Colloids and Surfaces

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Lecture - 42

Relation between Electrophoretic Mobility and Zeta Potential - 1

So, far we have looked at mobility of an isolated ion in an applied electric field. So, what we will do now is, we will extend this concept to understand what is the mobility of isolated colloidal particle in an electric field?

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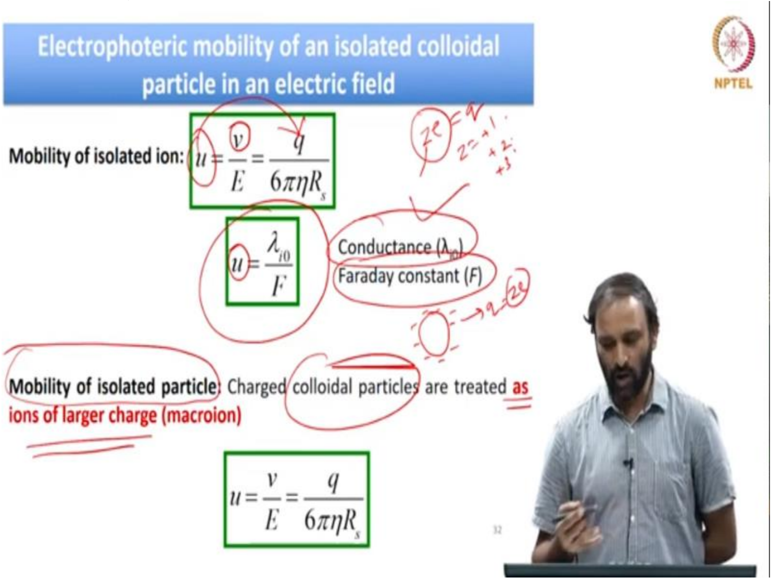

Electrophoteric mobility of an isolated colloidal particle in an electric field

Mobility of isolated ion: $u = \frac{v}{E} = \frac{q}{6\pi\eta R_s}$

$u = \frac{\lambda_{i0}}{F}$

Conductance (λ_{i0})
Faraday constant (F)

Mobility of isolated particle: Charged colloidal particles are treated as ions of larger charge (macroion)

$u = \frac{v}{E} = \frac{q}{6\pi\eta R_s}$

So, mobility of the isolated ion is given by u which is the velocity with which the ion is moving per unit field it depends on the charge of the isolated ion, eta is the viscosity of the fluid and R_S is the dimension of isolate ion that we are considering. If, we want to estimate q from this expression, that is the charge of the isolated ion which you can relate again to zeta potential of in the case of a charged colloidal particle.

What we should know is we should know what is the velocity, but however, because the ions are very, very small in dimension v cannot be measured. Therefore, what one does is you can actually measure the conductance which is the reciprocal of the resistance and if you know the conductance and from Faradays constant you can actually calculate what is u. Therefore, from the calculated value of u I can actually calculate what is the charge of the isolated ion? That is under consideration.

So, we can extend the same concept to essentially obtain the mobility of an isolated particle in an applied electric field. However by treating that the charged colloidal particles are what are called as larger ions or the macro ions. Instead of so, if you look at isolated ion so, you could have ions of different valency they could have z times e, where z is a valency of the ions multiplied by the charge of the electron is what gives the total charge of the isolated ion.

However, so, we know that z = + 1 or + 2 or + 3 depending upon whether we are considering a monovalent, divalent or trivalent ions. However, so if we can assume that when you have a charged particle that is, which has a large number of surface groups on the surface of the particle, so you can say that, we can still say that q is z times e however, we do not know what is z, because it depends on the total number of dissociable groups on the surface or the total number of adsorbed ions on the surface of the particle.

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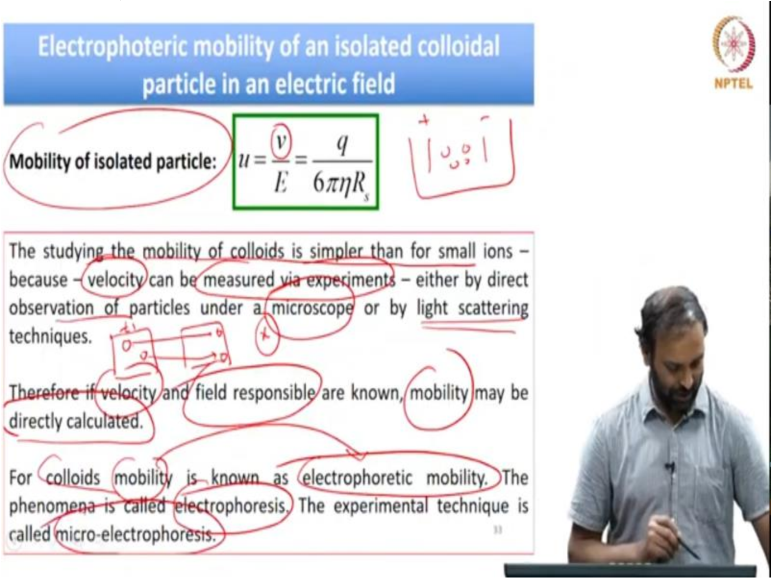

Electrophoteric mobility of an isolated colloidal particle in an electric field

Mobility of isolated particle: $u = \frac{v}{E} = \frac{q}{6\pi\eta R_s}$

The studying the mobility of colloids is simpler than for small ions – because – velocity can be measured via experiments – either by direct observation of particles under a microscope or by light scattering techniques.

Therefore if velocity and field responsible are known, mobility may be directly calculated.

For colloids mobility is known as electrophoretic mobility. The phenomena is called electrophoresis. The experimental technique is called micro-electrophoresis.

So, however, when one is dealing with the mobility of isolated particles, the studying mobility of colloids is much simpler than small ions, because the velocity with which the particles are moving in a given under the influence of a given external field can be experimentally measured by direct visualization. So, what I can do is you could have you know, two electrodes there could be particles in a fluid and I can look at video of the migration of particles.

Then, you could track these particles in different frames for example, if this is a time t_1, these are the position of the particle, I can say that this would have moved some further location under the influence of the field. So, therefore, I can calculate what is the displacement of the particle and if I know what is the displacement and the time that the particle has taken for the movement I can actually calculate velocity directly from simple experiments.

This can be either done by using microscope or one could use light scattering techniques to detect the position of the particle. So, therefore, once the velocity and the field that is responsible for the motion of the particles are known, one could actually calculate what is the mobility directly from experiments? Therefore, studying electrophoteric mobility of particles is much, much simpler than studying the mobility of ions because we have a chance of directly visualizing the motion of the particle in the presence of an electric field.

So, for colloidal particles the mobility is known as what is called electrophoteric mobility. And the phenomena, that is associated with this is what is called the electrophoresis. And one often combines a microscopy experiment with electrophoresis. Therefore the technique by which the mobility can be measured when an isolated colloidal particle moves in a field is what is called as a micro electrophoresis.

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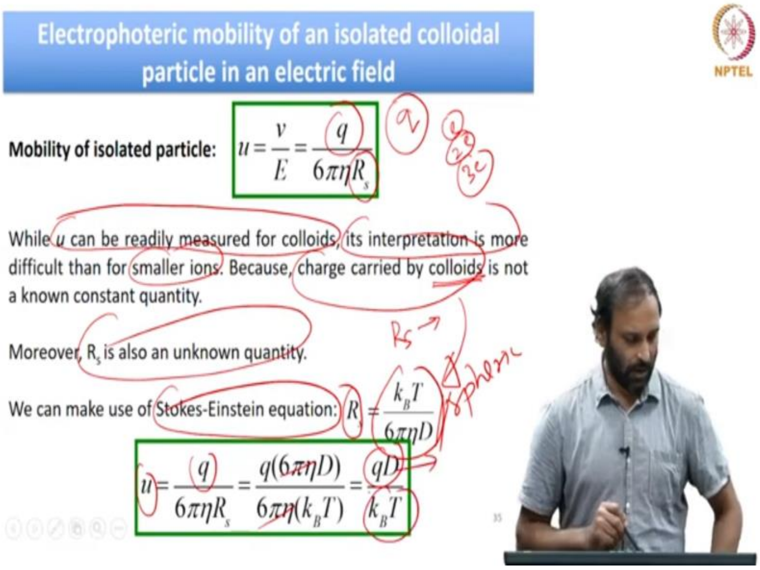

Electrophoteric mobility of an isolated colloidal particle in an electric field

Mobility of isolated particle: $\boxed{u = \frac{v}{E} = \frac{q}{6\pi\eta R_s}}$

While u can be readily measured for colloids, its interpretation is more difficult than for smaller ions. Because, charge carried by colloids is not a known constant quantity.

Moreover, R_s is also an unknown quantity.

We can make use of Stokes-Einstein equation: $R = \frac{k_B T}{6\pi\eta D}$

$$\boxed{u = \frac{q}{6\pi\eta R_s} = \frac{q(6\pi\eta D)}{6\pi\eta(k_B T)} = \frac{qD}{k_B T}}$$

So, now, if you want to calculate, so while u can be readily measured for colloids by doing simple experiments as we discussed its interpretation is a little bit more difficult than for simpler ions, because, once you calculate q for an isolated ion, we know that you know it could, the charge could be either e or 2 times e or 3 times e, depending upon what kind of ion, one is dealing with.

However, the charge carried by colloidal particles is not a known quantity therefore, and of course, it could vary depending upon the number of charges on the surface and other factors such as presence of electrolyte in the solution. So, therefore, and moreover if you want to estimate what is q that is the charge of the, charge carried by the colloidal particle in this expression R_S is again an unknown quantity.

Because R_S which is the size of the colloidal particle or the radius of the colloidal particle that is being investigated is an unknown quantity. So therefore, what one could do is instead of having an unknown quantity, you could use Stokes Einstein relation and substitute for R_S that is the radius of the particle under consideration in this case, we are specifically considering a spherical particle. Because the Stokes Einstein equation that has been written up here is valid for a spherical particle moving in a fluid.

So, therefore, u which is q / 6 pi eta into R_S, instead of R_S, so what we will do is we will substitute k_BT / 6 pi eta into D. Therefore, so we have 6 pi eta and 6 pi eta get cancelled. Therefore, the electrophoteric mobility goes as q times D / k_B T where D is the diffusivity of the particle.

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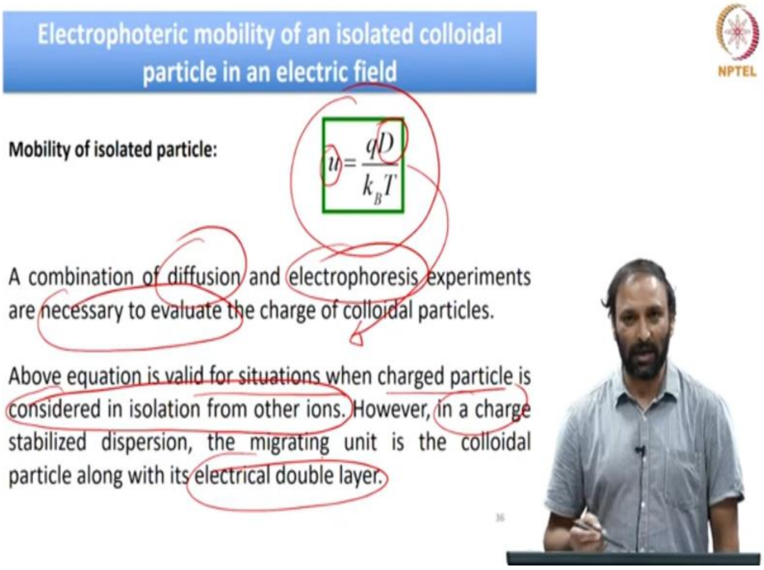

Electrophoteric mobility of an isolated colloidal particle in an electric field

Mobility of isolated particle:

$$\boxed{u = \frac{qD}{k_B T}}$$

A combination of diffusion and electrophoresis experiments are necessary to evaluate the charge of colloidal particles.

Above equation is valid for situations when charged particle is considered in isolation from other ions. However, in a charge stabilized dispersion, the migrating unit is the colloidal particle along with its electrical double layer.

So, therefore, a combination of diffusion experiments which will help us to find what is the diffusion coefficient of the particle and if you combine that with electrophoresis experiment, which give us what is the value of the electrophoteric mobility. Therefore a, combination of these two experiments are necessary to evaluate the charge of the colloidal particle. And of course, the equation that has been developed here it is valid for situations when the charged particle is considered in isolation from other ions which is of course, which is not the true case.

Because we know that there are going to be counter ions and there is going to be an electrical double layer as well. So, all these are going to complicate you know the issues. However, this expression can be used when we assume that the charged particle under consideration is in isolation compared to other ions, which is an assumption in developing this expression. And because of the fact that the charged particles would always have an electrical double layer.

Therefore, the migrating unit that in the electric field is not only the particle plus the associated electrical double layer along with the particle is what is a migrating unit. Therefore, one has to exercise caution when one is using these expressions.

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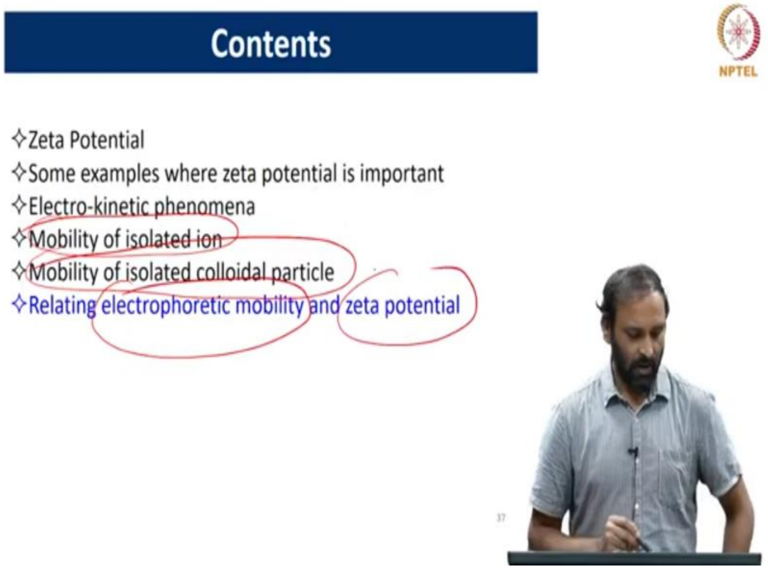

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- ✧Electro-kinetic phenomena
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- ✧Relating electrophoretic mobility and zeta potential

So, now that we know about the mobility of the isolated ions and electrophoteric mobility of charged particle, what we will do is we will develop expressions for relating electrophoteric mobility to the zeta potential.

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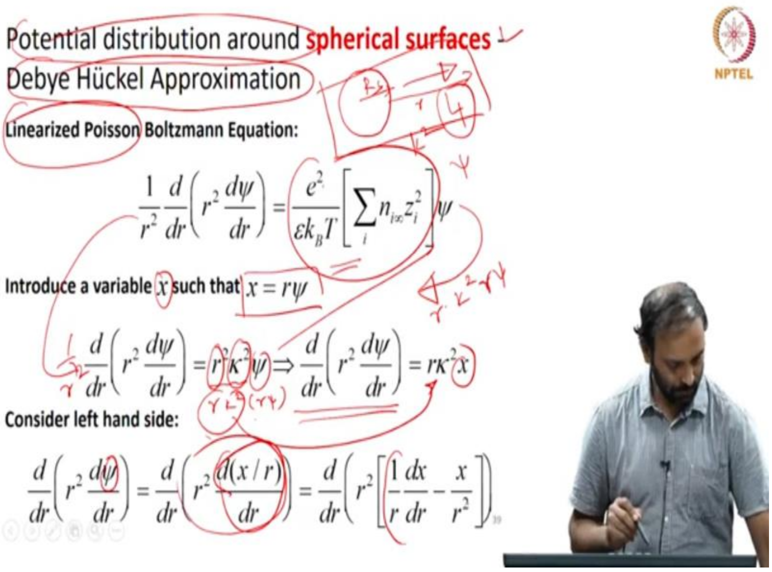

Potential distribution around spherical surfaces

Debye Hückel Approximation

Linearized Poisson Boltzmann Equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{e^2}{\varepsilon k_B T}\left[\sum_i n_{i\infty} z_i^2\right]\psi$$

Introduce a variable x such that $x = r\psi$

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=r^2\kappa^2\psi \Rightarrow \frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=r\kappa^2 x$$

Consider left hand side:

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d}{dr}\left(r^2\frac{d(x/r)}{dr}\right)=\frac{d}{dr}\left(r^2\left[\frac{1}{r}\frac{dx}{dr}-\frac{x}{r^2}\right]\right)$$

And so, for that what we will do is, we will go back and look at module 4, in which we looked at potential distribution around charged surfaces. And because we are dealing with mobility of a charged particle of radius R_S, we will consider a case where there is a spherical particle of radius R and that is being set into motion because of the applied electric field. Therefore, what we will do is, we will consider a case where we would like to obtain the potential distribution around a spherical surface.

How does the potential psi varies with distance or from the surface of the spherical particle? And in specific we will consider the Debye Huckel approximation, which is valid for the low potential cases. The starting point that we had considered is a linearized Poisson Boltzmann equation, which is 1 over r square into d / dr of r square d psi / dr = e square / epsilon k_BT sigma i n_i infinity z_i square times psi, this is kappa square.

So, in order to solve this equation, which is the 1 dimensional Poisson Boltzmann, linearized Poisson Boltzmann equation in the spherical coordinates, we will introduce a variable x such that x = r times psi, therefore, I can rearrange this expression as d / dr of r square into d psi / dr is equal to instead of this term there psi here, instead of so what we will do is, I have taken there was 1 over r square here, I have taken r to the right hand side.

Therefore, I have r square into kappa square in the right hand side times d psi. I can write this as d / dr of r square into d psi / dr. Because we have introduced x = r times psi, therefore, what I can do is, we will rearrange this. I can write this as r times kappa square times r times psi, that is what I have here. So this term, I can write this as r times kappa square into r times psi, therefore I have r times kappa square times.

Instead of r time psi I have replaced it with x because we have used a new variable x. But, if you look at the left hand side d / dr of r square into d psi / dr, I can write this as d / dr of r square into d / dr of x / r, because I am going to replace instead of psi I have x / r now. So therefore, if I differentiate the term in the bracket, so I what I will get is d / dr = r square into d / dr of x / r. This term essentially is 1 over r dx / dr - x / r square.

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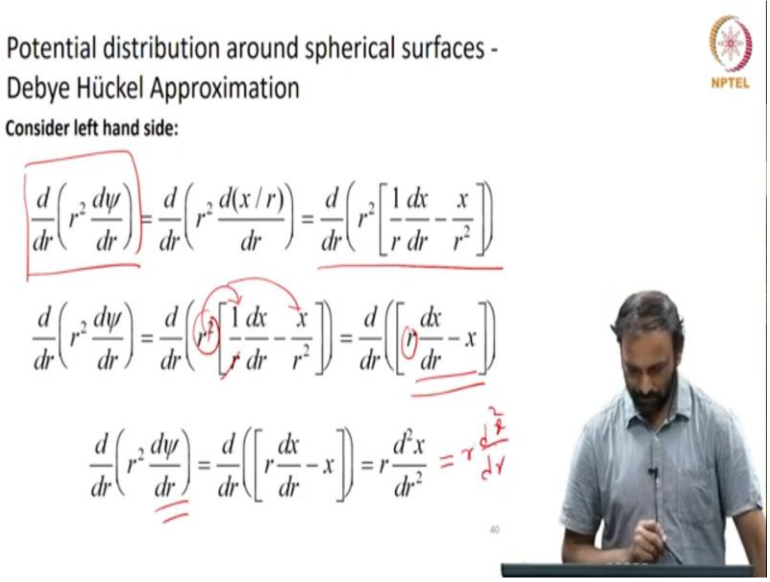

Potential distribution around spherical surfaces - Debye Hückel Approximation

Consider left hand side:

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d}{dr}\left(r^2\frac{d(x/r)}{dr}\right)=\frac{d}{dr}\left(r^2\left[\frac{1}{r}\frac{dx}{dr}-\frac{x}{r^2}\right]\right)$$

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d}{dr}\left(r^2\left[\frac{1}{r}\frac{dx}{dr}-\frac{x}{r^2}\right]\right)=\frac{d}{dr}\left(\left[r\frac{dx}{dr}-x\right]\right)$$

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d}{dr}\left(\left[r\frac{dx}{dr}-x\right]\right)=r\frac{d^2x}{dr^2}=r\frac{d^2x}{dr}$$

So, therefore, the left hand side term that is d / dr of r square d psi / dr can be written as d / dr of r square into 1 over r dx / dr - x / r square. I can take r square, inside the bracket. So therefore, this essentially becomes d / dr of there is one r and one r gets cancelled. Therefore, I have only one r there, minus times dx / dr - x. Therefore, d / dr of r square d psi / dr essentially becomes d / dr of r dx / dr - x which is equal to r into d square x / dr.

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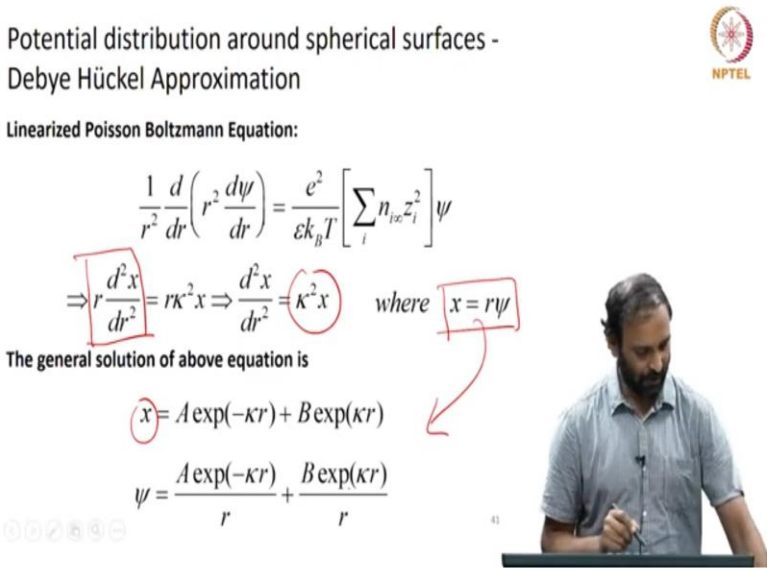

Potential distribution around spherical surfaces - Debye Hückel Approximation

Linearized Poisson Boltzmann Equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{e^2}{\varepsilon k_BT}\left[\sum_i n_{i\infty}z_i^2\right]\psi$$

$$\Rightarrow r\frac{d^2x}{dr^2}=r\kappa^2x\Rightarrow\frac{d^2x}{dr^2}=\kappa^2x \quad \text{where } x=r\psi$$

The general solution of above equation is

$$x=A\exp(-\kappa r)+B\exp(\kappa r)$$

$$\psi=\frac{A\exp(-\kappa r)}{r}+\frac{B\exp(\kappa r)}{r}$$

So, therefore, what we have done is we have been able to, the left hand side has been simplified to r into d square x / dr square, that is what we have done here. And the right hand side is kappa square into x, where x is r times psi. And the general solution of an equation of this sort is given by x = A times exponent - kappa r + B times exponent kappa r. We can substitute back for the value of r here. So, therefore instead of, so because we have x here, so I can replace this with x is r times psi, and I can take r onto the right hand side essentially I end up with psi = A / r times exponent of - k times r + B / r exponent of k r.

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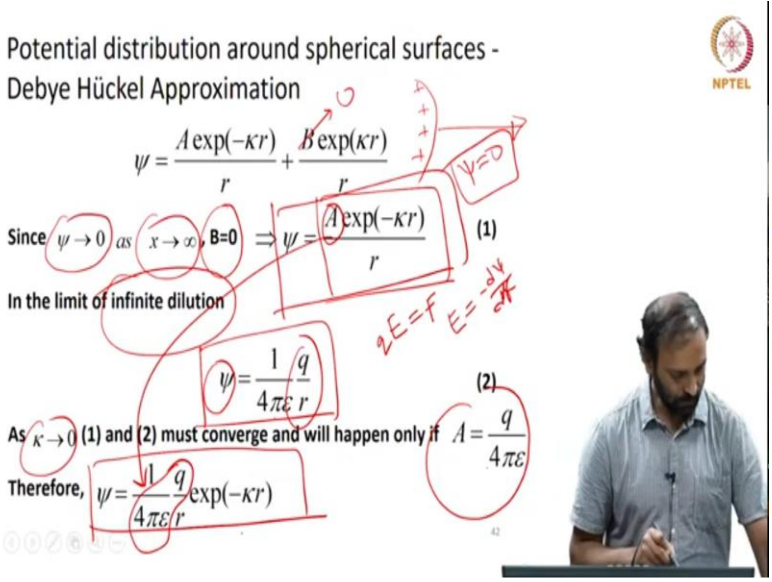

Potential distribution around spherical surfaces - Debye Hückel Approximation

$$\psi=\frac{A\exp(-\kappa r)}{r}+\frac{B\exp(\kappa r)}{r}$$

Since $\psi\to 0$ as $x\to\infty$, **B=0** $\Rightarrow \psi=\frac{A\exp(-\kappa r)}{r}$ **(1)**

In the limit of infinite dilution

$$\psi=\frac{1}{4\pi\varepsilon}\frac{q}{r} \quad \textbf{(2)}$$

As $\kappa\to 0$ **(1) and (2) must converge and will happen only if** $A=\frac{q}{4\pi\varepsilon}$

Therefore, $\psi=\frac{1}{4\pi\varepsilon}\frac{q}{r}\exp(-\kappa r)$

Of course, we can invoke the condition that the potential psi should go to 0 when x tends to infinity because if you have any charged surface whether it is positively charged or negatively charged, we know that if you go to a distance sufficiently far away from the surface of the particle, so essentially the total potential at a very large distance is going to be

0. Because of the fact that the total number of positive co-ions and counter ions in a solution is going to be essentially same.

Therefore, it turns out that this is true only when B is going to be 0. Therefore, the condition that psi tends to 0 as extends to infinity gives us a condition that B = 0 that is one of the integration constant can be left out. Therefore, psi essentially becomes A times exponent of minus k times r / r. Now, if we consider the limit of infinite dilution, that means we have added a really large number of salt. In such a case, we know that a potential psi.

So, electric field E is minus d psi by electric field E is q times E is force and therefore, and because of the fact that E goes as - d psi / dx, d psi / dr in this case, we know that the potential should be 1 over 4 pi epsilon into q / r this comes from the basic physics. So therefore, as k tends to 0 that is infinite dilution case equation 1, that we have developed and this expression should converge.

And that can only happen if, A takes a value of q / 4 pi epsilon. Therefore, the expression for the potential essentially goes as psi = 1 over 4 pi epsilon into q / r that is the constant that is derived, that is the constant that is A. So, therefore, psi goes as q / 4 pi epsilon into 1 over r exponent of minus kappa times r.

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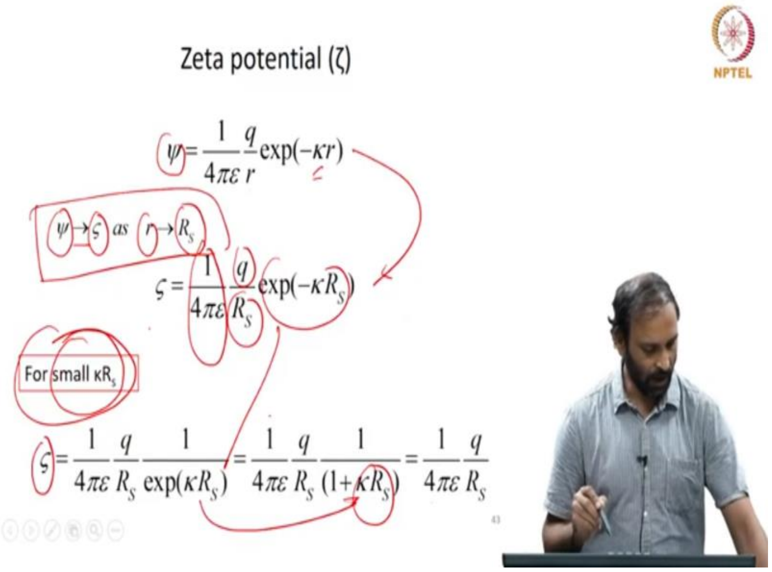

Zeta potential (ζ)

$$\psi = \frac{1}{4\pi\varepsilon}\frac{q}{r}\exp(-\kappa r)$$

$\psi \to \varsigma$ as $r \to R_S$

$$\varsigma = \frac{1}{4\pi\varepsilon}\frac{q}{R_S}\exp(-\kappa R_S)$$

For small κR_s

$$\varsigma = \frac{1}{4\pi\varepsilon}\frac{q}{R_S}\frac{1}{\exp(\kappa R_S)} = \frac{1}{4\pi\varepsilon}\frac{q}{R_S}\frac{1}{(1+\kappa R_S)} = \frac{1}{4\pi\varepsilon}\frac{q}{R_S}$$

So, therefore, and we know that zeta potential is defined as the potential at the plane of shear. Therefore, the potential psi tends to zeta when r goes to R_S, where R_S is the radius of the spherical particle that we are considering. So, therefore, I can use this condition and write this expression as zeta = 1 / 4 pi epsilon q divided by instead of r, I have R_S here, exponent of minus kappa times R_S.

Now, if we invoke the condition of small k times R_S. We will talk a little bit about what this condition essentially means zeta goes as 1 over 4 pi epsilon q divided by R_S. So, I can take this to the denominator, I can write it as 1 over exponent kappa times R_S .So therefore, and I can use a series expansion for exponent k times R_S. So, I can write it as 1 + k times R_S + k kappa square R_S square / 2 factorial and higher order terms.

And because we are considering a case of small k times R_S, we can neglect the higher order terms, therefore zeta becomes 1/4 pi epsilon into q/R_S times 1 / 1 + k times R_S and because k times R_S is small, I can write zeta as q / 4 pi epsilon into R_S.

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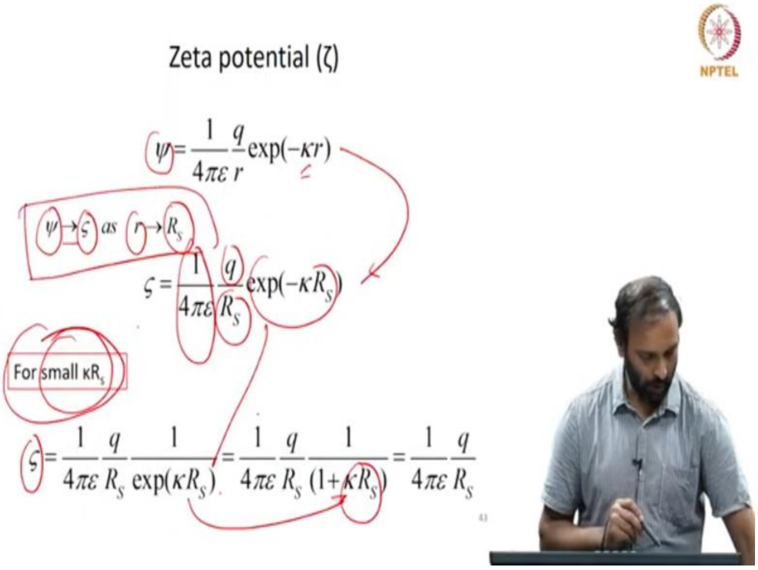

Zeta potential (ζ)

$$\psi = \frac{1}{4\pi\varepsilon}\frac{q}{r}\exp(-\kappa r)$$

$\psi \to \varsigma$ as $r \to R_S$

$$\varsigma = \frac{1}{4\pi\varepsilon}\frac{q}{R_S}\exp(-\kappa R_S)$$

For small κR_s

$$\varsigma = \frac{1}{4\pi\varepsilon}\frac{q}{R_S}\frac{1}{\exp(\kappa R_S)} = \frac{1}{4\pi\varepsilon}\frac{q}{R_S}\frac{1}{(1+\kappa R_S)} = \frac{1}{4\pi\varepsilon}\frac{q}{R_S}$$

So, therefore, for small k times R_S by using linearized Poisson Boltzmann equation for the spherical particle system, we have been able to show that the zeta potential is given by 1/ 4 pi epsilon into q / R_S. However, we have for the case of an isolated particle moving in a electric field, we have derived that u goes as q / 6 pi eta into R_S. So, I can replace for q from this expression.

So, I have q, I can write q as zeta times 4 pi epsilon into R_S that comes from this expression / 6 pi eta into R_S. So, this, this gets cancelled. So I have pi and pi also gets cancelled and therefore, you end up with 2 / 3 factor multiplied by zeta epsilon / n. Which is what is called as a Huckel equation, which is valid when k times R_S is small more specifically, when k times R_S is less than 0.1.

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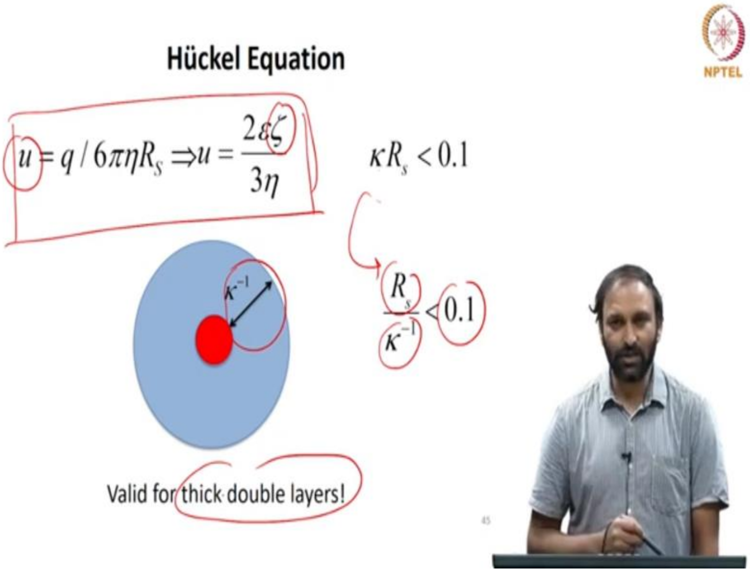

Hückel Equation

$$u = q / 6\pi\eta R_s \Rightarrow u = \frac{2\varepsilon\zeta}{3\eta}$$

$$\kappa R_s < 0.1$$

$$\frac{R_s}{\kappa^{-1}} < 0.1$$

Valid for thick double layers!

So, the case that we have considered here is valid for a situation which is what is called as a thick double layer, because of the fact that you know the k times R_S, this expression is valid for k times R_S is less than 0.1. I can rearrange this and I can write this as R_S / k inverse, where k inverse is the thickness of the electrical double layer. Therefore, this condition is met when k inverse that is the thickness of the double layer is much, much larger compared to the dimension of the particle.

So, therefore, this Huckel equation can be used to obtain zeta potential from the mobility measurements when we consider a case where the electrical double layer is thick that will occur when the concentration of electrolyte in the system is very, very low, that is in the case of dilute electrolyte conditions.

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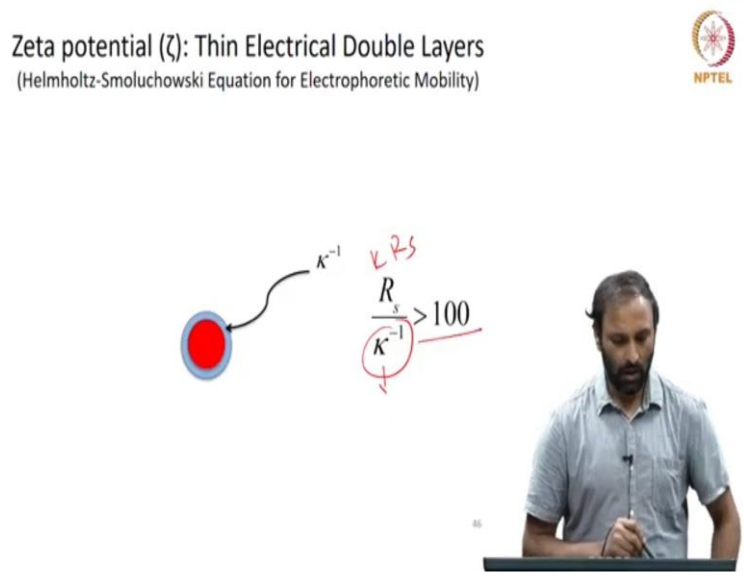

Zeta potential (ζ): Thin Electrical Double Layers

(Helmholtz-Smoluchowski Equation for Electrophoretic Mobility)

Now, we would like to look at a case where the other limit that is when k inverse that is the thickness of the double layer is very, very small that is that will occur when this k times kappa inverse is very, very small. So, this kappa times R_S would be very large, that is larger than about 100.

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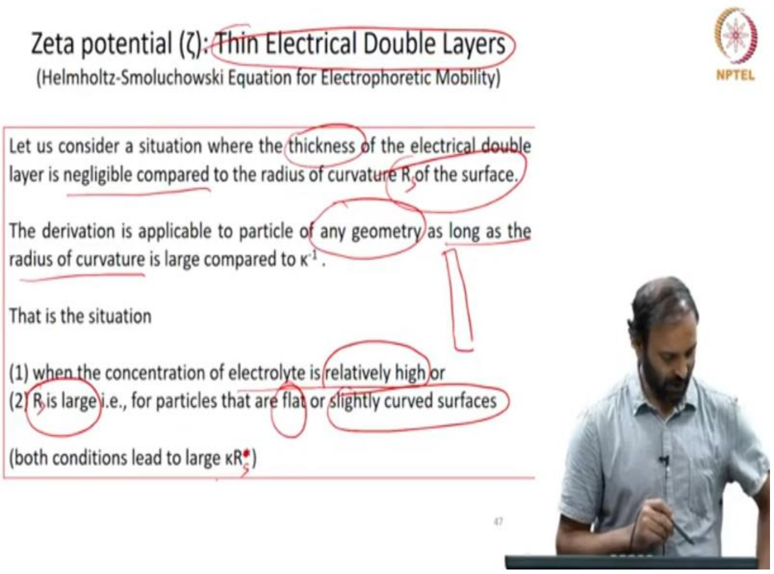

Zeta potential (ζ): Thin Electrical Double Layers

(Helmholtz-Smoluchowski Equation for Electrophoretic Mobility)

Let us consider a situation where the thickness of the electrical double layer is negligible compared to the radius of curvature R_s of the surface.

The derivation is applicable to particle of any geometry as long as the radius of curvature is large compared to κ^{-1}.

That is the situation

(1) when the concentration of electrolyte is relatively high or

(2) R_s is large i.e., for particles that are flat or slightly curved surfaces

(both conditions lead to large κR_s)

So, for this, what we are going to do is, so we will consider a situation where the thickness of the electrical double layer is negligible compared to the radius of curvature R of the particle or any surface that we are considering. And there, so essentially we are considering the thin electrical double layer limit. So, this derivation that we are going to do, it is applicable for any geometry as long as the radius of the curvature is large compared to a kappa inverse which this condition is of course met.

When we consider flat place for which the radius of curvature is infinity. So, therefore, that is very large compared to kappa inverse. And so, this k times R_S being large is met when the concentration of electrolyte is relatively high. That means we have added a very large concentration of electrolyte in the solution. So, that the electrical double layer is compressed that means, the dimension of the electrical double layer is very, very small.

Or for case where R that is a R_S that is a radius of the particle is much, much larger compared to much, much larger that will of course, occur if you consider flat particles or when you have cases where the we are considering slightly curved surfaces. So, therefore, both these conditions lead to k times R_S being very, very large.

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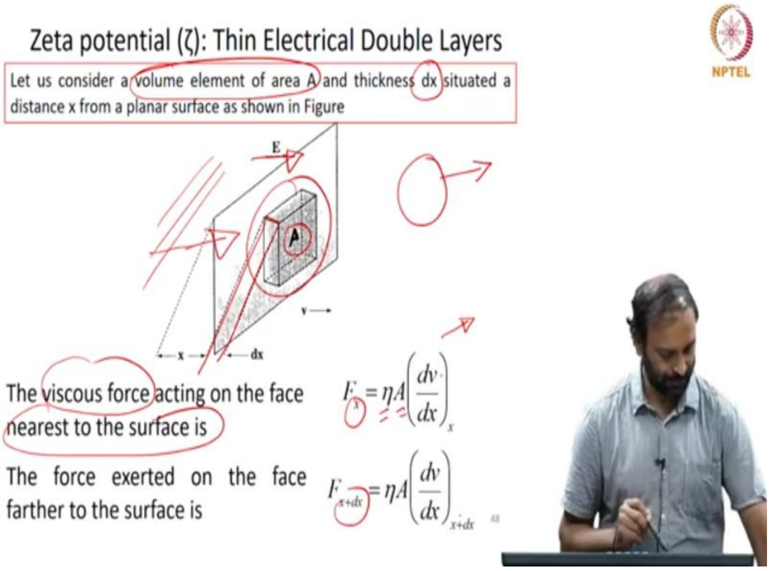

Zeta potential (ζ): Thin Electrical Double Layers

Let us consider a volume element of area A and thickness dx situated a distance x from a planar surface as shown in Figure

The viscous force acting on the face nearest to the surface is

$$F_x = \eta A\left(\frac{dv}{dx}\right)_x$$

The force exerted on the face farther to the surface is

$$F_{x+dx} = \eta A\left(\frac{dv}{dx}\right)_{x+dx}$$

So, whenever a colloidal particle is set into motion in the presence of an electric field, the fluid element around the particle is also going to move. So, therefore, what we got to do is to consider a fluid element, which is in the immediate vicinity of the charge surface. And we are going to do a force balance that we did when we looked at motion of a particle in the fluid. So, for that what we will do is we will consider a volume element of area A.

And the thickness of the volume element is dx that is what is represented here. That is the thickness of the volume element and the area is given by A and there is an electric field and that is applied and because of the electric field that is applied, the particle is going to move in a particular direction, and it is going to drag the fluid in the immediate vicinity also along with it.

So, what we could do is, we could write an expression for the viscous force that is acting on the face nearest to the surface of the particle. So, if you consider that the particle is here, so we can say that at distance x, the viscous force that is acting on the fluid element that we are considering, is given by eta times A / dv / dx, that comes from the Newton's law of viscosity and at a distance x + dx, the force exerted is given by F = eta times A dv dx at x + dx.

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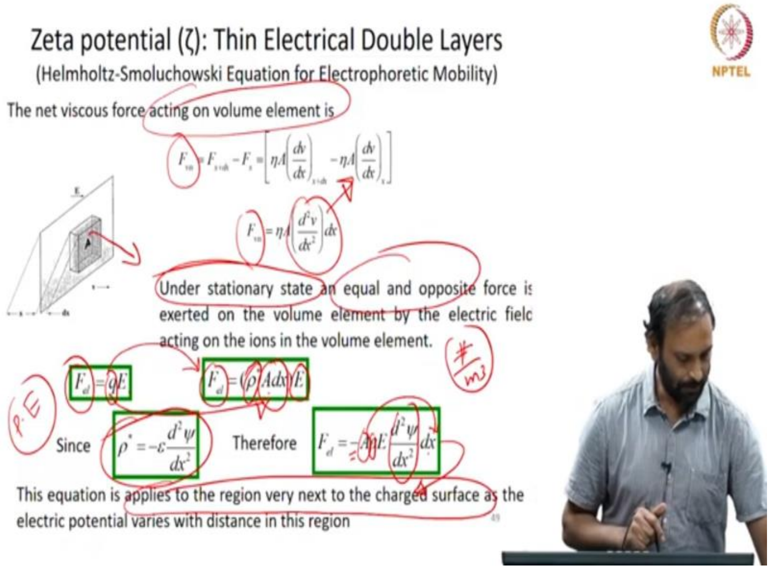

Zeta potential (ζ): Thin Electrical Double Layers

(Helmholtz-Smoluchowski Equation for Electrophoretic Mobility)

The net viscous force acting on volume element is

$$F_{vis} = F_{x+dx} - F_x = \left[\eta A\left(\frac{dv}{dx}\right)_{x+dx} - \eta A\left(\frac{dv}{dx}\right)_x\right]$$

$$F_{vis} = \eta A\left(\frac{d^2v}{dx^2}\right)dx$$

Under stationary state an equal and opposite force is exerted on the volume element by the electric field acting on the ions in the volume element.

$$\boxed{F_{el} = qE} \qquad \boxed{F_{el} = (\rho^* A dx)E}$$

Since $\boxed{\rho^* = -\varepsilon\frac{d^2\psi}{dx^2}}$ Therefore $\boxed{F_{el} = -A\varepsilon E\frac{d^2\psi}{dx^2}dx}$

This equation is applies to the region very next to the charged surface as the electric potential varies with distance in this region

Therefore, the net force that is acting on the volume element is given by which is F viscous is F at x + dx - F at x, therefore, F viscous becomes eta times A d square v / dx square into dx. This essentially comes from the definition of the double derivative. And however, we know that, although the particle will accelerate initially, at some time, there is going to be a stationary state or a steady state that is going to be achieved.

And that occurs because there is an equal and opposite force that is also exerted on the volume element. And considering that the volume element in the immediate vicinity of the charged particle will have ions in the volume element that means we are going to have co-ions and counter ions present in this volume element. So, there is going to be an electrical force that will come into picture which is given by q times E.

Now in this case, in the earlier case we looked at q is the charge of the particle. However, when we are considering a volume element, we are going to write q as the charge density that is rho star, which is the total charge per unit volume that multiplied by the volume of the fluid element that we have considered. That will give me what is the total that it gives me the charge contribution and that times the applied electric field is what gives F_{el}.

So, however, we know that rho star, that is the charge density, it is I can invoke the Poisson equation again for the variation of potential in 1 direction and the velocity with which the particles that we are, that is the fluid element that we are considering. So, we are looking at a plane which is perpendicular to the surface of the particle, therefore the movement of the particle is only in x direction.

That is perpendicular to the surface so, therefore, because of, I can use the Poisson equation and write F_{el} as there is A times dx that is the volume that we had here. And instead of rho star, I am going to substitute this with E times d square psi / dx square. Of course this is going to be a negative sign. So, this particular equation that we have written up, this equation applies to the region very next to the charge surface.

Because we know that if you go to sufficiently far away distance the potential is going to become 0, therefore this force is not going to be existent at all. So, therefore, F electrical is equal to - A times epsilon E, d square psi / dy / dx square times dx, is applicable to a fluid element, which is in the immediate vicinity of the charged surface.

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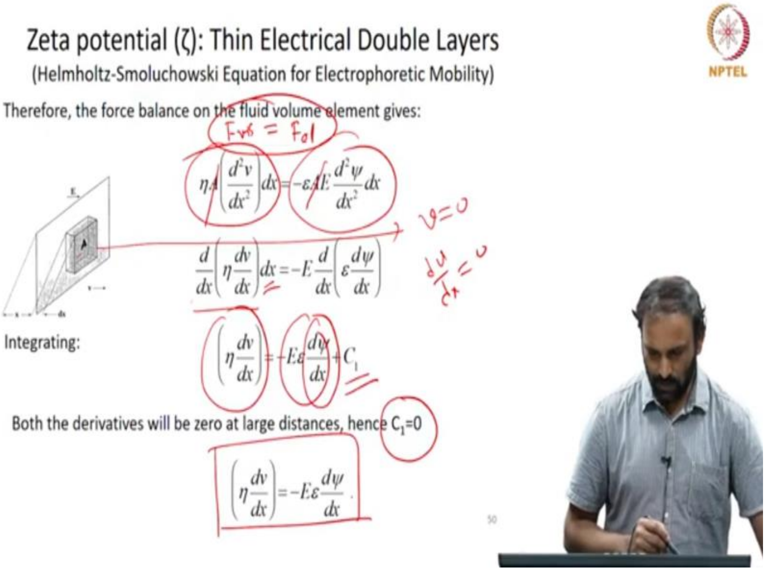

Zeta potential (ζ): Thin Electrical Double Layers

(Helmholtz-Smoluchowski Equation for Electrophoretic Mobility)

Therefore, the force balance on the fluid volume element gives:

$F_{vs} = F_{el}$

$$\eta \cancel{A}\left(\frac{d^2v}{dx^2}\right)dx = -\varepsilon \cancel{A} E\frac{d^2\psi}{dx^2}dx$$

$v = 0$

$\frac{dv}{dx} = 0$

$$\frac{d}{dx}\left(\eta\frac{dv}{dx}\right)dx = -E\frac{d}{dx}\left(\varepsilon\frac{d\psi}{dx}\right)$$

Integrating:

$$\left(\eta\frac{dv}{dx}\right) = -E\varepsilon\frac{d\psi}{dx} + C_1$$

Both the derivatives will be zero at large distances, hence $C_1=0$

$$\boxed{\left(\eta\frac{dv}{dx}\right) = -E\varepsilon\frac{d\psi}{dx}}$$

So, therefore, we will again go back to the force balance, so we had written that F viscous should be equal to F, electrical when the stationary state is reached. So, that is the expression for the viscous force that we have developed, and that is the expression for the electrical force. So, the A on both sides gets cancelled, I can write this as d / dx of eta times dv / dx times dx = - E times d / dx of epsilon times d psi / dx.

If I integrate this, so I will get this term is equal to this term plus an, integration constant. And because of the fact that if you look at a fluid element that is at a very large distance from the charge surface, the velocity is going to be 0, because the only the fluid that is in the immediate vicinity of the particle moves along with the particle. So therefore, v = 0 that therefore, dv / dx = 0 and of course, the potential is also is 0. Therefore, d psi / dx is also equal to 0. Therefore, we can invoke these conditions and set $C_1 = 0$.

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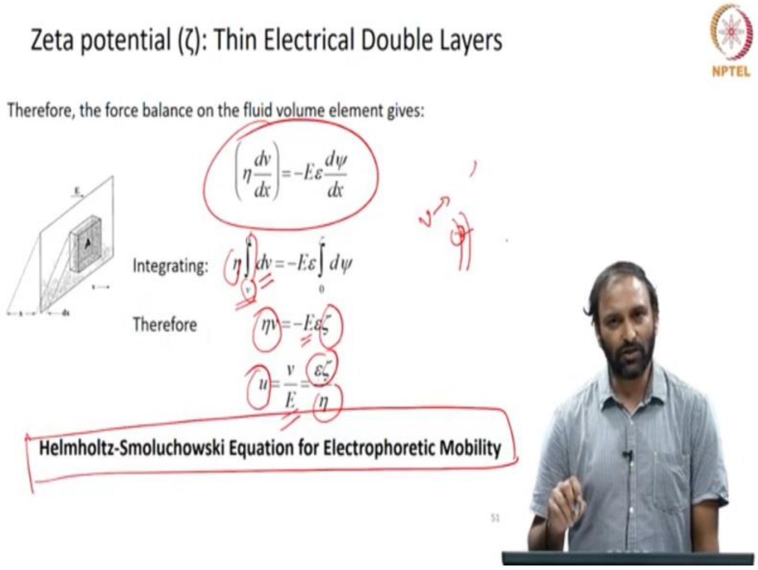

Zeta potential (ζ): Thin Electrical Double Layers

Therefore, the force balance on the fluid volume element gives:

$$\left(\eta\frac{dv}{dx}\right) = -E\varepsilon\frac{d\psi}{dx}$$

Integrating: $\eta\int_v^0 dv = -E\varepsilon\int_0^\zeta d\psi$

Therefore $\eta v = -E\varepsilon\zeta$

$$u = \frac{v}{E} = \frac{\varepsilon\zeta}{\eta}$$

Helmholtz-Smoluchowski Equation for Electrophoretic Mobility

So, now that the force balance is given us this expressions I can integrate this expression further integrating dv eta times integration of dv = - E times epsilon integration of d psi. If you look at the limits here, so we have used the limits for velocity from v to 0 and when the, so, if you look at, so the v is the velocity with which the particle is moving and therefore, the velocity with which the fluid is also moving is also the same.

And if I substitute these integration limits, eta times v becomes minus E times psi times zeta. Therefore, the electrophotereic mobility u which is given as v divided by the strength of the applied electric field is equal to epsilon times zeta / eta. So, this expression is what is called as a Helmholtz Smoluchowski equation for the mobility. We will just look at these limits.

So, we know that, so when, if we assume that this is the fluid element that is very next to the particle surface. We know that when at the surface of the particle, the velocity of the fluid and the velocity of the particle have to be same, and that is the velocity v, with which the particles are moving, at that location the potential is given by zeta. And however, if you look at a very far away distance from the surface that is when the velocity becomes 0 that is the potential is also 0.

Therefore we have used the condition that when velocity is v the potential is going to be zeta and when the velocity is 0, the potential essentially is 0. So, therefore, the electrophoteric mobility which is v / E goes as epsilon times zeta / eta for the case of thin double layers.

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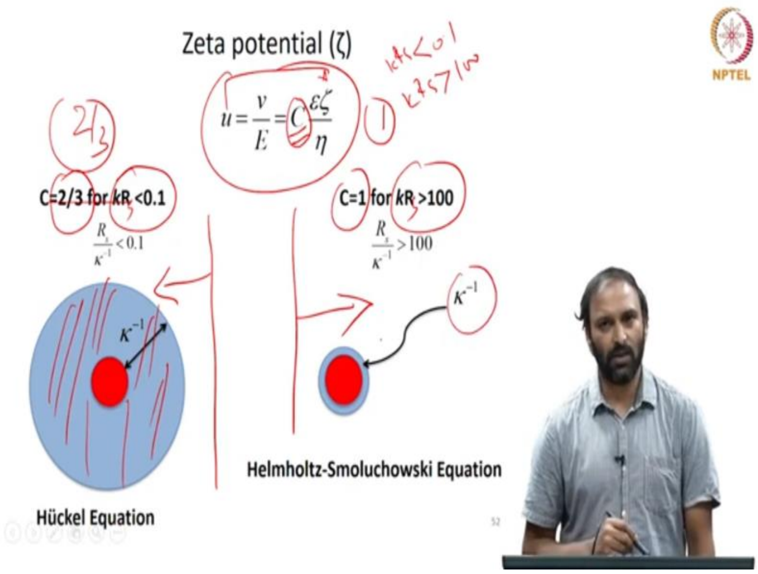

Zeta potential (ζ)

$$u = \frac{v}{E} = C\frac{\varepsilon\zeta}{\eta}$$

C=2/3 for kR <0.1

$\frac{R_s}{\kappa^{-1}} < 0.1$

C=1 for kR >100

$\frac{R_s}{\kappa^{-1}} > 100$

Hückel Equation

Helmholtz-Smoluchowski Equation

So, therefore, we can both, so we have developed two expressions one which is valid for kappa times R_S less than 0.1 other for kappa times R_S greater than 100. So you can write the expression for the relation between u and zeta in a, as a single expression where u is given by C times epsilon times zeta / eta and the constant C takes a value 2 / 3 when kappa times R_S is less than 0.1.

And the constant C takes a value of 1 when the kappa times R_S is greater than 100. So, this is the case of thick double layers and this is the case of thin double layers. And the fact that the coefficient is 2/3 in this case and 1 in this case, you can say that the mobility in the thick double layer case is smaller than the mobility in the case of thin double layer and that makes sense.

Because of the fact that whenever you have a thick double layer, there is going to be an additional drag that will come into picture because of the electrical double layer, thick electrical double layer around the charged particle and that is going to slow down the motion of the particle. Therefore, the mobility that is measured is smaller than the case when the mobility is going to be measured when the kappa inverse is very, very small. That is the case of very thin double layers.