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Lecture – 15 Electrokinetics (Continued...)

Okay, so let us continue our discussion on electroosmosis. We told that if you have a charge surface and there is an ionic liquid in contact with the charge surface, then we form an electrical double layer and by applying a voltage difference between the 2 ends of a capillary, for example, we will be able to derive the fluid, okay. So, it can create pumping action in doing so, okay.

So, what would happen is closer to the wall would create a diffuse layer and if the wall is negatively charged, it would create a positive charge rich region in the diffuse layer and if you create an electric field, the charges in the liquid in the diffuse layer they will tend to migrate towards the and in doing so they will carry the bulk of the liquid with it because of viscous run, okay.

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So, if you look at the Navier Stokes equation, what happens is you have rho*del v/del t+v dot del v=-gradient of pressure +del square v that is the viscous term-electrical charge density * the gradient of potential, okay. So, this is the electrical body force term, okay. So, this electrical body force term basically accounts for the force exerted on the fluid because of the electric field, okay.

So, if you were to solve a case where we would talk about how the electroosmotic velocity is going to look like, then we would have 2 consider the Navier Stokes equation and we have to include this electrical force as a body force term in the Navier Stokes equation, okay. So, let us look at a simple case flow between 2 infinitely long parallel plates and we apply appropriate boundary conditions to derive the expression for the velocity profile, okay. So, we look at the ideal electroosmotic flow between parallel plates, okay.

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So, there are some assumptions that we would make here. We would make some assumptions. So, the assumption is that the external electric field does not change the charge distribution, the charge density, okay. So, we assume that the charge density inside the liquid is because of the charge distribution that happens when the ionic liquid is in contact with the charged surface, okay and the external electrical field does not create any charge.

So, there is no change in the charge density. Here, we consider ideal electroosmotic flow meaning there is no external pressure gradient present here, okay. So, we also say that no external pressure gradient, okay.

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So, with those 2 assumptions if you look at the situation, this is the situation. We have 2 infinitely long parallel plates. So, this is the bottom plate okay and this is the top plate, okay. Because the surfaces are charged surfaces, so in this case the surface is positively charged, okay. So, we have the positive terminal and negative terminal there. Since, the surface is positively charged, we would how a negative charge region in the electrical double layer here, okay.

So, across this electrical double layer, we would have a negative charged rich region, so when we apply an electric field, this negative charges would try to migrate towards the (()) (05:47), thus it will create a velocity in this direction, okay in the opposite X direction. So, you know here we say that there is no external pressure gradient, so the external at X=0 is 0 and P external at X=L is 0 and potential on the left-hand side is 0 and on the right-hand side is delta v, okay.

So, you know we talk about here, so here we talk about infinite parallel plate channel and the charge was located at Z = +-h/2. So, we say that the centre is here at the middle between the 2 plates. So, at +- h/2 we have the charged walls, okay.

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finite paralle plate channel walls are located at 2=± h/2 gradient =0 elec. field : -ve x-direction ∇ +(+) = - = = E ex $\nabla \phi(\mathbf{r}) = 0$, $\vec{v}(\mathbf{r}) = u(\mathbf{z}) \mathbf{e}_{\mathbf{x}}$. 2/9

The assumption that external pressure gradient is 0 and the external electric field is in the negative Z direction because we have delta v here and 0 here. The direction of the electric field is in the negative X direction, okay. So, external electric field in negative X direction. So, we can write electric field E as negative E^*ex , this is (()) (08:05), so it means that the electric field in the negative X direction and we know that the gradient of the electric potential del phi r=negative of electric field, so it will be E^*ex .

Now, the gradient of external pressure is 0 and velocity vr is only in the x direction and it varies across Z, okay. So, the velocity is going to be only in the X direction and it only varies in the Z direction, so that it was this means.

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$$\nabla p(\mathbf{x}) = 0 , \quad \nabla (\mathbf{x}) = u(\mathbf{z}) e_{\mathbf{x}}$$

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$$Maxwell' eqn: : \quad f_{\mathbf{x}} = - \in \nabla^2 \phi(\mathbf{x})$$

$$X - componend \quad of \quad N-S eqn: :$$

$$P\left(\frac{\partial u}{f^{\pm}} + (u, p)u\right) = -\frac{\partial f}{\partial x} + \eta \nabla^2 u - f_{\mathbf{x}} \nabla \phi_{\mathbf{x}}$$

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You can write the Maxwell's equation for the electrical charge density which is given by electrical charge density=-epsilon*del square phi r, okay. So, with that if we write the X component of Navier Stokes equation, then I can write rho*del v/del t+u.del u=-del p/del x+eta del square u-electrical charge density*the potential gradient, okay. So, we are talking about steady flow.

So, this is 0 because we talk about steady flow and this is the acceleration term which is 0 because we are talking about uniform flow there and no pressure gradient. So, this term also vanishes.



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So, we have only these 2 terms in the equation. So, we say that eta del square u/del Z square because u is only a function of z and we have an expression for the charged density from her, okay. So, we can write +epsilon del square phi z/del z square*electric field is going to be 0. So, now we can integrate. We can say if we take this to the other side of the equation and integrate, we get –eta*u z =epsilon*phi z*electric field+C1z+C2, okay. So, that is equation we get. (Refer Slide Time: 12:02)

Boundary conditions:	
$O No-SLip: U(\pm W/2) = 0$	
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Now, what are the boundary conditions we have, one is the no-slip boundary condition, that means the velocity at +-h/2 at the plate okay will be 0 and the other condition is that the gradient of the velocity as we move away from the wall, okay as I said in the bulk, there are equal number of positive and negative charges, the velocity profile is flatter in the bulk liquid, so the gradient of the velocity as z tends to infinity will vanish, okay.

So, we have 2 boundary conditions; one is the no-slip boundary condition which is u + h/2=0 and the second condition is del u/del z as z tends to infinity=0, okay. (Refer Slide Time: 13:40)



Now, if you apply this second condition on this equation for the velocity profile, we would see that the C1 has to be 0, otherwise it is not possible to evaluate this equation, okay. So, to satisfy this you will see that constant C1 has to be 0. So, now if you apply the no-slip condition, we have uz=-epsilon phi in the electric field/eta-C2/over eta, right. So, if you say 0, so this is 0 at +-s/2=-epsilon eta E*xi.

So, at the wall this potential is going to be the zeta potential, okay, divided by eta-C2/eta. So, we get an expression for the constant C2 will be –epsilon*electric field*eta, right. So, with that we can write down the expression for the velocity profile, uz=zeta potential-phi z*epsilon E/eta, okay. So, this is the expression for the velocity profile in case of flow-through to infinitely long parallel plates.

So, it depends on the zeta potential, okay. Higher the zeta potential, the velocity magnitude will be higher and it also depends on the electric field, directly proportional to the electrical field as well as the permittivity of the liquid and it is inversely proportional to the viscosity, okay. Now, if we go the Debye-Huckel limit, why we say that, the electrical energy is small compared to the thermal energy, okay where the lambda d, (()) (15:47) length is very small compared to the length scale of the flow that we are talking about, then we see what happens, okay.

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Debye - Huckel Limit \rightarrow thin EDL

\rightarrow \frac{\partial^2 +}{\partial z^2} = \frac{1}{\lambda_p^2} + \rightarrow

Infinite parall plak channel: Surface are

at \pm h/L

\phi(\pm h/2) = \xi

\phi(z) = \xi \left[\frac{\cos h(z/\lambda_0)}{\cosh (h/2\lambda_0)}\right]
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So, under Debye- Huckel limit which is nothing but thin electrical double layer, we have derived this earlier del square phi/del z square=1/lambda d square*phi. So, this equation we derived earlier in case of thin electrical double layer limit. So, for the infinite parallel plate channel, the surfaces are at +- h/2, okay. So, the potential at +- h/2 is going to be zeta potential. Now, with this boundary condition if we solve this we get an expression for potential, okay. We get an expression phi as a function of z.

We get zeta*cos hyperbolic z plus lambda d, this is what we had seen earlier, okay cos hyperbolic h/2 lambda d. So, this is the expression for the potential within the Debye layer.

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Now, if we substitute this phi z, in this velocity expression, we have an expression for the velocity along z direction. So, we can have uz=1-cos hyperbolic z/lambda d/cos hyperbolic h/2 lambda d*a factor called, so you will have epsilon xi E/eta. Now, this is known as ideal electroosmotic velocity U come a subscript eo, okay.

So, if we assume that lambda d<< h which is nothing but the thin EDL approximation, then in that case, you will that this term at the bottom will be infinite, this term will be 0, okay. This complete term will vanish. So, uz will be equal to ideal electroosmotic flow which is nothing but epsilon xi E/eta, okay. So, this something we can tell when the electrical double layer is very thin as compared to the transverse length scale, okay.

Some typical values are the xi can be of the order of 100 mV and we can define a parameter called the electroosmotic mobility, okay.





So, we can define a parameter called electroosmotic mobility which is the ratio between the ideal electroosmotic velocity/the electric field, okay. This is given by the symbol mu subscript eo, so this is the electroosmotic mobility, okay which is the nothing but you can write this also as epsilon xi/eta, okay. Typically, this electroosmotic mobility mu eo is about 7*10 to the power of -8 m² per vs, okay. Now, if we use these typical values of zeta potential and electroosmotic mobility, the typical electroosmotic flow velocity is of the order of 1 mm/s, okay. So, in a typical

electroosmotic pumping, we can expect the electroosmotic velocity is of the order of few millimetre per second, okay.

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So, now we talk about the flow rate, okay, knowing the velocity profile or the ideal electroosmotic velocity, how you can the flow rate. So, just calculate the ideal electroosmotic flow rate, okay, Qeo=0 to W, so that is W is the width into the plate, okay*dy and then integration-h/2 to h/2 dz and the velocity is varying along uz. So, if you do that, if you say that uz can be approximated as Qeo ideal electroosmotic velocity, then we can find an expression for the flow rate which is Ueo*wh.

So, Qeo=Ueo*wh and this is at lambda d <<h/2, okay. So, this is the expression for the velocity profile and the total flow rate in case of a flow-through to parallel plates. Now, let us look at flow in a cylindrical tube situation, okay.

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So, let us look at flow-through in a cylindrical tube or channel. So, for cylindrical channel, if you solve this equation del square phi r=1/lambda d square phi r, solve for cylindrical channel, you get an expression for the potential phi r as this, (()) (24:40) I0 r/lambda d/I0 a/lambda d, okay. So, this is the expression for the potential in case of flow in a cylindrical channel. So, this is how the potential is going to vary along the radial direction where I0 is the Bessel function of first kind, okay.

So, there are I0, I1, I2, ... like that, so I0 is the Bessel function of first kind and V we can write is a function of r but in the X direction. So, the velocity is in the axial direction and you can write down the boundary conditions.

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So, we have mostly boundary condition which is velocity at right=a and the perimeter is going to be 0 and the second boundary condition is that when you are talking about flow-through tube, we are talking about symmetry, okay. So, the gradient of the velocity at r=0 should also vanish, okay. So, the gradient of del u/del r at r=0 should also be 0 and this is the symmetry boundary condition, okay.

Now, using these 2 boundary conditions, if you solve the velocity profile similar to this flow between flat plate case, okay. We would have an equivalent in the radial coordinate and if you solve that for flow-through tube, then you would get ur=1-I0 r/lambda d/I0 a/lambda d*Ueo, okay. So, this is the ideal electroosmotic flow velocity.

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So, we can find the ideal electroosmotic flow rate. So, we can write Qeo=integration 0 to 2pi d theta 0 to a, dr, ru, r theta. So, that is = Ueo. So, this is basically mean to be independent of theta, so we have only as a function of r, so that is from here. Now, if we impose the condition that lambda is less than less than a, then Ur could become Ueo, okay. So, under that condition, we can integrate this to get Ueo*pi a square.

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So, the electroosmotic flow rate=Ueo * the area of section, okay. So, now let us talk about Debye layer overlap. We have been talking about cases, you know we derived the expression for the velocity and flow rate for 2 different cases; one for flow between parallel plates and the second one is flow in a circular tube and in all these different cases we have been considering that the

lambda d is very small compared to the radius of length scale of the flow and but when the lambda d becomes comparable to the length scale, how the profile of the electroosmotic flow is going to change, okay. So that is something we can look at here.

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So, we look at Debye layer overlap, okay. So, you know we talk about different length scale. (Refer Slide Time: 30:46)



In one case we have lambda d/a, so let us talk about flow through a tube. If this is = 0.01 that means, we are talking about a tube of radius about 1 micron. So, micron size (()) (31:10). So, this results in a flat profile, okay. As you can see here, this is the value of lambda d/a for which this is the flow profile, okay. You can see that this is the radial velocity over this characteristic velocity

which is nothing Ueo, okay at the centre.

So, you can see that the profile takes a much flatter, okay. The profile is very flat at the significant part of the flow okay is flat. Now, if you take a value which is about 0.1, okay. So, you are talking about a tube radius about 100 nm, okay. Because lambda d is of the order of 10 nm, okay. So, that is what we have seen earlier. So, radius is about 100 nm, then we see that the profile is parabolic somewhat, close to the walls and towards the centre it becomes flat.

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So, here we see that a rounded profile, but it is flat near centre, okay. Now, if we go to lambda d/a as 1, that means we talk about a tube of radius 10 nm, this is what we see. This is the velocity profile, okay. So, the velocity profile is almost parabolic similar to the profile that we see in case of (()) (33:22) driven force, okay. So, here the flow is parabolic. So, I see a parabolic profile, okay. Now, if you write down the equation for the velocity Ur=1-I0 r/lambda d/I0 a/lambda d * Ueo.

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Now, if we do a tailor expansion of this equation and we have to learn how to expand when you have this Bessel function here, okay. So, we can write Ur to be a square/4 lambda d square*1-r square/a square*electroosmotic velocity plus some terms which are of the order of a/lambda d square, okay. So, this is the order okay.

Now, here you can see as lambda d becomes comparable to the radius, okay. So, the velocity is going to be suppressed, okay. So, the electroosmotic flow is going to be suppressed. So, as lambda d increases, the electroosmotic flow get suppressed, okay. So, that is what we also see here/ So, here if you see on the X-axis you have the lambda d/a and the Y-axis you have the maximum velocity of the centre divided by some characteristic velocity, okay.

Now as lambda d/a, so if it is small, even the lambda d is somewhere over here, you can see that the velocity is comparable to the ideal electroosmotic flow velocity and as lambda d/a increases as the Debye length becomes larger and larger, the (()) (36:33) this electroosmotic flow is heavily suppressed. So, the actual velocity at the centre is only 10% of the ideal electroosmotic velocity, okay.

So, what we learn is that the electroosmotic flow becomes beneficial only at the limit of low lambda d or when the electrical double layer thickness is very small, okay. So, here we have been looking at a electroosmotic flow when the pressure gradient is not present, okay but in most of

the practical situations we always have a pressure gradient present which opposes the electroosmotic flow. When we have such pressure gradient present, the velocity profile itself is going to get modified. So, we will like to see how it is going to get modified.

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So, we look at pressure driven flow, we look at electroosmotic flow with back pressure, okay. So, the situation we see it here. This is the situation, okay. So, this is a circular capillary, so we have this Debye layer here, okay and we have positive there and negative there and we say that the wall is positively charged. So, we have negative charge region in the Debye layer which migrate towards the (()) (38:41), so it creates a motion in this direction, okay.

But we have a backpressure that is acting because of the finite fluidic resistance, a backpressure acting. So, we can see that the P (()) (38:58) at X=0 is 0 but the pressure X=L is delta P. So, we have some backpressure which is acting in this direction. The potential here is 0 and the potential here is delta v, okay.

So, here what we are going to predict is that the velocity is going to be, we will see when we work with the Navier Stokes equation, we will end up with linear equation where we can find out the electroosmotic velocity and velocity due to the adverse pressure gradient independently, so we can find the net velocity by adding these 2 together in a vector sense, okay.

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So, here we are talking about external pressure gradient is presence, okay. So, the conditions are phi at X=0 is going to be 0 and phi at X=L is going to be delta V. The pressure at X=0 is going to be 0 and pressure at X-=L is going to be delta p, okay.

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$$-\nabla \phi = E = \left(-\frac{\Delta V}{L}\right) e_{x}^{d}$$

$$-\nabla \phi = \left(-\frac{\Delta \phi}{L}\right) e_{x}^{d}$$

$$\vec{u}(\mathbf{y}) = u(\mathbf{y}) e_{x}$$
Boundary Conditions:

$$u(\mathbf{a}) = u \in No-Slip$$

$$\frac{\partial u}{\partial Y}(\mathbf{o}) = o \in Symmetry$$

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Now, let us say we can write the potential negative gradient of the potential phi is nothing but the electric field, okay which can be written as -delta V/L, okay*Ex, this is the unit vector, okay. Similarly, we can write gradient of pressure is going to be –delta p/L along X direction. So, this unit vectors represent this along X direction, okay. So, here we say that the velocity is along X direction and it varies in the radial direction, so into Ex, okay.

We have the boundary conditions which are the velocity at r=a is 0 that is the no-slip and we have del u/del r at r=0 is 0 so that is the symmetry boundary condition.

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Now, if you look at the Navier Stokes equation, it is 0=eta del square u+epsilon del square pi*delta V/L-delta p/L. So, this equation is a linear equation, okay. So, it is a linear equation, so you can find the solution by breaking the equation into 2 parts and superimposing the solution, okay. So, we can say this is a linear equation, so we can solve by superimposing the electroosmotic flow and the Poiseuille flow, okay.

So, this part is going to give you the electroosmotic flow when there is no pressure gradient. Similarly, these 2 are going to give you the pressure driven Poiseuille flow, okay. So, we can write the velocity Ur to be the vector summation of the Poiseuille+ the electroosmotic, okay. So, this is what we can write because the equation is linear.

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So, the 2 equations that we get is one is 0=eta del square u-epsilon del square phi*delta v/L is nothing but the electric field, okay and we have 0=eta delta square u-delta p/L. So, you know, we have the 2 equations there is a correction here. So, 0 is eta del square u+epsilon del square phi*del v/L and this is for the electroosmotic flow and this is for the pressure driven flow which is 0=eta del square u-del p/L.

So, here this equation would be solved using the condition u electroosmotic at 0 is 0 and del Ueo 0/del r=0 and this equation will be solved based on Upa=0 and del Up/del r0=0, okay. So, we have to solve these 2 equations to get a solution. Now, we know the solutions for this independently. So, we can superimpose and write the expression for the velocity profile. **(Refer Slide Time: 46:30)**

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E o F velocity profile:

$$\begin{aligned}
U(r) &= \left[1 - \frac{I_{e}(r'/\lambda_{0})}{I_{b}(a',\lambda_{0})}\right] \left(\frac{\xi + \xi}{\eta}\right) \frac{\Delta V}{L} - (a^{2} - r^{2}) \frac{\Delta \beta}{4\eta L} \\
&= \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{b}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\Delta V}{L} - (a^{2} - r^{2}) \frac{\Delta \beta}{4\eta L} \\
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&= \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{b}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} - (a^{2} - r^{2}) \frac{\Delta \beta}{4\eta L} \\
&= \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{b}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} - (a^{2} - r^{2}) \frac{\Delta \beta}{4\eta L} \\
&= \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{b}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} - (a^{2} - r^{2}) \frac{\Delta \beta}{4\eta L} \\
&= \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{b}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} - (a^{2} - r^{2}) \frac{\delta V}{4\eta L} \\
&= \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{b}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} - (a^{2} - r^{2}) \frac{\delta V}{4\eta} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} \\
&= \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{e}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} - (a^{2} - r^{2}) \frac{\delta V}{\eta} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} \\
&= \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{e}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L} + \frac{E o F}{1 - \frac{I_{e}(a',\lambda_{0})}{I_{e}(a',\lambda_{0})}} \left(\frac{\xi + \xi}{\eta}\right) \frac{\delta V}{L}$$

So, the expression for the velocity profile would be for the electroosmotic flow, the electroosmotic velocity profile would be Ur=1-I0 r/lambda d/I0 a/lambda d*epsilon xi/eta*delta v/L. So, that is the electroosmotic velocity-a square-r square delta P/4 eta L, okay. So, that is how the velocity profile for the electroosmotic flow in presence of pressure gradient is going to look like, okay.

Now, we can find the electroosmotic flow rate, that will be doing in the limit of lambda d<<a. So, if we do that we would get Q total flow rate will be=Q electroosmotic + Q pressure driven. (Refer Slide Time: 48:20)

We can write this pia square*U electroosmotic and the Qp we can write this as -delta P/r

hydraulic, okay because this is in the negative direction. You know, we can see it here, the electroosmotic flow is going to be in this direction and the pressure driven flow is going to be in the opposite direction, so this is going to be Qeo and this is going to be the Qp.

So, there is a negative sign. So, we can say it is pia square epsilon xi/eta L*delta v-pi a4/8eta L*delta p. So, that is the expression for the flow rate, okay. You know, next we will look at how the PQ characteristics would look like, okay and that we will do in the subsequent class.