

Module 7: "Surface Thermodynamics"

Lecture 34: ""

The Lecture Contains:

- ☰ Gouy Chapman Theory
- ☰ Debye Huckel Approximation

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Gouy Chapman Theory

Gouy Chapman solved Poisson-Boltzmann equation for symmetric electrolyte. By symmetric electrolyte we mean an electrolyte in which valence of counter and co ion is same e.g. NaCl. For this case, the order of equation (9.11) can be reduced by multiplying its both sides by ' $2(d\psi/dx)$ '. Thus we get,

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

$$\Rightarrow \frac{d}{dx} \left(\frac{d\psi}{dx} \right)^2 = \frac{d}{dx} \left[\frac{2kT}{\epsilon} \right] \sum_i z_i n_{i0} \exp\left(-\frac{Ze|\psi|}{kT}\right)$$

Integrating the above equation and applying the boundary condition: $d\psi/dx \rightarrow 0$ and $\psi \rightarrow 0$, as $x \rightarrow \infty$, we get

$$\left(\frac{d\psi}{dx} \right)^2 = \left[\frac{2kT}{\epsilon} \sum_i z_i n_{i0} \exp\left(-\frac{Ze|\psi|}{kT}\right) \right] \quad (9.12)$$

Applying the condition of symmetric electrolyte to equation (9.12),

$$\left(\frac{d\psi}{dx} \right)^2 = \left[\frac{2kTn_0}{\epsilon} \left\{ \exp\left(-\frac{Ze|\psi|}{kT}\right) + \exp\left(\frac{Ze|\psi|}{kT}\right) - 2 \right\} \right]$$

where n_0 is bulk concentration and z is the absolute value of valence (no signs involved). The above equation can be simplified as

$$\left(\frac{d\psi}{dx} \right)^2 = \left[\frac{2kTn_0}{\epsilon} \left\{ \exp\left(-\frac{Ze|\psi|}{kT}\right) + \exp\left(\frac{Ze|\psi|}{kT}\right) \right\} \right]^2$$

If we take $y = \frac{ze\psi}{kT}$, the above differential equation can be written as

$$\left(\frac{dy}{dx} \right) = \frac{2n_0 e^2 z^2}{\epsilon kT} \left\{ \exp\left(-\frac{y}{2}\right) + \exp\left(\frac{y}{2}\right) \right\}$$

Thus we can write the solution as

$$\ln \left[\frac{\left(e^{\frac{y}{2}} + 1 \right)}{\left(e^{\frac{y}{2}} - 1 \right)} \right] = kx + c$$

where $k^2 = \frac{2e^2 z^2 n_0}{\epsilon kT}$ and c is the constant of integration. Applying the boundary condition $\psi = \psi_0$ at

$x=0$ and substituting the value for y we get,

$$\frac{\left[\left(\frac{ze\Psi}{e^{2kT}} - 1 \right) \right]}{\left[\left(\frac{ze\Psi}{e^{2kT}} + 1 \right) \right]} = \frac{\left[\left(\frac{ze\Psi}{e^{2kT}} - 1 \right) \right]}{\left[\left(\frac{ze\Psi}{e^{2kT}} + 1 \right) \right]} e^{-kx} \quad (9.13)$$

For simplicity we can write above as

$$\gamma(\Psi) = \gamma_0(\Psi_0) \exp(-kx)$$

where $\gamma = \frac{\left[\left(\frac{ze\Psi}{e^{2kT}} - 1 \right) \right]}{\left[\left(\frac{ze\Psi}{e^{2kT}} + 1 \right) \right]}$

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Note that κ^{-1} has the dimension of length and is called Debye length. It is the length scale corresponding to electrostatic interaction. Larger the value of κ^{-1} , lesser is the rate of potential drop with respect to x .

Value of κ^{-1} depends on concentration of ion, valence and temperature. Larger the concentration or valence of the ions, lower is κ^{-1} . At higher temperature, diffusion increases and κ^{-1} also increases so that electrostatic forces become significant for larger distance.

Equation (9.13) can be simplified when x is large or ψ is small. When Ψ is less than 10mV, exponential terms can be expanded. Neglecting the higher order terms equation (9.13) becomes

$$\frac{ze\Psi}{2kT} = \gamma_0 \exp(-\kappa x)$$

$$\Psi = \frac{4kT}{ze} \gamma_0 \exp(-\kappa x)$$

- When ψ_0 is small, the above equation can be further simplified to

$$\Psi = \Psi_0 \exp(-\kappa x)$$

- ψ is directly proportional to ψ_0 for smaller values of ψ_0 .

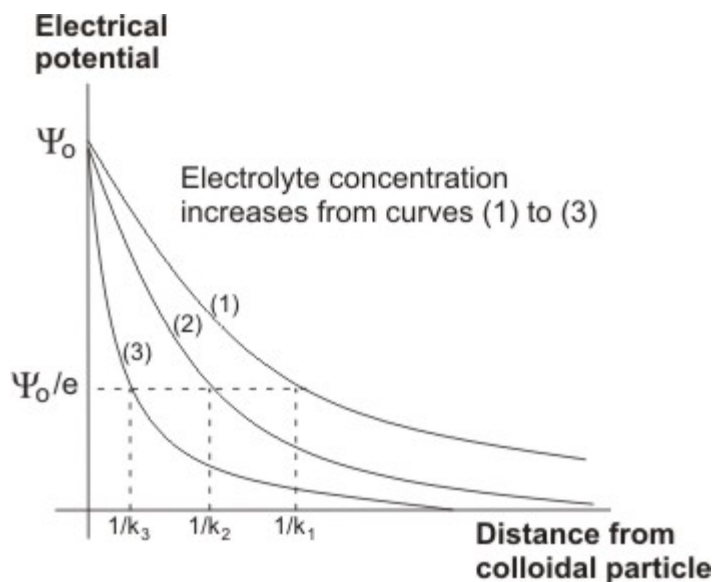


Fig. 9.3: Effect of electrolyte concentration on electrical potential

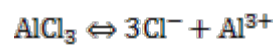
As the concentration of ions increases, the double layer thickness decreases. For larger value of ψ_0 (ψ_0 greater than 100mV), ψ_0 tends to 1. In that case,

- ψ will be independent of ψ_0 .

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Case 3 : 3-1 solute like AlCl_3 for 0.01 M solution.



$$\sum_i z_i^2 m_i = 9m + 3m + 12m = 0.12$$

$$\kappa^{-1} = 12.4 \text{ \AA}$$

We observe that there is not much of a difference in case 2 case 3.

Case 4: 3-3 salt for 0.01 M solution. We see that for this case,

$$\kappa^{-1} = 10.1 \text{ \AA}$$

Salts	Debye length (κ^{-1})
NaCl (1:1)	30.4
CaCl_2 (2:1)	17.6
AlCl_3 (3:1)	12.4
AlPO_4 (3:3)	10.1

NOTE: At higher temperatures κ^{-1} decreases.

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Debye Huckel Approximation

As discussed above, Poisson Boltzmann equation does not have a general solution, so to solve it for an asymmetric electrolyte we can take an approximation of low potential. This approximation was made in Debye-Huckel's Theory to solve equation (9.11). Under this approximation we can write

$$\frac{z_i e \Psi}{kT} < 1$$

Thus we can expand the exponential terms in equation (9.10) and neglect higher order terms.

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

$$\rho = \sum_i z_i e n_{i0} \left(1 - \frac{z_i e \Psi}{kT}\right)$$

$$\rho = \sum_i z_i e n_{i0} \sum_i \left(\frac{z_i^2 n_{i0} e^2 \Psi}{kT}\right)$$

First term goes to zero because of electrical neutrality. So we get

$$\rho = \sum_i \left(\frac{z_i^2 n_{i0} e^2 \Psi}{kT}\right) \quad (9.15)$$

Now, we see how Poisson-Boltzmann equation changes with low potential approximation.

$$\frac{d^2 \Psi}{dx^2} = \frac{e^2 \Psi}{\epsilon kT} \sum_i z_i^2 n_{i0} = k^2 \Psi \quad (9.16)$$

$$\text{where, } k^2 = \frac{e^2}{\epsilon kT} \sum_i z_i^2 n_{i0}$$

To solve differential equation (9.16) we need two boundary conditions. These boundary conditions will be

- $\Psi \rightarrow \Psi_0$ as $x \rightarrow 0$
- $\Psi \rightarrow 0$ as $x \rightarrow \infty$.

On solving equation (9.16) with these boundary conditions, we get

$$\Psi = \Psi_0 e^{-kx}$$

$$\Psi = \Psi_0 \exp\left(\frac{-x}{\lambda_D}\right) \quad (9.17)$$

$$\text{where, } \kappa^{-2} = \frac{\epsilon kT}{e^2 \sum_i z_i^2 n_{i0}}$$

κ^{-1} is called the Debye length. Note that equation (9.17) is similar to that of equation (9.14). We can see that κ^{-1} decreases as z_i or n_{i0} increase, thus by adding more salt or higher valence salt, the effect of the surface decreases. This is because of screening effect due to ions accumulated near the surface.

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Note that inducing coagulation by introducing an electrolyte AlCl_3 (has higher valence) does a better job compared to NaCl (lower valence).

To see the effect of valence let us calculate value of κ for different electrolytes in .01M aqueous solution at 25 °C. Let n_i be the number of ions per unit volume and m_i is the molar concentration of electrolyte. Thus,

$$m_i = n_i / 1000 N_A \text{ (kgmol/m}^3\text{)}$$

where N_A is the Avogadro constant.

$$\kappa^2 = \frac{1000 e^2 N_A}{\epsilon k T} \sum_i z_i^2 m_i$$

Let's put some constant values and parameters in equation (9.18).

$$e = 1.6 \times 10^{-19} \text{C}$$

$$N_A = 6.023 \times 10^{23}$$

$$k = 1.38 \times 10^{-23} \text{J/K}$$

$$\epsilon_0 = 8.8510^{-12}$$

$$T = 298 \text{K}$$

Value of dielectric constant of water at 25°C is $\epsilon_r = 78.54$

$$\kappa = 2.32 \times 10^9 \left(\sum_i (z_i^2 m_i)^{\frac{1}{2}} \right) (\text{m}^{-1})$$

Now we would see 4 examples of how κ varies with changing electrolyte.

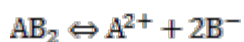
Case 1: 1-1 type solute like NaCl for 0.01 M solution.

$$\sum_i z_i^2 m_i = 2z^2 m = 2 \times 0.01$$

$$\kappa^{-1} = 30.4 \text{Å}$$

Charges are not felt after 100Å because of screening.

Case 2: 2-1 solute, for example CaCl_2 for 0.01 M solution.



$$\sum_i z_i^2 m_i = 4m + 2m + 6m = 0.06$$

$$\kappa^{-1} = 17.6 \text{Å}$$

