# Colloids and Surfaces
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## Lecture - 41
## Electrokinetic Phenomena

Having discussed zeta potential and the importance of zeta potential measurement in some of the problems, we will look at electrokinetics further.

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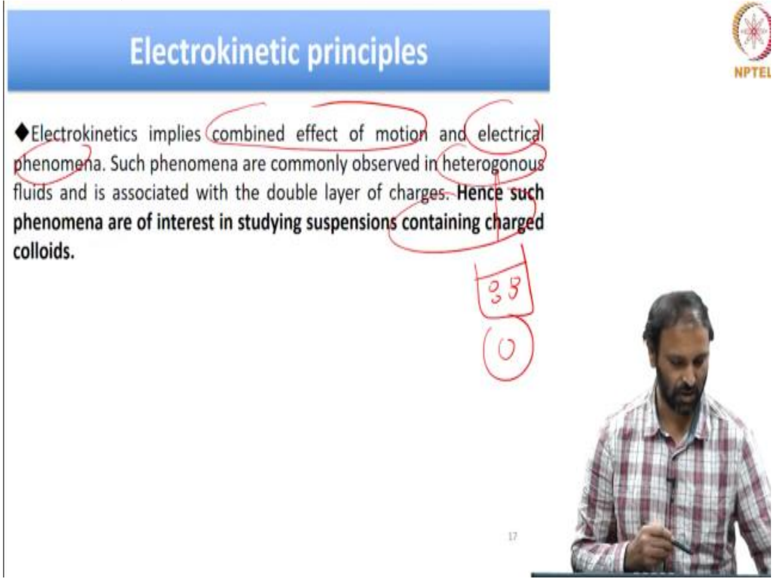

Electrokinetic principles

◆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.**

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Electro kinetics implies combined effect of motion and electrical phenomena and such phenomena can be observed whenever you have a heterogeneous fluid that is in case you have a particle filled fluids and if these particles are charged then you will have an electrical double layer associated with it. So, whenever you have systems like this the electrokinetics effects become important and such phenomena is of interest because that will help these phenomena will help us to study charge stabilized colloids or system in which the colloidal particles are charged.

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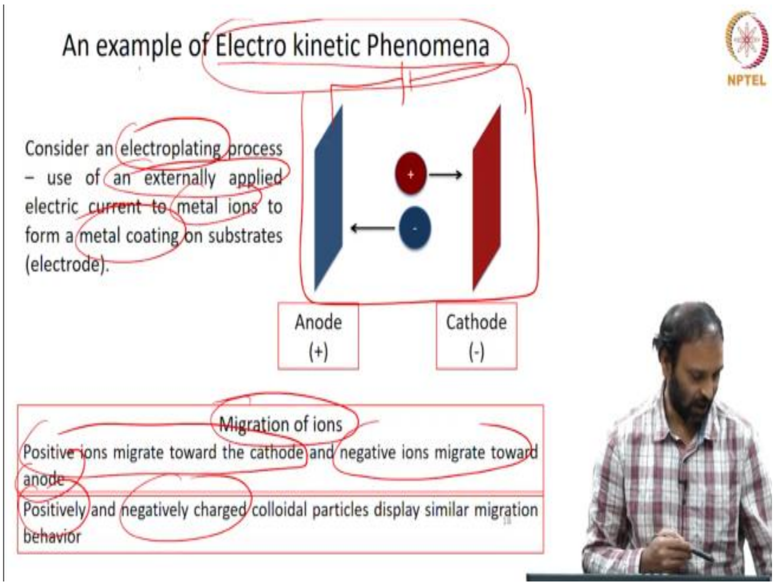

An example of Electro kinetic Phenomena

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

So, before we talk about electrokinetic phenomena in colloidal system, I would like to introduce electrokinetic phenomena from a concept that you may already be familiar with if you look at electroplating process in which what is done is an external electric field is applied to a solution which contain metal ions the schematic is given here. So, there is an anode and a cathode and you can imagine that you know there is a bath of electrolyte which contain like say metal salts.

And whenever electric field is applied, what happens is that there is a migration of ions and then these metal ions may get deposited on the electrode. So, that you can get a metal coating on substrates, this is one of the commonly used techniques called electroplating. And, so, what you see in electrokinetic in electroplating is that there is a migration of ion positive ions migrate towards the cathode and the negative ions migrate towards anode.

And so, similar to migration of ion, if you have positively charged particles or negatively charged particles, there will be a migration of colloidal particles similar to either the migration of ions that we have discussed. Therefore, the electroplating process is an example of a, phenomena where electrokinetics is observed.

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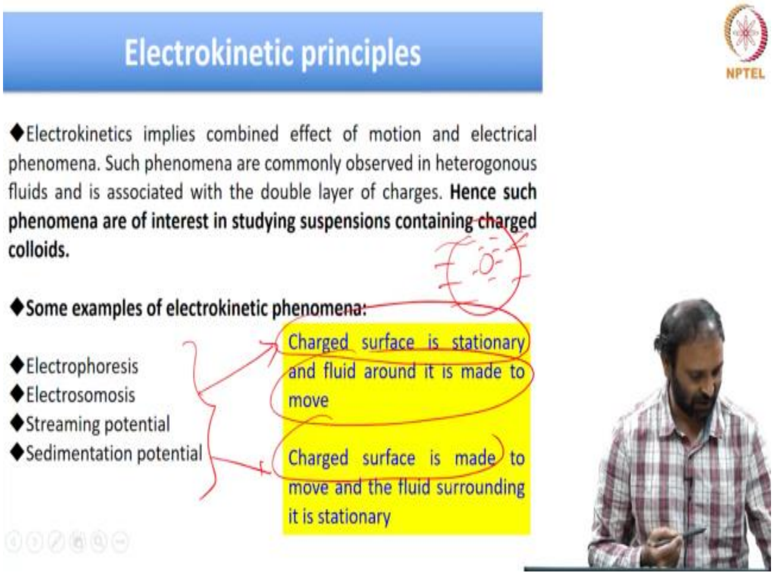

**Electrokinetic principles**

◆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

Charged surface is stationary and fluid around it is made to move

Charged surface is made to move and the fluid surrounding it is stationary

So, there are several examples of electrokinetic phenomena that we are going to discuss, we will mostly focus about the electrophoresis. However, there are also other techniques called electroosmosis, streaming potential, sedimentation potential, which are also important in the context of studying charged surfaces. So, mainly these 4 electrokinetic phenomena can be subdivided into 2 categories, one category where charged surface is stationary and the fluid is made to move around, fluid around it is made to move.

So, therefore, so, you could have a case where I have a charged particle for example, then there is fluid around it. So, if this is a fluid. So, in a class of technique, the charged particle is stationary or the charge surface is stationary. However, the fluid that is surrounding the charge surface is made to move in other class of technique, the charge surface is made to move while the fluid surrounding it is stationary, we will discuss some of these techniques not in great detail, but just to give an idea of what these methods are in electrophoresis.

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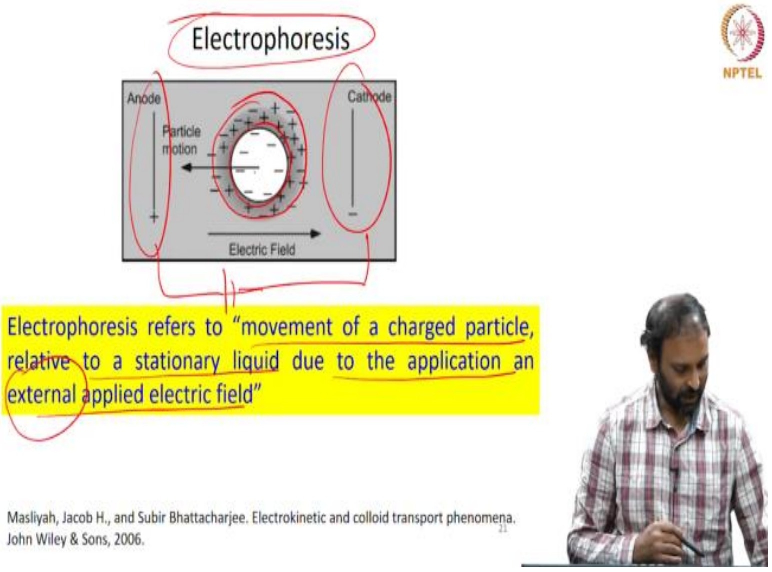

Electrophoresis

Electrophoresis refers to "movement of a charged particle, relative to a stationary liquid due to the application an external applied electric field"

Masliyah, Jacob H., and Subir Bhattacharjee. Electrokinetic and colloid transport phenomena. John Wiley & Sons, 2006.

Electrophoresis is very similar to what we saw in the case of electroplating. Electrophoresis refers to a movement of a charged particle relative to a stationary fluid due to the application of an electric field or due to the application of an external electric field. So, you have particles in a fluid, there is an anode and a cathode. And you have a charged particle that is depicted here. And there is an electrical double layer that is associated with the charged particle and whenever you apply an electric field, what happens is that the particle moves this phenomenon is what is called as electrophoresis.

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So, this is a video of an electrophoresis which is observed. So, what you are looking at is a video where the circular dots that you see here, these are all the particles and you will notice that the particles are moving in a particular direction until sometime let me just play the video again. So, the particles are moving in this direction initially, after a while, you will see that the particles start moving in the opposite direction that is now they are moving in the opposite direction.

So, now, this is a case where you have charged particles which are in between two electrodes and what is applied is an AC electric field and because of the alternating polarity, you will see that the particles move in 1 direction during you know one cycle and they move in the opposite direction in the other cycle. And you could of course, have a case where what is called as a DC electrophoresis.

When you will see that the charged particles depending upon whether positively charged or negatively charged they will start moving towards one of the electrodes as well. So, this is an example where there are charged particles in a fluid and you set the particle into motion by applying an external electric field.

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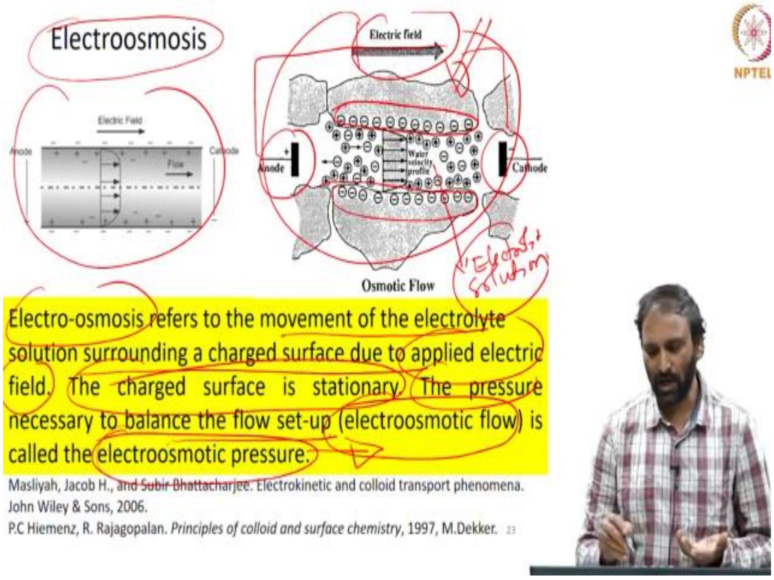

Electroosmosis

Electro-osmosis refers to the movement of the electrolyte solution surrounding a charged surface due to applied electric field. The charged surface is stationary. The pressure necessary to balance the flow set-up (electroosmotic flow) is called the electroosmotic pressure.

Masliyah, Jacob H., ~~and Subir Bhattacharjee~~. Electrokinetic and colloid transport phenomena. John Wiley & Sons, 2006.

P.C Hiemenz, R. Rajagopalan. *Principles of colloid and surface chemistry*, 1997, M.Dekker. 23

Now, another class of technique called electroosmosis there are two schematics here. And so, you could think about this schematic as a case where you have a pore and say that the surface of the pore is charged in this case it is negatively charged and what is contained between the charge surface is an electrolyte solution and now, what you could do is that you could apply an electric field which can be generated by you know having two electrodes and supply and connecting two electrodes to an external supply.

So, now, when you apply electric field what happens is that the electrolyte solution that is between the two charge surfaces is set into motion. So, electroosmosis refers to the movement of the electrolyte surrounding a charge surface and the movement of the electrolyte is achieved by the application of an electric field. However, the charged surface is stationary therefore, the electrolyte solution moves with the charge surface being stationary therefore, there is a relative motion that is set in because of the applied electric field.

The pressure that is necessary to balance the flow that is set up because of the applied external electric field is what is called as electroosmotic flow and this pressure which is called the electroosmotic pressure can be easily measured and one could correlate the electroosmotic pressure to the charged of the surfaces that we know we would like to investigate. So, therefore, in this technique, what is set into motion is the electrolyte and the motion is set by an applied external field and what is measured is the osmotic pressure and that can be related to the charge of the stationary surface.

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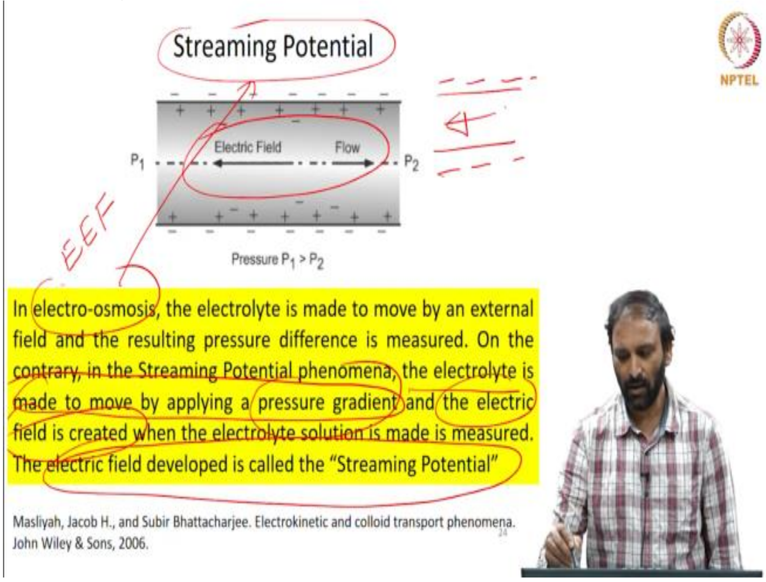

Streaming Potential

In electro-osmosis, the electrolyte is made to move by an external field and the resulting pressure difference is measured. On the contrary, in the Streaming Potential phenomena, the electrolyte is made to move by applying a pressure gradient and the electric field is created when the electrolyte solution is made is measured. The electric field developed is called the "Streaming Potential"

Masliyah, Jacob H., and Subir Bhattacharjee. Electrokinetic and colloid transport phenomena. John Wiley & Sons, 2006.

On the contrary, in what is called as a streaming potential what is done is the electrolyte is made to move by applying a pressure gradient we know that whenever you have a charged surface and if there is electrolyte, which is in between these two charge surfaces, I can set up a fluid motion by applying a pressure gradient. And because of the fact that now you have charged species in the electrolyte their motion is going to induce an electric field.

And that electric field is what is measured in streaming potential the effective electric field that has developed is what is called as a streaming potential. So, the difference between the electroosmosis and the electro and the streaming potential is essentially that the phenomena are similar that is you have stationary charge surfaces in both the cases and what is moving is the electrolyte however in the electroosmosis, the electrolyte is made to move by applying an external electric field. However, in the case of streaming potential the electrolyte is set into motion by applying a pressure gradient.

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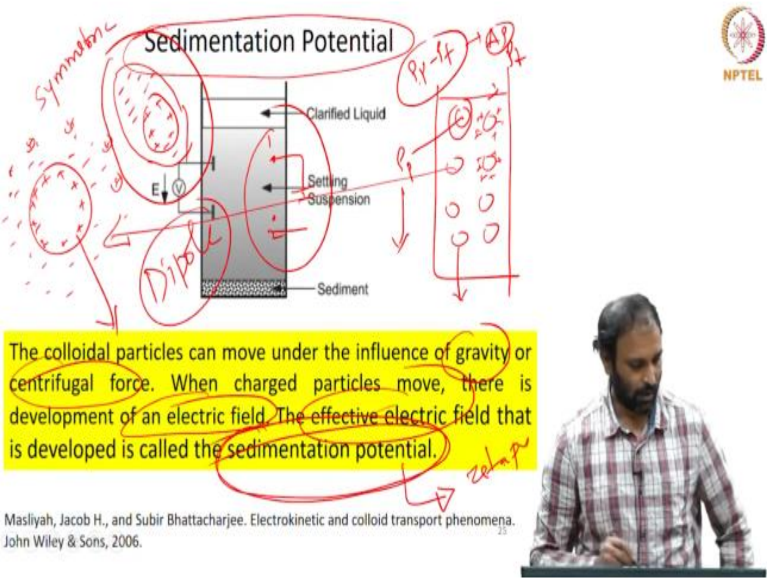

Sedimentation Potential

The colloidal particles can move under the influence of gravity or centrifugal force. When charged particles move, there is development of an electric field. The effective electric field that is developed is called the sedimentation potential.

Masliyah, Jacob H., and Subir Bhattacharjee. Electrokinetic and colloid transport phenomena. John Wiley & Sons, 2006.

The last of the electrokinetic technique is what is called as sedimentation potential. So, we know that if you have a system that contains particles and these particles can sediment to the bottom of the container either because of gravity or centrifugal force. So, if the fluid density is like say rho fluid and if the particle density is rho p. So, we know that rho p minus rho f is an important parameter which will dictate whether there is going to be sedimentation of particles which is driven by gravity or centrifugal force.

If there is a large difference between the densities of the particle the fluid we can expect that the gravity settling would be a prominent. However, if the delta rho or the density difference is small then you know one could you know make the particle settle by the application of an external field. Now, if these particles are charged let us consider these particles are positively charged now, because of the fact that you have charged particles now, and the motion of these charged particles can set up an electric field.

So, now, if you look at individual particles, so, we know that I have a particle that is charged. Now, every charged particle would have an electrical double layer associated with it, so we know that there is going to be a counter ions in solution and more counter ions as we go away from the surface. And of course, there is going to be co-ions as well. Now, because of the so, when the particles are stationary, this electrical double layer around a charged particles is symmetric.

However, when the particles move because of the gravity, there is going to be a distortion of the electrical double layers that means if they are moving in a particular direction you will see that the charged particle is here. Now, the electrical double layer around it is going to be somewhat distorted with more counter ions in one region versus the other. So, because of which the system of the colloidal particle and associated double layer looks more like a dipole.

So, whenever you have charged particles settling, you can imagine that instead of a colloidal particle, every particle and electrical double layer combination can be imagined like a dipole and the summation of all these dipoles will lead to an effective electric field and that effective electric field that has developed is what is called as sedimentation potential therefore, if you essentially take 2 regions.

For example, region 1 here and region 2 here and if you measure the potential difference, there is going to be a potential difference that has developed that will depend on the concentration of the particles that you have the surface charge and the particle and a lot of other parameters and this potential difference can be measured and that potential is what is called as a sedimentation potentials therefore, so one could measure sedimentation potential and of course, this can again be related to the charge of the particle or the zeta potential as well.

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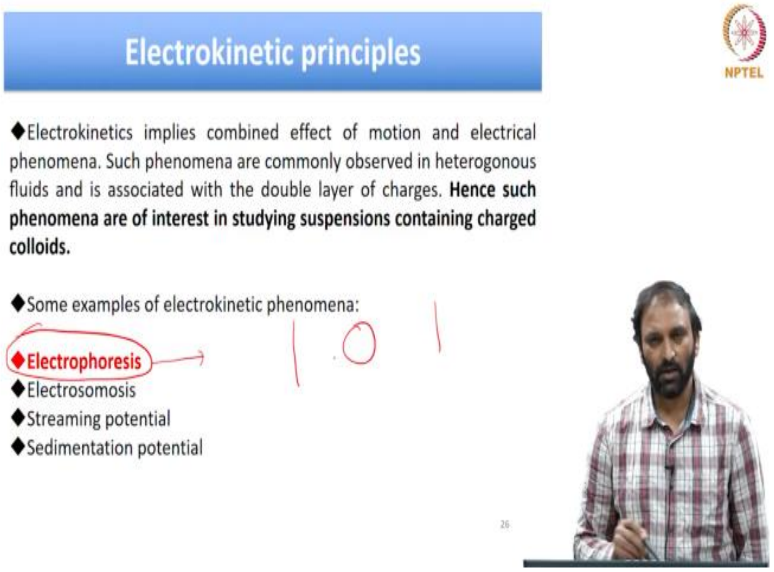

## Electrokinetic principles

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◆Some examples of electrokinetic phenomena:

◆Electrophoresis
◆Electrosomosis
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◆Sedimentation potential

So, now, we will look at electrophoresis in a little bit more detail. So, before we talk about electrophoresis of a, colloidal scale particles.

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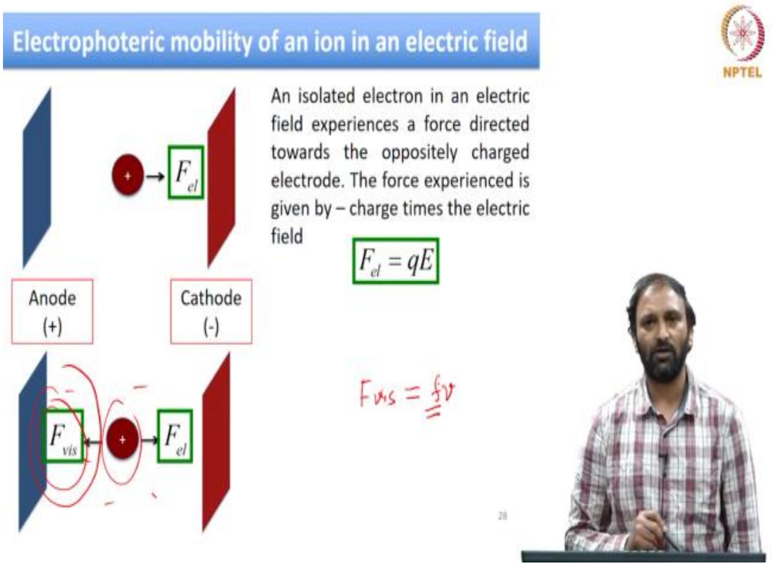

Electrophoteric mobility of an ion in an electric field

An isolated electron in an electric field experiences a force directed towards the oppositely charged electrode. The force experienced is given by – charge times the electric field

$$\boxed{F_{el} = qE}$$

$F_{vis} = \underline{\underline{f}}v$

What we will do is? We will consider a simple case of electrophoresis of an ion in an electric field. So, what you have is a positively charged ion it could be ion with any polarity. So, there is an anode and there is a cathode now, an isolated electron in a or an isolated ion in an electric field experiences a force that is directed towards the oppositely charged electrode so, if you have a positive charge it will move towards cathode and if you have a negative charge it will move towards anode.

So, that force essentially is proportional to the strength of the electric field that is applied the strength of the electric field times the q that is the charge of the isolated ion essentially gives you the force that the isolated ion is experiencing. So, initially the ion could be stationary or it could be moving about because of the Brownian motion. However, once the external field is applied, it will move with this force towards the oppositely charged electrode.

So, when the electric field is applied, so, first the ion is going to accelerate, that means there is going to be a sudden increase in the velocity of the isolated ion. However, this initial increase is going to die down with time that is because, you have and that is because there is an opposing forces that comes into pictures. So, because of the fact that whenever there is a relative motion between the particle and the fluid so, this ion is set into motion.

Now, whenever there is a relative motion between the ion and the fluid that is surrounding it, there is going to be a viscous force that can come into picture and this viscous force is going to oppose the motion of the isolated ion and this force F viscous is given by some friction factor f times the velocity with which the isolated ion is moving.

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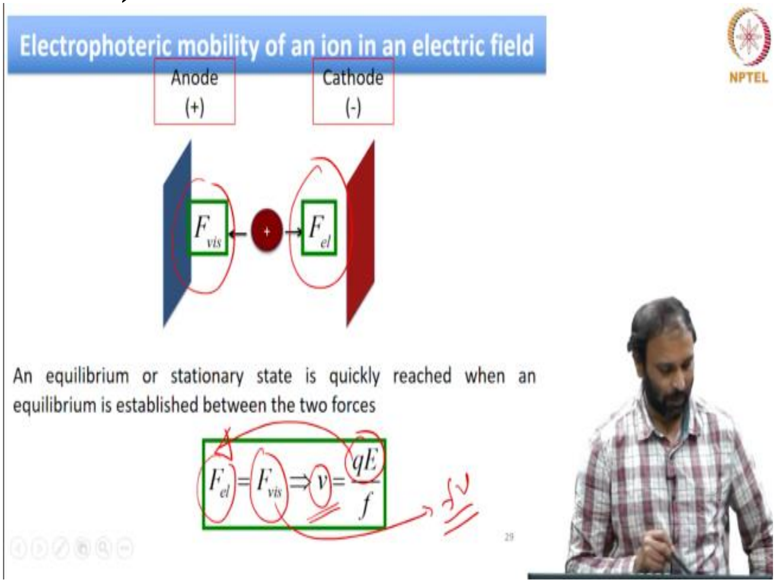

Electrophoteric mobility of an ion in an electric field

An equilibrium or stationary state is quickly reached when an equilibrium is established between the two forces

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

And soon an equilibrium will be set up between the two forces that are acting on the isolated ion and that is established when the two forces that are acting on the species are equal therefore, we could equate the electrical force that has generated because of the applied electric field and the viscous force that is f times v that is set up because of the drag that the moving ion experiences in the fluid. So, therefore, so, we could obtain an expression for the velocity with which the fluid is moving in the, we can obtain an expression for the velocity with which the ion is moving in the fluid and that is given by q times E/f.

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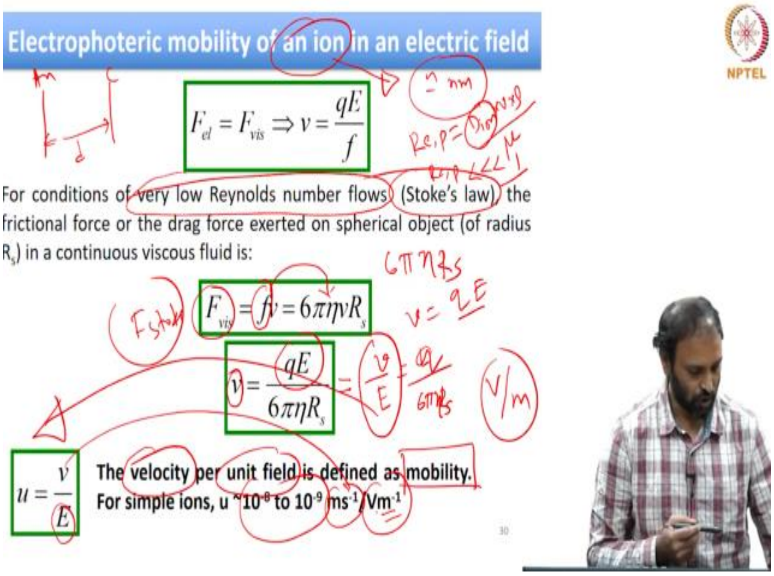

Electrophoteric mobility of an ion in an electric field

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

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:

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

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

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

The velocity per unit field is defined as mobility.

For simple ions, u ~$10^{-8}$ to $10^{-9}$ $ms^{-1}/Vm^{-1}$

Now, because we are dealing with species that are very, very small, the dimensions of these species are going to be you know of the order of sub nanometer. So, whenever you have such small species, if you calculate the particle Reynolds number, which goes as diameter of the ion that we are considering, times the velocity with which they are moving times the fluid density divided by viscosity of the fluid because of the fact that the dimension of the species are very, very small.

This Reynolds number if you calculate it will be much, much less than 1. So, under such condition these you can refer to this as a low Reynolds number flows therefore, we could use stokes law and therefore, the friction factor f can be replaced with 6 pi eta times $R_S$ this essentially comes from the F stokes the stokes law for low Reynolds number force therefore, in v = qE/f we could replace f with qE/ 6 pi eta into $R_S$.

So, therefore, we end up with an expression which is the velocity with which the particles are moving with which the ions are moving in the field goes as q times E / 6 pi eta times $R_S$. So, I can rearrange this expression further I can write this as v / E = q / 6 pi eta into $R_S$ and this quantity v / E is what is called as electrophoretic mobility that is the velocity with which the isolated ion is moving in the presence of an applied electric field of a given strength is what is called as mobility or the electrophoretic mobility.

And for simple ions, the typical value of electro phoretic mobility would be of the order of 10 power -8 to 10 power -9 meters per second inverse divided by volts per meter. So, if you look at this expression that E that is the electric field that is applied it is measured in terms of volts per meter. So, that is because, whenever one does electrophoretic experiments typically you have an anode and a cathode which are anode and a cathode which are separated by some distance some known distance like say d.

And so, you can manipulate the electric field that is applied by considering distance different distance between the electrodes. Therefore, the strength of the electric field that is applied in an electrophoretic mobility experiment is typically expressed in terms of volts per meter. Therefore, you will have units of a meter inverse that is from the numerator and E that is volts per meter, which is the unit in which the applied electric field is measured in electrophoretic mobility measurements.

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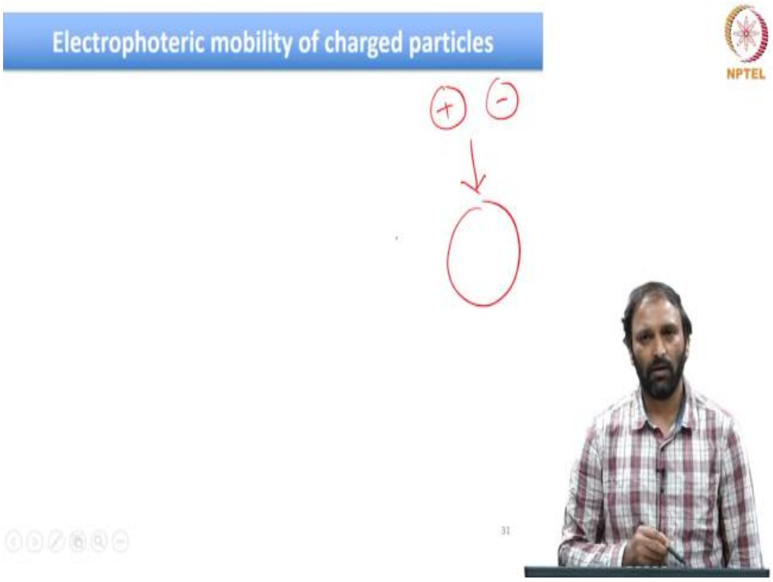

Electrophoteric mobility of charged particles

So, now, we would like to what we would like to do is to extend the concept that we have discussed about the electrophoretic mobility of the isolated ions into electrophoretic mobility of charged particles. We will do that in the next class.