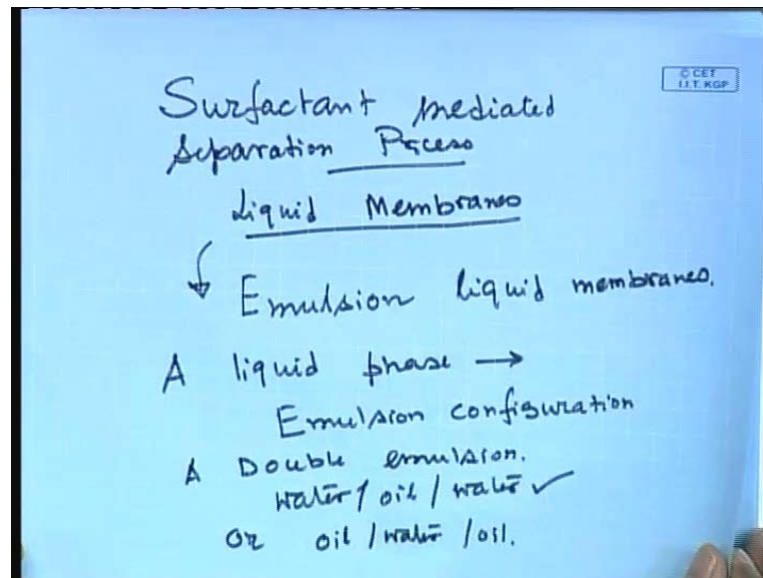


Novel Separation Processes
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Lecture No. # 33
Liquid Membrane

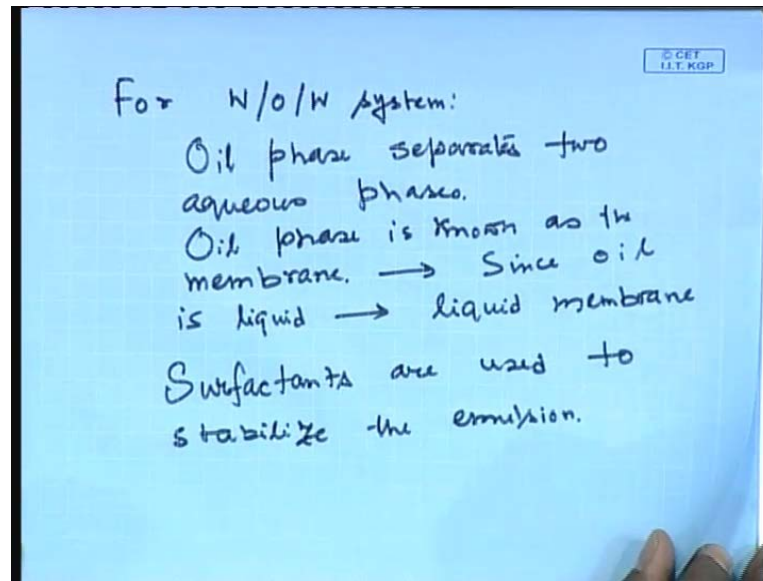
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We will now start the next at the third surfactant mediated separation process, that is the liquid membranes previously we discussed two more that will the cloud conduct extraction and (O) ultra filtration. Now, will talk about the liquid membrane and in this chapter we will be talking about the emulsion liquid membrane only. There are two things, there 2 liquid membrane one is supported by liquid membrane another is the emulsion liquid membrane and the talking about the emulsion liquid membrane only.

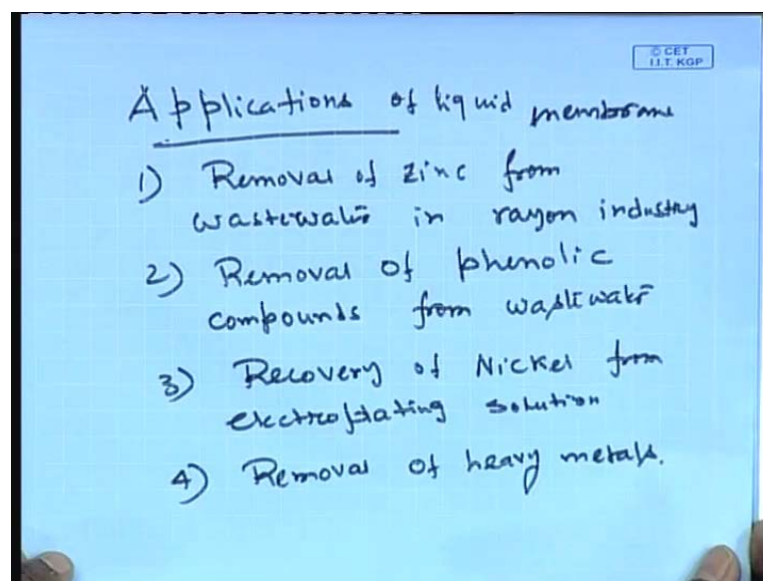
So, it is basically the liquid phase is involving in emulsion configuration. A liquid phase that has emulsion configuration and it is basically a double emulsion. That means, you must having a system like water, oil water or oil water, oil system that will be generate talking about the water oil water system will be talking about this system will not talking about the oil water oil system.

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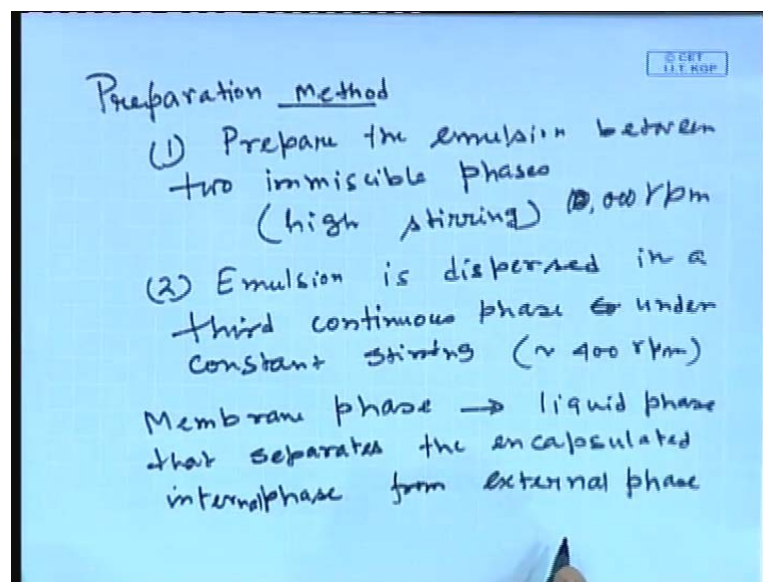
Now, for water oil water system, the oil phase separates 2 aqueous phases, the oil phase separates 2 aqueous phases and this oil phase is known as the membrane and since, the oil is in liquid phase is called a liquid membrane. Now, surfactant is used for stabilizing the emulsion. So, one uses the surfactants to stabilize the emulsion. So, will just look into some of the applications of the liquid membrane systems, application of the liquid membrane systems.

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So, it is a specific separation and extraction of metal ions then will be the metal ions for example, removal of zinc from waste water in rayon industry. Number 2, removal phenol this are the concentration phenol, an aniline, phenolic component like, Meta nitro phenol, Para nitro phenol, there are obtain in the refineries in the areas around refineries. Removal of phenolic components it is a group of components phenolic components, they customise (()) in nature from waste water. Recovery of nickel from electroplating solution, removal of heavy metals. So, for if there are loss of you know inorganic can be removed by using liquid membrane, there are loss of organic can be can be removed by using the liquid membrane as well as.

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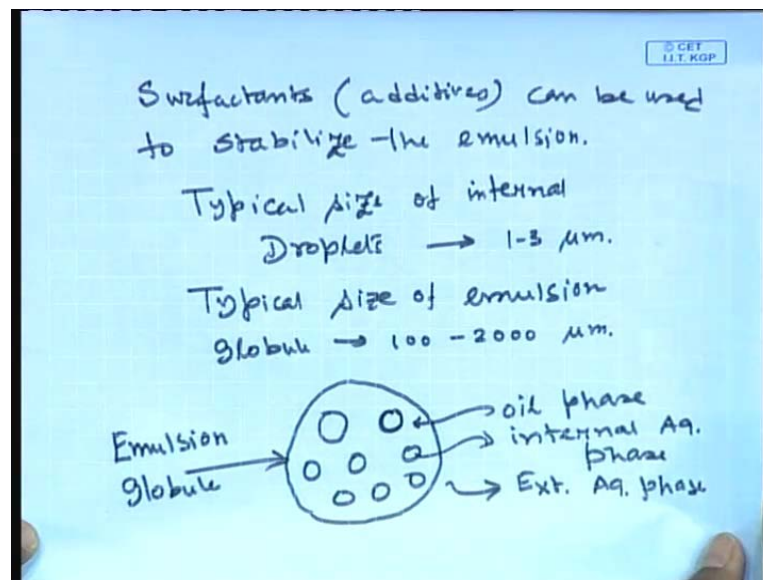
Now, next we see now these liquids membranes are prepared, preparation method. First you have to prepare the emulsion between two in visible phases, prepared the emulsion between 2 immiscible phases, that means oil and water, aqua phase and there are equipments called emulsion fire. What is emulsion fire? Is nothing but a tank which is attached to a starter and let say stirring is pretty high.

So, basically you need two phases and put it and the high stirring and the emulsion globules will be formed, then once the emulsion is produced, the emulsion phase is dispersed in a third continuous phase under the constant stirring and the stirring will be here, in the order of around 10,000 RPM, in that order and second their one emulsion is produced the emulsion is dispersed that means, it place it in a continue phase another

aqua phase may be dispersed in a third phase, third continuous phase under constant stirring and in this case stirring speed will be much **much** lower and it will be in the order of let say 300 to 400 RPM in that order of magnitude.

Now, membrane phase is the liquid phase is separates encapsulate internal droplets, in the emulsion from the external phase. What is the membrane phase? Membrane phase is the liquid phase that separates the trap or encapsulated internal phase from external phase. So, in the emulsion, the oil will be the aqua phase will be encapsulated in the oil phase now, you put this bigger babul **the** the oil droplet which is encapsulated in the inner phase, it will be outer phase. So, oil will be separating the outer aqua phase from the inner outer phase.

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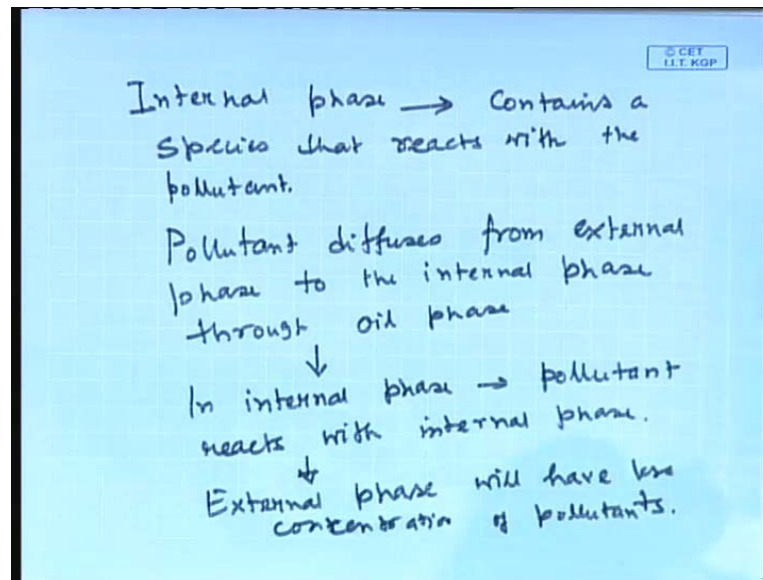


Now, we have to use the surfactants or additives are used surfactants, which are known as the generally the additives can be used to stabilize the emulsion. Otherwise, the emulsion will be will be broken. Typical size of internal droplets is 1 to 3 micron, on the other hand the typical size of emulsion globule will be 100 to 2000 micron. So, the basically will be having emulsion globule is something like this and with in here, we can we can take various internal droplets and will be having outer phase.

So, this is the oil phase, this is the internal aqua phase and the outside is the external aqua phase and this is an emulsion globule that means, it has a size of around 100 to 2000 micron. On the other hand each of the globule will be containing number of

internal globule the inner phase internal droplets, which will be in the size in the order of 1 to 3 micron. So, basically will be having a liquid membrane system and this oil phase is called a liquid membrane, that separate the internal aqua phase from the external aqua phase.

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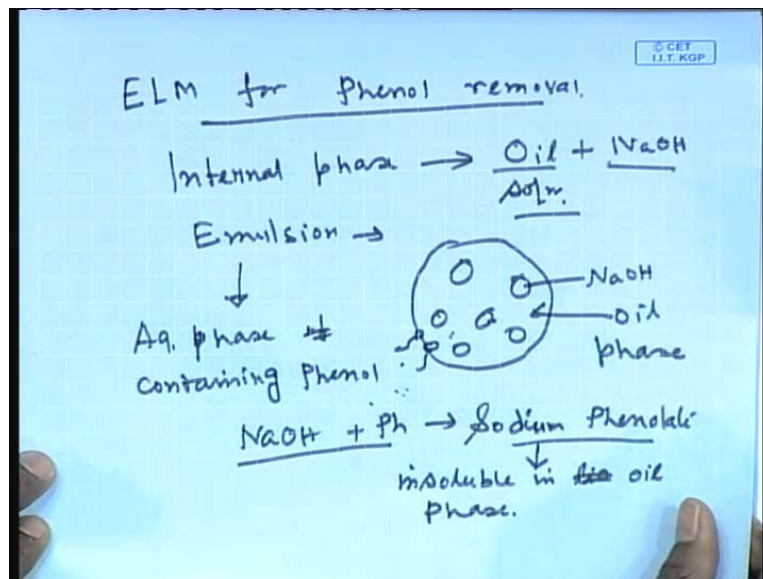
Typically, the internal phase contains some species, it contain a species that react with the pollutant. So, that concentration of the pollutant within the internal phase will be minimum. So, that mean you are maintaining a maximum driving force during the system then, what it does that the pollutant diffuses basically, pollutant is present in the external aqua phase that is first we have to produce the emulsion that will placed emulsion in to the pollutant containing external phase.

So, what the pollutant will do now, the pollutant diffuses from external phase to the internal phase through the membrane for the liquid phase, the oil phase through oil phase. So, when it reaches the internal phase it reacts with the species present in the internal phase. So, in internal phase the pollutant that means, solute can react with internal phase particular component present in the internal phase. Now, the product of the reactant reaction will be larger in side it cannot diffuse out. So, what will be the essence it will do?

So, therefore, the external phase after some time, this external phase will have less concentration of pollutants. Now, since therefore, after sometime all the pollutant some

in the external phase will diffuse to the membrane phase and going in to the internal phase within the emulsion globules. So, therefore, will be having after sometimes will be having a emulsion various emulsion globules, which are loaded with the pollutant. Now, since the emulsion globule in larger in size, we can separate them out by will using an ordinary filter paper. So, in the product in the filtrate what will be having the external phase, which will be having less concentration of the pollutant, which will be lean in the pollutant. So, thus the emulsion liquid membrane occurs, works.

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So, let us talk about the one particular example, emulsion liquid membrane for phenol removal. Now, you are internal phase will be basically produce by oil plus N a O H solution. So, you prepare the emulsion by adding a **fixed** fixed volume of oil and fixed volume of N a O H and then under high studying, the emulsion will be prepared. The emulsion globule will be having spheres, smaller spheres of N a O H there will be encapsulating the N a O H solution and this will be the oil phase. Now, when you place this emulsion in a aqua phase, then will be placed emulsion in a aqua phase of aqua phase containing phenol let say.

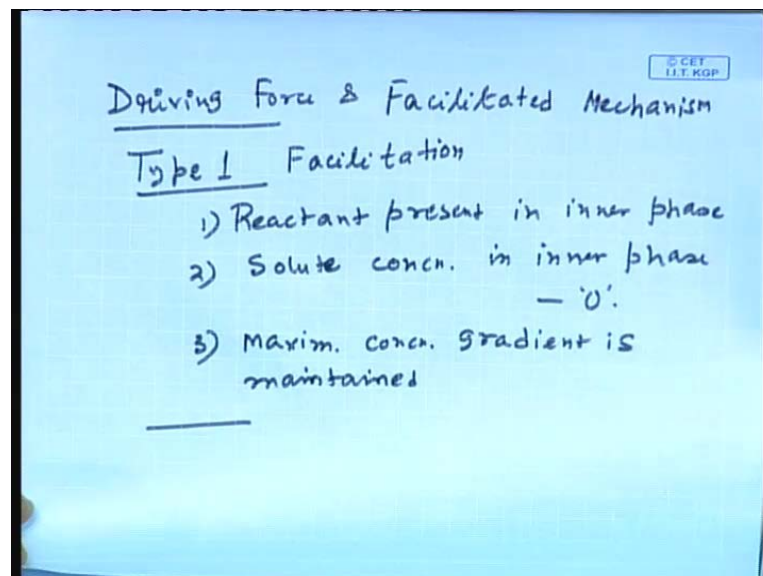
What phenol does? Phenol diffuse through the membrane phase let say this is phenol, this phenol diffuse through the oil phase of the membrane phase, it reaches into the sodium hydroxide. In the inner phase and sodium hydroxide react with phenol to form

sodium phenolate, this is sodium phenolate being larger in size, they are sodium phenolate is insoluble in the liquid phase, this is insoluble in oil phase. So, what it does?

It basically being it remains trap within the emulsion globule. So, all of the inner phase will be having the sodium phenolate and though will be trapped with in the inner phase, because they cannot come out because it is insoluble in the oil phase. Now, because of the reaction the concentration of what is the concentration of the phenol in inner phase? The concentration of phenol in the inner phase will be equal to 0 and the concentration of the phenol outside there is no phenol present in the inner phase, it is only sodium phenolate and phenol is present in of side out of outer confluence phase. So, it maintains the maximum concentration gradient that means $c_{out} - 0$.

So, it maintains the maximum concentration gradient across the inner phase and the outer phase and phenol will keep on diffusing through them through the oil phase. So, therefore, after sometime the emulsion of the will be loaded by solute phenol and this emulsion globule can be separate by a filter paper and you will be getting the water which will be very lean in phenol concentration, that is the typical fundamental principle of emulsion liquid membrane.

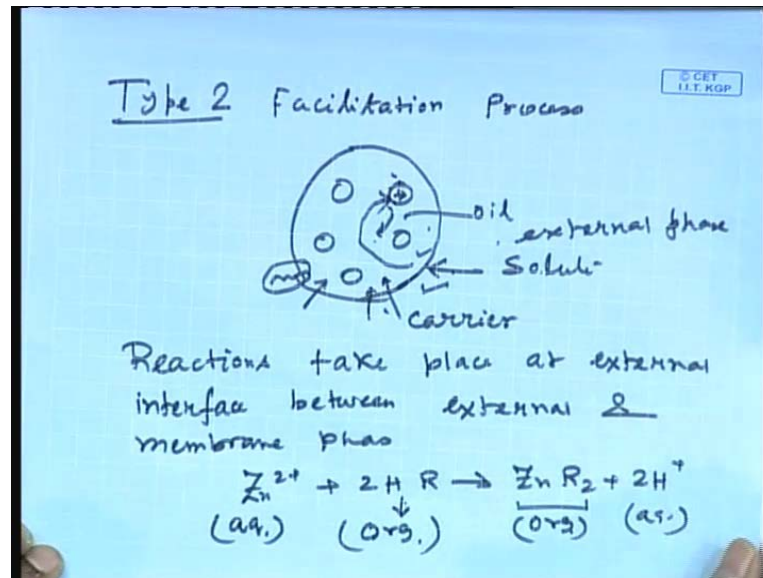
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Now, let us look into the driving forces and facilitated mechanism, there are two types of facilitation one can have, this is one is type 1 facilitation. In type 1, we have a reactant present in the inner phase number one laminar is writing the variant features. So,

therefore, this reactant reacts with the solute. So, therefore, the solute concentration in inner phase is 0. So, you maintained the maximum concentration gradient, the product being incapable to diffuse through the oil phase so, it remains in trap here.

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So, this is this is a, you know type 1 facilitation process. In type 2 facilitation process and this type 1 facilitation will just discussed, in the case of removal of phenol by using a inner phase loaded to sodium hydroxide. In type 2 (O) facilitation diffusion of species are carried out across the membrane phase by incorporating a carrier compound or complex present in the oil phase. In this case the diffusion will occur, let say this is the emulsion globule now, the solute is present.

Now, in the oil phase are in the membrane phase, we use 1 carrier or a compound, 1 carrier is used, these carriers make the complex with solute. So, this complex will be diffusing through the oil phase and it gets into the inner phase and in the inner phase, the complex break down and the solute will be moving in to the inner phase and the complex comes out the oil phase.

So, it maintains the composition of the oil phase and then this solute will be in the inner phase it will be reacting with another internal again. So, the concentration gradient becomes maximum, what is the facilitation it will be, this process will be faster or why it will be faster? Because whenever will be forming a complex of the solute carrier, the

concentration difference between the external phase and the oil phase will be maximum because there is no concentration, there is no solute present in the oil phase.

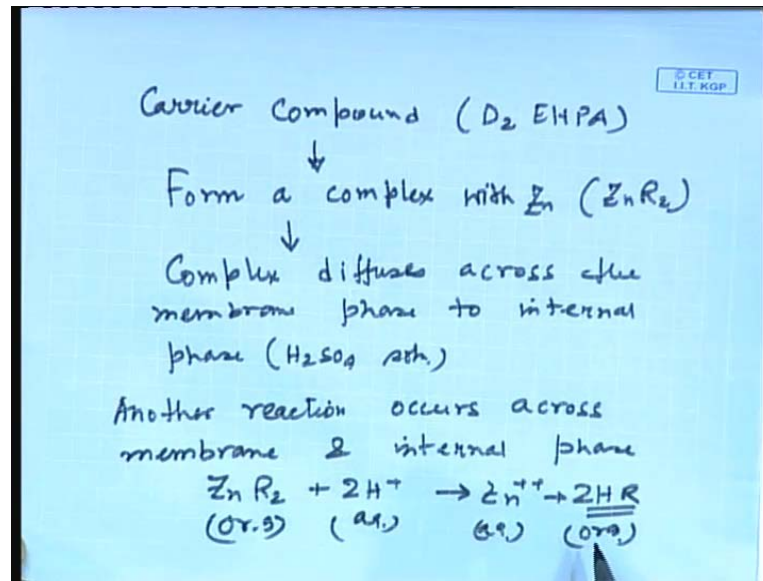
So, your maximizing the concentration difference of the driving force in two phases, one in across the oil external phase junction, this is the external phase at all external phase boundary you are maximizing the solute concentration, because in the in the internal, in the carrier phase, in the oil phase the carrier plus internal carrier plus the solute mix a complex. So, the solute concentration will be 0 there is basically a complex.

So, more solutes will be diffusing through it, we are making a maximum concentration, maintaining a maximum concentration gradient there. Now, once this carrier will **will** get to torch of the internal phase, it releases the solute and it indicates, the react, the solute. So, therefore, you are maintaining again a maximum concentration different there. So, it is the type 2 facilitation process.

So, what is the difference between the type 2 facilitation processes and type 1 facilitation process? In type 2 facilitation process, we have a facilitated or a carrier present in the membrane phase or in the oil phase, that makes a complex with the solute and transport the solute their as the internal phase more easily, it facilitates the transport of the solute as the internal phase. So, will be having the reaction. So, there are 2 reaction take place at external phase.

External interface between external and membrane phase and again about this boundary, this is the boundary talking about the first reaction occur. So, this reaction takes place, let us talk about the zinc transport of the Zn^{2+} plus plus. So, this is the solute Zn^{2+} plus plus, plus $2HR$, HR is an organic it is the carrier organic ZnR_2 , plus $2H^+$ plus this reaction take place. So, zinc was in the aqua phase or the external phase and HR is the carrier or it is an organic phase, this is the carrier present in the oil phase, this is the react to the zinc and produces a complex and releases protons, this also organic phase and this is the aqua phase.

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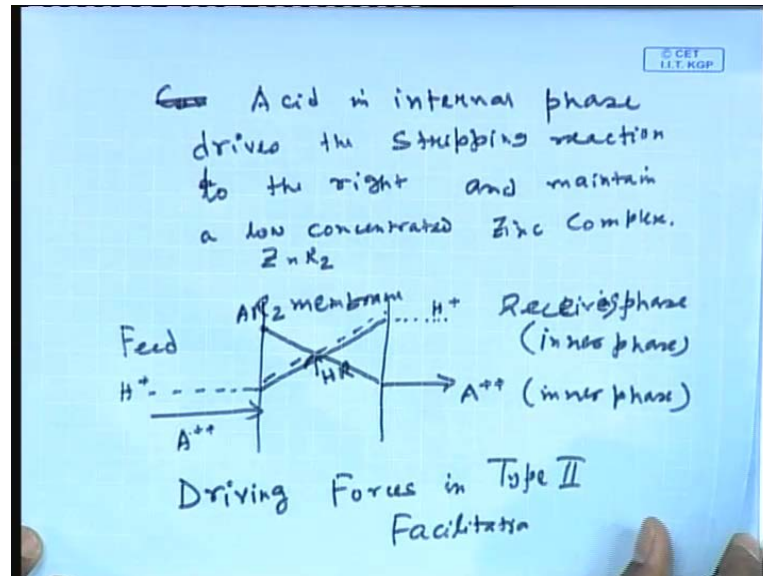
Now, what is the typical carrier compound? A typical carrier compound is called **deaf** D 2 EHPA, it is a big name and this forms a complex with the zinc and we have denoted these complexes as ZnR_2 . Now, this zinc complex diffuses through the internal phase to the **to the** through the oil phase to the internal phase right. This complex diffuses across the membrane phase to internal phase and internal phase contains sulphuric acid solution internal phase contains sulphuric acid.

Now, so there will be another reaction occurs at the interface of internal or oil phase or the membrane phase. So, another reaction occurs across membrane and internal phase what is the reaction will be ZnR_2 plus, $2H^+$ plus going into Zn^{2+} plus, plus $2HR$. So, again it is an organic phase and this is an aqua phase this is in aqua phase and this is organic phase. So, you get back your HR . So, the carrier medium get the carrier compound and it will be remain in the aqua in the oil phase or in the membrane phase. So, concentrate acid now, in internal phase strip Zn from the membrane phase to become Zn^{2+} ion and donates proton to the extracted in the membrane phase.

So, once it donates the proton to the membrane phase. So, once it donate the proton to the membrane phase to get back you carrier medium and zinc will be going to the internal phase. So, one can get back now, one can destabilize you can separate out the emulsion and you can break the emulsion by you can use the simply a filter paper, because the emulsion globule will having the phi in the order of 1000 micron, you use

the simple filter paper and separate out the emulsion, then break the emulsion and get back your pollutant separately pollutant internal phase separately.

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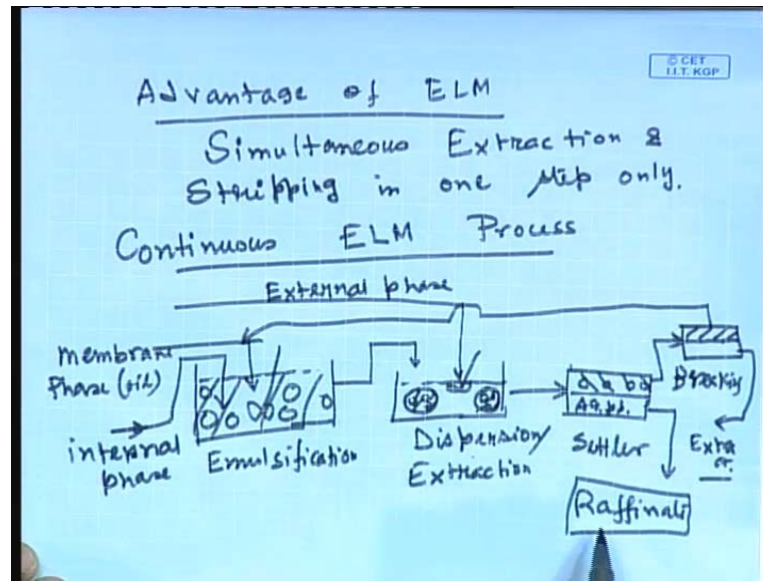
So, concentrated the acid internal in the internal phase, drives the stripping reaction to the right and maintain a low **low** concentrated zinc complex $Z_n R_2$, why means that zinc protons are present in the internal phase at higher quantity basic it is an acid solution. So, it drives the reaction for the right. So, at the internal phase this concentration will be absolutely low and it will be getting back to $H R$ and the zinc will be walking into the internal phase. So, in the first reaction will have the separation, in the second reaction we have the stripping or extraction.

So, if you like to write down the driving phase curve in type 2 facilitation, this is the feed are the external phase containing the react in a pollutant and let say zinc plus plus, it forms $H R$ their the $H R$ will be and this is let say the H plus profile and it forms $H R$ there. So, this is $H R$ profile and it donates protons in the receiving phase or the inner phase **or inner phase** and will be having a membrane phase here.

There is the oil phase and this A plus plus will react with $H R$ and it for this produces a complex of let say $A R_2$ this complex will be having a higher concentration at the interface because here there is no $H R$ there is no presence of a react to their and this will then diffuse to the membrane phase and it release the A plus plus in to the inner phase. There is the typical driving force diagram in a type 2 facilitation process.

So, there are the transport of the pollutant is being facilitated by a carrier by a complex in carrier compound present in the oil phase and this complex diffuses through the oil phase and the membrane phase. It goes into the inner phase and releases, another reaction expressed and releases the pollutant in to the internal phase and it will be strip and concentrate will in the internal phase that is the principle.

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Now, let us write down the advantage of liquid membrane of emulsion liquid membrane here, the at most the first and the strongest advantage is we have the simultaneous extraction and stripping in one step only. Next, we look in to a semantic of continuous ELM process, first we have the internal phase you produce you do the emulsification, we add the membrane phase that means, the oil phase put the membrane phase oil phase, then you add internal phase do a high stirring. What is the result?

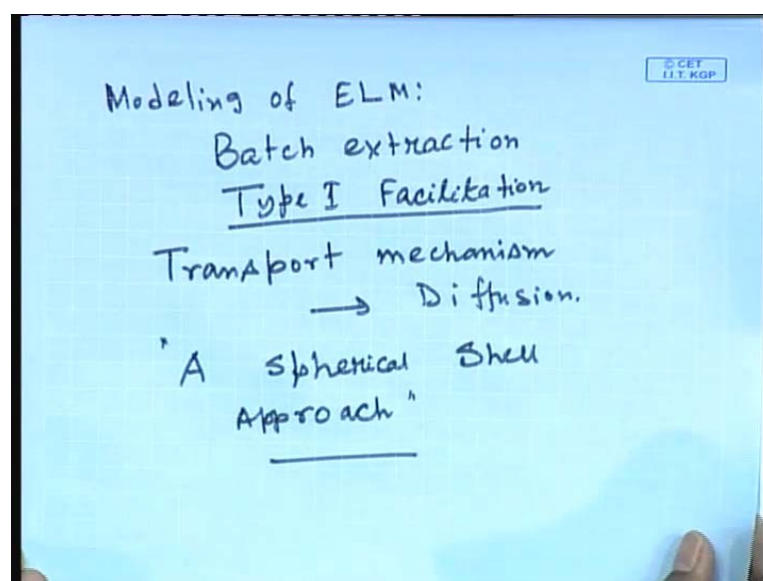
The result is will be producing the emulsions, will be producing the emulsion globules, this emulsion will be trapping will be containing various small droplets of inner phase, then the emulsion is taken out and it is feed into the dispersion or the external phase. Here the dispersion or extraction occurs and you add the external phase here that means, in the first box you are carrying out the emulsification. In the second box you are putting the emulsion in to the external phase it will be that much. Now, again this is will be must having the continuous stirring at lower stirring speed. So, that will be emulsion will not be settle on the bottom.

So, will be having the bubbles of emulsions having internal droplets with the oil phase along with them, will be having the bubbles are emulsion trapped in the internal phase in the oil phase, then once this is done then you send it to a settler. So, here what happens all the transport phase that means, solute from the external phase it gets transported through the oil phase into the internal phase and then you send this to a settler, this is the settler.

So, what happens the settler, this is the settler it **it it** separate into two phases will be having the oil rich phase and will be having the aqua phase, we having the emulsion here and will be having the aqua phase here this is called a Raffinate and this emulsion is taken out, it goes to a chamber it is known as you know demulsification or breaking of the emulsion and again it will be having the 2 phases, will be having a membrane phase and membrane phase will be recirculated to this phase and will be having extract phase.

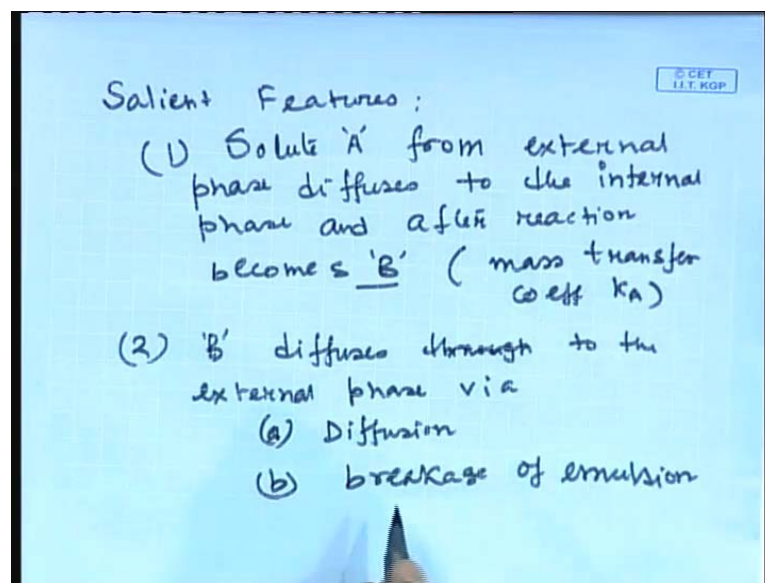
Now, in this whole process the Raffinate stream will be the external phase external continuous phase, which will be dividing of pollutant. That means, this is the final product where there is no pollutant present almost negligible amount of pollutant present. On the other hand in the extraction, in the extract phase, **extract phase** in the emulsion of that you get after the emulsion breaking with the extract phase contain the whole of pollutant present in a concentrate manner.

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So, you separate out the pollutants from the Raffinate into the Raffinate phase and get a concentration version of the pollutant in the extraction phase that is how a continuous liquid membrane system will occur. In the next what will see will try to module the mass transfer of the system, emulsion liquid membrane system and first will talk about a batch extraction process and will be talk talking about the type one facilitation. So, there is only one internal phase which is contains the reactor that react will be reactant, that react with the pollutant that will be diffusing to the oil phase, you are not assuming there is the another phase is the present in the oil phase that produce a complex in with the pollutant.

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So, then transport that involves transport mechanism, that involves in the type 1 facilitation is diffusion is nothing but diffusion mechanism and a spherical shell approach is taken to model the system, this know as a spherical shell approach there are the various salient features of this module early state first solute A form external phase solute A is the pollutant there you know heavy metal ion. So, citations from in external phase diffuses to the internal phase and after reaction, it becomes B.

The solute A reacts it diffuses to the membrane phase goes in to internal phase, you have to a reactant present A reaction that and produces the complex reacts the sodium phenolate, sodium phenolate is termed as B and this whole process will be associated with the mass transfer coefficient let say k times K_A substitute k substitute a we can

affective mass transfer coefficient K_A . The second step is that B diffuses **diffuses** to the external phase.

So, there are 2 the B can also diffuse to the external phase. In some cases the most of the cases it is not soluble in the oil phase. So, if there is diffusion is bulk, it is presented, it is encapsulate within the internal phase, but engine you can say the B be can diffuse to the external phase via through 2 mechanism. Via number 1 and number 1 is the diffusion and talking about the complex that is coming out through the oil phase through the external phase now, diffusion and second is via breakage of emulsion.

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(3) In external phase, B can get converted to A

Thus, 'A' can exist only in external phase
 'B' can exist only in internal phase

NaOH + Phenol → Phenolate

Diagram: A circle represents an emulsion globule. Inside is the internal phase containing B. Outside is the external phase containing A. An arrow points from B in the internal phase to A in the external phase. Another arrow points from H₂SO₄ in the external phase to the internal phase. A legend on the right states: B: NaOH, A: Phenol.

So, these are the only 2 mechanism by use the complex can come out to the external phase and the breakage of emulsion is always possible because when the emulsions are always stable, some of them some fraction of them will be always you know breaking at the same time. And in the external phase when the internal phase comes to the external phase, in external phase B can get converted to let say original pollutant A, A can exist in only internal phase. A can exist only in external phase right.

So, there is no A anywhere, it can it can be exist in a form only the external phase and B can exist B is the complex. So, it can exist only in internal phase and in internal phase that reaction occur, the reaction will be N a O H plus phenol giving it a phenolate. So, can have a typical semantic, this is an emulsion globule this is the internal phase, internal

volume of the internal phase that means, more be the internal phase, more will be the breakage, less will be the internal phase less will be the breakage.

So, therefore, the minus dV_i/dt is nothing, but the rate of loss, rate of reduction of the internal phase volume, this is proportional to interface volume, internal phase volume and this proportional constant is known as ϕ and it is known as the breakage coefficient. You can integrate this equation and finally, will be getting V_i is equal to V_{i0} exponential minus ϕT . So, internal phase volume at any point of time will be given as the initial internal phase volume this V_{i0} is the initial internal phase volume, multiplied by exponential minus ϕT . So, this is the internal phase volume at any point of time t total volume is constant.

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At any point of time,
 $V_e + V_i = V_0$

$V_e = V_0 - V_{i0} e^{-\phi t}$

→ Volume of external phase at any point of time.

Example: Ext. phase → Phenol + H₂SO₄
 Int. phase → NaOH.
 ↳ Sodium Phenolate

None of Sod. Phen. ← comes to external phase through breakage

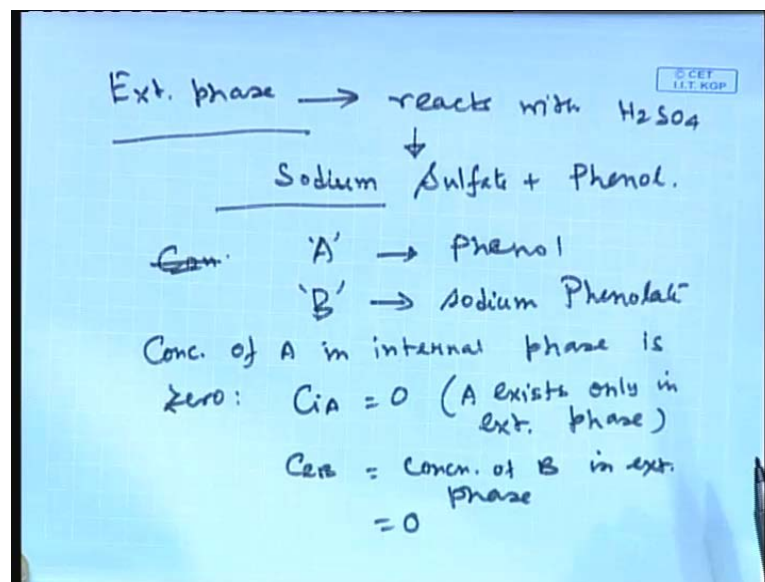
So, total volume is return as of the system is V_{naught} is equal to V_e naught plus, V_i naught, v_{naught} is the total initial volume, this is the total V_e naught is the total external phase volume. Initially, external phase volume, this is the total internal phase volume both of at all this are at time t equal to 0, later on it will be changed and at any point time will be having the volume, you know conformation will be met point of time will be having V_e plus V_i is equal to V_{naught} . The total volume will be comprised the two things, one is the external phase volume, one is the internal phase volume.

Now, you can combined this thing you can you can write V_i is equal to V_{i0} e to the power of minus ϕt and V_e can expressed as, v_{naught} minus V_{i0} e to the

power of minus phi t. So, this expression gives you the volume of external phase at any point of time. Now, in a present case you are considered the example, that we are considering in the present case is does removal of phenol.

So, the external phase has it is slightly acidic phenol plus sulphuric acid, that constitute the external phase, the internal phase is sodium hydroxide. So, in the internal phase the phenol and sodium hydroxide reacts and it produce a sodium phenolate. Now, some amount of sodium phenolate comes out to the external phase through breakage, some of sodium phenolate comes to external phase through breakage and when it comes out the external phase it react.

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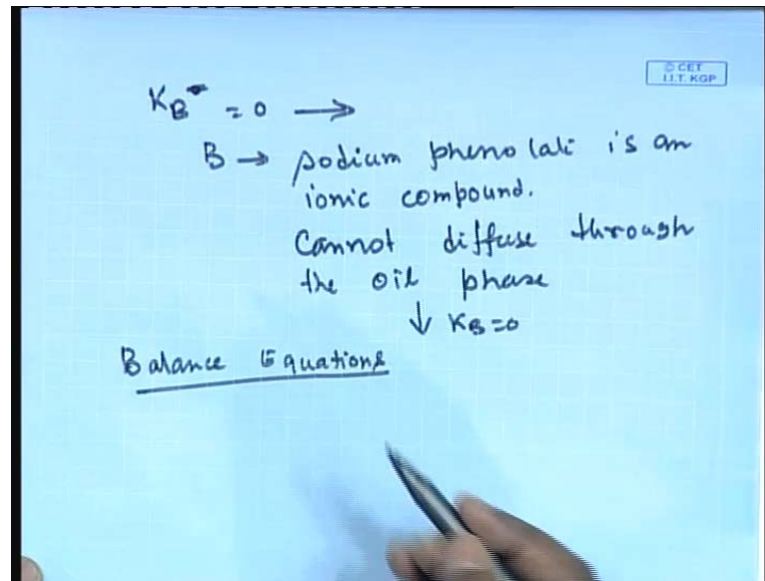


So, sulphuric acid again to produce phenol and sodium sulphate, when it comes to the external that amount will be extremely small. It reacts with sulphuric acid and produces sodium sulphate plus phenol back. So, that means, the concentration of phenolate will be will be allows constant in the external phase you know because this breakage itself will be very small. So, the amount the sodium phenolate, that is coming out of the internal phase into the external phase that is itself will be very small and. So, the phenol that is region hydrate will be extremely small.

So, in the long run the concentration of phenol will be really decreasing in the external phase. So, concentration of A means phenol and B is the final compound that is produced in the internal phase is sodium phenolate. So, concentration of A in internal phase is 0.

That means, sodium does not exist in the internal phase, because reacts with sodium hydroxide produced by sodium phenolate. So, $C_i A$ is equal to 0. So, A exist only in the external phase, that is simply mean A exist only in external phase concentration of B in a external phase is 0 $C_e B$ that means, concentration of B in external phase is equal to 0. That means, when the whenever, that B.

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That means, sodium chloride comes out to the external phase it reacts the sulphuric acid and produces sodium sulphate and phenol back therefore, sodium phenolate does not exist in the external phase. So, the concentration is always 0. Since, this concentration is in the external phase is 0, the K_B is equal to 0 the simply, because third assumption is the K_B is equal to $K_B = 0$, because the B that is the sodium phenolate is an ionic compound. That means, it is hydrophilic in nature, it does not like the hydrophobic environment of the oil of the membrane phase.

So, it cannot diffuse through the oil phase. That means, you are K_B is equal to 0, but some of the sodium phenolate can always come a small fraction of the sodium phenolate can always come to the external phase, via breakage as seen that have mention two mechanism by which the internal phase can come out to the external phase, one is diffusion number 1 and through the mass transfer coefficient K_B . Secondly, via breakage since the sodium phenolate itself is the ionic compound does not like the hydrophobic environment of the oil diffuse of the membrane.

So, therefore, it cannot be diffuse to the oil phase it remove their, but it some of it can always come back go to the external phase to the first mechanism there is the breakage. Next, will go to you know different assumption and balance equations. So, the governing equation of various species either in the external phase or in the internal phase can be develop, if you write down the species balance equation of various species in the internal phase, as well as in the external phase.

And we will be assuming there it is one dimensional ordinal differential equation, because it is a function of time only you are talking about a batch extraction process only. In fact, in the now in today is class is not possible, write down all the equation come to a conclusive solution. So, in the next class, what will be doing will write down all the balance equation of various species either in the internal phase and the external phase, then will try to see them, you know it to it will give you DAES system the differential algebraic equation system and will be able to solve this system almost analytically and can get an analytical solution.

So, in this class we can we have just what you are seen in summarize. We have seen the fundamental principles of liquid emulsion membrane system and there are 2 types of facilitation process one can have type 1 and type 2. We have defined the type 1 facilitation process and type 2 facilitation process. And we have look in to several type of examples and we have to know for the batch extraction of liquid emulsion membrane.

We have discussed various assumption and variation step go for involve and we have in a position now to write down the species balance equation. So, that we can model the whole system and or we can pre predict the performance of system at any point of time in a batch extraction process. So, we look in to all those details in the next class or the coming class. Thank you very much.