Colloids and Surfaces
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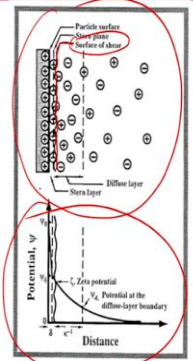**Indian Institute of Technology, Madras**

Lecture – 40
Electrokinetic Phenomena and Zeta Potential Measurement

We look at new module, module 5, in which we going discuss about what is called as electrokinetic phenomena, which is a useful tool for measuring what is called as zeta potential. So, this is going to be the contents for this lecture. So, will briefly again recap, what is zeta potential and we will look at some examples where zeta potential measurement becomes important and I will introduce electro-kinetic phenomena in this lecture.

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So, we have looked at what is zeta potential already. So, electrokinetic measurements are used for measuring zeta potential which is the experimentally determined potential measured in electrical double layers. So, this is a schematic of electrical double layer and this is how the potential falls with distance and we have learned that zeta potential is the potential at the plane of shear which is essentially given by this line that I am tracing.

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Zeta Potential

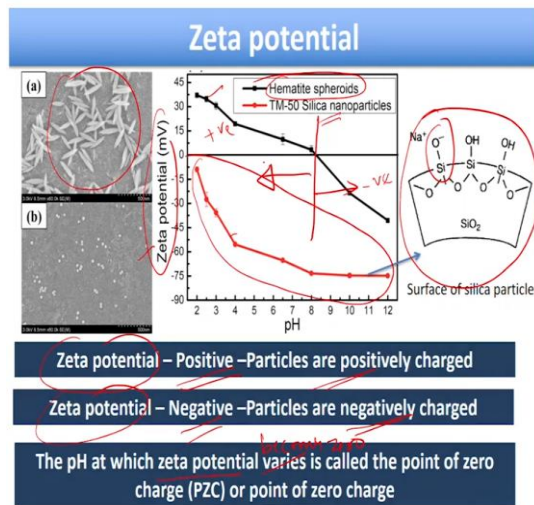So, we will so zeta potential depends on several factors the factors that influence are the surface chemistry and the surface charge density of the particles it does depend on solution conditions for example, pH of the fluid is important it also depends on the presence of additives such as electrolytes and electrolytes.

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Now, we look at some salient features of zeta potential for different materials. So, what you are looking at here is zeta potential measured for two types of particles one is hematite spheroids that is given by the black line and silica nanoparticles which is given by the red line and the corresponding SEM micrographs of the particles are given as well. So, you can see that the certain and what is plotted as a zeta potential as a function of pH in this particular case, and you will see that under certain pH conditions.

The zeta potential is positive and under certain conditions the pH conditions the zeta potential is negative for hematite particle However, if you look at silica nanoparticles, so, all throughout the pH window that has been considered the zeta potential is always negative. And the reason why the silica surface has negative value or the negative zeta potential is because of the surface chemistry of the particle itself.

There are certain all groups on the surface of silica particles and the dissociation essentially leads to SiO^- group on the particle surface which leads the particle to have a negative charge on the surface. So, in it is by convention, the zeta potential is positive for the particles that are positively charged and the zeta potential is negative for the particles that are negatively charged and you would always come across cases.

Where you will have under certain conditions you could have the zeta potential to be 0 as well. So, in this particular case concerning hematite particle the pH at which the zeta potential becomes zero, the potential becomes is called the point of zero charge and this is a useful quantity because whether a given dispersion of colloids is stable or not depends on how far you are from the isoelectric point.

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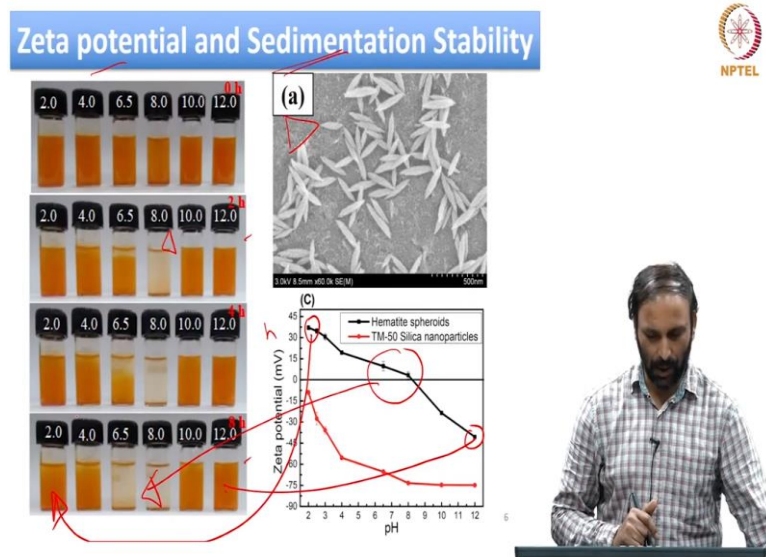
So we will again look at some examples of this in the next few slides. So, what you are looking at is connecting zeta potential measurements to sedimentation stability these are vials of images which contain hematite particles, these are iron oxide particles and that is why the dispersion appears reddish brown in colour. And what is done is this dispersion has been

prepared at certain particle concentration and the concentration of particles in all the vials is exactly the same.

However, the dispersion ph changed from 2.0 all the way up to 12 that means, there are some dispersions which are acidic in nature and there are some dispersions which are basic in nature. Now, what you are looking at is again, a time sequence images, where the images of vials have been taken at different time intervals, this is for 0 hour, this is for 2 hours, this is after 4 hour, this is after 8 hours.

And as you can clearly see that, at least visually, what one could see is that the dispersion of these particles at a pH of 12, you do not see any visual changes and so, is also the case if you look at the pH 2, however, if I look at intermediate pH values, you see that at the end of about 2 hours, at pH 8, there is all the settling of particles and if you look at pH 6 and a half there is some settling that occurs at about 2 hours.

But however, if you wait for long enough time, there is about 8 hours you see that all the particles are essentially sedimented at the bottom. So, this example tells us that the charge of the particular or the zeta potential is one of the important factors that can dictate the sedimentation stability of the given dispersion and looking at you know the zeta potential plot here.

So, if you so, the plots corresponding to so, this vials that we are looking at here, it corresponds to the pH 2, and this corresponds to pH of 12 that has this particular point. And however, somewhere in between we see that there is the sedimentation therefore, highly charged particles exhibit a better stability against sedimentation versus less charged or low charged particles.

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Zeta potential and Drying Problems
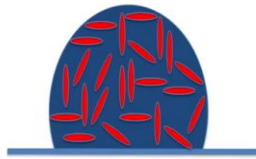
Such drop configurations are important for
(a) Inkjet Printing
(b) Spray Coating
(c) Deposition of pesticides and nutrients, etc..

The second example that I would like to point out as the application of zeta potential measurements and how they are important in drying problems so what you are looking at is a configuration where there is a substrate, and there is a drop and this drop contains particles and the fluid it would evaporates because you know, if you take like say, if there is a dispersion in water, you will see that with time, although the fluid will evaporate and the in the end, what you end up with is that you know, on the glass substrate.

I would have the deposition of particles. So, it turns out that this simple drying problem is important in several technological important processes, examples are inkjet printing spray coating, and as well as deposition of pesticides and nutrients, on leaves and so on and so forth.

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Measurement of zeta potential
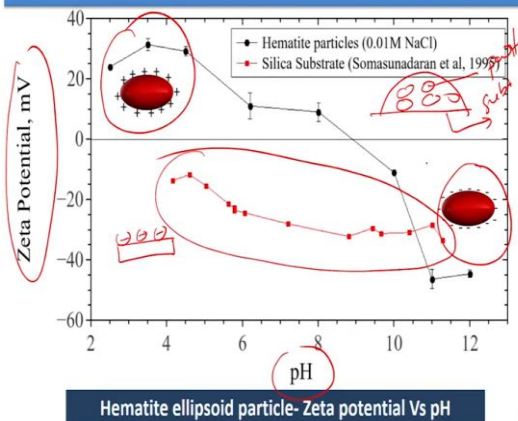
Hematite ellipsoid particle- Zeta potential Vs pH

So, if we look at the configuration that we had here, so, that is you had a glass substrate or you had a substrate in which you had particles. So, in such an example of what is important is the zeta potential of both the dispersed species that is the particles in this case, as well as the zeta potential of the substrate become important. So, what is plotted here is zeta potential as a function of pH and like we discussed earlier.

The substrate that is being used is silica surface, therefore, all through the pH window, the glass is negatively charged. Because the zeta potential is negative, and however, because these are hematite particles, so we have a pH window where the particles are positively charged, and there is a pH window where the particles are negatively charged.

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So, we look at some salient so, what happens in a drying problem is that when the liquid evaporates from the free surface of the drop there is what is called as a capillary flow that is established and this capillary flow drives the particles to the contact line. What we are looking at is a movie where there is a dispersion of particles, these are 3 micrometre particles 3 micrometre in diameter, and we are looking at what happens at edge.

This is the boundary or the three phase contact line and with time, what happens is that this capillary flow dries the particles and it helps in the deposition of particles at the contact line. So, this is a classic phenomenon called what is called as a coffee-ring effect, that is because, similar features are found when a droplet of coffee dries.

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Zeta potential and Drying Problems
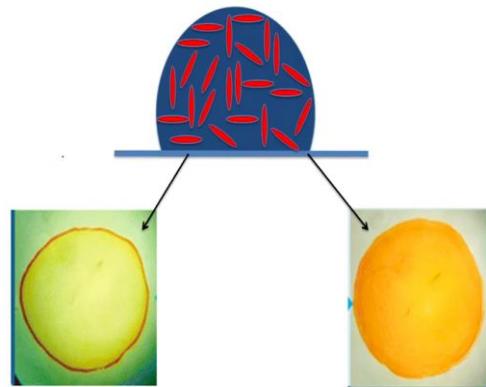
So, with this in mind, if we deposit or dispersion can containing elliptical particles, that is hematite particles on a glass substrate, it turns out that there are conditions where we get a classic coffee-ring effect. And of course, there are conditions where you get a more uniform deposition of particles to throughout the deposit.

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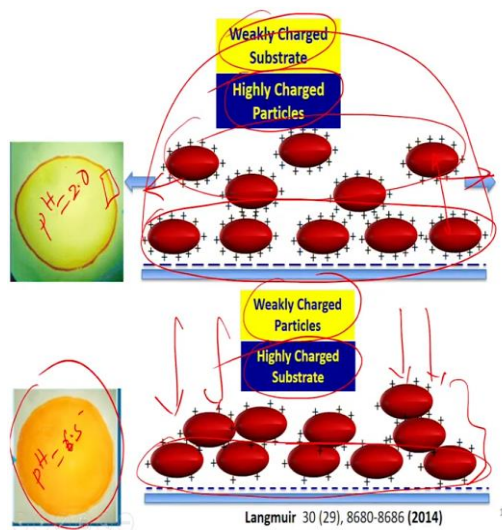
So, now, one could understand why such different deposition patterns have formed, even though we have considered dispersions of similar type by the fact that the result that you see here, this is for a case where the pH is about 2.0 and this is for a case where the pH is about 6.5. And it turns out that in the case of pH 2 the particles are highly charged and the substrate is weakly charged.

So, in such cases, because of the electrostatic attraction between the highly charged particles and the substrate, there is a deposition of a layer of particles on the substrate. However, once

a layer gets deposited, there is repulsion between the particles in the fluid and the particles that are already deposited on the substrate. Therefore, there are a lot of free particles in the dispersion or in the drying drop.

And these free particles are carried to the edge because of the capillary flow that we saw in the previous video and that leads to the deposition of particles at the edge giving such a pattern. However, if you look if you look at the case, where the pH is 6 and a half the substrate is highly charged and the particles are weakly charged. And therefore, there are many layers of particles deposited on the substrate, because of the fact that the substrate is highly charged now.

So, it cannot attract more layers of particles even though there is a deposition of particles, one layer of particles on the surface further deposition is still possible, because of the highly charged nature of the substrate. Therefore, all the particles are kind of attracted towards the substrate leaving no particles in the bulk therefore that leads to a more uniform deposit formation.

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So, therefore, in problems such as drying, of droplets, the fact that pH 2 you get a coffee-ring effect and pH 6 and a half, you get a more uniform deposition, it can be explained based on DLVO interactions, which essentially is the fact that the total DLVO interactions is a summation of the Van der Waals force of attraction and the electrical double layer attraction. However, in this case, the DLVO interactions have two components.

One is the particle-particle interactions and the particle-substrate interactions. Therefore, depending upon the overall DLVO interaction which is the summation of the DLVO interaction arising because of the particle presence of particles as well as the particle and the substrate that is what governs the deposition in such cases.

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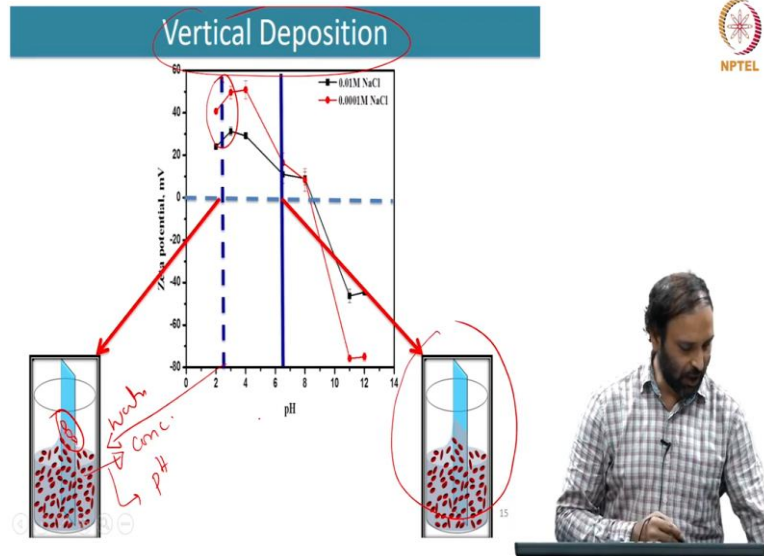
So, another example of how one could manipulate the arrangement of particles on the substrate is again from an example where there is a technique called vertical deposition. In this technique, what is done is there is a dispersion which contains particles and what you do is you maintain this dispersion at a certain concentration of particles and you maintain the pH under certain conditions.

And so, you let the fluid evaporate that is if the fluid is water under normal you know ambient conditions it would evaporate and as the evaporation of occurs, these particles that you have the dispersion they are drawn to the three phase contact point and then the particle start get the particles get deposited on the substrate. Now, what is done in this case is the conditions are chosen such that the pH is about a 2, 2 and a half. Such that the; particles are again highly charged and again a condition of pH such that the particles are weakly charged.

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Venkateshwar Rao Dugyala and Madivala G. Basavaraj. RSC Advances. 5, 60079-60084 (2015)
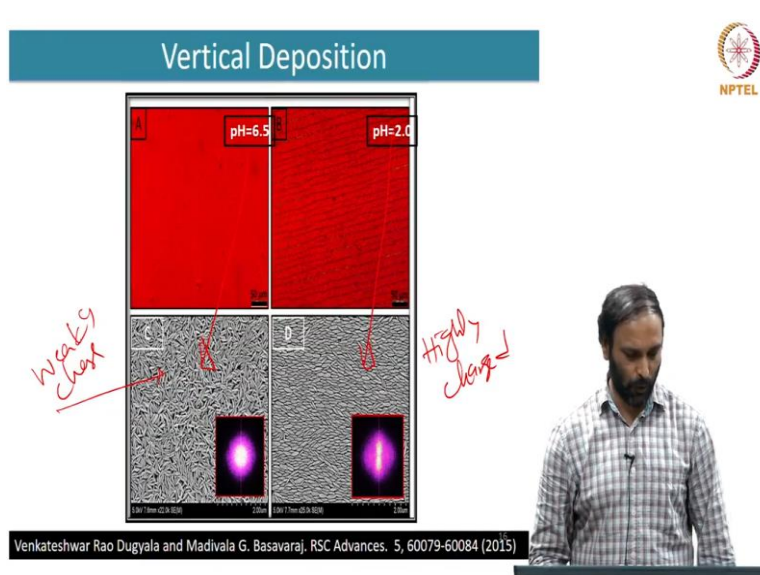
So, after the deposition if you look at the glass slides under microscope, you will see that the sample appears reddish brown because of the fact that these are again iron oxide particles However, if you look at the microstructure or the arrangement of particles on the substrate, it looks very different. When the pH is 6 and a half versus when the pH is 2 therefore, when the pH is 2 because of the fact that the particles are highly charged you have more ordered arrangement of particles and the substrate.

However, when the pH is 6 and a half that is weakly charged particles, there is a random arrangement of particles and the substrate therefore, one could use the zeta potential measurements and the fact that with the change in the zeta potential measurements. The total interactions or the contribution of the electrical double layer interactions can be manipulated and those aspects can be exploited to obtain different self-assembly patterns and this different deposition patterns as well as to control the stability of dispersions or the stability of particles in a fluid.

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Electrokinetic principles

◆ Electrokinetics implies combined effect of motion and electrical phenomena. Such phenomena are commonly observed in heterogonous fluids and is associated with the double layer of charges. Hence such phenomena are of interest in studying suspensions containing charged colloids.

◆ Some examples of electrokinetic phenomena:

◆ Electrophoresis
◆ Electrosomosis
◆ Streaming potential
◆ Sedimentation potential

So, with that background, so, we will look at what is electro kinetic phenomena electro kinetic essentially implies a combined effect of motion and electrical phenomena. And such phenomena are commonly observed in heterogeneous fluids when we say heterogeneous fluids this is these are fluids containing particles and it is associated with the double layer charges.

The fact that there is an electrical double layer around charged particles that essentially manifests in the electro kinetic effects and therefore, such phenomenon is of interest in studying dispersions containing charged particles and some of the examples of electro kinetic phenomena or what is called as electrophoresis, electro osmosis, streaming potential and sedimentation potential. So, we look at each of these aspects.

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An example of Electro kinetic Phenomena

Consider an electroplating process – use of an externally applied electric current to metal ions to form a metal coating on substrates (electrode).
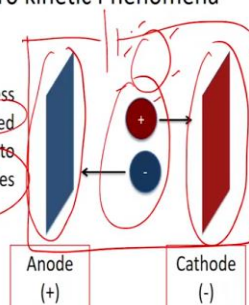
Anode (+)   Cathode (-)

Migration of ions
Positive ions migrate toward the cathode and negative ions migrate toward anode
Positively and negatively charged colloidal particles display similar migration behavior
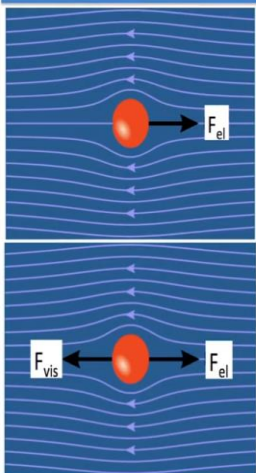
Before we do that, I would like to give an example of an electro kinetic phenomena that we all of us know if you look at processes such as electroplating. So, what is done is you use an externally applied electric current to deposit metal ions on substrate. So that you can obtain a metal coating. So, these phenomena called electro plating and a schematic that is given to you here is you have 2 electrodes anode and a cathode and you could have this in a bath of electrolyte and when you complete the circuit.

When you apply in an electric current, it turns out that there is migration of ions to different electrolytes the positive ions will migrate towards cathode and the negative ions migrate towards the anode. So this is an a classic example of electro kinetic phenomena where there is a combined effect of electric field combined with the motion of ions towards oppositely charged electrolytes, in a similar way, you instead of ions in the bath, if you have charged particles, and these charged particles would also migrate and will discuss some of the phenomena associated with the charged particles.

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So, in the next few slides, so, let us look at the migration of an iron in the electric field. So, what you have is a we will take a simplest case where or a simple case where you have an isolated iron you know a fluid and what is being done as an electric field is applied an isolated electron or an ion in an electric field it experiences a force that force is given by F_{el} which essentially is given by the product of the charge.
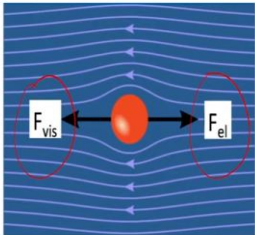
That the electron has or the ion has multiplied by the strength of the applied electric field and in and whenever you have an ion, so, it essentially migrates towards the oppositely charged

electrolyte electrode because of the force that the isolated ion experiences in the electric field. And so, whenever you have a motion of any particulate matter or any iron enough in a fluid, we know that there is going to be some opposing forces.

And this opposing forces arise because we have what is called viscous resistance in the medium and what this viscous resistance does is it essentially hinders the motion of the particle and it slows down the ion that is set into motion because of the applied electric field and this F viscous is given by f times v where f is what is called as the friction factor and v is the velocity with which the isolated iron is moving in the electric field.

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And although the particle would accelerate when the electric field applied initially, because of the balance between the viscous forces and the electrical forces, there is going to be an equilibrium or a stationary state is quickly reached when the equilibrium is established between the two forces, in the absence of other effects, we can equate F_{el} to F viscous therefore.

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Electrophoteric mobility of an ion in an electric field

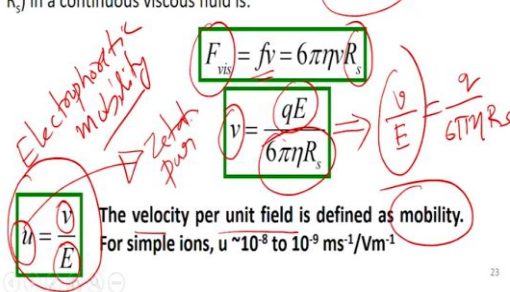$$F_{el} = F_{vis} \Rightarrow v = \frac{qE}{f}$$

For conditions of very low Reynolds number flows (Stoke's law), the frictional force or the drag force exerted on spherical object (of radius R_s) in a continuous viscous fluid is:

$$F_{vis} = fv = 6\pi\eta v R_s$$

$$v = \frac{qE}{6\pi\eta R_s}$$

The velocity per unit field is defined as mobility. For simple ions, $u \sim 10^{-8}$ to 10^{-9} ms^{-1}/Vm^{-1}

$$u = \frac{v}{E}$$

The velocity with which the electron or the ion is moving is given by q times E divided by f where f is the friction factor and, because of the fact that the dimension of the isolated ion that we are considering is very, very small the Reynolds number that is in N Rep that is the particle number which is given as diameter the particle the velocity which is the particular moving density of the fluid divided by mu because of the fact that the dimension of the particle under consideration is very, very small.

That is of the order of sub nanometer. Therefore, this Reynolds number is going to be much less than 1 therefore, we can assume that the flow is essentially low the low Reynolds number flows. Therefore, the friction force or the drag force experienced by the isolated iron is given by F viscous is equal to F_v is equal to 6 pi eta v times R_s where R_s is the dimension of the spherical object or the dimension of the isolated ion that are under consideration.

So, therefore, the velocity with which the particle is moving or the velocity with which the accelerated ion is moving is given by q times E divided by 6 pi eta times R_s. So, now I can rearrange this expression and I can write v divided by E = Q divided by 6 pi eta into R_s and this quantity v / E that is the velocity per unit field with which the ions are migrating that is what is called as a electrophoretic mobility this is what is called as.

So, whenever electro kinetic measurements are done, one of the quantity that is really extracted from electro kinetic measurements is this mobility that is the velocity with which the particles are moving in the field for a given for a field of given strength and this quantity

is what will be used to relate to the zeta potential of the particles and which we will discuss in the in the next lecture.