

Lecture 13

Stabilization of Charged Particles in Electrolyte Solutions

In this lecture, we will see another example in surface science that involves the electrical double layer: the stabilization of charged particles in electrolyte solutions. For example, proteins can be regarded as charged particles in aqueous solution due to the amine and carboxylic acid groups. Since aggregation of proteins always reduces the surface area, the proteins are **thermodynamically** unstable and tend to aggregate. However depending on the environment the proteins can be either **kinetically** stable (negligible aggregation over a long time span) or kinetically unstable (aggregates within a short time). The difference between kinetically stable and unstable colloidal systems can be seen in Figure 13.1. From daily life, we know that adding salts into the protein solution promotes aggregation. In this lecture, we will see the fundamental principle behind such phenomena and how the kinetic stability of charged particles is influenced.

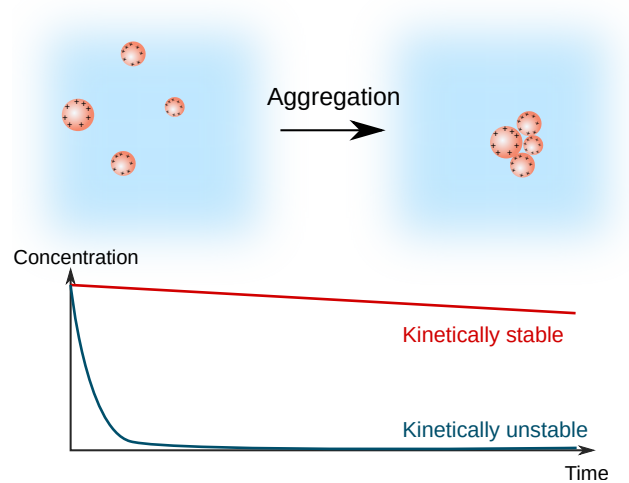


Figure 13.1: Kinetic stability of colloidal systems. Although thermodynamically all colloidal systems tend to aggregate, depending the time of aggregation, they can be categorized into kinetically stable or unstable systems.

13.1 The electrostatic repulsion

Consider two charged particles with same sign of charges in solution. There are two types interactions that counteract each other:

- Attractive force: van der Waals interactions
- Repulsive force: electrostatic repulsion between particles

Let's first deal with the electrostatic interactions. As we know the high ϵ_r of water greatly screens the electrostatic force between two charges. Therefore the repulsive force is prominent only if the distance between the particles h are very close to the Debye length λ_D . When two particles are close to each other, the EDLs overlap, causing changes to both the electrical potential ψ and ionic concentrations c_i between the junction. There are two forces involved in this system:

- Electrostatic interaction: caused by the change of ψ
- Osmotic force: caused by the change of c_i

Let's consider the situation of a $z:z$ electrolyte solution. If the particles are much larger compared with the distance of their junction, they can be regarded as two charged walls and the system is essentially 1D 13.2.

The osmotic force F_{osmotic} is created by the imbalance between the osmotic pressure inside the junction of the particles P_{inner} and the bulk solution P_{outer} . In an ideal solution, the osmotic pressure P_{osmotic} is related to the local concentration as:

$$P_{\text{osmotic}}(x) = kT(c_+(x) + c_-(x)) \quad (13.1)$$

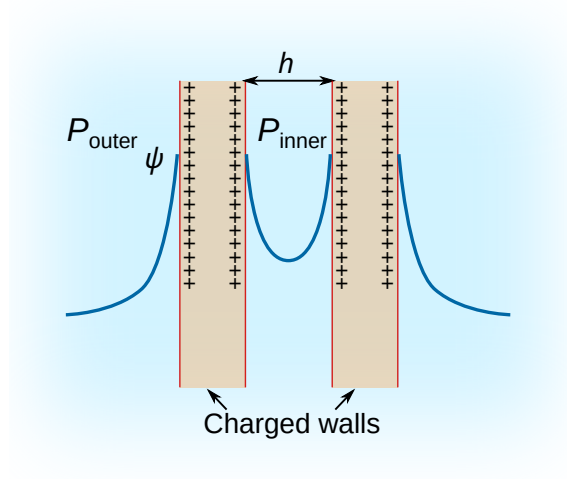


Figure 13.2: Approximation of colloidal particles as charged walls. The change of electrolyte concentration causes the osmotic pressure P_{inner} and P_{outer} , to be different.

Consider a infinitely small domain at position x with volume dV and area $A = dV/dx$, the differential osmotic force dF_{osmotic} is then:

$$dF_{\text{osmotic}} = dP_{\text{osmotic}} \frac{dV}{dx} = \frac{dP_{\text{osmotic}}}{dx} dV \quad (13.2)$$

On the other hand, the differential electrostatic force dF_{elec} is:

$$dF_{\text{elec}} = -(\rho dV) \frac{d\psi}{dx} = \varepsilon_0 \varepsilon_r \frac{d^2\psi}{dx^2} \frac{d\psi}{dx} dV \quad (13.3)$$

which uses the 1D Poisson equation $d^2\psi/dx^2 = -\rho/\varepsilon_0\varepsilon_r$ to derive the right hand side. At equilibrium, the osmotic force and electrostatic forces balance each other at every x position. Therefore we have:

$$\begin{aligned} \frac{dP_{\text{osmotic}}}{dx} &= \varepsilon_0 \varepsilon_r \frac{d^2\psi}{dx^2} \frac{d\psi}{dx} \\ &= \frac{\varepsilon_0 \varepsilon_r}{2} \frac{d}{dx} \left[\left(\frac{d\psi}{dx} \right)^2 \right] \end{aligned} \quad (13.4)$$

The solution is

$$P_{\text{tot}} = P_{\text{osmotic}} - \frac{\varepsilon_0 \varepsilon_r}{2} \left(\frac{d\psi}{dx} \right)^2 = \text{Const} \quad (13.5)$$

We can then calculate the total pressure in both the inner (junction) and outer (bulk) regions. Since in the inner region, $d\psi/dx = 0$ when $x = h/2$, P_{tot} becomes identical with $P_{\text{osmotic}}(x = h/2)$:

$$\begin{aligned} P_{\text{tot}}^{\text{in}} &= k_B T (c_+(x = \frac{h}{2}) + c_-(x = \frac{h}{2})) \\ &= 2k_B T c_0 \cosh \left[\frac{ze\psi_{h/2}}{k_B T} \right] \end{aligned} \quad (13.6)$$

On the other hand, in the outer region, $d\psi/dx = 0$ when $x \rightarrow \infty$, therefore:

$$P_{\text{tot}}^{\text{out}} = 2k_{\text{B}}Tc_0 \quad (13.7)$$

Combine Equations 13.6 and 13.7, we get the pressure difference between the inner and outer regions:

$$\Delta P_{\text{tot}} = \frac{F_{\text{R}}}{A} = 2kTc_0 \left[\cosh\left(\frac{ze\psi_{h/2}}{k_{\text{B}}T}\right) - 1 \right] \quad (13.8)$$

where F_{R} is the repulsive force (towards the outer region). The only unknown parameter here is the potential at the center of the inner region $\psi_{h/2}$. Depending on the system, the solution of $\psi_{h/2}$ can be different:

- Constant surface potential ψ_0

In this case the kinetics of the ion migration is very slow and surface potential ψ_0 on the walls remains unchanged compared with the bulk system.

- Constant surface charge σ_0

In this case the ions migrates fast enough that the surface potential ψ_0 can becomes different compared with the bulk system.

- Charge regulated system

The hydrolyzing and dissociation of the surface groups (e.g. NH_4^+ and COO^-) is influenced by local pH values and other interactions.

Here we only consider the constant surface potential situation. When the overlap between EDL is not great, we can assume that the potential between the walls is the superposition between potential of individual walls (ψ_{single}), therefore we have $\psi_{h/2} = 2\psi_{\text{single}}(x = h/2)$. Since $\psi_{h/2}$ is usually very small when the potential superposition assumption is valid, we can perform a Taylor expansion to Equation 13.8 to the first order:

$$\begin{aligned} \frac{F_{\text{R}}}{A} &\approx 2kTc_0 \left[1 + \frac{\left(\frac{ze\psi_{h/2}}{k_{\text{B}}T}\right)^2}{2} - 1 \right] \\ &\approx kTc_0 \left(\frac{2ze\psi_{\text{single}}(x = h/2)}{k_{\text{B}}T} \right)^2 \end{aligned} \quad (13.9)$$

From Equation 11.10 we know the solution of ψ_{single} from the GC method:

$$\begin{aligned} \tanh\left(\frac{ze\psi_{\text{single}}}{4k_{\text{B}}T}\right) &= \tanh\left(\frac{ze\psi_0}{4k_{\text{B}}T}\right) \exp(-\kappa x) \\ \psi_{\text{single}} &= \frac{4k_{\text{B}}T}{ze} \Lambda_0 \exp(-\kappa x) \end{aligned} \quad (13.10)$$

The last equation uses the zero-order Taylor expansion of \tanh on the left side and $\Lambda_0 = \tanh(\frac{ze\psi_0}{4k_B T})$. Insert Equation 13.10 into Equation 13.8 we finally get the solution of F_R :

$$\frac{F_R}{A} = 64kTc_0\Lambda_0^2 e^{-\kappa h} \quad (13.11)$$

Due to the domination of the exponential term, increasing c_0 decreases κ^{-1} and reduces F_R . In other words, by adding salts, the repulsive force is attenuated between the charged particles, which corresponds to the phenomenon called “salting” discussed in the beginning of this lecture.

The repulsive potential energy Φ_R per unit area between two charged particles at distance h is then calculated as:

$$\begin{aligned} \Phi_R(h) &= - \int_{\infty}^h \frac{F_R}{A} dh' \\ &= 64kTc_0\kappa^{-1}\Lambda_0^2 e^{-\kappa h} \end{aligned} \quad (13.12)$$

Note that such result is derived with two planar walls. For two spheres with same radii R , the Derjaguin approximation¹ shows that the repulsive potential Φ_R^{ss} (not normalized by area) between spheres with spacing of D should be corrected from the repulsive potentials of planar bodies in Equation 13.12:

$$\Phi_R^{ss}(D) = 64\pi kTc_0 R \kappa^{-2} \Lambda_0^2 e^{-\kappa D} \quad (13.13)$$

Such approximation is valid when:

- $R \gg D$, i.e. near the junction the surfaces from two particles are still considered as planar.
- $D \gg \kappa^{-1}$, i.e. small overlap between EDLs.

13.2 The vdW attraction

Finally we will add the vdW attraction term for the charged particles. From Lecture 1, the interaction potential between two planar bodies spaced at h is:

$$\Phi_A(h) = -\frac{A}{12\pi h^2} \quad (13.14)$$

where A is the Hamaker constant. Using the Derjaguin approximation again for two equal size particles with radii R and spaced at D , we get:

$$\Phi_A^{ss} = -\frac{AR}{12D} \quad (13.15)$$

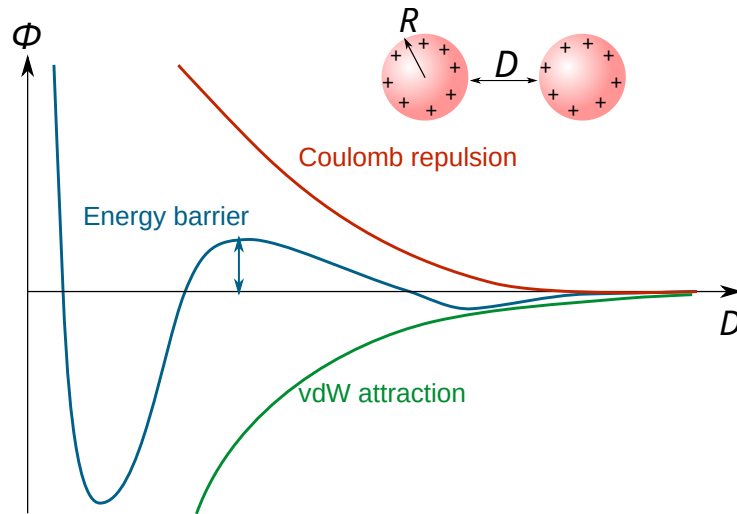


Figure 13.3: Interaction potential of two charges particles with radius R and spacing D from the DLVO theory. A energy barrier is observed, which makes colloidal systems kinetically stable.

We should note that both Φ_R^{ss} and Φ_A^{ss} are the *body* interaction energies between the particles and not normalized over the area. Therefore we expect the interaction potential to be higher for larger R . The total interaction potential $\Phi_{tot}^{ss} = \Phi_A^{ss} + \Phi_R^{ss}$ is then written as:

$$\Phi_{tot}^{ss} = 64\pi k T c_0 R \kappa^{-2} \Lambda_0^2 e^{-\kappa D} - \frac{AR}{12D} \quad (13.16)$$

The typical shape of Φ_{tot}^{ss} as a function of D is shown in Figure 13.3. When $d\Phi_{tot}^{ss}/dD = 0$ and $\Phi_{tot}^{ss} > 0$, a potential barrier is created which prevents the particles from aggregation. When the potential barrier height $\Phi_{barrier}$ is much larger than $k_B T$, the two particles are kinetically stable. Equation 13.16 is the main conclusion of the famous DLVO theory of colloidal aggregation [1].

References

- (1) Israelachvili, J. N., *Intermolecular and surface forces*, Third edition; Elsevier, Academic Press: Amsterdam, 2011.

