Molecules In Motion

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Lecture – 28
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules In Motion and we will continue on the explanations of whatever we had in the Debye Huckel theorem and we are trying to explain the Kohlrausch's Law.

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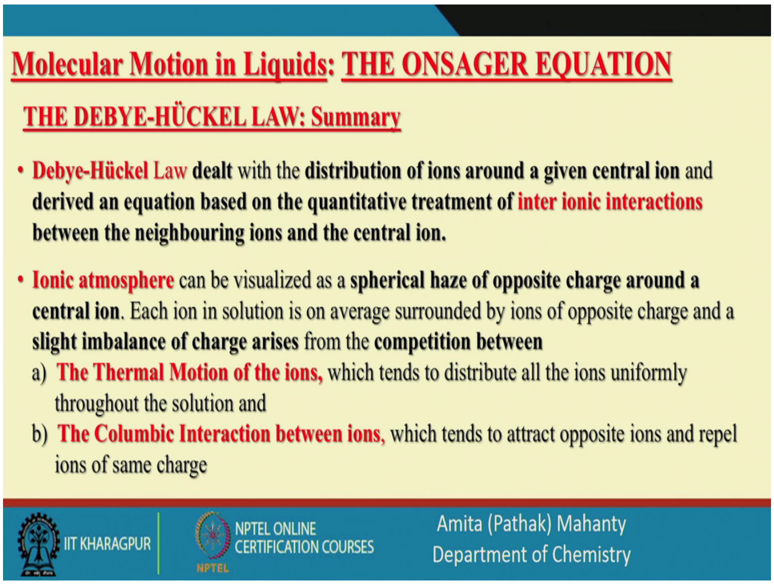

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL LAW: Summary

- **Debye-Hückel** Law **dealt** with the **distribution of ions around a given central ion** and **derived an equation based on the quantitative treatment of inter ionic interactions between the neighbouring ions and the central ion.**
- **Ionic atmosphere** can be visualized as a **spherical haze of opposite charge around a central ion**. Each ion in solution is on average surrounded by ions of opposite charge and a **slight imbalance of charge arises** from the **competition between**
  - a) **The Thermal Motion of the ions,** which tends to distribute all the ions uniformly throughout the solution and
  - b) **The Columbic Interaction between ions,** which tends to attract opposite ions and repel ions of same charge

Where you have the molar conductivity dependence on the concentration in terms of under root of concentration is what we are trying to explain and what we have done in the last class I am going to summarize because we are going to do a extension of the Debye Huckel law. So, what we have in the summary Debye Huckel theorem was when we Debye Huckel law what we had done in the last class was we were looking into the I mean ionic coefficient of the electrolytes being proportional or being having a dependence of under root of the ionic strength and that was the basis of what we had in Debye Huckel law was based on the having a ionic atmosphere around the central ion.

So, we are going to be looking into the summary of what we had talked about in the last class. So, the Debye Huckel theorem dealt with the distribution of ions around a central ion and based on that equation was derived on the qualitative treatment of interionic interactions between the neighboring ions and the central ion.

What we had visualized we had put in the concept we had discussed the concept of ionic atmosphere which can be visualized as a spherical haze of opposite charge around a central ion. Each ion in solution is on average surrounded by ions of opposite charge and a slight imbalance of the charge arises from the competition between two effects. The two effects are one of them is the motion thermal motion of the ions.

What does the thermal motion do? If you have a central ion at it is surrounded by a haze of oppositely charged ion and this haze which you have where along the central ion the number of the counter ions will be always outnumbering the central ion; however, the total charge we have a total charge neutrality; that means, the a charge of the central ion should be balanced by the haze of oppositely charged ion despite the fact that the haze of oppositely charged ions will be having a higher number of charge associated with themselves.

So, if we have each ion on average surrounded by ions of opposite charge then what causes imbalance? There is two competitive forces which is acting one is the thermal motion of the ions and the other is the columbic interaction between the ions. What does the thermal motion do? Because thermal motion or thermal energy we say it is KT the Boltzmann constant into the temperature in Kelvin. So, KT is the thermal energy. So, thermal energy is always there associated with any temperature of the system. So, whenever you have the ions in solution the thermal motion what does it do? The thermal motion tries to distribute the ions uniformly throughout the solution.

But there is another sort of force which is acting in a electrolyte solution it is the columbic interaction between the ions. Columbic interaction means if you have oppositely charged ions then you will have experience attraction. If you have oppositely same charge charges then you similar kind of charges then you have a repulsion.

So, if you have a ionic atmosphere if you have a central haze spherical haze around a central ion. Then what can cause this disturbance of the spherical haze around the central ion? One is the if there is a imbalance between the two the thermal motion and the columbic interaction between the ions.

So, if either of them is if the columbic interaction is more effective, then it takes over the thermal motions; which is trying to distribute the ions uniformly. So, the columbic interaction becomes a major player in the field.

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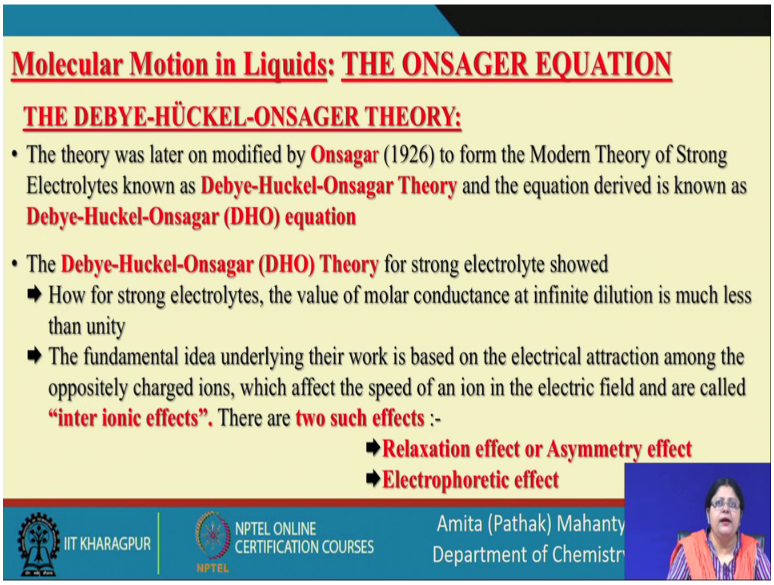

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL-ONSAGER THEORY:

- The theory was later on modified by **Onsagar** (1926) to form the Modern Theory of Strong Electrolytes known as **Debye-Huckel-Onsagar Theory** and the equation derived is known as **Debye-Huckel-Onsagar (DHO) equation**
- The **Debye-Huckel-Onsagar (DHO) Theory** for strong electrolyte showed
  - ➡ How for strong electrolytes, the value of molar conductance at infinite dilution is much less than unity
  - ➡ The fundamental idea underlying their work is based on the electrical attraction among the oppositely charged ions, which affect the speed of an ion in the electric field and are called **"inter ionic effects".** There are **two such effects** :-
    - ➡ **Relaxation effect or Asymmetry effect**
    - ➡ **Electrophoretic effect**

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So, what we have we have the theory which is going to be modified by was modified by Onsager in 1926 and that was the basis of the modern theory of strong electrolyte and the theory is known as Debye-Huckel-Onsager Theory. And then equation which was derived see all of these are experimental observations on based on which we try to model a for a model and formulate equation which will regenerate or reciprocate or we can get back the observed values using this formulated equation. So, these are model equations which is trying to explain something which is experimentally existing ok.

So, the Debye-Huckel-Onsager Theory for a strong electrolyte is the basis of what modern theory of strong electrolytes is known to us. So, Debye-Huckel-Onsager Theory for a strong electrolytes shows for a strong electrolyte the value of molar conductivity at infinite dilution is much less than unity and the fundamental idea under this work is based on the electrostatic attraction or electrical attraction among the oppositely charged ions and this effect the speed of the ions in when in when placed under a electric field and this is known as the Inter ionic effects.

So, what we are talking about? We are talking about that in we have a strong electrolyte what the observation is that you have the molar conductivity depending on concentrate under a square root of the concentration of the electrolyte and at infinite dilution it is less than unity and the fundamental idea lying behind this is the electrical or electrostatic attraction among the oppositely charged ions which affects the speed of the ions when they are placed in a electric field.

So, far we are talking about only the electrolytes in solution which were dissociated each ion was surrounded by a haze of spherical charge and we had not talked about them being affected under any electric field. So, if we have a electric field associated with a charged central charge surrounded by a ionic atmosphere a spherical haze of oppositely charged ion. Then what happens the speed of the ions with which the ions are going to move gets affected because of the inter ionic effects and what are the two in major inter ionic effects associated with a electrolyte system one is called as the Relaxation effect or Asymmetric effect and the other one is the Electrophoretic effect

Let us see what each of them means.

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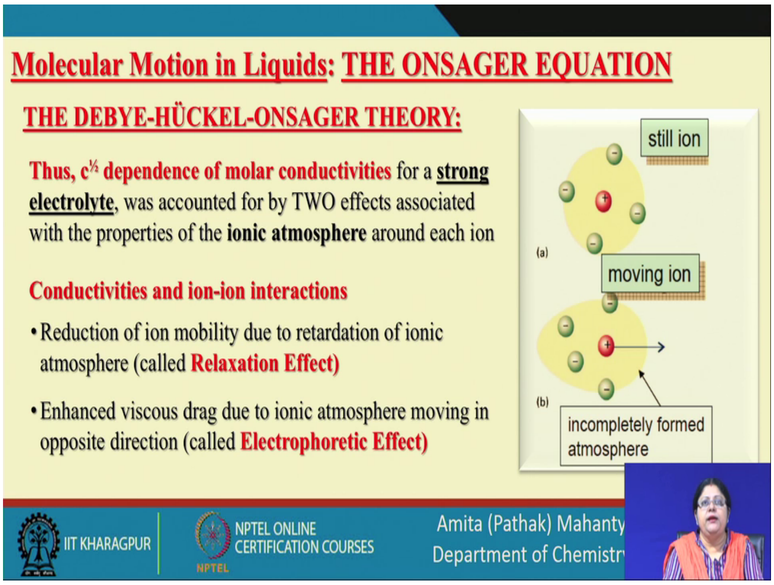

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL-ONSAGER THEORY:

Thus, $c^{1/2}$ dependence of molar conductivities for a **strong electrolyte**, was accounted for by TWO effects associated with the properties of the **ionic atmosphere** around each ion

Conductivities and ion-ion interactions

- Reduction of ion mobility due to retardation of ionic atmosphere (called **Relaxation Effect)**
- Enhanced viscous drag due to ionic atmosphere moving in opposite direction (called **Electrophoretic Effect)**

So, what we are trying to explain? We are trying to explain the square root of molar concentration of a strong electrolytes dependence on the molar conductivity and the two effects which is associated with the ionic atmosphere which tends to reduce the motilities of the ion and hence the conductivities other ion interaction reduction of ionic mobility due to retardation of ionic in the presence of the ionic atmosphere and because of the enhanced viscous drag due to ionic atmosphere moving in the opposite direction.

So, these are the two effects which is in its which play when we have a ion in a electric field. So, what we have you if you look at this picture here you have a central ion surrounded by oppositely charged ion that is here we have taken positive charge as the central ion and it is surrounded by negative ions

So, this is a symmetric haze which is we which we see it is a spherical symmetric haze around the positive central ion you can have a similar one with the negative ion being the central ion that is not the issue. Issue is when you have these ions which is not under any electric field you have a symmetric haze around the central ion and we see that the we have the molar conductivity is at infinite dilution is less than one; that means, when you have the molar conductivity dependence not on c, but under root of c is what we are trying to understand.

And why is that we are trying to interpret the lower value of molar conductivity in terms of the retarded value of the ionic movement in the solution and the retarding values retarding motion of the ions in under existence of an electric field can be explained on the basis of the ion interaction one is the reduction of the speed of the ion due to relaxation effect and another is the reduction in the mobility or the speed of the ions because of the electrophoretic effect.

So, let us see what we have; this is the symmetric charge which is still now suppose we have a ion in the placed under the electric field suppose you have a negative electrode here then the positive charge will go towards the cation will move towards the cathode. So, the cathode suppose is here its moving towards the cathode then what you see then the charge a charged atmosphere which was surrounding them gets distorted. When it is moving forward the charged atmosphere ionic atmosphere it is not completely formed while the one which is behind is not completely disappeared.

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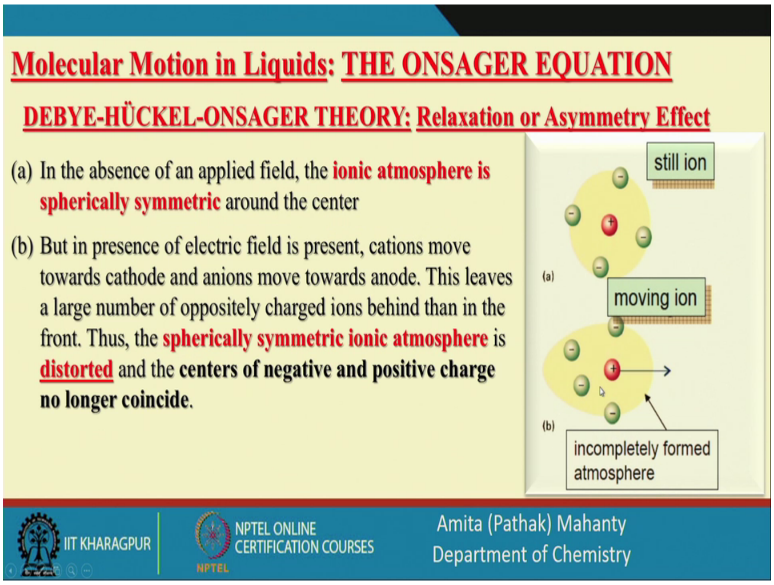

Molecular Motion in Liquids: THE ONSAGER EQUATION

DEBYE-HÜCKEL-ONSAGER THEORY: Relaxation or Asymmetry Effect

(a) In the absence of an applied field, the **ionic atmosphere is spherically symmetric** around the center

(b) But in presence of electric field is present, cations move towards cathode and anions move towards anode. This leaves a large number of oppositely charged ions behind than in the front. Thus, the **spherically symmetric ionic atmosphere** is **distorted** and the **centers of negative and positive charge no longer coincide**.

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Let us look at this. So, in absence of a electric field what we have the ionic atmosphere is spherical and symmetric around the central ion that is what we have seen, but in presence of a electric field cations move towards the cathode anions move towards the anode we are focusing only on the positive charge; obviously, you will have a negative charge very close by, but we are focusing on one particular central ion to have a simplistic picture ok.

So, in presence of a electric field the cations move towards the cathode the anions move towards the anode this leaves a large number of oppositely charged ion behind than in front. So, in the front at ionic atmosphere is not formed while this has moved what is having what we have if you have a large number of oppositely charged ion which was part of the ionic atmosphere being left behind.

So, what happens; the center here you see the center of the central ion and the center of the spherical sphere coincide, but here the center of the charge and the center of the sphere which we have ionic sphere do not coincide this symmetrical spherical symmetric ionic atmosphere is distorted the center centers of the positive and the negative charges no longer coincide ok.

So, you have generated some sort of asymmetry in the charge and the surrounding atmosphere so, this is what we have.

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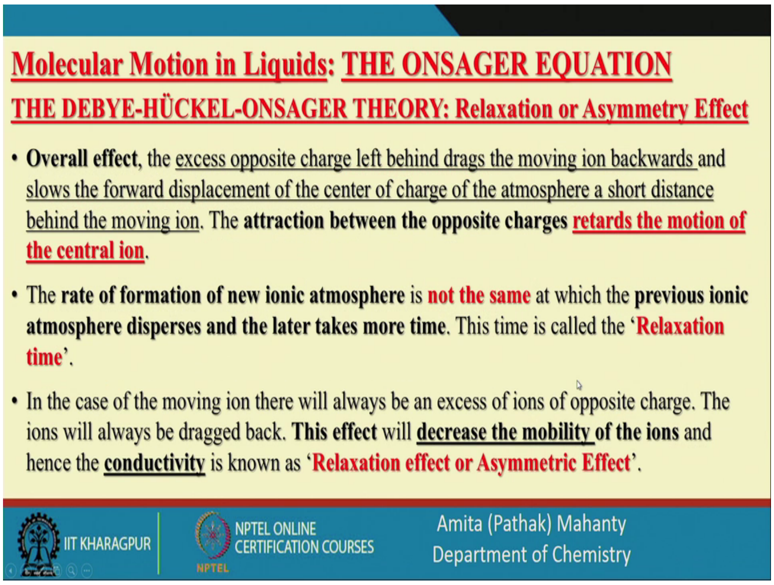

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL-ONSAGER THEORY: Relaxation or Asymmetry Effect

- **Overall effect**, the excess opposite charge left behind drags the moving ion backwards and slows the forward displacement of the center of charge of the atmosphere a short distance behind the moving ion. The **attraction between the opposite charges** **retards the motion of the central ion**.
- The **rate of formation of new ionic atmosphere** is **not the same** at which the **previous ionic atmosphere disperses and the later takes more time**. This time is called the '**Relaxation time**'.
- In the case of the moving ion there will always be an excess of ions of opposite charge. The ions will always be dragged back. **This effect** will **decrease the mobility of the ions** and hence the **conductivity** is known as '**Relaxation effect or Asymmetric Effect**'.

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The overall effect is the excess opposite charge which is left behind some of them are left behind we are in tries to drag the moving ion from moving forward and in the process slows down the forward displacement of the central ion the center of the charge of the displacement of the center of charge of the atmosphere is a shorter distance behind the moving ion.

The attraction between the opposite charges the retarded motion of the retards the motion of the central ion. What is happening is essentially the rate of formation of the new ionic atmosphere of the central ion which we will can visualize this is the central ion which we have it is moving forward. So, as they move forward they will have a ionic atmosphere generated; what happens the ionic when the ions are moving they are moving pretty fast and the amount of the ionic atmosphere which should be generated has does not have the time to be formed.

While what you have is the ions which were forming the these negative charges which is now this center of the negative ions some sort of distorted then that of the central ion corresponding to the central ion like this. So, the same this is no longer symmetric here you have the center of all the negative charges coinciding with the center of the positive charge here we do not have all the say negatively charges the center of all the negative charges do not coincide with the center of the positive charge. So, positive charges moved forward, but what is happening the charged ionic atmosphere for the forward movement ion is has yet to be formed, but what happens the formation the dispersed ion atmosphere which is having is not completely disappeared. What is the effect of it? It effect of it is this is going to this positive charge is going to have experience attractive force from behind because of the undispersed ionic negative counter ion atmospheres atmosphere ionic atmosphere because of the counter ion.

Like if you have a positive it is going to be the negative ions which is going to be pulling in back if it is a negative ion which is moving forward then it will be the counter ions of the positive ion charges will be trying to hold it back.

So, the rate of formation of the new ionic atmosphere is not the same at which the previous ions ionic atmosphere get is disappeared. Suppose you have in the same time the ions is moving immediately the charge is forming a atmosphere and this charge has disappeared then you will not see a effect. But what you have the ions will move under the electric field as it is, but what happens when you have the ion moving forward, but the ionic atmosphere is not yet formed, but the one which was there around the central charge which is now moved forward is going to pull it back, because of the electrostatic force of attraction, because they are counter ions and what will happen this will tend to retard the motion of the central ion.

So, the rate of formation of the ions is not the same rate of formation of the ionic atmosphere is not the same for the ion which is moving forward the previous one is not completely disappeared and that new one is not completely formed. So, this is there is a relaxation period and that is why this we call this as a relaxation effect. So, there is a relaxation time involved.

In case of the moving ions there will be always an excess of ions of opposite charge. The ions will always be dragged back; this affects the mobility of the ions and hence the conductivity. If mobility is increased conductivity increases if mobility decreases conductivity decreases. So, the whole effect which we see because of the asymmetry of the ionic atmosphere or because of the different relaxation time the relaxation time of the ionic atmosphere which is formed and which is getting dispersed which is formed and which is left behind. The formation of the new atmosphere ionic atmosphere and the disappearance of the previous ionic atmosphere do not match they have a time lapse or we can say there is a relaxation in time.

So, this effect which is going to eventually have effect on retarding the motion of the central ion by pulling it back and when again subjected against the electric field is known as the relaxation effect or the asymmetry effect. Asymmetry effect comes from the concept that the ionic atmosphere around the central ion is not going to be symmetric anymore. Because the ion is moving under experience of the electric field is moving faster and the opposite counter ions is still to be dispersed and they tend to have a attractive force on the central ion and try to pull it back.

So, this is the relaxation effect which is associated with the reduction in the mobility or speed of the molecules when subjected against the in a electric field.

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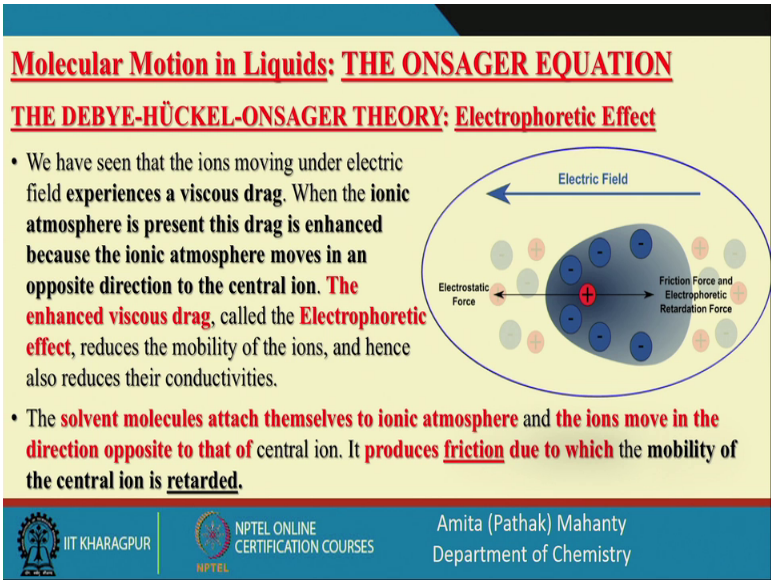

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL-ONSAGER THEORY: Electrophoretic Effect

- We have seen that the ions moving under electric field **experiences a viscous drag**. When the **ionic atmosphere is present this drag is enhanced because the ionic atmosphere moves in an opposite direction to the central ion**. **The enhanced viscous drag**, called the **Electrophoretic effect**, reduces the mobility of the ions, and hence also reduces their conductivities.
- The **solvent molecules attach themselves to ionic atmosphere** and **the ions move in the direction opposite to that of** central ion. It **produces friction due to which** the **mobility of the central ion is retarded.**

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There is another effect which we have talked about which is another in a ionic interaction is the electrophoretic effect you just see what we are have you can see the picture here you have a central ion you have suppose this side is the cathode positive charge is there the positive charge is going to move towards the cation is moving towards the cathode; that means, the negative electrode.

So, what happens when the ions are moving under the electric field if you remember when we were talking about we were deriving the drift speed we had seen that whenever ion is moving under the electric field it experiences a viscous drag.

Now, if there is a ionic atmosphere present this drag is going to be enhanced because of the ionic atmosphere moves in the opposite direction to that of the central ion. So, let us see what is there in this diagram what you have; you have a electric field applied this side so, the ions are going to be moving this side right. So, we have a frictional force which is going to be existing which is going to draw the ions backward and the frictional force and the electrophoretic retarding force will try to pull it back

So, what is this electrophoretic retarding force what you have when you are moving a the charge under the electric field we have said that the ionic atmosphere around the charged ion is not going to be formed the one which is previously there and the ion is moving forward this is not going to be distorted so, which is not going to be dispersed so easily. So, what happens the some portion of some amount of the oppositely charged ion will be always there. So, these you see when we are having a ion moving this side the forward ionic atmosphere of the charge is not yet formed, but the one which was there around this central ion is not completely dispersed it is still existing. So, these ions are still existing which is trying to pull it back this is a associate with the ionic atmosphere.

Now, see what happens you have the frictional force coming from the medium a cell because the solvent is going to be now attached to the ionic atmosphere. So, these are the solvent molecules which we are looking into when we are talking about a ion moving towards this side then another application of electric field what you have this force, this is the electrostatic force which is going to be generated for the new ionic atmosphere which is going to be yet to be generated completely, but you have some amount of ionic atmosphere which is distorted and yet not disappeared this solvent molecules will get attached to it and then you have the frictional force as well as the electric electrophoretic force this enhancement in the viscous drag is what is known as the electrophoretic effect ok.

So, the concept wise both electrophoretic and asymmetric effect will reduce the movement of the ions or reduce the mobility of the ions because both of them in both the cases the ion is trying to move forwards towards the direction of the cathode for a positive ion, but it is dragged for first one for asymmetric one it is dragged behind by the not completely dispersed ionic atmosphere and when you have a electrophoretic effect this not dispersed ionic atmosphere will get associated with some solvent molecules and this solvent molecules which is attached to that ionic atmosphere will move in the opposite direction and hence we will try to retard the motion in the direction of the applied field.

So, what we have here? We have produced a friction due to which the mobility of the center line is retarded. So, what we have here we have the two effects which is the asymmetry effect and the electrophoretic effect which is inter playing together we do not know to what extent the electrophoretic effect is a relevant and to what extent the asymmetry effect is effective, but both of them play together for the ions to be retarded in motion.

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Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL-ONSAGER THEORY:

If the solution of electrolyte is not infinitely dilute, the motion of the ions is retarded

- Because of the **electrical attraction between ions of opposite sign** (**Relaxation** or, **Asymmetry effect**), and
- Because the positive and negative ions are moving in opposite directions each carrying some solvent (**Electrophoretic effect**).

- **Both of these effects are intensified as the concentration of the electrolyte increases** so that the **retarding forces increase** and the **conductivity decreases**.

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So, when whenever the ions are retarded so, if the ions are retarded in motion; that means, their mobility is reduced both the effects electrophoretic and the relaxation effect it gives rise to a loss in mobility they retard the ion from moving forward and this is hence going to reduce the mobility of each of the ions and hence the conductivity ok.

So, if a solution is very dilute we can apply the solutions which we have looked into, but if the solution is not very dilute what happens the motion of the ions are retarded because the electrical attraction between the opposite ions between the ions of opposite sign opposite charge and also because the positive and negative charges are moving in the opposite direction and carry the solvent molecules both of these intensify as the concentration of the electrolyte increases.

So, whenever we are talking so, far we had talked about a very dilute solution what we are now putting it if the dilution is not sufficiently is not equal to 0 then what is effectively going to be concerned is the concent; if the concentration is in increase both of these effects the relaxation effect and the electrophoretic effect is intensified as the concentration of the electrolyte increases.

So, what happens when you increase the concentration? The retarding forces are more effective and so, this immobility of the ions are going to be reduced and so will be the conductivity. So, we will take into account what are the factors which are going to effect the electrophoretic effect for a particular system and what are the effect which is going to be going to be important when we talk about the relaxation effect. These two factors and how the new equation of the Debye Huckel Onsager theory is developed and what is the close monitoring of what based on the formulation which we have we do the experiment and see the experiment how their experiment as your or how far the experiment result is close to whatever we have formulated in the Debye Huckel Onsager theory.

Thank you so, much.