

**Molecules in Motion**  
**Prof. Amita Pathak Mahanty**  
**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Lecture - 31**  
**Molecular Motion in Liquids (Contd.)**

Welcome to another lecture on Molecules in Motion, what I would like to inform you that whatever lecture class was there on 30th we did not take up the effects of the Debye-Huckel theory what are effects are going to be there if we have the Debye-Huckel expression, we had skipped this in the thirtieth lecture it would have been better if we had taken up this earlier.

(Refer Slide Time: 00:32)

**Molecular Motion in Liquids: DEBYE-HÜCKEL-ONSAGER THEORY:**


- The final expression for the **molar conductivity** ( $\Lambda$ ), of an electrolyte which includes both the **asymmetry effect** and the **electrophoretic effect**, is (for uni-univalent electrolytes) can be written as:


$$\Lambda_m = \Lambda_m^0 - \left[ \frac{8.249 \times 10^{-4}}{(\epsilon_r T)^{1/2} \eta} + \frac{8.20 \times 10^5}{(\epsilon_r T)^{3/2}} \Lambda_m^0 \right] \sqrt{c}$$

where, constant  $A = \frac{8.249 \times 10^{-4}}{(\epsilon_r T)^{1/2} \eta}$  and  $B = \frac{8.20 \times 10^5}{(\epsilon_r T)^{3/2}}$

which is the **Debye-Hückel-Onsager** Equation ; it is usually abbreviated to

$$\Lambda_m = \Lambda_m^0 - [A + B \Lambda_m^0] \sqrt{c} \quad \text{where, } c \text{ is the concentration in mol/L}$$





NPTEL ONLINE  
CERTIFICATION COURSES

Amita (Pathak) Mahanty  
Department of Chemistry

Because we wanted to continue with the Debye- Huckel- Onsager theory and then go over to applying the molecules to uncharged charged molecules to non application of electric field.

So, before you can take this lecture to be supposed to be a little earlier than the 30th lecture. Anyway what we are going to be discussing here today is this is the expression which we had derived from the Onsager theory that is Debye- Huckel- Onsager theory, Debye Huckel theory was modified and we got the Onsager theory which from which we got the expression of molar conductivity. We have seen how for various one electrolyte

this equation can be taken up and to great extent can be satisfied with whatever we see in the observation through experiments.

So, these 2 parameters which we have in the Debye Huckel Onsager theory was parameter A and parameter B and parameter A and B were actually contributions from the asymmetric effect and the electrophoretic effect which we associated in a system of ionic charges are there in a solution.

So, I will not go into the detail discussion because we have already taken it up in 29th lecture. So, we have this equation and now based on this equation we will see what are the parameters in under which the electrophoretic effect or the asymmetry effects are going to be exaggerated or it will be diminished under the various conditions, I think these conditions need to be understood before we take up a system where we are not dealing with any electric field associated. If we do not have any electric field associated then; obviously, we are not talking about the asymmetry effect or electrophoretic effect in the solution.

So, we will take up whatever we continued in the 31st lecture in the next lecture, but today we are going to be discussing on the parameters which are going to affect the molar conductivity given by the Debye Huckel Onsager theory. So, this is the equation which we are going to see and we are not going to come back and discuss about what A and B stands for; obviously, A and B are given to you this is the in which you have the viscosity coefficient along with the dielectric constant of the medium and T is the temperature. So, this was the expression which we had talked about was coming from the asymmetric effect and this was the effect which we are associating with the electrophoretic effect.

(Refer Slide Time: 03:50)

**Molecular Motion in Liquids: DEBYE-HÜCKEL-ONSAGER THEORY:**

**Molar Conductivity under High Electrolyte Concentrations:**

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 **mobility decreases** so does the **conductivity decreases**.

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

So, what happens when you have a highly concentrated solution of electrolyte? If the solution is not this equation which we had seen for the Onsager theory was we had seen how it is it was verified or validated when the solution was very dilute.

What happens under the condition when the concentration is very high? If the solution concentration is not dilute then the motions of the ions are retarded the electrical attraction between the opposite signs the relaxation effect the asymmetry effect and also because of the positive charge and negative charge associated in the opposite direction can carry some solvent that is the electrophoretic effect.

So, because of these 2 effects what happens, in the solution we you have large number of ions in which are in motion and because of the asymmetry effect because it is a charged ion they are moving under electric field because of the charged ion moving under the electric field. If you have a numerous number of ions instead of being a very dilute solution where you have ions fairly a distant apart when you have the concentration high the ions are much closer.

So, what happens the electrical attraction between the opposites ions are there, ion is associated with a ionic atmosphere and the positive and negative ions also not only the ionic atmosphere, but the rate charges themselves will have the solvent molecules tagged along with them.

So, both these effect will be intensified as the concentration of the solution is increased because all these retarding forces as you remember relaxation forces and relaxation effect and electrophoretic effect are actually going to be opposite to the movement of the charged ion under electric field. So, they always will tend to retard the motion of the ions under electric field.

So, these retarding forces are going to be increased when you have a increased concentration and if you have something which is going to pull you back these forces are much more then what happens the mobility of the ions is; obviously, going to be affected they are going to decrease. And if the mobilities of the ions are affected mobility is directly related to the conductivity so, the molar conductivity will decrease ok.

So, the increased concentration of the electrolyte will have a impact of reduced conductivity as you have already seen when the when we had graphs for molar conductivity versus concentration at much higher concentration you had the values of molar conductivity much lower than at lower concentrations.

(Refer Slide Time: 07:01)

**Molecular Motion in Liquids: DEBYE-HÜCKEL-ONSAGER THEORY:**

**Molar Conductivity under High Temperature and Pressure:**

- The molar ionic conductivities **increase markedly** with **increase in the temperature**.
- For ions (**other than  $H^+$  and  $OH^-$** ) this **increase is principally** the consequence of the **decrease in the viscosity of the medium**. **Decrease** in **viscosity solvents** because the **motion** of **both** the ionic atmosphere and the ion is **increased** and hence the **molar ionic conductivities are increased**.
- The **decrease** molar ionic conductivities with **increase in pressure** is also mainly a result of the **increase in viscosity with pressure**.
- The conductivities of  **$H^+$  and  $OH^-$**  have **larger temperature coefficients** (about 14% and 16 % respectively) because of the **difference in the conduction mechanism**.

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

This is one effect what happens with the temperature. So, if you have the molar conductivities the molar conductivities increase markedly when you increase the temperature. Why does it so happen when you are talking about say ions other than say positive H plus and H minus which is in the solvent, which are different they propagate through the solution move through the solution in a different manner which we have

discussed it is the Grotthuss mechanism through which they move. So, it is by it is transfer of charge or hopping of charge that they conduct.

So, if we have to caught talking about ions other than the H plus and OH minus ion what is happening, why do with the molar conductivities in show a marked increase when increase the temperature of the solution, increases principally the consequence of decrease in viscosity of the medium. So, when you whenever we have medium when the medium is supposed to be having some viscosity. So, when we increase the temperature what happens that the system or medium has a lower viscosity they become thinner. So, they if they are becoming thinner the medium the retarding forces which they are going to be associated with the higher viscosity is going to decrease.

So, when we increase the temperature the solvent medium is going to have a decrease in viscosity and this increase in viscosity because both the motion of the ionic and mass ions are increase hence, the molar conductivities are also going to be increased. So, when you have a thinner medium the coefficient of viscosity of the medium is lower, then the ions and the ionic atmosphere can move faster and if they move faster than the ionic mobility is which we are going to see is going be increased.

So, when you have a increase in temperature what we essentially are associating with is the viscosity of the medium, whenever there is a increase in temperature the viscosity of the medium is decreased and if the viscosity of the medium is decreased the motions are less restricted and whatever effects which we are associating with the solvent like the electrophoretic effect will be much lower. So, we have lowering of the retarding forces hence the conductivity the mobility of the ions are increased and hence the conductivity of the ions at higher temperature is increased.

So, the temperature effect is understood, what happens when you have a pressure associated with we are doing all the experiments under normal atmospheric pressure. What happens when you are increasing the pressure of the system, you have a electrolyte system and you are increasing the pressure of the medium in which you are doing the measurement.

So, what happens with the observed value is a decrease in the molar ionic conductivity, this also results because of the viscosity effect when you increase for a liquid usually when you increase the pressure the viscosity of the system increases. So, if you

increasing the pressure the viscosity of the medium increases and since the viscosity of the medium increases the forces which are going to be letting the ions propagate through the solution are going to be more effective so, they cannot move. So, when you are increasing the pressure you have a decrease in the ionic conductivities associated.

The conductivities of H plus and OH minus have larger temperature coefficients like it is around 14 to 16 percent respectively because of this difference; because of the difference in the conductive conduction mechanism. They are that temperature coefficient means that for small range of temperature how much is the increase in the molar conductivity. So, molar conductivity increase is quite large because of the higher temperature coefficient of the H plus and OH minus associated and this is only because this is subjected to because of their mode of transfer through the medium that is how they are conducted through the hob jump mechanism ok.

(Refer Slide Time: 11:40)

**Molecular Motion in Liquids: DEBYE-HÜCKEL-ONSAGER THEORY:**

**Molar Conductance under High Electric Field: WIEN EFFECT**

- The concept of the **ionic atmosphere**, proposed in **Debye-Hückel-Onsager Theory**, is further substantiated by the **Wien Effect**
- Under very **high fields applied electric fields** ( $E > 10^7$  V/m) the ions **move so fast** that it **effectively loses its ionic atmosphere**, as a finite time (the relaxation time) is required for it to form **around the moving central ion**. Thus, the **ionic atmosphere around a moving central ion** does not have time to form and **cannot retard the motion of ions**
- So, the **asymmetry effect** associated with **ionic atmosphere** **also disappears and hence cannot slow/retard the motion of ions**
- This effect is **known** as the **Wien Effect**. Thus, **Molar Conductance** of electrolytes are **observed to increase under very high electric fields** ( $E > 10^7$  V/m) due to **Wien Effect**

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

Now, there is another effect which should we should be talking about is what happens to the molar conductivities we are talking about the molar conductivities keeping in mind whatever the expressions the postulations were put forward by Debye Huckel Onsager theory. Debye Huckel Onsager theory as we have seen before is valid or validated only under very low concentration of the electrolyte very dilute solution.

So, what happens if you are having a certain solution and you have a increase because we are talking about ions moving under a influence of electric field. So, what happens if

the electric field is increased this effect which we see on the molar conductance or molar conductivity of electrolyte when there is a increase in electric field is known as the Wien effect. And this Wien affect the, what is was further extension of whatever we had seen by the Debye Huckel Onsager theory. The concept of ionic atmosphere which was proposed by Debye Huckel Onsager theory was further substantiated by the Wien effect.

Under very high applied field to the order of  $E$  to the order of  $10^7$  volts per meter the ions move much faster. The ions will because it is if the potential applied is very high what happens, the ions are going to be rushing towards the respective electrode. So, if the positive ion is supposed to be moving towards negative electrode it is going to be accelerating because of the high electric field applied.

So, ions move so fast that it effectively loses the ionic atmosphere which is it is surrounded with and you have to be understanding this the ionic atmosphere which we are associating we are not disturbing that if the electric field is not that is high. They move if along with the ion and because of the asymmetric effect and the electrophoretic effect they trend to these 2 effects associated with the ionic atmosphere tend to retard their motion through the solution.

Now, if we have a very high electric field what happens as a finite time the relaxation time is required for it to form around the central charge, you need a definite time for it to form around the central charge. It is very small, but it does take a little amount of time for the ionic atmosphere to be formed along the central ion. That is the reason why, if you are pulling the electron pulling the central ion towards the electrode then the ionic atmosphere previously has not decayed and the in the front it is not completely formed.

If this is the condition you see the decay also takes time and the formation of the ionic atmosphere also takes some time this is that this time is known as the relaxation time. This relaxation time is not going to be available if you are having a very high electric field associated.

What happens the move ions are moving so fast that the ionic atmosphere does not get the chance to form around the central ion. So, the asymmetry associate effect associated with the ionic atmosphere also disappears hence, these solvents that the retarding forces which are supposed to be there associated with the asymmetry effect or the relaxation effect will not be visible to us. So, this effect is known as the Wien effect that the molar

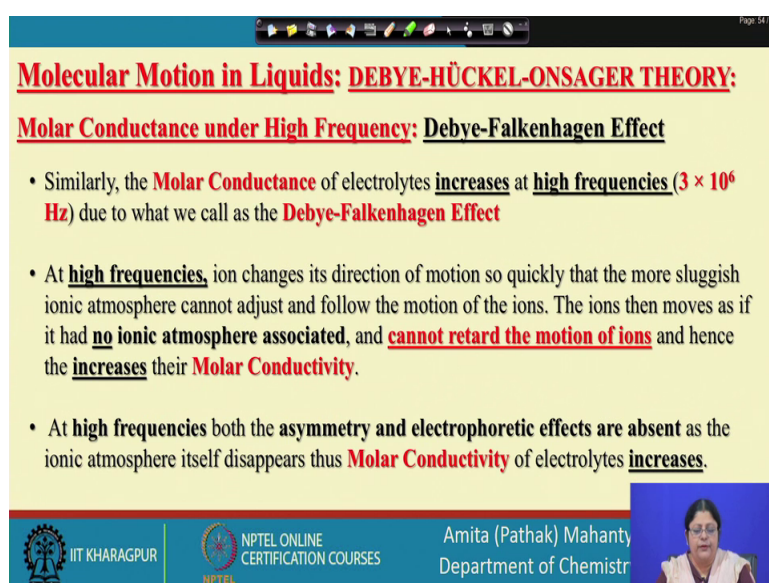


conductivity of electrolyte are observed to increase when we are increasing the electric field in the orders of 10 to the power 7 volts per meter am I clear.

So, the Wien effect is the extension or sub further substantiation of the Debye Huckel Onsager theory here we are not talking about the electrolyte concentration as such we are talking about the electric field associated if the electric field applied is very high. If the electric field applied is very high then the ions are going to be rushing towards the respective electrode, opposite electrodes like positive ion moving towards the negative and the negative ion moving towards the positive electrode. That this will be so fast that the time required for the formation of this ionic atmosphere will not be available to the ion. And if the ionic atmosphere is not available, then these ionic atmosphere is actually what is the root cause for having the retarding force to drag the ion back when it is under influence of electric field.

So, if the ionic atmosphere is not formed then this drag forces are not available; that means, the asymmetry effect which you are going to be seeing is not will be visible. So, if these retarding forces are not available the molecules will or ions under the electric field will be moving much faster will be accelerated and if the movement of the ions is accelerated the molar conductivity is will increase. So, the Wien effect is essentially talking about having the molar conductivity increased at high applied electric fields.

(Refer Slide Time: 17:53)



**Molecular Motion in Liquids: DEBYE-HÜCKEL-ONSAGER THEORY:**

**Molar Conductance under High Frequency: Debye-Falkenhagen Effect**

- Similarly, the **Molar Conductance** of electrolytes **increases** at **high frequencies** ( $3 \times 10^6$  Hz) due to what we call as the **Debye-Falkenhagen Effect**
- At **high frequencies**, ion changes its direction of motion so quickly that the more sluggish ionic atmosphere cannot adjust and follow the motion of the ions. The ions then moves as if it had **no ionic atmosphere associated**, and **cannot retard the motion of ions** and hence the **increases** their **Molar Conductivity**.
- At **high frequencies** both the **asymmetry and electrophoretic effects are absent** as the ionic atmosphere itself disappears thus **Molar Conductivity** of electrolytes **increases**.

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry



Now, another effect the Debye-Falkenhagen effect this is also a substantiation or extension of the Debye-Huckel theory. Here what we are talking about how the molar conductivity of electrolyte is going to be affected when we have high frequency. Similarly the molar conductivity of the electrolyte here also will increase as the frequency is increased.

The Falkenhagen effect is associated when we are applying a very high frequency the, it is in hertz which is the frequency which we are talking about in terms of the electrical field. So, the frequency at which we are using a alternating current. So, the frequency which by which we are going from a clockwise and anticlockwise field is going to be affected.

So, what happens when you have a high frequency, in the order of 10 to power 6 hertz; that means, when we are going to see the Debye Falkenhagen effect when we have the frequency associated in the order of mega hertz. So, at high frequency the ions change it is direction of motion as quickly that more sluggish ion ionic atmosphere cannot adjust and follow the motion of the ions. The ions then move as if it had no ionic atmosphere associated and the associated retarding force which is associated with the ionic atmosphere is not prominent and then hence you see a molar increase in the molar conductivity.

You are understanding what I am saying? When you have a frequency suppose we are doing the experiment; obviously, all are all the experiments are done in AC current. So, if you are having the frequency which is once it is going to be clockwise it is going to another time it is going to be anticlockwise if the frequency is high, then the ions are going to be moving in one direction and as soon as the frequency is changed the anticlockwise then it moves to the other direction.

But, what happens if you are having a very high frequency the change of moving from clockwise to anticlockwise will be so, fast that the ionic atmosphere which is going to be associated with the ion will not have sufficient time to adjust to the change in frequencies and if they if such a effect is seen what happens the motion of the ionic atmosphere gets disturbed. It does not get a time to form when the positive charge clockwise frequency is applied and when the anticlockwise frequency is applied then the charges are. So, if the

changes are so, fast then the ions cannot adjust to the changing in the frequencies of the applied field.

So, what happens the ionic, ionic atmosphere associated does not have any effect with on the motion of the ions. The motion of the ions does not get retarded and hence the mobility of this ions in the system will increase and if the mobilities are increasing the molar conductivity will also increase.

So, at high frequencies both the asymmetry effect and the electrophoretic effect become absent as the ionic atmosphere associated with the ion does not get the time to be completely formed. So, under these condition the molar conductivity is supposed to increase as the retarding forces associated with the ionic atmosphere do not exist to hamper their motion. And hence the molar mobility of the ions in the solution increases and hence the molar conductivity of the ions of the ions in solution an increased.

So, what we have seen we have seen the effect of concentration we have we have seen the effect of temperature we have changed the effect of pressure and high field and high frequency. These are going to be modifying or whatever we see as the deviations of Debye Huckel Onsager theory, whatever we see in the experiment and what we have proposed through the proposed equation will not match if these any of these parameters are going to be applicable or effective when we are doing the experiment.

(Refer Slide Time: 23:09)

**Molecular Motion in Liquids: Molar Conductivity in Nonaqueous Solvents:**

The principles governing **Molar Conductivity** of an electrolyte in **Non-aqueous Solvents** are the same as those for **Aqueous Solutions**

**Molar Conductivity and the Viscosity of the Solvent:**

- Similar to Aqueous Solvent, **Molar Conductivity** of an electrolyte in **Non-aqueous Solvents** is also expected to **decrease** with **increase in Viscosity** of the Solvent as is evident from the following expressions

$$\text{molar conductivity, } \lambda = z u F = \frac{z s F}{E} = \frac{|z|^2 e}{6 \pi \eta_o a} \quad \text{where,} \quad \text{Ionic mobility, } u = \frac{s}{E} = \frac{|z| e}{6 \pi \eta_o a}$$

where,  $s$  = drift speed;  $E$  = Electric Field;  $z$  = charge of the ion;  $\eta_o$  = solvent viscosity;  $e$  = electronic charge =  $1.602 \times 10^{-19}$  C;  $a$  = solvated radius of the ion. If water is the solvent, then " $a$ " as known as the **hydrodynamic radius**

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

So, in principle molar conductivity of electrolyte in non aqueous solvent, if you are seeing non aqueous solvent what happens, we have so far discussed all majorly in the conductivities in the solvent which is water.

So, if what happens when we are having a non aqueous solvent the effects which can be associated with that is one of them is the viscosity of the solvent similar to aqueous molar conductivity of electrolyte in non aqueous solvent is also expected to decrease with increase in viscosity. So, if you are having an increase in viscosity the molar conductivity is going to decrease as is in the case of aqueous medium. Because it is evident from this expression molar conductivity is going to be  $\lambda_{\infty}$  and  $\lambda_{\infty}$  is related to from the Stokes law is the viscosity, viscosity is always in the denominator. So, if you have increase in viscosity; obviously, the molar conductivity is going to decrease.

(Refer Slide Time: 24:28)

**Molecular Motion in Liquids: Molar Conductivity in Nonaqueous Solvents:**

**Molar Conductivity and the Dielectric Constant of the Nonaqueous Solvent:**

- In solvents of **low dielectric constants** ( $\epsilon_r$ ), there is a **lessening of the degree of ionization** of many electrolytes. Electrolytes that are completely dissociated in water may be only partially dissociated in solvents having low dielectric constant ( $\epsilon_r$ )

**Example:** HCl is a "strong" acid ( $K_a = 1.5 \times 10^{-3}$ ) is completely dissociated in water however, in ethyl alcohol, HCl is a "half-strong" acid, with a dissociation constant of about  $1.5 \times 10^{-2}$

- Suppose we have two ions with charges  $+ze$  and  $-ze$  at a distance  $r$  in a **medium** of dielectric constant ( $\epsilon_r$ ) solvent.

The **energy of interaction of between the two ions** will be given as:

$$V = -\frac{z^2 e^2}{4\pi\epsilon_0 \epsilon_r r}$$

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

So, what happens is next is the dielectric constant of the solvent, if the solvent is low dielectric constant then lessening of the degree of ionization of the electrolyte, electrolytes are the completely dissociated in water may not be completely dissociated in solvent it may be only partially dissociated having low dielectric constant.

So, suppose we have a solvent of low dielectric constant and compare that with water, water has a very high dielectric constant. So, in solvents which have low dielectric constant the degree of ionization; that means, formation of ions in the solution gets

hampered. The electrolytes that are completely dissociated in water may not be completely dissociated in a solvent which is having low dielectric constant.

For example HCl is a strong acid see  $10^{-3}$  is the dissociation constant, it is completely dissociated in water; however, in ethyl alcohol what happens because of this it does not behave like a strong acid it behaves like half the acid strength of what we have in aqueous medium. So, the dissociation constant is in the order of  $10^{-2}$ .

So, you can understand suppose 2 ions with positive and negative charges are at a distance  $r$  the medium of the dielectric constant of the solvent, the energy of interaction between the 2 ions. In a medium of dielectric constant say  $\epsilon$  of the solvent then the 2 ions which may interact is going to be given by the interaction energy is going to be given by  $V$  equal to  $-\frac{z^2 e^2}{\epsilon}$  you see the dielectric constant of the medium is in the denominator.

(Refer Slide Time: 26:22)

**Molecular Motion in Liquids: Molar Conductivity in Nonaqueous Solvents:**

**Molar Conductivity and the Dielectric Constant of the Nonaqueous Solvent:**

- If the **dielectric constants ( $\epsilon_r$ )**, is **large** (in  $H_2O$ ,  $\epsilon_r = 80$ ), the ions must come rather close together before the energy of interaction becomes appreciable. If we choose ethyl alcohol ( $\epsilon_r = 24$ ), then at the same distance of approach, the **interaction energy will be  $80/24 = 3.3$  times greater**
- Alternately, we can say, **the energy of interaction becomes appreciable at a distance 3.3 times greater than in water.**
- As a result, since **most solvents have much lower dielectric constants than water**, the **effects due to ionic interaction are much larger than in water.**

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

So, what happens, if you have dielectric constant which is large like water, the ions may come rather close together before the energy of interaction becomes appreciable. If we choose ethyl alcohol for which the dielectric constant 24 at the same distance of approach the interaction energy will be say 80 by 24, 3.3 times greater. So, alternately we can say the energy of interaction becomes appreciable at a distance of point 3.3 times greater than in water.

So, what happens if the dielectric constant as a result most solvents have much lower dielectric constant than water and effects due to the ionic interaction is much larger in water. So, the ionic interactions which we are seeing which is supposed to be much higher in when we are talking about solvent.

But this interaction energy if is going to be lower if the is going to be if the dielectric constant is lower this interaction energy is going to be higher and if for water this is pretty high. So, the interaction energy is going to be for water this is high, this is high. So, this is the energy of interaction between the ions is going to be lowered.

And what happens is the energy of interaction becomes appreciable at a distance of if I compare water and ethanol it is appreciable at a distance of 3.3 times the greater that in water. So, most solvents as a result most solvents since most solvents have dielectric constant lower than that of water, the effects due to ionic interactions are much larger in water compared to the other solvents.

(Refer Slide Time: 28:14)



**Molecular Motion in Liquids: Molar Conductivity in Nonaqueous Solvents:**

**Molar Conductivity and the Dielectric Constant of the Nonaqueous Solvent:**

- The **large ionic interaction** often renders the **Debye-Hückel-Onsager Equation** useless (it is still presumably correct) for the extrapolation to obtain  $\Lambda_m^\circ$ .
- The solutions for which the **Debye-Hückel-Onsager Equation** is valid are so dilute that it is **not possible to obtain reliable measurements of their Molar Conductivity**. In these cases, special methods of obtaining  $\Lambda_m^\circ$  are used.
- If the electrolyte is **weakly dissociated**, then the  $\Lambda_m^\circ$  can be obtained by application of the **Ostwald Dilution law**, modifying it in precise work to correct for the inter-ionic forces.  

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{c}{K} \cdot \frac{A_2}{(A_1^\circ)^2}$$
- In solvents of **low dielectric constant**, **ion association** occurs. The appearance of ion pairs  $A^+B^-$  and ion triplets  $A^+B^-A^+$  and  $B^-A^+B^-$  may result in a **very rapid variation of Molar Conductivity with concentration**.

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

So, if we see the effect of dielectric constant are coming from the Debye Huckel Onsager theory large ionic interactions will often render the Debye Huckel Onsager equation useless, it is still presumably correct for extrapolation of an to get the extrapolation value of the molar conductivity at infinite dilution.

The solutions for which the Debye Huckel Onsager equation is valid are so, valued that it cannot be possible it obtain a reliable measurement of their molar conductivity. In these cases the special methods are to be used to find out the  $\lambda_{\infty}$  value. The electrolytes if the electrolyte is weakly associate dissociated the limiting value of molar conductivity can be applied he found out by using the Ostwald dilution law.

In ions with low dielectric constant we also have ion association is occurring this appearance of ion pairing like  $A^+ B^-$  and triple ion of this sort of configuration may result in rapid variation of molar conductivity with concentration. Because of the association if which is effectively there going to be much higher when you are having a lower dielectric constant. So, the ions themselves get associated they appear as triplets or double ions.

So, if these ions are there then the molar conductivity is not going to be having a very rapid variation with concentration. So, these are effects which are going to be associated when you have a non aqueous solvent mediums. So, large interactions are going to be there when you are having the low dielectric constant ionic interactions will be higher, most of the times the Debye Huckel Onsager equation cannot be valid you cannot find out the limiting value of molar conductivity through extrapolation.

Usually if it is weakly dissociated in this medium then we can use the Ostwald dilution law which we have used here if we know the ionization constant we can find out the value from the plot of  $1/\lambda$  versus  $c/\lambda$  in the x axis. So, this is using the Ostwald dilution law we can find out only when the solvent medium is not aqueous. So, solvent we have you do not need to think about what it should be, just remember any solvent which we are talking about is going to have a dielectric constant lower than water.

If the dielectric constant is lower the anion interactions are going to be much stronger if the anion interactions are going to be stronger then the Debye Huckel equation fails then the substance dissolves which are supposed to be behaving like a strong electrolyte may not be completely dissociated in the non aqueous medium they may be formation of charge association and formation of ion pairs ion triplets. So, these will cause to have a rapid variation in the molar conductivity as the concentration of the electrolyte is

increased because if you increase the concentration of the electrolyte system becomes much more complex.

Thank you so much.