Microscale Transport Processes

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Lecture No. # 18

Dispersion (Contd.)

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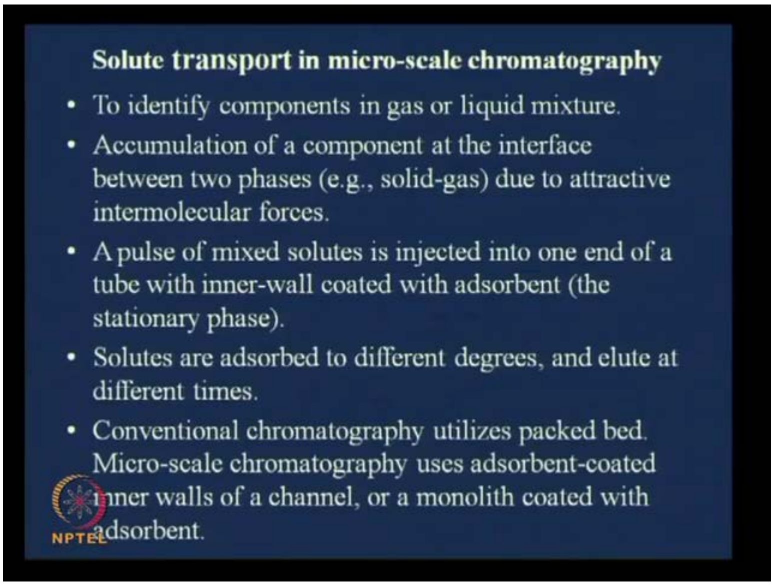

Solute transport in micro-scale chromatography

- To identify components in gas or liquid mixture.
- Accumulation of a component at the interface between two phases (e.g., solid-gas) due to attractive intermolecular forces.
- A pulse of mixed solutes is injected into one end of a tube with inner-wall coated with adsorbent (the stationary phase).
- Solutes are adsorbed to different degrees, and elute at different times.
- Conventional chromatography utilizes packed bed. Micro-scale chromatography uses adsorbent-coated inner walls of a channel, or a monolith coated with adsorbent.

I welcome you to this lecture of micro-scale transport process. What we have been discussing is the issue of dispersion in micro-scale chromatography. What we have discussed so far is how Taylor dispersion takes place, when you introduce a small, when you introduce a slug at the inlet; because of this parabolic velocity profile in a micro channel that slug gets deformed, and then that leads to a different kind of mixing, which we we referred this as dispersion; this is a different kind of mixing, and we tried to at least put together the available theories that define the the theories that define this this sort of mixing. And then we said that this kind of this type of mixing can be can be a problem this type of mixing needs to be addressed in in in case of a in case of a chromatography application, chromatography type application in a micro channel.

If I if I look at the my power point slide here, what we see is that this we discussed in the last class that solute transport in micro-scale chromatography, the objective of this is to identify components in gas or liquid mixture, this is happening because of accumulation of a component at the interface between two phases. Here, two by two by two phases what we mean is one stationary phase that is the adsorbent held next to the wall, and the other one is the gas phase or the the phase that is flowing that is called a mobile phase. And this is this accumulation is happening due to attractive intermolecular forces, a pulse of mixed solutes is injected into one end of a tube with inner wall coated with adsorbent. Now, solutes are adsorbed to different degrees, and elute at different times.

I tried to explain to you, these adsorption and desorption mechanism, and the why why a solute would be adsorbed, and then again it would be dissolved and it will elute, at the outlet. And last point is the conventional chromatography, utilizes packed bed micro-scale chromatography uses adsorbent coated inner walls of a channel or a monolith coated with coated with adsorbent. Basically, in a micro channel you probably cannot afford to have beads, which is commonly there in case of a micro-scale chromatography. So, there there would be some some adjustment to it.

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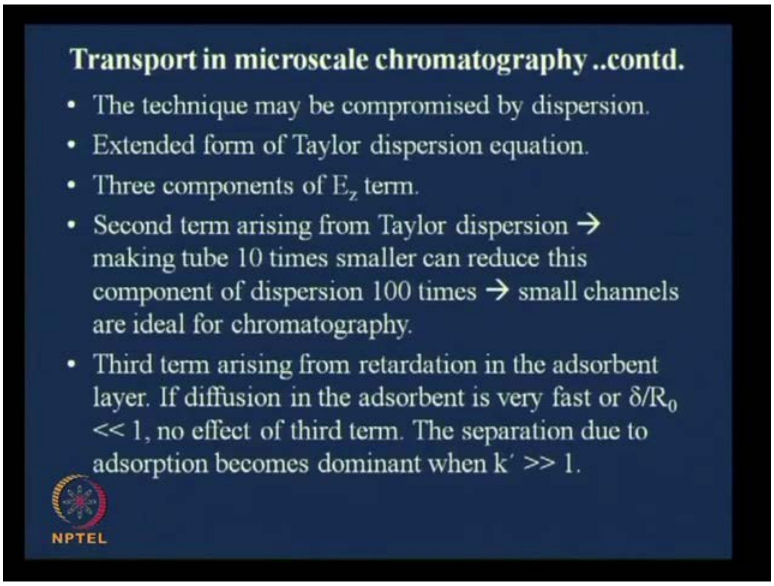

Transport in microscale chromatography ..contd.

- The technique may be compromised by dispersion.
- Extended form of Taylor dispersion equation.
- Three components of E_z term.
- Second term arising from Taylor dispersion → making tube 10 times smaller can reduce this component of dispersion 100 times → small channels are ideal for chromatography.
- Third term arising from retardation in the adsorbent layer. If diffusion in the adsorbent is very fast or $\delta/R_0 << 1$, no effect of third term. The separation due to adsorption becomes dominant when $k' >> 1$.

Now, what we have done next is, we we mentioned that this technique may be compromised by dispersion. This technique may be compromised by dispersion that means, the chromatography when you when you run it, I mean we we at least this was showed in the last class, that the the when the when say say you are you are introducing A, B, C, D, and they are eluting at different times. So, you get peaks of A, B, C, D at the outlet. Now, these peaks can be can get broadened because of this dispersion and so, if so, so, to find exactly. If would have been sharp peak, you could have identified this is the peak, but if it gets broadened there is always a possibility that some peak get lost, some peaks get lost, because of these these dispersion. So, I that is why that is why probably the first point in the power point slide means, the technique may be compromised by dispersion.

And then what we do here is we are trying to write down the governing equations. In the last class, we have we have we tried to put together, the mass balance equation for the mobile phase. This this is what we arrived at right. This is the accumulation term, this is this is basically the radial diffusion and on top of that there was these axial diffusion and this is the convective term as before and we have discussed in the last class, various boundary conditions.

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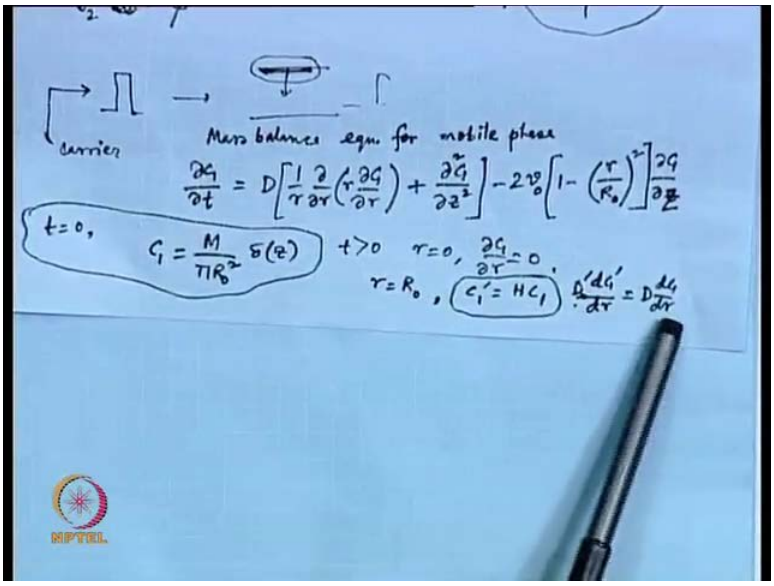

Mass balance eqn. for mobile phase

$$\frac{\partial C_1}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_1}{\partial r}\right) + \frac{\partial^2 C_1}{\partial z^2}\right] - 2v_0\left[1-\left(\frac{r}{R_0}\right)^2\right]\frac{\partial C_1}{\partial z}$$

$t=0, \quad C_1 = \frac{M}{\pi R_0^2}\delta(z)$

$t>0 \quad r=0, \quad \frac{\partial C_1}{\partial r}=0$

$r=R_0, \quad C_1' = HC_1 \quad D'\frac{dC_1'}{dr} = D\frac{dC_1}{dr}$

The initial condition is that you introduced pulse at the inlet and then when t greater than 0 you are assuming that at r equal to 0 symmetry exists and at the wall and and next to the adsorbent not to wall. At the at the interface between the mobile phase and adsorbent. There exists this this equilibrium, which is govern govern by this equation, you are assuming linearity here and the continuity of flux. This is something, which you assumed in this is something, which we discussed in the last class. This is for a mobile phase and for the stationary phase; what we have is that for the this is for the for the adsorbent that means, the stationary phase. So, that is why it was superscripted with a prime.

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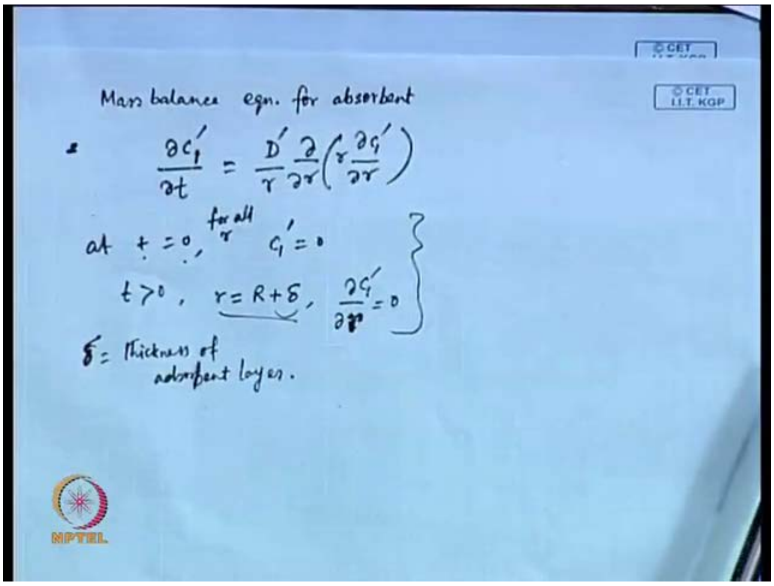

Mass balance eqn. for absorbent

$$\frac{\partial C_1'}{\partial t} = \frac{D'}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_1'}{\partial r}\right)$$

$$\left.\begin{aligned} &\text{at } t = 0, \overset{\text{for all}}{r} \quad C_1' = 0 \\ &t > 0, \quad \underline{r = R + \delta}, \quad \frac{\partial C_1'}{\partial r} = 0 \end{aligned}\right\}$$

δ = Thickness of adsorbent layer.

So, concentration of that same species in the adsorbent phase that this is the accumulation term and this is the radial diffusion and I mentioned this in the last class, that there will not be any convective term of course, and there could be some that that axial diffusion is is neglected. Because you are assuming that the concentration gradient in the axial direction is is not appreciable. So, here also you have a boundary initial and boundary condition at t equal to 0 the entire adsorbent is is untouched. So, C 1 prime is equal to 0 and at t greater than 0 at the wall that means, beyond the adsorbent. I am not talking about that means, r is equal to capital R is the interface of gas and adsorbent and r is equal to capital R plus delta that means, that gives the that that is we are talking about the wall; beyond the adsorbent.

And there there is not any diffusive flux, there that is that is the end of the story, because nothing can pass through the tube is impermeable. So, this is D del C 1 prime del r is equal to 0. So, this is something, which you are working with delta is thickness of adsorbent layer. So, these are these are primarily the governing equations and various boundary conditions that you can have. Now, what? If I go back to the power point slide once again, I mentioned here that extended form of Taylor dispersion equation is used and three components of E z term. What do we what we mean by this? What we mean by this is that you have what we what we write here is that C 1 bar what was the original? I mean this equation by now, we have written it so, many times you should be you should be able to you should be able to write this; I mean you do not have to refer any text by wrote you can just write this.

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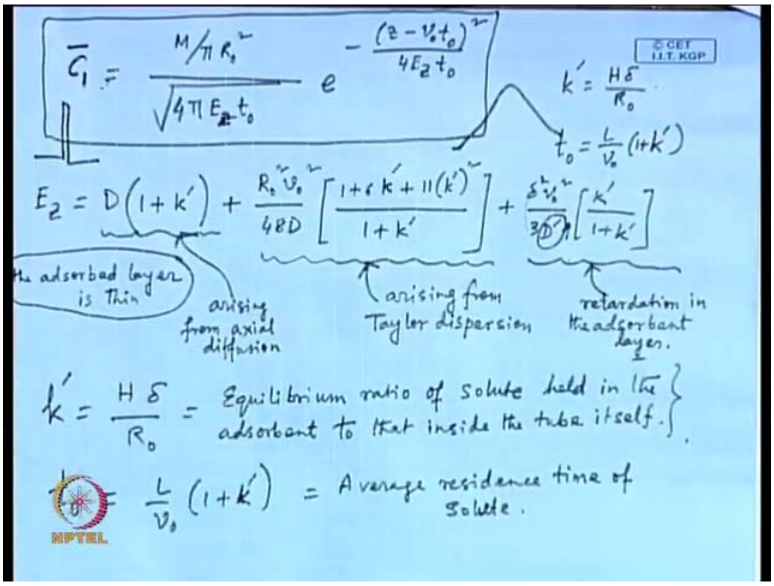

$$\boxed{\bar{C}_1 = \frac{M/\pi R_0^2}{\sqrt{4\pi E_z t_0}}\, e^{-\frac{(z - V_0 t_0)^2}{4 E_z t_0}}}$$

$$k' = \frac{H\delta}{R_0}$$

$$t_0 = \frac{L}{V_0}(1+k')$$

$$E_z = \underbrace{D(1+k')}_{\text{arising from axial diffusion}} + \underbrace{\frac{R_0^2 V_0^2}{48D}\left[\frac{1+6k'+11(k')^2}{1+k'}\right]}_{\text{arising from Taylor dispersion}} + \underbrace{\frac{\delta^2 V_0^2}{3D'}\left[\frac{k'}{1+k'}\right]}_{\text{retardation in the adsorbant layer.}}$$

the adsorbed layer is thin

$$k' = \frac{H\delta}{R_0}$$ = Equilibrium ratio of solute held in the adsorbant to that inside the tube itself.

$$t_0 = \frac{L}{V_0}(1+k')$$ = Average residence time of solute.

So, this is this is the equation, we had All Right this is the equation we had earlier this is the equation we had earlier. So, you have the this is this is the equation that same equation that we had earlier for Taylor dispersion. Now, what we are what what is new here? What is what is different from the conventional Taylor dispersion is first of all we said that this E z term, we need to we need to look into this E z term once again. And also, we need to look into this t 0. What is this t 0? Because this t 0 is something which is new to us, I mean earlier we were working with t.

So, the idea behind doing this exercise, I have already pointed out the governing equations. I have already pointed out that there are two governing equations, two mass balance equations; one for the solid phase and the other for the mobile phase and there are boundary conditions or initial conditions that are in place. Now, you have to solve this equation, but your objective here is to, I mean at least that is the way the people have the researches have thought about it is what they have done they have come up with this solution. They are saying that this is the this is the solution, we have and let us now talk about; the E z and t 0. Such that these becomes the solution of the those to governing equations.

So, that is that is what the researches have already obtained. What the difference here is, what was the E z term for for say Taylor dispersion, you must have must be remembering V naught R naught whole square divided by 48 D that was just a single term, small term. Here, this E z would be comprising of three different some of three terms because it is complicated and you you are working with the different more complicated equations than Taylor dispersion. So, this E z has to be then then that that is adsorb in the E z. So, what what researches have done is they have not they have not touched this form this functional form they said that let it be, because this functional form let is allows me to compare, how things are, because this functional form was in place for just say diffusion of a small spot of dye in an infinite medium.

So, this let us continue with this functional form and write a compact expression for E z this. So, see where the how this E z is changing, because we started with D when when we talked about the diffusion of a small spot of tracer in infinite medium, they have what we have done is we we start we started with this expression, but there we had instead of E z we had D, that is diffusion co-efficient. Which is something we know, which is which is available a bulk property. Then we said, if we go to Taylor dispersion we continue with the same form, but instead of D we have something called a dispersion coefficient coefficient E z. And, we said the expression for E z you already know, V naught, R naught square by 48 D I mean that we have already looked into.

Now, what researches are saying as that we continue with the same compact functional form; however, we we work with we work out, how this E z would be affected, because of this complications. So, that that is a that is a idea here. So, what they have done is they have written E z as a as some of three terms. And those three terms are D into 1 plus k prime plus R naught square V naught square by 48 D into 1 plus 6 k prime plus 11 k prime square divided by 1 plus k prime plus delta square V naught square divided by 3 D prime into k prime divided by 1 plus k prime. Now, what is k prime here? First of all, the k prime here is equal to H delta divided by R 0 and t naught is equal to L divided by V 0 into 1 plus k prime.

What do we have here? What we have here is first of all you got to understand that there I mean I mean you you got appreciate that this equation system is pretty complex. You you have already notice this while, when we tried to at least identify the steps, by which this Taylor dispersion has been the equation for Taylor dispersion has been arrived at. So, this here you are working with a two different governing governing equations, clubbed or or put put together. So, this equation system is pretty complex one of the assumption here, when while arriving at this expression for E z is that the adsorbed layer is thin. The adsorbed layer is thin that means, the delta is small compared to R 0, this is that is what it means. Now, this is one of the assumptions you have, and this C 1 bar is of course, what is C 1 bar? C 1 bar is the average concentration, which is averaged over the entire cross section.

I hope this you should you should keep in mind well that one is species one, the subscript one. C 1 bar that one talks about species one, if you have 1, 2, 3, 4, then you will have C 2, C 3, C 4. And this bar, replace a bar represents the concentration, which is averaged over the entire cross section; that means, the you have a micro channel and at the outlet you have detector and the detector will detect the average concentration for the entire cross section, because detector will not detect individual layers. Though, you have a parabolic velocity profile in one layer is moving at a higher velocity, but detector will detect over the entire cross section, detector cannot detect the that that level dimension of the micro channel is small.

So, you so, so, this C 1 bar is the concentration, which is averaged over the entire cross section. So, this is the expression that you have here, this is the expression that you have here and this is the this is the expression for E z. Now, as I said, at the very outset this E z is comprising of three different terms and this here we have made use of this and and t naught is used here here we have used this t naught, instead of t and this t naught is given by this quantity t naught is equal to L divided by V 0 into1 plus k prime. Can you tell me what would be this L divided by V 0? I think, it it this itself represents time. Only thing is we on top of that you have another another factor added which is 1 plus k prime.

Now, what is k prime? K prime is equal to H delta by R 0. So, what is H delta by R 0? H delta by R 0, if I if I look at it here clearly k prime is equal to H delta by R 0. So, this is basically, Equilibrium ratio of solute held in the adsorbent layer held in the adsorbent to, that inside the tube itself that is that is what is k prime? Equilibrium ratio of solute held in the adsorbent to that inside the tube itself. Now, this is k prime and so, what you are doing is you, when you are writing this t 0 as L divided by V 0 into 1 plus k prime. If I write this once again, t 0 is equal to L by V 0 into 1 plus k prime. So, what this gives is, the this gives you the average residence time of solute. Now, if I try to with this understanding now, if I try to identify, what are these various terms in E z. I said that there are three terms. That is they are clubbed into three components E z has been clubbed into three components.

So, what does where are they arising from, this first component D into 1 plus k prime, this is arising from axial diffusion and here you have another term, this is arising from, I mean this must be obvious to you, we have at prefix R naught square, V naught square by 48 D. So, this is this term is basically arising from Taylor dispersion All Right. And this term; this is arising from retardation in the adsorbent layer. Why there is retardation? Retardation in the adsorbent layer, why there is retardation? Because you have this this chromatography effect present so, the solute is getting adsorbed. So, this E z is comprising of three different components; first component is arising from axial diffusion, the second component is arising from Taylor dispersion and the third component is retardation in the adsorbent layer and all these three components they are contributing to the spreading of the spreading of that peak and what you want to do is you want to minimize this spreading.

So, now if I go back to the power point slide, what we have here is we said that the technique may be compromised by dispersion, extended form of Taylor dispersion equation that is what we have already written here. And it has three components of E z term. The second term arising from Taylor dispersion, what that means is that making tube ten times smaller can reduce this component of dispersion hundred times. Because you have R naught square type dependence. So, small channels are ideal for chromatography. So, smaller the channel the better of course, you cannot endlessly you cannot you cannot make this small endless, because you will encounter very high pressure drop in that case, I mean as you make it smaller, but at least from the dispersion point of view that this is the smaller is the better.

The third term, arising from retardation in the adsorbent layer, third term is arising from retardation in the adsorbent layer that that you have already pointed out this, if diffusion in the adsorbent is very fast or delta by R 0 is much less than 1, no effect of third term, on the other hand, this separation due to adsorption becomes dominant when k prime is much greater than 1. What do we mean here? We let us let us focus on what I have written here. On the third term, we have this diffusion in the adsorbent, when the diffusion in the adsorbent is very fast. Diffusion in the adsorbent is very fast means this D prime is very high. When the D prime is very high automatically the value of this component would be low or delta by R 0 is much less than 1. Delta by R 0 much less than 1 that means, delta square would be very small.

So, either D prime is much higher or delta is much small both have the same effect that will make this term insignificant. On the other hand, if k prime is much greater than 1. If k prime is much greater than 1, then this separation due to adsorption becomes dominant. So, this term becomes dominant if k prime is much greater than 1. If k prime is much greater than 1 then this will cancel out and this remains there, but if k prime is much smaller than 1 and this term would be, much smaller. So, this is so, this is the idea here that because your objective here is to is to reduce this E z, as much as possible then only you can have this in the C 1 bar you can have least amount of spreading, the concern concentration profile profile. I mean you have put a peak here, you you put a peak here. This is the peak you have given and what you get at the outlet of the tube is something like this and you want to minimize this ideally you want this peak to be this also should come out as a peak.

So, the how you can reduce this broadening is you can reduce this E z term and for reduce reduction of E z term of course one thing is you can reduce this R 0 to the extent possible. I mean without hurting, I mean because there will be huge amount of pressure drop. And pressure drop means, that even if you keep the outlet, at atmospheric pressure the inlet of the channel will have very high pressure and it will step the first place it will start leaking is through that through the port, through which you are injecting. So, this is this is the problem there or otherwise you can play with the third term and you try to reduce this I mean or or I mean in case the D prime is big. D prime is high then denominator is high means this quantity will become smaller or if delta is low that means, delta by R 0 is low then also this will become then then also this will become smaller.

So, that that also can help you in the in reducing the broadening so, this equation sort of this expression for so, so we we do not care about this expression, this equation anymore because this is the same equation that we have been talking about, but we focus on this E z and we will see, we see how this how much would be the spreading or if you have two different systems, how much spreading will take place for each case which one will have broader peak and which will which one will have sharper peak. So, that can be worked out through this equation systems; through through this through this functional form.

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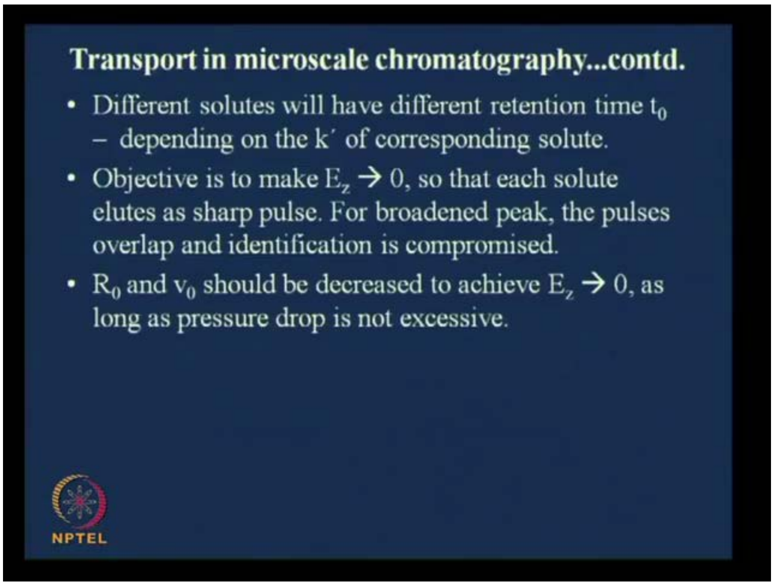

Transport in microscale chromatography...contd.

- Different solutes will have different retention time t_0
  - depending on the k′ of corresponding solute.
- Objective is to make $E_z \rightarrow 0$, so that each solute elutes as sharp pulse. For broadened peak, the pulses overlap and identification is compromised.
- R_0 and v_0 should be decreased to achieve $E_z \rightarrow 0$, as long as pressure drop is not excessive.

Now, if what you need to look at in this in this power point slide is that different solutes will have different retention time t 0, depending on the k prime of corresponding solute. What is t 0? Here are if I if I look at look at this what we have written here or here, t 0 is equal to L by V 0 into 1 plus k prime and k prime would be different for different solutes; we have 1 2 3 4 for one you have some k prime for two you have another k prime. So, you have depending on the value of the k prime it would be different solutes will have different retention time. Objective here is to make E z tending to 0. Ideally E z should be the spreading should be made close to 0. So, that each solute elute as sharp pulse, for broaden peak the pulses overlap and identification is compromise this you already you have appreciated it. R naught and V naught should be decreased to achieve E z tending to 0.

Because because R naught, V naught they are appearing in the Taylor dispersion term in the in the in the second term. So, R naught should be small, V naught should be small. R naught and V naught should be decreased to achieve E z tending to 0 as long as pressure drop is not excessive. Now, if V naught is reduced the pressure drop would be less, but if R naught is also reduced then the that will have an adverse effect on the pressure drop. So, you that the that the system has to be designed appropriately, but these are the, at least from the dispersions point of view these are the terms and this is the type of dependence you have as far as the broadening of the peak is concerned.

So, this is this is I think all I have as far as the dispersion is concerned. We have we have talked about first of all that difference between a diffusion and dispersion and we have come with the functional form just for diffusion and we retained that same functional form C 1 bar, we retained at same functional form and then we continued defining what is Taylor dispersion and we showed that in case of a chromatography in a micro channel. What all terms would be playing but retaining the same functional form how the individual terms would be effected; because of various contribution from various parameters. So, with that practically, I with that I would be closing this discussion on dispersion.

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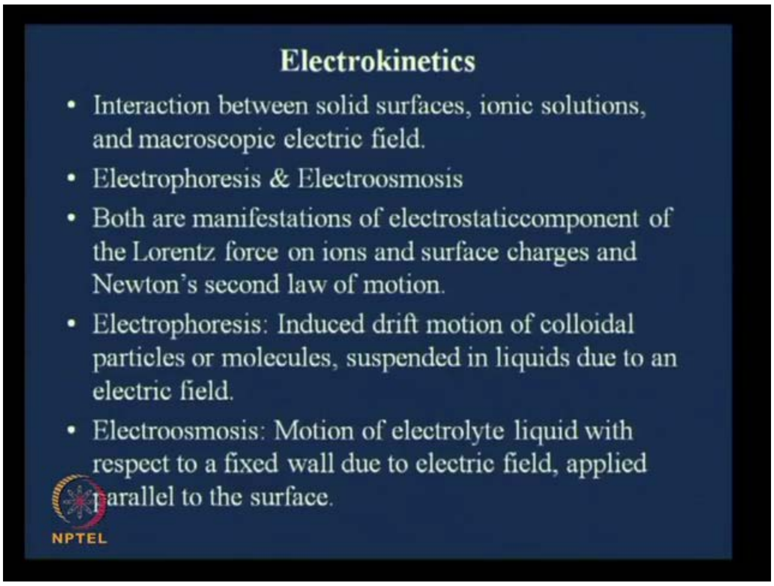

Electrokinetics

- Interaction between solid surfaces, ionic solutions, and macroscopic electric field.
- Electrophoresis & Electroosmosis
- Both are manifestations of electrostaticcomponent of the Lorentz force on ions and surface charges and Newton's second law of motion.
- Electrophoresis: Induced drift motion of colloidal particles or molecules, suspended in liquids due to an electric field.
- Electroosmosis: Motion of electrolyte liquid with respect to a fixed wall due to electric field, applied parallel to the surface.

The next topic that I pick up here is on Electro-kinetics. So, this is the this is the new topic. So, we are we are moving away from mixing. So, we started with first we discussed about the fabrication of various devices, then next we worked on passive mixing, and we tried to show that remaining within the framework of that same mass balance equation over a over a differential element, and then taking the solution how we can mix mix and match, how we can have elongational deformation or linear stretching, and and I and and we are basically in between somewhere, but the two extremes we discussed and and various how how we can treat these mixing? How we can derive? How we can obtain a functional form for mixing? And what are the various passive mixers that are available various mixings schemes that are available?

And then next, we said that there is a problem in the hand, a problem in hand here, which is called dispersion, which can have adverse effect in this this dispersion is also another form of mixing; however, this mixing is unwanted that may the passive mixing that we have discussed was the desired mixing, but here it is not desired; however, you cannot avoid it, because it is it is defined by the fluid fluid mechanics itself. So, next topic that we we pickup is something called Electro-kinetics. Electro-kinetics basically, it is it concerns interaction between solid surfaces, ionic solutions and macroscopic electric field interaction between solid surfaces, ionic solutions and macroscopic electric field.

So, all these three aspects are involved here. We are mostly focusing on electrophoresis and electro osmosis here in this lecture though there are other forms of Electro-kinetics there there are other forms also present.

Here, we are not we are not talking about electro wetting. I think that would be taken up separately, I mean it will not be taken up by me. This electro wetting is another very important topic where basically, the contact angle gets change, but that is that is not we are taking up here. We are mostly focusing on electrophoresis and electro osmosis. Now, these both are manifest manifestations of electrostatic component of the Lorentz force on ions and surface charges and Newton's second law of motion. So, here you are talking about electrostatic component of Lorentz force on ions and surface charges. So, you are looking at first of all the electrostatics, the electrostatic forces and also you are looking at the Newton's second low. So, it is it is a mixture of both basically what we will write is we will write down the I mean our governing equation here, in this in this scheme of things would be Navier stokes equation; however, we have additional body force term arising from these interactions these electrostatic components etcetera.

So, basically we are working with the framework of Navier stokes equation only with an additional body force term. So, that is that is basically, this what we would be working on, and this electro. So now, we define quickly what is Electrophoresis? And what is electro osmosis? Electrophoresis is induced drift motion of colloidal particles or molecules, suspended in liquids due to an electric field. And electro osmosis is motion of electrolyte liquid with respect to fixed wall due to electric field applied parallel to the surface. What are these now? Electroosmosis; motion… What is the last point? Motion of electrolyte liquid with respect of fixed wall due to electric field applied parallel to the surface.

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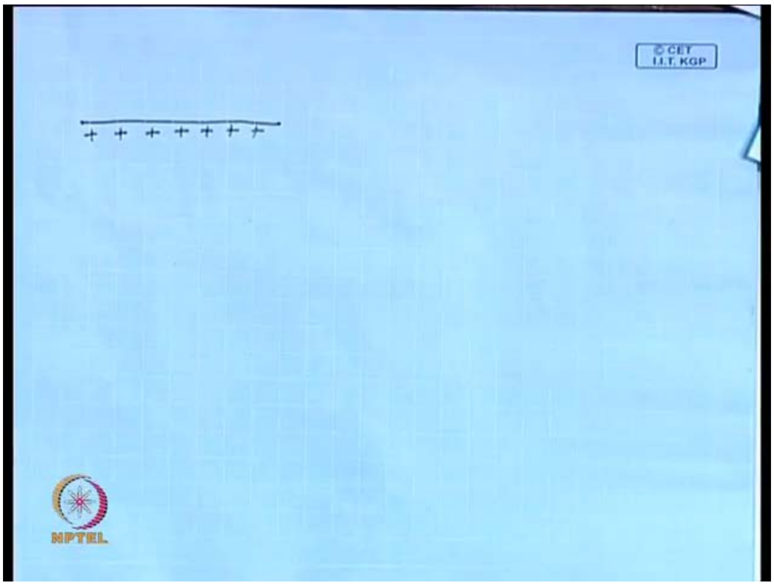

What that means is suppose, you have a surface here and you have an electrolyte present on the surface what is an electrolyte? I mean how do you define that? For example, see in a c l, breaking down into n a plus and c l minus something like that which is which is giving you ions there and you have a surface here. Now, you can first first let me tell you what what will happen here, for some reason this surface will acquire some charge, maybe positive or negative. What could be the reason of this charge developing on this surface? There are various reasons possible.

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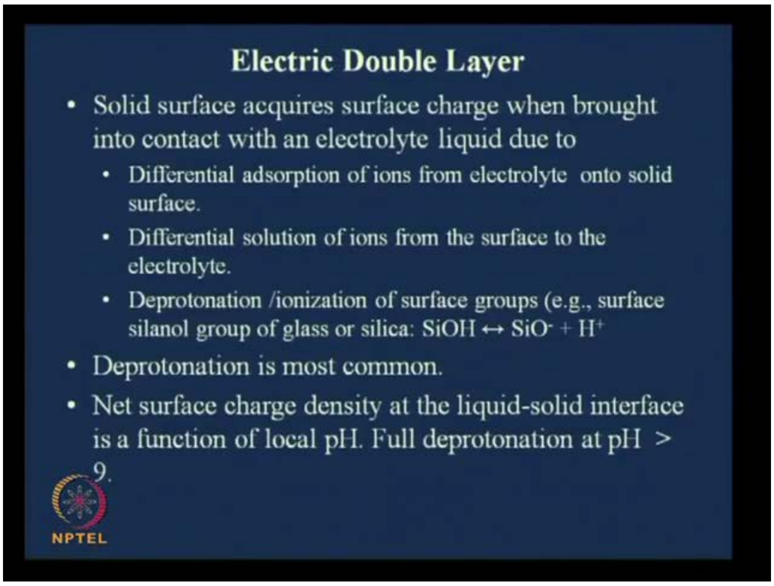

Electric Double Layer

- Solid surface acquires surface charge when brought into contact with an electrolyte liquid due to
  - Differential adsorption of ions from electrolyte onto solid surface.
  - Differential solution of ions from the surface to the electrolyte.
  - Deprotonation /ionization of surface groups (e.g., surface silanol group of glass or silica: $SiOH \leftrightarrow SiO^- + H^+$
- Deprotonation is most common.
- Net surface charge density at the liquid-solid interface is a function of local pH. Full deprotonation at pH > 9.

In fact, if we look at this power point slide, solid surface, acquires surface charge when brought into contact with an electrolyte liquid. Due to there are three points given here, differential adsorptions of ions from electrolyte onto solid surface differential adsorptions of ions from electrolyte onto solid surface. So, this solid surface is these ions that are present here, ions are present plus and minus these ions are roaming around everywhere on the top on top of the surface. There is differential adsorption that means, some particular ions are adsorbed more by this surface than other and thereby you are developing some extra charge.

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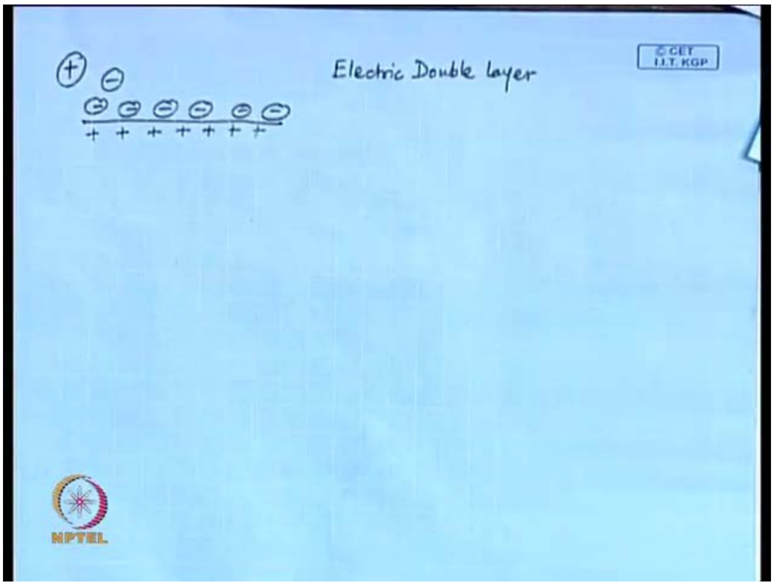

The second point is differential solution of ions from the surface to the electrolyte. So, from the surface something is going back to the solution, from the surface something is going to the solution some differential solution of ions, differential solution; that means, differential means plus is more than the minus that is what I mean by differential so, differential solution of ions from the surface to the electrolyte. At the third point here is Deprotonation or ionization of surface groups such as, silanol group of glass or silica. Since, we are we have been extensively talking about glass and silica, we have been talking about this glass as a micro channel device as a material for micro channel device. So, that will have silanol group S i O H, which breaks down into S i O minus and h plus. So, this H plus is available and this H plus goes away. So, this gives. So, you have deprotonation of the surface group. So, if H plus goes away so, automatically the minus charges they are left there and these minus charges will be, these minus charges will be sitting there. So, the surface will be, having all minus charges All Right.

So, for various reasons there could be, the something some some charges may develop on the surface. Deprotonation deprotonation is most common, what we have here deprotonation is most common and net surface charge density at the liquid solid interface is a function of local pH full deprotonation at pH greater than 9. Net surface charge density at a liquid solid interface is a function of local pH. I mean this you must appreciate, because pH is what? It gives you some and say what what is the hydro hydrogenion concentration Right. So, what p H you are holding this surface and that has a tremendous effect on how much H plus is going from the surface to the to the electrolyte. So, so the local p H is it is functional to local p H, net surface charge density at the liquid solid interface is a function of local p H and full deprotonation at p H greater than 9. So, this is a fact which is which is there, I mean if you have a surface you will develop some charge there.

And because of this charge developing, the opposite charge from the electrolyte would be attracted to the wall. So, if you have all plus here, you will have all minus sitting here like this. Now, this this is happening with any any wall material. So, if you have a pipe on the wall this is happening, but for a macro-scale you probably do not care much about it. Because this is insignificant, but in a micro-scale when when it comes to a micro channel, this particular phenomena can be important. I mean this because of the scale of the problem this this particular phenomena needs to be studied. So, what we have is ions of opposite charge in the electrolyte are attracted and the like charges are repelled. So, opposite charges are coming to the wall and the like charges; that means, the plus that will be repelled from the surface that that is that is the idea that is that that is how it happens everywhere.

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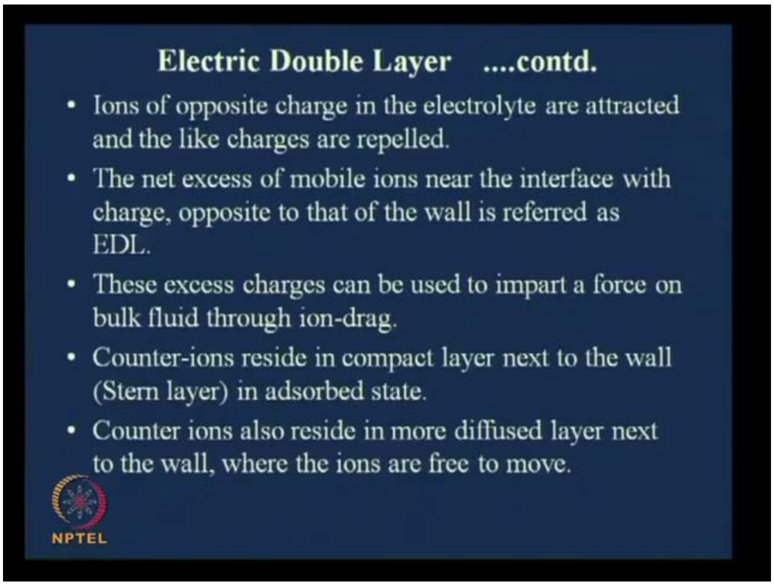

Electric Double Layer ....contd.

- Ions of opposite charge in the electrolyte are attracted and the like charges are repelled.
- The net excess of mobile ions near the interface with charge, opposite to that of the wall is referred as EDL.
- These excess charges can be used to impart a force on bulk fluid through ion-drag.
- Counter-ions reside in compact layer next to the wall (Stern layer) in adsorbed state.
- Counter ions also reside in more diffused layer next to the wall, where the ions are free to move.

Net excess of mobile ions net excess of mobile ions near the interface with charge opposite to that of the wall is referred as EDL, electric the full form is Electric Double Layer. These excess charges can be used to impart a force on the bulk fluid through ion drag. These these excess charges can be used to impart a force on a bulk fluid through ion drag what what is meant here? What what this statement means here is that if you have a channel, If you have a channel; then you will have similarly, the upper part of the wall also will have upper part of the wall will also have this positive see you have a flow between two parallel or you have two parallel plates we have not talked about flow, we have say say we have two parallel plates.

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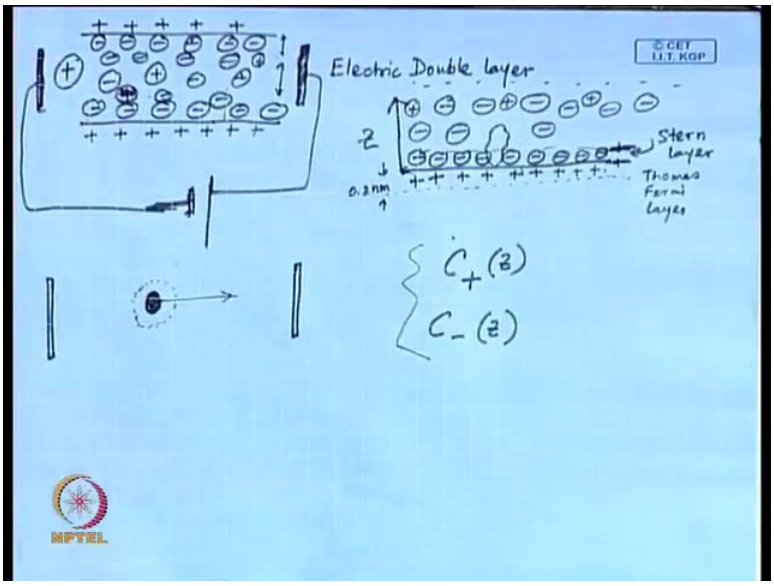

So, the upper plate also will have the same thing and then you will have opposite charges attracted to it. And, then these other charges are floating around here and there right. So, what this is saying, is that you will have the concentration of some opposite charges next to the wall of course there would be one layer which is immediately adjacent to the wall which would be so, called a static layer. Which is which is call which is which is static, but there would be a diffused layer, I mean would be up to some distance away there would be a concentration of negative ions, I mean there would be some positive charges, but the negative ions the concentration would be more and that is a diffused charge which is which is mobile charge, which which is mobile. So, maybe maybe immediately next to the wall there would be a compact layer, but little bit away from there there is a concentration of opposite ion which is mobile.

So, that is that is very much present around. And of course, the positive because positive negative they are all they have to be equal should be in equal numbers so, then there are positives everywhere. So, this this is next to the wall and this is probably the away from the wall which is which is probably you would say the bulk. Now, if you put the electrodes if you put the electrodes here suppose, you put an electrode here, this is an electrode here and this is another electrode here. And then you put this electrode here and you put so, this is acting as an anode and this is acting as a cathode. So, what will happen is this these negative charges they would be pulled towards this direction, these negative charges would be pulled towards this direction, negative charges from the diffused layer, the negative charges which are mobile, which are free to move, which is not sitting next to the wall held permanently, but which is free to move.

So, that would be that would be moving and that while these ions are moving from one direction to the other this is generating a drag force, this is generating. So, if I look at the power point slide, what we see here? Is that ions of opposite charge, if we look at the power point slide, here the ions of opposite charge in the electrolyte and attracted and the like charge are repelled. The net excess of mobile ions near the interface with charge opposite to that of the wall is referred as electric double layer these excess charges can be used to impart a force on bulk fluid through ion drag through ion drag. So, now, if I if I look at what I have drawn here on this page, what what we are saying is that these negative charges would be pulled to one electrode and the positive charge, I mean negative charges would be pulled towards one electrode and this while while this pulling while this pulling it would be pulling the that would be a bulk there there will be a force on the bulk fluid through ion drag.

So,so, what what? In fact, in fact we can we can show that from from Navier stokes equation we said there would be a body force term, I am right? An additional body force term coming in here. So, what we will be doing here is from the Navier stokes equation we can show that there would be viscosity, there would be everything, but because of that body force term that extra body force term that we are talking about because of that body force term there would be a net movement of the fluid from one direction to the other. And that is arising because of this body force term as I said so, you can call this that these excess charges can be used to impart a force on bulk fluid through ion drag that is what you can say here. So, this we will we will get into the theories of it, how we can really have. In fact, what we will do is I will give the velocity gradient, I mean what is delta V and I will ask you to find out what would be the velocity. So, you you will be having those theories in hand, how we can find out the velocity here.

In fact, this is one one pumping mechanism people have researchers are proposed electro osmotic pumping I mean you might have heard of this term. So, this is based on this principle. So, I mean why I have gone so far here is if we now look at what we have said so far. I repeat once again what we have what we studied before what what we learned here is that interaction between solid surfaces, ionic solutions and macroscopic electric field that is what we are talking about here. We will be discussing about electrophoresis and electro osmosis here. Both are manifestation of electrostatic component of the Lorentz force on ions and surface charges. And Newton’s second law of motion now now if I if I look at the electro osmosis.

If I look at the electro osmosis the second the last component, electro osmosis is motion of electrolyte liquid with respect to a fixed wall, due to electric field applied parallel to the surface do you do you agree to this what we have discussed here here. On this on this paper what we have discussed is basically the motion of electrolyte liquid, with respect to a fixed, wall the wall was fixed electrolyte liquid is moving due to electric field applied parallel to the surface. Field is applied parallel to the surface field is in this direction. So, field is applied parallel to the surface. So, that is that is what referred as electro osmosis. Now, if we look at what is electrophoresis in the power point slide. Induced drift motion of colloidal particles or molecules suspended in liquids due to an electric field, what that means is, that you have similarly, a positive and a negative electrode and you have a colloidal particle or think of a particle all together.

You have a particle, you have a particle, if the particle is big if the particle is big, you will you we can one can show that you have an electric double layer developing around the particle. And this particle as a whole will be pulled to one one electrode on the other hand there would be drag force acting on the particle because moving a particle to one electrode it has to overcome the drag force. So, it would be an inter-play between the drag force on the particle and electric double layer that is developed around the particle, which would be pulled by the electrode. So, this this would be a another another game, where these these concepts of electric double layer will be important, but in a in a different way. So, this sort of scheme is referred as electrophoresis. So, depending on how what is the size of the particle etcetera that will be or how much of charge it has on the particle, it will be pulled by different velocities.

And velocity by that I mean the terminal velocity so, that means, if you if you take this system apply the voltage, run it for some time and then freeze it. Then you will see that that over that delta t time each particle has moved by some distance, depending on the size of the particle and depending on the charge that it has. So, you will find that the particles of same size or particles of same charge they will be forming band and by identifying this bands you can or probably from p calibration and then running the sample then you can identify the particle is having these properties or the sample that you have it contains A, B, C, D and A is A is of this size and this charge, B is of this size this charge. So, this kind of analysis you can do.

So, these these are essentially. So, what I what I want to mention here is the we so, we we understand interaction between solid surfaces, ionic solutions and macroscopic electric field; we understood what is at least that interplay of electrostatic component of the electrostatic components and this Newton’s second law motion and I mean we have some idea of what is. So, electrophoresis is induced to drift motion of colloidal particles or molecules suspended in liquids, due to an electric field and electro osmosis is motion of electrolyte liquid as a whole, this we already discussed. So, this is what we had? Now, this electric double layer once again, the solid surface why solid surface will acquire a surface charge because when it comes into contact with an electrolyte liquid there are so many, things that can happen 1 2 3. Deprotonation is most common and of course, the p H has good effect on the so, so the net surface charge would be functional local p H.

Then we said that these ions of opposite charge in the electrolyte are attracted and the like charges are repelled. The net excess of mobile ions, net excess of mobile ions near the net excess of mobile ions near the interface with charge opposite to that of the wall is opposite to that of the wall is referred as electric double layer, these excess charges these excess charges can be used to impart a force on bulk fluid through ion drag and a counter ions counter ions reside in compact layer next to the wall, which is referred as the stern layer. That is in adsorbed state and counter ions also reside in more diffused layer next to the wall where the ions are free to move.

Now, now one thing I would like you to appreciate here, is that if I if I look at what we what we are writing here on this paper. We said that we have we have some charge. We have some charge here, say these these are all this is the wall and we have positive charges here. This is I mean then I mean even if even if this wall is a metal, still we can have this kind of charge, there would be a layer, which is referred as Thomas-Fermi layer. The thickness of this layer is maximum it goes to 0.2 nanometer even it is less than that. That is where these these charges are predominant. Beyond this I mean these these when it comes to metals, I mean it has it has electrons it has the they have they are the they have they have practically excess charges available.

So, what what the essentially, what these what these researchers they have they they found is that this these charges are heavily screened. Heavily screened in the sense that these charges will remain this way, I mean it will not you will not expect, even if this is a metal that this charges will escape. So, this there is a screening involved, this screening this so, this is this is referred as a Thomas-Fermi layer within which this there would be concentration of charges, but that does not, because as such there would be lot of charges inside, I mean there there are lot of I mean, I do not want to get into the distribution of atoms etcetera, but there are available charges as such, which will ensure that this charges is screened next to the wall up to a distance which is less than 0.2 nanometer. That is that is what you have to keep in mind though so, even even if you have a metal wall still you can have this possible.

It is not it need not be it has to be a colloid or something like that. So, this is this is what you have one thing. Second thing is this existence of this opposite charge. So, this is this is the end of the wall. So, this bold line is the wall. So, this plus these are this is little bit inside the wall. Now, immediately outside the wall there would be opposite charge we said right. So, you will you will be having a very small distance a very small distance where these negative charges are held. One thing, I want you to appreciate, I mean this we are work still working with the framework of whatever studied in a microscopic scale. So, there would be say adsorption of neutral atoms possible on the wall. So, it is not that it will be all arrange plus and minus, there could be a large atom, large neutral entity sitting there adsorbed on the surface. There could be there could be so, many other things happening, but as far as the charges are concerned, they are there that is what and since we are talking about electric double layers so, we are only focusing on charges we are not talking about other other entities.

But there will be other entities also present for example, a neutral neutral molecule will be adsorbed on the surface and which is very much possible there will be adsorption, desorption everything is going on; plus on addition on top of it there would be these array of charges present. Now, this layer a very small, very thin layer, where the charges which are there inside this layer these these these charges are held strongly, these charges are held adsorbed to the wall and these charges are referred this layer this layer is referred as stern layer s t r e n stern layer. Now, this existence of this layer, I mean it is very difficult to confirm, I mean what what exactly is happening. In fact, the researcher who who was doing the pioneering work here is Helmholtz? Helmholtz is the person. In fact in fact this layer in lot of places you will find that the the initially it used to be referred as Helmholtz layer.

Now, this the problem would the problem was there is that this layer what what researchers have is found is that there exists another layer, which is probably much on a wider level, where you have predominantly minus charges and some plus charges as well little one some plus charges as well, but predominantly minus charges. But some plus charges here and there. And these charges they are mobile, they are not strong they are not adsorbed by the wall they are mobile and these charges can be pulled by application of an by putting an electrode, these charges can be pulled. And these charges can give body force to the Navier-stokes equation and pull the rest of the liquid as a whole.

So, so these charges are what what matters? So, then probably they differentiated into this stern layer which is next to the wall and these these diffused layer. It is it is this called Chapman layer there are there are various scientists who have. So, initially it was some proposition and then later on from initially there it was it was proposed from the proposed from the free energy point from thermodynamics point of view and then they said there should be provision like this and then people have showed, I mean electro osmotic pump is an existence, people have shown movement of fluid by this method. So, so, the naturally that this there has to be a diffused layer so, then then these so, these these things continue to develop.

I should I have to wrap up this discussion here, what I will do in the in the next class is, I will start start solving, I mean I will start writing the governing equation that defines what would be the concentration of plus ions. C plus as a function of z, C minus as a function of z what is z? Z is distance from the wall z is distance from the wall. So, How plus concentration changes with z? How minus concentration changes with z? Because this information is very important once we have that then only we can develop we can write down the body force term in Navier stokes equation and then and then because our final aim is to find out what would be the velocity. From Navier stokes equation, I do not apply any pressure drop, I do not apply any pressure delta p, I mean p inlet and p outlet they are held at same pressure p inlet and p outlet held at same pressure.

I have applied just the voltage and now, I am seeing the bulk movement of the fluid and what is the velocity, what is the average velocity, by which the fluid is moving that velocity I have to find out. So, I have to use Navier stokes equation only with the body force term would be, arising from these ion drag. So, before before we find out it is very important that we find out how the concentration changes plus ion concentration and minus ion concentration, because here you can see the minus ion concentration would be, higher at z equal to 0, and then it goes down then if that is so, then the opposite ion concentration would be just the reverse. So, what would be the functional form? So, we will start from there. So in the next class, we will start from there. That is all I had for today is discussion.