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

**Lecture-10**
**MF Membrane characterization: Bubble point, Mercury intrusion, Permeability method**

Good morning students today is the lecture 10 under module 4 as you know that we are discussing the characterization of membranes. Today we will discuss microfiltration correct membrane characterization under which will cover the bubble point method bubble point with gas permeation mercury intrusion and permeability method. Then will learn the characterization of ultrafiltration membranes.

So in which we will discuss about gas adsorption desorption thermoporometry and permporometry. And then liquid displacement and finally the solute rejection method which is called as molecular weight cut off experiment which is mostly used by the membrane and manufacturers to decide the molecular weight cut off of their particular membrane. So let us start so let us understand the fermentation process. So I do not know how many of you understand the fermentation process.

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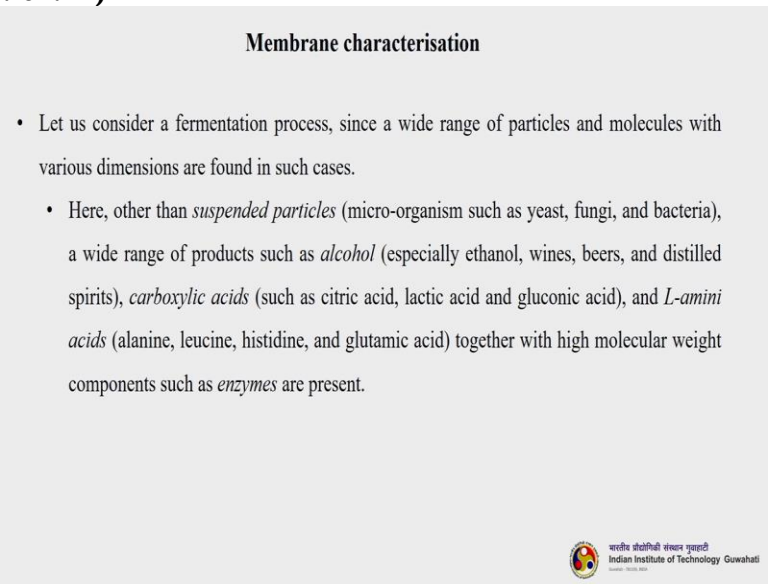


So those who have biotechnology background there must be knowing what is fermentation. So actually why I am asking or taking this example because this is one of the classic example, in

which will find so many different types and sizes and molecular weights as well as shapes of particles. So like that there will be suspended particles which are our microorganisms it can be yeast, fungi, algae, bacteria, anything.

Then we will have different kinds of alcohol where we have ethanol, wine, beers, distilled spirits, then we will have carboxylic acid such as citric acid, lactic acid, gluconic acid and then L - amini acid like alanine, then leucine histidine together with other different high molecular rate components such as enzymes.

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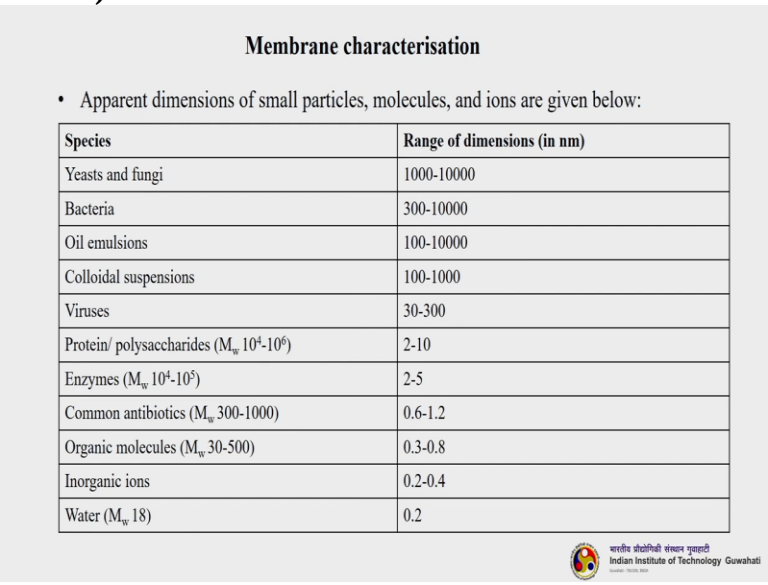


And these are the apparent dimensions of the different types of particles and their respective ions, you can see the yeast, fungi, bacteria, they are of the order of this 1000 to 10000 this is these are all in nanometers then we will have viruses in 30 to 300 nanometers we have proteins, enzymes in organic ions and the water molecular weight is 18. 0.2 nanometer is the hydrodynamic radius of water molecules.

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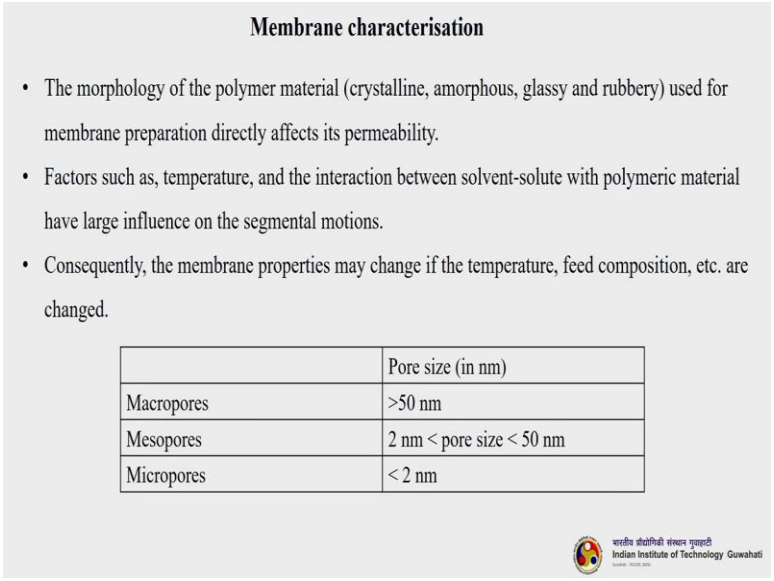


So the morphology of the polymeric material that is whether it is crystalline, amorphous, glassy or rubbery. So these are all used for preparation of membranes. So and they affect directly the membrane permeability. So factors such as temperature interaction between solvent solute with polymeric material they also have large Influence on the segments and motions. Consequently membrane properties may change if the temperature feed composition etc. changed.

So let us again understand though we have been discussing it many times and I have shown you in many slides, since, each classes are different let us again try to understand the sizes of the pores that we are going to characterize. So the macro pores greater than 50 nanometer major pores 2 nanometer to 50 nanometer and micro pores less than 2 nanometers. So this is the pore size classification and given by a IUPSC.

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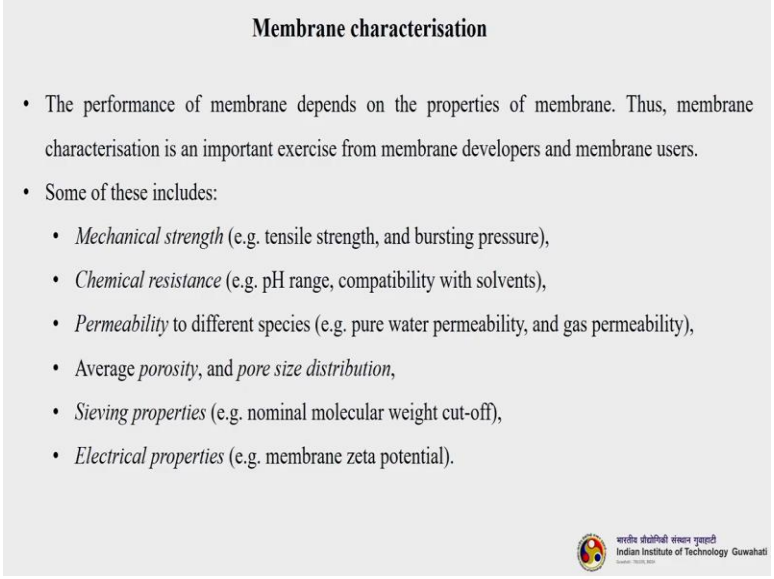


Now the performance of the membranes depends on the properties of the membrane. Thus membrane characterization is an important technique exercise from membrane developers and membrane users now some of the properties include mechanical strength so basically tensile strength and the bursting pressure, then chemical resistance like pH range compatibility with other organic solvents permeability to different species for example pure water permeability and then gas permeability.

Average porosity and pore size distribution the most important membrane properties then sieving properties like our nominal molecular weight cut off and electrical properties. So which is decided by the membrane zeta potential?

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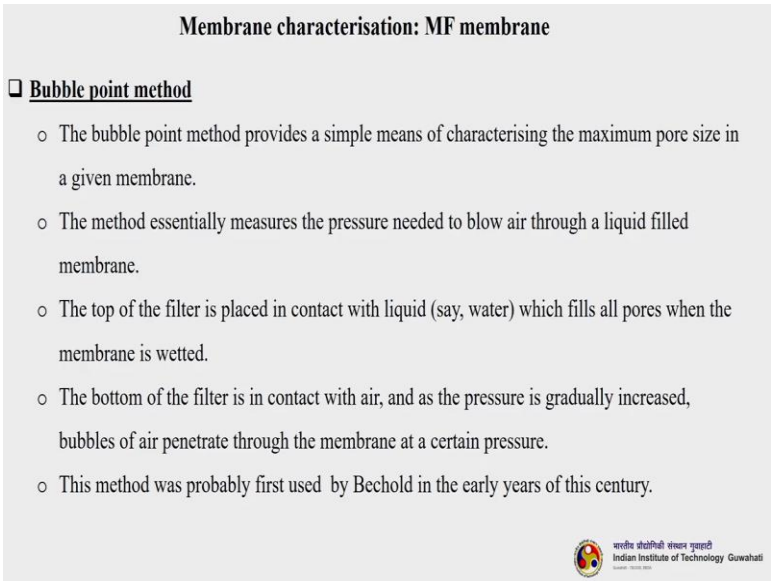


Let us see the first method of today's lecture which is called bubble point method it is one of the classic and most easily adoptable techniques for membrane microfiltration and membrane characterization can be done easily in any lab. So the method essentially measures the pressure needed to blow air through a liquid filled membrane. And the top of the filter is placed in contact with liquid essentially it is water which fills all the pores of the membrane.

And the membrane gets wetted the bottom of the filter is in contact with air and as the pressure is gradually increased bubbles of air penetrate to the membrane at certain pressure. So, this method was first used by Bechold in the early years of this century now let us understand how this process works.

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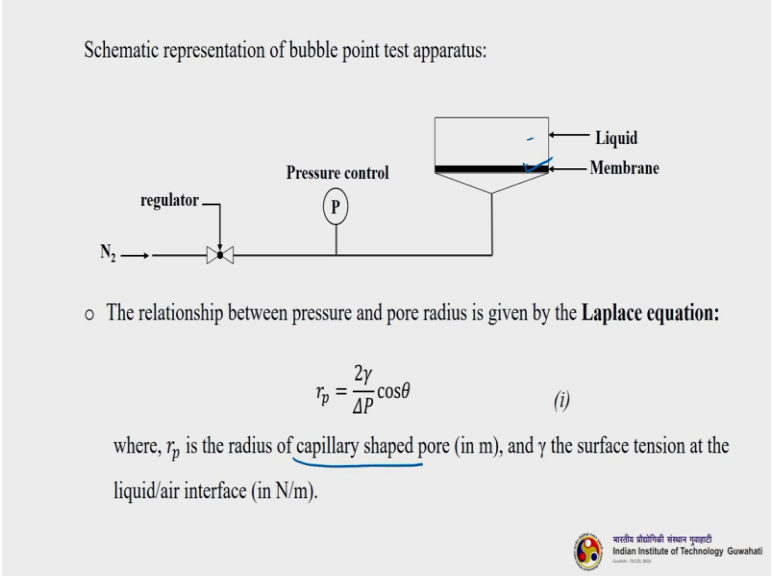


Please see this particular image as you can see that there is a module or some sort of arrangement which is holding your membrane so this is your membrane and here the liquid is present now I am passing nitrogen from the bottom of this membrane the membrane is getting already is wetted with the liquid or water. So, we can use laplace equation the classic laplace equation to find out the pore radius so it is given by this r p = 2 gamma / delta P cos theta.

So, r p is the radius of the capillary shaped pores why we are talking about capillary because it is assume in particular this equation that the pore are capillary shaped and gamma is the surface tension in the liquid air interface.

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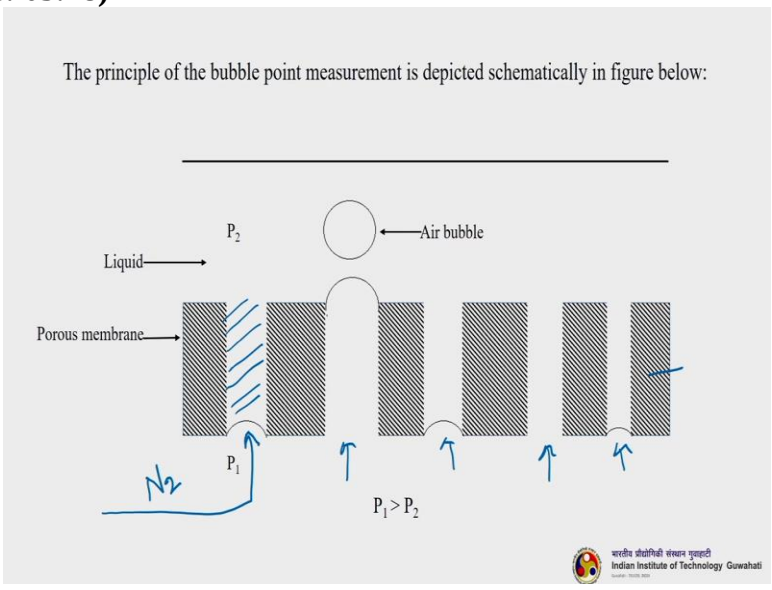

Now how this happens? What will happen basically this is a principle. So as you can see P1 is the pressure from the bottom side of the this one membrane which we are supplying and P2 is the pressure at the upstream side of the membrane that is basically the liquid pressure and obviously P1 is greater than P2 because P1 is what we are supplying from the bottom side now what will happen? So these pores are actually filled with liquid.

So basically these are actually filled with liquid try to understand this is one of the pore which is filled with liquid now what I am doing is that I am passing nitrogen through this what will happen so similarly here also nitrogen is coming here also it is coming and here also it is coming everywhere these are all pores and whatever you are seeing by sketches so these are this is your membrane material.

So what will happen basically so nitrogen will try to pass through the pores of the membranes? So in nitrogen trains tied to pass through the pores of the membrane initially what will happen? The largest pores will be emptied because the pressure that is required to empty a large pore is much lesser than that is required to empty a small pore. So the pore size actually matters then when the gas is passing through the liquid filled pores of the membrane. It will flows slowly through like this becomes like this then it keeps on moving then it moves, then it moves out basically and you get air bubble on the top of the membrane.

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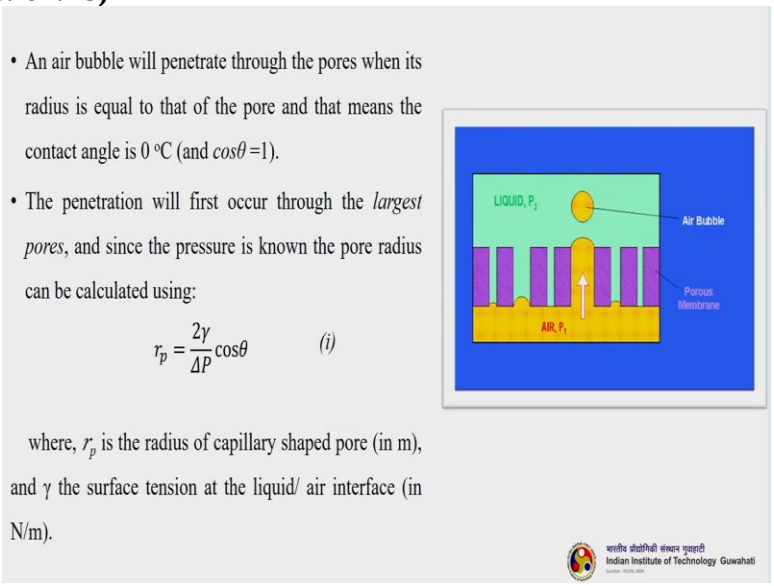

So an air bubble will penetrate through the pores when its radius is equal to that of the pore that means yet the contact angle is 0 degrees here cos theta in the Laplace equation becomes 1. So the penetration will first occurred to the largest pores since the pressure is known as the pore radius and since the presser is known the delta p we know so that is why we can calculate the pore radius from this particular equation.

So you can see again I am trying to show this the same image is a color image only. So air or nitrogen passing through this you can see the initially this is the largest pore among all these pores you can see this the largest pore at least from the side bottom side. So, that is getting displaced liquid is displaced from the largest pore then again when we increase the pressure smallest pore which also displaced.

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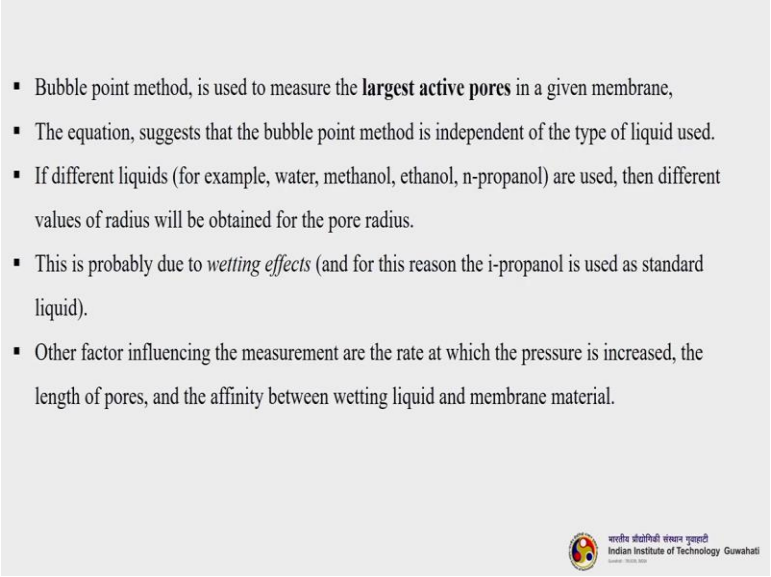


So bubble point method is used to measure the largest active pores in a given membrane now please understand that this is one of the most this one though it is a simple technique and one of the most important technique to measure the microfiltration membrane why because only the largest and only the active pores actually are getting characterize since we are characterizing we have pressurizing the membrane from the bottom side.

So any pore that is dead and that is not taking part in this particular exercise. So the equation suggests that bubble point metal is independent of the type of liquid now but if different liquids are using because the type of liquid has nothing to do because of the equation is stuck. RP equals

to here in this equation, it is 2 gamma / delta P cos theta. Cos theta it is 1 then it is 2 gamma / delta P.

So your RP is a consequence of nothing but delta P and here surface tension of course that is a constant so such type of liquid has nothing to do with in this equation however, let us assume that you are taking different types of liquids then what will happen, you will get different results. Now there is a reason for that is that different types of liquids are wetting the membrane differently. So that is where most of the time isopropanol is being used. So, other factors that can influence this particular measurement technique is that the length of the pores and the affinity between the wetting liquid and the membrane material that is also very important.

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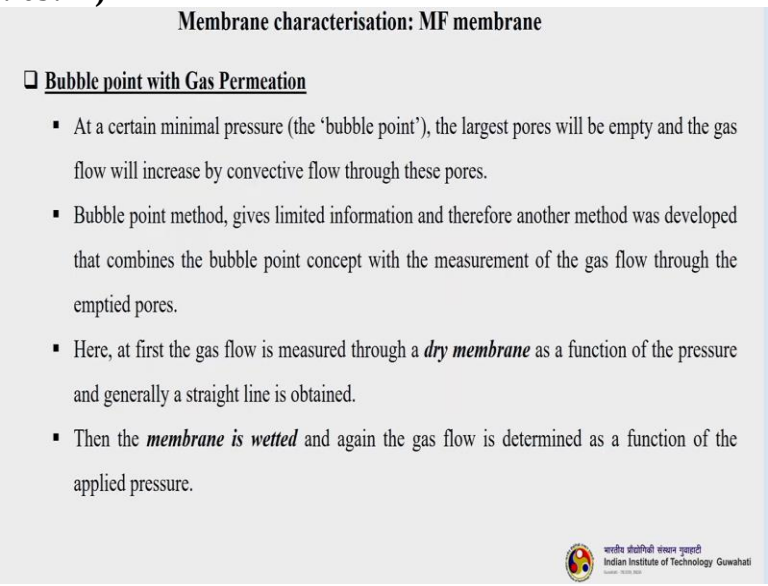


Now the next method is bubble point with gas permeation. Now at a certain minimal pressure which is called actually the bubble point the largest pores will be empty and the gas flow will increase by convective flow through these pores. Now bubble point methods it had some limited information and therefore another method was developed that combines the bubble point concept with the measurement of the gas flow of the emptied pore.

So what we are what is happening in this particular technique is that initially the bubble initially there is a membrane there is a dry membrane through which we are passing the gas and we are measuring the flux of the gas. So gas flow is being measured as a function of pressure and we

will get a straight line because the pores are there. So the gas will pass through unhindered. Now, what is happening in the next place now the membrane is the same membrane is being wetted?

Using a particular liquid using most of the times or you can go for isopropanol or water. Now again the gas flow through the membrane is being measured. So this second part is nothing but here our earlier bubble point method.

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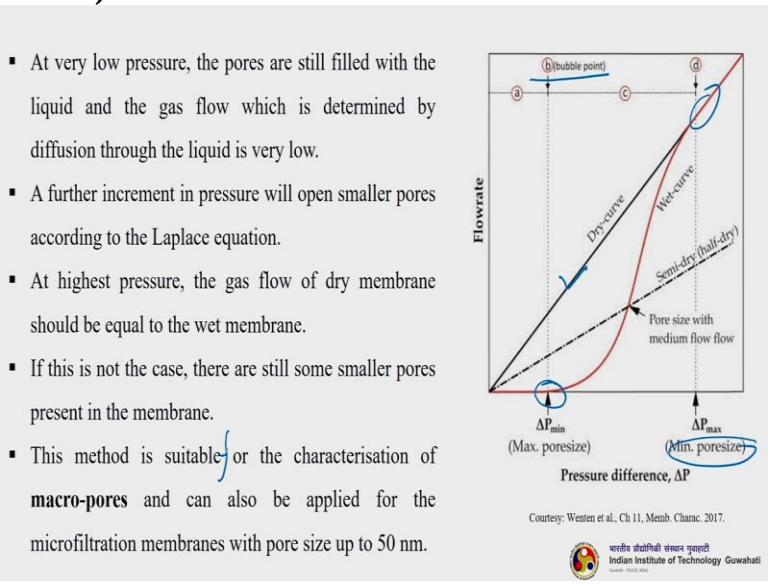


So at a very low pressure the pores are still filled with liquid and the gas flow which is determined by the diffusion to the gas through the liquid is very low. Now when you increase the pressure it will the smaller the smaller pores will be emptied actually or they will take part in this particular gas flow and it has at highest pressure the gas flow dry membrane should be equal to the wet membrane so this is what.

So you can see that this is the dry curve so that is it is a straight line and this red line is the representation of the wet curve. So, you can see this is what is the maximum delta P minimum here that corresponding to the maximum pore size and that Is the bubble point you can see this is the bubble point then the maximum pressure is same for both here dry method as well as wet method. And we will get the minimum pore size this method is suitable for the characterization of macro pores and can also be applied for the microfiltration membrane with pore size up to 50 nanometers so there is a F missing here.

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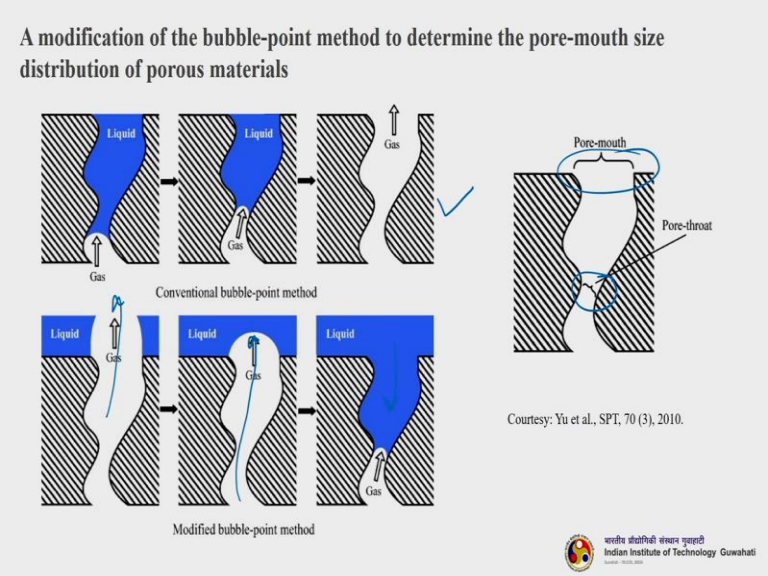


Now let us understand another method this is actually a modification of the bubble point method to determine the pore mouth size distribution of porous material. Now what we have discussed these are all the 2 we have discussed 2 bubble point method one is bubble point the usual bubble point in which the liquid that is filled inside the pores of the membranes are displaced in the second method of the gas permeation.

So we are measuring the gas flow rate for a dry membrane and then we are wetting the membrane and again one measuring I mean all these things what is happening that what we are characterizing is the pore through now please look at this particular image you can understand this is a pore here and you can see this is a pore throat or you can tell is the constriction inside the pore you can call even call it the smallest constriction in the pore.

Because eventually that will determine its size will determine what type of solute will pass through it. And but what is actually required because initially it happens that we need to characterize the suppose you are characterizing from the membrane from the top side you can do it using here SCM and other methods. So which will take into account the dead pores also deaden pores also and it will the SCM method which we have learned earlier.

So it takes it talks about characterizing from the top surface so, that means it is characterizing your pore mouth. So this is the this is what is being characterized. So in this method it will use

this modified method then we can correlate our results. This is what is the basically intention so instead of characterizing the pore throat let us characterize the pore mouth. So this is the conventional bubble point method in this particular method what is happening so the pore of the mouth is dry is filtered through the liquid when the gas is passed.

So when the gas is passing I am dropping liquid on the on the mouth on the pore mouth. So what will happen? You can see this so initially before putting the liquid on the top of the on the mouth of the pore the gas is passing through here freely then I am putting it so putting the liquid on that top of the membrane or the pore mouth itself what will happen? You can see gas here it is coming but it is trying to escape through this liquid. And we will make this one convex type of surface here then what is happen I am still increasing the pressure and I am and the liquid is there. So you can see the liquid is coming here. And the gas flow is still continuing.

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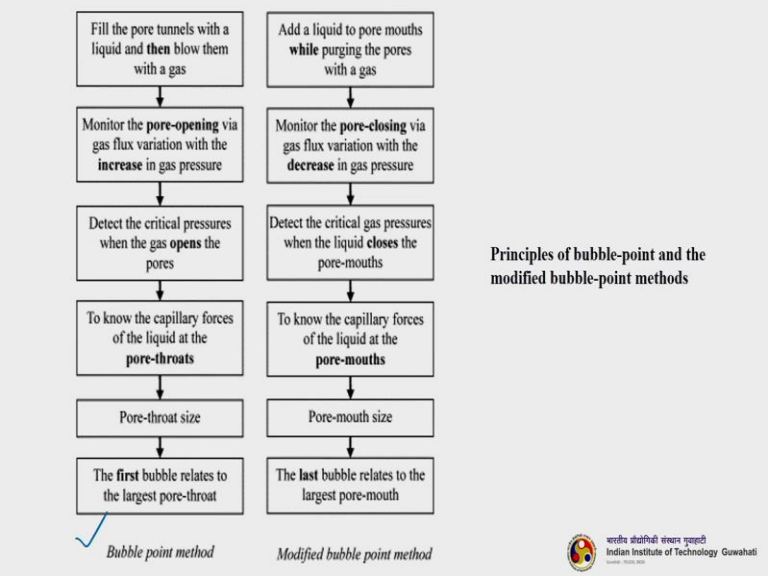


So he can again do this let us understand it clearly. So this is our classical bubble point method here what is happening so we are adding a liquid to the pore mouth while purging the pores to the gas. So the gas is purging and that time only simultaneously I am adding the liquid to the pore mouth so it can be water. So monitor the pore closing via gas flux variation with the decrease in gas pressure so detect the critical gas pressure.

When the liquid closes the pore mouth so when the liquid closes the pore mouth something like this here this time you determine the critical gas pressure. Now then from here only we can

understand what is the size of the pore mouth? And the last bubble that relates to the largest pore whatever that peg and the last bubble is getting created. So, that is corresponding to the largest pore mouth.

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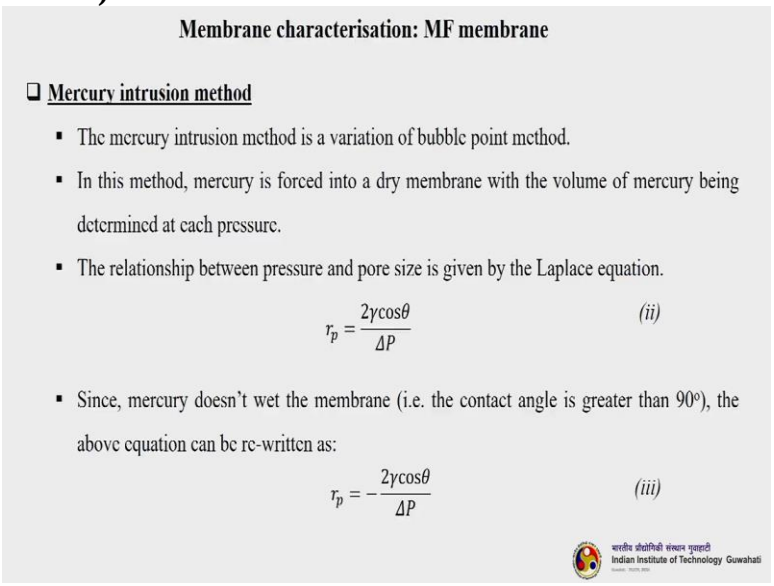


So students the next method that we are going to discuss today is the mercury intrusion method. So this is very important method as because most of the membranes and the catalyst and absorbents always use this method to find out the pore volume. So we have discussed about pore sizes, pore sizes distribution how to find out the pore radius all these things but we have never talked about pore volume.

Pore volume is also very important especially in adsorbents and catalyst. But this is also important for membranes because in many times if you are using the membrane in membrane contactors reactors and bio reactors so the time pore volume is also plays a big or important role. So this is this method is a variation of bubble point method in this method mercury is forced to a dry membrane.

So membrane is not getting wet and the relationship between the pressure and pore size is again given by the Laplace equation. Now since mercury does not wet the membrane so mercury does not wet the membrane that is the contact angle is greater than 90 degrees. So the above equation can be rewritten is r p = 2 gamma cos theta / delta P so gamma is being so negative sign is being

used to take care of the cos theta. Since the contact angle of mercury for polymeric material most of the polymeric material is 141.3 degree and the surface tension is 0.48 Newton's per meter.

So the equation reduces to r p = 7492 / delta P. So again you can see from this particular equation 7490 is become constant. So r p is a consequence of delta p. So the volume of mercury can be determined very accurately why because the mercury is not wetting the membrane whatever is getting inside the membrane pores we are knowing the volume and pore size distribution can be determined quite precisely.

So the equation achieves that capillary pores are present. However, this is not generally the case and for this reason a morphologic constant also must be introduced. Most importantly very high pressure must be avoided because they may damage the porous structure and leads to erroneous pore size distribution. So to push the mercury actually inside the pore smallest pore you need to apply very high pressure. So, certain times it happens that if the membrane is very thin, then membrane will rupture.

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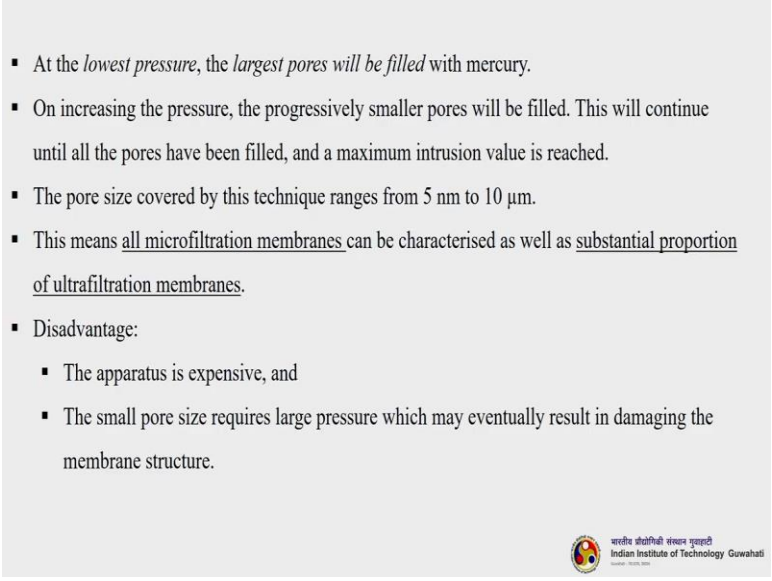


So at the lowest pressure the largest pores will be filled and only increasing the pressure the progressively smaller pores will be filled. This will continue until all the pores have been filled. Maximum intrusion value is reached. Now the pore size can covered by this technique usually from 5 nanometer to 10 micron. This means most of the microfiltration membranes of almost all

microfiltration membranes can be characterized with a substantial proportion of the ultrafiltration ranges also.

So how about the disadvantage in this particular method is the apparatus is very expensive and the small pore size requires a large pressure so, the membrane may get rupture or it will eventually it may get cracks or develop cracks and gets ruptured then we will get erroneous results.

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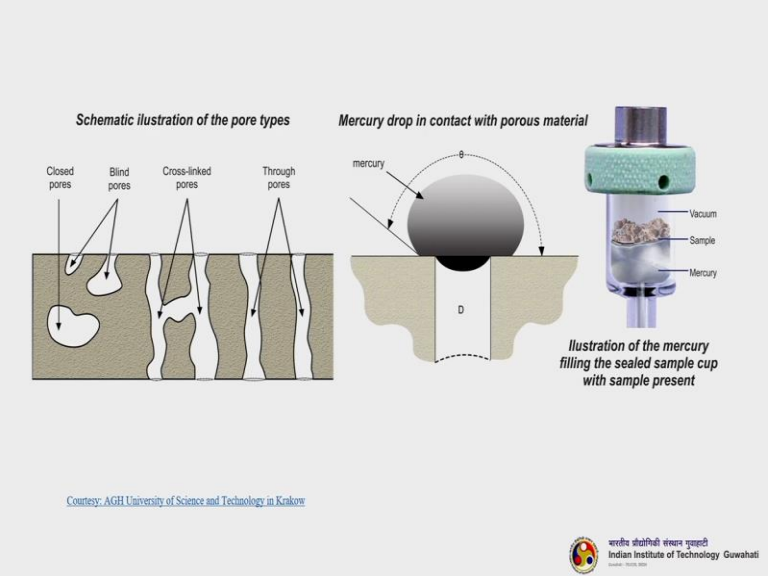


This is how actually it happens. So, this is a schematic illustration of the different types of pore we have never discussed something called a closed pore you can see this is it closed pore. So, it closed pore is a pore inside the membrane material but it has no openings either to the upstream side or to the bottom side. Then we have blind pores so this blind pores nothing but deaden pores.

Many times blind pores can come up to this also it depends what type of it is and it is open here. Then we have crosslink pores so the 2 or more than 2 pores are linked with each other then we have through pores actually whatever our intention is a membrane scientists or resistors would be that we should get maximum this type of pores which are called through pores. So, this is the mercury contact angle with the porous material and this is how it actually happens and this is a vacuum the sample is hold here and Mercury's here. And now when we are pressurizing it, mercury is getting inside that sample.

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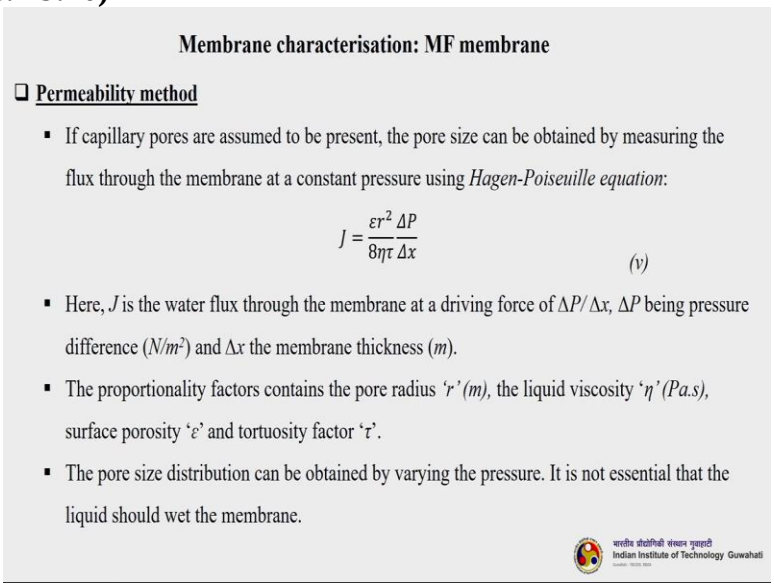


And the next method that we are going to discuss is permeability method. This is again one of the most important methods for characterization of our microfiltration membranes. So if capillary pores are assumed to be present, the pore size can be obtained by measuring flux through the membrane at constant pressure is in the Hagen Poiseuille equation. So, here you see the equation epsilon r square / 8 mu tau and this one here delta p / delta x.

So, here J is the water flux, which is as a result of the driving force which is delta p / delta x and delta p being the pressure difference and delta x is the membrane thickness. Like the r is the pore side of the radiation then you have the liquid viscosity, which is given in Pascal second surface porosity and the tortuosity factor, tortuosity factor is actually geometric parameter and the pore size distribution can be obtained by varying the pressure it is not essential that the liquid should wet the membrane.

Essentially what we are doing here in this method is that we are measuring the flux of either liquid or liquid that is passing through the membrane. So, that is the amount also we are collecting the volume of the permeate basically and measuring it.

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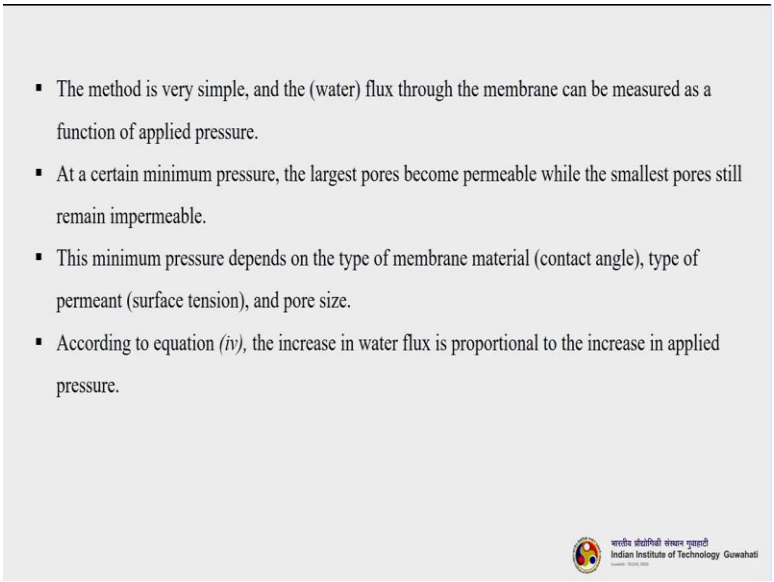


So, this method is very simple and usually water is used, water flux through the membrane can be measured as a function of applied pressure at a certain minimum pressure the largest pores becomes permeable with the smallest pores still remain impermeable and when we increase the pressure then the smallest water will also flow through the smallest pores. So, this minimum pressure depends on the type of membrane material that is contact angle type of permeant also surface tension and also the pore size.

So, according to the Laplace equation the increase in water flux is proportional to the increase in applied process. So, this is very simple method you have a membrane you just put it in a dead end filtration module and filled it with water and then pass pressurized it once you when you are pressurizing it, then we are getting permeate that permeate you measure and you get flux from that.

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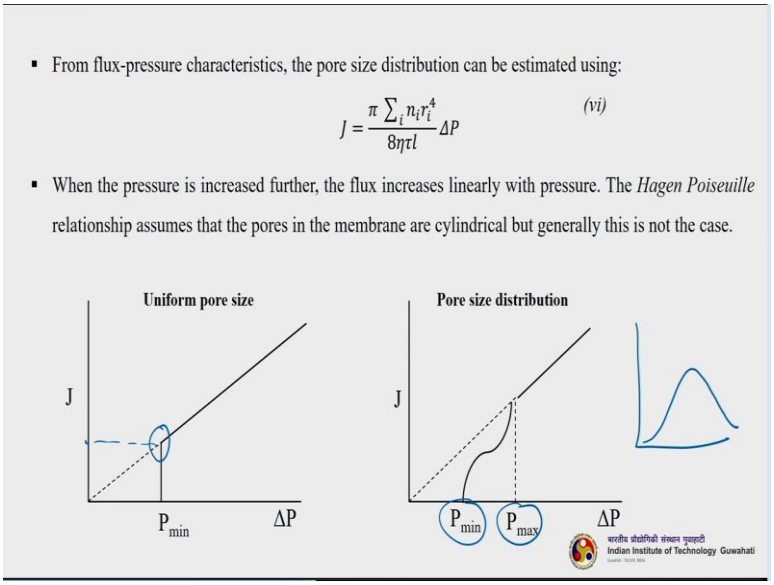


So, from flux pressure characteristics the pore size distribution can be estimated using this particular equation, So, when pressure is increased further, the flux increases linearly with pressure and the Hagen Poiseuille relationship assumes that pores in the membrane or cylindrical, but generally this is not the case, you remember in one class we have discussed that Hagen Poiseuille equation assume that pores are cylindrical of nature and there is another equation which is called Kozeny Carman equation.

There it is assumed that the pores are the interfaces between the closely packed spheres. So, let us look at this 2 fingers here. So, the first figure is flux versus delta p which is giving me at a P minimum this is a P minimum you can see and the corresponding minimum flux here. So, this particular straight line is getting obtained. So, this is for the uniform pore size if a membrane is having uniform pores if a membrane is having a pore size distribution then you will get the flux and versus delta p grab something like this.

So here this is the P minimum and this is the maximum pressure that we are getting. So it can be anything if you have a pore size distribution can be anything like something like this, and usually the uniform pores there should not be distribution. So, usually it is a (())(23:04) type of membrane.

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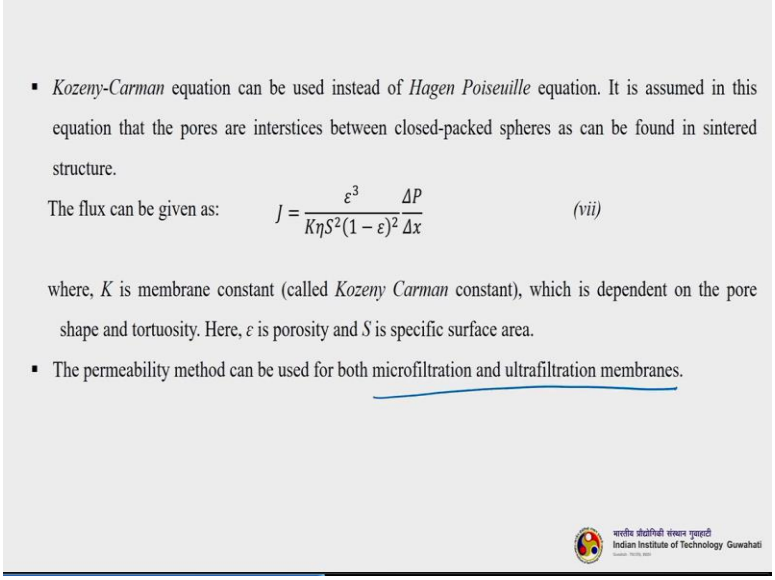


So, as I was just mentioning about the Kozeny Carman equation, so, this is the Kozeny Carman equation here K is the membrane constant also called Kozeny Carmen constant. So, which is dependent on the pore shape and tortuosity and here epsilon is the porosity and S is this specific surface area. Now, the permeability method can be used for both microfiltration and ultrafiltration membranes. So, this is also very important to note that, so, both MF and UF membranes can be characterized using this method.

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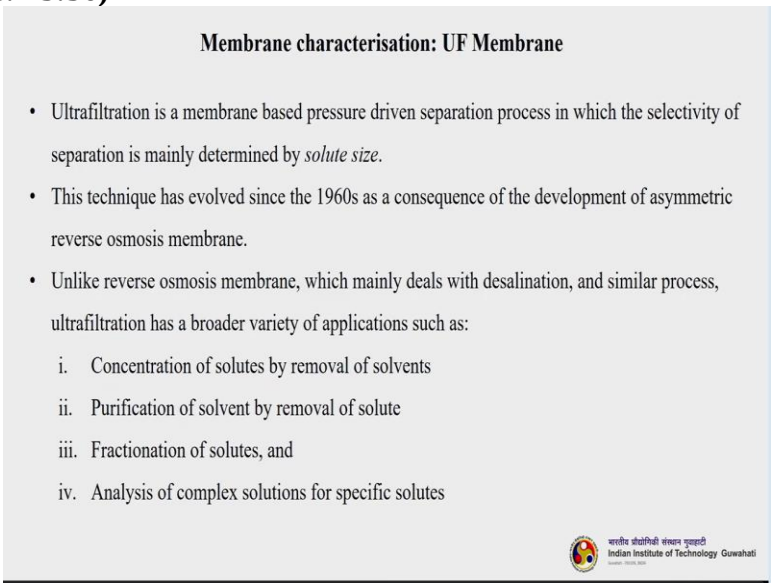


Then, let us understand that and try to learn the different characterization techniques for the ultrafiltration membrane. So, ultrafiltration is a membrane based pressure driven separation process in which the selectivity of separation is mainly determined by the solute size, size

exclusion, and separation basically, this technique has evolved since 1960s as the consequences of the development of asymmetric reverse osmosis membrane. So, our membrane developed by (())(24:05) as you have discussed that many times. So, unlike reverse osmosis membrane, which mainly deals with the desalination and similar processes, ultrafiltration has a broader variety of applications.

So, I have listed only the 4 different broader applications. So, the first is concentration of solutes by removal of solvents, 2nd is purification of solvent by removal of solute, 3rd is fractionation of solutes and 4th analysis of complex solutions for specific solutes.

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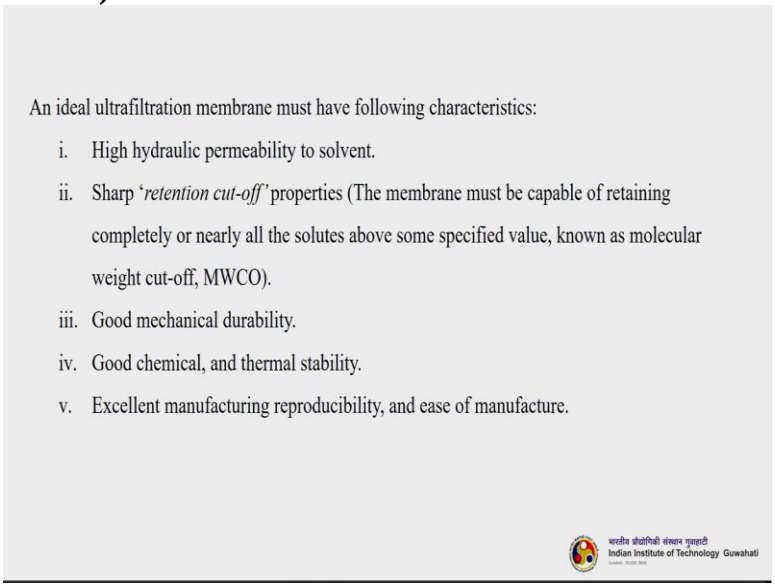


Then an ideal ultrafiltration membrane must have the following characteristics. So, what are those, so, this would have a high hydraulic permeability to solvent and that means the most of the solvents would pass through sharp retention cut off so, the membrane must be capable of retaining completely or nearly all solutes above some specified value which is known as the molecular weight cut off. Subsequently, we will discuss this molecular weight cut off at the end of our lecture today.

Then members should have a good mechanical durability, it should have good chemical and thermal stability and it should have excellent manufacturing the reproducibility and ease of manufacture, which is more important for the membrane manufacturers.

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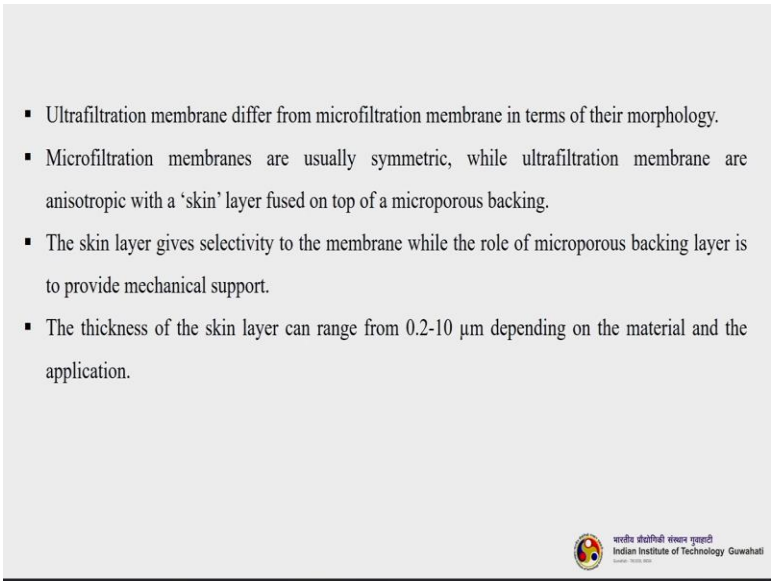


Ultrafiltration membrane differs from microfiltration membrane in the terms of their morphology, because Ultrafiltration membranes are usually asymmetric membranes. So, we have a skin layer we have discussed this many times. So, there should be there is a skin layer, it is a symmetric nature. So, this is skin layer which is fused on the top of the micro porous backing, that is micro porous support actually, the skin layer gives selectivity to the membrane.

And the role of the micro porous backing layer is providing the mechanical support the thickness of the skin layer can range from point 2 to 10 micron. So, depending on the material and application what is our intended application? So, but it is very clear, I have told you earlier many times also that, whether it is a composite membrane, whether it is asymmetric membrane for Ultrafiltration applications, the skin layer the top layer should be as thin as possible, because if it is more thick, then it will provide it additional membrane resistance to the flow. So, which is actually not good?

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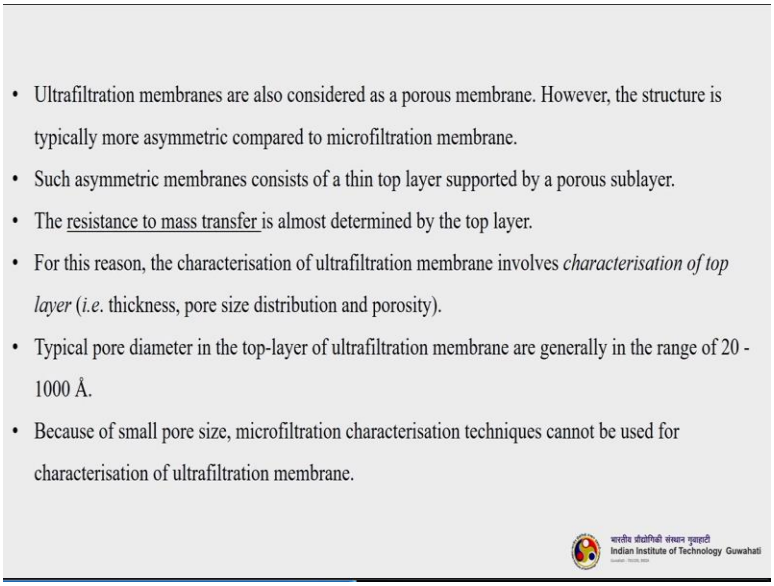


Ultrafiltration membranes are also considered as porous membrane however, the structure is typically asymmetric. So, such asymmetric membranes consist of a thin top layer, the resistance to mass transfer is almost determined by the top layer. So, for this reason the characterisation of ultrafiltration membrane involves the characterization of the top layer so, what they are going to this is what to why we are discussing this now, you can understand that we are discussing the ultrafiltration characterization is asymmetric membrane.

And what I am going to characterize is that top layer, and the thin or top layer the skin layer, that is what I am going to characterize because that is actually doing the separation. So, the thickness pore size distribution and porosity of this skin layer we are going to characterize, so typical pore diameter will be usually in the range of 20 to 1000 armstrung. Since the pore size is small microfiltration characterization techniques cannot be used for characterisation of ultrafiltration membrane, though here we know that we can use a permeability method for ultrafiltration membrane also.

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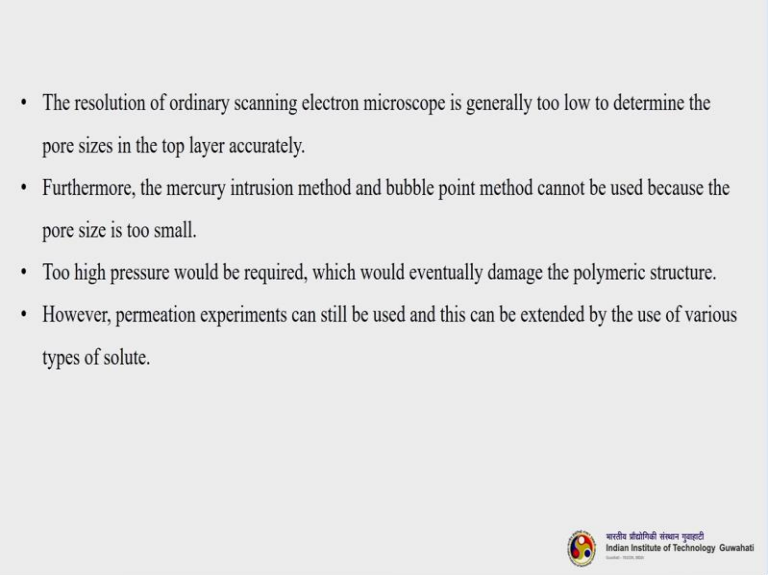


The resolution of ordinary scanning electron microscope is generally too low to determine the pore sizes, for the top layer in the ultrafiltration region. Basically, furthermore the mercury intrusion method and bubble point method cannot be used, because the pore size is too small. And so you need to apply high very high pressure, the moment you go beyond a proper certain pressure, what will happen that remembered and really damaged then too high pressure would be required, which would eventually damage the polymeric structure. However, permeation experiments can still be used and this can be extended by use of various types of solute.

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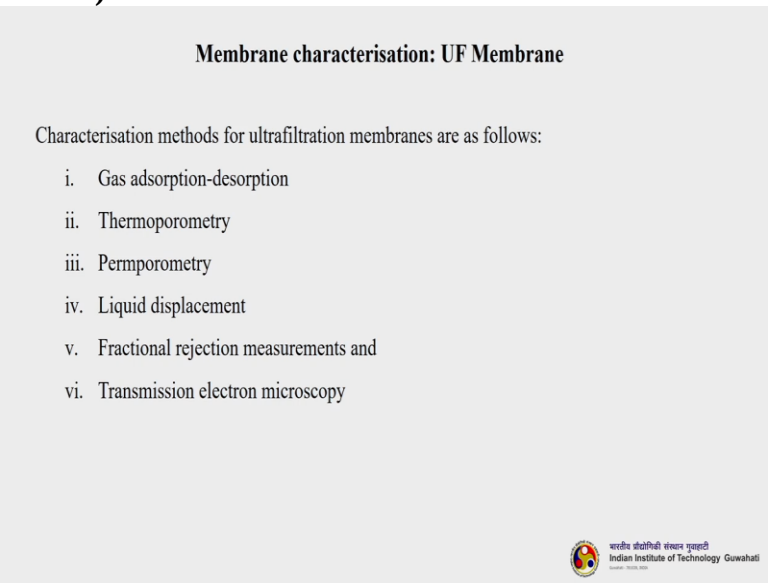


Now let us understand and discuss what, are the different types of techniques that we are going to discuss today. So first one is gas absorption desorption, then thermoporometry then

permporometry, the liquid displacement then fractional rejection measurements and transmission electron microscopy. So these are the techniques which are being used. We have already discussed them in one of our earlier class and we are going to discuss the other methods today.

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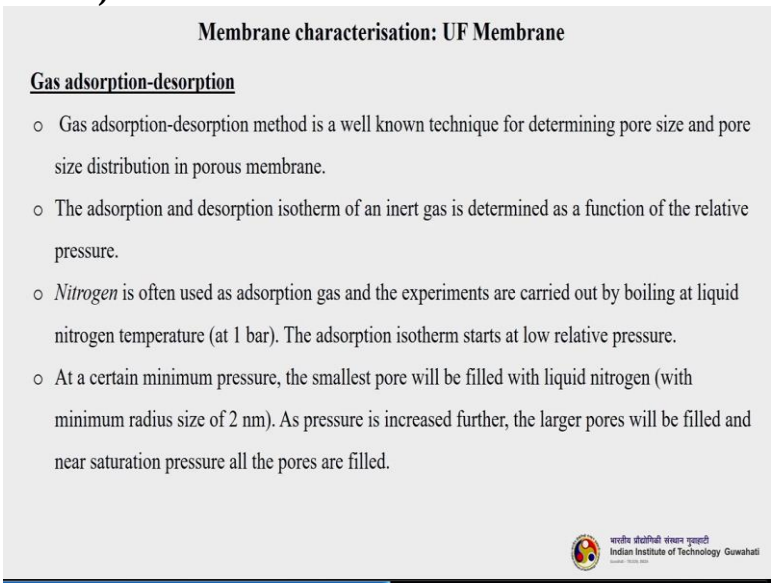


So, let us discuss the gas adsorption desorption technique and method. So, this is a well known technique for determining the pore size and pore size distribution in porous membrane the adsorption and desorption isotherm of an inert gas is determined as a function of the relative presser usually nitrogen is used as a adsorption gas and the experiments are carried out by boiling at liquid nitrogen at almost 1 bar the adsorption isotherm starts at relatively low pressure.

At certain minimum pressure the smallest pore will be filled with liquid nitrogen almost the size is 2 nanometer as pressure is increased further, the larger pores will be filled and near saturation pressure, all the pores will be filled. So, this is the method is all about? So, we are adsorbing the liquid nitrogen over the surface of the membrane and then inside the pores also that we are deserving. This is what it is been done for this particular method.

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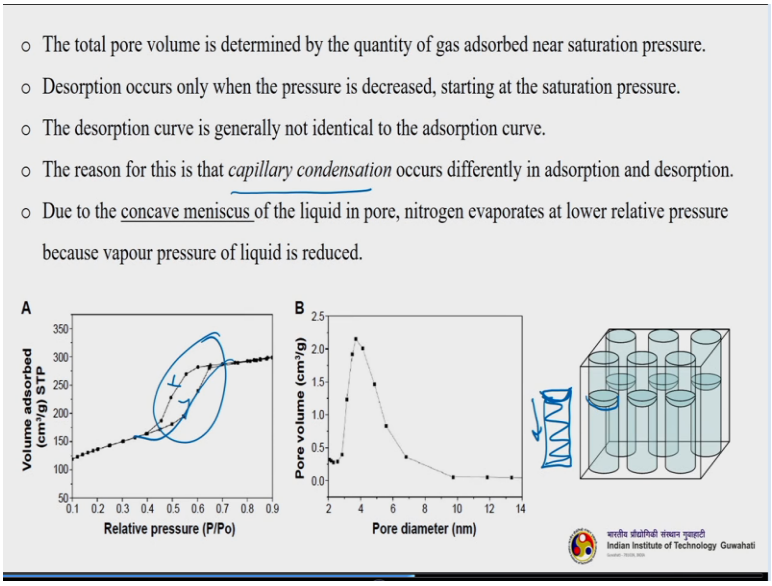


**T**otal pore volume is determined by the quantity of the gas absorbed near saturation pressure. So, this is another method to find out the pore volume apart from your mercury intuition in microfiltration membrane. So, desorption occurs only when the pressure is decreased starting at saturation pressure. So, the desorption curve is generally not identical to the adsorption curve that is why and this is the reason for this is that capillary condensation occurs differently in adsorption and desorption and due to this there is something called hysteresis.

So, as you can see this is hysteresis ideally this called adsorption this is actually adsorption and this is desorption ideally a desorption should have follow something like this, but it is not following due to the capillary condensation that is occurring differently for adsorption and desorption. And this is called hysteresis actually. So, capillary condensation why it is different for desorption.

The reason is that the concave meniscus of the liquid in the pore this is you can see when it is adsorbing pores let us say this is the pore when it is getting inside the pores of pore is getting filled. So, it will be filled something like this. So, this is happening this is pore filling during adsorption, but when I am decreasing the pressure and going put deception, so, whatever is inside the pores it should actually come out.

So, that is what desorption. So, during that process initially it will form meniscus something like this you can see this is. So, this is a concave meniscus the liquid in the pore. So, now that is due to this the evaporation of nitrogen happens at a relative low air pressure because the vapor pressure of liquid is actually reduced inside the pores.

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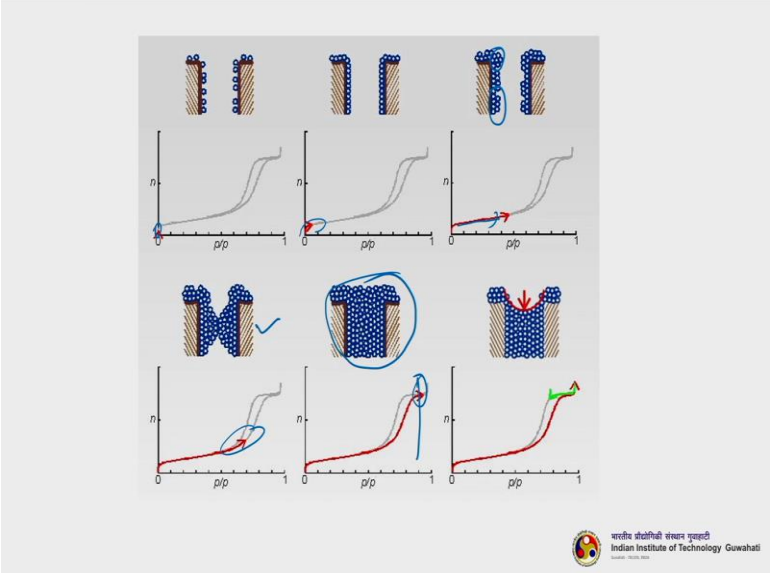


Let us try to understand the process little in detail by seeing this particular slide you can see whatever it is seeing in the first plot here, the line corresponding it is showing actually the adsorption and desorption plot how ideally it should happen. So, we are starting adsorption. So, you can see is a few molecules that are getting adsorption on the surface of the pore as well as inside the pore as well as on the top of the membrane also.

So, our adsorption starts here then and we are preceding the adsorption. So, most of it is they have formed a particular monolayer adsorption system here, then we are further in proceeding our adsorption you can see by layer deposition starts, here you can see tri layer deposition starts, now we have further increasing and we can see how the pores is getting filled here for that increasing so this is what we actually reached saturation. As we have this comport is completely filled by the liquid nitrogen.

Now what? Now we have to decrease the pressure to start desorption. So decreasing the pressure start once we reach saturation, so each situation here, now we are decreasing it. So start decreasing the moment to decrease what will happened due to the relatively low vapor pressure

inside that there is a meniscus that is formed here you can see and that is actually preventing the escape of the liquid nitrogen is a much slower rate than that of the adsorption that is why the hysteresis curve is coming into picture. I hope it is now clear to you.

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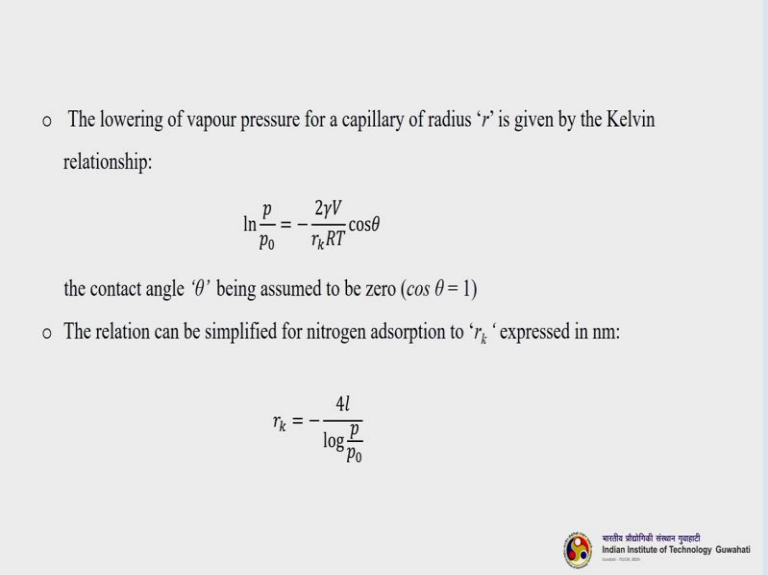


The lowering of vapor pressure for a capillary of radius r is given by Kelvin equation you can use this particular equation so P / P 0 = - 2 gamma V / r k RT cos theta. So here theta is the angle that assumed to be 0 so that cos theta becomes 1and this relationship can be simplified if you are taking a nitrogen adsorption so r k can be expressed in minus 4 l log p / p 0.

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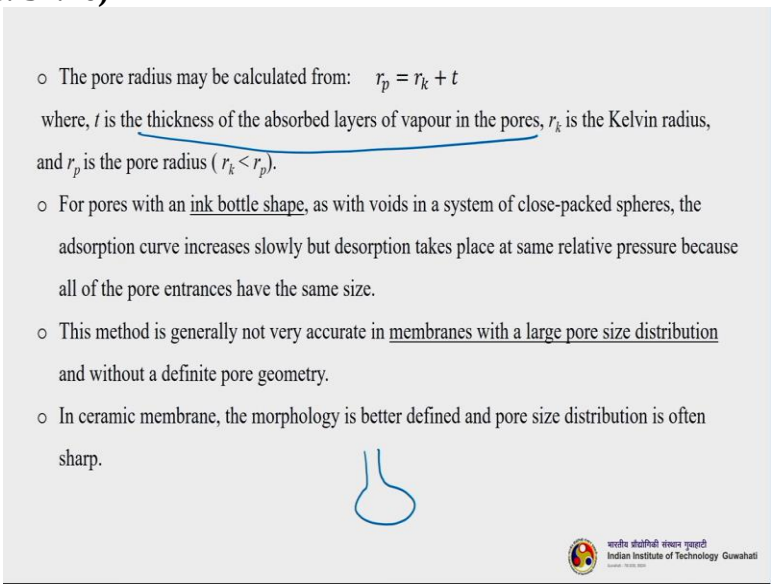
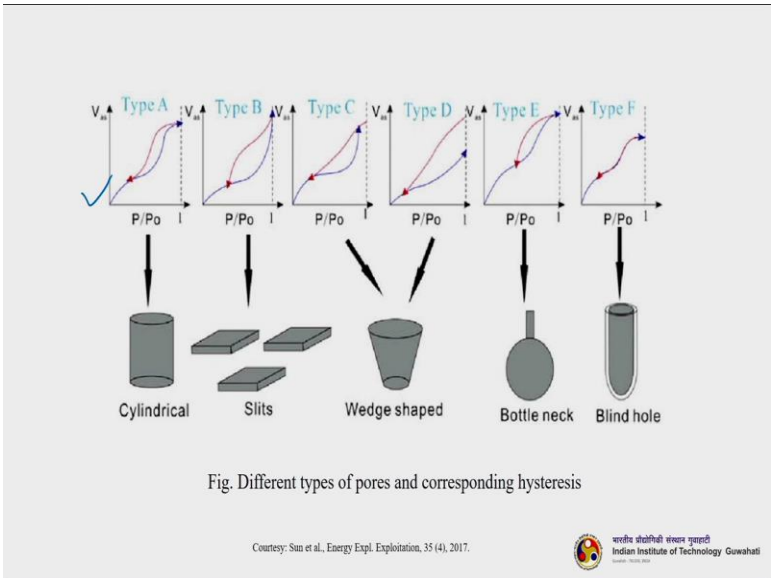


The pore radius maybe calculated from this equation r p = r k + t. Now what is t? t is the thickness of the adsorbed layers of vapour in the pores. So that is actually t and r k is the Kelvin radius. So r p, is the pore radius and obviously it is true that r k will be less than r p. So pores with the ink bottle shape ink bottles shape something like this with voids in a system of close packed spheres, that adsorption curve increases slowly by desorption takes place at same relative pressure, because all of the pore entrances have the same size.

Now, this method is generally not very accurate in membranes with large pore size distribution and without definite pore geometry. In ceramic membrane the morphology is better defined. So, we can characterize ceramic, ultrafiltration membrane easily using this particular technique. **(Refer Slide Time: 33:38)**




This slide will make you understand the different types of pores and their corresponding hysteresis please understand that hysteresis curves also are up different nature it is not that everything is following whatever where I show you earlier, it is never happens like that. So, for the cylindrical pores that was actually for the cylindrical pores this one, so for the cylindrical pores here, hysteresis curves look something like this (())(34:02) then we can have a broader hysteresis plot and if we have wide separate pore.

So, we can have these 2 different types of hysteresis curve type C and type D if the pores are a bottleneck then E type of hysteresis curve is being obtained and if we have a blind hole then you can see the adsorption and desorption actually falling on the same particular line.

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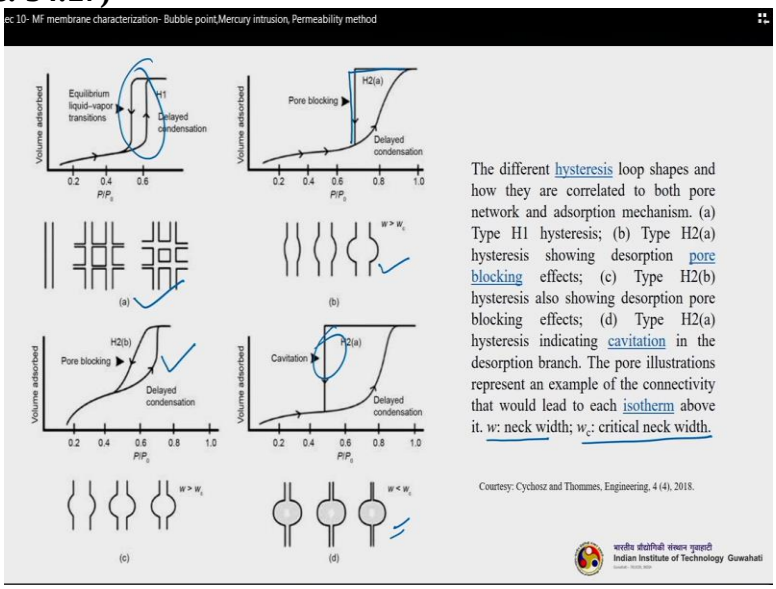


So, here again little extension of the earlier slide actually, So, if you see this a is type 1 H1 type of hysteresis here the pores are very uniform here. So, you can have a delayed condensation, you have hysteresis looks something like this. Then in a if we have pores up something like this have different up sizes. So, you have pore neck width, the liquid, is more than neck width of the critical neck width w actually w.

So, you can see here w is the neck width w c is the critical negative neck width if w is greater than w c in this particular this one, so, poor blocking will take place. So, we are poor blocking takes place because of the small size of the pore when poor blocking happens, and then you get something like this. So, you have desorption curve plots like this. So you get some hysteresis here. So here, again when w is greater than w c for a different type of pore geometry, So you will have to see something like this and

When w becomes w c, so, this is basically the 4th one this particular one here actually hysteresis indicating cavitation and in the desorption branch. So here cavitation is happening during the desorption and we get a response something like this. So these are actually isotherms.

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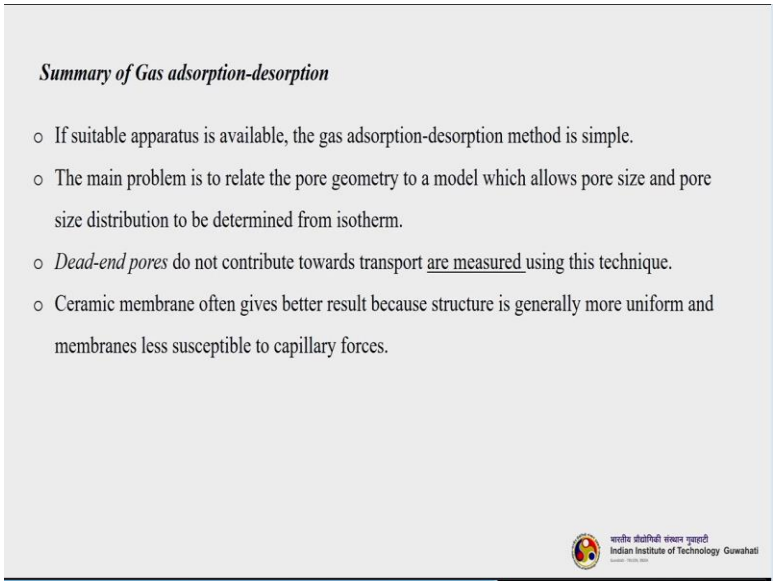


So in summary, we can understand that if suitable apparatus is available, then gas adsorption and desorption method is very simple. The main problem is to relate the pore geometry to the model which allows pore size and pore size distribution to be determined from the isotherm. It is nothing complicated, actually, it is easy process, but it should have an apparatus fine and dead end pores do not contribute, but they are getting measured.

So, that is another actually disadvantage of this particular method. Because what we are doing actually we are adsorbing the liquid nitrogen from the top of the membrane and the pores are open to the top side. And what is that is closed from the bottom side that we are also characterizing because the liquid nitrogen also getting deposited on the surface inside the dead end pores. So ceramic membrane often gives better result because their structure is very uniform, and they are less susceptible to capillary forces.

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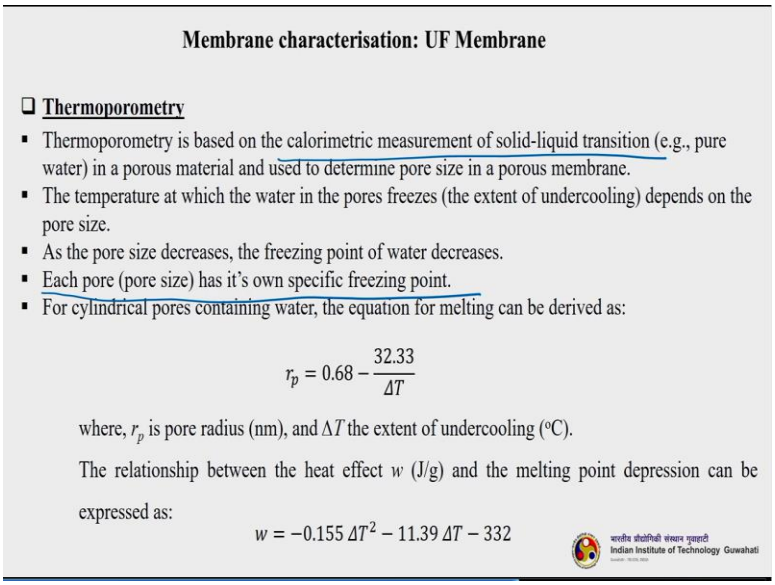


The next method is thermoporometry. So this is based on calorimetric measurement of solid or the liquid transition. So this is a very different method will try to understand what is simple mechanism. Here we will study the transition of pure water. So transition means from its solid to liquid or liquid to solid, so phase transition we are studying and that will tell us the pore size for a particular membrane usually for ultrafiltration membrane.

So the temperature at which the water in the pore size decreases so that means the extent of under cooling that is what we are going to measure that is also dependent on the pore size is the pore size decreases the freezing point of the water also decreases. So, a large pore it will freeze faster at the small pore it will freeze a little later. So, each pore size has its own specific freezing point. So, this is the important take away message. So, each pore size or pourer pore size has its own specific freezing point.

So, for a cylindrical pore containing water the equation can be utilizes this r p = 0.68 - 32 point 33 divided by delta T. So, here r p is the pore radius and delta T is the extent of under cooling. The relationship between heat effect that is the w and the melting point depression can be expressed is W = - 0.155 delta t square - 11.39 delta 23 - 32. So, these equations can be utilized to calculate our pore radius.

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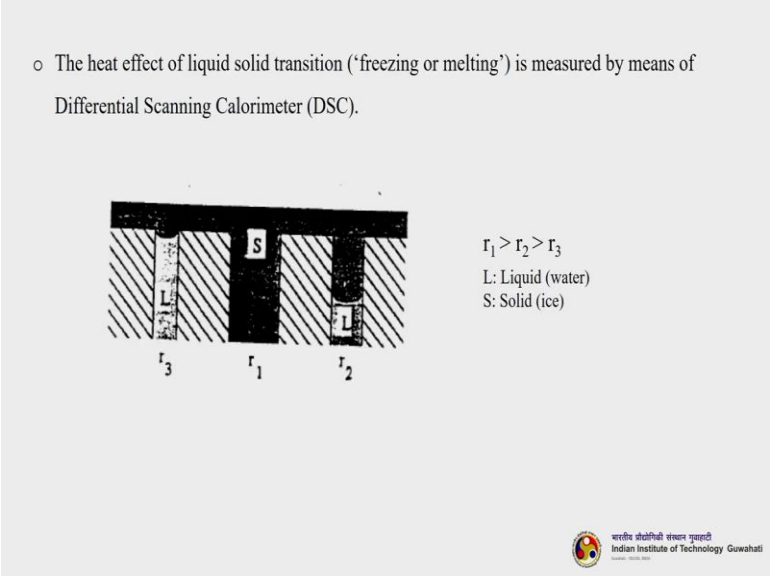


So, I could not find a proper figure this figure is taken from older actually. So, you can let us try to understand actually so the effect of liquid solid transition that is freezing or melting is measured by means of a differential scanning calorimeter. So, you should have a DSC apparatus, if you have a DSC apparatus, you can easily do that otherwise it is you cannot do it. So, that is another disadvantage is for this particular technique. So, you can see there are 3 different types of pores I have seen, one is r 1 one is r 2 one is r 3. So, each will have different radius. So, r 1 is a bigger pore size and so, and which is greater than r 2 which is greater r 3, so r 3 is the smallest one so.

You can see when the process is happening initially as I told the largest pore will be will freeze faster. So, you can see that the largest pore the water is freeze and it has become solid, solid means it is actually ice. Then you can see in second pore which pore sizes little smaller than the r 1 here it is half liquid and half solid and in r 3 at the same time. Since it is the smallest pore it is completely liquid. So, this is how it happens actually.

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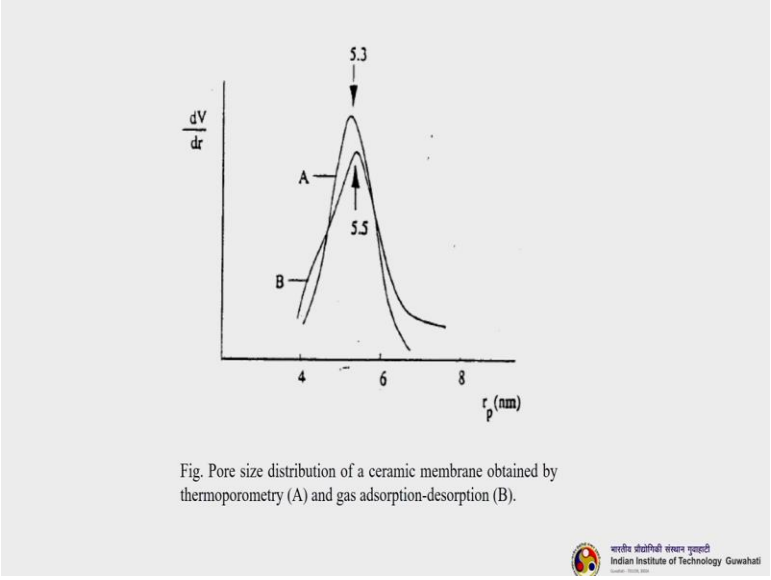


Fig. Pore size distribution of a ceramic membrane obtained by thermoporometry (A) and gas adsorption-desorption (B).

So, this is just an example of competition of 2 methods. So using thermoporometry gas absorption and desorption. Now, please understand that both these methods so they are actually measuring and taking into account the dead end pores. So that is why their results are very close. You can see 5.3 and 5.5. They are very, very close to each other.

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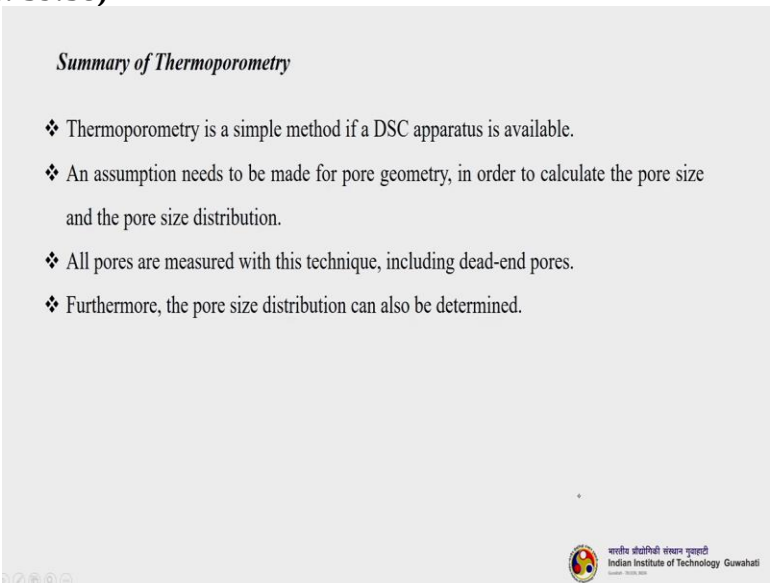


So the summary of thermoporometry we can say that it is a good method very, very reliable, it is fine if we have a DSC apparatus. Now, assumption needs to be made for pore geometry in order to calculate the pore size and pore sizes distribution. All pores are measured including the dead end pore probably that is one of the disadvantages and pore size distribution also can be measure.

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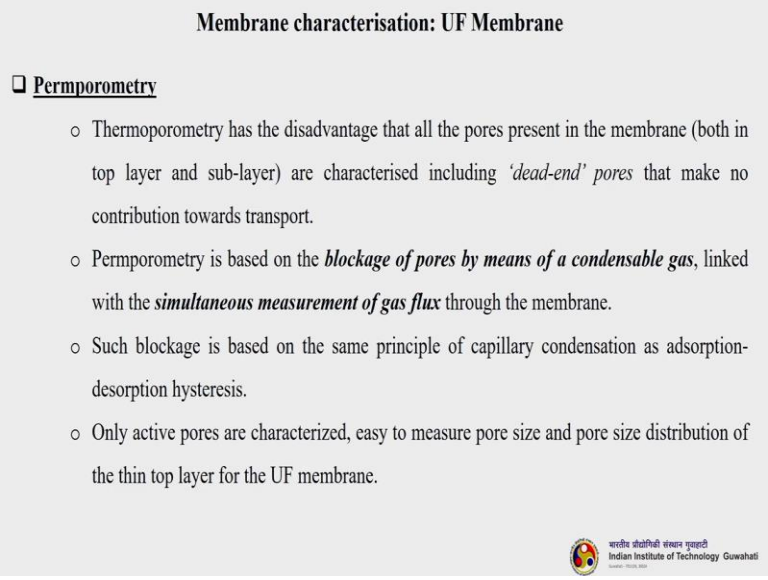


So the next method is permporometry. So, thermoporometry has a thermoporometry has a disadvantage that all the pores present in the membrane are getting characterized. So including the dead end pores. So which actually is not good understanding of the actual separation that is what is happening fermium and permporometry based on the blockage of pores by means of a condensable guess.

And linked with simultaneous measurement of gas flux we will see in the next slide how it happens. So we are blocking the pore using a condensable gas now such blockage is based on the same principle of capillary condensation as absorption and desorption hysteresis so only active pores are characterized easy to measure pore size and post size distribution of the thin top layer of the ultrafiltration.

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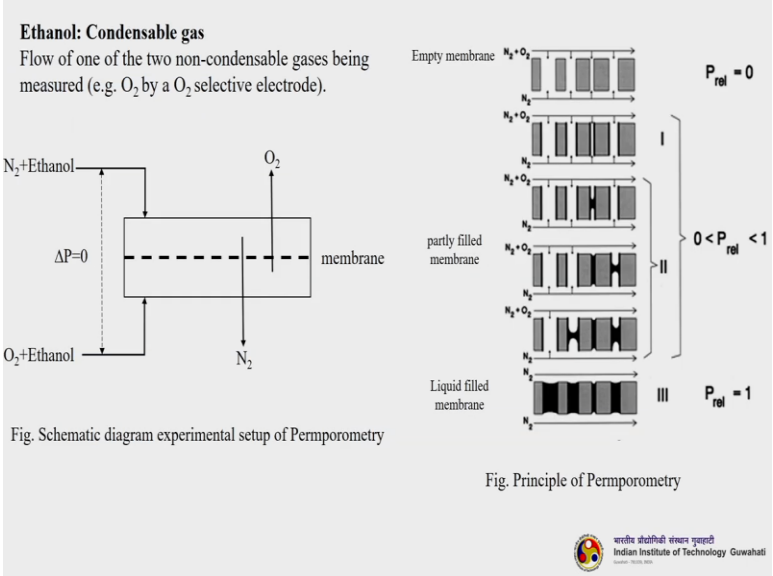


Fig. Schematic diagram experimental setup of Permporometry

Fig. Principle of Permporometry

Let us understand how it happens. So, this is the membrane module which is happening this is your membrane. So here we are using ethanol as condensable gas it is not mandated to use ethanol you can use any other condensable will gas, but you need to understand the properties of the properties of that particular gas with respect to the properties of the membrane. So, here in this example, ethanol is being used as the condensable gas.

And then nitrogen and oxygen being used as the 2 non condensable gases and out of these 2 non condensable gases we can measure the flux of anyone gas so let us say if I am measuring the flux of oxygen. So oxygen is flowing from the backside of the this one of the pore and it is getting passed like this from the top side, then we can use the oxygen flow using the oxygen selectivity electrode.

Now, let us understand how the process actually happens. Now, please look at this particular image here this is the principle. So, in a relative pressure that P / P 0 the relative pressure equals to 1 unity this means all the pores are filled with the condensable gas that means, one on the condensable gases filled becomes liquid and that is why it is written actually liquid film membrane that you can see everything is filled then what we are what is the next step we are decreasing the pressure.

So, your relative pressure is between 0 to 1 somewhere between that slowly decreasing you can see the largest pores will be emptied fast you can see the largest pores it has emptied fast then smallest pores are getting emptied at a certain particular decreasing pressure. So, then when the relative pressure equals to 0, then what will happen and there is no liquid everything is gone out and we have an empty membrane completely empty membrane. So what we understand is that by decreasing the pressure slowly. We can find out the pore size distribution.

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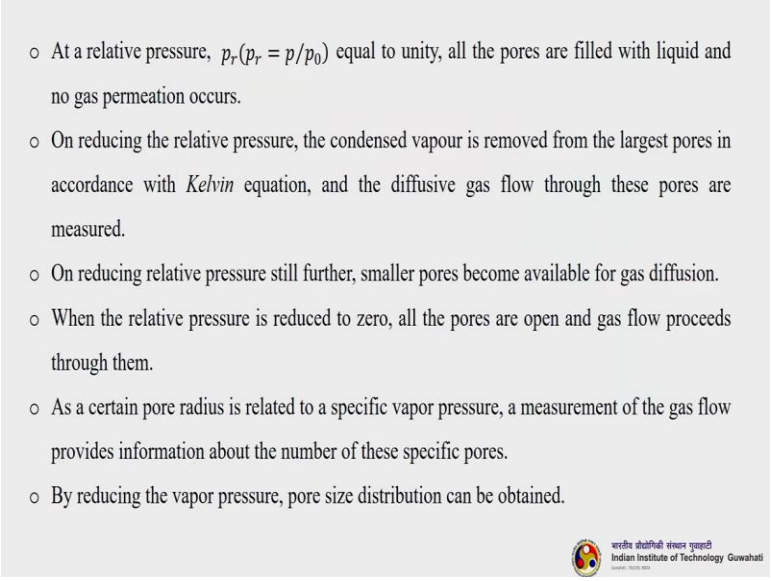


So, this is what actually have described so on reducing the relative pressure the condensed vapour is removed from the largest pore in accordance with the kelvin equation and the diffusive of gas flow through these pores are measure. So, on reducing relative pressure further small pores become available for gas diffusion. When the relative pressure is reduced to 0, all the pores are open and gas flow proceeds through them.

Now, as a certain pore radius is related to a specific vapour pressure. This is what is the principle as a certain pore radius is related to a specific vapour pressure the measurement of the gas flow provides information about this number of the specific pores. So, by reducing the vapour pressure pore size distribution can be obtained.

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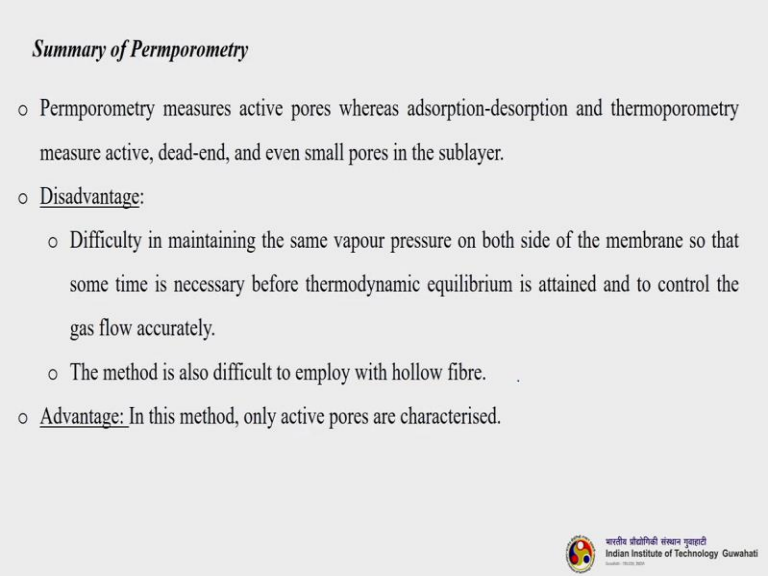


So, in summary, we can say that it is measures active pores only that is the beauty of this particular technique. And whereas, the absorption desorption thermoporometry measuring dead end pores so, however the disadvantage is difficulty in maintaining the same way professor on both side of the membrane. So, there is a trick basically here and you need to maintain the vapour pressure on both side of the membrane.

Because from one side we are flowing 1 non condensable gas either nitrogen and from other side another one oxygen so, the method is difficult to employ with hollow fibre. So, hollow fibre membrane characterization is very difficult, but advantages only active pores are being characterized.

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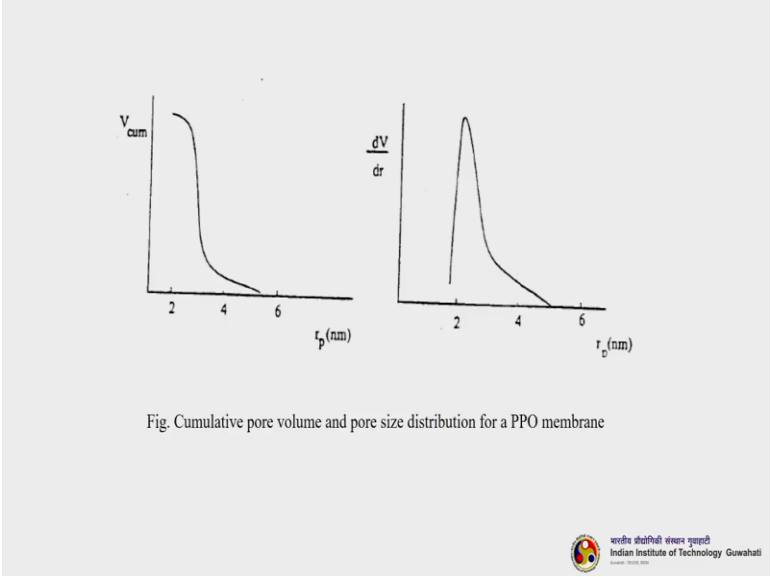


Fig. Cumulative pore volume and pore size distribution for a PPO membrane



So, you can see how the cumulative pore volume figure looks from this particular experiment and how you get a particular pore size distribution using this particular method for a PPO membrane.

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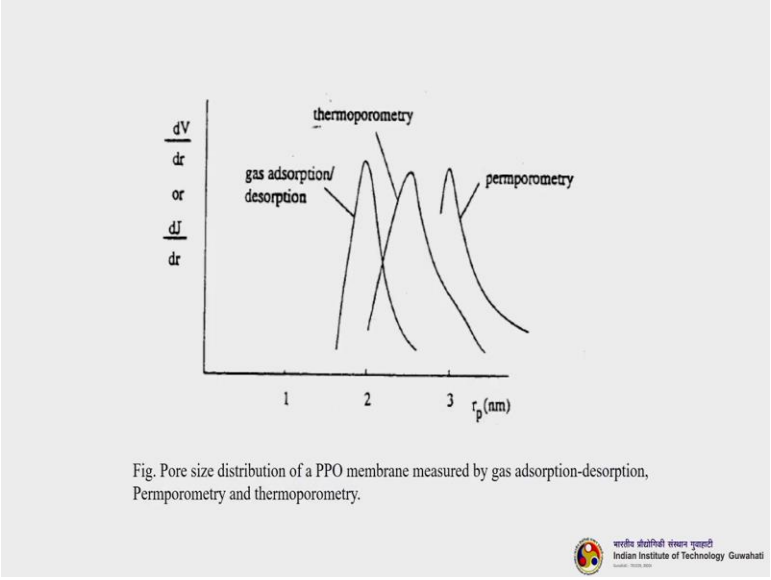


Fig. Pore size distribution of a PPO membrane measured by gas adsorption-desorption, Permporometry and thermoporometry.



Now, in a summary we can understand from this particular figure the relationship between or the competition between 3 different techniques that we have learned gas absorption desorption thermoporometry and permporometry. You can see that gas absorption, desorption and thermoporometry they are that data, whatever we are getting is very close is to each other and they both them are measuring the dead end pores. So what since permporometry it is giving it a higher side data, the reason that it is characterizing only the active force.

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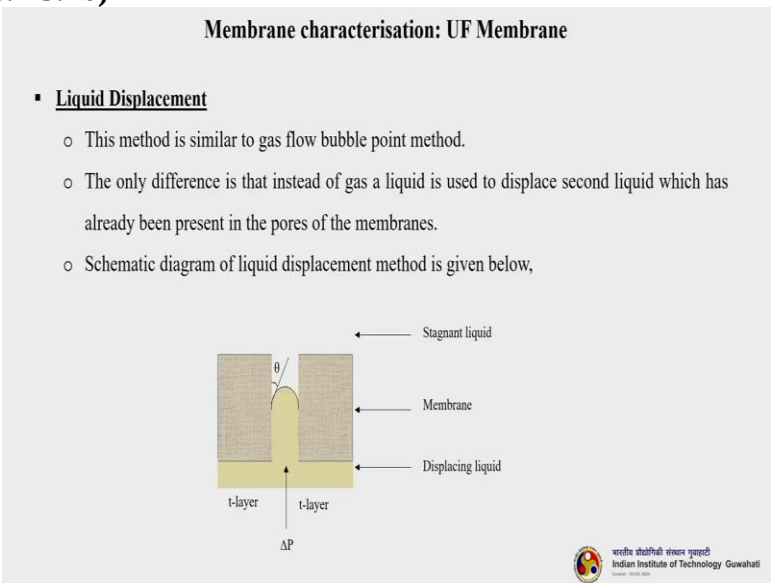


So on the next method is liquid displacement to characterize the ultrafiltration method membrane. So this method is similar to gas flow bubble method. So here, the only difference between the gas flows bubble point with the gas flow basically, is that instead of a gas we use a liquid. So, what we are doing a liquid is displacing another liquid which is already filled in the pores of the membrane.

So, you can understand from this particular image, how it happens. So, this is actually one pore of the membrane, which is filled with a liquid, this is liquid one of the liquid. And it is already filled this particular liquid and this is another liquid. Which is being pushed from the bottom side of the membrane? And that particular liquid is displacing the liquid whatever is already there. So here, here there is a stagnant liquid that is present and this particular liquid is pushing and displacing the liquid, which is already filled in the inside the pores. So, this is actually simple method

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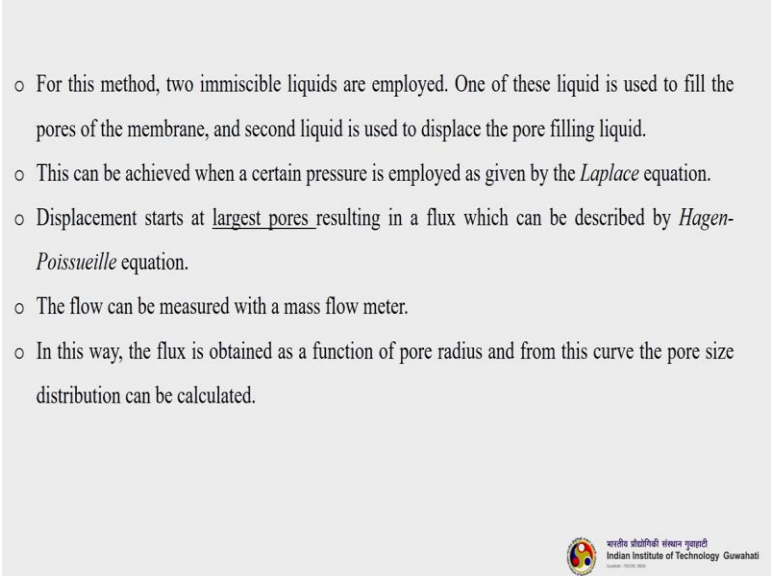


And just like bubble point permeation and however the condition is that 2 immiscible liquids will be employed completely immiscible liquids. So, one of these liquid will be used to fill the pores of the membranes which is present on the top side of the membrane also and the second liquid is used to displace which is from the bottom side of the membrane. Now, this can be achieved when a certain pressure is employed by given by Laplace equation.

And displacement starts at the largest pore this is true for our usual gas bubble point method also. So, again poissueille question can be used to calculate the flux and the pore size. The flow can be measured with a mass flow meter in this way, the flux is obtained as a function of pore radius and from this curve the pore size distribution can be calculated.

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- The method can be carried out in two ways:
  - i. the pressure is varied stepwise, and the liquid flow is measured, or
  - ii. a fixed flow is varied stepwise (by an HPLC pump), and the pressure is maintained.
- The former method is more easily performed with a flat membrane but with hollow fibre membrane system the pressure build up may result in irreproducible values and in such case the second method is preferred.

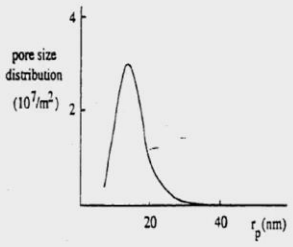


Fig. Pore size distribution of a Celgard membrane measured by liquid displacement.



Now, this can this method can be carried out in 2 ways. The first one is that pressure is varied stepwise and the liquid flow is measure. So, we can measure that we can varied the pressure in a stepwise manner and we then we measure the flow in the second method, a fixed flow is varied stepwise so the flow is married actually stepwise using basically HPLC pump and the pressure is maintained constant. So, the former method the first one is more easily performed with a flat membrane.

But with hollow fibre membrane system pressure build up may result in irreproducible values. And in such case the second method is preferred. So basically flat sheet membrane we can go for the first one, which is easy to do, and for the second, the second method will usually being used to characterize the hollow fibre membrane. So, this is an example of pore size distribution from product using this particular liquid displacement method for a celgard membrane celgard is a commercial membrane.

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- In Laplace equation, γ is surface tension between two liquids and by proper selection a low value of γ can be obtained.
- The Table below summarises the interfacial tension of various liquid/air and liquid/liquid interfaces.

| Phase 1 | Phase 2 | Surface tension, γ (mN/m) |
|---|---|---|
| Water | Air | 72.0 |
| Methanol | Air | 72.6 |
| Ethanol | Air | 21.8 |
| Hexane | Air | 18.4 |
| Iso-pentane | Air | 13.7 |
| Water | Isobutanol | 1.85 |

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So, in Laplace equation, the surface tension between the 2 liquids is very important and the proper selection of a low value can be obtained. So, this actually gives us a surface and value from different types of liquids. So, you can go water and air we can go for methanol air, we can have ethanol air we can have hexane air we have iso pentane air and we have water isobutanol for the liquid displacement method both are liquids and you can see the surface tension is very low the lowest 1.85.

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***Summary of Liquid displacement measurements***

- Liquid displacement is a membrane characterisation method used to determine pore size distribution in microporous and macroporous material.
- Advantage: Only active pores are characterised.
- Disadvantage:
  - The occurrence of swelling due to the stagnant liquid that changes the pore sizes.
  - The set-up is quite complicated, and the pressure build-up may occur which interferes with the measurements.

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So, in summary, we can say that liquid displacement is a membrane characterisation method used to determine pore size distribution in both micro porous and micro porous material. So, advantage is the that only active pores are characterized however, the disadvantage is that the

occurrence of swelling due to the stagnant liquid that changes the pore size. Now, if you are using the liquid 1.

Which is actually used to pre fill the pores of the membrane and we add them and liquid is actually in contact with the membrane for certain time or little hard time, and if the liquid is not chosen properly that it may swell the membranes and when the membrane is swelling, its pores are also getting swell. So, you may get an erroneous value and the setup is a little complicated and the pressure build up may occur which interprets with the measurements. So this is the disadvantage. Nevertheless, it is an easy method to do; it measures both micro porous, macro porous.

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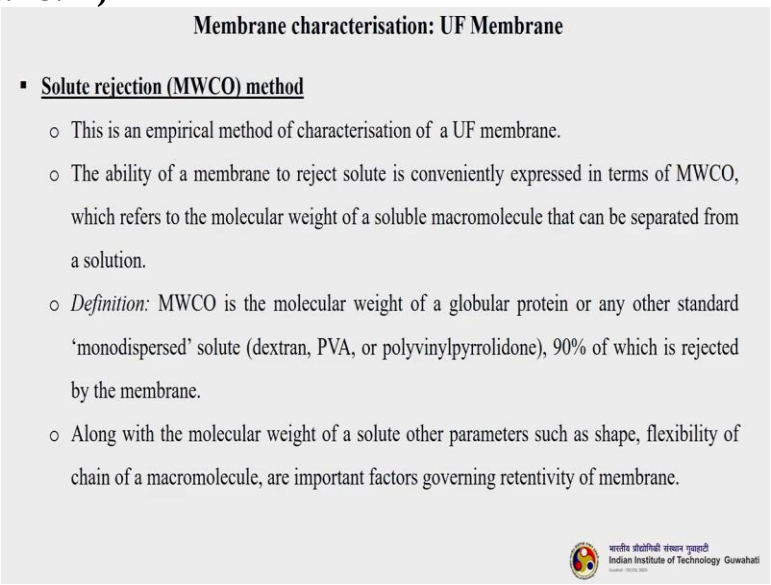


So, the next one, it is the solution rejection method, which is also called molecular weight cut off membrane method. So, students MWCO is called molecular weight cut off and when you buy a commercial membrane and you can see on the packing itself, it will be written either MWCO is 100 kilo Dalton 150 Dalton 1000 kilo Dalton so something like that or it will be returned a membrane cut off.

So, anyway are simple cut off so many companies write in different ways. So, what is it means basically the ability to reject solute conveniently is expressed by this. So, molecular weight cut off so, weight molecular weight solute is getting rejected and how much is getting rejected. So,

we have seen the nominal rating we have seen the absolute rating based upon that the cut off will be determine.

So, by definition, definition is given by actually (())(50:37), his group so ease really. So, molecular weight cut off is the molecular weight of a globular protein or any other standard mono dispersed solute like dextran and PVA then polyvinylpyrrolidone 90% of which is rejected by the membrane. So this is how the difference of molecular weight cut off. So, that means 90% of the particular solute having a particular molecular weight must be rejected by the membrane.

If that is the case then we can say that is the cut off of that molecular weight of the protein will be called as the molecular weight cut off of that particular membrane. So, along with the molecular weight of a solid other parameters such as say flexibility of chain of a macro molecule are important factors which also determine receptivity of the membrane.

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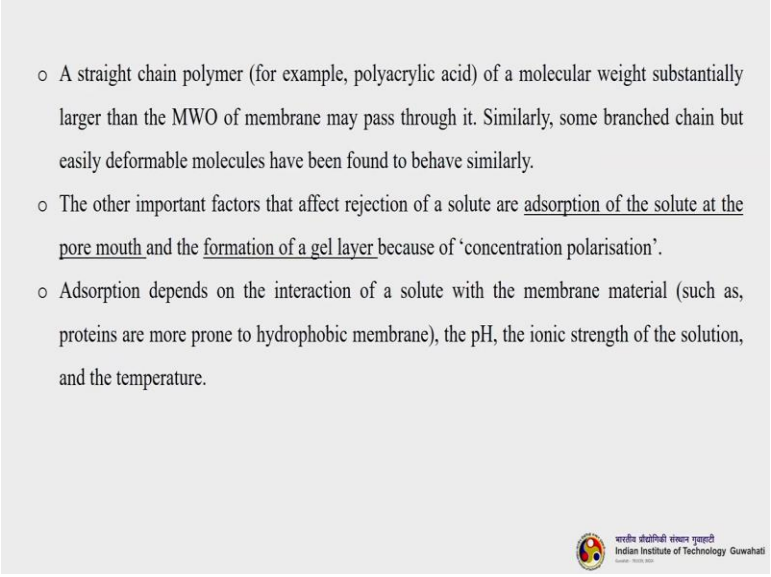


So, a straight chain polymer for example, let us say polyacrylic acid of a molecular weight substantially larger than the molecular weight of the membrane may pass through it. Similarly, some branched chain and proteins, but easily deformable molecules have been found to behave similarly. So, these are not good actually. So, other important factors that affect rejection of a solute are adsorption of the solute at the pore mouth.

So, you know (())(51:56) is very instantaneous process and we should also take care. So, that adds I deserve of the solutes proteins whatever it is we are using for the measurement must not get added on the surface of the membrane, you do whatever there will be some adsorption, but basically to minimize that (())(52:11) there is an if they starts absorbing that there will be gel layer information. So, then we cannot go for this particular measurement.

So, adsorption depends on interaction of a solute with the membrane material and you know proteins are very prone to hydrophobic membrane the pH and ionic strength of the solution as well as sometimes temperature also play a role.

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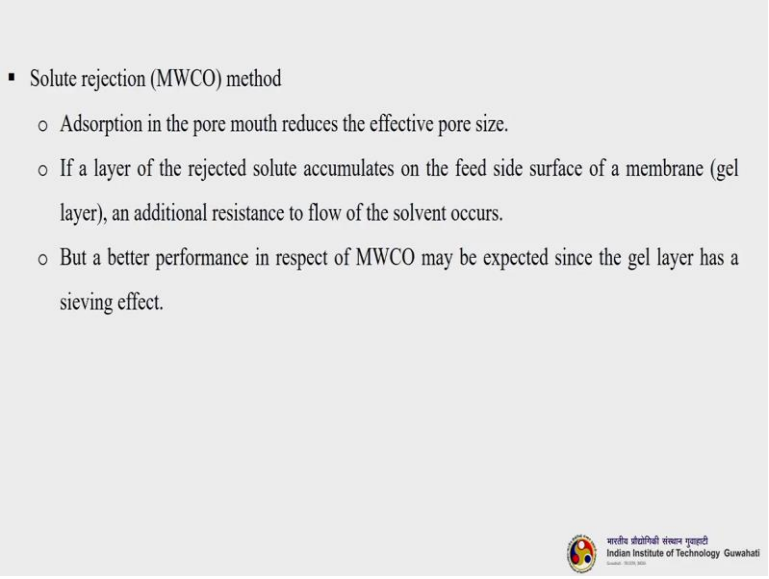


So, absorption in the pore mouth reduces the effective pore size it a layer of rejected solute accumulates on the feed side surface of the membrane. So, that is basically the gel layer then additional resistance to flow actually happening for a better performance in respect of particular but cut off may be expected since the gel layer has a sieving effect.

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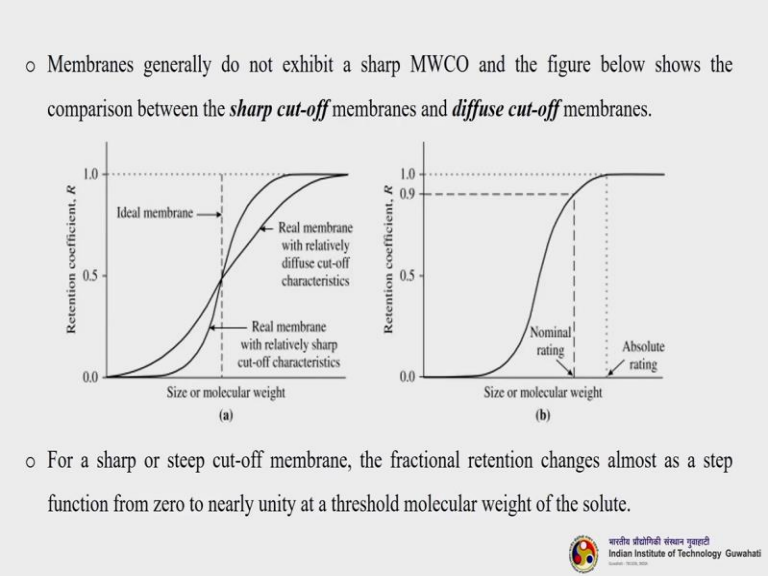


So, you can see this how actually I was talking about a sharp cut off and diffuse cut off so a sharp cut off is the so this is the actually ideal membrane. So here ideal membrane molecular this one retention verses in molecular size is a straight line. However, the real membranes with relatively diffuse cut off so this is with a diffuse cut off and the other are car this car is with a cut off so usually actually we wish that membranes.

When we are making a membrane whether at lab or in commercial scale will usually we try to aim that we have a sharp cut off membrane, but it never happens because the membrane is a pore size distribution due to that actually the cut off becomes a diffuse cut off in this we have discussed earlier also normal and rating 90% 90 to 95% and absolute rating is 100% rejection.

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- Most real membranes, with the pore size distributed over a range, have a diffuse MWCO, and the retention changes from 0-100% over a range of molecular weight.
- Table below gives the MWCO, operating temperature and pH ranges of a few UF membranes:

| Membrane material | Typical MWCO | Operating pH range | Max. operating temperature | $Cl_2$ resistance | Membrane configuration |
|---|---|---|---|---|---|
| Cellulose acetate | 1000-5000 | 3.5-7 | 35 | Good | Flat sheet, tubes |
| Polysulphone | 5000-50000 | 0-14 | 100 | Good | Flat sheet, tubes, hollow fibre |
| Aromatic polyamides | 1000-50000 | 2-12 | 80 | Poor | Flat sheet, tubes, hollow fibre |
| Polyacrylonitrile | 30000-100000 | 2-12 | 50 | Fair | Flat sheet, tubes, hollow fibre |

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Support most real membranes with pore size distributor over a range. They have a diffuse molecular weight cut off most of the commercial membrane. That defuse cut off membrane and the retention is from 0 to 100% for different molecular weights. So, this gives us membrane materials, typical molecular weight cut off their operating pH range maximum operating temperature.

That is actually recommended by the company of the manufacturer their chlorine resistance and membrane configuration means using that particular let us say this polysulphone. So, the polysulphone is very good chlorine resistance and it can be used to make flat sheet membranes tubular membrane as well as hollow fibre membranes.

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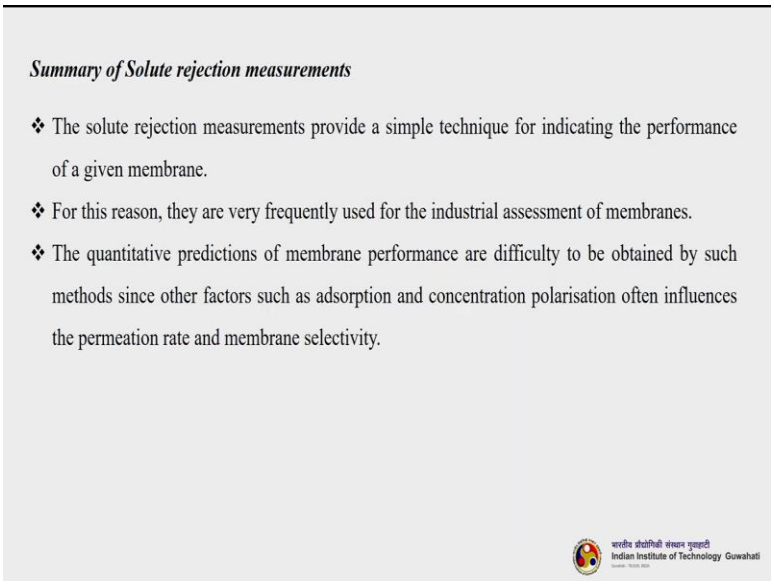


So, let us summarize the solute rejection measurement technique. So, this technique provides a simple method for indicating the performance of a given particular given membrane. For this reason they are very frequently used for industrial assessment of membranes. So, that means that I was telling some commercial manufacturers or the companies which make membrane they all of the them and go for this particular measurement technique which is the molecular rate cut off a membrane.

Because unless until they do they cannot say that what is the cut off of the membrane the quantitative predictions of membrane performance at differently to be obtained can by such method since other factors such as desorption and concentration polarisation often influence the permeation rate and membrane selectivity.

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So, we came to the conclusion of this lecture today. So, students I have been giving this text and references. So, most of the material in today's lecture was taken from the M. H. Mulder the basic principles of membrane technology please try to have this book if it is possible and go through this particular today's lecture. Otherwise you can refer other books also, which is listed here.

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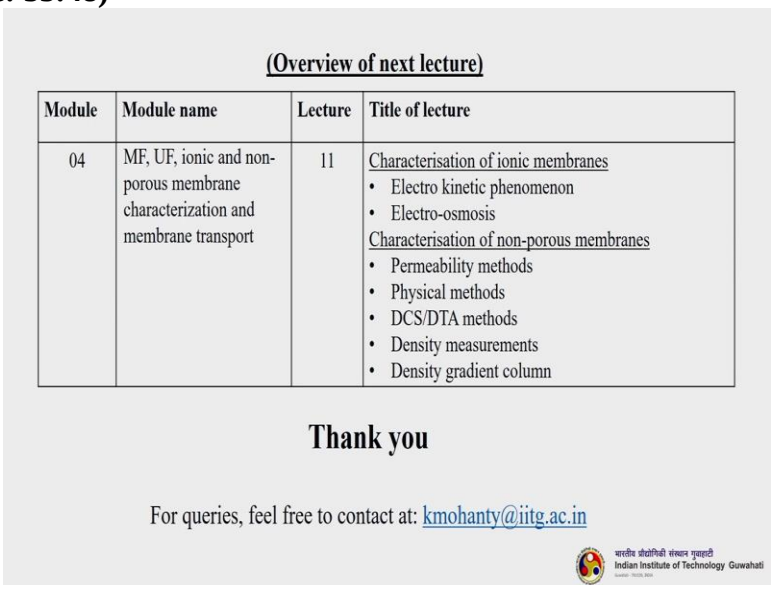


And in the next class, we are going to wind up this membrane characterization lecture section actually. So, you will learn about the characterization of ionic membranes. The characterization of non porous membrane, so non porous membrane also needs to be characterized. So their characterization and methods are little different than the porous membrane. So that will done. So

thank you very much. So, if you have any queries please feel free to write to me kmohanty@iitg.ac.in. Thank you