Elementary Electrochemistry

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Lecture 33

Hydration of Ions and Their Ionic Mobility

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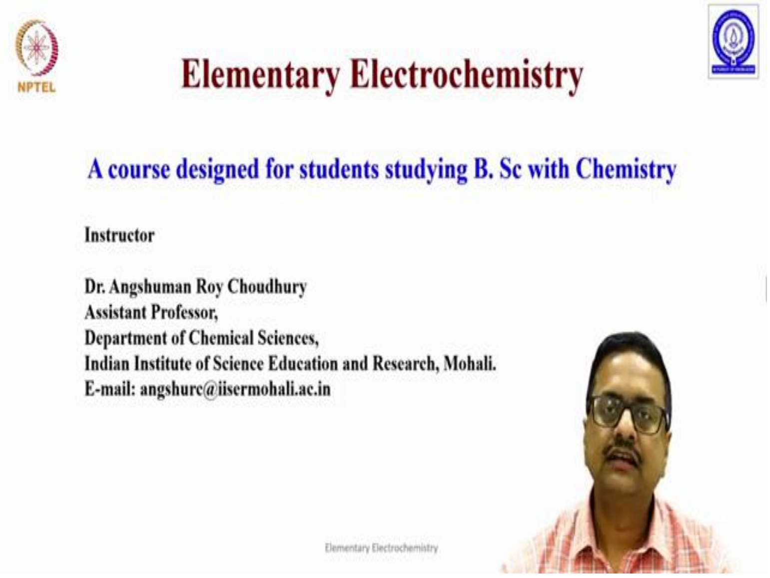

Elementary Electrochemistry

A course designed for students studying B. Sc with Chemistry

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Elementary Electrochemistry

Welcome back to the course entitled Elementary Electrochemistry, we are in the seventh week of this course.

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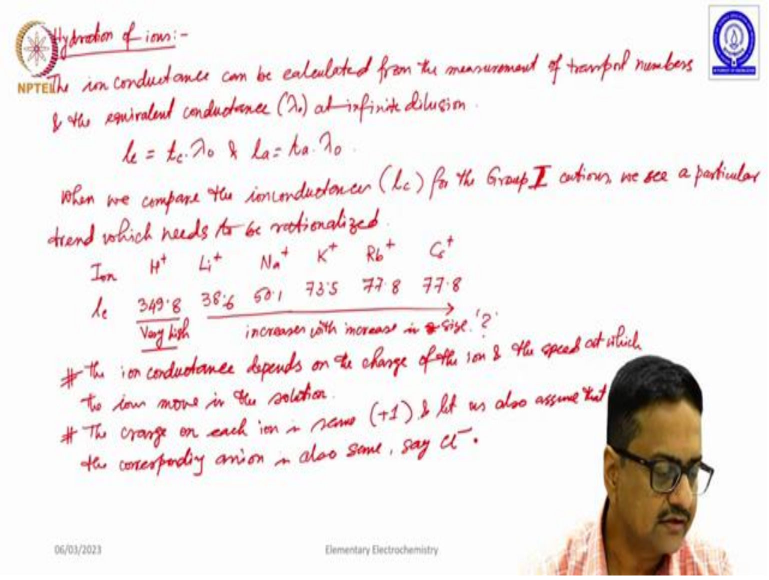

Hydration of ions:-

The ion conductance can be calculated from the measurement of transport numbers & the equivalent conductance (λ_0) at infinite dilusion.

$$l_c = t_c \cdot \lambda_0 \quad \& \quad l_a = t_a \cdot \lambda_0$$

When we compare the ionconductance (l_c) for the Group I cations we see a particular trend which needs to be rationalized.

Ion	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+
l_c	349.8	38.6	50.1	73.5	77.8	77.8

Very high

increases with increase in size. '?'

\# The ion conductance depends on the charge of the ion & the speed at which the ions move in the solution.

\# The charge on each ion is same (+1) & let us also assume that the corresponding anion is also same, say Cl^-.

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Today, I am going to discuss about the topic of hydration of ions and because of hydration how their mobility is affected. So, what we know is that the ion conductance can be calculated from the measurement of transport numbers and the equivalent conductance that is lambda at infinite dilution. So, what we know is lc is equal to tc that is t transport number of cation multiplied by lambda 0, similarly, la is equal to ta into lambda 0.

So, when we compare the iron conductance's that is suppose lc for the group 1 cations we see a particular trend which needs to be rationalized. What do we see? We see that, if I write down the corresponding ions and their ion conductance values for different ions h plus the value is 349.8, li plus is only 38.6, n a plus is 50.1, K plus is 73.5, Rb plus is 77.8 and Cs plus is again 77.8.

So, what we see is that this value is very high compared to all others, but then when we are going down from lithium to cesium it increases with increase in size, why does it happen, what is the reason behind this kind of observation that hydrogen h plus ion has a very high ion conductivity compared to others and then others slowly increase from lithium to sodium to potassium up to cesium.

So, one thing one you must accept that the ion conductance depends on the charge of the ion and the speed at which the ions move in the solution. In this particular case in case of group 1 cations the charge on each ion is same that is plus 1 and let us also assume that the corresponding anion is also same say Cl minus chloride anion.

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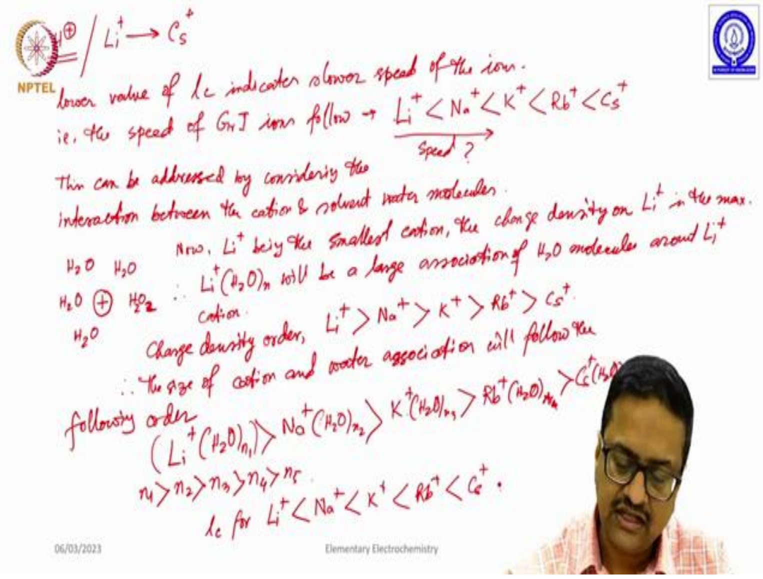

$H^{\oplus}$ / $Li^+ \rightarrow Cs^+$

lower value of l_c indicates slower speed of the ion.

i.e. the speed of Gr I ions follow → $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ $\xrightarrow[\text{speed ?}]{}$

This can be addressed by considering the interaction between the cation & solvent water molecules.

Now, Li^+ being the smallest cation, the charge density on Li^+ is the max.

∴ $Li^+(H_2O)_n$ will be a large association of H_2O molecules around Li^+ cation.

Charge density order, $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.

∴ the size of cation and water association will follow the following order

$(Li^+(H_2O)_{n_1}) > Na^+(H_2O)_{n_2} > K^+(H_2O)_{n_3} > Rb^+(H_2O)_{n_4} > Cs^+(H_2O$

$n_1 > n_2 > n_3 > n_4 > n_5$.

l_c for $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

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So, when we have this scenario we at the moment keep the h plus ion aside because that has abnormally high value, so there must be a particular different reason for that high value, let us first discuss about the case of Li plus to Cs plus. Now, this lower value of l c indicates slower speed of the ions that means the speed of group 1 ions follow this trend speed trend lithium plus is small lowest then Na plus then K plus then rubidium and then Cs plus.

So, why does that happen? Why the speed continuously increases, it is of course in a general consideration when you think about motion of any object in a large crowd of motion of one human being in a large crowd a thinner person would move faster, so the speed of that small person will be faster than a fat person.

So, in if you consider that concept then lithium plus should have the highest speed and CGM plus would have the lowest speed, but here again this situation is totally reversed from the values of ion conductance that we see that means looks like lithium has a very small slow speed and CGM has a high speed.

This can be addressed by considering the interaction between the cation and solvent water molecules, because you see the cations in solution do not stay as an independent ion all the cations will be associated with solvent water molecules around it, lots of water molecules will be associated with the central cation.

So, now Li plus being the smallest cation among all these the charge density on Li plus is the maximum among all these cations, therefore, Li plus H2O whole n will be a large association of water molecules around Li plus cation. So, this size of the ion increases from lithium to sodium to potassium to rubidium to cesium as a result the charge density reduces in the same direction.

So, if you arrange them in charge density order in the decreasing order of charge density order then Li plus has the highest charge density compared to Na plus compared to K plus compared to Rb plus compared to Cs plus. So, now the size of cation to, cation and water association will follow the following order Li plus H2O say N1 is much greater than Na plus H2O N2 is greater than K plus H2O N3 greater than Rb plus H2O whole 4 or N4 rather greater than Cs plus H2O whole N5 such that N1 is greater than N2 is greater than N3 greater than N4 greater than N5.

So, now what is happening is what we now can understand that lithium has a much larger size of the cation water complex that is cation water association and hence the motion of that cation water complex under the influence of a potential difference is much less compared to others and as the size of these cation water complex decreases the mobility of those ions increase and hence the order of lc for lithium is greater than that of Na plus then greater than K plus and sorry the order is the reverse, the motion for lithium water is less.

So, lc for Li plus is less than that of Na plus less than that of K plus less than that of Rb plus and less than that of CGM plus which was observed from the experimental measurements. So, now if you follow this argument, if you accept this argument that the cation hydration makes the complex size different because of charged difference in charge density then you must come back and tell me that then h plus ion has the smallest size among all these. So, h plus will have large number of much larger number of water molecules associated with it because of its very high charge to radius ratio, therefore, the h plus ion should have got the lowest value of ion conductance that is Lc.

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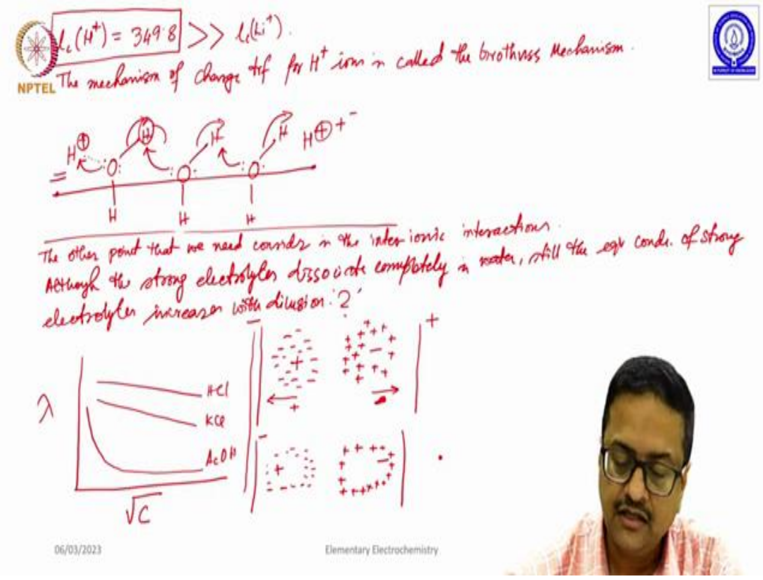

$\boxed{l_c(H^+) = 349.8} >> l_c(Li^+)$.

The mechanism of charge trf for H^+ ion is called the brothuss Mechanism.

The other point that we need consider is the inter-ionic interactions.

Although the strong electrolytes dissociate completely in water, still the eqv cond. of strong electrolytes increases with dilution. '2'

But in case of h plus this situation is totally different as you have seen I have written that Lc for H plus is 349.8 which is much, much greater than Lc of l i plus, so this difference this the very high value of Lc for charge h plus is attributed to a different reason that is the how the charge this H plus ion carries the charge from one end to another, the mechanism of that charge transfer.

So, the mechanism of charge transfer for H plus ions is called the brothms mechanism. So, what is this mechanism? You see that the advantage of H plus ion is in water is that this H plus ion is in close proximity of water molecules which has lone pair of electrons, so this H plus can accept lone pair of electron and get bonded to this water molecule and this H plus can be kicked out.

Similarly, enabling water molecule will accept that proton and if another proton will be removed. So, like this when you have a very fast transfer of proton from one water to another water this takes place this proton, this H plus moves out leaving the electrons back, so you end up getting H plus ion in the other end.

So, instead of this H plus ion moving from this point to that point individually this transfer mechanism of proton helps H plus ion to conduct electricity much more efficiently and that is why the Lc value for H plus is much much higher compared to the other cations in the group. So, this mechanism is called brothms mechanism and this is possible only for H plus ions in water.

The other point that we need to consider is the inter ionic interactions although the strong electrolytes dissociate completely in water still the equivalent conductance of strong electrolytes increases with dilution, why does it happen? If you remember the plot that I had shown for strong and weak electrolyte for lambda, it varies with square root of C and you get this kind of plots for different strong electrolytes I think this will be HCL, this is KCl and for weak electrolyte acidic acid it was like this.

So, what is the reason for that kind of increase in conductance increase in equivalent conductance with dilution, the reason is that whenever you have a cation suppose a monopositive cation that monopositive cation is surrounded by a large number of anions of course because of electrostatic interactions. Similarly, each anion is associated with a large number of cations around it and this is the scenario with moderate to strong solutions of the electrolyte.

So, now when you try to apply a potential difference across these ions suppose this is the positive electrode and this is the negative electrode what we will try to happen is that the anions will start negative ions will tend to move towards the positive electrode and the positive ions will tend to move to the negative electrode and what will happen is this second scenario that the positive ion tries to come closer to the electrode when the negative ion atmosphere is pulling the cation to the other direction because negative ions are moving away from the negative electrode.

And similarly, on this side when the negative ion tries to go to the electrode the positive ions tend to pull the negative ion to the other side. So, this inter ionic interaction becomes very very important and this also changes the capability of conducting in charge by those cations and anions.

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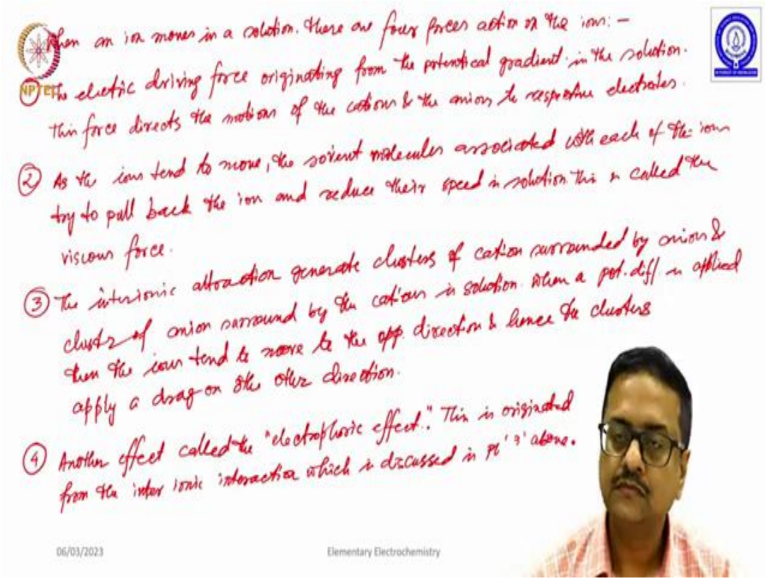

When an ion moves in a solution. there are four forces acting on the ions:-

① The electric driving force originating from the potential gradient in the solution. This force directs the motion of the cations & the anions to respective electrodes.

② As the ions tend to move, the solvent molecules associated with each of the ions try to pull back the ion and reduce their speed in solution this is called the viscous force.

③ The interionic attraction generate clusters of cation surrounded by anions & cluster of anion surround by the cations in solution when a pot. diff is applied then the ions tend to move to the opp. direction & hence the clusters apply a drag on the other direction.

④ Another effect called the "electrophoretic effect." This is originated from the inter ionic interaction which is discussed in pt '3' above.

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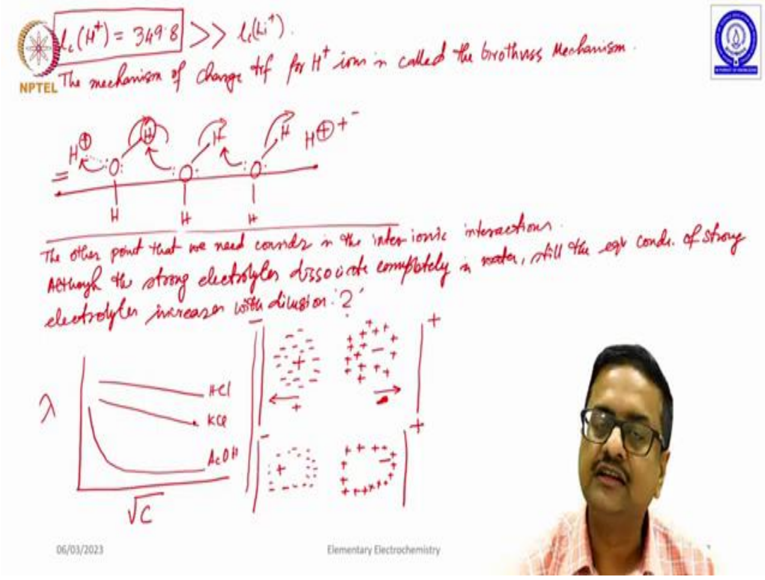

$\boxed{\lambda_c(H^+) = 349.8} >> \lambda_c(Li^+)$.

The mechanism of charge trf for H^+ ion is called the Grotthuss Mechanism.

The other point that we need consider is the inter-ionic interactions.

Although the strong electrolytes dissociate completely in water, still the eqv condc. of strong electrolytes increases with dilution. '2'

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So, when an ion moves in a solution there are four forces acting on the ions, number 1, the electric driving force originating from the potential gradient in the solution, this force directs the motions of the cations and the anions to respective electrodes. Number 2 is as the ions tend to move, the solvent molecules associated with each of the ions try to pull back the ions and reduce their speed in solution. So, this is called the viscous force. So, this tends to reduce the speed of the ions.

Number 3 is that the inter ionic attractions generate clusters of cation surrounded by anions and cluster of anion surrounded by the cations in solution when a potential difference is applied, then the ions tend to move to the opposite directions and hence the clusters apply a drag on the other direction, this I have already explained here that the cations were associated with many anions, anions were associated with many cations and when you apply a potential difference the cations move towards the minus electrode anions move towards the positive electrode.

But then there is a drag of cation on that negative ion retarding its motion towards the cation cathode and the positive electrode and the anion when it is moving towards the sorry cation when it is moving towards the negative electrode anions pull it back. So, this force also exists in that. And the number 4 is the is another effect called the electrophoric effect, so this effect called electrophoric effect and this is originated from the inter ionic interactions which is listed which is discussed in point number 3 above.

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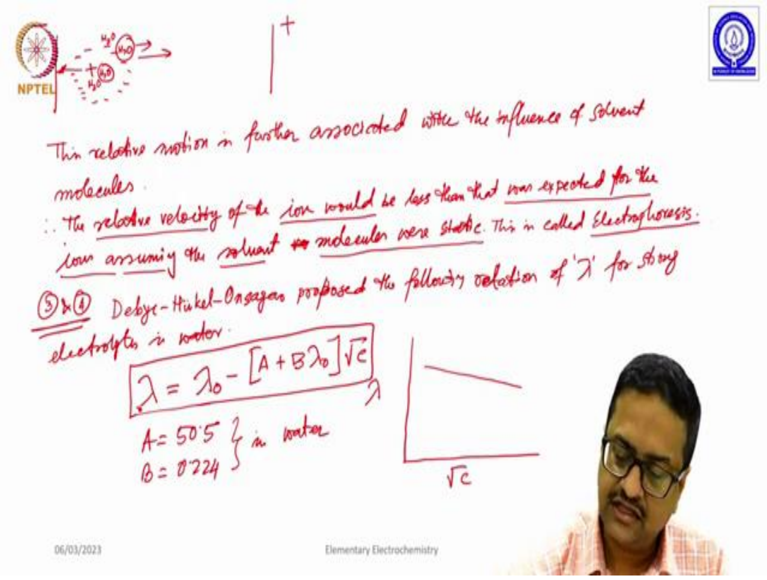

This relative motion is further associated with the influence of solvent molecules.

∴ The relative velocity of the ion would be less than that was expected for the ions assuming the solvent molecules were static. This is called Electrophoresis.

⑤ & ④ Debye-Hückel-Onsager proposed the following relation of 'λ' for strong electrolytes in water.

$$\boxed{\lambda = \lambda_0 - [A + B\lambda_0]\sqrt{c}}$$

$A = 50.5$, $B = 0.224$ } in water

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So, in this condition what happens is the positive ions get a drag of negative ions in the opposite directions because positive ions are trying to move towards the negative electrode but these electrons it is these negative ions are trying to pull it towards the opposite direction and this relative motion is further associated with the influence of solvent molecules.

So, the relative velocity of the ion would be less than that was expected for the ions assuming the solvent molecules were static, see what we are trying to propose here is that when you have a cation which is surrounded by the anions is also surrounded by lot of water molecules anions are also surrounded by lot of water molecules.

So, when you apply a potential difference the anions tend to move towards the positive electrode by taking the corresponding solvent molecules with it and cations when it tries to move towards the negative electrode that also tries to drag the water molecules along with it as a result these solvent molecules are no longer static, they are moving along with the corresponding ion with which they are associated as a result the relative velocity of the ion may be relative velocity of cation is much less than that was expected for the ions assuming that the solvent molecules were static. So, this is called the electrophoresis.

Considering all these effects the effects of 3 and 4 Debye-Hukel-and Onsager proposed the following relation for the equivalent conductance lambda for strong electrolytes in water that lambda equal to lambda 0 minus A plus B into lambda 0 square root of C, where A is a constant 50.5, B is a constant whose value is 0.224 in water to explain the nature of the plot that we have already discussed for the strong electrolytes that is lambda versus square root of C you get to see a plot like this. So, to explain this plot this equation was proposed. So, I would like to stop here in this class and we will continue from here in the next class. Thank you.