Analytical Chemistry
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Module 11
Lecture No 54
Electrochemical Methods 3(Contd)

Good morning everybody, so welcome to this class where we are still continuing about the electron transfer processes and basically we are looking for the different types of electrode processes. So all these different techniques starting from your potentiometric to ultimately what we are discussing right now the cyclic voltammetry, so the voltammetric techniques are basically very important to understand the corresponding electrode processes and these electrode processes are based on where we have the working or indicator electrode, so we want to study whatever thing is happening at that particular working electrode and is very important that is why.

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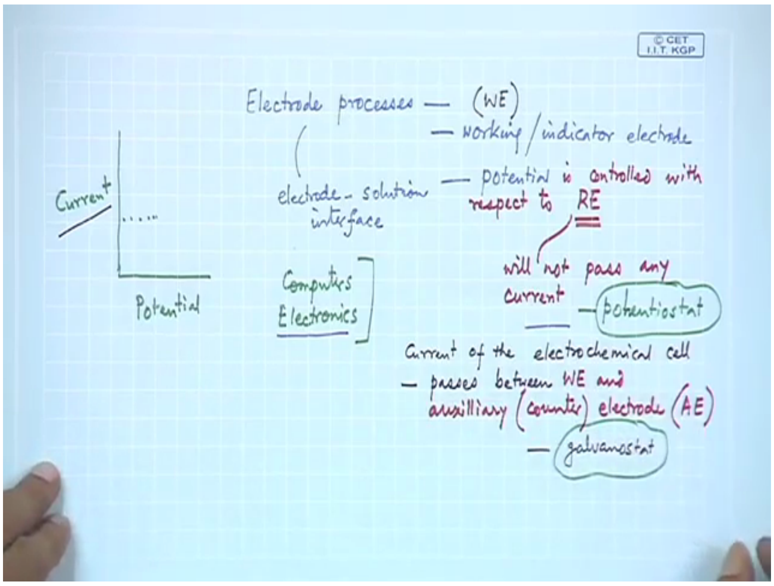

So basically what we are looking for the electrode, not only electrode but it is electrode and the analyte solution interface, so how that particular interface is important and how these are important in terms of the electron transfer reactions. So what we see, we just want to plot 2 things that is we call as the current potential plot so we have the current in one axis and potential on the other and the typical development what we achieve so far is due to not only the modification of these different electrode types but also the advent of new generation of computers and the related electronics which are very important to improve these particular types of electrode processes and we can have different variations but the most basic one what we are looking for is your potential measurement.

So what the potential of the working or the indicator electrode, so what we basically measure is your potential of this working or the indicator electrode is controlled with respect to what with respect to the corresponding reference electrode. So this reference electrode we have certain condition what we impose as that this reference electrode will not pass any current so will not pass any current that is very important. So in that way we basically measure that thing and the electronics parts for that basically what is the particular part which is responsible for measuring the potential is therefore that we can have a static potential and the different potential values we basically get.

So what we get is that particular types of potentials were there so is by potentiostat so the electronic part of that is that arrangement for potentiostat should have and that potentiostat will be responsible for measuring that potential with respect to the reference electrode. And the second component now we want to measure is your current, so the current of the electrochemical cell how we get the particular current because we are not allowing the current to pass through the reference electrode so whatever current we are allowing to pass is through the corresponding auxiliary electrode so we have the same working electrode, so this was your WE the working electrode so here also you will have the working electrode.

So the current which we will be going to measure for this particular type of plot is passed or passes between what? Between the working electrode because we will have the definitely the current and auxiliary electrode or counter electrode or counter electrode so we if we consider it as AE as the auxiliary electrode. So there something else will be there so one particular part will be responsible for measuring your potential and other parts of the electronics will be responsible for measuring your current which will be our galvanostat.

So these two things always we should keep in our mind that we are without knowing the very details of the electronic arrangement and all this, but the name of this thing the basic components what we can have, we have the potentiostat and the galvanostat for all the different types of electrochemical measurements and the electrochemical workstation what we can have. And we get the corresponding current potential plot and we can analyse for these things.

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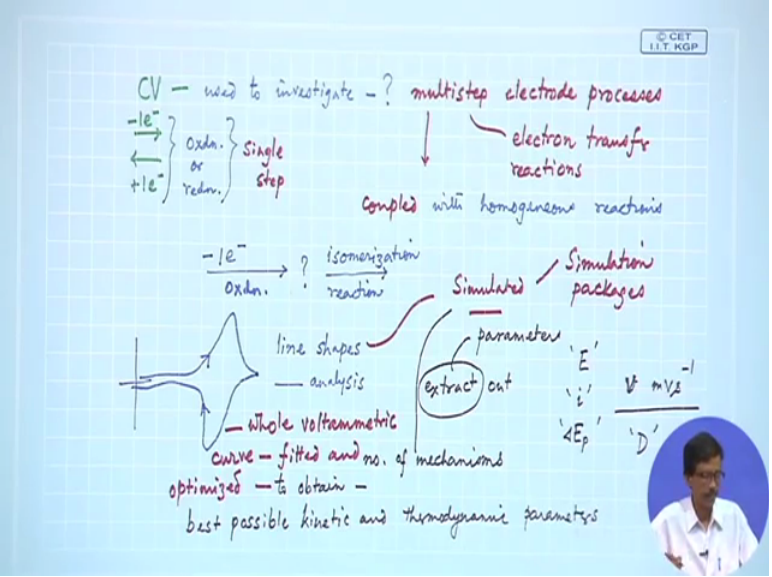

CV – used to investigate – ? multistep electrode processes

$\xrightarrow{-1e^-}$ / $\xleftarrow[+1e^-]{}$ } Oxdn. or Redn. } Single step

electron transfr reactions

coupled with homogeneous reactions

$\xrightarrow[\text{Oxdn.}]{-1e^-}$? $\xrightarrow[\text{reaction}]{\text{isomerization}}$

Simulated / Simulation packages

line shapes

— analysis

— whole voltammetric curve – fitted and optimized – to obtain – best possible kinetic and thermodynamic parameters

extract out parameters

no. of mechanisms

'E'

'i'

'ΔE$_p$'

ν mVs^{-1}

'D'

So the first thing what we are getting is your cyclic voltammetry, so cyclic voltammetric arrangement can also be used because once we have seen that it can go for one electron oxidation that means – electron or it can go for + one electron reduction process, so these two processes we can monitor very nicely but if the situation is little bit complicated how we can handle that particular thing also we can see, so it also investigate so used to investigate part that means more complicated reactions or the corresponding follow-up reactions, so if we have not a single step so whatever electron transfer for oxidation or reduction we are getting oxidation or reduction and those we can consider as the single step electrode processes so those are single step electrode processes.

So if we can have some multistep electrode process or processes so multistep electrode processes we can consider that means one electron followed by another electron transfer all these things can happen and sometimes not only that, always there will be a chance we all know that if the corresponding oxidised species or the corresponding reduced species are not very much stable in the solution they can perform further reactions to undergo, so this multistep electrode processes or the electron transfer reactions because electrode processes are nothing but multistep electron transfer reactions so those are your electron transfer reactions.

So those multistep electronic transfer reactions can be coupled with some homogeneous reactions can therefore be coupled that means it is coupled with some homogeneous reactions. That means if we can follow that there is some electron transfer reactions that means electron transfer one electron reduction in the state is oxidation and whatever species is produced over there it will have some reference for some reaction. If there is a mixture of isomer, we will see now that how we can detect within a solution the two isomer also so that can be considered as the follow-up reactions the homogeneous reaction what is falling electron transfer is isomerisation reaction and that we can also follow very nicely.

And in fact whatever cyclic voltammogram you get from say a potential starting potential and then you have the corresponding switching potential then it gets like this say forward scan and the backward scan but all the different types of plots basically what I have drawn here and what I showed earlier from the textbook also that they are having the different line sets and we all know that a corresponding type of plot suppose the upper part of this lot we can fit it. So theoretically the fitting procedure we can for a corresponding Gaussian analysis type or the Lagrangian analysis that means the shape is either Gaussian shape or the Lagrangian shape for its lines shape.

So the line shape analysis is the most important and the most crucial state to understand this type of electron transfer reaction so what we can do thus these lines steps what we achieve experimentally can be simulated so those can be simulated and now commercially available simulation packages are also available so we can have the commercially available solution packages which we can use it for that. So this simulated spectrum what we get that means the theoretically predicted spectrum with the exact line line shape are matching with that experimentally obtained.

So we get the different parameters because basically we can say here we can extract out the different parameters like the potential what we can have current, what we can have Delta EP, what we can have and how they are dependent on one particular important thing is the corresponding scan rate small v basically, so is millivolts per second scan speed so how it is related to all these things so we can through that that means through simulation we can therefore be able to establish a number of mechanisms because all these electron transfer mechanisms are so important from materials from our life processes and everywhere so what we can do that for using this software packages the whole voltammetric plot or whole voltammetric curve can be fitted so whole voltammetric curve can be fitted and optimised.

That means, it is not that you can exactly reproduce the experimental curve but as much as possible you can match the corresponding experimental curve and from that what we can do, we just basically extract the data extract the parameters and therefore, we basically obtain the best possible which otherwise is not possible from the typical experimental plot, so best possible kinetic from the rate and all this and thermodynamic because in doing so what we can get that we can have to feed some equation and that is why we can have some simple equations like starting from the last equation then Ilkovic situation and all these different equations can be established.

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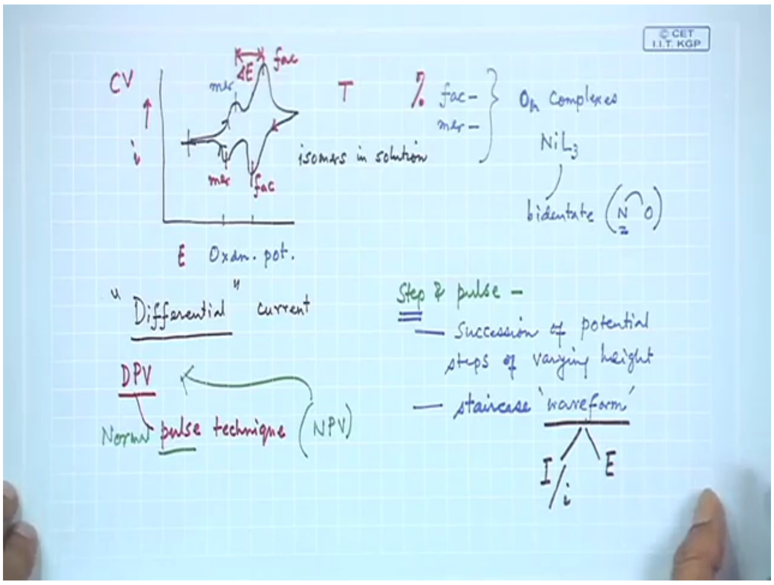

And once we establish these in terms of either the current or the potential, we can extract out so many other parameters like the deficient coefficient what we have discussed earlier. So is the best possible way to extract out your kinetic and thermodynamic parameters. So these things are very important and if we have therefore very overlapping plots so they are not very much separated such as when we starts from here we can get one thing and before going for its resolution that means going to the baseline once again, a second voltammogram starts appearing and you can get the first one as well as we can get the second one.

So this we get for a typical scan and if we have isomers in solution then only we get this sort of plot and we expect this sort of plot particularly when we talk in terms of the corresponding (())(15:38) complexes we can have these 2 isomers, we all know that the facial and the meridional isomers so you see that with respect to the corresponding potential for say oxidation that means if we try to measure the corresponding oxidation potential so the first isomer is oxidising here so if you have the main isomer over here is fast oxidising that means in a medium these are all octahedral complexes because we get these 2 isomers in some NiL3 type of complexes where L is your bidentate ligand and you have definitely of 2 different donor atoms like nitrogen and oxygen.

So NO donor type of ligand when it binds to the face where one face is basically occupying all nitrogen and another face is also occupying all oxygen, so we get the corresponding facial isomer and other one is also the meridional is spanning same donor group. So if you get the first oxidation potential for that isomer is say the meridional then the second one will be the facial isomer. Then if we go for your reverse scan, the facial isomer that has been oxidised over here they will now be reduced over here and next is your meridional isomer.

So if we can able to do this thing and also the corresponding temperature effect for this voltammetric processes and how we can vary it, how we can go for this or we change the corresponding proportion of these 2 isomers will also change and that can also be shown for their relative responses in the cyclic voltammogram where we measure the corresponding current against the corresponding potential E. So if we find that what should be your corresponding differences because this difference this separation this Delta E value for these 2 isomers are sometimes so overlapping that we cannot get the sort of thing very nicely. So what we expect, we get something where we can go for the derivative one or the differential one.

So what we can go, we can go for differential current you can follow, so differential current measurement you can achieve it and that is why a new technique basically because the differential current measurement basically gives rise to a technique like your this was your CV and the next one is your DPV differential pulse voltammetry. So you have differential current and the P stands for your pulse technique. So the very first thing what we will be getting over here is the one where we do not have this differential one so will be your normal one. So your normal voltammetry will be NPV, so before going to your DPV we should no little bit about the normal pulse voltammetry.

So what do we get? We get the state and pulse technique so it is not the state as well as the pulse 1 so once you have the pulse one so state and pulse technique is useful. So again with the development of your electronics part and the available computers and their small computations also are very much needed so the development from that part electronics part in the computer part is very much important to get this state and pulse technique. And what we have, we have succession of potential steps we use of different heights of varying heights so that basically gives you the step, shape of the different steps and next we get the corresponding pulse, so is not the continuous one it is the pulsed one.

So what we get there is a staircase waveform, so as we discussed earlier that the different waveforms are available and these different waveforms are the triangular waveform is used for your cyclic voltammetry measurement. So now we are looking for something where we can consider it as a staircase waveform so how the nature of this waveform is useful for getting the corresponding E value and corresponding I, sometimes we also write it in the small ‘i’. So the current, so how we generate those potential pulses so short potential pulses are generated and which are given to the electrodes.

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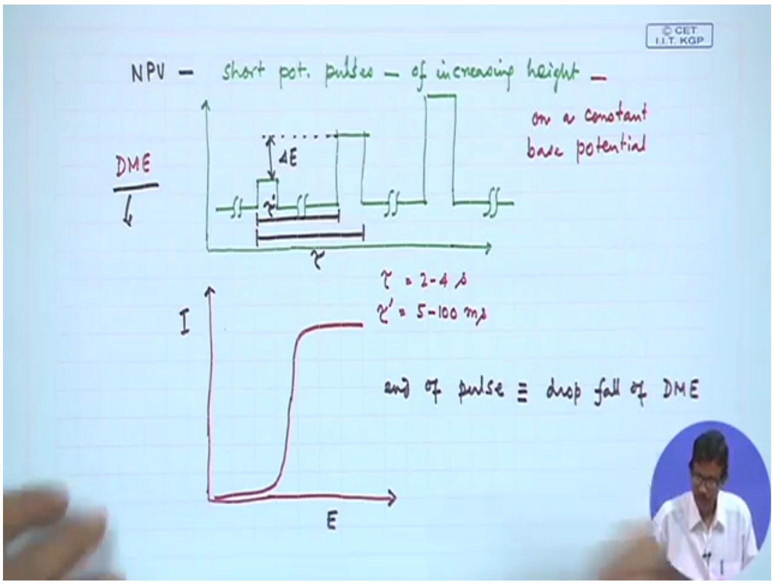

NPV – short pot. pulses – of increasing height – on a constant base potential

τ = 2-4 s

τ' = 5-100 ms

end of pulse ≡ drop fall of DME

So in normal pulse voltammetry in NPV what we do, we basically use there the short potential pulses, so they are very short potential pulses are used of increasing height so what we see there because we should know about the nature of these so it is the break so it is going and is breaking at some point so its height is increasing but this particular time axis is not changing so that means the time width for these different pulses are same, only the strength of these pulses are changing so it is coming back again to the base line. So when it is coming back to the baseline and we get something and this basically the separation between the first one to the second one we get and the timeframe from here to up to this point is your Tau prime and the time from here to this point is your Tau because this Tau and Tau prime values have some significance for this.

And when we get this your this change this the pulse changes because the Delta E values are there so these are the corresponding potential values so is the corresponding potential axis and this is your time axis and when we figure out for these for the normal pulse voltammetry is that Tau values will be the range of seconds, it will be 2 to 4 second range where the Tau prime in the range of 5 to 100 3 seconds so the separation, so these are the corresponding various (())(23:56) the continuous variation what we can impose for this sort of measurement so you see everything is computer-controlled or rather electronics control for this sort of measurement.

So when we get this as increasing height of Delta E values of these pulses, so what we have again the potential is coming back so you get will give the short pulses this confusing height pulses are giving on a constant base potential because it is coming back to the original potential values so that is why we get original plot. So what sort of our current potential plot would be then, you should know that what should be the normal pulse voltammetry and how the corresponding plot will look like so it will be like this so it is a typical staircase type of plot like our all cases we find for potentiometric measurements also, so this can also be done in using the dropping mercury electrode what we know from the beginning that the historical it is also important to get that dropping marker electrode for the development of polarography.

So this is your I axis small i or capital I whatever it is so it is your current axis and this is your potential axis is your E. So this potential axis you can have and is moving in this way, so when we use the dropping marker electrode so the drop life time is there. If we consider sure that drop life time is same to that of your this corresponding generation of these pulses, it will be very easy to monitor these things in terms of that so when we finish it when we come back to this particular position is your end of pulse. So when you finish that, that means end of pulse will be equal to your drop falling of the drop or drop fall of DME, so you get a fresh or new dropping marking electrode, new drop of marker you are getting and that new drop of marker is utilised for your second pulse and the third drop is for the third pulse so in this way it will be very useful for this normal pulse voltammetric measurement.

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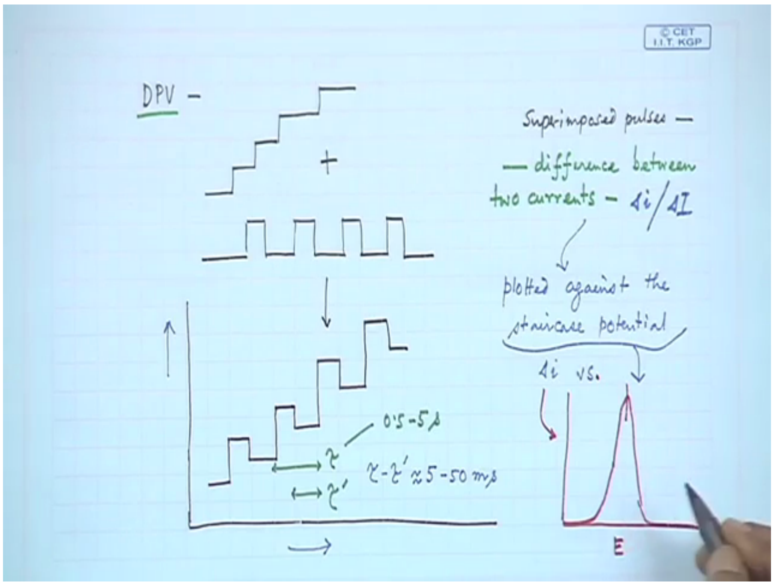

But nowadays with the development of other parts also we can go for a differential one which is your DPV so how we know that because it is a very useful technique why it is useful that we will see just now what we have seen that is if you have a very overlapping potential so cyclic voltammetry cannot give the good resolution for that. So you have now for the DPV we have the superimposed pulses so how one of them is your staircase one and another one is the square steps so if 2 of them basically matched together, we get the corresponding pulses again in the basis of Tau and Tau prime. So what we get now is very important and interesting also, you get this and you come back and you get this and it go up like this.

So this is the waveform so we should know the shape and nature of the waveform particularly for your differential pulse voltammetric measurements. So this differential pulse voltammetric measurements are useful in that way that you have not that earlier we have seen a normal pulse voltammetry your base potential was not changing so it is coming back to the base potential. Now your base potential is your staircase so this base potential is changing in a staircase manner because the staircase we have imposed on something where this is of the same height.

So this particular one from here so what are those your tau and Tau prime values so this is your one will be your Tau and another would be your Tau prime values for this so we get this superimposed pulses so we get basically the corresponding current responses because this is the potential versus time axis so whatever current responses we get over there so is then plotted so we get the difference between two currents. We basically get 2 different currents and you have these pulses again, so Tau is basically going from 0.5 to 5 seconds it can range it can have the corresponding range from 0.5 to 5 seconds and your Tau – Tau prime would be in the range of 5 to 50 milliseconds.

So these timeframes are very important that how short or long durations you are utilising for generating those pulses so you get the difference between these 2 currents so this difference in current that can be whether you consider as Delta I or Del i and we plot this basically so this when we plot, so it is plotted against the staircase potential so is plotted therefore against the staircase potential because this potential is changing, this is your time so staircase potential so we get this Delta i versus your staircase potential. So Delta I versus staircase potential will give rise to all these things and how we will analyse it and all these things we can discuss in our next class but what we plot if it is your Delta I and is the plotting against the potential so we get from the very baseline is basically change like this and are very sharp plot we get.

Corresponding to the potential only one potential is fine for this oxidation reduction, we do not get the reverse one, so this is your corresponding plot for your DPV. So in the next class we will see how we can utilise this and how we can find out this when we have the corresponding overlapping plots okay.