

## Module 8: "Stability of Colloids"

### Lecture 37: ""

The Lecture Contains:

- DLVO Theory
  - Effect of Concentration

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Studying the stability of colloids is an important topic in the study of colloids. The manipulation of the state of dispersions, from stable to unstable, or the reverse is important for many applications. This manipulation can be carried out by altering the interactions between the particles, mainly through Electrostatic or Steric phenomena. In the current chapter we will focus on the former method which can be achieved through changes in the properties such as salt concentration, ion valence and pH. An important theory in this regard is the DLVO Theory (named after Derjaguin, Landau, Verwey and Overbeek).

## DLVO Theory

DLVO Theory is the classical explanation of the stability of colloids in suspension. It looks at the balance between two opposing forces — Electrostatic repulsion and Van-der Waals attraction — to explain why some colloidal systems coagulate while others do not. For example, by adding Alum ( $\text{AlCl}_3$ ), suspended colloidal particles in dirty water could be made to settle down. Addition of the salt (Alum) causes the destabilization of the colloid. This theory has applications in predicting the stability of colloids in a number of Industrial processes such as liquid-liquid extraction, alkaline flooding operations, floatation of Hydrocarbons, stability of oil droplets in emulsions etc.

Consider two identical parallel flat plates (of type '1') in an electrolyte medium (of type '2') (a typical case of two colloid particles in a medium at a very close distance). These plates may have an excess surface charge due to an unequal distribution of lattice forming-ions, dissociation of surface groups or preferential adsorption of ions/surfactants.

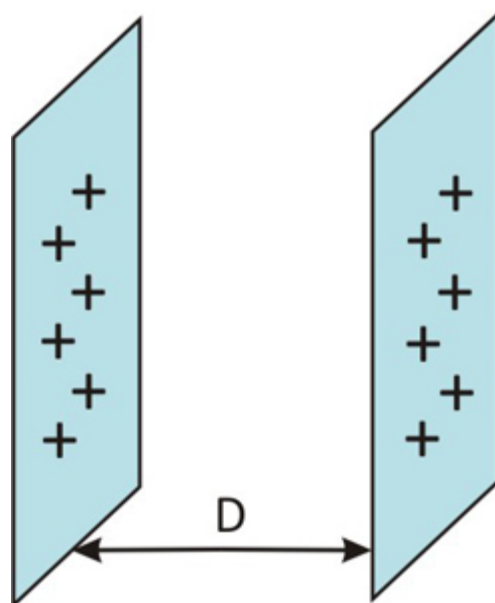


Fig. 10.1: Two identical flat plates in an electrolytic medium

For now, we consider that the surfaces have an excess charge and a surface energy of  $G^{\text{TOTAL}}$  per unit area.

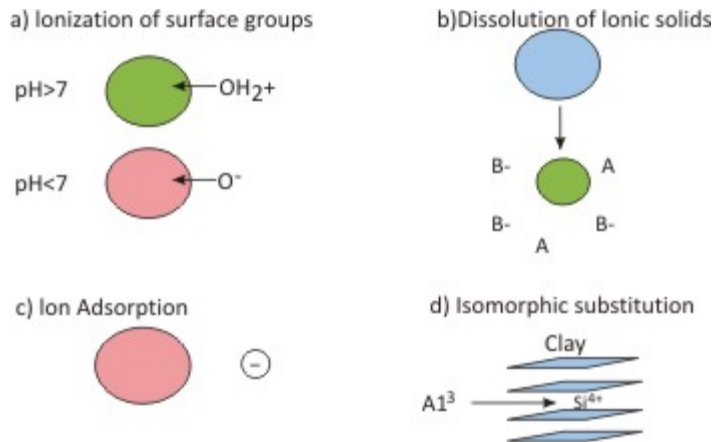


Fig. 10.2: Methods of charging of a surface immersed in an electrolyte [4]

The total energy of interaction per unit area between the two plates is given by:

$$G^{TOTAL} = G^{LW} + G^{EL} + G^{AB} + \dots$$

In the original theory provided by Deryaguin et al, the acid-base interactions are not considered while writing the expression for  $G^{TOTAL}$ . In fact, they were not even known at that time to have been affected the interactions between two particles. So, continuing with that we will, in our current discussion, neglect Acid-Base term.

$$G^{TOTAL} = G^{LW} + G^{EL}$$

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We have already derived a few models for evaluating  $G^{EL}$  (Energy per unit surface area) using some approximations in the previous chapters. Let us consider the Gouy-Chapman model for a symmetric electrolyte. So, the expression for  $G^{EL}$  now becomes,

$$G^{EL} = \frac{64n_0 kT \gamma_0^2 \exp(-\kappa D)}{\kappa}$$

where,

$$\gamma_0 = \tanh\left(\frac{Ze\psi_0}{4kT}\right)$$

$$\frac{1}{\kappa} = \left(\frac{\epsilon kT}{2e^2 Z^2 n_0}\right)^{\frac{1}{2}} = \text{Debye Length}$$

If the two surfaces have unequal potentials,  $\psi_1$  and  $\psi_2$  (viz  $\gamma_1$  and  $\gamma_2$ ), the expression for  $G^{EL}$  becomes:

$$G^{EL} = \frac{64n_0 kT \gamma_1 \gamma_2 \exp(-\kappa D)}{\kappa}$$

It is important to note that the Electrostatic repulsion ( $G^{EL}$ ) decreases, and  $\kappa^{-1}$  increases as the solute concentration increases ( $n_0$ ). As we'll see later this decrease in repulsion favors coagulation of colloidal particles.

For the Van-der Waals attraction term (for flat plates) we know that,

$$G^{LW} = -\frac{A_{121}}{12\pi d^2}$$

where  $A_{121}$  is the Hamaker constant for the system.

Therefore, the total energy could be written as:

$$G^{TOTAL} = -\frac{A_{121}}{12\pi d^2} + \frac{64n_0 kT \gamma_0^2 \exp(-\kappa D)}{\kappa} \quad (10.1)$$

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These two terms in the total free-energy have quite different dependence on separation,  $D$ , which varies with different electrolyte concentrations. The Van-der waal Attraction term has inverse-square dependence whereas the Electrostatic Repulsion term has exponential decay.

A typical variation of energy with separation is depicted in the figure below-

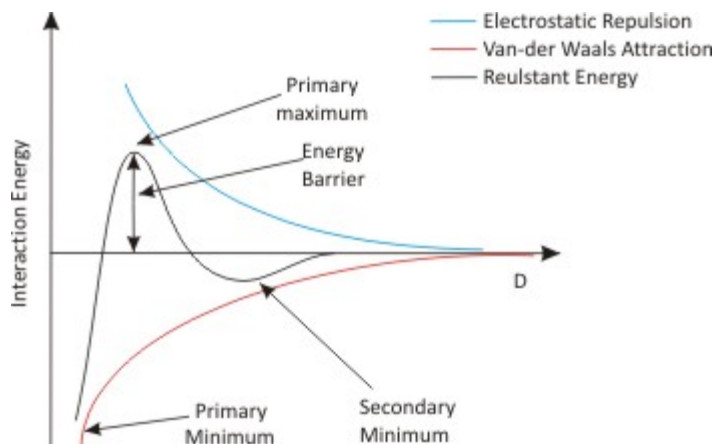


Fig. 10.3: Typical Energy barrier for two charged plates in an electrolytic medium

1. The *primary minimum* indicates that the aggregated state is of the lowest-energy condition and this is where we would expect the particles to reside .
2. The *primary maximum* acts as an activation barrier that must be exceeded for aggregation to occur. As two particles come closer, they must collide with sufficient energy to overcome the barrier provided by primary maximum.
3. The *secondary minimum* could be seen as a flocculated state but the particles still have to cross the energy barrier to come into close contact at the minimum energy state.

To pose a suitable barrier to aggregation, the primary maximum must be at least  $10k_B T$  in order to achieve a stability which can be relied upon over an extended period of time.

Effect of Concentration

We saw above that these interaction energies also depend upon the salt concentrations. At low salt concentrations ( $n_0$ ), the Electrostatic Repulsion term dominates and the overall interaction energy is positive. For high salt concentrations, the repulsive interactions have short-range effect and here Van-der Waals attractive term becomes dominant, leading to an overall Attractive Interaction.

Let us look the effect of concentration on energy as we increase the electrolyte concentration. In the above figure, the concentration increases from curve 1 to 5.

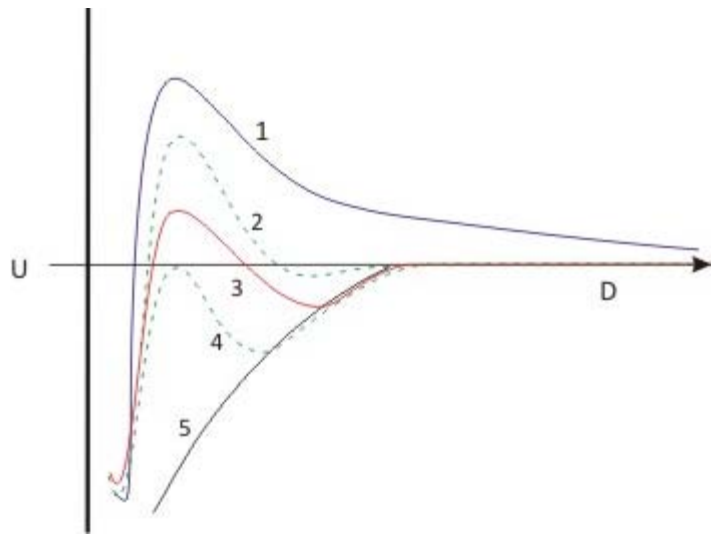


Fig. 10.4: Variation of Energy with solute concentration. point P represents CCC

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Graph 1: This is the curve for pure water or very low electrolyte concentration. The Repulsion term dominates and the overall interaction energy becomes positive. The energy barrier is very high and hence, the colloid remains stable.

Graph 2: The secondary minimum starts appearing but the Energy barrier is still very high, so the colloid is kinetically stable. i.e. there may be a little flocculation but true coagulation is difficult.

Graph 3: The Energy barrier is lowered further and the coagulation may increase. If the barrier is sufficiently low, than the particles may even be able to cross it due to their Thermal energy.

Graph 4: Energy barrier has become zero, and fast coagulation is possible. The concentration at this point is called 'Critical Coagulation Concentration (CCC)' at which coagulation can occur spontaneously. Hence, the colloid becomes unstable

Graph 5: As the concentration of ions has become very large, there is a large attractive Van-der Waals force, due to which there is no barrier and very fast coagulation takes place.

We should remember that LW component cannot be altered by changing any parameter as Hamaker constant is fixes for a given set of interacting bodies.

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