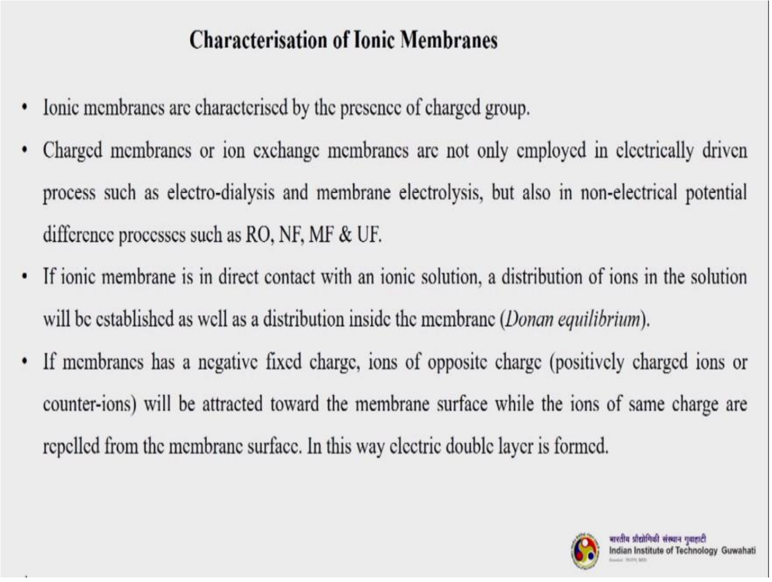
Membrane Technology
Prof. Kaustubha Mohanty
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture – 11
Plate Tectonics (Part V)

Good morning students. Today is lecture 11 of module 4. So in today's lecture, we will discuss about the characterization of ionic components and characterization of nonporous membranes. So, various techniques one by one we will see.

(Refer Slide Time: 00:47)



Characterisation of Ionic Membranes

- Ionic membranes are characterised by the presence of charged group.
- Charged membranes or ion exchange membranes are not only employed in electrically driven process such as electro-dialysis and membrane electrolysis, but also in non-electrical potential difference processes such as RO, NF, MF & UF.
- If ionic membrane is in direct contact with an ionic solution, a distribution of ions in the solution will be established as well as a distribution inside the membrane (*Donan equilibrium*).
- If membranes has a negative fixed charge, ions of opposite charge (positively charged ions or counter-ions) will be attracted toward the membrane surface while the ions of same charge are repelled from the membrane surface. In this way electric double layer is formed.

So, before we move on let us understand what are ionic membranes. So, if you remember, during our introduction class and during our discussion on classification of membrane and membrane processes, we have briefly discussed what are ionic membranes. So, if you recall, we can have 3 different types of ionic membranes, one is cation-exchange membrane and another is called on anion-exchange membrane and other one is bipolar membrane.

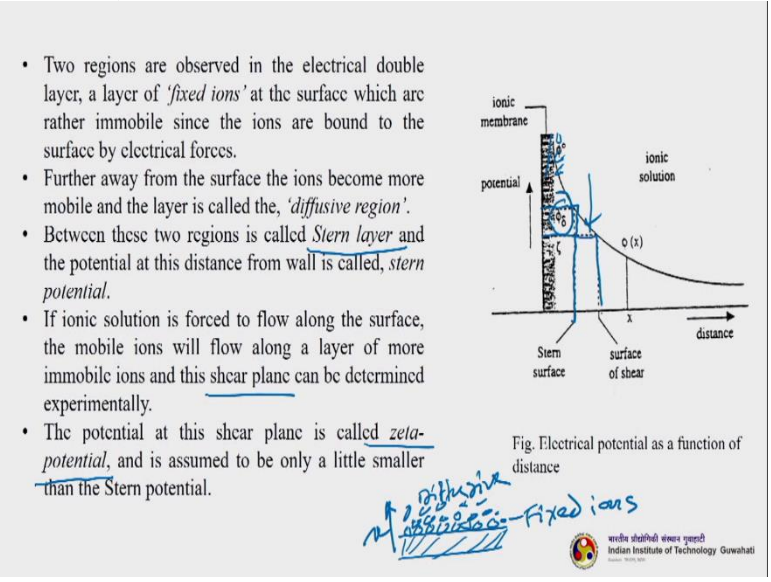
So, cationic exchange membrane and is something in which there are fixed and anionic groups. So, it is exchanging cations. So, that is the name actually similarly in anionic exchange membrane they have fixed cations and they are exchanging anions and bipolar membrane is something in which both cations and anions or presented fixed charges but they are separated by a particular layer.

Or layer that is a layer of separation in between 2 different charged groups. So bipolar membrane has its own specific applications. Now, charged membrane or ion exchange membrane are not only employed in electrically driven processes, such as electro-dialysis and membrane electrolysis, but also in non-electrical potential processes such as reverse osmosis Nano filters and micro filters and ultra-filtration.

If ionic membrane is in direct contact with an ionic solution, then what happens? What will happen basically there will be distribution of ions and the solution and the distribution of ions will be present in 2 different phases, some of the ions will come and sit on the surface of the membrane. So, they will become immobile because there will be charged interaction between the surface groups already present on the charged membrane and they are counter ions and there will be distribution also inside the membrane.

So, this distribution will continue in the donor equilibrium is reached and then if the membrane has a negative fixed charge then properties just like positively charged anions and counter ions will be attracted to the membrane surface and while the ions of the same charges are repelled from the membrane surface and vice versa. So, in this way electric double layer is actually formed.

(Refer Slide Time: 02:55)



- Two regions are observed in the electrical double layer, a layer of *'fixed ions'* at the surface which are rather immobile since the ions are bound to the surface by electrical forces.
- Further away from the surface the ions become more mobile and the layer is called the, *'diffusive region'*.
- Between these two regions is called *Stern layer* and the potential at this distance from wall is called, *stern potential*.
- If ionic solution is forced to flow along the surface, the mobile ions will flow along a layer of more immobile ions and this shear plane can be determined experimentally.
- The potential at this shear plane is called *zeta-potential*, and is assumed to be only a little smaller than the Stern potential.

Fig. Electrical potential as a function of distance

Diffusive

Fixed ions

So, let us closely look into this particular figure, which is showing you the electrical potential is a function of distance. Now, 2 regions can be observed in the electrical double layer, a layer of fixed ions at the surface which are rather immobile since ions are bound to the surface by electrical forces. So, basically what is happening this is your membrane actually.

So, here is some ions will come and deposit on the surface and by virtue of the charge exchange between them, so they will become immobile they are not in the dispersed medium. So, that is the fixed ions at the surface which are immobile and there are bound to the surface though by the by some charges this one exchange and electrical forces whatever you can say in that way.

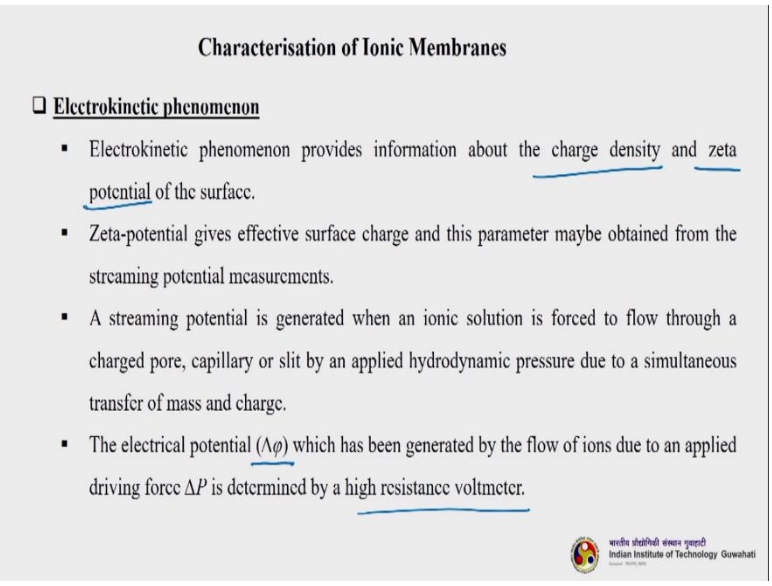
So, further away from the surface ions becomes more mobile and the layer is called diffusive layer. So, somewhere here we can say while you come down this side somewhere you, so, I can try to draw something here. So, let us say this is actually the membrane. So, when the ions are coming in getting deposited the surface of the membrane and this particular group we can called fixed ions.

Then above this there are also answer coming here. If you also getting deposited on the surface. It is just something like concentrated polarization that we discussed long back if you remember, recall how it happened actually monolithic deposition bilateral deposition that it goes on. So here actually this diffusive region comes. So, this is here X the distance from the surface of the membrane.

Now, between these regions there is something called a stern layer you might have been called about stern potential many times? So, this is what is called you can see this is from here. So, this is your stern surface and the corresponding potential is that stern potential this one phi delta so, if ionic solution is forced to flow along the surface and the mobile ions will flow along a layer of more immobile ions and this shear plane can be determined experimentally.

What we are going to determine is basically the shear plan and the potential at this shear is called zeta potential. One of the most important features or characterization parameter for membranes as well as polymers and other materials also. How about the sustained potential the value is higher than the zeta potential. So you can see this is the zeta potential.

(Refer Slide Time: 05:30)



Characterisation of Ionic Membranes

❑ **Electrokinetic phenomenon**

- Electrokinetic phenomenon provides information about the charge density and zeta potential of the surface.
- Zeta-potential gives effective surface charge and this parameter maybe obtained from the streaming potential measurements.
- A streaming potential is generated when an ionic solution is forced to flow through a charged pore, capillary or slit by an applied hydrodynamic pressure due to a simultaneous transfer of mass and charge.
- The electrical potential $(\Lambda\varphi)$ which has been generated by the flow of ions due to an applied driving force ΔP is determined by a high resistance voltmeter.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

Often it is assumed that ions in the solution are uniformly distributed and the electric potential decreases exponentially with distance that can be expressed by this particular equation phi = phi not exponential to the power – k x. Now, at a distance of k inverse, now, what is k inverse k inverse is known as the Debye length. So, the potential has decreased to a value of exponential to the power of minus 1.

So, that is 0.37 and this value is frequently taken as the potential which gives the thickness of the double layer. So, this value actually is the thickness of that gives that the thickness of the double layer. The specific properties which we can measured up by for this particular membranes anionic membranes, so, they are surface charge the zeta potential, electrical resistance and ionic permeability.

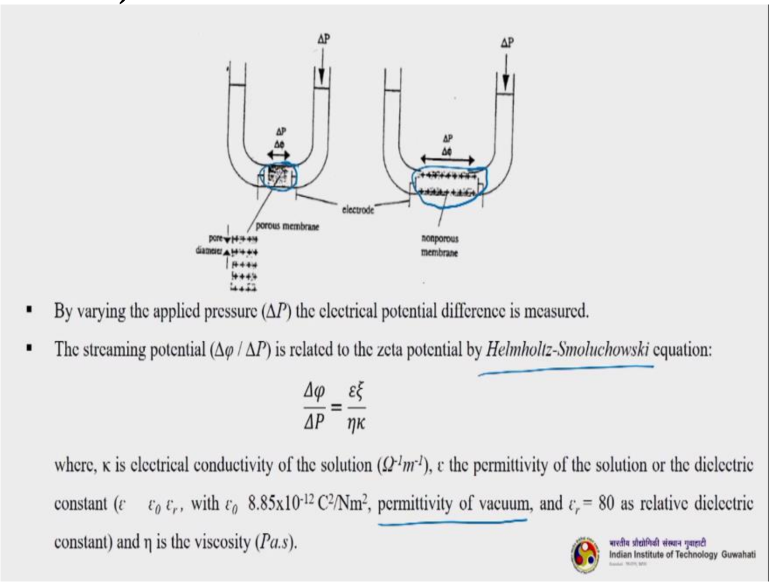
Now, let us this is what we discussed in general about the ionic membranes and how the charged electrical potential actually plays an important role in characterizing the ionic membranes. Now we will discuss in general different types of one by one different types of ionic membrane characterization techniques. So, under this the first one is called electro kinetic phenomena.

Now, electro kinetic phenomenon provides information about the charge density and zeta potential it tells us 2 things. It will tell us about the it will give the charge density as well as the zeta potential of the surface. Now, zeta potential gives effective surface charge and this parameter may be obtained from the streaming potential measurements. Streaming potential when the streaming potential is generated that also we need to understand.

So, what will happen so, when an ionic solution is forced to flow through a charged pore there is a porous membrane and the porous membrane is having certain let us say charged pore or capillary or slit then by applying a hydrodynamic pressure due to a simultaneous transfer of mass transfer mass and charge a streaming potential will be generated. Now, the electrical potential donated by this delta phi which has been generated by the flow of ions due to an applied driving force delta P is determined by a very high resistance voltmeter.

So need a voltmeter actually, to measure zeta potential there are particular instruments they are also costly but in a crude oil zeta potential and streaming potential also can be measured.

(Refer Slide Time: 08:10)



- By varying the applied pressure (ΔP) the electrical potential difference is measured.
- The streaming potential ($\Delta\varphi / \Delta P$) is related to the zeta potential by *Helmholtz-Smoluchowski* equation:

$$\frac{\Delta\varphi}{\Delta P} = \frac{\varepsilon\xi}{\eta\kappa}$$

where, κ is electrical conductivity of the solution ($\Omega^{-1}m^{-1}$), ε the permittivity of the solution or the dielectric constant ($\varepsilon \quad \varepsilon_0 \varepsilon_r$, with ε_0 $8.85\text{x}10^{-12}$ C^2/Nm^2, permittivity of vacuum, and $\varepsilon_r = 80$ as relative dielectric constant) and η is the viscosity ($Pa.s$).

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

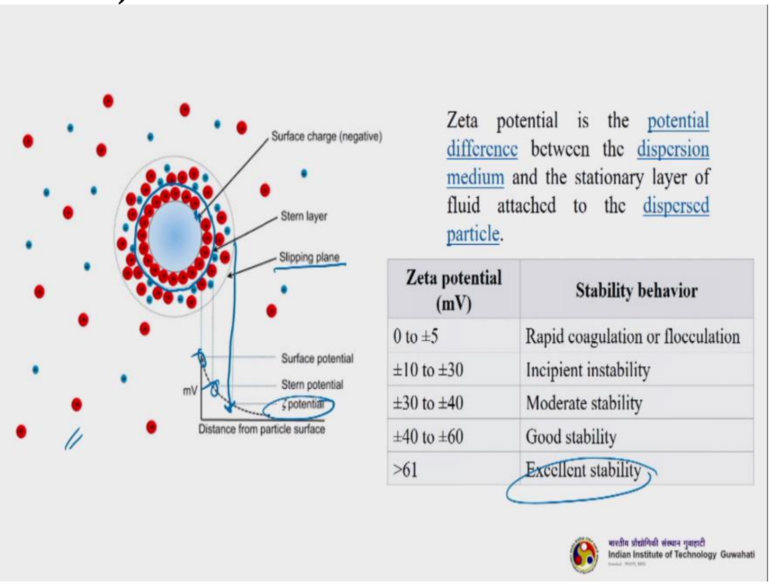
Now we will discuss actually how it happens. So you can see there are 2 figures here. So, capillary tube or u tube manometer type of arrangements in which are holding porous membrane as well as non-porous membrane. So porous membrane is fixed here. So this is actually a porous membrane this is non-porous membranes are arranged in his slit since they do not have pore so they are arranged in a particular way edge slits.

Then what is happen and you can see there are electrodes here both sides of the membrane there are electrodes and then voltage is applied. So, we are varying the applied pressure, what we are doing actually we are varying the delta P that means that pressure then electrical potential differences measured corresponding electrical potential difference now the streaming potential that delta phi / delta P is related to the zeta potential.

By this equation which is called Helmholtz Smolchowski equation. So, it is a delta phi / delta P = epsilon zeta then it eta K. So, where K is the electrical conductivity of the solution epsilon is the permittivity of the solution or the dielectric constant so, epsilon = epsilon 0 epsilon r with epsilon 0 is given it is a constant basically 8.85 10 power of minus 12 C square / N meter square that is a actually permittivity of vacuum.

And epsilon r = 80 as relative dielectric constant. So and eta it is the viscosity in Pascal per second. So, what we are going to do is this once in this particular type of arrangement please look at the figure once again. So, here electrodes are placed and the charges and voltages are applied it and we are varying the delta P and measuring the corresponding electrical difference and from this particular Helmholtz Smolchowski equation we can find out what is the streaming potential.

(Refer Slide Time: 10:09)



Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.

Zeta potential (mV)	Stability behavior
0 to ±5	Rapid coagulation or flocculation
±10 to ±30	Incipient instability
±30 to ±40	Moderate stability
±40 to ±60	Good stability
>61	Excellent stability

So, now please look at this particular figure, so, here this is also tells you about what is zeta potential. You can see that the surface charges negative this is for example. It is not that all surfaces are negatively charged surfaces can be positively charged also. So then their corresponding ions which will be deposited on immediately on the surfaces this will be the negatively charged just a reverse of this phenomena.

That is been shown here. You can see this is the surface. So, here since the surface is negatively charge so, the immediate ions, which are attached to the surface are all positively charged ions and then there is a layer which is surrounding on the surface of this particular positively charged ions. So, that is called actually stern layer. So, you can see that corresponding potential here.

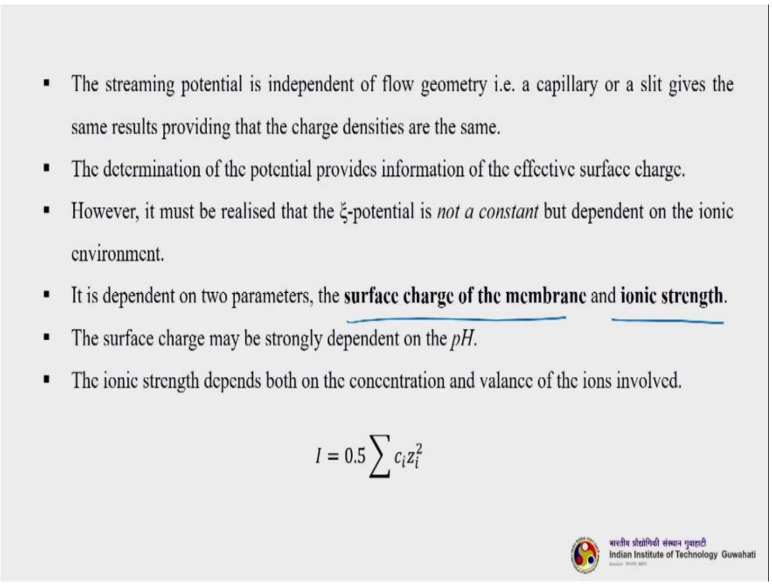
You can see so, this is the stern potential and this is what this surface potential then what is happening so, what is zeta potential so zeta potential actually is the potential difference between that dispersion medium so, this is dispersion medium here and the stationary layer of fluid attached to the dispersed particle so, this is a particle which is negatively charged over that surface, positively charged particles are there.

And that layer actually is giving a stern layer. Above that there are certain ions both positive and negatively charged and so they are existing inner layer however that loosely dispersed. And however though they are loosely dispersed above there is a layer existing are we can call it is slipping plan here. So that is actually the zeta potential. So here you can see this layer so this is given by zeta potential. So, zeta potential actually is given though the many times we write actually, it is a particular.

So you can see the potential and the stability behavior. So, this is what the collides. The stability we are which I am showing here is this is what a collides if it is it can be plus and minus both positive or negative if the zeta potential is from 0 to + - 5. Then rapid coagulation or flocculation will occur. If it is + - 10 to + - 30. Then stability will be in incipient and if it is + – 32+ - 40 it is moderate stable, if it is + - 40 to + - 60 the stability will be good and anything that is > 61 will have excellent stability.

Now, this please remember that whatever I am showing this stability behavior is for the colloidal dispersion. As this is zeta potential actually measured initially for the colloids.

(Refer Slide Time: 12:46)



- The streaming potential is independent of flow geometry i.e. a capillary or a slit gives the same results providing that the charge densities are the same.
- The determination of the potential provides information of the effective surface charge.
- However, it must be realised that the ξ-potential is *not a constant* but dependent on the ionic environment.
- It is dependent on two parameters, the **surface charge of the membrane** and **ionic strength**.
- The surface charge may be strongly dependent on the *pH*.
- The ionic strength depends both on the concentration and valance of the ions involved.

$$I = 0.5 \sum c_i z_i^2$$

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

And it was derived like that. So, the streaming potential is independent of flow geometry that is a capillary or the slit gives the same results providing that the charge densities are the same. The determination of the potential provides information of the effective surface charge. However, it must be realized that zeta potential is not a constant but dependent on the ionic environment.

Now, immediately you change the ionic environment zeta potential will change. So, you cannot say that this particular membrane zeta potential is this then you have to tell what is the environment under which this particular zeta potential measurement is carried out. Now, it is dependent on 2 parameters first is the surface charge of the membrane and then ionic strength the surface charge may be strongly dependent on the pH of the environment.

Now, the ionic strength depends on the concentration and valance of the ions and given by this particular equation, where I = 0.5 summation of c i z i square i is the ionic strength and c i is the concentration of the ions z i is the valance of ions.

(Refer Slide Time: 13:49)

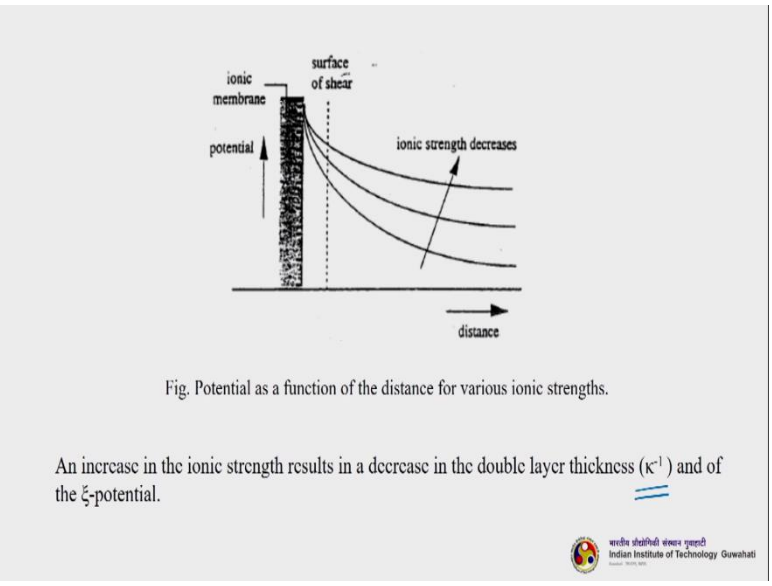


Fig. Potential as a function of the distance for various ionic strengths.

An increase in the ionic strength results in a decrease in the double layer thickness (κ^{-1}) and of the ξ-potential.

Please look at this particular figure this is what I was just telling the slide before that in increasing the ionic strength result in a decrease in the double layer thickness and this was K inverse which is the divide length and of zeta potential. So, when you are increasing the ionic strength so, the double layer thickness actually is getting decreased. So, the zeta potential will also decrease. This particular figure shows that.

(Refer Slide Time: 14:17)

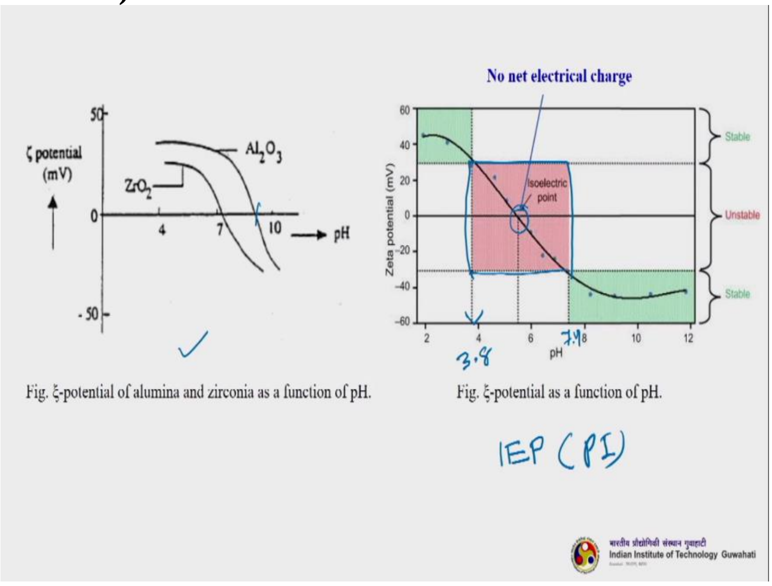


Fig. ξ-potential of alumina and zirconia as a function of pH.

Fig. ξ-potential as a function of pH.

IEP (PI)

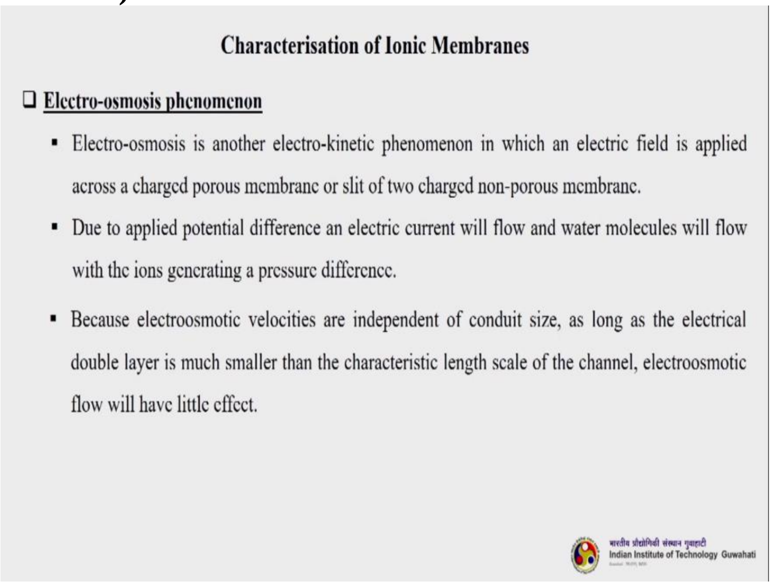
Now have a close look at this particular figures there are 2 distinct figures I am showing here. To understand more about a little better zeta potential it you can see this this particular left hand side figure. So, it is showing zeta potential of alumina and zirconia is a function pH. So alumina zirconia are materials to prepare ceramic membrane in organic membrane. So, what it says this particular figure says this particular figure from here we are finding zeta potential absolutely true.

But we can still understand in a very better way that that had what particular pH that particular material whether alumina, zirconia will be either positively charged or negatively charged. So, you can see that alumina is positively charged till almost somewhere here maybe it is 9 around beyond that 99.2 something like that. So aluminized positively charged. Now, you can please look at this right hand side figure you can see this.

It says zeta potential as a function of pH is given. So, you can see this here, this is the isoelectric point. Now, what is the meaning of isoelectric point, so it is the point in which there is no net electrical charge? Now isoelectric point which is called as IEP or P I many times it is written like that. So, that is basically a point where there is no electrical charges there is no net electrical charges now do not confuse with point of 0 or point of 0 charge many times they are loosely used, both this terms.

Now, you can understand that here you can see this particular region which is marked like this particular region tells us that this region is highly unstable. Let us say from the pH here is maybe somewhere around 3.8 or something like that. Are here it will be around 7.4 or something like that. I am just telling approximately right and this to make you understand, so, apart this is for a particular actually material I do not remember actually what that material is and above that let us say from pH 2 to 3.8 or something like that. The material is very stable and again above 7.5 to 12 around 12 the material the system or material is very unstable.

(Refer Slide Time: 16:49)



Characterisation of Ionic Membranes

❑ Electro-osmosis phenomenon

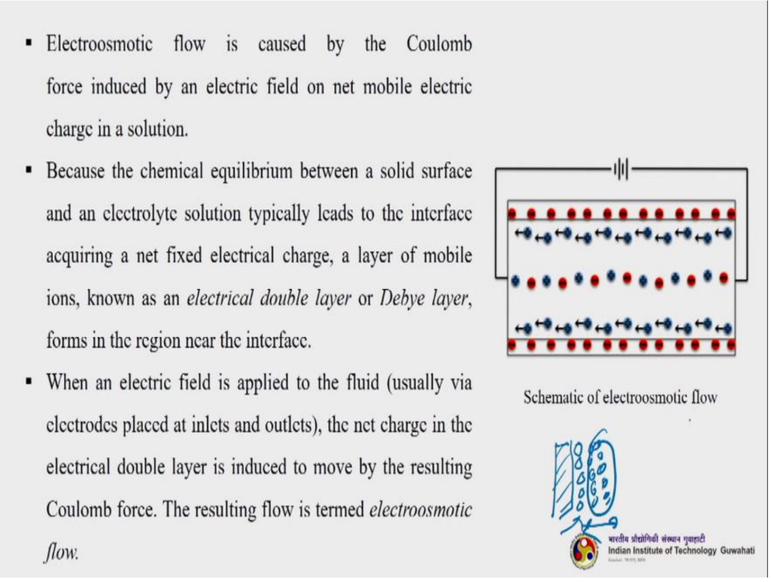
- Electro-osmosis is another electro-kinetic phenomenon in which an electric field is applied across a charged porous membrane or slit of two charged non-porous membrane.
- Due to applied potential difference an electric current will flow and water molecules will flow with the ions generating a pressure difference.
- Because electroosmotic velocities are independent of conduit size, as long as the electrical double layer is much smaller than the characteristic length scale of the channel, electroosmotic flow will have little effect.

When you draw this particular figure zeta potential and the pH we can understand the stability and unstability as well as we can find out the isoelectric point. Now, the next characterisation technique is electro osmosis phenomenon. Now, electro osmosis is another electro kinetic phenomenon only in which the electric field is applied across a charged porous membrane or the slit of 2 charge non porous membrane.

This can be used for a porous membrane also, if I am using a non-porous membrane then, I have to make a slit of this 2 non-porous membrane, now due to applied potential difference in electric current will flow and water molecules will flow when the ions with the ions generating pressure difference, because electroosmotic velocities are independent of conduit size, as long as electrical double layer is much smaller than the characteristic length of the channel, electroosmotic flow will have very little effect.

So, this means it is telling that the velocity of the electroosmotic flows actually that is independent of the conduit size in which we are measuring actually. But however, this will have no impact, if the electrical double layer is very very small to that of that length the characteristic length of the tube other conductors, you can say.

(Refer Slide Time: 18:10)



- Electroosmotic flow is caused by the Coulomb force induced by an electric field on net mobile electric charge in a solution.
- Because the chemical equilibrium between a solid surface and an electrolyte solution typically leads to the interface acquiring a net fixed electrical charge, a layer of mobile ions, known as an *electrical double layer* or *Debye layer*, forms in the region near the interface.
- When an electric field is applied to the fluid (usually via electrodes placed at inlets and outlets), the net charge in the electrical double layer is induced to move by the resulting Coulomb force. The resulting flow is termed *electroosmotic flow*.

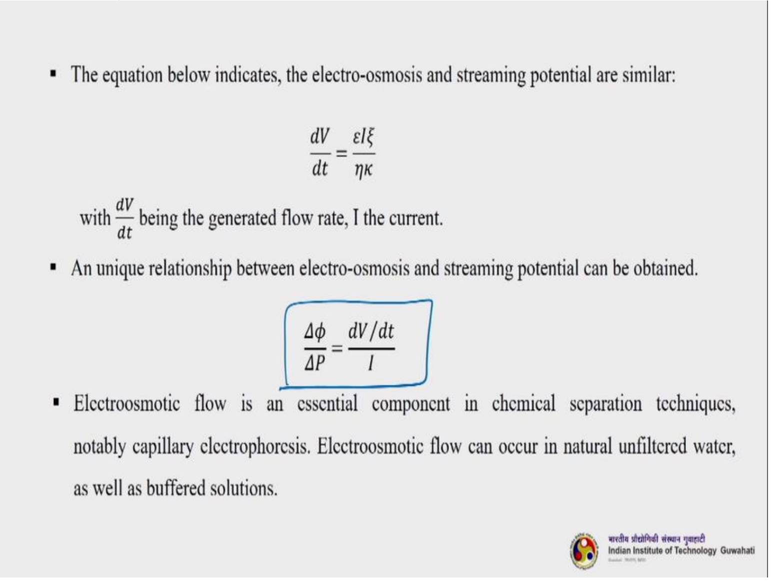
Schematic of electroosmotic flow

So, electro osmotic flow is caused by the Coulomb force induced by an electric field on net mobile electric charge in a solution. Now, because the chemical equilibrium between a solid surface and an electrolyte solution typically leads to the interface acquiring a net fixed electrical charge a layer of mobile ions, known as electrical double layer or Debye layer forms in the region near the interface.

This is what we just discussed earlier also. So, there is a surface here let us say this is the surface here this is surface. So, charged surface so, some ions will come and deposit now what is that the ions positive or negative depends upon what is the charge of the surface, then again there will be loosely bound ions. So, this is a fixed layer that I that we have already fixed ions there in immobile.

Then we have loosely attached dispersed a particular dispersed layers, so, they are mobile. So, this is particularly actually this layer will form the electrical double layer or Debye layer, so that is forming of the interface. So, when an electric field is applied to the fluid, usually via electrodes placed in as both sides inlets and outlets we just show how it was done using U-tube manometer type of system. The net charge in the electrical double layer is induced to move by the resulting coulomb force the resulting flow is termed electroosmotic flow. You can see actually how that electro osmotic flow takes place.

(Refer Slide Time: 19:36)



- The equation below indicates, the electro-osmosis and streaming potential are similar:

$$\frac{dV}{dt}=\frac{\varepsilon I\xi}{\eta\kappa}$$

with $\frac{dV}{dt}$ being the generated flow rate, I the current.

- An unique relationship between electro-osmosis and streaming potential can be obtained.

$$\boxed{\frac{\Delta\phi}{\Delta P}=\frac{dV/dt}{I}}$$

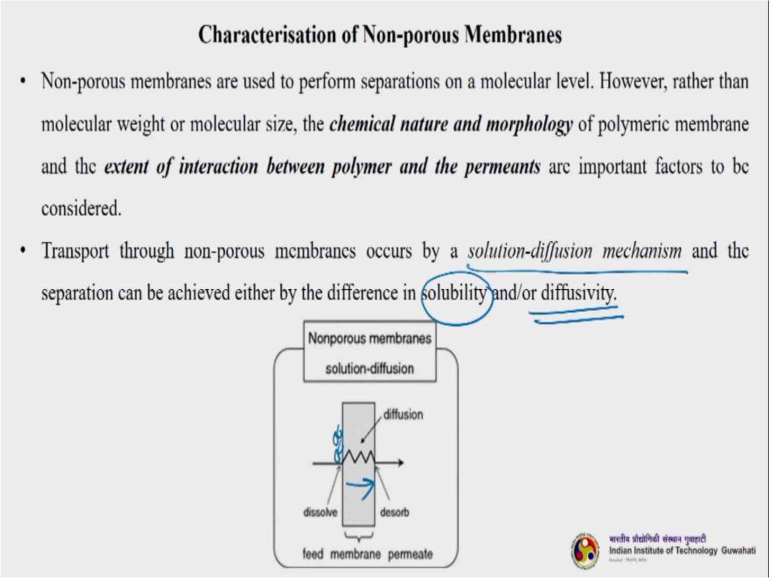
- Electroosmotic flow is an essential component in chemical separation techniques, notably capillary electrophoresis. Electroosmotic flow can occur in natural unfiltered water, as well as buffered solutions.

Indian Institute of Technology Guwahati

Here this particular slide figure will tell you now, the equation below indicate the electro osmosis and streaming potential are similar. So, d V / d t, which is the generated flow and = epsilon I zeta / eta K d V / d t. So, I is that current, so, unique relationship between electro osmosis and streaming potential can be obtained. So, the streaming potential delta phi / delta P = d V / d t / I.

So, from this equation we can understand that there is a relationship between the streaming potential as well as the electroosmotic flow. Now, electroosmotic flow is an essential component in chemical separation techniques and notably capillary electrophoresis. Now, electroosmotic flow can occur in natural unfiltered water as well as buffered solutions also.

(Refer Slide Time: 20:24)



Characterisation of Non-porous Membranes

- Non-porous membranes are used to perform separations on a molecular level. However, rather than molecular weight or molecular size, the ***chemical nature and morphology*** of polymeric membrane and the ***extent of interaction between polymer and the permeants*** are important factors to be considered.
- Transport through non-porous membranes occurs by a *solution-diffusion mechanism* and the separation can be achieved either by the difference in solubility and/or diffusivity.

So, now, let us understand the characterization of non-porous membranes So, will exclusively discuss about non porous membranes and non-porous membranes are used to perform separations on a molecular level however, other than molecular weight or molecular size, the chemical nature and morphology of the polymeric membrane and the extent of interaction between the polymer and the permeants are important factors to be considered.

So, now, you understand that when we are talking about actually porous membranes, so, you are finding out certain parameters which are essentially integral part of the porous membrane. So, what are those pore size, pore size distribution pore volume all these things porosity surface porosity because they have fixed force. But in non-porous membrane when there are no force, so, what we are going to characterize.

And how the separation is happening. Now, the parameters which will affect the non-porous membrane separation are basically the chemical nature and morphology of the membrane. It may be polymeric it can be anything else also, but most it is polymeric only. So, what is the membrane material and its characteristic features both physical chemical parameters actually will define the rate of separation.

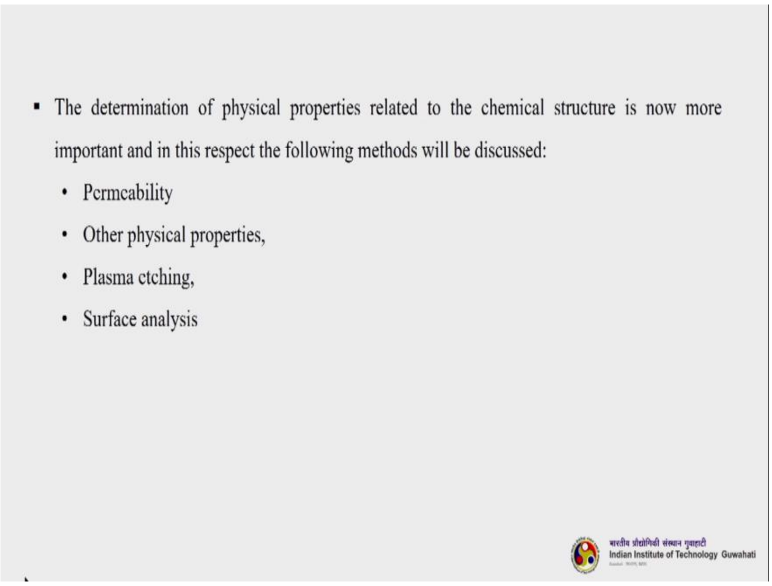
How the separation is going to happen. So that is not all then the extent of interaction between the polymer and the permeate, which is going to be to the permeate side or we want to, because we are still taking it to the permeate side or passing through the membrane. Their interaction and the interaction between the polymer is also very important. So, that means, let us say, let us understand this solute is getting transported to this particular non porous membrane.

So, what is the interaction of this particular solute with that membrane material is very important. Now, we have never taken into consideration than membrane material and each feature when you discuss non porous membrane though in charge members they have certain importance. However, the importance is more in case of non-porous membranes. Now transport through non-porous membranes occurs by solution diffusion mechanism and the separation can be achieved either by difference in solubility and or diffusivity.

The solution diffusion mechanism will discuss in detail when you will discuss our transport models and allow. So now for today's class to understand that is non-porous membrane how it is happening. How the transport will happen when there are no pores. So, what will happen the solute will come and get this deposited on the surface of the membrane here then they have to be dissolved in the membrane material.

So, that is why it is solubility very important solubility of solute inside the membrane material the once they are dissolved, now they will have to diffuse by virtue of that potential difference. Now, that is why diffusivity comes into picture. So the solutes diffusivity plays a very important role. Now, what is that they come across permeate side they will dissolve now this is what is called a solution diffusion mechanism where solubility and diffusivity of the solute inside the membrane material is the mechanism of transport.

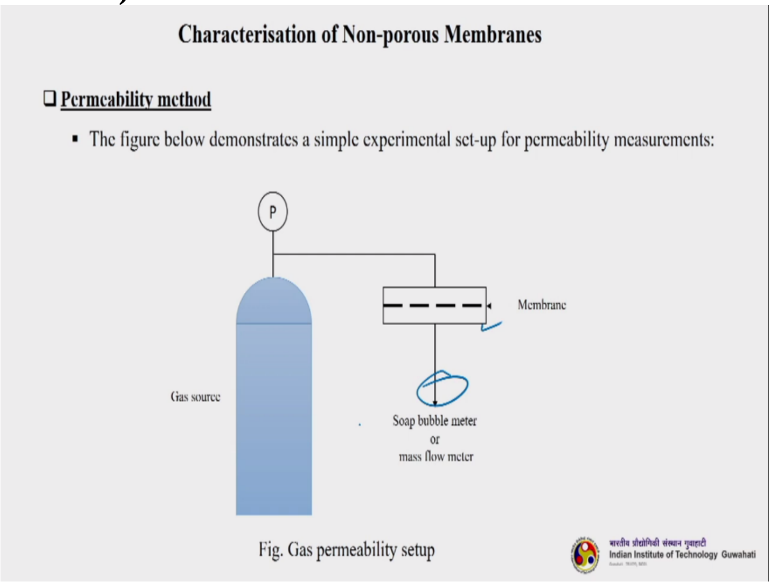
(Refer Slide Time: 23:38)



- The determination of physical properties related to the chemical structure is now more important and in this respect the following methods will be discussed:
  - Permeability
  - Other physical properties,
  - Plasma etching,
  - Surface analysis

The determination of physical properties related to the chemical structure is now more important and in this respect the following methods will be discussed. So, we will be discussing permeability, different physical properties, plasma etching and surface analysis these methods will discuss as characterized and techniques for the non-porous membrane.

(Refer Slide Time: 23:56)



Characterisation of Non-porous Membranes

❑ Permeability method

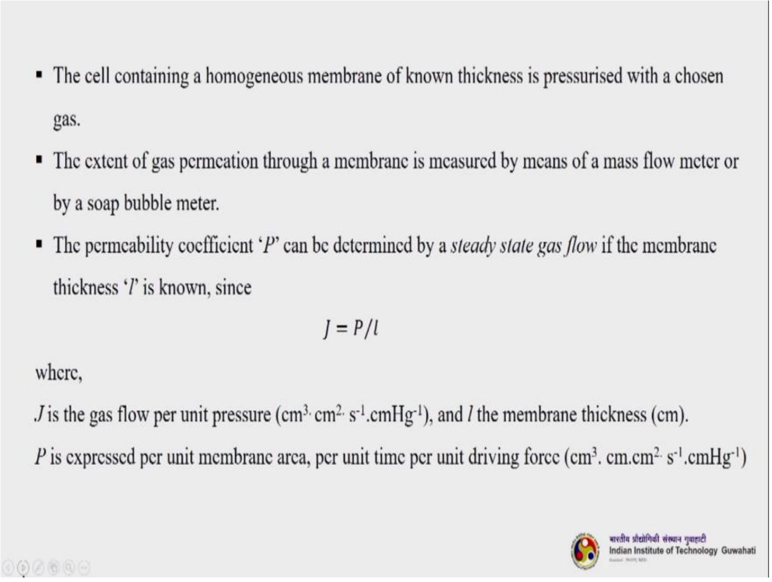
- The figure below demonstrates a simple experimental set-up for permeability measurements:

Fig. Gas permeability setup

So, the first one is permeability method. So, you remember we discussed permeability of how to calculate water flux and all during our porous membrane characterisation also micro filters and membrane. Now, we will quickly discuss about the permeability method here in non-porous membrane also. Now, here actually instead of water here, we are using gas because since the water flow inside the non-porous membrane will be very difficult.

That is why gas is being used as a source of for permeate that will pass through the membrane. So, you can see the schematic measurements is very simple. So, there is a membrane model here. So, this one which is holding the membrane then you can pass the gas one particular from a gas source usually the gas cylinders and you can measure the flow here the permeate flow. By using a soap bubble meter or a mass flow meter.

(Refer Slide Time: 24:51)



- The cell containing a homogeneous membrane of known thickness is pressurised with a chosen gas.
- The extent of gas permeation through a membrane is measured by means of a mass flow meter or by a soap bubble meter.
- The permeability coefficient '*P*' can be determined by a *steady state gas flow* if the membrane thickness '*l*' is known, since

$$J = P/l$$

where,

J is the gas flow per unit pressure ($cm^{3\cdot} cm^{2\cdot} s^{-1}.cmHg^{-1}$), and *l* the membrane thickness (cm).

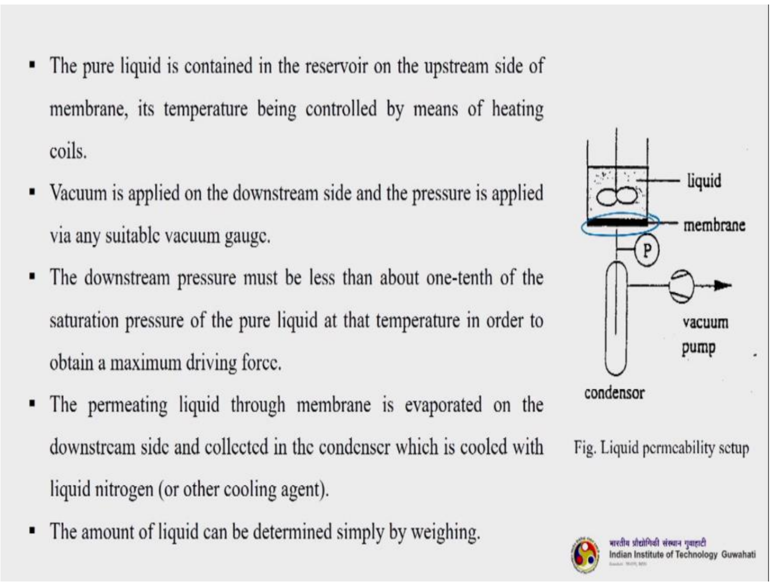
P is expressed per unit membrane area, per unit time per unit driving force ($cm^3.\ cm.cm^{2\cdot} s^{-1}.cmHg^{-1}$)

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

This very simple technique. Now, the cell containing a homogeneous membrane of known thickness is pressurized. The extent of gas permeation through the membrane is measured by means of a mass flow meter or by soap bubble meter. The permeability coefficient P can be determined by a steady state gas flow, if the membrane thickness l is known no membrane thickness l can be characterized or found out by various mechanisms.

Usually the electron microscopy like cm or Hgcm. So, J = P / l so here J is the gas flow per unit pressure, and l is the membrane thickness in centimeter. So, P is expressed per unit membrane area per unit time per unit driving force.

(Refer Slide Time: 25:35)



- The pure liquid is contained in the reservoir on the upstream side of membrane, its temperature being controlled by means of heating coils.
- Vacuum is applied on the downstream side and the pressure is applied via any suitable vacuum gauge.
- The downstream pressure must be less than about one-tenth of the saturation pressure of the pure liquid at that temperature in order to obtain a maximum driving force.
- The permeating liquid through membrane is evaporated on the downstream side and collected in the condenser which is cooled with liquid nitrogen (or other cooling agent).
- The amount of liquid can be determined simply by weighing.

Fig. Liquid permeability setup

Indian Institute of Technology Guwahati

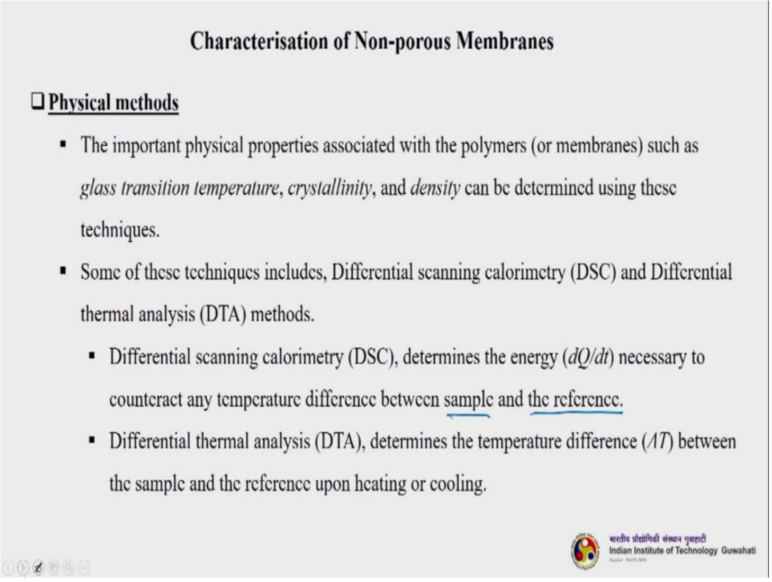
Now pure liquid is contained in the reservoir now when we talk about actually liquid permeability, the mechanism by which both air permeability or gas permeability and liquid permeability or this one carried out are mostly the same. So, the liquid is contained in the reservoir on the upstream side of membrane and its temperature being controlled by means of heating coils.

So, here this is the membrane here the liquid is there. Now, the vacuum is applied on the downstream side and the pressure applied via any suitable vacuum gauge. Now, if you recall what we discussed the liquid permeability of the water permeability or water flux measurement or during the micro filters membrane characterization then that time we have not vacuums the system the downstream system downstream side of the membrane.

That was not done only how much of liquid is that is coming out so, that is being measured. Now since liquid will not come out as it is so easily in porous non-porous membrane that is why a vacuum is required at the permeate size needs to be so, that liquid flow take place. So, the actually the vacuum is applied on the downstream side as you can see this is the permeate side.

So, the liquid is so, the vacuum is applied there so, you can do it by having a vacuum pump or vacuum gas so, the downstream pressure must be less than about 1 10 th of the saturation pressure of the pure liquid at that temperature in order to obtain the maximum driving force and the permeating liquid through membrane is evaporated on the downstream side and collected in the condenser. Which is cold with a liquid nitrogen or other cooling agent the amount of liquid can be determined simply by weighing.

(Refer Slide Time: 27:19)



Characterisation of Non-porous Membranes

❑ **Physical methods**

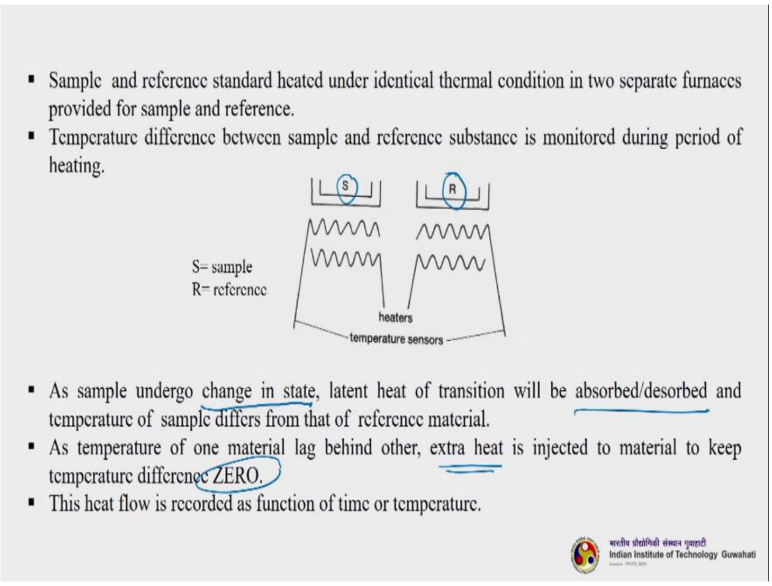
- The important physical properties associated with the polymers (or membranes) such as *glass transition temperature*, *crystallinity*, and *density* can be determined using these techniques.
- Some of these techniques includes, Differential scanning calorimetry (DSC) and Differential thermal analysis (DTA) methods.
  - Differential scanning calorimetry (DSC), determines the energy (dQ/dt) necessary to counteract any temperature difference between sample and the reference.
  - Differential thermal analysis (DTA), determines the temperature difference (ΔT) between the sample and the reference upon heating or cooling.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

So, the next is physical methods. So, under the physical properties which are associated with polymers or polymeric membranes or glass transition temperature crystallinity and density. So, some of these techniques include the DSC which is called differential scanning calorimetry and differential thermal analysis DTA methods, not differential scanning calorimetry determines the energy d Q / d t.

That is necessary to counteract any temperature difference between the sample and reference. There is a sample and the difference sample is something which we are going to measure the transition and there is a difference we will discuss in our next lecture about this and in DTA the differential thermal analysis this determines the temperature difference delta t between the sample and the reference upon heating or cooling.

(Refer Slide Time: 28:05)



- Sample and reference standard heated under identical thermal condition in two separate furnaces provided for sample and reference.
- Temperature difference between sample and reference substance is monitored during period of heating.

S= sample
R= reference

- As sample undergo change in state, latent heat of transition will be absorbed/desorbed and temperature of sample differs from that of reference material.
- As temperature of one material lag behind other, extra heat is injected to material to keep temperature difference ZERO.
- This heat flow is recorded as function of time or temperature.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

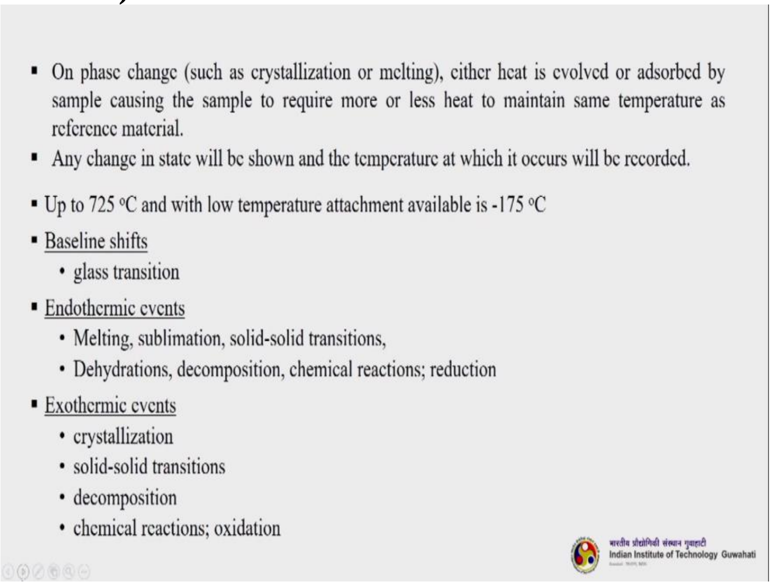
So, let us understand what DTA is so the sample in reference standard heated under identical thermal condition in 2 separate furnaces provided for sample and reference. So, there are 2 furnaces another single furnace DTA. So, you can see here this furnace is holding the sample this furnaces is holding the reference now and both sample and references are getting heated. Or heat is being supplied to them and uniform heat is being supplied to them. Now as sample undergo change in state.

So, the latent heat of transition will be absorbed or desorbed depending upon what is the sample and the temperature of sample differs from that of the reference material. So, because that material is degrading either it is absorbing heat or it is the deserving heat. So, as temperature upon of the material of one material leg behind other extra heat is injected to material to keep the temperature difference zero. That means what is happening so, there is a sample and there is a reference both are supplied equal amount of heat.

Now, references is a enough material into not thermally degrade will not degrade, nothing will happen to it. So, what is but that sample which is being kept there under the thermal under the temperature, this one that is the heat that is being supplied to this sample, it will degrade. So degradation and maybe either it is absorbing or deserving or whatever it is depending upon the type of the material nature of the material. So, it is this one temperature will drop or will increase.

So, it will not be equal to that of the reference material. So, there is a delta t between them now that delta t amount of his to be supplied to here sample, so that the temperature will remain same for both the sample and the reference. So, the delta t between the sample and the reference will must be 0. So, that is the concept of actually DSC how the DSC operates, this heat flow is recorded as a function of timer temperature.

(Refer Slide Time: 30:10)



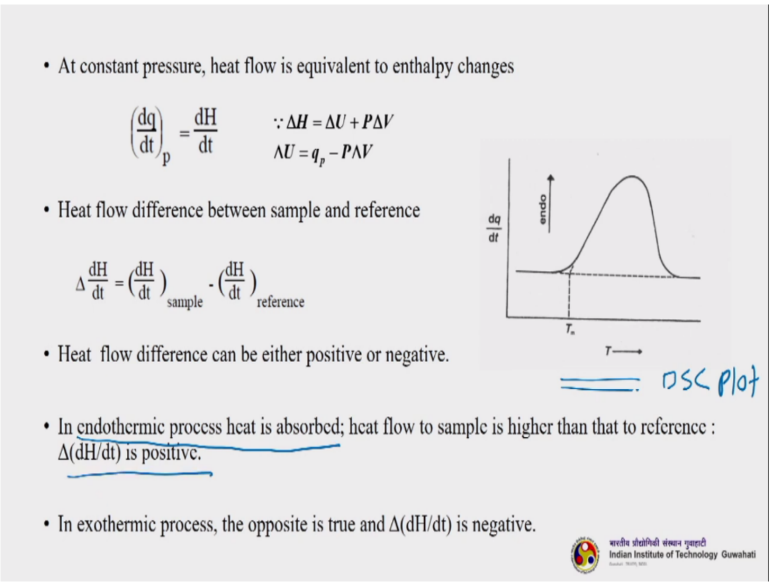
- On phase change (such as crystallization or melting), either heat is evolved or adsorbed by sample causing the sample to require more or less heat to maintain same temperature as reference material.
- Any change in state will be shown and the temperature at which it occurs will be recorded.
- Up to 725 °C and with low temperature attachment available is -175 °C
- Baseline shifts
  - glass transition
- Endothermic events
  - Melting, sublimation, solid-solid transitions,
  - Dehydrations, decomposition, chemical reactions; reduction
- Exothermic events
  - crystallization
  - solid-solid transitions
  - decomposition
  - chemical reactions; oxidation

Indian Institute of Technology Guwahati

Now, on phase change such as crystallization or melting, either heat is evolved or adsorbed by the sample causing the sample to require more or less heat maintain this is what I will just telling that either the sample will degrade by taking heat or by releasing heat so, any change in state will be shown and the temperature at which occurs will be recorded. Now usually up to 725 degrees centigrade and with low temperature at almost up to minus 175 degrees.

This is a range of DSC that can be most of the commercial DSC manufacturer they operate in this particular range minus 175 to 725. Now, when actually the baseline in the DSC curves, so, then we can understand that that glass transitions region is going on. Because of endothermic events that can be exothermic events also so, endothermic events are melting sublimation solid solid transition. Apart from dehydration decomposition chemical reaction and reduction so, whereas crystallizer solid solid transitions decomposition chemical reaction oxidation these are exothermic events.

(Refer Slide Time: 31:17)



- At constant pressure, heat flow is equivalent to enthalpy changes

$$\left(\frac{dq}{dt}\right)_p = \frac{dH}{dt} \qquad \because \Delta H = \Delta U + P\Delta V$$
$$\Delta U = q_p - P\Delta V$$

- Heat flow difference between sample and reference

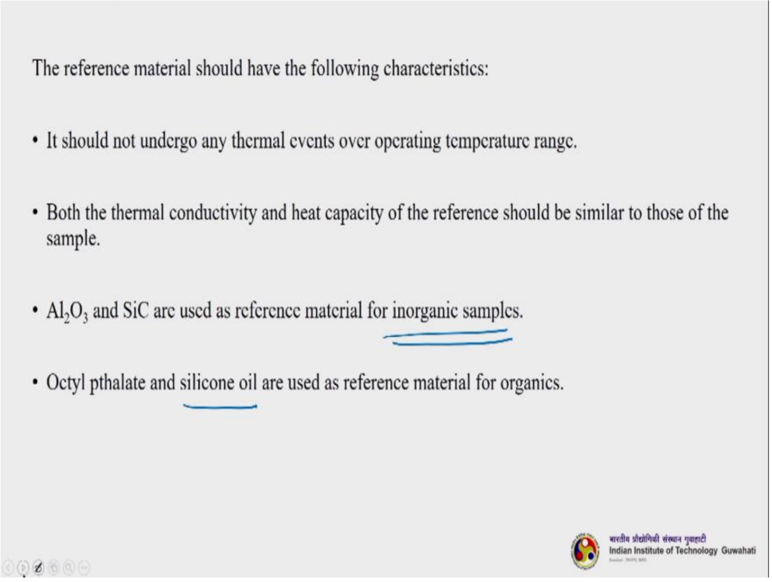
$$\Delta\frac{dH}{dt} = \left(\frac{dH}{dt}\right)_{sample} - \left(\frac{dH}{dt}\right)_{reference}$$

- Heat flow difference can be either positive or negative.
- In endothermic process heat is absorbed; heat flow to sample is higher than that to reference : Δ(dH/dt) is positive.
- In exothermic process, the opposite is true and Δ(dH/dt) is negative.

Now, let us understand this is a particular actually DSC plot. It is a typical plot not all DSC plots will look like this. So, at constant pressure heat flow is equivalent to enthalpy changes. So, here d q / d t at constant pressure = d H / d t because delta H = delta U + P delta V. So, from that you can find out delta U = q p - p delta V and so, that heat flow difference between the sample and the reference can be calculated in this equation.

So, delta d H / d t of sample – d H / dt of reference. Now, that is way it can be positive or negative. So depending upon that only the heat will be supplied. So heat flow difference can be either positive or negative. So in endothermic process heat is absorbed. So heat flow to the sample is higher than that to reference. So here delta d H / d t is positive. So in exothermic process, the opposite is true and delta d H / dt is negative.

(Refer Slide Time: 32:18)



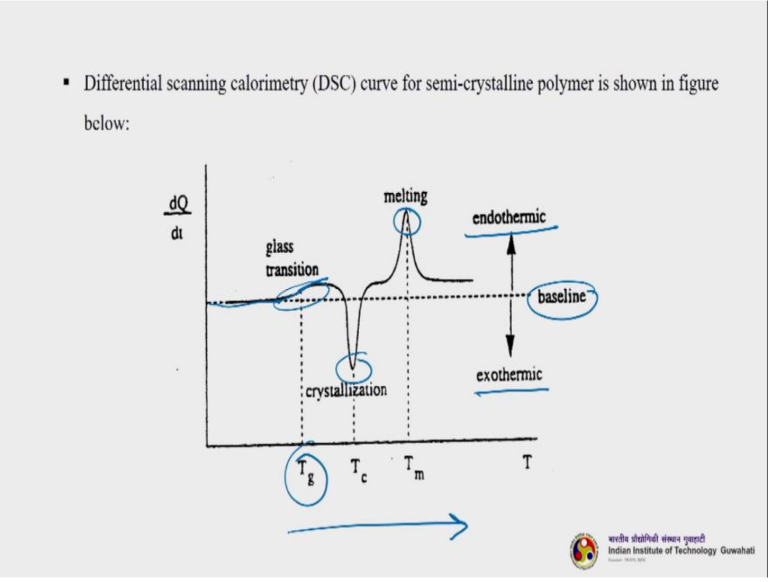
The reference material should have the following characteristics:

- It should not undergo any thermal events over operating temperature range.
- Both the thermal conductivity and heat capacity of the reference should be similar to those of the sample.
- Al_2O_3 and SiC are used as reference material for inorganic samples.
- Octyl pthalate and silicone oil are used as reference material for organics.

So what is the reference material. What is it is important that we understand the importance of reference material. It is inner material mostly and it is not the with whatever the amount of it that is being supplied. So, it should not undergo any thermal events over operating temperature range. I am telling you about the characteristic which is up the reference materials.

So, both thermal conductivity and heat capacity of the reference should be similar to those of the sample. So for example, alumina Al 2 O 3 and SiC which is silicon carbide are used as reference materials for inorganic samples. Now, please remember that for organic and inorganic samples reference materials are different. Now, octyl pthalate and silicone oil are used as reference material for organic silicon oil is mostly used. And silicon carbide also mostly use silicon oil and silicon carbide they are mostly used as a reference material for inorganic and organic samples.

(Refer Slide Time: 33:15)



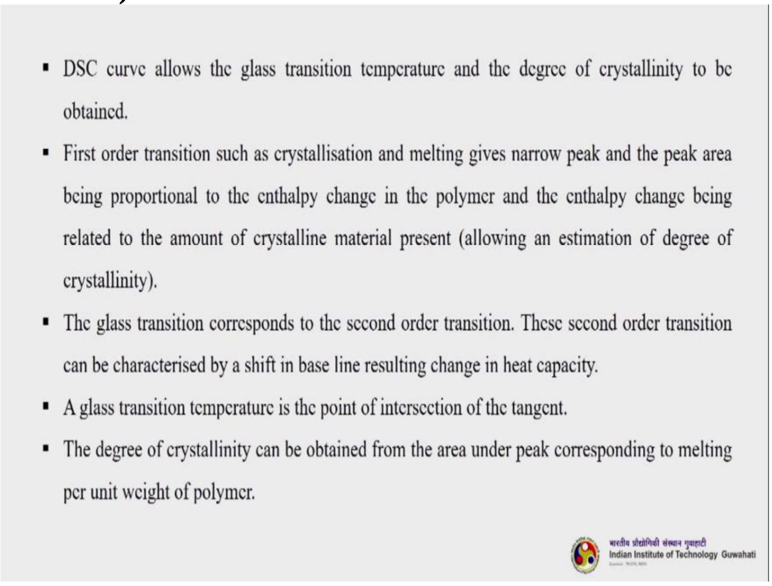
- Differential scanning calorimetry (DSC) curve for semi-crystalline polymer is shown in figure below:

Now, please have a close look at this particular DSC curve this is representative DSC curve or polymeric sample. So, you can see d Q / d t is plotted versus temperature. So, when we start the process we heat basically we start, we are heating in this direction, we are increasing the temperature so, what is happening that something will call there is a glass transition phase will come.

This is a glass transition is crystallization it is not a particular thing um temperature so, from here we can find out the T g. T g is the glass transition temperature. Now what is happening so, you can understand like that below T g the material will be crystalline and when we go above T g glass transition temperature, it will become like. So, when we further move across go ahead, beyond the glass transition temperature crystallization will occur. So crystallization then followed by melting, so the crystallization is the exothermic process you can see here.

Where is melting agent endothermic process then this is what is we are talking about baseline, when there is a baseline as I told you know, when there is a baseline then glass transition occurs so, you can see here that till this point there is no baseline change just when the glass transition occurs then there is a shift. So, this shift occurs so, that means, we can immediately see from the plot. When the progress is happening actually the plot is getting as generated in your computer. So, you can see when the baseline shift occurs, then you can understand that glass transition regions starts.

(Refer Slide Time: 34:54)



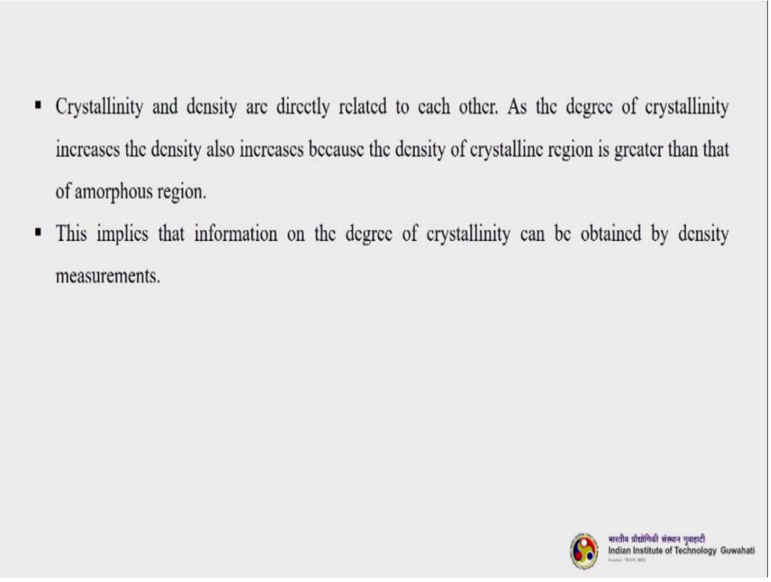
- DSC curve allows the glass transition temperature and the degree of crystallinity to be obtained.
- First order transition such as crystallisation and melting gives narrow peak and the peak area being proportional to the enthalpy change in the polymer and the enthalpy change being related to the amount of crystalline material present (allowing an estimation of degree of crystallinity).
- The glass transition corresponds to the second order transition. These second order transition can be characterised by a shift in base line resulting change in heat capacity.
- A glass transition temperature is the point of intersection of the tangent.
- The degree of crystallinity can be obtained from the area under peak corresponding to melting per unit weight of polymer.

Indian Institute of Technology Guwahati

So, DSC curve allows the glass transition temperature and the degree of crystallinity to be obtained. First order transition such as crystallization and melting gives narrow peaks and the peak area being proportional to the enthalpy change in the polymer and the enthalpy change being related to the amount of crystalline and material present. So, this allows you to estimate the degree of crystalline material present.

During the glass transition corresponds to the second order transition. The second order transition can be characterized by a shift in the base line resulting change in heat capacity. A glass transition temperature is the point of intersection of the tangent. The degree of crystallinity can be obtained from the area under the peak corresponding to the melting per unit weight of the polymer. So, you basically calculate the area under the peak to find out the degree of crystallinity.

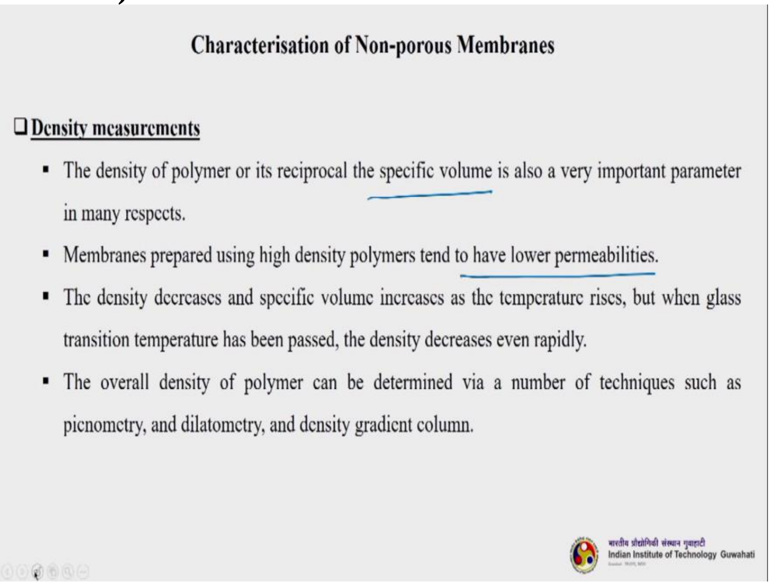
(Refer Slide Time: 35:39)



- Crystallinity and density are directly related to each other. As the degree of crystallinity increases the density also increases because the density of crystalline region is greater than that of amorphous region.
- This implies that information on the degree of crystallinity can be obtained by density measurements.

Crystallinity and density are directly related to each other. So, is the degree of crystallinity increases the density also increases, because the density of crystallinity region is greater than that of that amorphous region? That this implies that information on the degree of crystallinity can be obtained by density measurements.

(Refer Slide Time: 35:55)



Characterisation of Non-porous Membranes

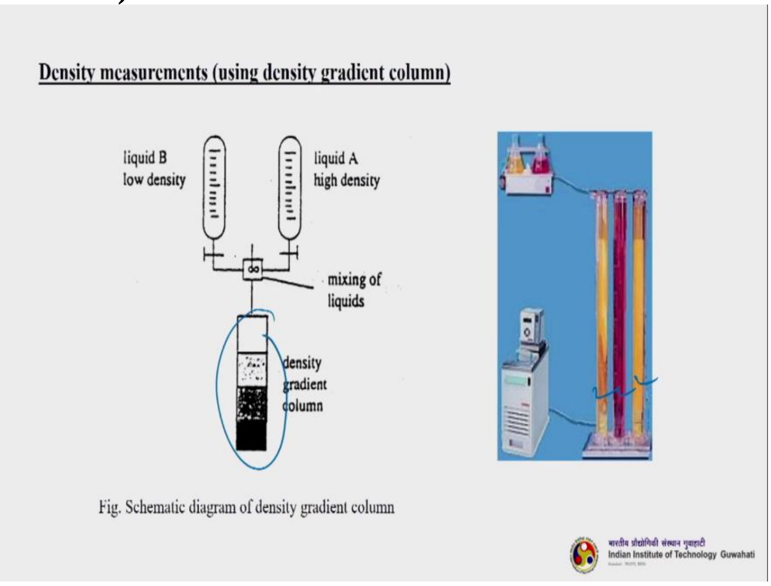
❑ **Density measurements**

- The density of polymer or its reciprocal the specific volume is also a very important parameter in many respects.
- Membranes prepared using high density polymers tend to have lower permeabilities.
- The density decreases and specific volume increases as the temperature rises, but when glass transition temperature has been passed, the density decreases even rapidly.
- The overall density of polymer can be determined via a number of techniques such as picnometry, and dilatometry, and density gradient column.

Then the next technique to characterize of non-porous membrane is the density measurement are the density of polymer reciprocal that is specific volume is also very important parameter in many respects. Now, membrane material but please again understand that since this is non-porous membrane the membrane material and needs properties plays a important role. That is our density also plays a role.

So, membranes prepared using high density polymers tend to have lower permeability. So, from here you can understand what the importance grams of density is actually. So, the density decreases the specific volume increases as the temperature rises, but when the glass transition temperature has been passed, the density decreases even rapidly. Now, the overall density of polymer can be determined via a number of techniques such as picnometry and dilatometry and density gradient column.

(Refer Slide Time: 36:45)



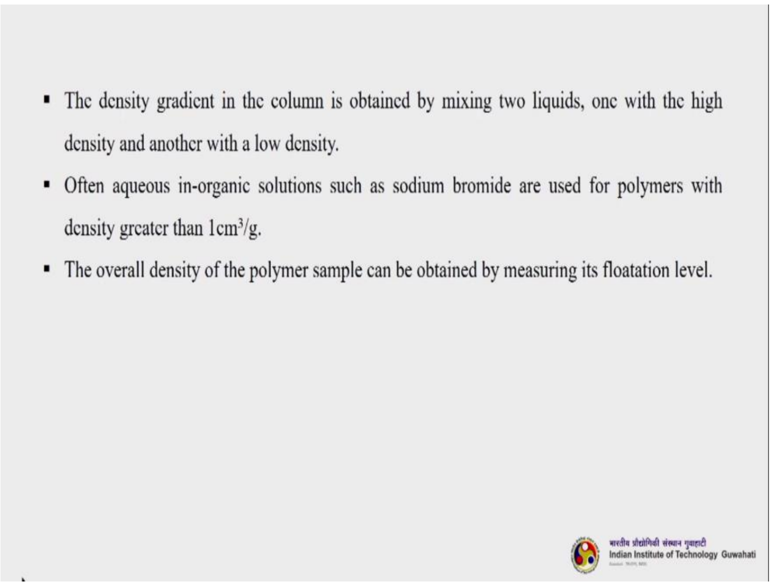
Density measurements (using density gradient column)

Fig. Schematic diagram of density gradient column

We will see the density gradient column. So, let us look at this particular image. So, this is a schematic representation of the density gradient column what is happening is there are 2 different types of liquids, one having high density and other have been low density and mixed at different proportions in a mixing chamber and they are allowed to flow through my density gradient column.

So, this is a simple column, you can see these are columns actually. So, you can see here different coloring agents are added, so it is 2 different set 2 different liquids with having different densities, now they will float here and they will settle here, one upon each other, you can see from the color you can see and the yellow how much is that you can measure in centimeter actually and find out the density.

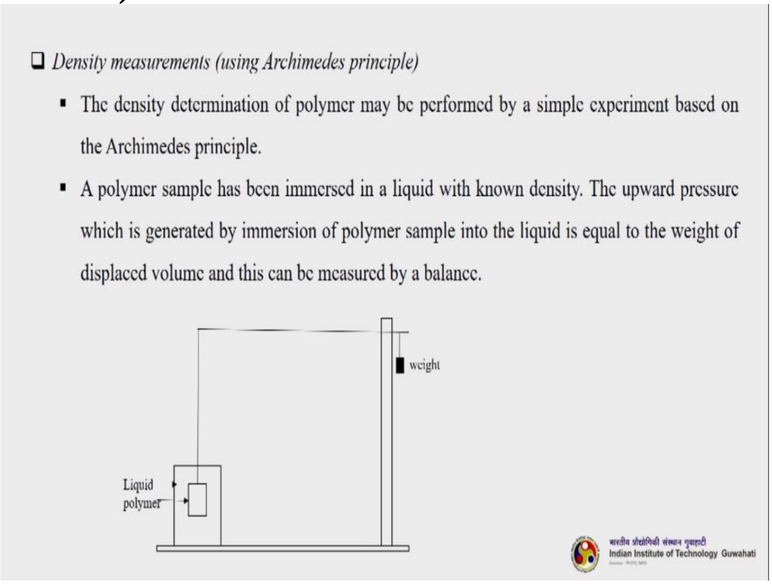
(Refer Slide Time: 37:31)



- The density gradient in the column is obtained by mixing two liquids, one with the high density and another with a low density.
- Often aqueous in-organic solutions such as sodium bromide are used for polymers with density greater than $1 cm^3/g$.
- The overall density of the polymer sample can be obtained by measuring its floatation level.

So, the density gradient in the column is obtained by mixing 2 liquids one with the high density another the low density of one equals inorganic solutions such as sodium bromide are used for polymers with density greater than 1 centimeter cube per gram. So, the overall density of the polymer sample can be obtained by measuring its floatation level. So, you are measuring the floatation level actually from the density gradient color.

(Refer Slide Time: 37:52)



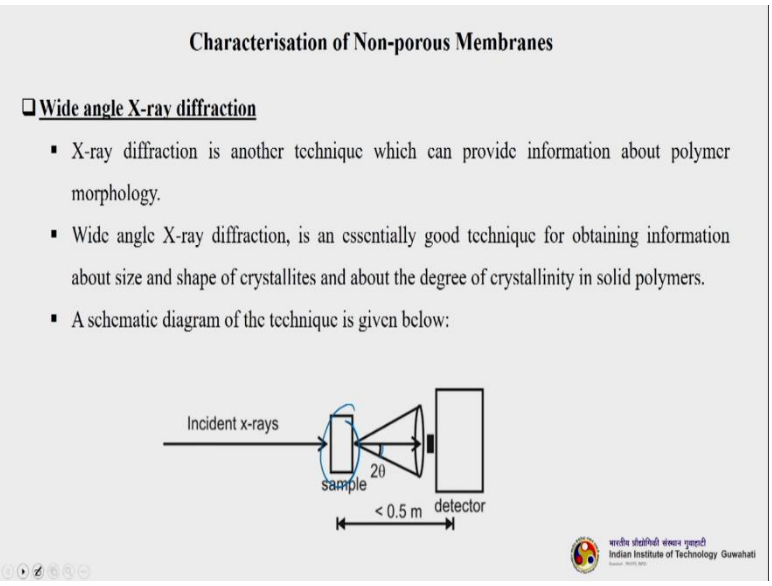
❑ *Density measurements (using Archimedes principle)*

- The density determination of polymer may be performed by a simple experiment based on the Archimedes principle.
- A polymer sample has been immersed in a liquid with known density. The upward pressure which is generated by immersion of polymer sample into the liquid is equal to the weight of displaced volume and this can be measured by a balance.

So, you can measure density by Archimedes principle also very easy. So, then density determination of polymer may be performed by simple experiment based on Archimedes principle. So, what is been happening here you can see here a polymer sample has been immersed in a liquid within non density. So, we are taking a polymer sample of which we want to measure the density we are immerse it in a liquid whose density is known to us.

Now, the upward pressure which is generated by immersion of polymer sample into the liquid is equal to the weight of the displace volume and this can be measured by a balance. So, how much actually upward pressure is generated when you immersing of this polymer sample in the liquid that should be equal to the weight of the displaced volume. How much amount of liquid is being displaced, and that can be measured by a balance. It is a very simple technique, this is a schematic of how actually it is being done.

(Refer Slide Time: 38:42)



Characterisation of Non-porous Membranes

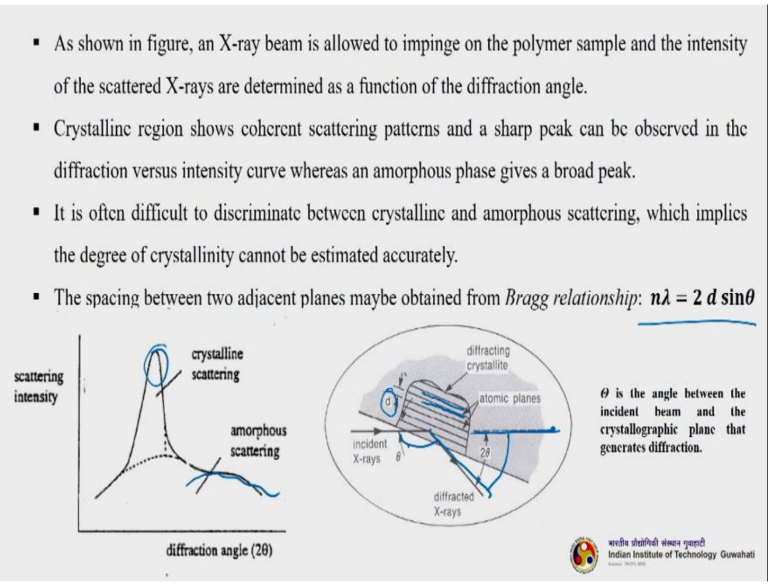
❑ **Wide angle X-ray diffraction**

- X-ray diffraction is another technique which can provide information about polymer morphology.
- Wide angle X-ray diffraction, is an essentially good technique for obtaining information about size and shape of crystallites and about the degree of crystallinity in solid polymers.
- A schematic diagram of the technique is given below:

So, the next is one of the most important and sophisticated measurement technique, analytical technique, which is called WAX, wide angle X-ray diffraction of the X-ray d. So, X-ray diffraction is another technique, which can provide information about polymer morphology. Wide angle X-ray diffraction is an essentially good technique for obtaining information about size and shape of crystallites. So, what it gives us, it gives us the crystallinity, the size and shape of crystallites in solid polymers.

So, this is the schematic representation in a very simple way. I am showing you this. So, the incident trends. This is a sample on which the incident x rays are falling. Then whatever is getting passed to the sample documents, it is generating the secondary electrons. Those are getting detected. So the angle, this angle actually is called 2 theta. We will see in another image that will be a little more clear in this particular image.

(Refer Slide Time: 39:38)



- As shown in figure, an X-ray beam is allowed to impinge on the polymer sample and the intensity of the scattered X-rays are determined as a function of the diffraction angle.
- Crystalline region shows coherent scattering patterns and a sharp peak can be observed in the diffraction versus intensity curve whereas an amorphous phase gives a broad peak.
- It is often difficult to discriminate between crystalline and amorphous scattering, which implies the degree of crystallinity cannot be estimated accurately.
- The spacing between two adjacent planes maybe obtained from *Bragg relationship*: $n\lambda = 2\,d\,\sin\theta$

θ is the angle between the incident beam and the crystallographic plane that generates diffraction.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

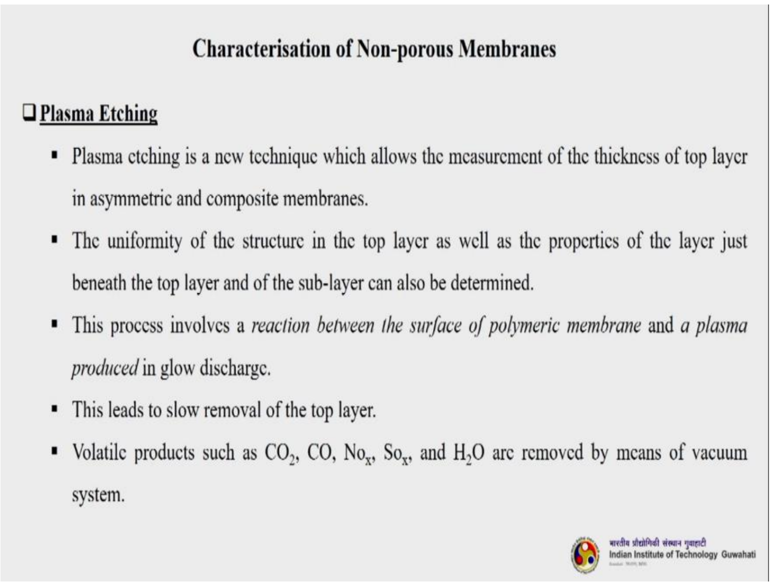
So, as shown in this figure an X ray beam is allowed to impinge on the polymer. So, this is a polymer sample, on which the X ray beam actually is impinging on. And at a particular diffraction angle, that angle is called theta. Now, crystalline region shows coherent scattering patterns and a sharp peak can be obtained in the diffraction versus intensity curve whereas an amorphous phase gives a broad peak.

So, this is the scattering intensity versus the 2 theta the angle you can see the sharp peak here, this sharp peak is due to the crystalline region and amorphous region always gives this type of broad peaks. So, you can see this particular this one image here. So, here theta is the angle between the incident beam this is theta is the angle between the incident beam and the crystallographic plane that generates the deflection and 2 theta is the angle between this incident beam and if it is passing you can see from here.

And whatever it is getting the diffracted. So this is your 2 theta. Now, you know, in earlier the exotic systems theta systems. Now, most of the accepted systems, or whatever it is available that theta 2 theta system. But it is being shown here. Now, it is often difficult to discriminate between crystalline and amorphous scattering, it is very difficult actually, which implies the degree of crystallinity cannot be estimated very accurately the spacing between the 2 adjacent planes.

So, these are atomic plane, this is 1 atomic plane. This is another atomic plane. So, you can see that the distance between these 2 planets are given by can be calculated from the Bragg relationship, which is this particular equation n lambda = 2 d sin theta. So the d is the distance between the 2 atomic plans theta is this angle of incidence. And lambda is the wavelength which is falling on the surface.

(Refer Slide Time: 41:39)



Characterisation of Non-porous Membranes

❑ **Plasma Etching**

- Plasma etching is a new technique which allows the measurement of the thickness of top layer in asymmetric and composite membranes.
- The uniformity of the structure in the top layer as well as the properties of the layer just beneath the top layer and of the sub-layer can also be determined.
- This process involves a *reaction between the surface of polymeric membrane* and *a plasma produced* in glow discharge.
- This leads to slow removal of the top layer.
- Volatile products such as CO_2, CO, No_x, So_x, and H_2O are removed by means of vacuum system.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

Now, the next technique is called plasma etching, the plasma etching is a new technique which allows the measurement of the thickness of top layer in asymmetric and composite membranes. Now, please note this very importantly, because this is one of the most important technique which will measure or will help us in characterize the asymmetric membranes. Those moments whichever skin layer or the top layer. So, in composite membranes also so, the uniformity of the structure in the top layer as well as the properties of the layer just within the top layer and the sub layer can also be determined.

So, it is not that only the top layer is being characterized we can characterize the sub layer also which is supporting basically, but the process involves a reaction between the surface polymeric membrane and a plasma that is produced in a flow distance. This leads to slowly move up the top layer that material itself getting removed and by the virtual plasma interaction what is happening that we get different types of vapors or volatile products such as carbon dioxide, carbon monoxide and knocks socks and water.

(Refer Slide Time: 42:42)

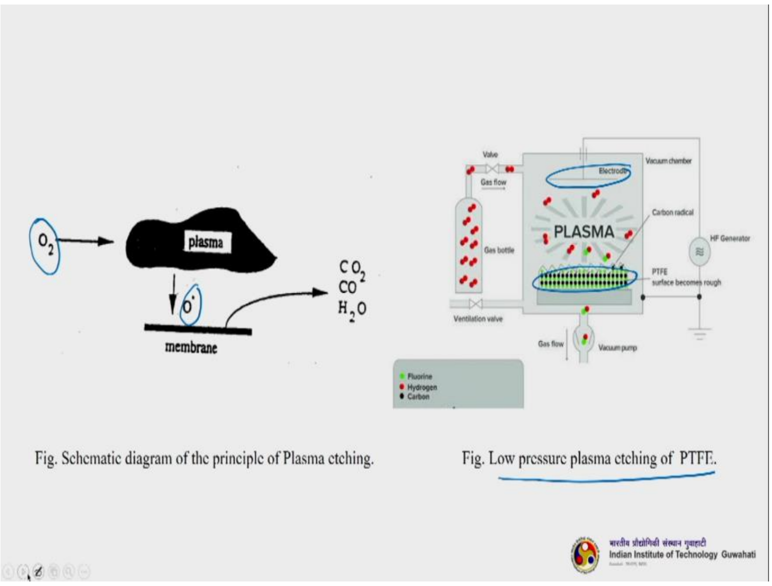


Fig. Schematic diagram of the principle of Plasma etching.

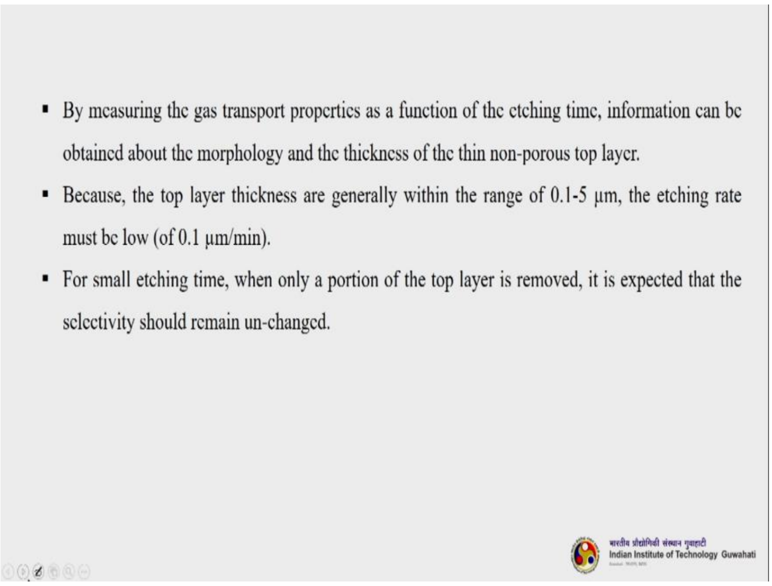
Fig. Low pressure plasma etching of PTFE.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

So, let us see how this is actually happening. So, this is a schematic representation. Here your are seeing oxygen is using being used as ionizing gas when we put it inside a plasma generating chamber so it will ionized and it will generate what it will generate oxygen radicals. So you can see this, now they are hitting to the membrane surface and then the degradation starts. There is some states so you get carbon dioxide, carbon monoxide, water and other things. So, this particular figure is a low pressure plasma etching of a poly tetra fluro ethylene polymer.

So you can see how it happens actually, this is a better schematic representation. So here the guest is coming and then entering to this particular reactor plasma reactor basically under the electrode discharge the gas will be generating different types of radicals. Now these radicals is hitting the surface of the membrane and then it is degrading and then it is generating different other components such as carbon monoxide carbon dioxide, here this was nocks socks depending upon extremely what is the composition of the particular polymer.

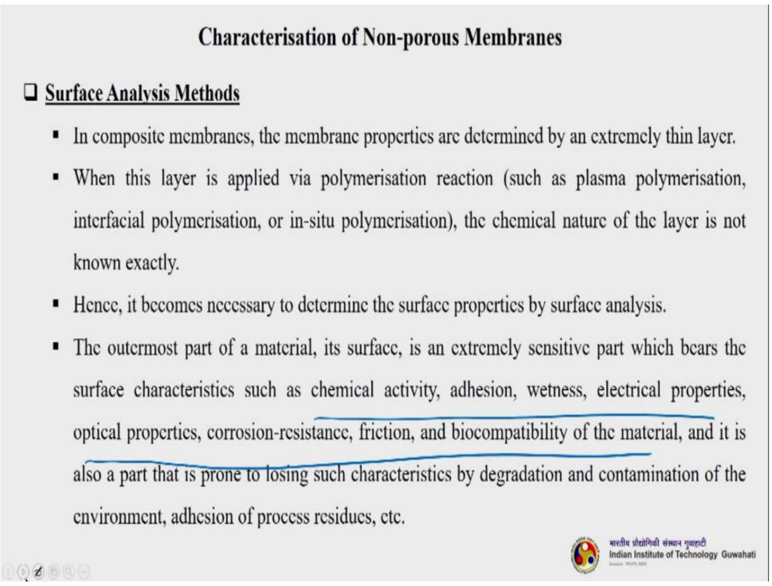
(Refer Slide Time: 43:55)



- By measuring the gas transport properties as a function of the etching time, information can be obtained about the morphology and the thickness of the thin non-porous top layer.
- Because, the top layer thickness are generally within the range of 0.1-5 μm, the etching rate must be low (of 0.1 μm/min).
- For small etching time, when only a portion of the top layer is removed, it is expected that the selectivity should remain un-changed.

So, by measuring the gas transport properties as a function of the etching time information can be obtained about the morphology and the thickness of the thin non porous top layer because the top layer thickness generally within the range of 0.125 micron the etching rate must be below. For small etching time only when a person of the top layer is removed it is expected that the selectivity should be unchanged. This is a good process actually good technique however, little costly apparatus is required because we are talking about generating plasma.

(Refer Slide Time: 44:22)



Characterisation of Non-porous Membranes

❑ **Surface Analysis Methods**

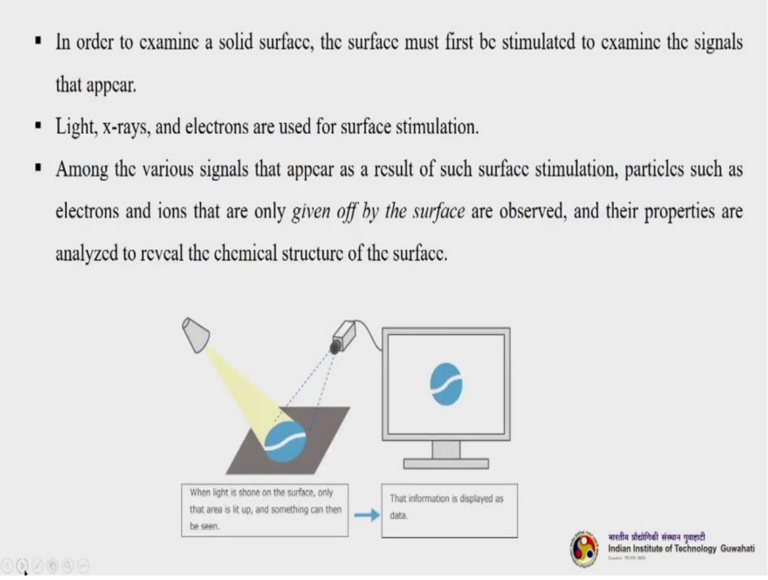
- In composite membranes, the membrane properties are determined by an extremely thin layer.
- When this layer is applied via polymerisation reaction (such as plasma polymerisation, interfacial polymerisation, or in-situ polymerisation), the chemical nature of the layer is not known exactly.
- Hence, it becomes necessary to determine the surface properties by surface analysis.
- The outermost part of a material, its surface, is an extremely sensitive part which bears the surface characteristics such as chemical activity, adhesion, wetness, electrical properties, optical properties, corrosion-resistance, friction, and biocompatibility of the material, and it is also a part that is prone to losing such characteristics by degradation and contamination of the environment, adhesion of process residues, etc.

Now, the next method is surface analysis methods. So, in composite membranes, the membrane properties are determined by the extremely thin layer, the top layer of the skin layer. So, when this layer is applied via polymerization reaction, so, we have discussed about all these techniques know, techniques to make a symmetric membranes or composite membranes, such as plasma polymerisation, interfacial polymerisation or in-situ polymerisation, the chemical nature of the layer is not known exactly.

So, that is why it need to characterize it. So, the outermost part of the material that is its surface is an extremely sensitive part, which bears the surface characteristics. So, what are those, so, the chemical activity, adhesion, wetness, electrical properties, optical properties, corrosion-resistance, friction and biocompatibility of the material, and it is also a part that it is prone to losing such characteristics by degradation and contamination of the environment, adhesion of process residues etc.

So, you can see there are so many surface properties these are all of them plays a certain role to care, when the separation is actually going on through the membrane.

(Refer Slide time: 45:26)



- In order to examine a solid surface, the surface must first be stimulated to examine the signals that appear.
- Light, x-rays, and electrons are used for surface stimulation.
- Among the various signals that appear as a result of such surface stimulation, particles such as electrons and ions that are only *given off by the surface* are observed, and their properties are analyzed to reveal the chemical structure of the surface.

When light is shone on the surface, only that area is lit up, and something can then be seen.

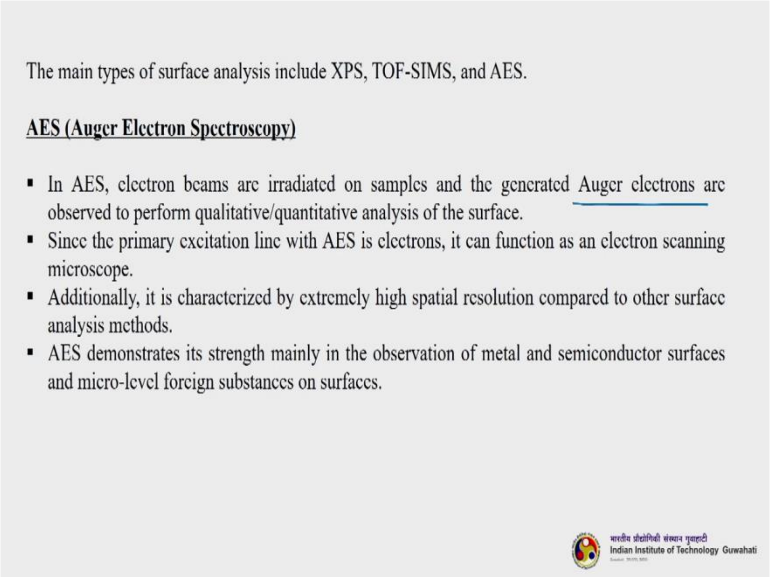
That information is displayed as data.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

Now, in order to examine a solid surface the surface must be first stimulated to examine the signals that appears. So, to stimulate that we can use either light or x rays in electrons. Different types of electrons per surface stimulation. So, among the various signals that appear as a result of soft surface stimulation particles, such as electron center that are only given above the surface.

So, what actually we are doing is that we are using light extra electrons to stimulate the surface. So, what is the surface is getting stimulated, the surface is emitting certain electrons, anion, so, whatever it is, so, that what is being emitted is being actually observed or being that is goes to the detector that has been detected actually. So, their properties are analyzed to reveal the chemical structure of the surface.

(Refer Slide time: 46:18)



The main types of surface analysis include XPS, TOF-SIMS, and AES.

AES (Auger Electron Spectroscopy)

- In AES, electron beams are irradiated on samples and the generated Auger electrons are observed to perform qualitative/quantitative analysis of the surface.
- Since the primary excitation line with AES is electrons, it can function as an electron scanning microscope.
- Additionally, it is characterized by extremely high spatial resolution compared to other surface analysis methods.
- AES demonstrates its strength mainly in the observation of metal and semiconductor surfaces and micro-level foreign substances on surfaces.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

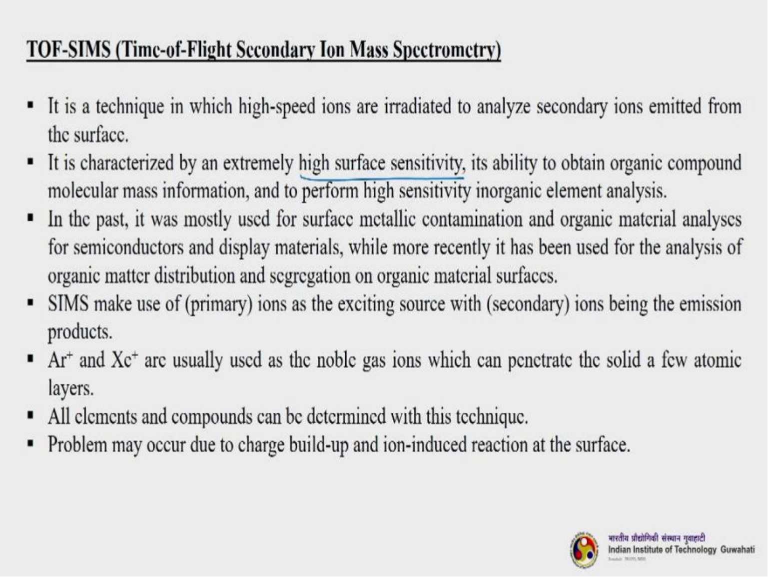
So, under these techniques we will discuss 3 different analytical methods. One is called XPS then is one and then the next is TOF-SIMS and another AES. So, let us first see that AES which is called auger electron spectroscopy. So, AES the electron beams are irradiated on samples and the generated auger electrons are observed to perform the qualitative quantitative analysis of the surface.

We can have both qualitative and quantitative measurement. So, basically something like electron microscope you can understand and correlate with that. So, electrons are being or x rays being actually put on the surface of the membrane material and it will generate some electrons. In same also it will generate the electron those are called secondary electron. The secondary electrons are actually detected.

We are not talking about any that is any other electrons so, only the secondary electrons are being detected. So, here auger electrons are detected there may be some other electrons also. So, since the primary excitation line with AES electrons it can function as an electron scaling microscope. So that is what I was telling about scanning microscope. Additionally it is characterized by extremely high spatial resolution compared to other surface and analysis methods.

So the resolution is extremely high in AES. So AES is demonstrates its strength mainly in the observation of metal and semiconductor surfaces and micro level foreign substances on surface. It is a very good technique. I will show you sketch later on.

(Refer Slide time: 47:50)



TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry)

- It is a technique in which high-speed ions are irradiated to analyze secondary ions emitted from the surface.
- It is characterized by an extremely high surface sensitivity, its ability to obtain organic compound molecular mass information, and to perform high sensitivity inorganic element analysis.
- In the past, it was mostly used for surface metallic contamination and organic material analyses for semiconductors and display materials, while more recently it has been used for the analysis of organic matter distribution and segregation on organic material surfaces.
- SIMS make use of (primary) ions as the exciting source with (secondary) ions being the emission products.
- Ar^+ and Xe^+ are usually used as the noble gas ions which can penetrate the solid a few atomic layers.
- All elements and compounds can be determined with this technique.
- Problem may occur due to charge build-up and ion-induced reaction at the surface.

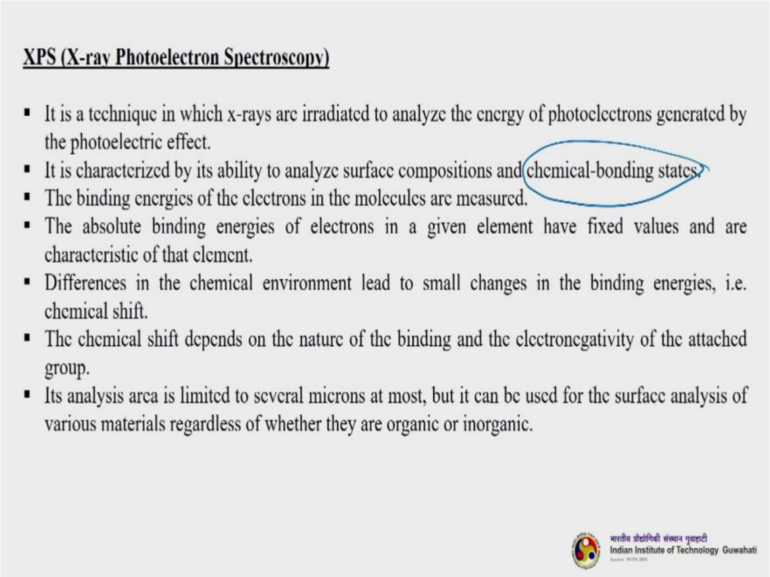
भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

The next method is TOF-SIMS, it is actually called time of flight secondary and mass spectrometry. So what is happening in this, so it is a technique in high speed ions are irradiated to analyze secondary ion that is emitted from the surface. Now it is characterized by an extremely high surface sensitivity. That is its ability to obtain organic compound molecular mass information and to perform high sensitivity inorganic elemental analysis.

Now, in the past, it was mostly used for surface metallic contamination and organic material analysis, usually for the semiconductors and display materials while more recently it has been used for the analysis of organic matter distribution and segregation on organic material surfaces. Now SIMS make use of primary and ions as the exciting source with secondary ions being the emission products that is being detected.

So, Argon and Xenon are usually used as the noble gas ions which can penetrate the solid few atomic layers is that is why the elements and capabilities more that is why they are being used with a small excitation they actually go to a very with small amount of this one excitation. So, they actually penetrate very deep. So, they can go to the sub layer of the support layer also. So, all elements and compounds can be determined with this technique problem may occur due to the charge build-up and ion induced reaction at the surface.

(Refer Slide time: 49:13)



XPS (X-ray Photoelectron Spectroscopy)

- It is a technique in which x-rays are irradiated to analyze the energy of photoelectrons generated by the photoelectric effect.
- It is characterized by its ability to analyze surface compositions and chemical-bonding states.
- The binding energies of the electrons in the molecules are measured.
- The absolute binding energies of electrons in a given element have fixed values and are characteristic of that element.
- Differences in the chemical environment lead to small changes in the binding energies, i.e. chemical shift.
- The chemical shift depends on the nature of the binding and the electronegativity of the attached group.
- Its analysis area is limited to several microns at most, but it can be used for the surface analysis of various materials regardless of whether they are organic or inorganic.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

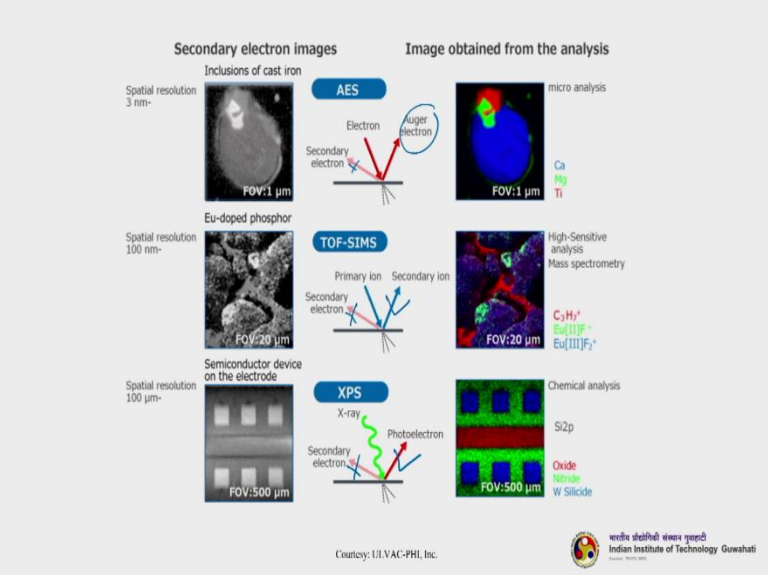
So the next method is called XPS, which is called X-ray photo electron spectroscopy. So, it is one of the most important analytical method people those who are working with membrane materials then you adsorbents catalysts and all. So, they have to go through all the XPS actually analysis. It is a technique in which x rays are irradiated to analyze the energy of the electrons generated by the photo electric effect this is how it is difference from the usual accepted.

So, it is characterized by its ability to analyze surface composition and chemical bonding states. So, I was telling units very important to excite very important for catalyst polymeric materials like per membrane and all applications as well as adsorbent because of this chemical bonding states. So, it will tell me the bonding state actually, as well as the composition.

Now, the binding energies of the electrons in the molecules are measured that is what, how much energy is there that can be measured and the absolute binding energy of electrons in a given elements of fixed values and are characteristics of that element. Difference in the chemical environment will lead to small changes in the binding energies that will result in the chemical shift. The chemical shift depends on the nature of the binding as well as electronegativity of the attached group.

Now, its analysis area is limited to several microns at most, but it can be used for the surface analysis of various metals regardless of whether they are organic or inorganic. So, we have seen the 3 methods.

(Refer Slide time: 50:45)



Secondary electron images

Image obtained from the analysis

Inclusions of cast iron

Spatial resolution 3 nm-

AES

micro analysis

Eu-doped phosphor

Spatial resolution 100 nm-

TOF-SIMS

High-Sensitive analysis

Mass spectrometry

Semiconductor device on the electrode

Spatial resolution 100 µm-

XPS

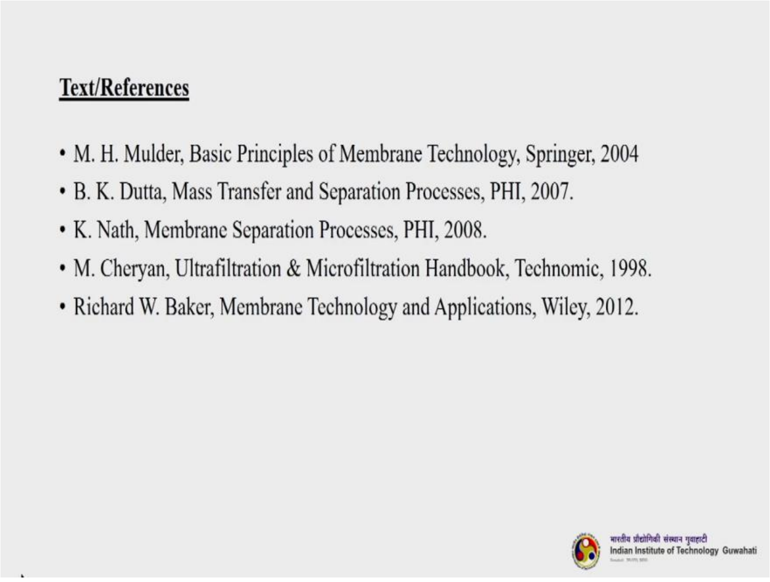
Chemical analysis

Courtesy: ULVAC-PHI, Inc.

Now, the next slide is showing you understanding or in the form of images of this particular 3 methods which we discussed, that AES the TOF-SIMS and the XPS. In case of AES that resolution is very high, it is 3 nanometer for TOF-SIMS it is 100 nanometer for XPS it is 100 micron and these are the images actually micron analysis. This is the image obtained from the analysis from you can see the what we are measuring is the auger electron.

This is not being measured. In AES what we are measuring is the secondary ion, not this one not the secondary electron in case of TOF-SIMS and what we are measuring in XPS is the porter electron not this secondary electron. So, please see this is in a nutshell in this single picture will tell you the differences between AES and TOF-SIMS and XPS and these are the corresponding images from the analysis you can see this is the resolution at 1 micron. This is 20 micron. This is 500 micron. In XPS we are able to see the oxide nitride and different phases also.

(Refer Slide time: 52:01)



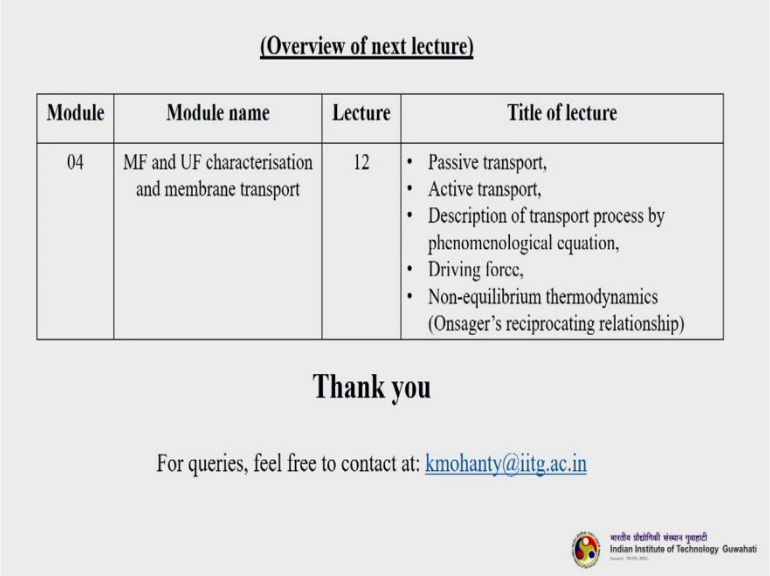
Text/References

- M. H. Mulder, Basic Principles of Membrane Technology, Springer, 2004
- B. K. Dutta, Mass Transfer and Separation Processes, PHI, 2007.
- K. Nath, Membrane Separation Processes, PHI, 2008.
- M. Cheryan, Ultrafiltration & Microfiltration Handbook, Technomic, 1998.
- Richard W. Baker, Membrane Technology and Applications, Wiley, 2012.

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

So, students today we discussed about the characterization of this non-porous membranes and an ionic membranes also. So, you can use this references and books actually Mulder is the text as I keep on telling you and apart from other books also like which are Baker and Cheryan for today's topic most it is taken from the Mulder.

(Refer Slide time: 52:25)



(Overview of next lecture)

Module	Module name	Lecture	Title of lecture
04	MF and UF characterisation and membrane transport	12	• Passive transport, • Active transport, • Description of transport process by phenomenological equation, • Driving force, • Non-equilibrium thermodynamics (Onsager's reciprocating relationship)

Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

So, thank you very much in the next class. We are going to solve characterization its topics are over. So once we characterisation is over as I discussed in the introductory lecture what is the next is basically we need to understand the transport. Before we move on to a particular processes now in the transport we will discuss about the membrane transport, how the transport is happening.

What is passive transport what is active transport, then phenomenological equation, driving force and we will discuss in nutshell in a brief actually the non-equilibrium thermodynamics the on suggest reciprocating relationship it is very important when you go for any design of membrane processes, you must understand this actually. So then only you can model and design a particular membrane process. So thank you very much. So you have any query please drop a mail to me at kmohanty@iitg.ac.in. Thank you