Membrane Technology
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Lecture-31
Concept, Types of LM, Mechanism of Mass Transfer in LM, Choice of Solvent and Carrier

Good morning students today is lecture 31 under module 11 in today's lecture we will cover liquid membrane. Liquid membranes are very interesting if you recall during the introduction class I told you that any membrane is made up of liquid is a liquid membrane. So, they are very interesting they have lots of positive features for which the researchers attention has been drawn to this particular technology.

And we will discuss about the concept that different types of liquid number and how to prepare liquid membrane then how mass transfer happens in liquid membrane. Then there are applications I will show you one case study also the work which is carried out in my own lab.

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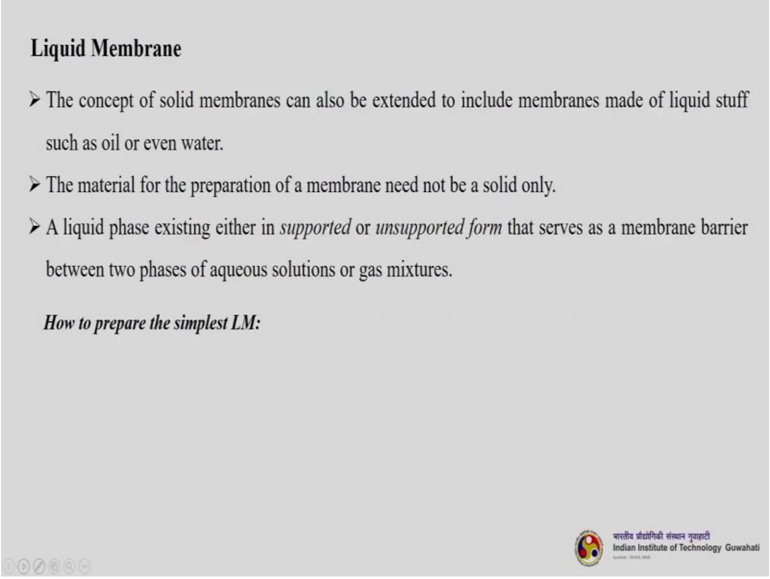

Liquid Membrane

- The concept of solid membranes can also be extended to include membranes made of liquid stuff such as oil or even water.
- The material for the preparation of a membrane need not be a solid only.
- A liquid phase existing either in *supported* or *unsupported form* that serves as a membrane barrier between two phases of aqueous solutions or gas mixtures.

How to prepare the simplest LM:

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So, let us begin a liquid membrane is as I told you that it is nothing but the membrane itself is a liquid so the concept of solid membranes I was extended to include membranes made up of liquid stuff such as oil or even water or any organic other organic solvents. The material for the preparation of the membrane need not be a solid only a liquid phase existing either in supported or unsupported form we will see and learn what is the meaning of supported an unsupported that serves as a membrane barrier between two phases of aqueous solutions and gas mixtures.

Now let me try to explain you by showing that how we can prepare a liquid membrane in a very simple way may be in the lab. So, most of you have seen the U-tube manometers which are used to measure pressure readings. So, let us say something like that we have a U-tube manometer right this is the simplest form which I am trying to actually draw, the simplest that we can make it in the lab itself and something like this.

So it has two limbs basically so you pour your membrane which is a lipid either water or oil or any organic solvent into one of the limbs so then it will come down and settle down here, let us say it comes and settle here right. So, this is your liquid membrane part so basically here so this is your liquid number but right. So, now there is a limb 1 here this is limp 2 here. So, in the limb 1 you will have your feed you can pass on your feed here.

And here you will have an extract phase please understand that there is extract phase here this is something extra which is not present in other membrane systems. So, this phase will basically extract the materials which we want to remove from the feed phase then is let us say in the feed phase the solutes are there we want to remove, the solids will travel through this liquid membrane and will come to this phase.

Now extract phase will be chosen in such a way that this will trap these solutes which we want to remove from the feed phase and will not allow the back diffusion to happen otherwise it will happen that again they will transport from here to here to feed size. And after some time you are seeing that again you are back to the original state so that this should not happen. So this is how you can prepare a liquid membrane in the simplest way.

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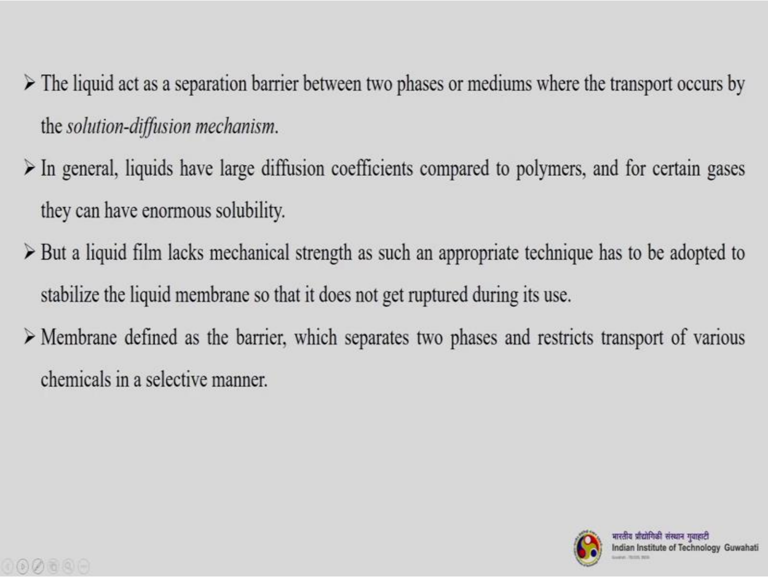

- The liquid act as a separation barrier between two phases or mediums where the transport occurs by the *solution-diffusion mechanism*.
- In general, liquids have large diffusion coefficients compared to polymers, and for certain gases they can have enormous solubility.
- But a liquid film lacks mechanical strength as such an appropriate technique has to be adopted to stabilize the liquid membrane so that it does not get ruptured during its use.
- Membrane defined as the barrier, which separates two phases and restricts transport of various chemicals in a selective manner.

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Now the liquid as a separation barrier between two phases or medium where the transport occurs by the solution diffusion mechanism, the mechanism of transport is solution diffusion. In general liquids have large diffusion coefficients compared to polymers and for certain gases that can have enormous solubility. Now but a liquid film lacks mechanical strength so this is one of the most important disadvantages of this liquid membranes.

As such an appropriate technique has to be adapted to stabilize the liquid membrane so that it does not get ruptured during its use and membrane defined as the barrier which separates two pages and restrict transport of various chemicals in a selective manner.

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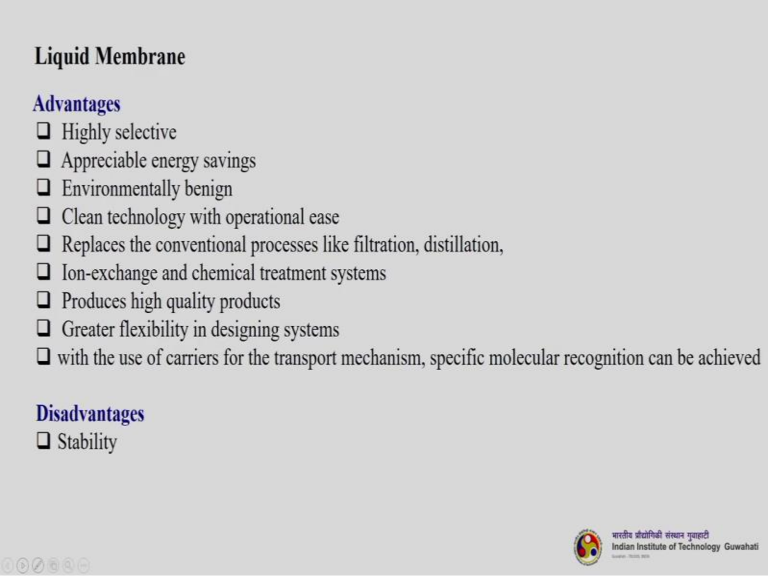

Liquid Membrane

Advantages

- ☐ Highly selective
- ☐ Appreciable energy savings
- ☐ Environmentally benign
- ☐ Clean technology with operational ease
- ☐ Replaces the conventional processes like filtration, distillation,
- ☐ Ion-exchange and chemical treatment systems
- ☐ Produces high quality products
- ☐ Greater flexibility in designing systems
- ☐ with the use of carriers for the transport mechanism, specific molecular recognition can be achieved

Disadvantages

- ☐ Stability

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Now advantageous are liquid membranes are highly selective as I told in the beginning of this lecture that I can actually target and make a liquid membrane which will remove and separate the solute which we want to separate from the feed phase. So, they are very highly selective then we can have different modes of transport also not only restricted to solution diffusion we can have carrier mediated transport where a particular group or carrier will help to remove the component more efficiently than that of the use a liquid membrane without having a carrier.

Now it does not require an energy say appreciable energy savings and environmentally benign, clean technology with operational, it is easy to operate, replaces the conventional process like filtration and distillation, ion exchange and chemical treatment systems, produces high quality products, greater flexibility in designing systems with the use of carriers this is what I was just telling a specific molecular recognition can be achieved and disadvantage is stability.

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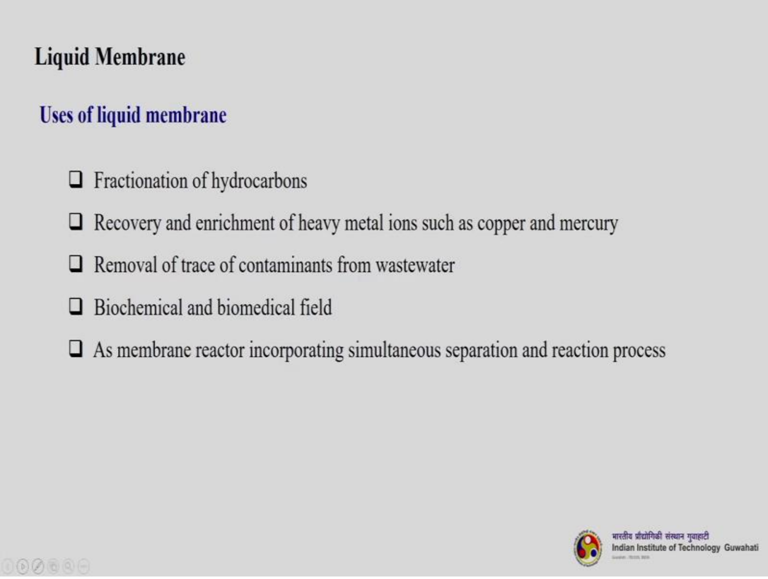

Liquid Membrane

Uses of liquid membrane

- ☐ Fractionation of hydrocarbons
- ☐ Recovery and enrichment of heavy metal ions such as copper and mercury
- ☐ Removal of trace of contaminants from wastewater
- ☐ Biochemical and biomedical field
- ☐ As membrane reactor incorporating simultaneous separation and reaction process

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Now the uses have there are manifold uses fractionation of hydrocarbons, recovery and enrichment of heavy metal ions such as copper and mercury removal of trace contaminants from waste water biochemical and biomedical field applications, membrane reactor incorporating simultaneous separation and reaction process.

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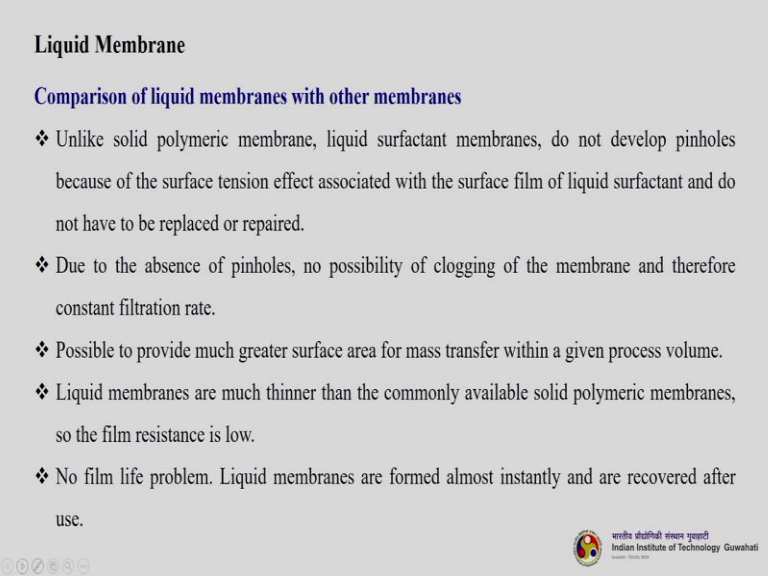

Liquid Membrane

Comparison of liquid membranes with other membranes

- Unlike solid polymeric membrane, liquid surfactant membranes, do not develop pinholes because of the surface tension effect associated with the surface film of liquid surfactant and do not have to be replaced or repaired.
- Due to the absence of pinholes, no possibility of clogging of the membrane and therefore constant filtration rate.
- Possible to provide much greater surface area for mass transfer within a given process volume.
- Liquid membranes are much thinner than the commonly available solid polymeric membranes, so the film resistance is low.
- No film life problem. Liquid membranes are formed almost instantly and are recovered after use.

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So, let us now compare the liquid membrane with other membranes. So, unlike solid polymeric membrane liquid surfactant membranes do not develop pinholes because of the surface tension effect associated with the surface film of liquid surfactant and do not have to be replaced or repaired. So, this is one of the biggest advantage then due to the absence of panels no possibility of clogging of the membrane and therefore called strand filtration rate so there is no question of any concentration polarization that is happening as in the case of solid membranes.

So possible to provide much greater surface area for mass transfer within a given process volume liquid membranes are much thinner than the commonly available solid polymeric membranes so the film resistance is low see this is also another advantage and no film life problem liquid membranes are form almost instantly and are recovered after use.

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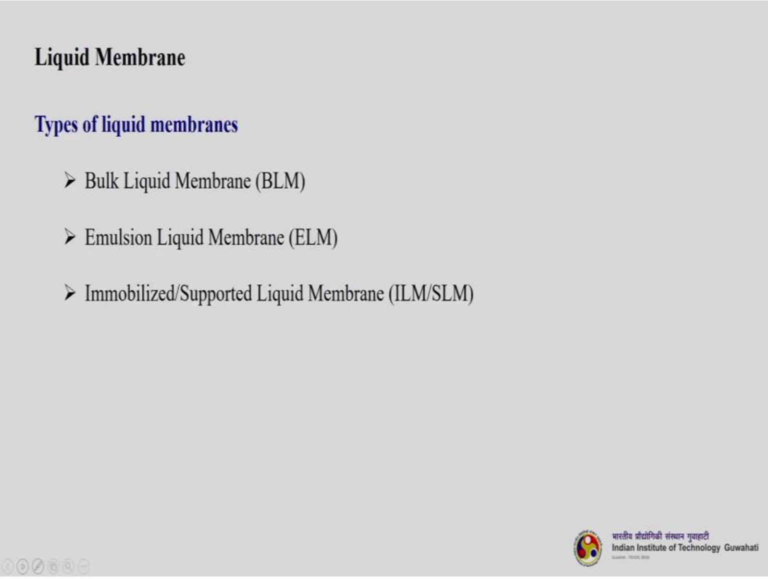

Liquid Membrane

Types of liquid membranes

- Bulk Liquid Membrane (BLM)
- Emulsion Liquid Membrane (ELM)
- Immobilized/Supported Liquid Membrane (ILM/SLM)

So, let us now try to understand the different types of liquid membranes. Basically we can categorize them into three different types one is BLM which is bulk liquid membrane second is ELM which is emulsion liquid membrane which has a lot of practical applications then the third is immobilized or supporter liquid membrane. Now immobilization or supported liquid membrane has come into picture basically to increase the mechanical stability of the membrane right.

So the most of the liquid membranes their mechanical stability is very poor so to improve it, it was thought that liquid the membrane which is like will be impregnated inside a porous support, so it may be another porous membrane inside which you will immobilize the liquid membrane and this porous membrane or support will provide the mechanical stability to the membrane. So, in this way those are either called is immobilized liquid membrane or supported liquid membrane.

So a lot of applications are there so the mechanical strength has actually increased by making supported liquid membranes or immobilized liquid membranes.

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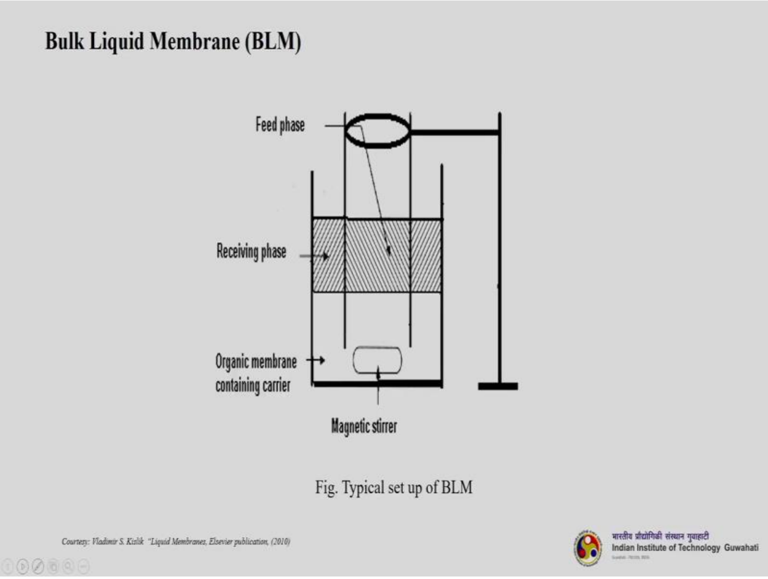

Bulk Liquid Membrane (BLM)

Fig. Typical set up of BLM

Courtesy: Vladimir S. Kislik "Liquid Membranes, Elsevier publication, (2010)

Well let us say one by one so this is BLM this is the most simplest top one which I was just showing showed you in the first slide itself drawing a U-tube manometer in how we can convert it to a liquid membrane setup. Here you can see there is a; it is a glass beaker you can call this is a beaker type of thing, so in which we can put two different there is a partition we can call. It made up of usually glass and then your organic membrane containing carrier or whatever we without carrier also does not matter containing carrier or no carrier also.

So this is your part where your liquid membrane part is being faced then there is a receiving phase here. So, this side and this side this air is receiving phase and this is from here from where you are entering your feed phase. So, there is a magnetic starter which is rotating to just increase enhance the rate of mass transfer right. So, this is a typical BLM setup.

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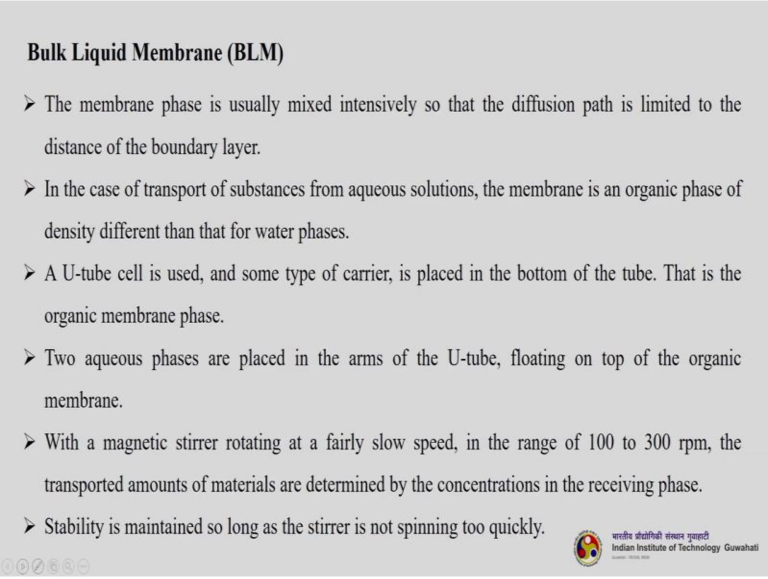

Bulk Liquid Membrane (BLM)

- The membrane phase is usually mixed intensively so that the diffusion path is limited to the distance of the boundary layer.
- In the case of transport of substances from aqueous solutions, the membrane is an organic phase of density different than that for water phases.
- A U-tube cell is used, and some type of carrier, is placed in the bottom of the tube. That is the organic membrane phase.
- Two aqueous phases are placed in the arms of the U-tube, floating on top of the organic membrane.
- With a magnetic stirrer rotating at a fairly slow speed, in the range of 100 to 300 rpm, the transported amounts of materials are determined by the concentrations in the receiving phase.
- Stability is maintained so long as the stirrer is not spinning too quickly.

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Now the membrane phase is usually mixed intensively so that the diffusion path is limited to the distance of the boundary layer this is very important. So, in this case of transport of substances from aqueous solution the membrane is an organic phase of density different than that of the water phases. A U-tube cell is used some type of carrier is placed at the bottom of the tube that is the organic membrane phase.

And that 2 aqueous phases are placed in the arms of a U-tube floating on the top of the organic membrane with a magnetic stirrer rotating at a fairly slow speed in the range of 100 to 300 rpm the transporter amounts of materials are determined by the concentrations in the receiving phase. So, stability is maintained as long as the steroid is not spinning too quickly.

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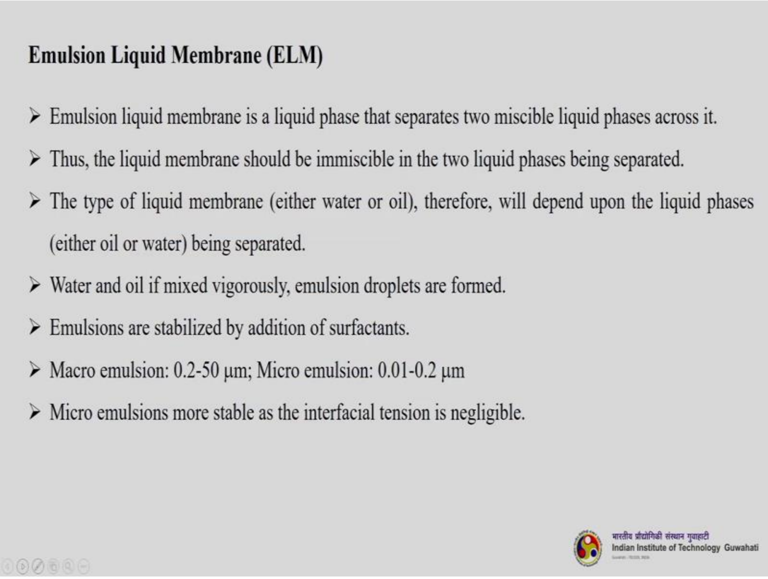

Emulsion Liquid Membrane (ELM)

- Emulsion liquid membrane is a liquid phase that separates two miscible liquid phases across it.
- Thus, the liquid membrane should be immiscible in the two liquid phases being separated.
- The type of liquid membrane (either water or oil), therefore, will depend upon the liquid phases (either oil or water) being separated.
- Water and oil if mixed vigorously, emulsion droplets are formed.
- Emulsions are stabilized by addition of surfactants.
- Macro emulsion: 0.2-50 μm; Micro emulsion: 0.01-0.2 μm
- Micro emulsions more stable as the interfacial tension is negligible.

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Otherwise the liquid membrane will break but these BLM's of the bulk liquid membranes do not have any commercial applications there is in the lab scale to generate data or to characterize a particular liquid membrane that was developed. So, then the next one is emulsion liquid membrane, emulsion liquid membrane is a liquid phase that separates two miscible liquid phases across it. Now thus the liquid membrane should be immiscible in that two liquid phases being separated.

So liquid membrane phase should be in such a way that there are two miscible liquid phases in between one immiscible membrane phase, now the type of liquid membrane either water or oil will therefore depend upon that liquid phases either oil or water being separated. Usually it is oil water type locations basically oil water separations. So, water and oil if mix vigorously emulsion droplets are form emulsions are stabilized further by addition of some surfactants.

Macro emulsions are of the size of 0.2 to 50 micron micro is 001 to 0.2 micron micro emulsions more stable because the interpersonal tension is negligible.

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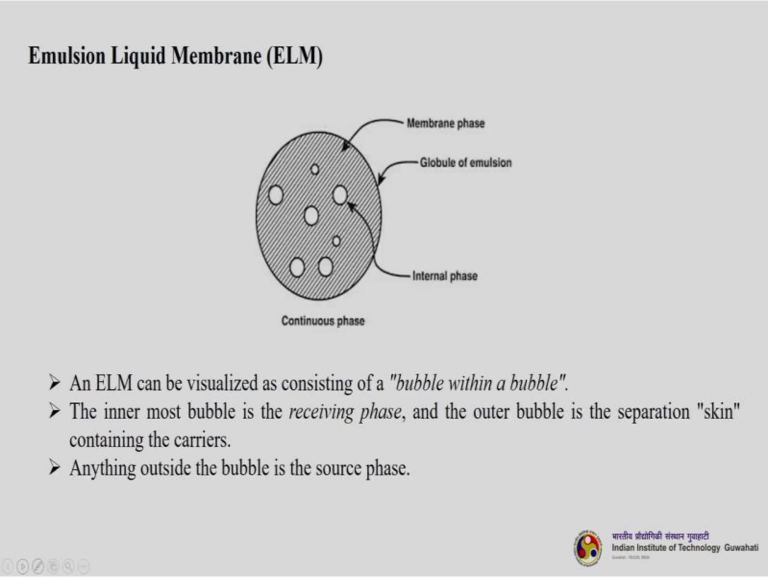

Emulsion Liquid Membrane (ELM)

- An ELM can be visualized as consisting of a *"bubble within a bubble"*.
- The inner most bubble is the *receiving phase*, and the outer bubble is the separation "skin" containing the carriers.
- Anything outside the bubble is the source phase.

This is just a schematic representation to try to understand let us try to understand what is this so here whatever it is here these are continuous phase okay outside this emulsions. So, this hatched portion what you are seeing is the membrane phase and whatever is the small bubbles you are seeing this is this one this is all these are all internal phase or we can call it as receiving phase. We can call it extract phase or extract phase.

Now you are understanding so this is your continuous phase or feed phase this is the hatching person so this is all your membrane phase right and inside that there is a internal phase. You can visualize at a bubble within a bubble this is looking like now it is a big bubble and there are so many small, small bubbles exactly it looks like this if you take it take the emulsions and put it under a microscope and see it just look like this.

So the innermost bubble is the receiving phase and the outer bubble is the separation skin containing the carriers anything outside the bubble is the source phase or your feed phase.

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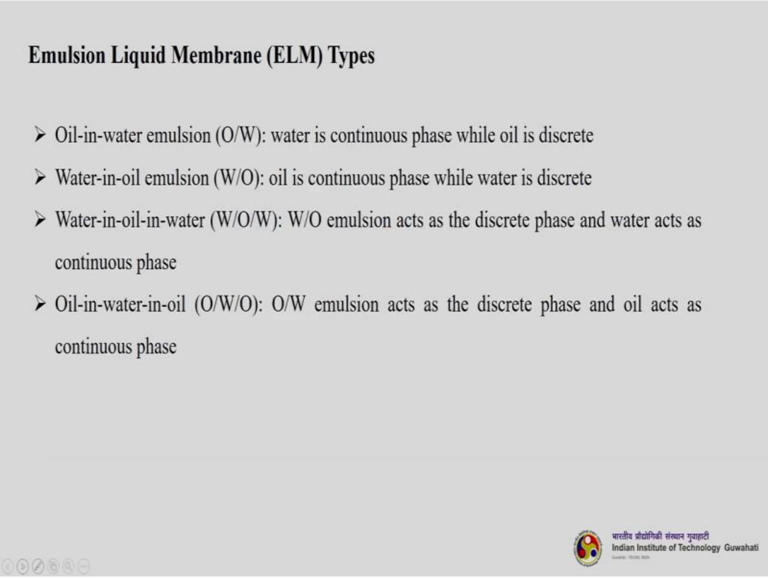

Emulsion Liquid Membrane (ELM) Types

- Oil-in-water emulsion (O/W): water is continuous phase while oil is discrete
- Water-in-oil emulsion (W/O): oil is continuous phase while water is discrete
- Water-in-oil-in-water (W/O/W): W/O emulsion acts as the discrete phase and water acts as continuous phase
- Oil-in-water-in-oil (O/W/O): O/W emulsion acts as the discrete phase and oil acts as continuous phase

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Now different types of LMS are there usually 3 or 4 distinct types the first one is oil in water emulsion. So, here water is continuous phase while the oil is the discrete phase then second is water in oil emulsion so here oil is continuous phase and the water is discrete phase. Then third one is water in oil in water, so here water and oil emulsions all excess the discrete phase and water excess the continuous phase.

Another is the reverse of this oil in water in oil. So, here oil and water emulsion act is the discrete phase and oil acts as the continuous phase.

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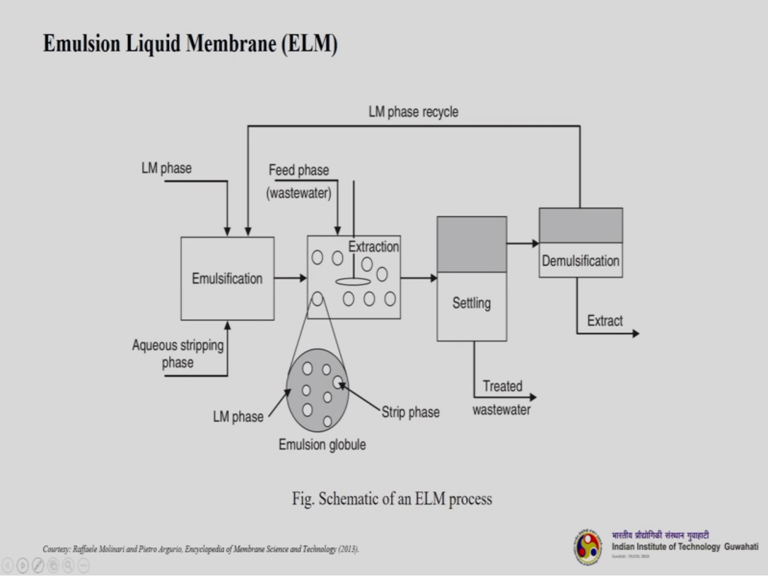

Emulsion Liquid Membrane (ELM)

Fig. Schematic of an ELM process

Courtesy: Raffaele Molinari and Pietro Argurio, Encyclopedia of Membrane Science and Technology (2013).

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So, this is the emulsion liquid membrane schematic setup you can see how actually you will from this you can understand that how ELM's are prepared. Let us see here so this is the first chamber which is emulsification here a quest dripping press and liquid membrane phase are mixed together right and then they will form something like this just what we have seen, this is what will be formed here.

Then you add your feed phase here, so then there is discrete phase so basically this is what is there here. Now this goes to the extraction process so you just store it little very low agitation speed sorry this is not the feed phase the feed phase is coming here. So, this is what is present here you are putting your feed phase here and slowly stirring it during that your mass transfer will takes place and the components are the solutes which you want to transport from the feed phase to that of the receiving phase will travel through the emulsion membrane phase and eventually it will get inside or trapped inside the receiving vessel so or stripping face whatever it is you come.

So once that is done then you leave it to a settling tank where the treated wastewater will be collected at the bottom and the oil trees face will be collected and a will be sent into a demulsifier, so this is a demulsifier. So, this is emulsifier this is demulsifier here you are making emulsion see where you are breaking emulsions. so whatever you break it then you got the extract phase here the same being phase.

Basically what is done here this is break into this plus this, so two different phases one is the membrane phase and this is the extract phase right. So, you can take the extra phase again and put it here right a stripping phase and the liquid membrane phase is being recycled to the main stage. So, this is how it happens so in industry there are so many emulsifiers then demulsifier various settling tank, central settling tanks mostly in series, they operate in series.

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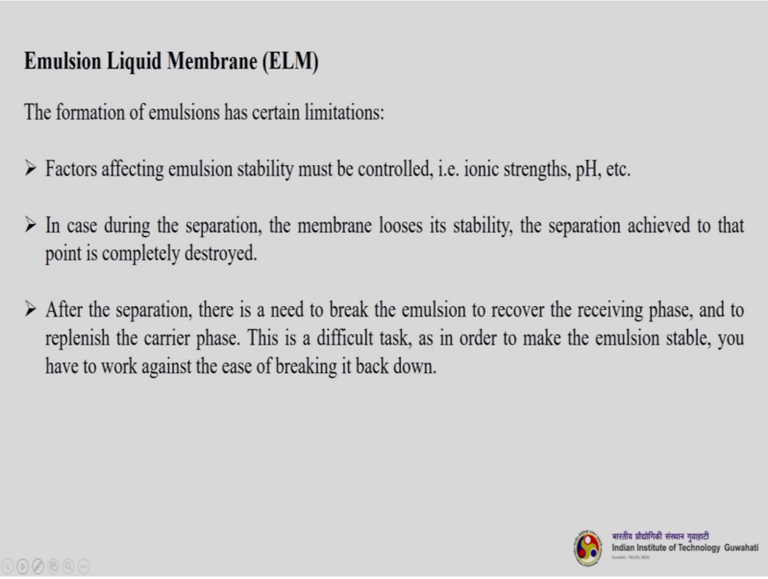

Emulsion Liquid Membrane (ELM)

The formation of emulsions has certain limitations:

- Factors affecting emulsion stability must be controlled, i.e. ionic strengths, pH, etc.
- In case during the separation, the membrane looses its stability, the separation achieved to that point is completely destroyed.
- After the separation, there is a need to break the emulsion to recover the receiving phase, and to replenish the carrier phase. This is a difficult task, as in order to make the emulsion stable, you have to work against the ease of breaking it back down.

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So, the formation of emulsions has certain limitations so factors affecting emulsion stability must be control so this is very important. So, these factors are ionic strength and pH. So, in case during the separation the membrane loses its stability then the separation achieved to that point is completely destroyed so this is one of the biggest disadvantage of these ELM membranes. In case let us say the separation is happening almost 30-40% separation is done and in the next test you would have got 60 to 70 % of your desired separation.

In case the emulsions breaks then you are just back to the starting point. So, after the separation there is a need to break the emulsion to recover the receiving phase and to replenish the carrier phase. Now this is a difficult task as in order to make the emulsion stable you have to work against the ease of breaking in break it down because many times you are supplying stabilizing agent such as certain surfactants to increase its mechanical strength.

Now you want to break it so you are going against the entire forces up whatever is present to break it down so it is a tough task basically.

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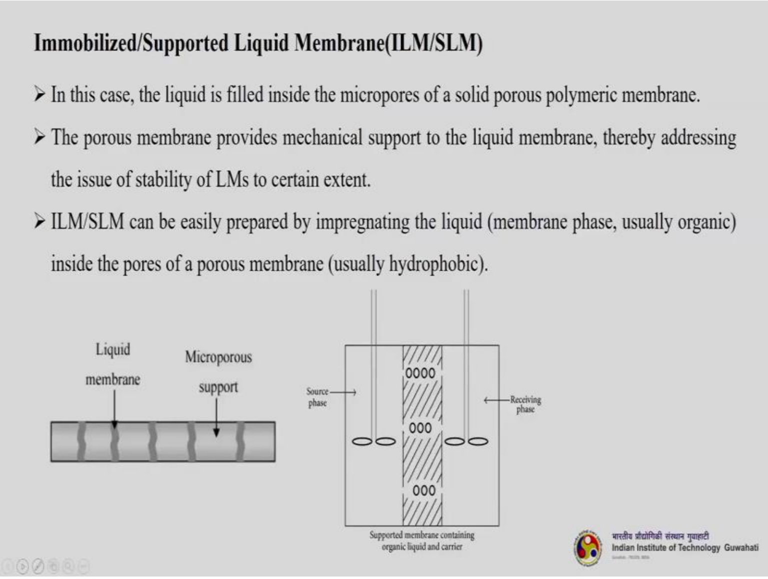

Immobilized/Supported Liquid Membrane(ILM/SLM)

- In this case, the liquid is filled inside the micropores of a solid porous polymeric membrane.
- The porous membrane provides mechanical support to the liquid membrane, thereby addressing the issue of stability of LMs to certain extent.
- ILM/SLM can be easily prepared by impregnating the liquid (membrane phase, usually organic) inside the pores of a porous membrane (usually hydrophobic).

So next one is immobilized or supported liquid membrane it is either you can call it ILM's or SLM. Now in this case the liquid is filled inside the micro pores up a solid porous polymeric membrane just like this. Let us assume this is a micro porous support and these are the pores these are the pores these pores are filled with the liquid membrane. It is very easy to do it in the lab actually so the porous membrane provides mechanical support to the liquid membrane thereby addressing the issue of stability of the liquid membranes to certain extent.

Now ILM SLM can be easily prepared by impregnating the liquid that is the membrane phase usually organic inside the pores of a porous membrane usually hydrophobic. Now once you have the impregnation membrane so how do you do it? You take a this one let us say micro porous membrane micro filtration membrane basically 0.45 micron pore size or any pore size that is actually required. Then what you do basically you can take it in a Petri dish put the micro porous support on that and over that you just pour the membrane phase, the liquid membrane phase it is either oil or any other organic solvent over it.

So, slowly, slowly by gravity what will happen the pores will get filled so this is a lengthy process or what do we do in the last basically we put the micro porous support in a vacuum filtration unit and then slowly and then pour the liquid membrane phase about the surface of the membrane of the micro porous support and gradually very slowly just reach on here vacuum filtration unit and in a controlled manner you have to do it very low pressure. Otherwise it will suck everything and all the membrane phase will come to the permeate side so that should not happen.

So once it is done then you can take it out wipe it the membrane surface so that the extra liquid membrane phase whatever is present on the top surface of the membrane has to be wiped out. And then you either you can go for dry it or no need of it up drying also you can just take it and use it. So, you use it something like this, so you can have a let us say some sort of cell system right. So, here you can have your liquid membrane here so this is liquid membrane so you studied you studies one is feed one is here receiving our extract phase.

So we are studying both sides just to enhance the rate of mass transfer from here also the component should move to the liquid phase and once they come here they also should be properly trapped inside the receiving phase.

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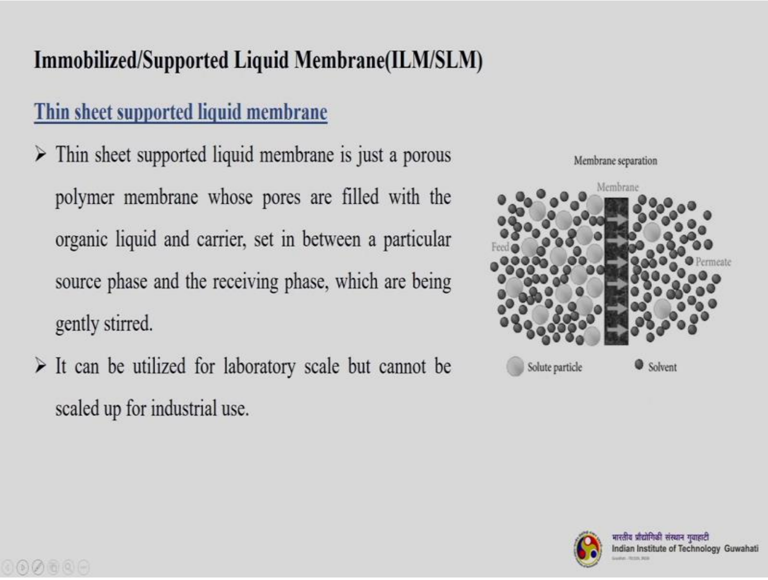

Immobilized/Supported Liquid Membrane(ILM/SLM)

Thin sheet supported liquid membrane

- Thin sheet supported liquid membrane is just a porous polymer membrane whose pores are filled with the organic liquid and carrier, set in between a particular source phase and the receiving phase, which are being gently stirred.
- It can be utilized for laboratory scale but cannot be scaled up for industrial use.

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So, there are different types of supported liquid membranes thin sheet supported liquid membranes. So, thin sheet support liquid membrane is just a porous polymer membrane which pores are filled with the organic liquid and carrier set in between a particular source space and the receiving phase which are being gently stirred just whatever we discussed. So, it can be utilized for laboratory scale but cannot be scaled upon for industrial use that is another thing for this type of thin sheet supported liquid membrane.

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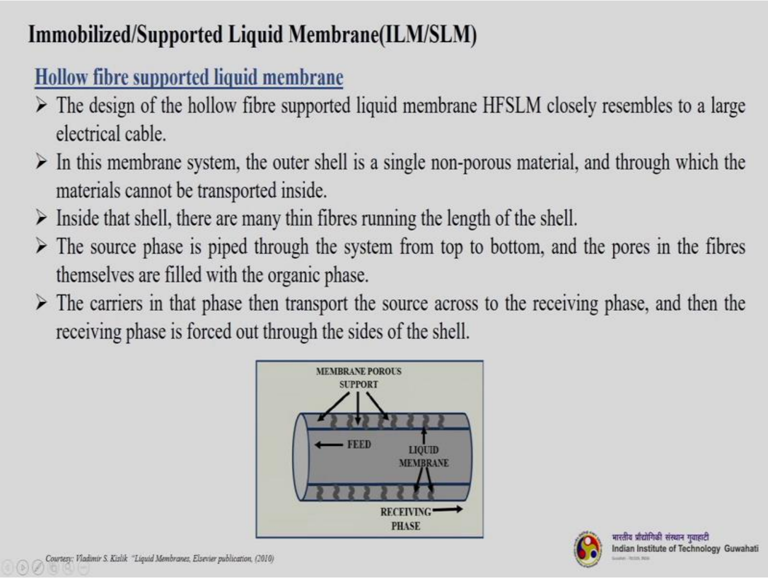

Immobilized/Supported Liquid Membrane(ILM/SLM)

Hollow fibre supported liquid membrane

- The design of the hollow fibre supported liquid membrane HFSLM closely resembles to a large electrical cable.
- In this membrane system, the outer shell is a single non-porous material, and through which the materials cannot be transported inside.
- Inside that shell, there are many thin fibres running the length of the shell.
- The source phase is piped through the system from top to bottom, and the pores in the fibres themselves are filled with the organic phase.
- The carriers in that phase then transport the source across to the receiving phase, and then the receiving phase is forced out through the sides of the shell.

Courtesy: Vladimir S. Kislik "Liquid Membranes, Elsevier publication, (2010)

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So hollow fiber supported liquid membrane now we have discussed a lot about hollow fiber it is different types of properties, how it is used in different applications. So, here also we can have all the fiber supported liquid membranes so the design of the hollow fiber supported liquid membrane closely resembles to a large electrical cable. So, in this membrane system the outer cell is a single non porous material and through which the materials cannot be transported inside.

So here you can see the membranes this is the membrane porous support right these are holes basically inside which you have the liquid membrane impregnated feed is being passed from this side and receiving phases outside. So, what will happen whatever it is the solute is coming here it will be transported through this and will go to the receiving phase, will be transported through this liquid membrane phase and will go to the receiving phase.

This is how it works so inside the cell there are many thin fibers running the length of the cell so the porous the source phase is piped through the system from top to bottom and the pores in the fiber themselves are filled with the organic phase. Now the carriers in the face then transport source across the receiving phase and then the receiving present forced out through the sides of the wall.

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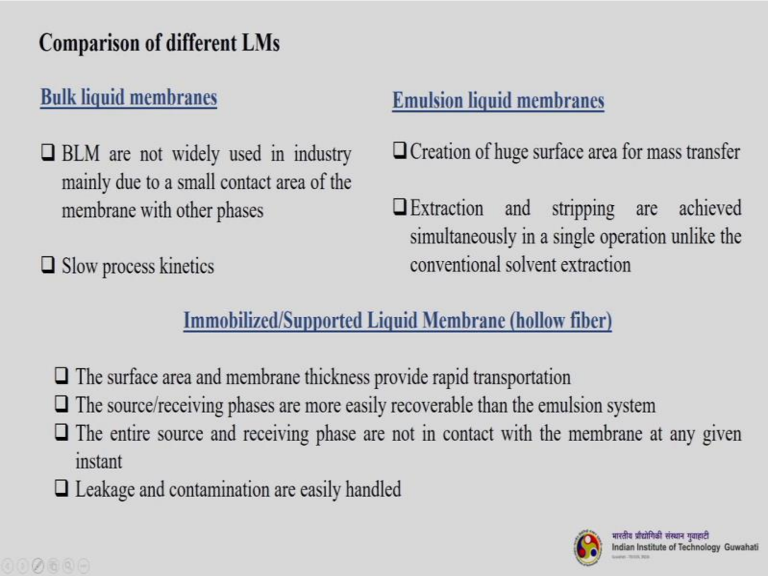

Comparison of different LMs

Bulk liquid membranes

- BLM are not widely used in industry mainly due to a small contact area of the membrane with other phases
- Slow process kinetics

Emulsion liquid membranes

- Creation of huge surface area for mass transfer
- Extraction and stripping are achieved simultaneously in a single operation unlike the conventional solvent extraction

Immobilized/Supported Liquid Membrane (hollow fiber)

- The surface area and membrane thickness provide rapid transportation
- The source/receiving phases are more easily recoverable than the emulsion system
- The entire source and receiving phase are not in contact with the membrane at any given instant
- Leakage and contamination are easily handled

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So, let us now understand the comparison between the three different types of liquid membranes bulk, emulsion and immobilized. So, bulk liquid membranes are not widely used in industry mainly due to the small contact area of the membrane with other phases and very slow process kinetics. In emulsion liquid membrane there is huge surface area equation for mass transfer this is the biggest advantage of emulsion liquid membrane.

And extraction and stripping of achieved simultaneously. In a single step both extraction and stripping are going on in a single operation like the conventional solvent extraction. And in immobilized and supported liquid membrane system including the hollow fiber systems the surface area and the membrane thickness provide rapid transportation the source of receiving faces are more easily recoverable than the emulsion system.

The entire source and receiving phase are not in contact with the membrane at any given time instead leakage and contamination are easily handled.

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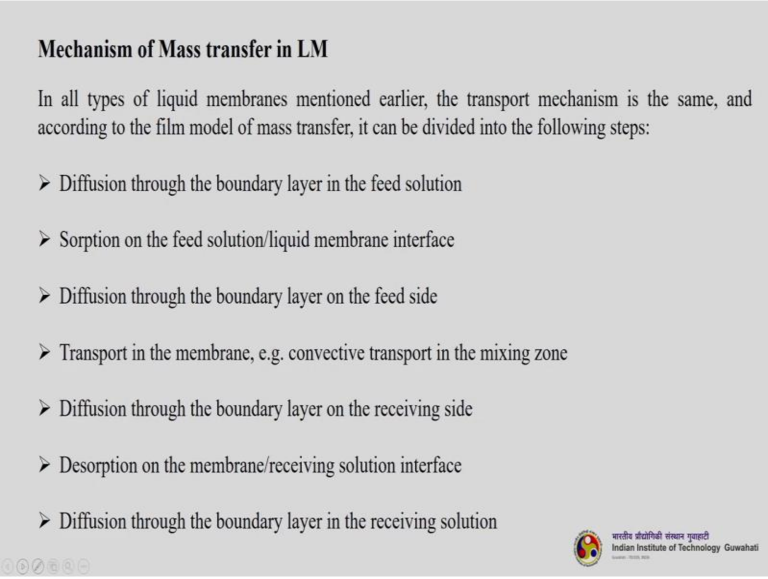

Mechanism of Mass transfer in LM

In all types of liquid membranes mentioned earlier, the transport mechanism is the same, and according to the film model of mass transfer, it can be divided into the following steps:

- Diffusion through the boundary layer in the feed solution
- Sorption on the feed solution/liquid membrane interface
- Diffusion through the boundary layer on the feed side
- Transport in the membrane, e.g. convective transport in the mixing zone
- Diffusion through the boundary layer on the receiving side
- Desorption on the membrane/receiving solution interface
- Diffusion through the boundary layer in the receiving solution

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Now let us try to understand the mechanism of mass transfer in liquid membranes. In all types of liquid membranes mentioned earlier the transport mechanism is the same and according to the film model of mass transport it can be divided into the following step the first is that diffusion through the boundary layer in the feed solution. Then substance on the feed solution or liquid membrane interface. So, basically if you try to explain it let us say this is a emulsion in which there are receiving phases and this is the membrane right.

So this is receiving well this is membrane phase and this is your feed phase. Now what will happen there will be a thin boundary layer here so what will happen initially the solute will diffuse through the boundary layer from the bulk to the boundary layer, so here. Once it comes here then it comes to this place which is the speed solution liquid membrane interface. It will diffuse through this then the boundary layer and on the feed side then transport in the membrane side then once it reaches here it got transported in that this is all membrane side it transported to the membrane side that is convective transport basically.

Once the diffusion through the membrane is happening then it will reach to the diffusion through the boundary layer on the receiving side, so there is some thin boundary layer here then it gets transported and it reaches here it will diffuse through this boundary layer and then it will get inside the receiving phase. The disruption on the membrane or receiving solution interface diffusion through the boundary layer in the receiving solution this is how it happens but all different types of liquid membranes.

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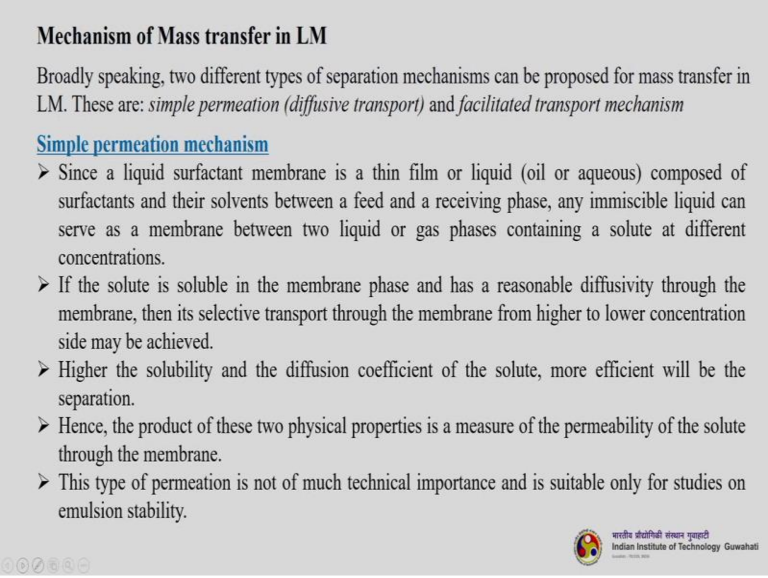

Mechanism of Mass transfer in LM

Broadly speaking, two different types of separation mechanisms can be proposed for mass transfer in LM. These are: *simple permeation (diffusive transport)* and *facilitated transport mechanism*

Simple permeation mechanism

- Since a liquid surfactant membrane is a thin film or liquid (oil or aqueous) composed of surfactants and their solvents between a feed and a receiving phase, any immiscible liquid can serve as a membrane between two liquid or gas phases containing a solute at different concentrations.
- If the solute is soluble in the membrane phase and has a reasonable diffusivity through the membrane, then its selective transport through the membrane from higher to lower concentration side may be achieved.
- Higher the solubility and the diffusion coefficient of the solute, more efficient will be the separation.
- Hence, the product of these two physical properties is a measure of the permeability of the solute through the membrane.
- This type of permeation is not of much technical importance and is suitable only for studies on emulsion stability.

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So, broadly speaking two different types of separation mechanisms can be proposed for mass transfer in liquid membrane. So, these are simple permeation which is due to diffusive transport and then facilitated transport mechanism. Now let us understand the simple permeation mechanism. Now since a liquid surfactant membrane is a thin film or liquid either oil or aqueous phase composite of surfactants and their solvents between a feed or receiving phase any immiscible liquid can serve as a membrane between the two liquid and gas phases containing a solute at different concentration.

So basically we are talking about a ELM here. So, if the soluble is the membrane phase and has a reasonable diffusivity through the membrane then its selective transport through the membrane from higher to lower concentration side may be achieved. So, higher the solubility and the diffusion coefficient of the solute more efficient will be the separation. Hence the product of these two physical properties is a measure of the permeability of the solute through the membrane.

This type of permeation is not of much technical importance and is suitable only for studies on emulsion stability just for lab scale studies basically because in industrial parlance where you need continuous separation we need a higher permeability and separation so this is not going to help us.

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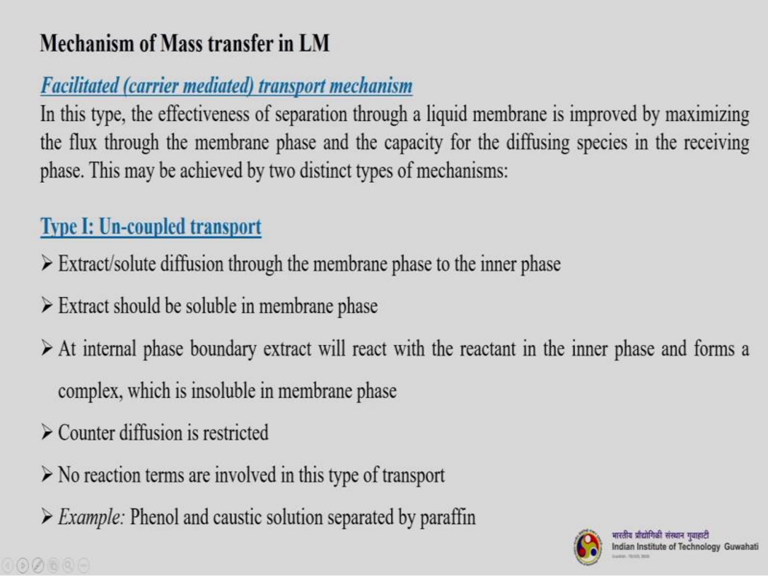

Mechanism of Mass transfer in LM

Facilitated (carrier mediated) transport mechanism

In this type, the effectiveness of separation through a liquid membrane is improved by maximizing the flux through the membrane phase and the capacity for the diffusing species in the receiving phase. This may be achieved by two distinct types of mechanisms:

Type I: Un-coupled transport

- Extract/solute diffusion through the membrane phase to the inner phase
- Extract should be soluble in membrane phase
- At internal phase boundary extract will react with the reactant in the inner phase and forms a complex, which is insoluble in membrane phase
- Counter diffusion is restricted
- No reaction terms are involved in this type of transport
- *Example:* Phenol and caustic solution separated by paraffin

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So, next is facilitated carrier mediated transport mechanism so in this type the effectiveness of separation through a liquid membrane is improved by maximizing the flux through the membrane phase and the capacity for diffusing spaces in the receiving phase. Now this we can do it by two distinct different mechanisms the first one let us understand is uncoupled transport. Now here what is happening now extract and solute diffusion through the membrane press to the interface and the extracts which were on to remove or the solute will diffuse through the membrane press to the inner phase?

Now extract should be soluble in the membrane phase that is very important at internal phase boundary extract will react with the reactant in the interface and forms a complex which is insoluble in the membrane phase. Now counter diffusion is restricted no reaction terms are involved in this type of reaction one classic example is phenol and caustic solution separation using paraffin. So, this is uncoupled transport so nothing is to getting coupled together.

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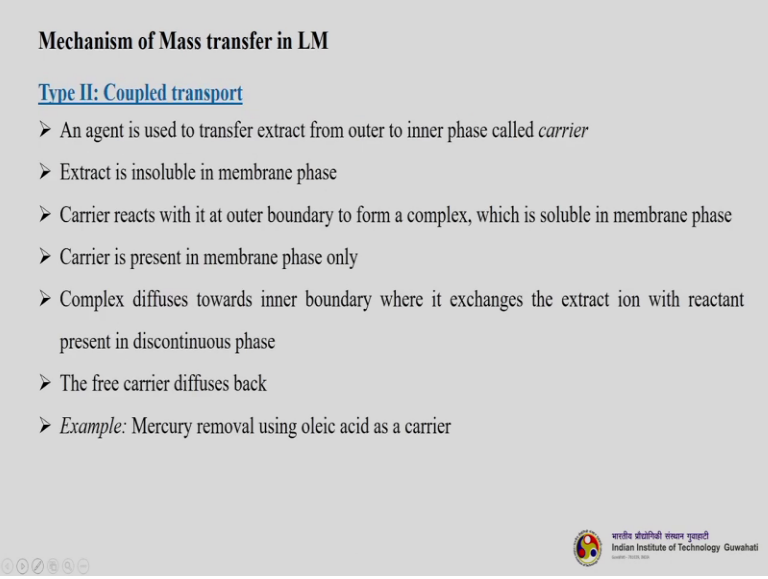

Mechanism of Mass transfer in LM

Type II: Coupled transport

- An agent is used to transfer extract from outer to inner phase called *carrier*
- Extract is insoluble in membrane phase
- Carrier reacts with it at outer boundary to form a complex, which is soluble in membrane phase
- Carrier is present in membrane phase only
- Complex diffuses towards inner boundary where it exchanges the extract ion with reactant present in discontinuous phase
- The free carrier diffuses back
- *Example:* Mercury removal using oleic acid as a carrier

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And the second is coupled transport so here an agent is used to transfer extract from outer to inner parts called a carrier there is a third component which is added to the membrane phase. So, extract is insoluble in the membrane phase carrier reacts with it at outer boundary to form a complex which is soluble in the membrane phase otherwise it will not transporter diffusion set the membrane phase carrier is present only in membrane phase.

Complex diffuses towards the inner boundary where it exchanges the extract ion with the reactant present in the discontinuous phase the carrier becomes free it will again diffuses back. One classic example is mercury removal using oleic acid as a carrier.

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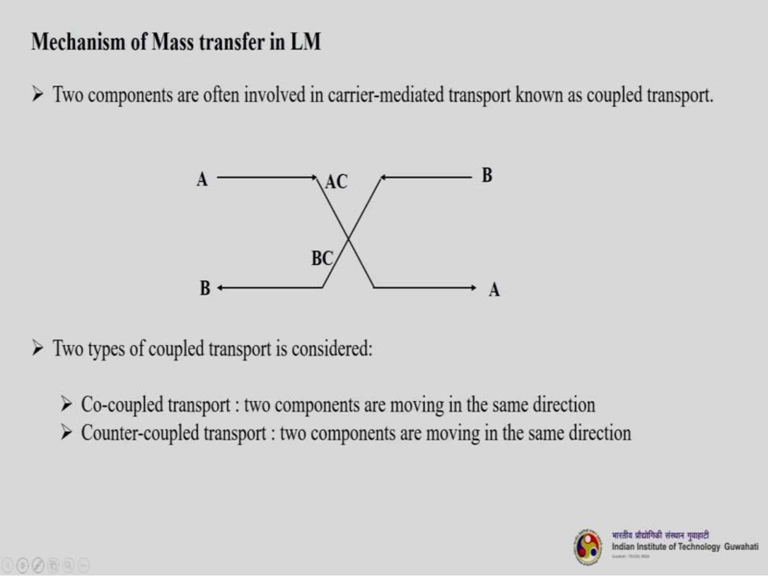

Mechanism of Mass transfer in LM

- Two components are often involved in carrier-mediated transport known as coupled transport.

- Two types of coupled transport is considered:
    - Co-coupled transport : two components are moving in the same direction
    - Counter-coupled transport : two components are moving in the same direction

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So, there are many such examples actually of couple and non coupled or transport. So, this is how actually it is happening so two components are often involved in a carrier mediated transport known as coupled transport. So, a component A and component B right, so here two types of copper transport are considered first is co-coupled transport second is counters coupled transport. In co-coupled transport two components are moving in the same direction.

So that means A and B both are diffusing in the same direction and in counter coupled transport two couples are moving in the opposite direction. So, just at is being shown here so A is moving here in this direction B is moving in counter coupled and direction. So, when it comes here so it is the A is bound to the carrier which forms a complex AC then it transports through the membrane phase and once it comes to this side it will release the A and the C is back.

Now simultaneously the C is getting bound to the B also so BC will again diffuse from the BC complex will diffuse from this inside the membrane phase we will release the B will get a B here and the C is again going back. So, this is how the counter coupled transport happens.

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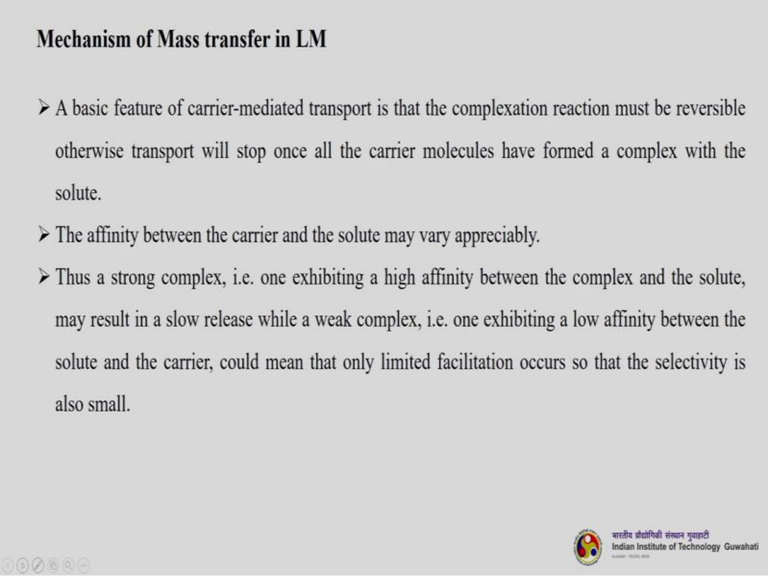

Mechanism of Mass transfer in LM

- A basic feature of carrier-mediated transport is that the complexation reaction must be reversible otherwise transport will stop once all the carrier molecules have formed a complex with the solute.
- The affinity between the carrier and the solute may vary appreciably.
- Thus a strong complex, i.e. one exhibiting a high affinity between the complex and the solute, may result in a slow release while a weak complex, i.e. one exhibiting a low affinity between the solute and the carrier, could mean that only limited facilitation occurs so that the selectivity is also small.

So, the basic feature of carrier mediator transport is that the complexes and reaction must be reversible otherwise transport will stop once all the carrier molecules have formed a complex with the solute right. Do you get it now so if there is no carrier molecule free to bind with the solute then there will be no more separation it will be say some sort of equilibrium. So, the affinity between the carrier and the solute may vary appreciably this is strong complex that is one exhibiting a high affinity between the complex.

And the solute may result in a slow release while a weak complex that is one exhibiting a low affinity between the solute in the carrier could mean that only limited facilitation occurs so that the selectivity is also very small.

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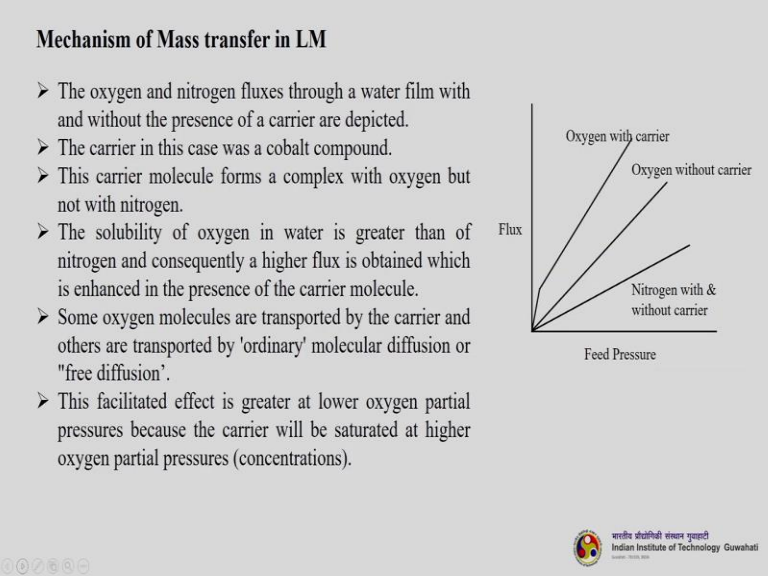

Mechanism of Mass transfer in LM

- The oxygen and nitrogen fluxes through a water film with and without the presence of a carrier are depicted.
- The carrier in this case was a cobalt compound.
- This carrier molecule forms a complex with oxygen but not with nitrogen.
- The solubility of oxygen in water is greater than of nitrogen and consequently a higher flux is obtained which is enhanced in the presence of the carrier molecule.
- Some oxygen molecules are transported by the carrier and others are transported by 'ordinary' molecular diffusion or "free diffusion'.
- This facilitated effect is greater at lower oxygen partial pressures because the carrier will be saturated at higher oxygen partial pressures (concentrations).

So, let us understand the transport of oxygen and nitrogen the oxygen and nitrogen fluxes through a water film only water with and without the presence of a carrier depicted. So, this is a flux versus flux versus the feed pressure data. So, the carrier in this case is a cobalt compound this carrier molecule forms a complex with oxygen but not with nitrogen. So, this is oxygen specific carrier so it will form cobalt oxide basically with oxygen but it will not react with nitrogen.

So the solubility of oxygen water is always greater than that of nitrogen and consequently a higher flux is obtained which is enhanced in the presence of a carrier molecule. So, already the solubility of oxygen is higher in water than that of the nitrogen so it will diffuse very fast but with the presence of a specific carrier the flux will increase further. So, some oxygen molecules are transported by the carrier and others are transported by ordinary molecular diffusion or pre diffusion.

So please remember that even if there is a carrier presence it is not that only the carrier mediated transport is happening there are some molecular diffusion orders ordinary diffusion transport is also happening without the carrier. Now this facilitated effect is greater at lower oxygen partial process because the carrier will be saturated at higher oxygen partial pressure or concentration. So, you can see the flux is high with oxygen with carrier oxygen without a carrier then nitrogen within without carrier is the same because nitrogen is not reacting with the carrier.So this figure tells us that what is the importance of a specific carrier mediated transport.

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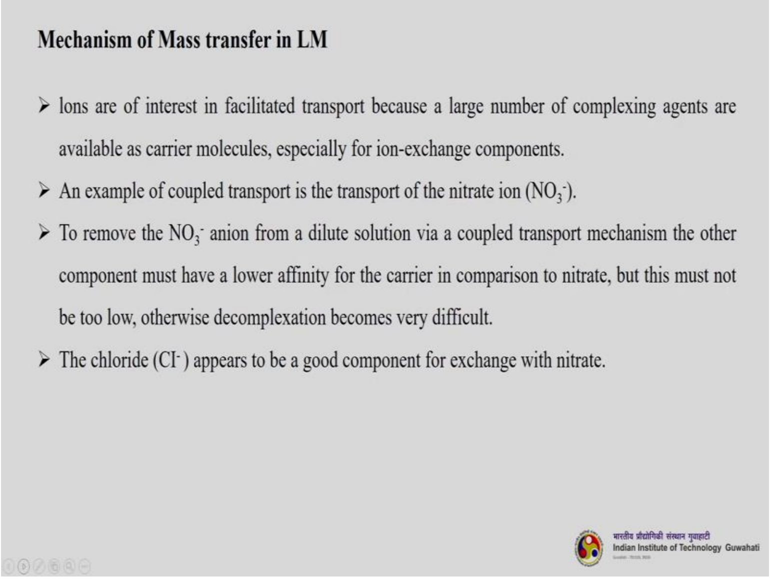

Mechanism of Mass transfer in LM

- Ions are of interest in facilitated transport because a large number of complexing agents are available as carrier molecules, especially for ion-exchange components.
- An example of coupled transport is the transport of the nitrate ion (NO_3^-).
- To remove the NO_3^- anion from a dilute solution via a coupled transport mechanism the other component must have a lower affinity for the carrier in comparison to nitrate, but this must not be too low, otherwise decomplexation becomes very difficult.
- The chloride (Cl^-) appears to be a good component for exchange with nitrate.

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So, I am set up interest in facilitated transport because a large number of complexing agents are available as carrier molecules especially for ion exchange components. Now an example of couple transport is the transport of nitrate ion. Now to remove nitrate anion from a dilute solution via a couple transport mechanism the other component must have a lower affinity for the carrier in comparison to nitrate.

Otherwise it will try to bind to the carrier but this must not be too low otherwise decomplexation system becomes very difficult. So, the chloride appears to be a good component for exchange with nitrate.

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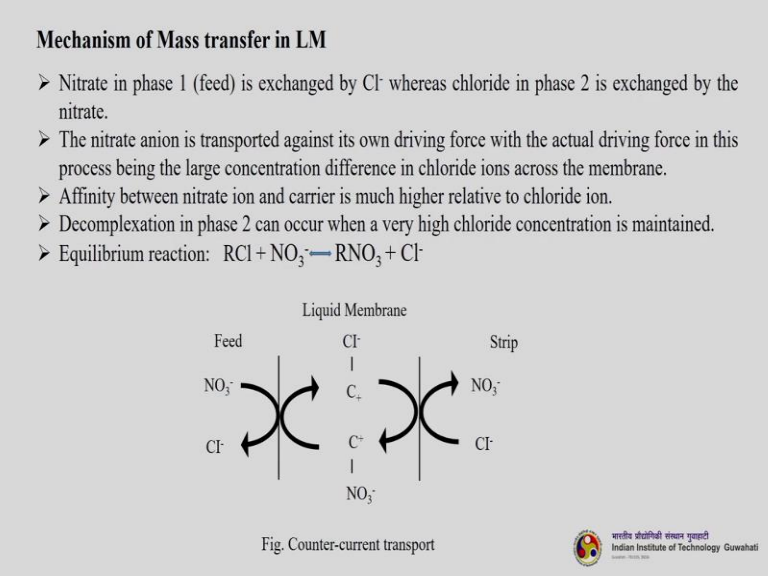

Mechanism of Mass transfer in LM

- Nitrate in phase 1 (feed) is exchanged by Cl^- whereas chloride in phase 2 is exchanged by the nitrate.
- The nitrate anion is transported against its own driving force with the actual driving force in this process being the large concentration difference in chloride ions across the membrane.
- Affinity between nitrate ion and carrier is much higher relative to chloride ion.
- Decomplexation in phase 2 can occur when a very high chloride concentration is maintained.
- Equilibrium reaction: $RCl + NO_3^- \longrightarrow RNO_3 + Cl^-$

Fig. Counter-current transport

So, you just see this how it is happening so nitrate in phase 1 or feed well this is phase 1 first true it is exchange by chlorine whereas chloride in the phase 2 is exchange by nitrate. So, the nitrate anion is transported against its own driving force with the actual driving force in this process being the large concentration difference in chloride ions across the membrane. Now please try to understand this what is happening though nitrate is having a concentration difference or concentration gradient higher.

But that is not helping what is helping is the chloride ions concentration difference between two sides that is driving force because nitrate is binding to the chlorides. So, affinity between nitrate ion and that carrier is much higher relative to the chloride and decomplexation and in Phase two can occur when a very high chloride concentration is maintained equilibrium where RCI plus nitrate equals to R NO3 plus CL minus.

So this is how the counter current transport is happening you can just have a look here. So, this is the entire liquid membrane phase this is feed phase and here it is the stripping phase.

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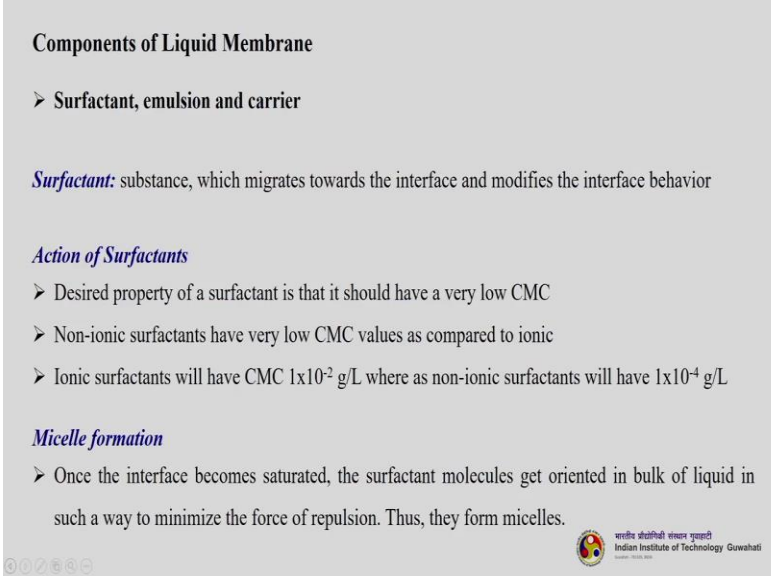

Components of Liquid Membrane

- **Surfactant, emulsion and carrier**

Surfactant: substance, which migrates towards the interface and modifies the interface behavior

Action of Surfactants

- Desired property of a surfactant is that it should have a very low CMC
- Non-ionic surfactants have very low CMC values as compared to ionic
- Ionic surfactants will have CMC $1x10^{-2}$ g/L where as non-ionic surfactants will have $1x10^{-4}$ g/L

Micelle formation

- Once the interface becomes saturated, the surfactant molecules get oriented in bulk of liquid in such a way to minimize the force of repulsion. Thus, they form micelles.

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Let us now try to understand the different components of a liquid membrane the different component sets are surfactant, emulsion and carrier, if at all carriers are prejudiced not mandatory. So, surfactant see the substance which migrate towards the interface and modifies the interface behavior we have already discussed a little about surfactant when we have discussed MEUF or your micellar enhanced ultra filtration.

So the extern of surfactants the desired property of a surfactant is that it should have a very low CMC. So, non ionic surfactants are very low CMC values are compared to ionic. Ionic surfactant will have CMC about 1 to 10 to the power of -10 grams per liter whereas non ionic surfactant will be 10 to the power of -4 grams per liter. So, once the interface becomes saturated the surfactant molecules get oriented in the bulk of liquid in such a way to minimize the force of repulsion thus the form micelles.

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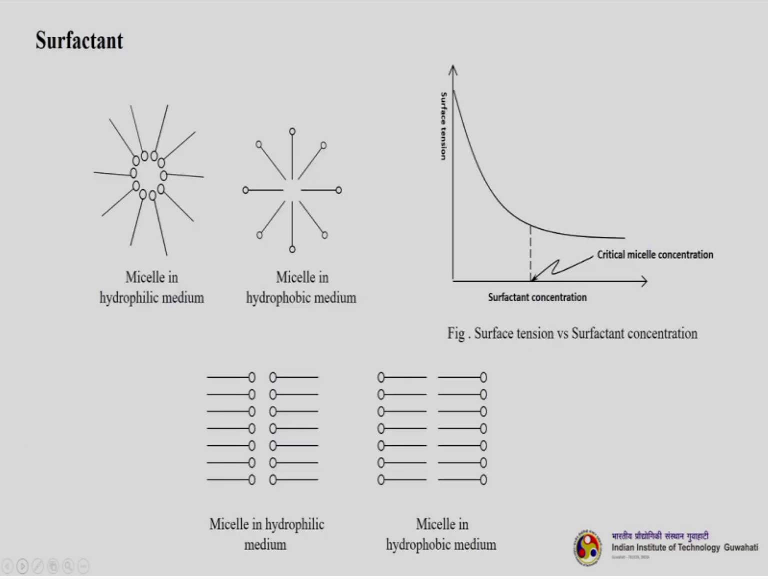

Surfactant

Fig . Surface tension vs Surfactant concentration

We have already discussed this you can see that how micelle is forming in a hydrophilic medium this is in a hydrophobic medium. You can see in hydrophilic medium the heads are inside the micelles and in a hydrophobic medium that tails are joined each other. It is not joined exactly some sort of interaction is happening okay and this is in hydrophilic medium micelle this is in hydrophobic medium and this is about the surface tension versus surfactant concentration.

You can see this is critical micellar concentration this we have already discussed just to again make you understand easily without going back to the earlier lecture.

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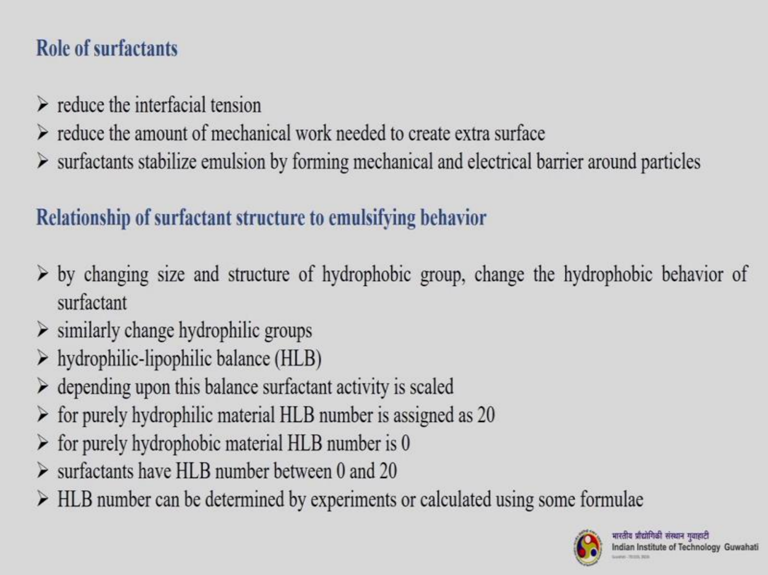

Role of surfactants

- reduce the interfacial tension
- reduce the amount of mechanical work needed to create extra surface
- surfactants stabilize emulsion by forming mechanical and electrical barrier around particles

Relationship of surfactant structure to emulsifying behavior

- by changing size and structure of hydrophobic group, change the hydrophobic behavior of surfactant
- similarly change hydrophilic groups
- hydrophilic-lipophilic balance (HLB)
- depending upon this balance surfactant activity is scaled
- for purely hydrophilic material HLB number is assigned as 20
- for purely hydrophobic material HLB number is 0
- surfactants have HLB number between 0 and 20
- HLB number can be determined by experiments or calculated using some formulae

So, that all of surfactant is to reduce the interfacial tension reduce the amount of mechanical work that is needed to create extra surface, a surfactant stabilized emulsion by forming mechanical and electrical barrier around particles. Now relationship of surfactant structure to emulsifying behavior now by changing size and structure of hydrophobic group change the hydrophobic behavior of the surfactant right.

Similarly change hydrophilic groups also hydrophilic lipophilic balance is very important it is called HLB and then depending upon this balance surfactant activity is scaled for purely hydrophilic material HLB number is assigned as 20 for purely hydrophobic material HLB is 0, surfactants have HLB number anything between 0 and 20 and HLB number can be determined by experiments or calculative using some formula.

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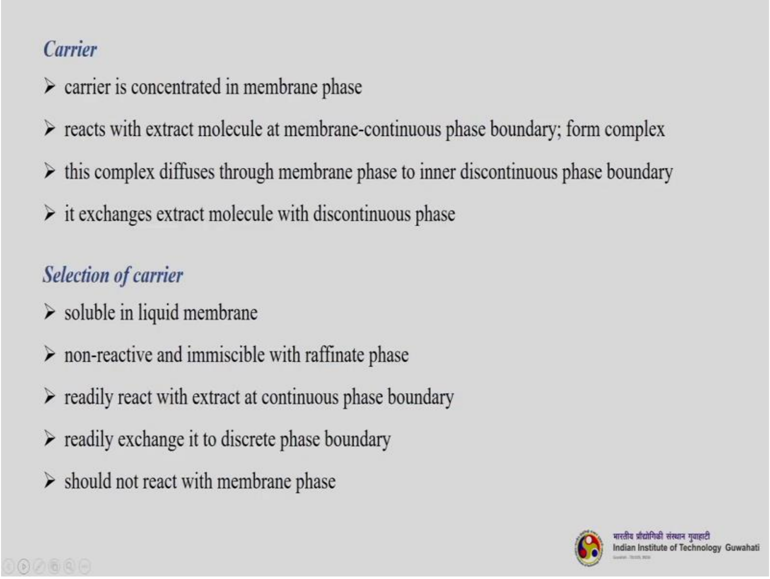

Carrier

- carrier is concentrated in membrane phase
- reacts with extract molecule at membrane-continuous phase boundary; form complex
- this complex diffuses through membrane phase to inner discontinuous phase boundary
- it exchanges extract molecule with discontinuous phase

Selection of carrier

- soluble in liquid membrane
- non-reactive and immiscible with raffinate phase
- readily react with extract at continuous phase boundary
- readily exchange it to discrete phase boundary
- should not react with membrane phase

Now carrier now carrier is concentrated in the membrane phase it should be dissolved in the membrane phase it reacts with the extract molecule at membrane continuous phase boundary form complex. Now this complex diffuses through the membrane press to the inner discontinuous phase boundary it exchanges extract molecule with discontinuous phase by virtue of the concentration difference again.

The selection of carrier is very important parameter which carrier to be chosen. Now it should be soluble in the liquid membrane it should be non reactive and immiscible with repeated phase or your extract phase. So, otherwise it will try to dissolve or get into inside the extract phase. So, readily react with the extractor continuous phase boundary readily exchange it to the discrete phase boundary should not react with the membrane phase. So, these are some of the properties of the carrier so which one need to take into account when you are choosing a carrier.

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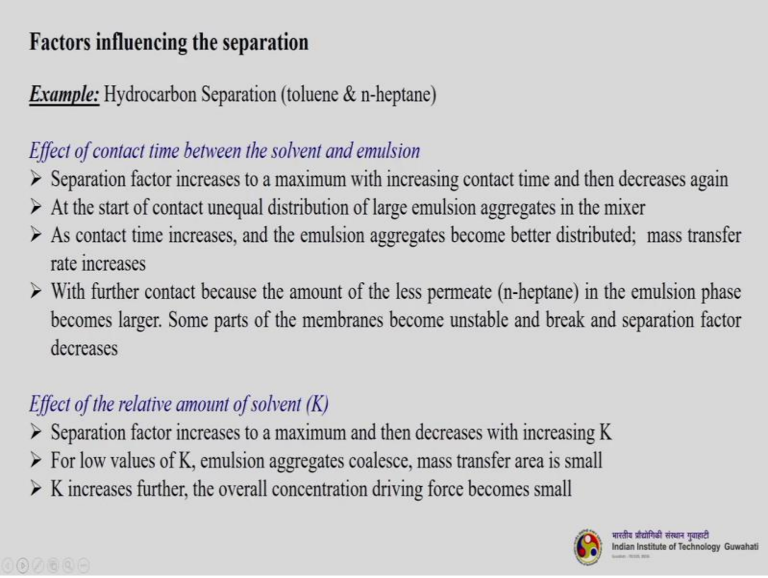

Factors influencing the separation

Example: Hydrocarbon Separation (toluene & n-heptane)

Effect of contact time between the solvent and emulsion

- Separation factor increases to a maximum with increasing contact time and then decreases again
- At the start of contact unequal distribution of large emulsion aggregates in the mixer
- As contact time increases, and the emulsion aggregates become better distributed; mass transfer rate increases
- With further contact because the amount of the less permeate (n-heptane) in the emulsion phase becomes larger. Some parts of the membranes become unstable and break and separation factor decreases

Effect of the relative amount of solvent (K)

- Separation factor increases to a maximum and then decreases with increasing K
- For low values of K, emulsion aggregates coalesce, mass transfer area is small
- K increases further, the overall concentration driving force becomes small

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So, factors influencing the separation so for example hydrocarbon separation toluene and n-heptane so based on this particular example it is discussed actually how the different factors are influencing the separation so affect up contact time between the solvent and emulsion. So, always in any separation you know or any mass transfer that is happening or even reaction that is happening contact time is extremely important.

So contact time should be optimized it should not be too less it should not be too high there should be some optimized value, so, which needs to find out by doing different experiments. So, separation factor increases to a maximum with increasing contact time and then decreases again so at the start of contact unequal distribution of large emulsion aggregates in the mixer as contact time increases and the emulsion aggregates become better distributed mass transfer rate increases.

With further contact because the amount of the less permeate n-heptane in the emulsion phase becomes larger some parts of the membrane become unstable and break and separation factor decreases. So, effect of the relative amount of the solvent so separation factor increased to a maximum and then decreases with increasing K. For low values of K emulsion aggregates coalesce mass transfer area is small k increases for the overall concentration driving first become small.

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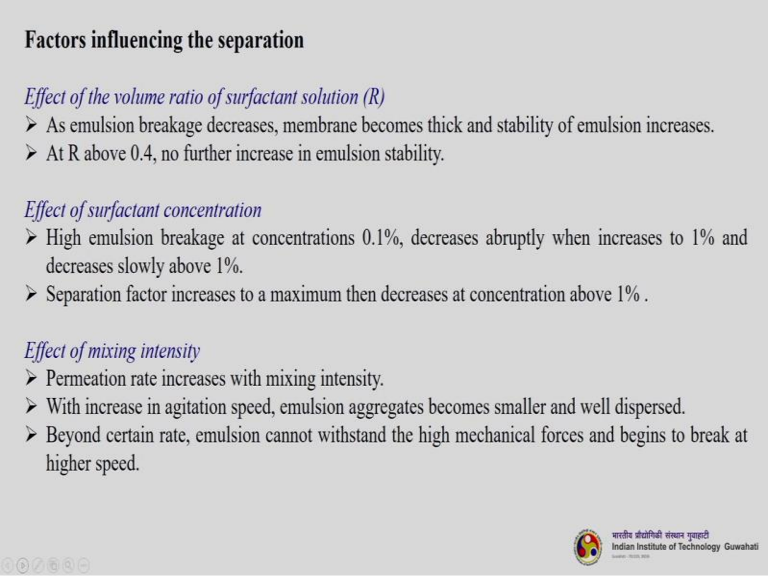

Factors influencing the separation

Effect of the volume ratio of surfactant solution (R)

- As emulsion breakage decreases, membrane becomes thick and stability of emulsion increases.
- At R above 0.4, no further increase in emulsion stability.

Effect of surfactant concentration

- High emulsion breakage at concentrations 0.1%, decreases abruptly when increases to 1% and decreases slowly above 1%.
- Separation factor increases to a maximum then decreases at concentration above 1% .

Effect of mixing intensity

- Permeation rate increases with mixing intensity.
- With increase in agitation speed, emulsion aggregates becomes smaller and well dispersed.
- Beyond certain rate, emulsion cannot withstand the high mechanical forces and begins to break at higher speed.

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So, the next is effect of the volume ratio of the surfactant solution so as emulsion breakage decreases membrane becomes thick and stability of emulsion increases. Now at our above 0.4 no further increase in the emulsion stability will be noticed. So, then effect of surfactant concentration high emulsion breakage at concentration of 0.1% decreases abruptly when concentration increases up to 1% and decreases slowly above 1%.

Separation factor increases to a maximum and then decreases at concentration above 1%. Effect of mixing intensity they also so plays a very important role permission that increases with increasing mixing intensity with increase in agitation speed emulsion aggregates becomes smaller and well dispersed beyond certain rate emulsion cannot withstand the high mechanical percents and begins to break at higher speed.

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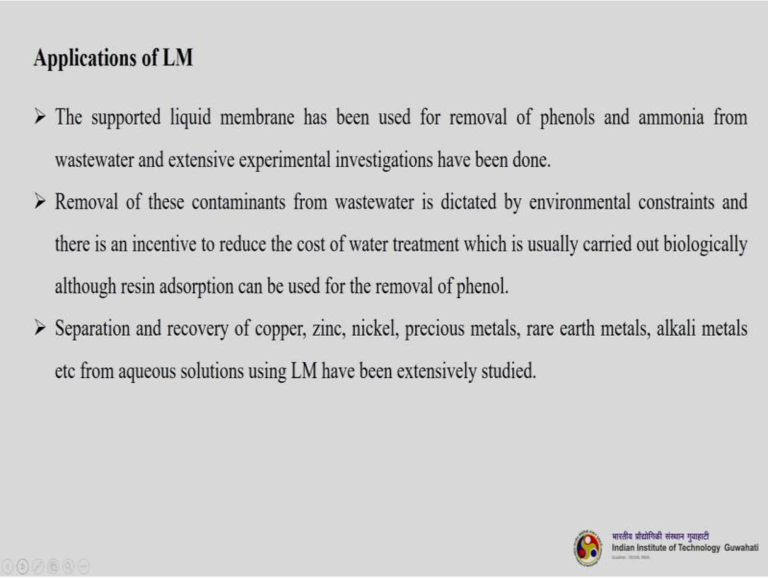

Applications of LM

- The supported liquid membrane has been used for removal of phenols and ammonia from wastewater and extensive experimental investigations have been done.
- Removal of these contaminants from wastewater is dictated by environmental constraints and there is an incentive to reduce the cost of water treatment which is usually carried out biologically although resin adsorption can be used for the removal of phenol.
- Separation and recovery of copper, zinc, nickel, precious metals, rare earth metals, alkali metals etc from aqueous solutions using LM have been extensively studied.

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Now let us now discuss the different applications of liquid membrane. The unsupported liquid membrane has used for removal of phenols and ammonia from we started an extensive experimental investigations have been carried out. Removal of these contaminants from wastewater is dictated by environmental constraints and there is an incentive to reduce the cost of water treatment which is usually carried out biologically although resin adsorption can be used for removal of phenol.

Separation and recovery of copper, zinc, nickel, precious metals rare earth metals alkali metals etcetera from aqueous solution using LM have been studied extensively.

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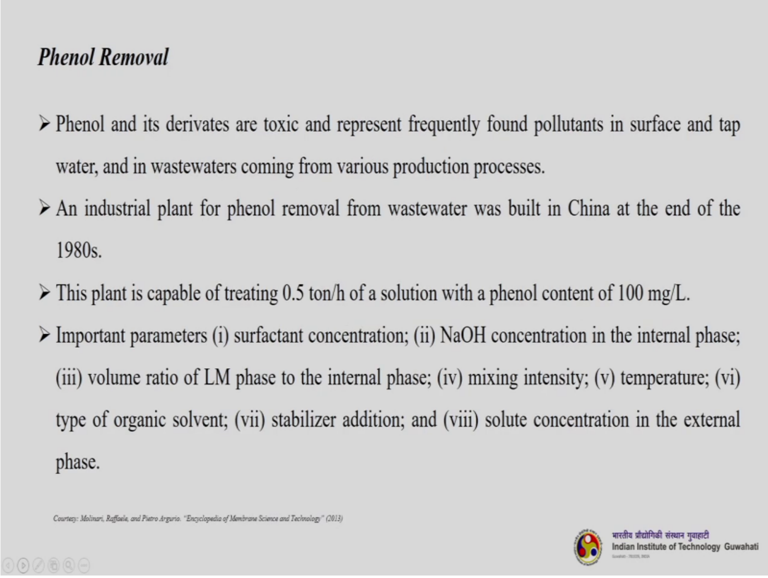

Phenol Removal

- Phenol and its derivates are toxic and represent frequently found pollutants in surface and tap water, and in wastewaters coming from various production processes.
- An industrial plant for phenol removal from wastewater was built in China at the end of the 1980s.
- This plant is capable of treating 0.5 ton/h of a solution with a phenol content of 100 mg/L.
- Important parameters (i) surfactant concentration; (ii) NaOH concentration in the internal phase; (iii) volume ratio of LM phase to the internal phase; (iv) mixing intensity; (v) temperature; (vi) type of organic solvent; (vii) stabilizer addition; and (viii) solute concentration in the external phase.

Courtesy: Molinari, Raffaele, and Pietro Argurio. "Encyclopedia of Membrane Science and Technology" (2013)

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So, phenol removal, phenol and its derivatives are toxic and represent frequently found pollutants in surface and tap water and in wastewaters coming from various products and processes like refinery metal finishing industries phenol hugely present. So, an industrial plant for phenol removal work from wastewater was built in China at the end of 1980s. So, this plant is capable of treating 0.5 ton per hour of solution with a phenol concentration of 100 milligrams per liter 100 ppm.

So important parameters surfactant concentration sodium hydroxide concentration in the internal phase sodium hydroxide is the dripping phase that will finally take the phenol inside it and will trap it and it will make sodium phenolate basically. So, then volume ratio per liquid membrane refers to the internal phase mixing intensity, temperature, type of organic solvent, stabilizer radiation, solute concentration in the external phase. So these are the parameters which is actually all optimized for this particular plant.

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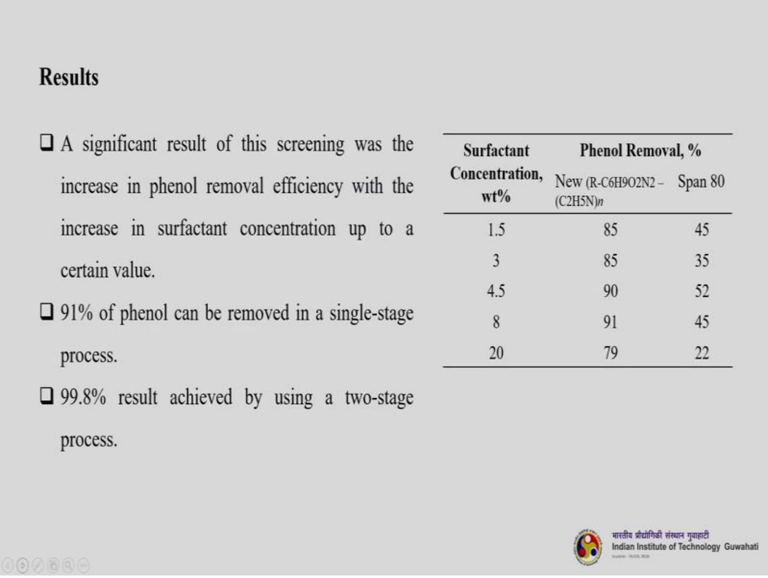

Results

- ❑ A significant result of this screening was the increase in phenol removal efficiency with the increase in surfactant concentration up to a certain value.
- ❑ 91% of phenol can be removed in a single-stage process.
- ❑ 99.8% result achieved by using a two-stage process.

Surfactant Concentration, wt%	Phenol Removal, %	
	New (R-C6H9O2N2 – (C2H5N)*n*	Span 80
1.5	85	45
3	85	35
4.5	90	52
8	91	45
20	79	22

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So results is that a significant result of this cleaning was that the increase in phenol removal efficiency with the increase in surfactant concentration up to a certain value. So, it has been seen that you keep on increasing the surfactant concentration here so your phenol removal percentage is happening up to let us say 91 here then it decreases right. So, it is increasing then it decreases further here so up to 8 we can say it is fine right.

So, 91% phenol can be removed in a single stress present 99.8% result achieved by using it 2 stage process.

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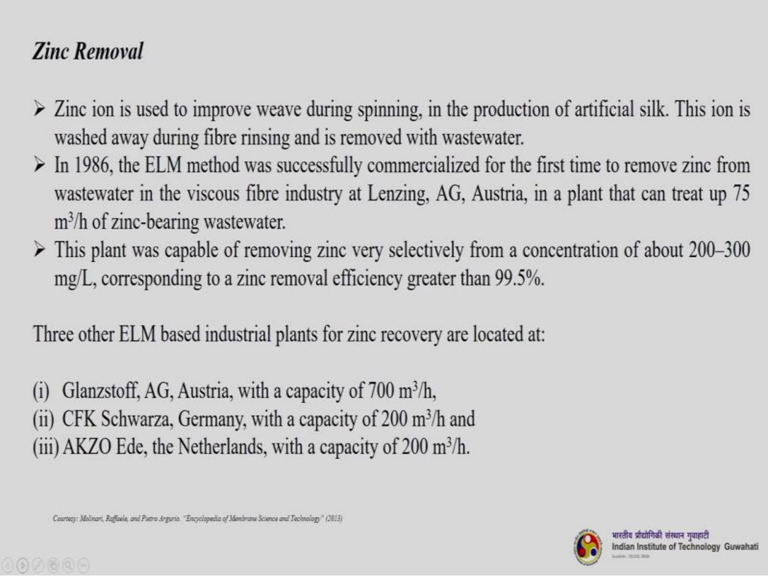

Zinc Removal

- Zinc ion is used to improve weave during spinning, in the production of artificial silk. This ion is washed away during fibre rinsing and is removed with wastewater.
- In 1986, the ELM method was successfully commercialized for the first time to remove zinc from wastewater in the viscous fibre industry at Lenzing, AG, Austria, in a plant that can treat up 75 m^3/h of zinc-bearing wastewater.
- This plant was capable of removing zinc very selectively from a concentration of about 200–300 mg/L, corresponding to a zinc removal efficiency greater than 99.5%.

Three other ELM based industrial plants for zinc recovery are located at:

(i) Glanzstoff, AG, Austria, with a capacity of 700 m^3/h,
(ii) CFK Schwarza, Germany, with a capacity of 200 m^3/h and
(iii) AKZO Ede, the Netherlands, with a capacity of 200 m^3/h.

Courtesy: Molinari, Raffaele, and Pietro Argurio. "Encyclopedia of Membrane Science and Technology" (2013)

So, another example is zinc remover. So, zinc ion is used to improve weep during spinning. So, in the production of artificial silk, so, this iron is washed away during fiber ranging and is removed with waste water zinc is high toxic so in 1986 ELM method was successfully commercialized for the first time to remove zinc from wastewater in the viscous fiber industries at Lenzing AG in Austria.

In the plant that can treat up to 75 meter cube per hour of zinc being used at this plant was capable of removing zinc very selectively from a concentration of about 200 to 300 huge concentration 200 to 300 ppm corresponding to a zinc removal efficiency of greater than 99.5%. Three other ELM based in the steel transferred zinc removal are also working so they are at a Glanstoff in Austria with a capacity of 700 meter cube per hour.

CFK Schwarza at Germany with a capacity of 200 meter cube per hour and AKZO Ade in Netherlands with a capacity of 200 meter cube per hour.

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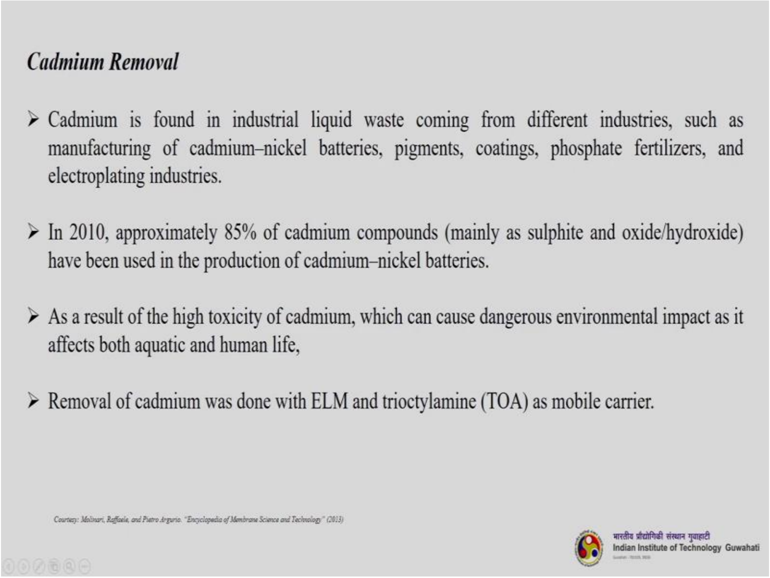

Cadmium Removal

- Cadmium is found in industrial liquid waste coming from different industries, such as manufacturing of cadmium–nickel batteries, pigments, coatings, phosphate fertilizers, and electroplating industries.
- In 2010, approximately 85% of cadmium compounds (mainly as sulphite and oxide/hydroxide) have been used in the production of cadmium–nickel batteries.
- As a result of the high toxicity of cadmium, which can cause dangerous environmental impact as it affects both aquatic and human life,
- Removal of cadmium was done with ELM and trioctylamine (TOA) as mobile carrier.

Courtesy: Molinari, Raffaele, and Pietro Argurio. "Encyclopedia of Membrane Science and Technology" (2013)

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So, then next one is cadmium removal, so cadmium is found in industry liquid coming from different industries such as manufacturing of cadmium nickel batteries, pigments, coatings phosphate fertilizers and electroplating industries. In 2010 approximately 85% of cadmium compound mainly a sulfite and oxide and hydroxide have been used in the production of cadmium nickel batteries. So, as a result of the high toxicity of cadmium which can cause dangerous environmental impact as it affects both the aquatic as well as human life human of cadmium was done with ELM and TOA that is a trioctoylamine was used as the mobile carrier.

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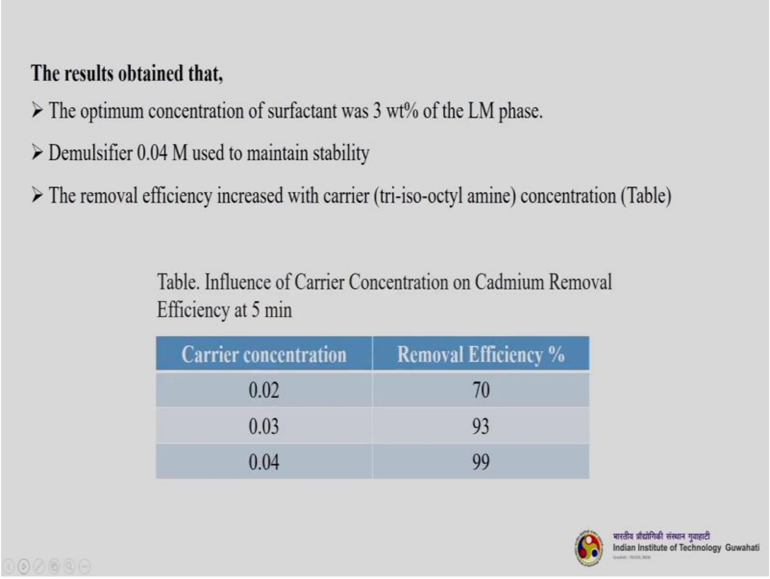

The results obtained that,

- The optimum concentration of surfactant was 3 wt% of the LM phase.
- Demulsifier 0.04 M used to maintain stability
- The removal efficiency increased with carrier (tri-iso-octyl amine) concentration (Table)

Table. Influence of Carrier Concentration on Cadmium Removal Efficiency at 5 min

Carrier concentration	Removal Efficiency %
0.02	70
0.03	93
0.04	99

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So, the results that is obtained at the optimum concentration of surfactant was found to be 3% for this particular replication demulsifier 0.04 molar was used to maintain the stability. The removal efficiency increased with carrier concentration. The concentration carrier concentration is increased from 0.2 to 0.04 you see the removal efficiency increased from 70% to 99% so excellent removal is obtained.

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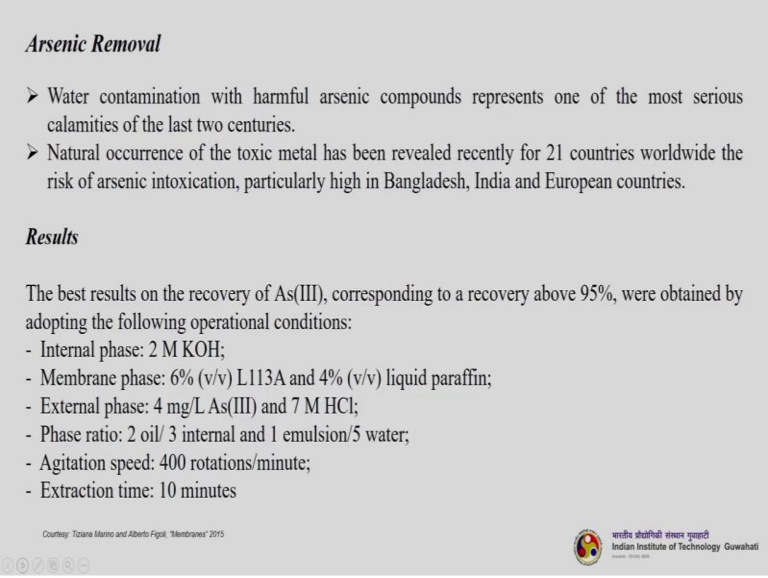

Arsenic Removal

- Water contamination with harmful arsenic compounds represents one of the most serious calamities of the last two centuries.
- Natural occurrence of the toxic metal has been revealed recently for 21 countries worldwide the risk of arsenic intoxication, particularly high in Bangladesh, India and European countries.

Results

The best results on the recovery of As(III), corresponding to a recovery above 95%, were obtained by adopting the following operational conditions:

- Internal phase: 2 M KOH;
- Membrane phase: 6% (v/v) L113A and 4% (v/v) liquid paraffin;
- External phase: 4 mg/L As(III) and 7 M HCl;
- Phase ratio: 2 oil/ 3 internal and 1 emulsion/5 water;
- Agitation speed: 400 rotations/minute;
- Extraction time: 10 minutes

Courtesy: Tiziana Marino and Alberto Figoli, "Membranes" 2015

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Then another cases arsenic removal arsenic is a big menace in SEM some of the ASEAN countries especially indo-Bangladesh border. So, water contamination with harmful arsenic compounds represents one of the most serious calamities of the last two centuries. Natural occurrence of the toxic metal has been revealed the for 21 current countries worldwide the risk of arsenic in toxification particularly high in Bangladesh, India and European countries.

So results is that the best result on the recovery of arsenic 3 corresponding to a recovery of above 95% was obtained by adopting the following operational conditions internal phase is 2 molar potassium hydroxide membrane phase is 6% volume by volume L11 3A this is a particular organic component and 4% by volume by volume liquid paraffin external phases 4 ppm, arsenic 3 and 7 M hydrochloric acid, 7 molar hydrochloric acid phase ratio is 2 oil into 3 internal and 1 emulsions 2 pipe water as it agitation speed is almost 400 rotations per minute and 10 minutes is the extraction time that was given.

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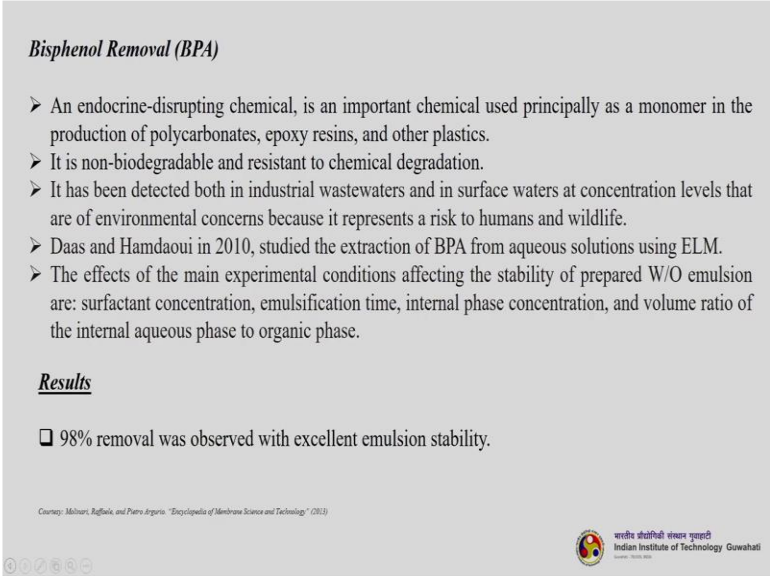

Bisphenol Removal (BPA)

- An endocrine-disrupting chemical, is an important chemical used principally as a monomer in the production of polycarbonates, epoxy resins, and other plastics.
- It is non-biodegradable and resistant to chemical degradation.
- It has been detected both in industrial wastewaters and in surface waters at concentration levels that are of environmental concerns because it represents a risk to humans and wildlife.
- Daas and Hamdaoui in 2010, studied the extraction of BPA from aqueous solutions using ELM.
- The effects of the main experimental conditions affecting the stability of prepared W/O emulsion are: surfactant concentration, emulsification time, internal phase concentration, and volume ratio of the internal aqueous phase to organic phase.

Results

☐ 98% removal was observed with excellent emulsion stability.

Courtesy: Molinari, Raffaele, and Pietro Argurio. "Encyclopedia of Membrane Science and Technology" (2013)

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So another case is Bisphenol removal endocrine disrupting chemicals is an important chemical used principally as a monomer in the production of polycarbonate, epoxy resins and other plastics. It is very big nuisance in the baby feeding bottle actually and for which there is a hue and a lot of cry. So it is non biodegradable and resistance to chemical degradation it has been detected both in industrial waste waters and in surface waters at concentration levels that are of environmental concerns because it represents a risk to humans and Wildlife.

Daas and Hamdaoui in 2010 studied the extraction of BPA from aqcuous solution using any LM. So, the effects of the main experimental conditions affecting the stability of the propeller oil water emulsion or surfactant concentration emulsification time, internal phase concentration, volume ratio of the internal phase to the organic phase 98% removal was observed with excellent emulsion stability.

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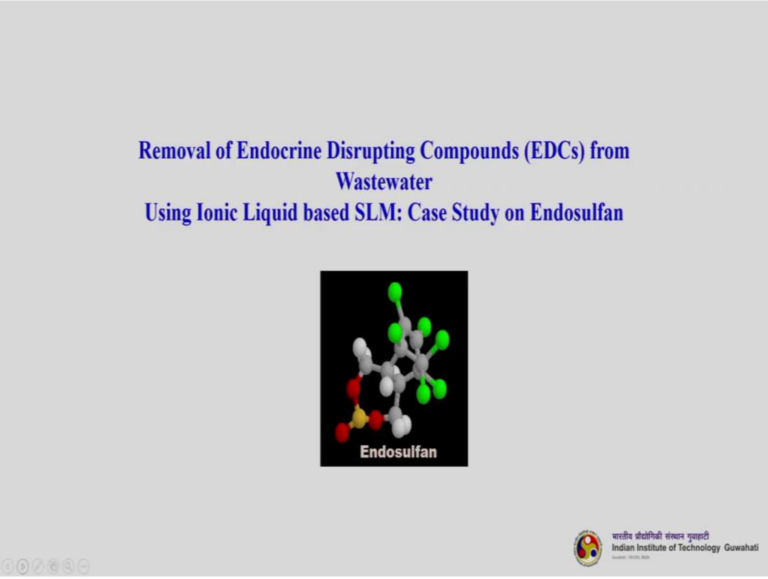

Removal of Endocrine Disrupting Compounds (EDCs) from Wastewater
Using Ionic Liquid based SLM: Case Study on Endosulfan

So very quickly I will show you one of the case study which was done by one of my PhD students Dr. Shanthiraja Pillai so what he has done is that he has removed endocrine disrupting chemical here it is Endosulfan from waste water using a ionic liquid based supported liquid membrane.

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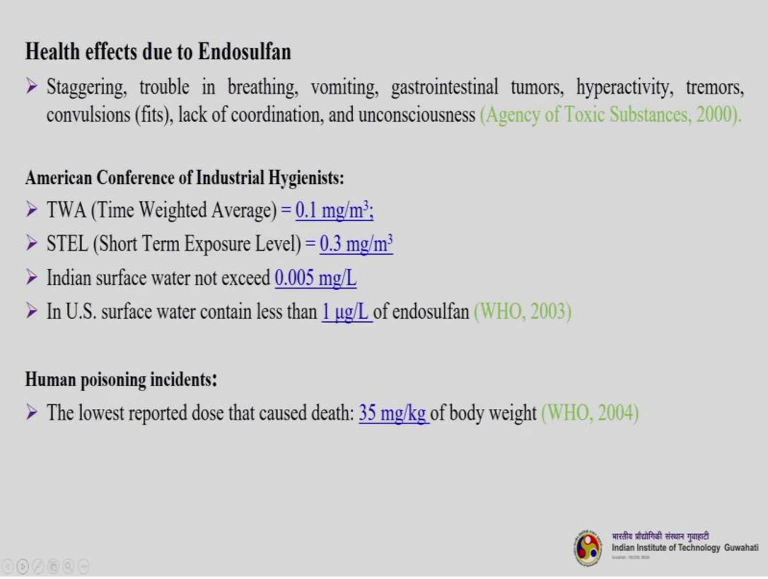

Health effects due to Endosulfan

- Staggering, trouble in breathing, vomiting, gastrointestinal tumors, hyperactivity, tremors, convulsions (fits), lack of coordination, and unconsciousness (Agency of Toxic Substances, 2000).

American Conference of Industrial Hygienists:

- TWA (Time Weighted Average) = 0.1 mg/m^3;
- STEL (Short Term Exposure Level) = 0.3 mg/m^3
- Indian surface water not exceed 0.005 mg/L
- In U.S. surface water contain less than 1 μg/L of endosulfan (WHO, 2003)

Human poisoning incidents:

- The lowest reported dose that caused death: 35 mg/kg of body weight (WHO, 2004)

Now let us quickly go through so Endosulfide is highly toxic so it is staggering trouble in breath it creates targeting trouble in breathing, vomiting, gastrointestinal, tumors, hyperactivity tremors convulsions, lack of coordination and unconsciousness says if you are continuously being exposed to and a endosulfan and you can see this time weighted average and short-term explosive levels is very high. So, human poisoning incident is already reported the lowest reported does that cause death is 35 milligrams per kg of body weight. So you can understand so this is highly toxic.

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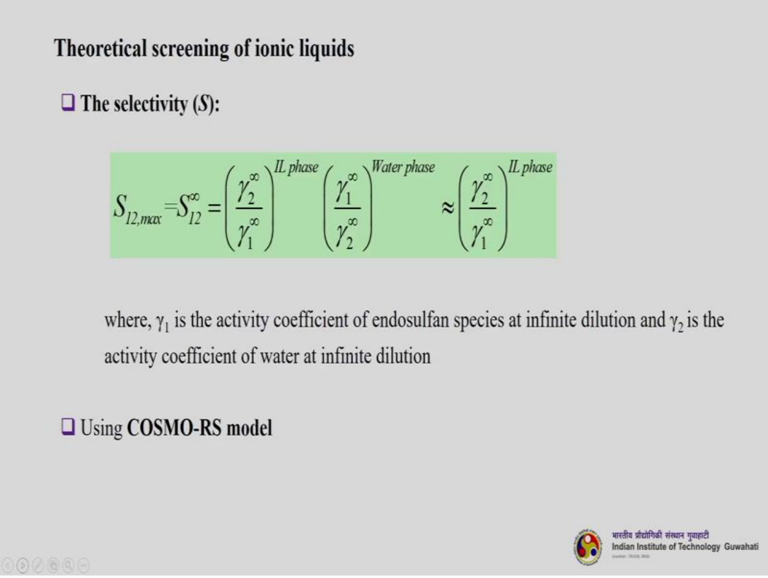

Theoretical screening of ionic liquids

- ☐ **The selectivity (S):**

$$S_{12,max} = S_{12}^{\infty} = \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right)^{IL\ phase} \left(\frac{\gamma_1^{\infty}}{\gamma_2^{\infty}}\right)^{Water\ phase} \approx \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right)^{IL\ phase}$$

where, γ_1 is the activity coefficient of endosulfan species at infinite dilution and γ_2 is the activity coefficient of water at infinite dilution

- ☐ Using **COSMO-RS model**

So, what we did actually we took to get chilly ionic liquids as one of the component of the membrane phase, basically the membrane phase is ionic liquid. So, ionic liquids are very resting solvents they are actually salts made up of one cationic group one and ionic groups we can choose a particular cation and choose a particular and anion fuse them together you would get ionic liquid. So, at room temperature there are room temperature ionic liquids which are called actually RTIL room temperature ionic liquids.

So, they are liquid at room temperature so we have used mostly RTILs so there are n number of ionic liquids available both commercially as well as you can prepare. So, which ionic liquids to choose for our particular application, so that is why you have done some theoretical calculations I will not go into detail about this so used on COSMO-RS model this based on activity coefficient thermodynamic concept actually. And you find out the selectivity using this equation right.

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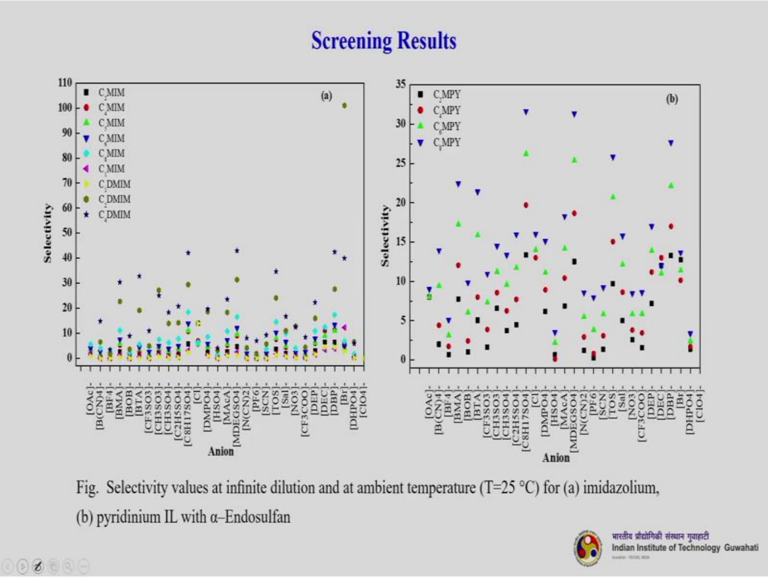

Screening Results

Fig. Selectivity values at infinite dilution and at ambient temperature (T=25 °C) for (a) imidazolium, (b) pyridinium IL with α–Endosulfan

So what you get is something like this so these are selectivities values at infinite dilution and ambient temperature for imidazolium, pyridium ionic liquid with alpha endusulfine. So, you can see then whichever is best let us say this is best here in this particular case in this particular case let us say this is best you take this ionic liquids. See if this is not commercially available then we have gone for the next one which is the next selective highest elective one over whose selectivity is the second highest and see if it is available commercially then take it. So this is how we have done some theoretical calculation so let us not anyway not go into that.

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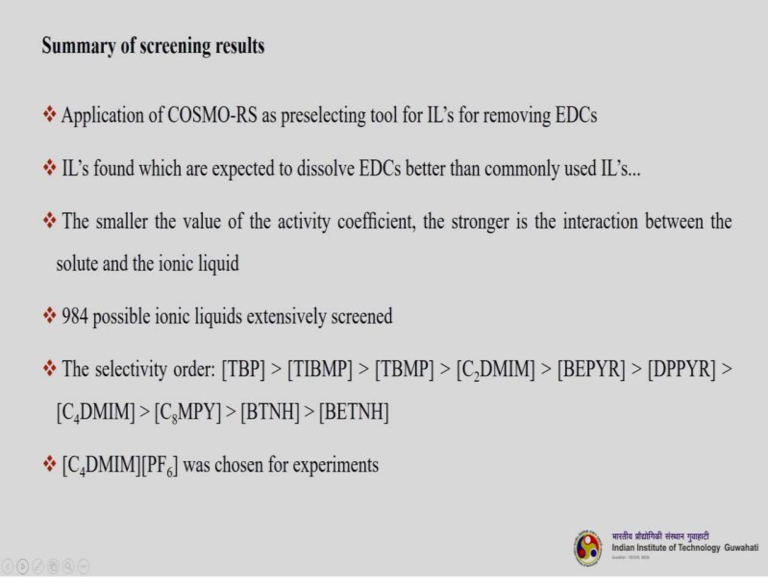

Summary of screening results

- Application of COSMO-RS as preselecting tool for IL's for removing EDCs
- IL's found which are expected to dissolve EDCs better than commonly used IL's...
- The smaller the value of the activity coefficient, the stronger is the interaction between the solute and the ionic liquid
- 984 possible ionic liquids extensively screened
- The selectivity order: [TBP] > [TIBMP] > [TBMP] > [C$_2$DMIM] > [BEPYR] > [DPPYR] > [C$_4$DMIM] > [C$_8$MPY] > [BTNH] > [BETNH]
- [C$_4$DMIM][PF$_6$] was chosen for experiments

So, applications of COSMO-RS pre-selecting tool for ionic liquid for removal of EDC's it is a oils found which are expressed to dissolve EDC's better than commonly used IL's. The smaller the value of the activity coefficient the stronger is the interact between the solute and the ionic liquid 984 possible ionic liquid we have screened. So, this is done using simulation see our theoretical skinning.

So this is the selectivity order that TBP is one particular ionic liquid is the hashed followed by T IBM PM so on. So, since we do not have a this ionic liquids available commercially so we have gone put the C4 DMIM PF 6 was chosen for our experiment. You have seen imidazolium based ionic liquid which hexafluorophosphate as the ion. So, this is your cationic group this is your anionic group.

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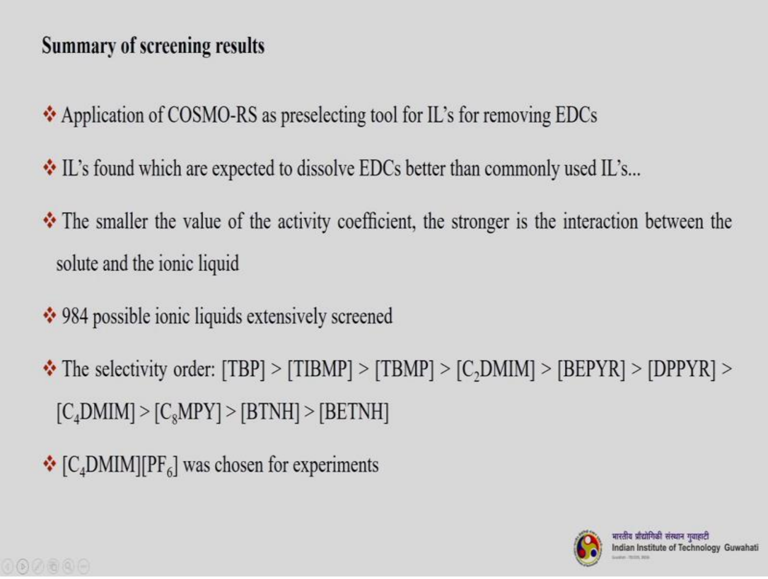

Summary of screening results

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So then we have to prepare the supported ionic liquid membrane, so we have prepared as I have just told you in few slides before how to prepare supported ionic liquid membrane. So, then you have to measure the flux using this equation minus V by A dC by dt later permeation.

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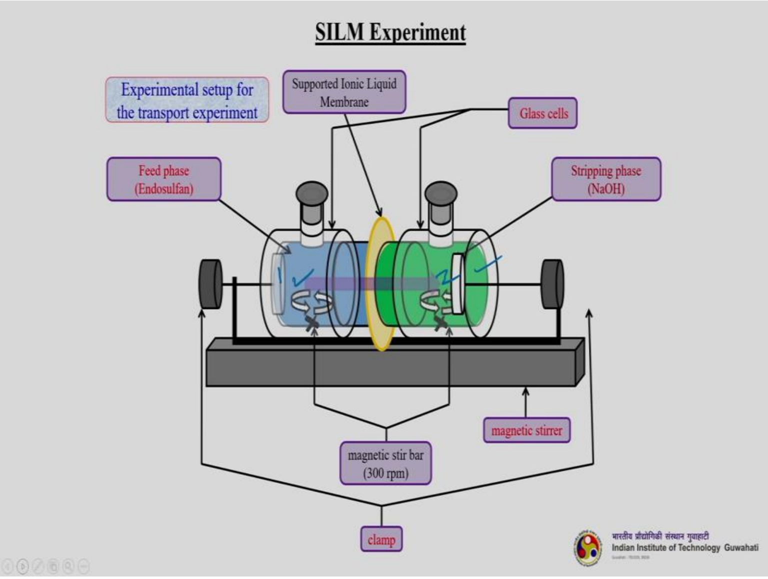

SILM Experiment

Experimental setup for the transport experiment

Supported Ionic Liquid Membrane

Glass cells

Feed phase (Endosulfan)

Stripping phase (NaOH)

magnetic stirrer

magnetic stir bar (300 rpm)

clamp

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Let us see how it has been prepared and done the experiments so SLM experiment. So, we have a magnetic stirrer plate something like this then what then we have a clamps fixed into that magnetic stirrer. Then we have two different cells glass cells. So, you can see this is one glass cell here which has come here then we have placed the supported ionic liquid membrane to the mouth of the glass the first glass chamber let us say the glass number one.

Then another glass chamber comes so let us see this is glass chamber 2 then it is printed and clamped to the setup. So, we have transport the feed phase here and we have to transport the receiving phase here. So, feed phase is under surfactant aqueous medium and stripping phase is your sodium hydroxide. Then it will be stirred then it is stir magnetic stirrer bar it is stir and this is closed and then stirrings takes place then your diffusion will start. This is the experimental setup for the transportation element.

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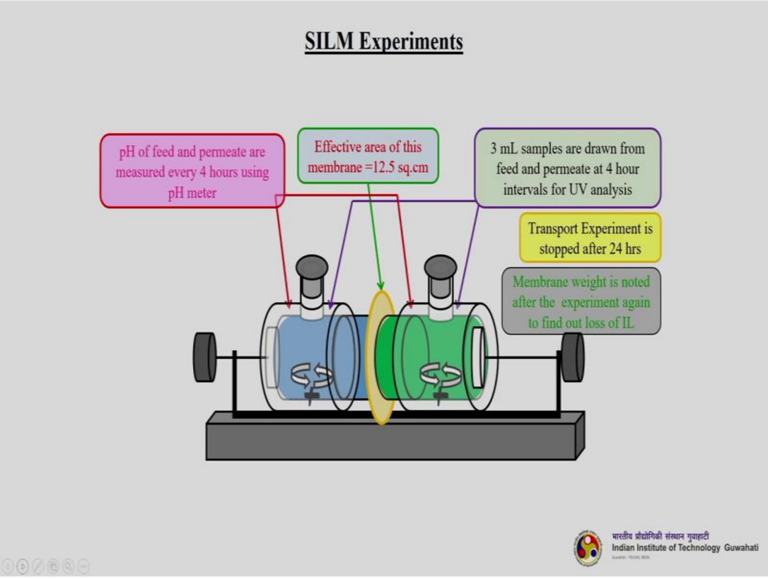

SILM Experiments

pH of feed and permeate are measured every 4 hours using pH meter

Effective area of this membrane =12.5 sq.cm

3 mL samples are drawn from feed and permeate at 4 hour intervals for UV analysis

Transport Experiment is stopped after 24 hrs

Membrane weight is noted after the experiment again to find out loss of IL

So, the membrane area is 12.5 square centimeter, centimeter square small membrane area in the lab scale. So, 3 ml of the samples are drawn from feed and permeate at 4 hour interval for UV analysis then pH and of the feed and permeate are measured every 4 hours using pH meter because since and endosulfine is moving so the pH of the feed as well as the receiving phase is keep on changing need to adjust that.

We have adjusted the pH also we have done some control experiments without adjusting the pH also. So, transport experiments is carried out for 24 hours then membrane weight is noted after the experiment again to find out the loss of pile. To see and to understand how effective is this supported ionic liquid membranes myself choose an ionic liquid basically they are green solvents. Second thing is that they are highly viscous so if the liquid membrane viscosity will be more high or will be higher, then its impregnation inside the porous membrane or the pores of the membrane support will be better, so that is the idea actually.

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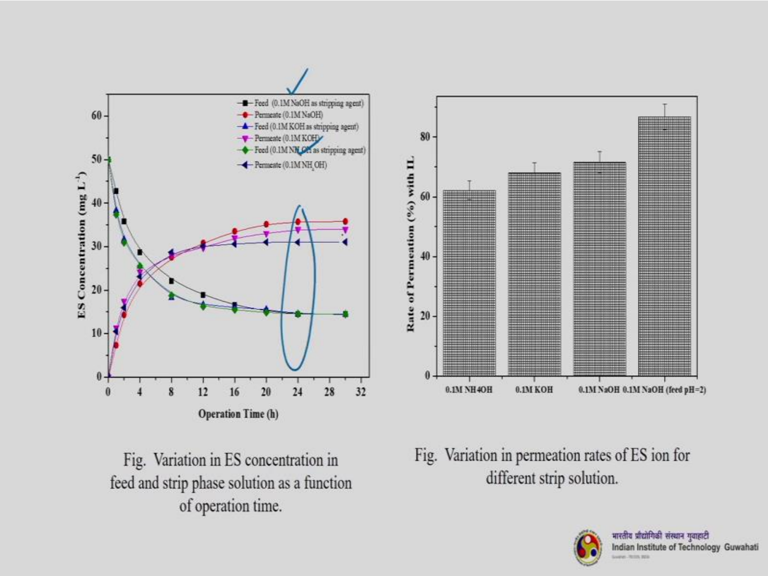

Fig. Variation in ES concentration in feed and strip phase solution as a function of operation time.

Fig. Variation in permeation rates of ES ion for different strip solution.

So this let us just quickly go through these are some of the results of the experiments basically you can see that here the concentration these have the concentration of the feed and result on how it is decreasing in the feed side and this is how it is increasing in the receiving side. This is same plotted in a different way then with different 0.1 molar sodium hydroxide then this one ammonium hydroxide as using as and another stripping phase.

So various in ensulfine concentration in feed in strip is as a functioning time so at time how so we have seen that almost after 24 hours no more change is there so we have stopped at 24 hours. So, this is with different stripping solution you can see that we have a ammonium hydroxide potassium hydroxide sodium hydroxide 0.1 molar, sodium hydroxide 0.1 molar which feed pH adjusted to 2. So, this particular has given the best separation more than close to 90% separation. So here we use that as the stripping phase.

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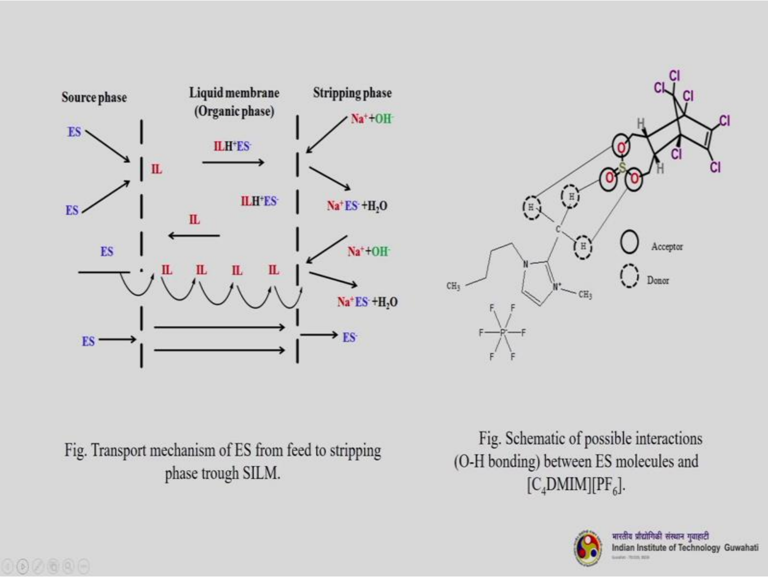

Fig. Transport mechanism of ES from feed to stripping phase trough SILM.

Fig. Schematic of possible interactions (O-H bonding) between ES molecules and $[C_4DMIM][PF_6]$.

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So this is the mechanism actually how what is happening so this is again try to understand this is one type of carrier mediated transport you can call it as a facilitated transport. Here that ionic liquid groups are behaving is actually a carrier so the endosulfine which is actually negatively charged when it comes then this is source feed it comes and sit here on the membrane and feed interface then diffuse to the membrane press and bind to the ionic liquid phase.

So you will get ILH plus EL minus this is an intermediate complex. Another intermediate complex is not stable so then it is moving in this direction by virtue of the concentration dependence but it comes here at the interface of the receiving phase and the membrane phase. So, by virtue of your concentration difference it will break and it will remove the endosulfine. The endosulfine result one will bind to the sodium hydroxide what about it to present here and will give you Na plus ES minus it becomes a salt.

Since the molecular weight of this particular component is much higher there will be no back diffusion. So, back diffusion has been discarded out.

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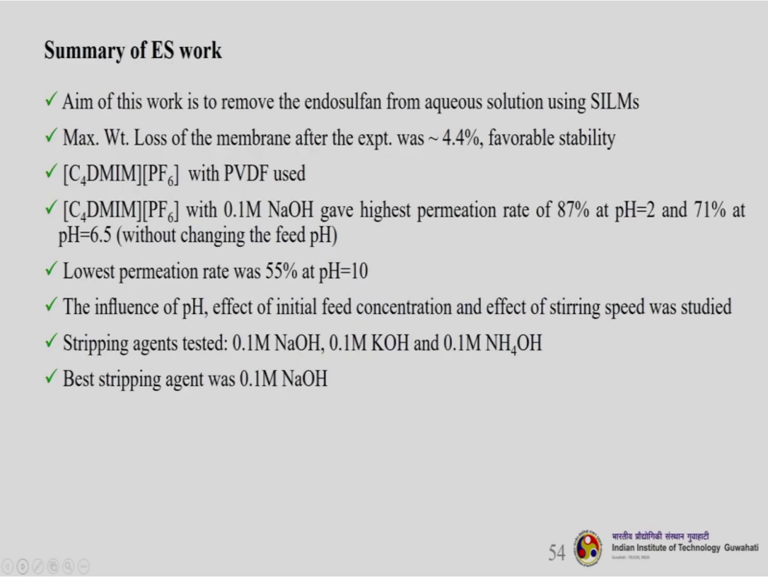

Summary of ES work

- ✓ Aim of this work is to remove the endosulfan from aqueous solution using SILMs
- ✓ Max. Wt. Loss of the membrane after the expt. was ~ 4.4%, favorable stability
- ✓ $[C_4DMIM][PF_6]$ with PVDF used
- ✓ $[C_4DMIM][PF_6]$ with 0.1M NaOH gave highest permeation rate of 87% at pH=2 and 71% at pH=6.5 (without changing the feed pH)
- ✓ Lowest permeation rate was 55% at pH=10
- ✓ The influence of pH, effect of initial feed concentration and effect of stirring speed was studied
- ✓ Stripping agents tested: 0.1M NaOH, 0.1M KOH and 0.1M NH_4OH
- ✓ Best stripping agent was 0.1M NaOH

So, I hope you will understand how actually we have carried out the experiment. So, in a nutshell we can say that aim of this work of study is to remove the endosulfine from aqueous solution using the supported ionic liquid membrane. Some maximum weight loss of the membrane and after experiment was 4.4%. so, we can say that it is favorable is stable so C4 DMIM PF6 with PVDP is used PVDP is the support polyvineyldiflouroethelene porus support was used.

And this particular ionic liquid with 0.1 molar sodium hydroxide gave the highest permeation that is 87% at pH 2 and 71% at pH 6.5 that means without changing the pH. So, lowest permeation was 55% at pH stem the influence of pH effect up initial feed concentration an effect of stirring speed was studied. Stripping agents used the sodium hydroxide, potassium hydroxide and ammonium hydroxide.

And by stripping agent was 0.1M sodium hydroxide. So, I hope you have got a test of how these liquid membranes were being used experimentally to remove certain compounds with this I conclude today's lecture.

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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.

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So, mostly it is taken from this scanner and Mulder pro liquid membrane okay. So, please refer these books and in the next class will be discussing about gas separation. So, different types of membranes and modules used for gas separation how the transport happens inside and during gas separation and factors that affect gas separation and various applications. So, thank you very much in case you have any query please feel free to write to me at kmohanty@iitg.ac.in thank you very much.