

Novel Separation Processes
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Lecture No. # 23
External Field Induced
Membrane Separation Processes (Contd.)

Good morning everyone. So, we were discussing about the filtration of charged colloid particles in presence of external electric field. Now these charge colloid particles are typical characteristic, because they are charged. Now, under an action external electro kinetic phenomena will initiate, and that is known as electrophoresis. In fact, under the presence of external electric field, there are several electro kinetic phenomena that will occur at a type in a solution that we have discussed in the last class, and they follow under the category of electrophoresis, electro osmosis, sedimentation potential, so and so forth.

Now in this case, it is very important to understand how an external electric field will facilitate the transport of the charged particles in an acquired solution that will enhance the performance of the filtration, and that will enhance the performance of the as well as enhance the productivity of the whole filtration process, but before going into quantification of the enhancement that will occur due to the presence of external electric field for the filtration of the charged solutes will come to know, we need to know some of the fundamentals of the electro kinetic phenomena.

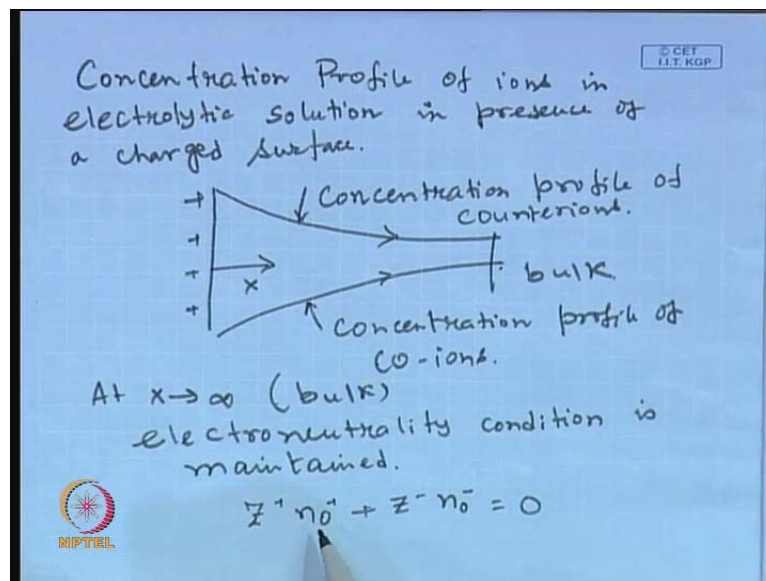
And let us we just looking into how to how the behaviour will occur of the **of the** electrolytic solution in presence of a charge surface. So, we are **we are** already seen, and will rewrite it again in this the class that why you placed a charged solute in an electrolytic solutions, there will be a new distribution of the charges that will occurred inside the solution. And that distribution will be the counter to be very close to the charge surface and co ions will the concentration of the co ions will be very small.

So, there will be increase in counter and concentration closed to the surface that will give rise to the concept of zeta potential, and if you remember what is zeta potential. It is basically a an envelope of the solid particles that move under an external electric field in an electrolytic solution where the viscosity will be infinite. That means, it moves an

envelope; it moves in electrolytic solution under the presence of external electric field. And that envelope will be always attaching to it, and that envelope will be mainly constituted by the counter ions.

So, the actual potential of the charged particles will never be measured. The what one can measure? The one can measure the potential of the charged particles on the outer surface of the envelope, and that potential is known as the zeta potential, and that can be measured by a zeta sizes or zeta metre. So, what zeta metre will do? Zeta metre exactly will measure the potential on the outer surface of the charged particles not on the actual particles outer surface. So, in order to quantify all this phenomena, we have to find out how the concentration profile will look like when you place a charge surface in an electrolytic solution.

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So, let us look into the concentration profile of ions in electrolytic solution in presence of a charged surface. Suppose, we place a positively charge surface in a electrolytic solution; as we have discussed that the, if you place a charged positively charged surface in an electrolytic solution, the counter ions will be **will be** accumulating over near the surface and the co ions will be not. There will be build up of concentration of the counter ions closed to the surface, and that will **that will** keep on decreasing and going into the bulk. Similarly, on the other hand the co ion concentration will be **will be** pretty less will

be very **very** less, and it will be depleted near the surface, and it will gradually increase and at the bulk the electro nutritive will be maintained.

So, this is the concentration profiles of counter ions, and this is the concentration profile of co ions, and here will be having the bulk of the solution. And the bulk of the solution; in the bulk always electro nutritive will be maintained. And this is the distance away from the charged surface at X tends to infinity; that means, the bulk of the solution electro nutritive condition should be maintained always. So, $Z^+ n_0^+ + Z^- n_0^-$ will be always equal to 0; or a Z^+ is the valency of the positively charged ion; Z^- is the valance of the negatively charge ions; and n_0^+ is the concentration of positively charged ions.

This is expressed in number concentration that means number of such ions per unit volume of the solution in number per meter cube. So, if you know the molar concentration, you change the molar concentration into molar means gram per litre; you change into gram per meter cube multiply by 1000. So, gram per and then you can divide by molecular will be gram mole per meter cube and then multiplied by the Avogadro number that will give you the number concentration numbers per meter cube. So, that is the **that is the** how one can have a unit change form molar concentration into the number concentration.

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$Z^+ \rightarrow$ valency of +vely charged ions
 $Z^- \rightarrow$ " " -vely " "
 $n_0^+ \rightarrow$ } number concn. of cations
 $n_0^- \rightarrow$ } "no./m³" " anions.
 $|Z^+| n_0^+ - |Z^-| n_0^- = 0$
 Potential energy of an ion in an electric field at a distance x from the surface.
 $\Phi(x) = Z e \Psi(x)$ Potential at that point.

So, Z plus is valency of cations positively charged ions; Z minus is valency of negatively charged ions; n_0 plus is the number concentration of cations; cations means positively charged ions; and n_0 minus is number concentration of anions or negatively charged ions. So, all these are expressed number per meter cube. So, you can write down this expression if you would like to. So, it becomes Z plus n_0 plus minus Z minus n_0 minus will be equal to 0. Now, we define so that is the form of electrolytic condition at the bulk potential. The potential now defined the potential energy of an ion in an electric field at a distance X from the surface. This potential energy is defined as ϕ of X equal to $Z e \psi$ at X . So, this is the potential energy **this is the potential energy** and this is the potential at a particular point. It should be multiplied by the electronic charge and Z will be the valency. So, if you remember the energy potential energy will be nothing but the charged multiplied by the potential at the particular point. So, if you remember the a loss of the electrolytic. Now, at the steady state we say net ions flux will be is equal to 0 **equal to 0**.

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At the steady state:
 Net ion flux = 0. = J (no/m².s.)

↓
 There are 2 components.

(i) diffusive flux (due to concentration gradient)
 (ii) Due to electric Potential gradient.

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

concentration gradient ↑ Potential gradient
 friction factor.

At the net ion flux is denoted by J and flux is number per meter square per unit time. There is the **there is the** net ion flux and these ion flux will be constituted by two components. So, there are two components of this flux. One is the diffusive flux; what is the diffusive flux? Diffusive flux is basically that will arise, because of the concentration gradient of the ions between two locations. So, the ion will move from the location one to location two, because of the presence of the concentration gradient, and that is that

will **that will** be occurring, because of the presence of diffusive flux. So, this is due to concentration gradient. Secondly, flux due to electric potential gradient. Since there is a electric potential present and this potential will be different between the two locations, that gradient will drive the ions from location one and location two; so, because of the presence of these two fluxes, the net flux will be equal to 0. So, if you write down the net flux equation at the steady state, it will be minus $D \frac{dn}{dx}$ plus $n \int d\phi dx$. So, this is the concentration gradient fixed law; and this is the potential gradient; and f is the friction factor. Now, this friction factor f will depend on the geometric of the solute and the size of the solute so and so forth.

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At steady state, $J=0$

$$-\frac{dn}{n} = \frac{d\phi}{fD}$$

$f = \frac{k_B T}{D}$ ← Stokes-Einstein Equation.

k_B = Boltzmann Const.
 T = Temp. in K.
 D = solute diffusivity.

$$\frac{dn}{n} = \frac{1}{k_B T} d\phi$$

$$n(x) = n_0 \exp\left[-\frac{\phi(x)}{k_B T}\right]$$

Boltzmann Distribution.

So, if at the steady state J should be equal to 0 and will be having minus dn by n is equal to $d\phi$ divided by fD ; and f is given as $k_B T$ divided by D ; and this is known as Stokes Einstein equation; and what is k_B ? k_B is the Boltzmann constant; T is the temperature in Kelvin; D is solute diffusivity. So, one can integrate this equation out. So, if you can integrate the equation out; what will be getting is something like this; gain by gain is the equal to 1 by $k_B T$ $d\phi$ from 0 to ψ at any X location, and this form n_0 to n at any X location. Now, what the implication of boundary condition is very important; at any X location, the potential energy is ψ , and the concentration number concentration is n at any X location.

On the other hand, the potential energy will be 0 at the bulk of the solution. That means, bulk phase do not realize or experience the presence of the charged surface in the electrolytic solution. So, the potential energy of the bulk will be equal to 0, and what is the concentration of the solute there? It will be the bulk concentration. Suppose, you are using 0.01 molar in a solution so the number concentration will be corresponding to the 0.01 molar. Then, you have to convert the number to molar concentration into number concentration the way we have discussed earlier.

So, if you do this then it will be getting a distribution of number concentration of the ions in the electrolytic solution as $n_0 \exp(-\phi / K_B T)$. Now this distribution is known as Boltzmann distribution. That means, the concentration of the co ions concentration of counter ions will decrease exponentially from the surface. The concentration for the co ions will increase from the **from the** surface exponentially up to the bulk.

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Charge Density (ρ)

Concentration of i^{th} type of ion

$$n_i = n_{i0} \exp\left(-\frac{\phi}{k_B T}\right)$$

$$n_i = n_{i0} \exp\left(-\frac{z_i e \psi}{k_B T}\right)$$

ψ = Potential at any location 'x'

For +vely charged surface

$$n_{i/\text{counterions}} = n_{i0} \exp\left(\frac{z_i e \psi}{k_B T}\right)$$

$$n_{i/\text{counterions}} = n_{i0} \exp\left(-\frac{z_i e \psi}{k_B T}\right)$$

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Next we define the charge density is given as ρ . Now concentration let us write down the concentration of i^{th} type of ion is given by the Boltzmann distribution n_i is equal to $n_{i0} \exp(-\phi / K_B T)$; and what is ϕ ? It is nothing but $Z e \psi$; and what is ψ ? ψ is the potential at the location X . So, n_i is given as $n_{i0} \exp(-Z_i e \psi / K_B T)$. So, if a talking about the chloride ion concentration then Z_i will be minus. If you talking about the sodium then Z_i will be

plus 1. So, and ψ is the potential at any location X. So, for positively charged surface suppose, you insert a positively charged surface in electrolytic solution, the number concentration of counter ions will be n_i naught exponential $Z_i \psi$ over $K_B T$, right because Z_i will be positive; if negative so negative **negative** will be positive and number concentration of counter ions will be n_i naught exponential minus $Z_i \psi$ over $K_B T$. Now actually, if you know the distribution of the potential as a **as a** function of location X, the X is from the distance from the charged surface will be able to know what is the exactly concentration profile as the function of location. So, our next aim is to find out how ψ values with X, but before that we have to find out what is the definition of charged density, because that will be requiring the definition time and again.

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Consider a symmetric electrolyte
 $Z_+ = Z_-$ NaCl
 $|Z_+| = |Z_-| = Z$
 CaCl₂ → 2:1 electrolyte } Asymmetric Electrolyte
 AlCl₃ → 3:1

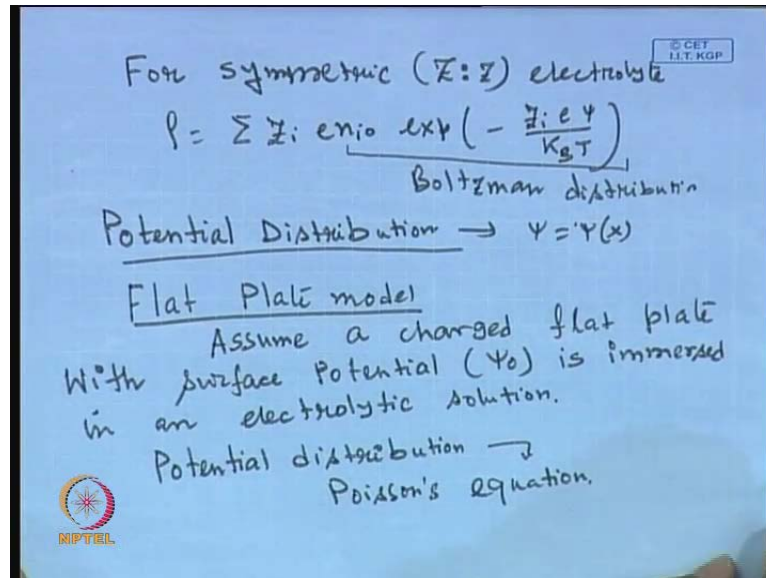
Concentration profiles:
 $n_+ = n_{+0} \exp\left(-\frac{Z_+ \psi}{k_B T}\right)$
 $n_- = n_{-0} \exp\left(+\frac{Z_- \psi}{k_B T}\right)$

Net charge density ρ (no. of charges/vol.)
 $\rho = \sum_{i=1}^2 Z_i e n_i$

Now, let us consider a symmetric electrolyte. Symmetric electrolyte let say Z is to Z that means, NaCl the both the valency are equal. That means, Z plus mod of Z minus will be equal to Z. So, it is sodium chloride for example, if it is a calcium chloride, it is 2 is to 1 electrolyte. If it is a aluminium chloride, it is 3 is to 1 electrolyte and these are called asymmetric electrolyte. So, concentration profiles of **sorry** Z is to Z electrolyte you have the concentration profile of counter ions and co ions; n_+ is n_{+0} exponential minus $Z_+ \psi$ over $K_B T$; and n_- is n_{-0} exponential plus $Z_- \psi$ over $K_B T$. And net charged density is defined as ρ . So, this number of charges per unit volume of the solution. It is defined as ρ is nothing but summation of $Z_i e n_i$; i is equal to 1 to 2 or 1 to 3 whatever. So, basically if you have the summation of all the number concentration

multiplied by the coulombic charge 1.6×10^{-19} coulomb multiplied by the valency of the corresponding ion. The whole thing over a summation will give you the charged density that will give you the number of charges per unit volume.

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So, for symmetric electrolyte, ρ is summation of $Z_i e n_i$ naught exponential minus $Z_i e \psi$ over $K_B T$, where this ψ will be function of distance at every location. So, this we know this n_i is nothing but given it is given by the Boltzmann distribution. This is nothing but the Boltzmann distribution. Now, let us look into the potential distribution; how ρ is varying as a function of X . Why the potential distribution is important? We got to find unless and until you know what is the variation of ψ as the function of X , you will be unable to find out how the number concentration varies of the function of X ; how the charged density varies as a function of X in the solution. That is important to know as the to know to estimate the potential distribution. And for the first case, we consider a flat plate model. What is the flat plate model? We assume that a charged flat plate is involved in an electrolytic solution with its surface potential ψ_0 . Assume a charged flat plate with surface potential ψ_0 is immersed in an electrolytic solution. And the potential distribution that you know, it is given by the Poisson's relationship **right** is given by the Poisson's equation.

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Poisson Equation:

$$\rho = \text{div} (-\epsilon \text{ grad } \psi)$$

ρ : Charge density; ψ : potential
 ϵ : ~~dielectric~~ ^{Permittivity} constant of medium
 $= \epsilon_0 D$ Dielectric const. of medium.
↑ Permittivity in vacuum.

For constant value of dielectric const.

$$\nabla^2 \psi = -\frac{\rho}{\epsilon}$$

1 Dimensional Cartesian co-ord.

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho}{\epsilon}$$

Let us look in to the poisons equation and how it takes the form in one dimensional case is given by rho is nothing but divergence of minus epsilon of gradient of psi. This is the generalised of poisons equation. Now, what is the rho? Rho is the charge density and we have already defined the charge density earlier. And what is psi? Psi is the potential at in a location X let us say, and what is epsilon? Epsilon is dielectric constant of the medium. And what is dielectric constant? Dielectric constant is given as epsilon 0 times D; this is the epsilon 0 is permittivity in vacuum; and D is the dielectric constant of the medium; again this is **this is** known as permittivity **right** Epsilon is permittivity. So, it has two component dielectric constant and medium multiplied by the permittivity in vacuum. So, dielectric constant of medium and for water.

What the value of dielectric constant? Is 80; it is correct and permittivity of the vacuum is 1 by 9 into 10 to the power of 9 something like that. So, we will look into that. So for constant value of dielectric constant, the form of Poisson equation this equation take this form delta square psi is minus rho by epsilon. So, this is the form of dielectric constant of the poisons equation. The potential distribution for constant dielectric constant and the under one dimensional Cartesian coordinates this will be nothing but d square psi dX square will be is equal to minus rho over epsilon **right**. And since we have already defined the definition of expression of charge density, and charge density will be in terms of number concentration of the ions which is known as the **as the** Boltzmann distribution just insert there in this equation and see what you get.

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$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} \sum_{i=1}^2 z_i n_{i0} \exp\left(-\frac{z_i e \psi}{k_B T}\right)$$
 Poisson-Boltzmann Equation.

For $\frac{z_i e \psi}{k_B T} \ll 1 \rightarrow$ Simplification

Debye-Huckel approx.

Valid for $\psi_0 < 25$ mV

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} \left[\sum z_i e n_{i0} - \sum z_i^2 e^2 \frac{n_{i0} \psi}{k_B T} \right]$$
 Electroneutrality condition.

So, will be getting $d^2\psi/dx^2$ will be minus $1/\epsilon$ summation $Z_i n_i$ naught, I think there will be an e here; $Z_i e \psi$ naught exponential minus $Z_i e \psi$ over $k_B T$. This equation is known as the and this summation is over 1 to 2 if there are ionic phases of that for example, NaCl there will be two times only in the **in the** summation. In one case **one case** Z_i will be plus 1; in another case that will be minus 1. Now, this is the Poisson equation and here we have inserted the Boltzmann equation. So, this equation is known as Poisson Boltzmann equation.

Now, there is the simplification of this whole problem if we neglect if we **if we** explain the exponential term; that exponential term can be expanded if the quantity $Z_i e \psi$ over $k_B T$ will be much **much** less than 1. So, for $Z_i e \psi$ over $k_B T$ much **much** less than 1, there is a simplicity; there is a mathematical simplification of this Poisson Boltzmann equation and this assumption is known Debye Huckel approximation. And typically, this approximation is valid if you have a surface potential around 25 millivolts or less valid for surface potential is less than 25 millivolts. That means, it has a fairly good applicability even surface potential around 40 millivolts; still you can use the Debye Huckel approximation.

Now, under the approximation and if you open up this summation series; if you open up the exponential term **if you open up the exponential term** you will be getting $1 - Z_i e \psi$ exponential it will be minus $Z_i e \psi$ by $k_B T$ will be approximated as $1 - Z_i e \psi$

by $k_B T$ and would you neglect the all terms. So, you will be getting $d^2 \psi / dx^2$ square is equal to minus 1 by epsilon summation $\sum z_i e n_i$ naught minus summation $\sum z_i$ square $e^2 n_i$ naught psi over $k_B T$. Now, if you remember the. First there are two terms of the on the **on the** right side now; the first time will correspond to the electro neutrality condition. If you remember, the bulk of the solution always the electro neutrality will be maintained. So, summation of $\sum z_i e n_i$ naught will be equal to 0, because to satisfy the electro neutrality condition. So, this term will vanish, because of electro neutrality condition. And then this term will be 1 minus **minus** will be epsilon multiplied the second term, and minus **minus** will be plus and the whole equation.

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$$\frac{d^2 \psi}{dx^2} = \frac{1}{\epsilon k_B T} \sum z_i^2 e^2 n_{i0} \psi$$

Where, $k = \sqrt{\frac{e^2 \sum z_i^2 n_{i0}}{\epsilon k_B T}}$ (length⁻¹) (m⁻¹)

$k^{-1} \rightarrow [m]$

↓ Debye length.

$f(\text{Concn. of electrolyte, nature of " solution environment, Temperature})$

Counter
 EDL
 bulk
 NIPTEL

Now becomes the Poisson Boltzmann equation now becomes $d^2 \psi / dx^2$ square is equal to 1 by epsilon $k_B T$ summation of $\sum z_i^2 e^2 n_i$ naught psi. Now, if you remember this psi is same for the both terms if you open up the summation those only terms that will differ whether it will be plus 1 or minus 1 result. And now these can be return as copper square psi you can write copper square is equal to under root e^2 square summation $\sum z_i^2 n_i$ naught divided by epsilon $k_B T$. Now, if you put do a dimensional analysis of this copper will be under root of this. And this will be having a unit of length inverse. That means, it is having a unit of meter inverse. So, copper inverse will be having a unit of length. This particular length is unknown as the Debye length. So, on which factors the Debye length will depend? The Debye length will depend. What

is the. It is totally entirely a characteristic of electrolytic solution, electro electrolytic concentration, nature of the electrolyte at the solution environment.

So, this will be a function of concentration of electrolyte; how the concentration it will be appearing? That will be appearing in the number concentration n_i naught, and nature of the electrolyte; how the nature of the electrolyte will basically reflected in the value of Z_i . And solution environment that means, epsilon and of course the temperature. And what is the physical significant of the Debye length? This physical significant is that it gives an idea what is the region; suppose you put an charged surface in an electrolytic solution and there will be a concentration profile of the counter ions, and this will be the co ions and this becomes the this is the bulk of the solution.

So, these distribution of the charges as we have discussed in the last class, this is known as the electric double layer or EDL. So, this thickness is nothing but EDL and thickness of the electric double layer will be dictated by the value of the Debye length. That means, if you have a very small Debye length then we can **we can** call it say thin double layer and if it is a high Debye length, we can call it say thick double layer or is known as the diffused double layer. So, double layer thickness will be dictated by the Debye length, and gives an idea what will be the region **the region** of influence of the charged surface in the electrolytic solution. That means, beyond the value of the Debye length from the charged surface, the influence of the charged surface on the electrolyte solution will be negligible small. There is the physical interpretation of Debye length.

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$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

at $x \rightarrow \infty$, $\psi = 0$
at $x = 0$, $\psi = \psi_0$

After integration,
 $\psi(x) = \psi_0 e^{-\kappa x}$

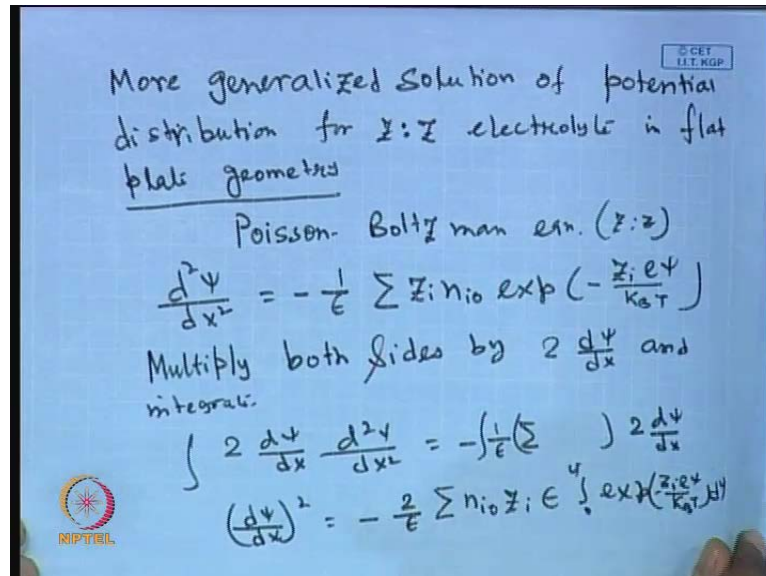
Debye-Huckel Appx
(DH approx) if ψ_0 (25mV)

Now, what we can do? The governing equation of the Poisson Boltzmann equation is nothing but it is based onto copper square psi, and you can integrate this equation with the boundary condition at X tends to infinity psi is equal to 0. That means, at the X tends to infinity means, at the bulk of the solution there is no influence of the charged surface. That means, potential will be exactly is equal to 0. And at X is equal to 0, the surface potential is known to us it is psi 0. If you integrate it out, the solution that you get after integration is it will give you the potential distribution as a function of X psi 0 exponential minus copper X. So, these distribution so is generally after so you should remember what if the you know the underlying principles or assumption that are those are required to have this distribution.

This is of course obtained under the Debye Huckel approximation. And the Debye Huckel approximation you can say, the potential will be decreasing will decline exponentially from the surface towards the bulk. Now of course, Debye Huckel approximation is valid if your psi naught will be less than 25 mille volt. If your **if your** surface will be having a high zeta potential or high surface potential the beyond let us say, 50 mille volt or 60 mille volt or 80 mille volt you cannot use this analysis. There is the short coming of this analysis. If you have the surface potential in the order of 25 mille volt even it works better if you go up to a potential up to around say 40, 50 micro mille volt. Beyond that if you have a high surface potential, you cannot use the this equation as a potential distribution, because the validity is not in **in in** the validity is not

valid under those situations. So, one has to get a more valid situation if you have a high surface potential.

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More generalized solution of potential distribution for $Z:Z$ electrolyte in flat plate geometry

Poisson-Boltzmann eqn. ($Z:Z$)

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\epsilon} \sum z_i n_{i0} \exp\left(-\frac{z_i e \psi}{k_B T}\right)$$

Multiply both sides by $2 \frac{d\psi}{dx}$ and integrate.

$$\int 2 \frac{d\psi}{dx} \frac{d^2\psi}{dx^2} = -\frac{1}{\epsilon} \left(\sum z_i n_{i0} \exp\left(\frac{z_i e \psi}{k_B T}\right) \right) 2 \frac{d\psi}{dx}$$

$$\left(\frac{d\psi}{dx}\right)^2 = -\frac{2}{\epsilon} \sum n_{i0} z_i \exp\left(\frac{z_i e \psi}{k_B T}\right)$$

Now, let us look into a more generalized solution **more generalized solution** of potential distribution for Z is to Z electrolyte in flat plate geometry. So, we write down the Poisson Boltzmann equation for Z is to Z electrolyte. The simplest version of Z is to Z electrolyte is NaCl. This becomes $d^2\psi/dx^2 = -1/\epsilon \sum z_i n_i$ naught exponential minus $Z_i e \psi$ over $K_B T$. Now you have to solve this equation; in order to solve this equation, you multiply both side by $2 \psi d\psi/dx$ **right** and then integrate. You will be getting If you do that that means, you multiply both side by $2 d\psi/dx$ $d^2\psi/dx^2 = -1/\epsilon \sum z_i n_{i0} \exp(z_i e \psi / K_B T)$ and then integrate it out, the integration result will be $(d\psi/dx)^2 = -2/\epsilon \sum n_{i0} z_i \exp(z_i e \psi / K_B T)$ it has left hand side right hand side; it will be $2/\epsilon \sum n_{i0} z_i \exp(z_i e \psi / K_B T)$.

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$$\left(\frac{d\psi}{dx}\right)^2 = \frac{2k_B T}{\epsilon} \sum n_{i0} \left[\exp\left(-\frac{z_i e \psi}{k_B T}\right) - 1 \right]$$

For symmetric electrolyte
 $z_+ = -z_-$
 $|z_+| = |z_-| = z.$

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{2k_B T n_0}{\epsilon} \left[\exp\left(\frac{z e \psi}{k_B T}\right) + \exp\left(-\frac{z e \psi}{k_B T}\right) - 2 \right]$$

$$\frac{d\psi}{dx} = - \frac{2\kappa k_B T}{z e} \sinh\left(\frac{z e \psi}{2k_B T}\right)$$

one more integration.

So, these will be simplified to $d\psi/dx$ whole square will be $2k_B T$ divided by epsilon summation of $n_i n_0 \exp(-z_i e \psi / k_B T) - 1$. So, for symmetric electrolyte, we have z_+ is equal to minus z_- minus **right**. So, basically mod of z_+ is equal to mod of z_- will be equal to left side denoted by z NaCl **right**; plus 1 minus 1 so mod value will be 1. So, modulus of z_+ and modulus of z_- will be denoted by let say it is z . So, $d\psi/dx$ whole square becomes, if you now open up the summation series or species ionic species is 1 and ionic species 2; it will be $2k_B T n_0$; n_0 is the bulk concentration; $n_i n_0$ will be basically, n_0 for both the ions divided by epsilon exponential $z e \psi / k_B T$ as exponential minus $z e \psi / k_B T$ minus 2.

And these expressions can be simplified; I am just overlooking the one step and it will be finally taken as $d\psi/dx$ will be minus 2κ ; **kappa** is nothing but the inverse of Debye length that we have discussed earlier; $k_B T / z e \sinh(z e \psi / 2k_B T)$. Now, you can integrate and this assure one you take the square root of this equation, you take the negative value plus negative root of the right hand side simply, because ψ will be decreasing as you as x is increasing, because x is the distance from the surface. So, one mole integration, it will be one more integration and that will be giving you the, you know the distribution as a function of x .

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$\tanh\left(\frac{Z\bar{\psi}}{4}\right) = \tanh\left(\frac{Z\psi_0}{4}\right) \exp(-\kappa x)$

$\psi = \frac{e\psi}{k_B T}$

boils down to $\psi = \psi_0 \exp(-\kappa x)$
if $\psi_0 < 25 \text{ mV}$

Double layer Analysis around the charged sphere.

$\psi_0 = \frac{w}{q \cdot \text{Area}}$
 $\psi_1 < \psi_0$

Stern layer

And this becomes $\tanh\left(\frac{Z\bar{\psi}}{4}\right) = \tanh\left(\frac{Z\psi_0}{4}\right) \exp(-\kappa x)$. And what is $\bar{\psi}$? $\bar{\psi}$ is nothing but the non dimensional ψ that is $e\psi / k_B T$. So, this is the generalized distribution of surface potential as a function of X for a Z is to Z **Z is to Z** electrolyte, and if you remember this equation does not give an explicit expression of ψ as a function of X . This gives the transcendental equation. So, if you would like to find what is the value of ψ at a factor X location, you have to **you have to** solve it by challenge, because it does not give the explicit expression.

So, the advantage of getting expression is expression using the Debye Huckel approximation if you **if you** have the surface charge less than 30 mille volts. So, these expression will boiled down; it boils down to the earlier expression is ψ is equal to $\psi_0 \exp(-\kappa X)$ if the ψ_0 is less than 25 mille volt. So, in rare cases in our applications will be utilizing these expression. In most of the cases will be using the simplified version using the Debye Huckel approximation, and also the we have done this analysis is basically, this is not relevant to our case. Our case is will be having charged protein solution or charged mical solution which will be moving around the electrolytic solution and you are filtering it by using ultra filtration or something. Why you are doing this analysis, because in electro find the solution environment the charge environment what is the value of surface potential around the charge sphere. It is easier to solve the rectangular coordinates. That is why to give a demonstration of how the

potential distribution will be occurring even if you **if you** insert a charged surface flat plate in a **in a** electrolytic solution we have done this analysis.

Next will be doing the actual analysis what is the charged distribution or the potential distribution around a **around a** sphere, because that will be of primary interest towards, because we are talking about the spherical colloidal particles charged colloidal particles for example, the protein solutions, **solutions** like that. So, will look into next the double layer charge double layer analysis around the charged sphere; this very important that we are going to do. Now, why this is important let me clarify it once again, because we are talking about the filtration of a protein particle or a colloidal particle which is charged by using the ultra filtration and by applying an external electric field. So, it is known as the electro ultra filtration electric or field enhanced ultra filtration or electric field assisted ultra filtration.

Now in presence of electric field what we can do? Basically, the problem that will arise is the declaim of permeate flux. That means, during the filtration all the charged colloids will be depositing about the membrane surface. By doing that, it will increase the resistance against the solvent flux of productivity will decrease. We do not want to do that; we would like to increase the productivity. So, what we should do? We apply an external electric field **we apply an external electric field** such that, its polarity will be opposite compared to the polarity of the charged sphere or the charged colloids. How you know? How is the polarity of the charge colloids? If you know the point of no charge that is **that is** known as the iso electric pH. If you know the iso electric point of all the various proteins or colloids by simply we can change the solution pH. If you set a solution pH suppose, we are talking about the protein molecule let us say which is **which is** having a iso electric pH around 4.7. All the proteins or the most of the proteins they are iso electric points of known.

Now, if you know the iso electric point you can set your operating Ph, because you can **you can** use some drops of hydrochloric acid to bring down the pH or if you can add some drops of alkali solution, and can you now increase the pH of the solution. Now, if you set your operating pH lower than the iso electric point the protein will be positively charged. If you set your iso electric point; if you set your operating pH above the iso electric point, the protein will be negatively charged; the charged colloids will be negatively charged. So therefore, you can have your colloid particles charged as per your

wish by changing the operating pH. So, once you know the operating pH, you will be able to know what is the charge resulting of the protein of the colloid particle whether it is positively charged or whether it is negatively charged. If you if it is positively charge then you can set an external electric field which will be having the let us say, it will be depositing on the bottom plate and top plate will be let us say negatively charged. Then what will happen? The proteins will be attracted by the electrostatic attraction and it will move through the electrolytic solution under the effect of external electric field.

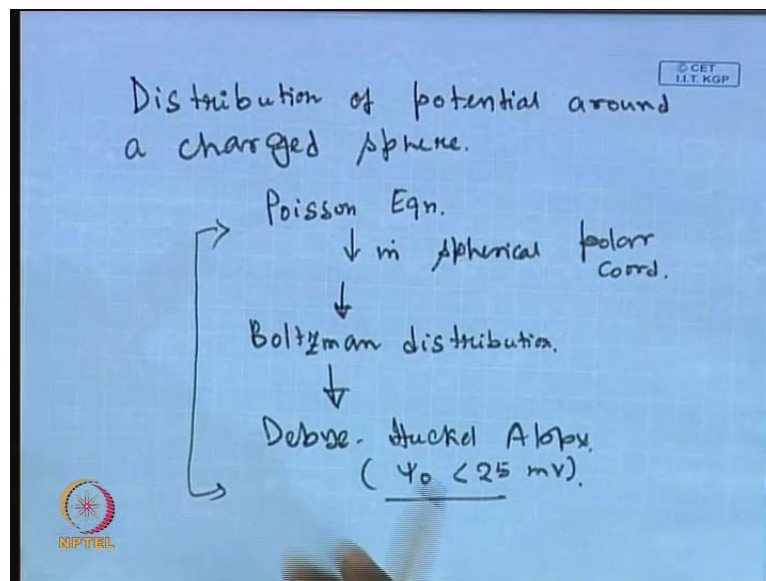
So basically, it will be complicated phenomena and the electrophoresis comes into play and we are going to you know quantify that. So, the most important thing as far as your course is concerned the potential distribution around the charge sphere. Now, the potential on the charge sphere is also is not very clear, because when the protein particles on the **on the** charge sphere will move the along electrolytic solution; since it is electrolytic solution, it will be having free positively enhanced and free cat ions. So, whenever, a charged protein or charged sphere is moving in an electrolytic solution, it will be immediately have an envelope of counter ions. That is known as the stern layer that we are discussed in the last class.

So, when a protein on a sphere will move in an electrolytic solution it will be having a stern layer associated with it. So therefore, the measurement of the surface potential will not be exactly the potential on its particle, but it will be the potential on the sterns outside surface of the stern layer. That means, this is the solid particle which will be having let us say positively charged; let us say this positive charge it amounts to be 25 e. This positive charge is around 25 e. Now, when it moves in an electrolytic solution in the last class that we have defined that, it will carry layer of oppositely charged ions along with it; there will be **there will be** strictly you know they will be very close to the protein surface or charged colloids, and there will be infinite viscosity; the viscosity will be infinity. That means, there will be no motion of the material that is within the stern layer compact to the motion of the sphere. That means, when the sphere moves it moves along with the stern layer associated with it intact with it. So, this known as the stern layer.

So, if the surface potential is ψ_0 ; what is ψ_0 ? ψ_0 is nothing but q by $4\pi\epsilon_0 a$; a is the radius of the particle and $4\pi\epsilon_0$ types. So, if you know the surface charge let us say 25 e. So, you can know the surface potential from the electro static. Now, when a layer of counter ion will be associated with it, what will be potential

outside the surface? Some of the counter ions will neutralise the charge on residing on the surface. So therefore, this potential will be ψ_1 , and ψ_1 will be definitely less than ψ_{naught} . If you see the zeta meter to calculate the potential on this charged sphere, it will never calculate; it is true potential. It will calculate the potential on the it will measure the potential on the outer surface what is known **what is known** as the zeta potential that we have to discussed in laboratory in the last class. So therefore, this system will be very important the as far as our application is concerned. So, if you write down.

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So, if you want to have a distribution of potential around a charged sphere, the first thing you have to do for starting equation point is the Poisson equation, and the and this time this Poisson equation will be in the polar coordinate spherical polar coordinate, and since we are assuming it is one dimension. So, it is a it say **it say** will be the using the parameter the operator corresponding to the spherical polar coordinate will be in not theta in bi direction. So, and then we use the Boltzmann distribution to formulate the Poisson Boltzmann equation. Now the Poisson Boltzmann in the equation spherical coordinate that will become say two clamze. So, use the Debye Huckel approximation. That means, surface potential is less than 25 mille volt. When you are applied the Debye Huckel approximation then, you will be getting a equation which will be very easy to solve. So, under utilizing this steps. I am now going into details, because these already done in the flat plate the governing equation.

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$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \kappa^2 \psi$$

↑
 $\kappa^{-1} \rightarrow$ Debye length

↓ $\psi = u/r$

$$\psi = \frac{A}{r} e^{\kappa r} + \frac{B}{r} e^{-\kappa r}$$

as $r \rightarrow \infty, \psi = 0$
 $r = a, \psi = \psi_0$

$$\psi(r) = \psi_0 \left(\frac{a}{r} \right) \exp[-\kappa(r-a)]$$

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That becomes for the spherical colloidal particles becomes $1/r^2$ by $r^2 dr$ of r^2 $d\psi/dr$ is equal to $d\psi/dr$ right is equal to $\kappa^2 \psi$; this is nothing but the Debye length. So, this is basically approximated version of Debye Huckel approximation version of the Poisson Boltzmann equation in spherical coordinate. And if you define a dummy variable you know ψ is equal to u/r , the solution becomes very simple, and it becomes solution becomes ψ equal to A/r plus B/r $e^{-\kappa r}$. And the boundary condition are as r tends to infinity ψ becomes 0 at the basically at the bulk of solution, and r is equal to a ; ψ is equal to ψ_0 . That means, we know the surface potential. So, under these two condition the potential distribution around the charged sphere it becomes ψ is equal to $\psi_0 a/r$ exponential minus $\kappa(r-a)$.

So, this gives the surface potential around the charged sphere as a function of location or radial position from the **from the** centre. Now a is the radius of the particle, r is the any radial location, and based on this point onwards, what will do in the next class? We will calculate what will be the surface potential, zeta potential that one can get under a set of electrolytic constant under an electrolytic solution, and that will be entirely depending on the solution concentration electrolytic concentration, nature and things like that. Then will do simple calculations and see, how that will be influence about our filtration performance. Thank you.