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

Lecture - 22 Review Lectures of 11 to 13

Hello and welcome to this review lecture for lecture 11 to 13 will be reviewing the various things which have been covered in these lectures today. So, basically in this lectures we discussed about the various techniques for realising physically the ion selective electrode and some of the ways which were described by the use of glass membranes. For example, particularly relevant for the pH measurement application, there are certain glasses which are the carbonates - the silicates which would be very, very selective to hydrogen ion over the other competing or interfering ions of interest.

We also talked about various crystalline membrane based ion selective electrodes which would involve crystal membranes like Lanthonm fluoride for doing selective detection of fluoride ions, and so and so forth. So, we also talked about the various natural extracts which are available from trees, etcetera which would be in a same manner as it has happens biologically or naturally would be able to measure one ion of interest. For example, we discussed about valinomycin, which is a very important organic extract and which is available at the membranes membrane or surface of the cells for doing ion transportation calcium, calcium or potassium ions

So, such naturally available extract can be easily used for similar application while measuring ion selective electrodes. We described about the various enzyme based membranes which would be selectively able to create a reaction or influence on a certain target species of interest. So, this is another class of the ion selective electrode. Having said that we also talked various gas electrode which are available the most fundamental measurements that are done are for example, detection of ammonia from... Let us say ammonium chloride and in that light everything converges to the measurement of pH across a glass selective electrode.

Following this we also talked about the various electrodes are related to the biological measurements for systems. Here, in we discussed things like penicillin sensors where by using an enzyme called betalactin would be able to change penicillin in to penicillite, and a hydrogen ion and essentially that hydrogen ion using pH electrodes. We discussed about how

to measure glucose again by change again with an enzyme glucose oxidise of the glucose into gluconic acid an H2O2, which would effectively result in increasing the pH of the solution which would again measured by a pH electrode.

We talked about urea sensors, we talked about various other sensors related to measurements of creating phosphate. For example, within the human body or finilalon which is again which an alpha amino acid, and a kind of generates information about catecholamine's the presence of catecolaminas within the human body which are hormones released by the abdominal glands in situations of physiological stress etcetera within the body. So, effectively what we saw is that one way or the other the conversion of these analytes has to be made in the manner. So, that it generate hydrogen ions which can be measured using a pH electrode. So, at the end of the day everything is measured in terms of those hydrogen ion releases, which have been back librated to the concentration of target ion of interest. We also studied about the electrodes related to carbon dioxide gas sensing or sensing of oxalates as commonly happens for investigation of kidney stones etcetera, where calcium oxalate percentage goes up in particularly urine, so on and so forth.

So, we also described the various processes associated with the formation of the interfacial double layer we theorised about why this double layer comes in to existence, because of the random motion of some atoms at the interface of a solution. And the metal the random motion is in terms of a sudden release of the atoms in to the solution as an ion, because of very minute changes of surface energy at the surface of the electrode, the electron cannot escape as a result of the electron is always trapped within the electrode. And the atom goes in to the solution as an ion, and the moment goes in to the solution there is a separation done by again a dielectric as thin dielectric layer of water having a dielectric constant, which does not let the atom come back and take its position on to its parent electrode which it got generated.

So, this results in the formation of an interfacial double layer, which has a very high electric field going to the extremely thin nature of the monolayer of water, which is absorbed on the surface by surface energy concentrations, and this potential can go up to a very high level almost of the level of 1 volt per 10 to the power of minus 9 meters, so it about 10 to the power of 9 volt per meter level.

So, that is how high this electric potential can be, and it generally balls down to the fact that all electrochemical measurements have to be in consonance with the presence of this layer, because whenever there is a metal immersed in a solution, this double layer would automatically prop up. And there is a capacity to behaviour of this double layer as well as a resistive behaviour and particularly these issues become very prominent when use high frequency measurement, you know when the signal is along DC in question.

Therefore, very accurate modelling etcetera has to be done associated with this double layer. So, we started theorising that how this dual layer can be modelled in real systems, and then whatever was associated with the one charge to its environment consideration done earlier in the while evaluating the gamma i or the activity co efficient of the ions of interest. In this particular case we thought the surface to be composed as if of an array of such charges, and dual layer being formulated, because of an array of charges. And then we tried to again in a unidirectional x directional manner solve for the potential function and ultimately the variation along the radial direction in a cylindrical manner starting from the surface of the electrode, all the way to the infinity was accomplished which would result in the formulation of the potential at a surface of this electrode very near, we start of the dual layer and we would call this potential this zeta potential associated with the surface.

So, we derived a formulation for this zeta potential at the surface corresponding to a radius r equal to the ion size parameter a, and then we modelled this you know a bi potential form associated with the electrode as a Helmholtz layer or a Helmholtz potential and the diffused potential. And we also further assume that as the electric field in to the space filled with the dielectric fluid and as it goes beyond the helm holds layer, there is a rapid depreciation of the electric field as a square of the inversely as a square of the distance from the particular surface.

Therefore, a potential plot if made would surmise to the linear drop of potential across this helm holds layer following which almost the exponential 1 by r square drop 1 by r drop of the potential across the diffuse layer. And therefore, the diffuse layer would be self thinning in nature it would automatically thin out with a distance as a function of r from the start of the diffuse layer onwards as you move in to the solution, and basically it would again come down to 0 theoretically at very large value of radius almost equal to infinite distance, although it would actually come down to a realisably smaller negligible value at much earlier point of time. So, what we essentially now looked was a capacitor model with the Helmholtz capacitance and a diffuse capacitance, and try to model a surface based on a parallel combination series combination of these 2 capacitance as across 2 potential points.

So, from this there emerged a very interesting concept and theory that what happens; for example, in a micro channel when the surface would be charged and developed a zeta potential in contact with the fluid of a certain pH. And we try to now look at the different flows of interest varying from the simple Couette flow across a single flat plate as the fluid would move against the flat plate to a model where this fluid would move between 2 flat plates, which would essentially result in the generation of the parabolic flow profile. And we derive for the velocity using the Navier-stokes conservation of momentum equations under certain boundary conditions, and found out what is the variation of the velocity from the axial centre of such a combination of a twin plate all the way to the this static layer or the immobile layer of the fluid which is more towards the surface.

So, once we generated that we try to estimate in a similar manner, what would happen when there is a formulation of zeta potential in addition to a simple pressure driven flow case, and there we sort of try to model that what kind of force would be needed to separate this dual layer. So, that the charges in the diffuse layer would move perpendicular in a direction perpendicular to the direction of the field as associated by this dual layer and diffuse, layer and we found out that there is a condition corresponding to a situation when the electric field would give enough force.

So, that the layer would separate across the dual layer and move as a plug. So, we try to derive what would be an ideal velocity or velocity, what would be an ideal force or a velocity in such a situation, where shear would happen exactly at the dual layer interface and this phenomena is also known as the electrostatic flow. So, we talked about how this flow would be influencing. Let us say a silica surface which has been charged to its point of 0 charge, and then taken slightly above the point of 0 charge may to the negative pH or may be slightly below the point of 0 charge to the positive pH. And then associated dual layer which would be formulated how it would move, we try to find that how using electro kinetic theory and essentially that would result in to the mobility equation whereas a function of electric field, you can equate how much the ions would be mobile for a unit field and multiply that with the electric field to find the overall velocity of the ions in question.

So, this was in a nut shell what we try to do for estimating the electro static velocity, and then we applied this further for designing the electro kinetic network of flows particularly for a case, where there would be a crisscross based channel like this which is present. And then we would try to apply potentials at different end points of this cross, and would deterministically find out what is the mobility of an ion, and with the certain field what would be the velocity of flow the flow discharge of such a system. So, we design this electro kinetic network of flow. And here we use to the simple network theory for predicting, what is the current associated between unequal potential points on sides if exists on such a network, and this way we realize the very strong you know design of the electro osmotic pump.

We also talked about several other electro kinetic phenomena which emerges from what is the cause, and what is the effect? For example, in the electro osmotic flow the cause really is the electric field which is the driving factor. And the effect is really the velocity which gets formulated of the charges because of this electric field. So, there are several other associated phenomena which are also grouped under the domain of electro kinetic phenomena where in one case just as the electro osmoses case. If you consider motion caused by EMF the other important phenomena associated with such a motion would be the electrophoresis.

So in electro osmosis the whole dual layer moves as a plug, but in electrophoresis it is the movement of a single ion probably to the opposite direction in applied field of interest. So, again the motion is the cause and the effect is electric field, there is also a reverse way out of looking at electro kinetic phenomena that if you cause motion it may change or it may result in a potential coming out because of the motion.

For example, we discussed the phenomena of streaming potential, where a potential would be produced by a liquid being forced through a diaphragm through a sort of micro capillaries and one of the reasons why that would be. So, is that you are disturbing the electrical double layer by physically applying pressure to make a shear action possible between the electrical double layer, which would force this layer to move against each other.

So, there would be the tendency or generation of an electric potential, because of that motion. So, we also talked about sedimentation potential which is used more from a chemical industry concept, where because of gravity action whatever particles come into motion in a stream of flow of fluids would generally result in some kind of a potential associated with that kind of a flow. So, as the particle is falling with because of gravity through that kind of a flow. So, as the particle is falling with because of gravity through the fluid there is always an increase in the potential or the charge on the particle, because flow there again the cause is the motion and the effect is the potential. So, it is a reverse. So, we discussed all these electro kinetic phenomena from a standard point of their models estimated the various parameters like velocity, pressure of flow the surface charge density, which would happen and also estimated the zeta potential in terms of several of these phenomena several of these parameters which would otherwise be experimentally determined. And finally, arrived at a way of defining or determining the zeta potential associated with the surface. So, this in a nutshell is what we covered in lecture 11 to13, and we would again follow another review for the later on lectures.

Thank you.