

Interfacial Engineering

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Lecture-34

Gouy-Chapman-Stern EDL model

A combination of parallel plate and diffuse double layer, Debye-Huckel parameter, and Debye screening length

Time : 1.11mins

The diffuse double layer: Gouy-Chapman model

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NPTEL

The distribution of ions is described by the Boltzmann distribution as follows.

$\nabla^2 \psi = k^2 \psi \rightarrow$ Linearized Poisson - Boltzmann

$$k^2 = \frac{\sum_i n_i z_i^2 e^2}{k_B T \epsilon_0 \epsilon_r}$$


Welcome back. So in this video lecture, in this video lecture, we will look at the Gouy Chapman Stern electrical double layer model. This model considers both the parallel plate as well as the diffuse boundary layer assumptions. Okay. And we can look at how we can continue to use this, you know, the Gouy-Chapman model by making a slight modification in the equation. Okay.

Apart from this, we will also look at how to determine the Debye screening length. Right. For a given electrolyte strength. Right.

And the temperature. So let's begin. Yeah. Yes, so before we move on to the electrical double layer model governed by Gouy, Chapman, and Stern, we can look at the linearized Poisson-Boltzmann equation, which you actually missed during the last lecture.

So the equation that we obtained in the form of ψ (psi) in our right,

$\nabla^2\psi = \kappa^2\psi$ is actually a linearized equation.

This is because κ (kappa) is obtained from the Boltzmann distribution function. The equation that we obtained using this approach is called the linearized Poisson-Boltzmann equation.

Time: 2.13mins

Gouy-Chapman-Stern double layer model

$\psi = \psi_0 e^{-kx}$

$\psi = \psi_0 e^{-k(x-x_h)}$

Two models for the double layer: (a) a diffuse double layer (Gouy-Chapman); and (b) combination of parallel plate and diffuse double layer (Gouy-Chapman-Stern)

In parallel plate, distribution of ions is assumed to follow rigid arrangement.

Hiemenz, P. C., & Rajagopalan, R. (2016). *Principles of Colloid and Surface Chemistry, revised and expanded*. CRC

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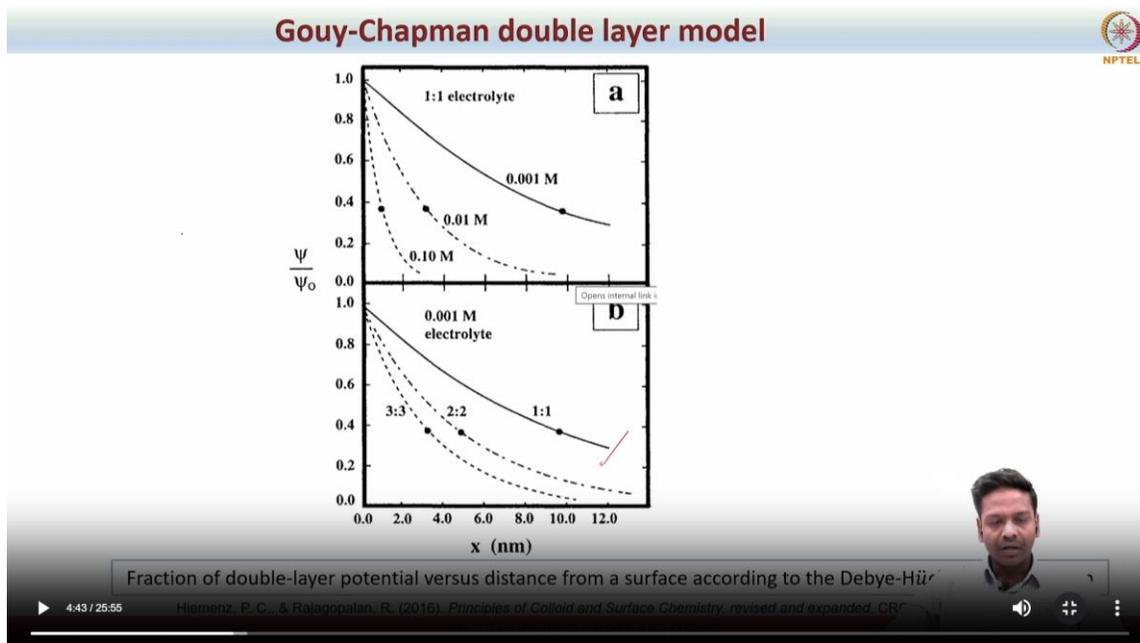
This is actually a very important one. We forgot to highlight this during our last lecture. Kindly make a note of it. We'll now move on to the next electrical double layer model. The Gouy-Chapman-Stern double layer model is given here. The Gouy-Chapman-Stern model considers both the parallel plate as well as the diffuse double layer.

So you have parallel plate as well as the diffuse double layer assumption given by Gouy Chapman. Because you are incorporating both the parallel plate as well as the diffuse double layer assumption, this particular model is called as Gouy-Chapman and Stern model right and in this you can see so the Guoy-Chapman considers only the diffuse counter ions right whereas the Stern considers this model which is combination of Guoy-Chapman and Stern considers that there is there exists both strongly bound counter ion okay right after

the charged surface and then followed by the diffuse layer okay so he uses the combination of this in assumption that is there is linear variation right after the charge the surface and then exponential variation after the you know, once the diffuse boundary layer starts to, you know, occur, right? So since it is a combination of parallel plate as well as the diffuse layer, we can call this a Gouy-Chapman Stern layer. In this case, the slight modification made to the equation is that you subtract the Stern layer thickness (x_h) from the distance x .

So the modified distance becomes: $x - x_h$.

Time : 4.43mins



In the Stern plane, there is a linear variation of the electrostatic potential ψ . Therefore, evaluating ψ based on this modification gives the Gouy-Chapman-Stern model.

This is the small change that must be incorporated into the model. Now, we consider the influence of the electrolyte.

To simplify, we define the normalized potential as: ψ / ψ_0 .

Here, ψ_0 is the maximum potential, so the normalized value will vary between 0 and 1. This gives us the fractional potential.

Refer to Figure A and Figure B. In Figure A, we show the case of a symmetrical electrolyte (e.g., 1:1 electrolyte), and how the potential varies as a function of electrolyte concentration. If we change the concentration of electrolyte keeping the type of electrolyte

the same right how the fraction of double layer potential varies that is what exactly shown in the figure here displayed by the figure a right so you can see that as the concentration of salt goes up the the variation right. The variation of the normalized potential ψ / ψ_0 as a function of distance also changes.

In the case of the highest salt concentration, the distance over which the fraction of the double layer potential varies is reduced.

This is due to the screening of electrostatic charges by the salt ions.

In Figure B, for different electrolyte types (e.g., 1:1, 2:2, 3:3), even when the electrolyte concentration is kept constant, the variation in the fraction of double layer potential across the surface can be observed.

This behavior can be explained using the Poisson-Boltzmann equation. In the equation, we have:

$n_{i\infty}$ → Bulk concentration of ion species i

z_i^2 → Square of the valence of ion species i

By tuning $n_{i\infty}$ (bulk concentration) while keeping z_i (valence) constant, one can observe the effect on the potential.

Conversely, by keeping $n_{i\infty}$ constant and varying z_i (as in changing the electrolyte type from 1:1 to 3:3), the effect of valence on the potential can also be demonstrated.

In this case, we actually tune the valence. That's why the potential, the fraction of double layer potential is also varying. Okay. Right. So now we can look at the physical significance of the Debye Huckel parameter.

Time : 8.43mins

Physical Significance of the Debye-Hückel Parameter K



$$K^2 = \left[\left(\frac{e^2}{\epsilon k_B T} \right) \sum_i z_i^2 n_{i\infty} \right]$$

$$n_{i\infty} = 1000 M_i N_A$$

$$K = \left[\left(\frac{e^2}{\epsilon k_B T} \right) \sum_i z_i^2 n_{i\infty} \right]^{1/2}$$



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As you can see, Debye-Hückel parameter, which is k^2 , is defined as:

$$k^2 = (e^2 / (\epsilon_0 \epsilon_r k_B T)) * \sum (z_i^2 * n_i^{\infty})$$

Here, the variable z_i is the valence, and n_i^{∞} is the bulk concentration.

It is often convenient to express n_i^{∞} using molarity, M_i . So we express concentration of salt as:

$$n_i^{\infty} = 1000 * N_A * M_i$$

where:

- M_i is the molarity (mol/L),
- N_A is Avogadro's number,
- 1000 converts liters to cubic meters for SI units.

Now, although we have the Debye-Hückel parameter k , it is also useful to consider the inverse:

$$1/k = \lambda_D$$

λ_D is called the Debye screening length.

This λ_D represents the characteristic length of the diffuse boundary layer. Let's say you have a negatively charged solid surface. There will be counter-ions (positively charged)

attracted to the surface, forming a compact layer. Beyond that, a diffuse layer forms. However, after a certain distance (λ_D), the potential becomes negligible and ions beyond this zone are unaffected by the surface charge.

Therefore, λ_D defines the domain beyond which:

- Counter-ions and co-ions are no longer influenced by the surface,
- No electrostatic interactions occur due to surface charge.

So that is the understanding. So it will be interesting to know what is the characteristic length of this diffuse layer that is indicated by what is known as K^{-1} , which is nothing but Debye screening length. So sometimes it is very important to know what is Debye screening length for a given problem. So that's why we need to do this exercise. You know, how to determine the K^{-1} , which is inverse of K .

So K^{-1} is actually expressed in terms of unit of length, which is meter. Okay. So this you should know. Right. Okay, so now what we can do is we can actually solve, understand one problem tutorial.

So we have a tutorial, we'll see the tutorial session now. Okay.

Time : 13.39mins

Tutorial



Calculate the Debye lengths in 10 mol/m³ aqueous solutions of NaCl, CaCl₂ and AlCl₃ at 298 K.

$$k^{-1} = \left[\frac{5.404 \times 10^{15}}{\sum_i z_i^2 M_i} \right]^{-\frac{1}{2}}$$

$(1)^2 \times 10 + (2)^2 \times 10 = 20$



16:36 / 25:55

And here the problem is to determine the Debye length okay okay so what is k inverse is what we have to calculate for a given concentration that is 10 moles per meter cube aqueous solutions okay so you make this aqueous solution 10 moles per meter cube based on these three solutions. One is NaCl, which is 1:1, and CaCl₂, which is 2:2, and AlCl₃, which is

3:3, right? So this is what we are going to look at. So remember, in this problem, excepting this part, so if I incorporate this n_i^{∞} over here, I will have M_i instead of n_i^{∞} , and $N_A \times 1000$ will be outside this summation, right? So all this will be a constant.

Okay, and excepting z_i and M_i , the rest of the terms will be constant. So what you can do, excepting this 1000 multiplier—we are not using the 1000 multiplier because the problem is given in mol/m³ itself—so you don't need to multiply with 1000. Okay, so what you have here is M_i in mol/m³. So rest of these constants can be grouped into one bracket and that is nothing but:

$$5.404 \times 10^{15}$$

So what you need to do is evaluate only this bracketed term given within the summation:

$$\Sigma(z_i^2 \times M_i)$$

Let's take an example now. This constant will remain as it is. Now for this case, how can we calculate it? So we know NaCl, you've got two species: Na⁺ and Cl⁻. The valence of Na⁺ is 1² and $M_i = 10 \text{ mol/m}^3$, so:

$$1^2 \times 10 = 10$$

$$\text{Cl}^-: 1^2 \times 10 = 10$$

So total:

$$\Sigma(z_i^2 \times M_i) = 10 + 10 = 20$$

Multiply with the constant:

$$5.404 \times 10^{15} \times 20$$

$$K^{-1} = 3 \times 10^{-9} \text{ m} = 3 \text{ nm}$$

Okay, right. So this is done. Now, what about the calcium chloride? So Ca²⁺: $2^2 \times 10 = 40$
Cl⁻ (2 ions): $2 \times (1^2 \times 10) = 20$

Total:

$$\Sigma(z_i^2 \times M_i) = 40 + 20 = 60$$

Multiply with constant:

$$5.404 \times 10^{15} \times 60$$

$$K^{-1} = 1.76 \times 10^{-9} \text{ m} = 1.76 \text{ nm}$$

Okay. What about aluminum chloride? So Al³⁺: $3^2 \times 10 = 90$

$$\text{Cl}^- (3 \text{ ions}): 3 \times (1^2 \times 10) = 30$$

Total:

$$\Sigma(z_i^2 \times M_i) = 90 + 30 = 120$$

Multiply with constant:

$$5.404 \times 10^{15} \times 120$$

$$K^{-1} = 1.24 \times 10^{-9} \text{ m} = 1.24 \text{ nm}$$

As you can see, as the electrolyte type is varied from 1:1 to 3:3, the screening length (K^{-1}) decreases. This is because the valence affects the ionic strength. Although the salt concentration is the same, valence impacts K^{-1} , hence it changes.

This is how you determine the Debye screening length K^{-1} for a given problem. There can be many more applications based on this information.

This problem is given for you to do this exercise yourself:

Determine K^{-1} for aqueous solutions of $MgSO_4$ at 298 K for:

$$M = 1 \text{ mol/m}^3$$

$$M = 10 \text{ mol/m}^3$$

Time : 21mins

Tutorial



Calculate the Debye lengths in 10 mol/m³ aqueous solutions of NaCl, CaCl₂ and AlCl₃ at 298 K.

$$k^{-1} = \left[5.404 \times 10^{15} \sum_i z_i^2 M_i \right]^{-\frac{1}{2}}$$

(Handwritten notes: (1)² × 10 + (1)² × 10 = 20



Okay. The next tutorial is to generate the potential profile.

We consider variation of potential ψ with distance x from the surface in a 1 mol/m³ NaCl solution at 298 K.

Given:

$$\psi_0 = 150 \text{ mV}$$

The potential decays as:

$$\psi(x) = \psi_0 * \exp(-k * x)$$

Where:

$$K^{-1} = 9.58 \text{ nm} \Rightarrow k = 0.104 \text{ nm}^{-1}$$

For x from 0 to 75 nm:

$$\text{At } x = 0: \psi = 150 \text{ mV}$$

As x increases, ψ decreases

Eventually:

$\psi \rightarrow 0$ as $x \rightarrow 75$ nm (approaches bulk)

Plotting x vs. ψ gives the surface potential decay profile.

This concludes the current explanation. We will continue from here in the next lecture.

Thank you.