BioMEMS and Microfluidics
Prof. Dr. Shantanu Bhattacharya
Department of Mechanical Engineering
Indian Institute of Technology, Kanpur

Lecture - 21
Review Lectures of 7 to 10

Hello and welcome to this review lecture for lecture 7 to 9, and basically this will all about electrochemistry and the way that measurements happen electrochemical system. So, we talked about the various calibration methods which were available for electrodes; for example, there were 3 methods that were specified - one was the direct measurement method, another was the standard addition method, third was the gran plot. And as the theory would go the direct measurement typically indicated that you have to calibrate, an electrode electrochemical electrode with reference to standard pH solutions.

So, you have 3 different pH's over which measurements are made of the EMF of the electrode, and then you have a calibration plot and the idea is that whatever the read out comes in terms of particular concentration, it would be read directly the concentration would be read directly by looking at this calibration plot. Assuming that the Nernst equation is obeyed and the potential verses log of concentration follows a linear characteristic.

So, as we also indicated this was a method which was more based on experiments and insufficient experiments, because the calibration would really depend on the number of points that we would make. And when the manufacturer decides to make an electrode and sell it typically not more than 3 or 4 solutions of different pH's are provided, because of logistic reasons. And therefore, based on these 3 or four points of pH EMF verses log of concentration relationship may not be accurate representation of the actual calibrated electrode.

So, there were requirements felled for different other methods for calibration; one of them was a standard addition method where there would be solution of known concentration of a known volume added to the one the analyte of interest which had an unknown concentration and a known volume. And there was a series of calculations through which it was shown how the 2 EMFs with the unknown concentration as well as the concentration after addition of this standard solution were taken. And based on the EMF difference you could correlate what is the unknown concentration of the species in question.

So, this was one step further to the direction method, because now there would be the possibility of introduction of some variability by introducing a new concentration, and let the electrode behave towards the new concentration. So, the randomization which would happen in the measurements as a natural process would be more limited, because of this addition and inclusion of that in the calibration scheme itself. The other requirement was that can we do multiple additions, because standard addition was only one step towards this minimisation of the random elements for measurements of the potential.

So, we did multiple additions meaning there by that, now you have different concentration different known concentrated solutions, which would add to your unknown concentration. And then you would plot the 10 to the power of delta e by s with respect to the concentration at hand, and then would extrapolate it all the way to the point when this 10 to the power of delta e by s would be 0. So, that your unknown concentration is your standard concentration which is added, this actually gives rise to a more variability or a more variable nature solution and EMF being measured every time by the by the electrode.

Then calibration is based on such variability meaning there by this would be more accurate representation of the actual calibration that the electrode should have in measurements. So, after doing these three addition methods we started talking about ion selective electrodes, and we started briefly describing about how this ion selective nature of the electrode can be introduction of iron activity was raised, where iron activity as we find earlier is a factor to the concentration of the analyte of interest which is added, because of the fact that there is a substantial interference from the other irons which are present near the target iron in the solution, meaning there by supposing there is a solution which contains the target ions.

Many other ions which are probably non-interfering in nature, but still they are present, and then the electrode needs to get influenced by electrode does not I mean electrode should be in a situation, where it need not have any influence from those interfering ions or even non interfering ions, and it should be able to measure the particular iron of interest of the target iron.

So here the idea is that how the target iron would be resulting in the reduction oxidation process or how the charge transduction would happen between the electrode, and the solution is also quite dependent on this environment of the target iron. So, as we properly sort of studies that what are the different causes for influencing this ion movement of charge exchange with the electrode, and the interface of electrode one of them would be simply that the irons would move randomly with respect to each other in a solution itself, because of Brownian motion, you cannot attain absolute 0. And therefore, at room temperatures defiantly there is going to be some motion some movement of the ions of the solutions.

So, then there would be columbic force of attraction between the irons of opposite kinds. And similarly there would be forces of repulsion between irons of opposite of similar kinds and there is always a tendency that they the central ion of interest drags an ionic environment around it of the opposite charge. The opposite nature although the overall charge neutrality concept would be or principal would maintained, but still there are going to be several positive charge canters surrounded by a bunch of different negative charges and. So, therefore, it is very definite to say that the influence from this columbic forces would be substantial in terms of ions moving getting reduced or oxidised at the electrode solution surface interface.

Electrochemistry has to considered these aspects, and then of course the facts that whenever there is a localised movement from one such environment to another environment going towards the electrode of its opposite charge kind, where ultimately the charge would be Diswaited or disappear, there is always going to be some kind of forces are interplay between such environment.

So, because of all these complex reasons, it is always important to say that the solution will not be represented in terms of 2 concentration there is going to be some difference between the 2 concentration of the analyte, and the actual concentration which is contributing towards any EMF change of an electrode one of the reasons why activity coefficient is brought in which is typically a factor of the concentration. And it was very clearly illustrated that earlier before electrochemical theory was not.

So, advanced probably 1920's or before that there was always an experimental validation of what is the activity looking at only the Nernst equation, and trying to find out what the log of, so called apparent concentration. So, which is actually the activity would behave like with the measured potential of an electrode, but later on of course, there was a theory which was described by detailed in the lecture where we talked about several aspects of electrode electrical charges, and columbic forces between a central charge which may be positive in nature to its ionic environment, which it would drag and in that light we tried to solve the equation which is of course, the solution for the potential function.

If we consider the central iron to be of spherical symmetry, and if you consider that the potential only varies radially outwards from the centre of the iron all the way to the infinite domain or infinite distance from the iron. So, we formed a very good theoretical background about how the ion of interest could actually result in its environment by doing some work by the system a distribution was assumed at infinite infinity in terms of numbers per unit volume. And then by using the Boltzmann equation, it was sort of analyse that add the point of interest where the potential function is been evaluated.

What would be the charge distribution, because the distribution, because of the presence of this distribution at infinity, and the potential associated with the central charge? So, we got a series of equations where by solving for the potential function. Finally, we obtain a very interesting form of the equation, which was related to a e to the power of minus k r by r, where a would be a constant coming out from the a b the general solution for the o d in question and e to the power of minus k r where r is the radius associated from the central of the iron of interest, all the way to the infinity. And this k coefficient was determined in terms of the summary charges of both positive, and negative kind which was there in the particular environment of a single charge in concentration.

So, finally we try to find out this a factor by using an equation, where we integrated the volume charge density, all the way from the surface of the iron which would be also known as the ion size parameter, all the way to the infinite distance, where the charge density assumes complete equivalence and there is no distribution before infinity of one charge over the other kind. And then we would equate that to the exact magnitude of the central charge assuming that the electro neutrality principle is obeyed.

From that we could actually find out what a value is and subsequently could determine the density of charges near the central ion of interest, which was in question. So, once we did that then of course, we found out that if we evaluate the potential function at the surface of the charge which is also nothing but the ion size parameter, it has 2 contributing components. One component would be resulting from the potential imposed by the central charge, and the other component would be the potential imposed due to the atmosphere the ion atmosphere as bound by the central charge.

So, an equivalent radius for the iron atmosphere was arrived at and it was actually nothing but 1 divided by 1 by k plus a, where is a ion size parameter, and subsequently we tried to see what is the work done per mole of the charge in order to bring the at least one mole of the environment very near to the central charge of the interest by virtue of the work done by the central charge itself. And then equated that to the free energy of the system, which would give us a very important relationship between the activity coefficient gamma i.

The amount of work done by the potential function psi i at a certain point probably at the surface of the charge at radius r equal to the ion size parameter in order to contribute, in order to build up an environment around, it its basically the total amount of work done by the system by one particular charge to built an environment of exactly the opposite charge around it. So, with this equating entity we could actually bring out a very simple relationship between gamma i the activity coefficient, and several other interesting parameters like the amount of valence of the charges which are different charges, which are present their actual charge values Boltzmann coefficient k, the temperature, the absolute temperature t the dielectric constant d. And then finally, things associated with this equivalent ionic radius which has which is in question.

Finally, we arrived at a very short concise form of how to define the iron activity coefficient which we use later on in several solved examples in order to evaluate the efficacy of each iron in the presence of each other. So, we did some problem examples towards that direction, where we try to see what is the effective influence of this activity coefficient onto the EMF generated at a particular electrode while sensing a solution. In fact, we tailored some problems wherein we mixed some 2, 3 different ions of interest and tried to modulate before mixing and after mixing, what is the contribution from the particular target ion of a change in activity going to the presence of other ion.

So, we did a very important design step here and this contributory equation was also called the Nichols chrysie equation, where we tried to find out what would be the contributing factor of one ion in the presence of the other, and in this light. We also discuss something called as ion selectivity coefficient. In fact, the ion selectivity coefficient could be determined through a series of experiment as was also designed earlier for different ionic systems.

For example, if there is a sodium ion present, and we want to measure the sodium ions concentration, and we put series of different ions like calcium ions probably you know some chloride ions some sulphate ions some potassium ions, so and so forth. And then try that at each level of mixing we tried to find out what are the contributing EMF’s, which would result in some way for us to gauge what is the selectivity of calcium ion over the other ions, which are present in the systems itself. So, this in a nutshell completes our lectures 7 to 9 and also lecture 10. So, following this we will be doing another review section for lectures to complete out.

Thank you.