead to a change in the value of the isoelectric point

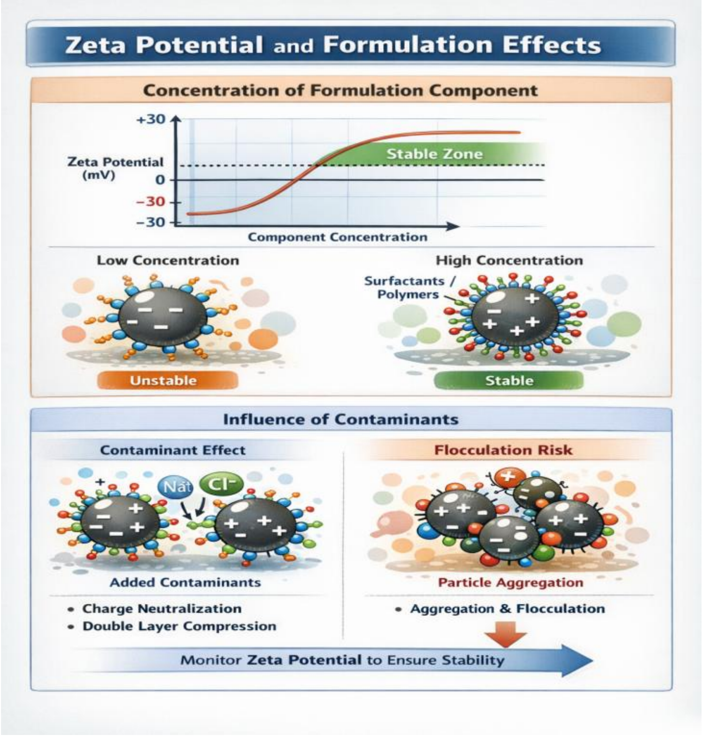
[**Ions bind directly to the surface groups, via coordination or chemical bonding** (binding can neutralize or reverse the surface charge and shifts the isoelectric point either higher or lower depending on the ion and the surface) e.g: Adsorption of multivalent ions like Al^{3+} or Fe^{3+} onto a negatively charged surface, which can raise the IEP by neutralizing more surface charge].

(3) Concentration of a formulation component

a) **The effect of the concentration of a formulation component** on the zeta potential can give information to assist in formulating a product **to give maximum stability**.

b) **The influence of known contaminants on the zeta potential** of a sample can be a powerful tool in formulating the product to resist flocculation for example.





Electrokinetic Effects

The existence of electrical charges on the surface of particles to **detect their interact with an applied electric field**.

There are four distinct effects depending on the way in which the **motion is induced**:

1. **Electrophoresis:** the movement of a charged particle relative to the liquid it is suspended in under the influence of an applied electric field.
2. **Electroosmosis:** the movement of a liquid relative to a stationary charged surface under the influence of an electric field.
3. **Streaming potential:** the electric field generated when a liquid is forced to flow past a stationary charged surface.
4. **Sedimentation potential:** the electric field generated when charged particles sediment.

Electrophoresis

When an **electric field is applied across an electrolyte**

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Charged particles suspended in the electrolyte are **attracted towards the electrode of opposite charge.**

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Particles move with constant velocity when equilibrium is reached between these two opposing forces.

Note: Viscous forces acting on the particles tend to oppose this movement.

The velocity is dependent on:

A. Strength of electric field or voltage gradient
B. Dielectric constant of the medium
C. Viscosity of the medium
D. Zeta potential.

- **The velocity of a particle in a unit electric field is referred to as its electrophoretic mobility.**

- **Zeta potential** is related to the **electrophoretic mobility** by the Henry equation:

$$UE = \frac{2\ \varepsilon\ z\ f(\kappa a)}{3\eta}$$

where UE = electrophoretic mobility, z = zeta potential, ε = dielectric constant, η = viscosity and f(κa) = Henry's function. The units of κ, termed the Debye length, are reciprocal length (measure of the "thickness" of the electrical double layer).
'a' refers to the radius of the particle
Ka ratio of particle radius to electrical double layer thickness (figure 9).

- **Electrophoretic determinations of zeta potential in aqueous media and moderate electrolyte concentration:**

a) **If f(κa) is 1.5, referred as Smoluchowski approximation** (particles larger than about 0.2 microns dispersed in electrolytes containing more that 10 molar salt).
b) **If f(ka) is 1.0, referred as the Huckel approximation** (for small particles in low dielectric constant media (eg non-aqueous media)).

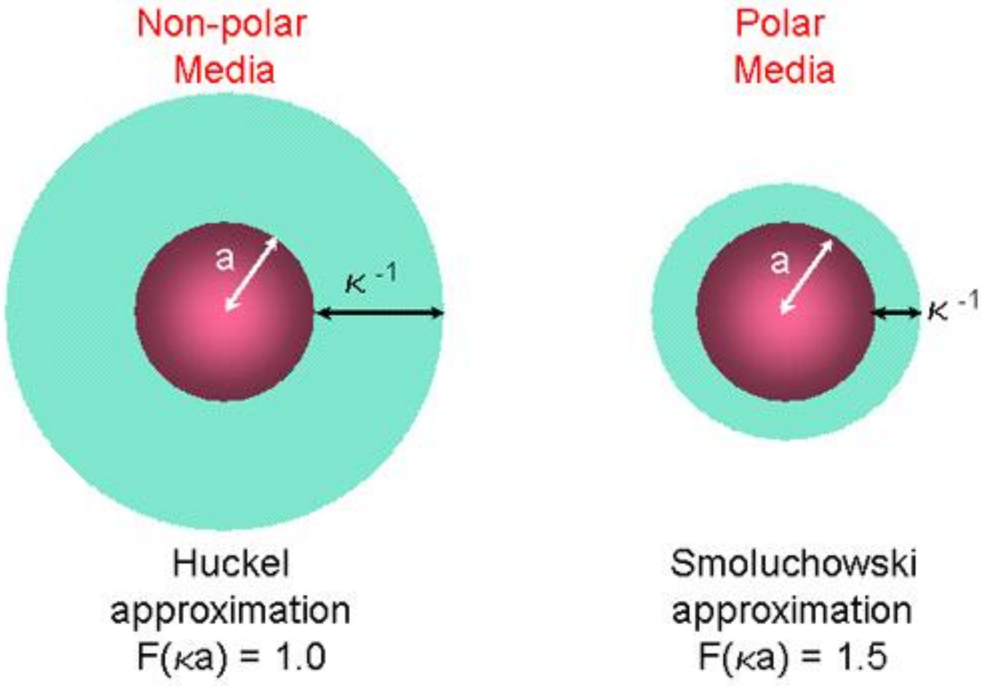

Figure 9: Schematic illustrating Huckel and Smoluchowski's approximations used for the conversion of electrophoretic mobility into zeta potential

Measuring Electrophoretic Mobility

- The Zetasizer uses a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) in a patented technique called **M3-PALS** to measure particle electrophoretic mobility.

Advantages of PALS:

1) High performance of greater than 100 times.
2) Measurement of high conductivity samples.
3) Accurately measure samples that have low particle mobilities (samples dispersed in non-aqueous solvents).
4) Low applied voltages used to avoid risk of heating effects on sample.

Optical Configuration of a Zeta Potential Instrument

A zeta potential measurement system comprises of seven main components (figure10):

1. **Laser:** provides a light source to illuminate the particles within the sample.
2. **Beam splitter:** split the light source to provide an incident and reference beam.
3. **Attenuator:** adjusts the intensity of the light reaching the sample and hence the intensity of the scattering.
4. **Sample Cell:** the incident laser beam passes through the center of the sample cell, and the scattered light at an angle of about **13° is detected**.
5. **Detector:** measure the intensity of the detected, scattered light must be within a specific range.
6. **Digital signal processor: get information when an electric field** is applied to the cell (any particles moving through the measurement volume will **cause the intensity of light detected to fluctuate with a frequency** proportional to the particle speed).
7. **Computer:** The Zetasizer Nano software produces a frequency spectrum from which the electrophoretic mobility and hence zeta potential is calculated.

- To correct for any differences in the cell wall thickness and dispersant refraction, compensation optics are installed to maintain optimum alignment.

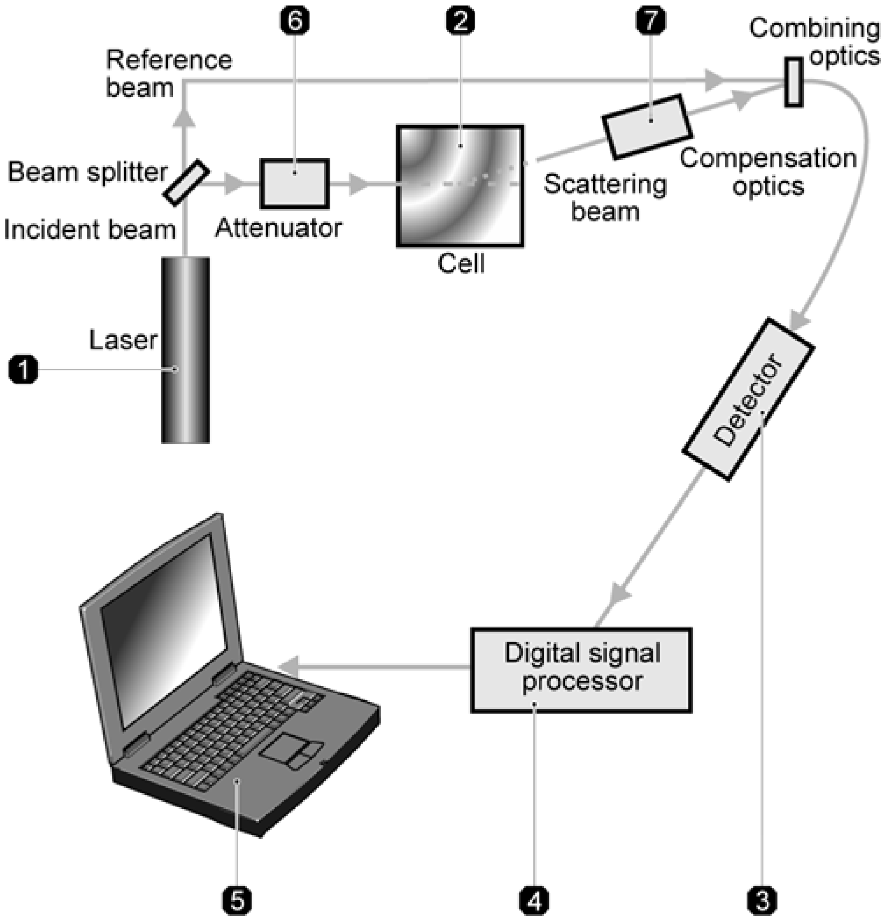

Figure 10: Optical configuration of the Zetasizer Nano series for zeta potential measurements

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