

Module 7: "Electrostatic Interaction"

Lecture 33: ""

The Lecture Contains:

- Electric Interaction in Colloidal Particles
- Electrostatic Interaction (Double Layer)

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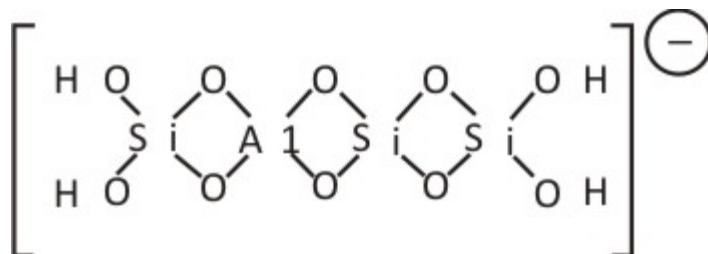
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Electric Interaction in Colloidal Particles

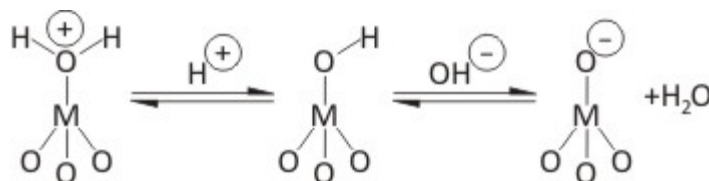
Most bodies attain a surface electric charge when they come in contact with a polar (e.g. aqueous) medium. Mechanisms by which charge is acquired in colloidal particles are:

1. For ionic crystals due to the presence of lattice defects or imperfection.



Example : Lattice substitution in Kaolin

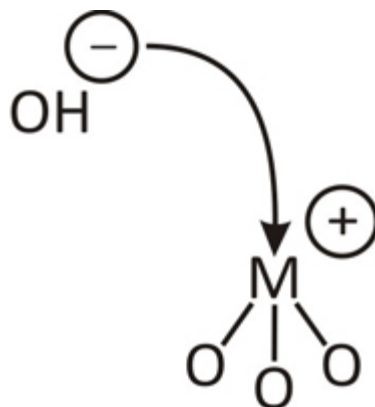
2. Ion adsorption in colloid solution.



3. Some ionic crystals have a slight imbalance in number of lattice cations or anions on surface,
eg. AgI, BaSO₄, CaF₂, NaCl, KCl

4. **Differential solubility of ions** : e.g. silver iodide crystals are sparingly soluble in water and silver ions dissolve preferentially to leave a negatively charged surface.

5. Dissociation of surface sites



- Protein groups have both dissociable groups
- By changing the pH we can regulate charge on surface

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Metals ions like Ba^{2+} , Al^{3+} , Si^{4+} , Zr^{4+} etc combine with oxygen to form metal oxide on top of surfaces. These oxides acquire either positive or negative charge depending on the pH of the solution. In the acidic solution colloid particles acquire positive charge represented by chemical reaction as:



Here OH_2 is bound water on the surface. When the solution is basic, surface of particles acquire negative charge as:



Acquiring charge by adsorption on particles can be represented by :



Surface gets positively charge by combining with A^{n+} . Dissociation of surface in ions can happen as :



Hydrogen ions are released in the solution so surface acquires negative charge in this case. Let K be the equilibrium constant of this reaction.

$$K = \frac{[\text{A}^-][\text{H}^+]_s}{[\text{AH}]}$$

$$N_0 = [\text{A}^-] + [\text{AH}]$$

$$k = \frac{[\text{A}^-][\text{H}^+]_s}{N_0 - [\text{A}^-]}$$

Surface charge depends on the pH of the solution. In acidic medium H^+ concentration is large so charge acquired by surface is less. Example of strong acid and base can be

Acids	Base
Sulfate $-\text{OSO}_2.\text{OH}$	Quaternary Ammonium N^+R^3
Sulphonate $-\text{SO}_2.\text{OH}$	Amine $-\text{NH}_2$
Sulphite $-\text{OSOOH}$	
Carbonyl $-\text{COOH}$	

Electrostatic Interaction (Double Layer)

If we put a charged particle in a suspension with ions, then the primary charge will attract counter ions (opposite charged ions) by electrostatic attraction. The primary charge cannot attract an equal amount of counter charge because a gradient of counterions is established that drives the counterions away from the surface.

Consider a plate having an electric potential ψ_0 in a neutral electrolyte solution. Due to the presence of the plate an electric potential will develop in the solution as a function of distance of distance from the plate.

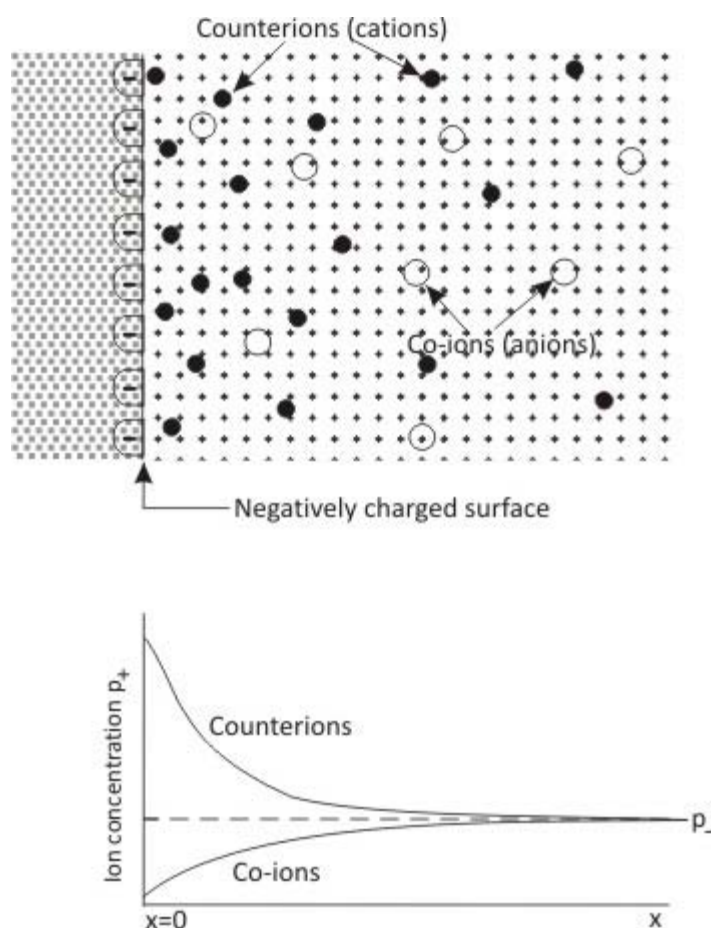


Fig. 9.1: Distribution of ions in presence of charged surface

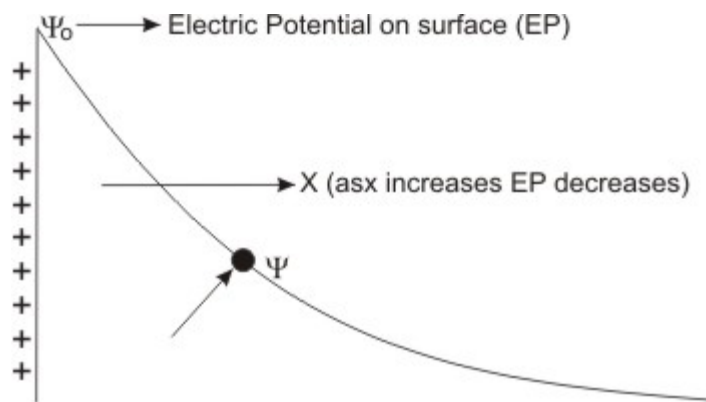


Fig. 9.2: Formation of double layer due to charged surface.

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Since the solution is electrically neutral,

$$\sum_i z_i n_{i0} = 0$$

where n_{i0} is the bulk concentration of ion or the number of ion per unit volume and z_i is its valence.

As a sign convention for valence (z), we use negative sign for counter ion valence and positive sign for co-ion valence. The counter-ions refer to the ions having a charge opposite to that of the plate where as the co-ions possess a charge similar to that of the plate.

Potential energy (u) of an ion in the solution is given by

$$\Phi = ze|\Psi| \quad (9.1)$$

where ψ is the electric potential at the ion location and e is the charge on an electron. The variation of potential with distance from the charged surface is given by Poisson equation,

$$\nabla^2 \Psi = \frac{-\rho}{\epsilon} \quad (9.2)$$

where ρ is the charge density of the system and ϵ is the absolute permeability of the electrolyte ,

$\epsilon = \epsilon_0 \epsilon_r$ where ϵ_r is the dielectric constant of the electrolyte,

In SI units $\frac{1}{4\pi\epsilon_0} = 8.99 * 10^9 \text{ J.m.C}^{-2}$

$\epsilon_r \sim 80$ for water at 20°C

Charge density at any location in the electrolyte is given by

$$\rho = \sum_i z_i e n_i(x) \quad (9.3)$$

where n_i is the number of ion per unit volume which is a function of x . So, we see that charge density is a function of x . To solve the Poisson equation we have to calculate charge density in terms of electric potential. For this we have to calculate n_i first.

Flux at any point in the electrolyte is defined as number of ion crossing per unit area per unit time at that point. Flux will depend on the concentration gradient of the ions in the electrolyte and electric force on the ions due to electric field due to the plate. Thus,

$$\text{Flux} = j = -D \frac{dn}{dx} + nv \quad (9.4)$$

where v is the velocity of the ions and D is the diffusion coefficient of the electrolyte. First term in the expression of J is due to concentration gradient called conductive flux and the last term is due electrostatic force called convective flux.

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Force/friction factor = v

$$\text{Force on an ion is} = -\frac{d\phi}{dx}$$

$$v = \frac{\text{force}}{f} = -\frac{1}{f} \frac{d(\Psi ze)}{dx} \quad (9.5)$$

Substituting ' v ' from equation (9.5) in equation (9.4), we get,

$$J = -\left[D \frac{dn}{dx} + \frac{n}{f} \frac{d\phi}{dx}\right]$$

At steady state, there will be no net flux i.e., conductive term will be equal to convective term. Thus,

$$J = -\left[D \frac{dn}{dx} + \frac{n}{f} \frac{d\phi}{dx}\right] = 0 \quad (9.6)$$

General expression of diffusion coefficient D is given by,

$$D = \lim_{t \rightarrow \infty} \frac{\langle \Delta r^2 \rangle}{t}$$

where $\langle \Delta r^2 \rangle$ is the mean square average displacement of an ion.

$$D = \frac{\sqrt{\langle \Delta r^2 \rangle} \sqrt{\langle \Delta r^2 \rangle}}{t}$$

$$D = \frac{v \sqrt{\langle \Delta r^2 \rangle}}{f}$$

$$D = \frac{v \sqrt{\langle \Delta r^2 \rangle}}{f}$$

Order of numerator of right hand side in above equation for colloidal particles is around kT . Thus,

$$D \approx \frac{kT}{f} \quad (9.7)$$

where ' kT ' is the energy for thermal diffusion. This equation is known as Einstein's relation for Brownian particle. We can assume validity of Stoke's law (since dimension of ion is very small) to find friction factor (f). Substituting f from equation (9.7) in equation (9.6), we get

$$-\left(D \frac{dn}{dx} + \frac{nD}{kT} \frac{d\phi}{dx}\right) = 0$$

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We see that D cancels out and has no role to play at steady state. This can be physically attributed to the fact that mobility for both forces is same.

$$\Rightarrow \frac{dn}{dx} + \frac{nD}{kT} \frac{d\Phi}{dx} = 0$$

$$\Rightarrow n = ce^{-\frac{\Phi}{kT}} \quad (9.8)$$

where c is the constant of integration which can be calculated by applying the boundary condition. When potential energy is zero the number of moles per unit volume will be equal to n_0 which is equal to concentration far from the surface. This can be used as the boundary condition.

Thus,

when $F = 0$; $n = n_0$. So,

$$c = n_0$$

$$\Rightarrow n = n_0 e^{-\frac{\Phi}{kT}}$$

$$\Rightarrow n_i = n_0 e^{-\frac{\Phi}{kT}} \quad (9.9)$$

Potential energy of an ion in terms of electric potential is given by

$$\Phi = ze|\Psi|$$

As discussed earlier F is negative for the counter ions and is positive for the co-ions.

Finally, we get:

$$\Rightarrow n_i = n_0 e^{-\frac{ze|\Psi|}{kT}}$$

Using this relation along with equation (9.3), we get the charge density as a function of ψ .

$$\rho = \sum_i z_i e n_{i0} \exp\left(-\frac{ze|\Psi|}{kT}\right) \quad (9.10)$$

Substituting charge density from equation (9.10) in Poisson equation (equation 9.2) we get,


$$\frac{d^2\Psi}{dx^2} = -\frac{e}{\epsilon} \sum_i z_i e n_{i0} \exp\left(-\frac{ze|\Psi|}{kT}\right) \quad (9.11)$$

which is known as Poisson-Boltzmann equation. On solving this equation we can get ψ as a function of x . However this equation does not have any general solution. Thus certain limitations or approximations have to be made in order to solve equation (9.11).

Poisson-Boltzmann equation is applicable as the basis for analysis of electrolyte solutions, electrochemical processes, membrane transport, conduction in nerve cells, transistor behavior and interaction in colloidal particles.

Stability of colloidal particles against coagulation can be determined with the help of double layer.

For instance, when two parallel plane double layer systems are brought close to each other, electrostatic repulsion is observed which can be correlated with coagulation of system.

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