Principles and Practices of Process Equipment and Plant Design
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Module - 02
Lecture - 35
Liquid- liquid extraction (LLE)

Hello everybody. We have come to almost the end of the separation processes. We have been doing this for a very long time. We have first covered distillation and then absorption, then adsorption and today we have come to extraction process. Now, what is this extraction process?

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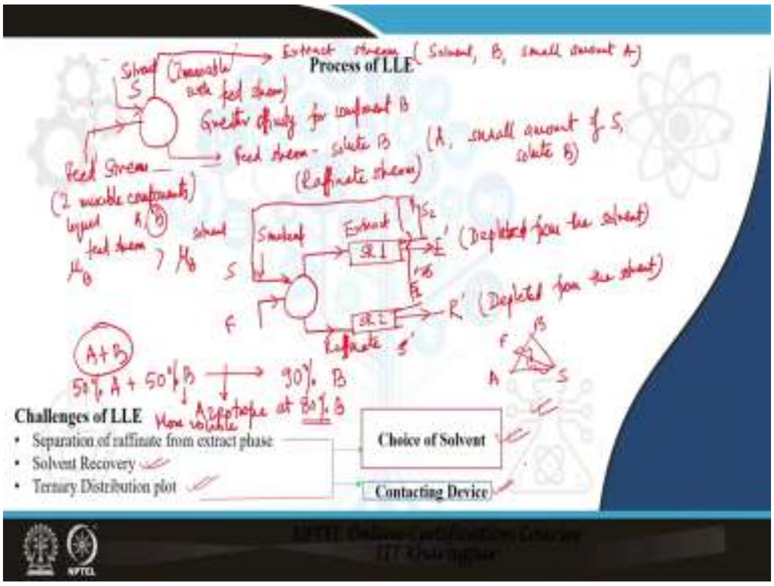

Process of LLE

Challenges of LLE

- Separation of raffinate from extract phase
- Solvent Recovery
- Ternary Distribution plot

Choice of Solvent

Contacting Device

In this particular extraction process what we do is, this is basically like this. We have say one particular feed stream. This particular feed stream, it contains said a minimum of two miscible components, this is a liquid feed stream.

So, therefore this is a liquid feed stream. It has at least minimum of two miscible components and we want to separate it. Say, the components are A and B; say, we would like to separate B from A, it will either B for purifying A or for recovering B from A.

What do we do? We put it in an extractor and we add another liquid which is known as the solvent S which is immiscible with the feed stream and this solvent S, this is mixed up with the feed stream and after mixing up, what happens, this S firstly, it is immiscible with the feed stream and it has a greater affinity for component B.

So, greater affinity for component B. So, naturally what happens, component B it diffuses from feed stream to the solvent stream or in other words, there is transfer of component B from the feed stream to the solvent stream after the mixing is over naturally. How long this transfer will go on?

As long as the chemical potential of B is not equal in the feed stream and the solvent stream or in other words mu B in the feed stream as long as this is greater than mu B in the solvent stream, the mass transfer goes.

And after the mass transfer we get two streams. One particular stream that we get that is the feed stream depleted from the solute. This particular feed stream minus the major portion of the solute B. This is known as the Raffinate stream.

This was already mentioned to you when we were doing our equilibrium classes and what else we have? We have one more stream which is the solvent stream which is rich in the solute B.

This particular stream this is known as the Extract stream which contains a large amount of solvent. It contains the solute B and also, it contains a small amount of feed liquid A and this feed stream what it contains? It contains a primarily maybe a small amount of solvent depending upon the solubility and it also contains definitely a small amount of solute B.

Now, from this remember we have definitely removed B from A which we wanted, but again if you see both the liquids, you will find that in both the liquids what you have? You have B mixed with both A and S. There will be more or less little A the whatever it is, but there will be B mixed with A. So, therefore, just like for all separation processes where we add a mass separating agent.

You have already done two such separation processes. One was absorption; the other was adsorption and in both of them you have seen that solvent regeneration recovery and recovery of the solute is something very important.

In this case also, we will find that recovery of the solute and also the regeneration of the solvent, these are extremely important. So, if you have just this process which is the extraction process, it is actually incomplete. So, what we do after this? We have got two streams; both these streams they are sent separately to a solvent recovery unit and the extract is sent to a solvent recovery unit. The raffinate is sent to a solvent recovery unit.

Generally, thus recovery is done the process normally in industries is that we undergo a flash distillation, maybe two flash distillations. One at under pressure, one under vacuum and after that if required we go for a steam stripping or a distillation once we have got here, from here what do we get? We get the extract E which the solvent has been recovered.

So, we get the extract E which is depleted from the solvent and in this case also after solvent recovery, we get R prime which is again depleted from the solvent or in other words, both E prime and R prime, they are rich in the solute that we had wanted. This solute B, and from both S R 1, we get the recovered solvent S from here also we get the recovered solvent S.

So, therefore from here we get the recovered solvent, from here also we get the recovered solvent. This recovered both these recovered solvent or they are then recycled back and they come and join the main solvent stream here.

So, from here we get some amount of recovered solvent say S 1, from here we get the recovered solvent say S 2. Both of these are joint and then the two streams they are once more recycled. And remember one thing in the entire process, there will be some amount of solvent losses. So, as a result we would also give some amount of makeup solvent here and then, the process continues in this particular way.

This is the process of extraction. Now from this particular process, you can very well understand what are the challenges which are involved in liquid liquid extraction. Tell me what are the challenges? The first thing is we cannot consider just the extraction, this particular extraction unit in isolation whenever we have to consider the extraction unit; we also need to consider the solvent recovery step.

Quite often it happens that the solvent recovery step is the more expensive process, therefore there economics is guided by the solvent recovery step which is usually as I have told you a flash followed by steam stripping or distillation. Therefore, several times we find that when we select the solvent, it is more keeping in mind the ease of recovering the solvent or the cost of recovering the solvent in the solvent recovery step stages rather than get selectivity.

Although selectivity is also important, this is one particular thing that we have to remember. This is true for all the processes which involve separation using mass separating agents as we had discussed in the very beginning of the introduction of the separation processes. What is the next thing? Which is important here which you have to remember; after the solvent and the feed are mixed, then they are separated the extract and the raffinate are taken away.

This is done for absorption distillation. Everywhere in absorption distillation stripping what are the two phases that are taken out? One is a vapor and a gas phase or a gas phase and the other is a liquid phase. They are having high differences dense in density. So, the separation of the two phases after the intimate contact that does not present any challenge. It is just gravity separated.

But in this particular case, if you see the extract and the raffinate their liquids. Usually there is not a very high density difference between the two. As a result what we find is that the separation of the extract and raffinate just by gravity is often incomplete and therefore, this also presents a special challenge for liquid liquid extraction processes which is not present for other processes involving mass separating agents.

Very frequently we find that gravity is not sufficient and we have to use a centrifugal force for separating the two, the extract and the raffinate phase. In fact, I will tell you one thing. You will often find that the efficiency of the process is quite low. Normally we take us 50 percent maybe maximum 70 percent efficiency much less than the efficiency, the tray efficiency that we get for distillation processes.

Remember one thing. This particular we decrease or the reduced efficiency that we get, it is mainly for the insufficient or mainly for the insufficient separation between the extract and raffinate phases rather than the equilibrium considerations. This is something which we need to remember.

In Liquid-liquid extraction processes, there is one other also very important challenge. If you remember when we were discussing the equilibrium processes or the equilibrium considerations, I had mentioned one thing. For vapor liquid equilibrium in distillation we refer to the t x y p x y or xy plots for gas absorption. We refer to solubility plots all of these are 2D plots, we have a x axis, we have a y axis.

Usually the mole fractions of the two are plotted on the two axes or rather the mole fraction of the component which is to be transferred in case of distillation. It is the more volatile component in case of absorption, it is the component that is to be transferred. So, that components mole fraction in the two phases are plotted as the two axes.

In case of Liquid-liquid extraction. If you see the way I have shown here we find that it is very difficult to get two liquids which are completely immiscible with one another. There even if small there will be some limited miscibility of the solvent and the feed liquid.

As a result if you find what I have shown you here that in the extract stream also, there will be a small amount of feed liquid in the feed stream also, there will be a small amount of solvent liquid.

Therefore, how what do we do for representing the equilibrium? If you recollect correctly we use a ternary plot. If you remember I will be going into the details of this particular turn ternary plot where the apices they refer to the completely pure A, completely pure B and completely pure solvent S and the each particular arm that represents a binary mixture.

So, if we have started with A and B, then this sum represents the composition of A and B. As we go more towards the vertex B, it means that the proportion of B is increasing and the proportion of A is decreasing. Now suppose in this particular liquid we add component S, so therefore maybe we had started from this feed composition and we add S. Immediately what happens? The composition instead of staying on this on this particular line AB, it shifts to inside the triangle.

And depending upon the composition, we find that on addition of S, the composition it shifts into the triangle and it moves along the line which joins the feed composition to the vertex S. I have considered the vertex S under the condition where I have taken fresh feed, fresh solvent or even if I have taken regenerated solvent, it contains very less amount of A and B.

So, under that condition I can join the vertex S to the feed composition and with addition of S, the composition of the mixture it shifts from this straight line into inside the triangle. The more amount of S we add the more the point is going to shift. So, therefore the composition of the feed on addition of S, it moves along the straight line say from the feed the line joining the feed composition to the S. The more we add solvent, the more it moves.

And therefore, the proportion of the solvent to the proportion of feed is given by the ratio of it is. It is from lever rule. It is given by the ratio of the feed point to the mixture point and the solvent point to the mixture point. So, quite naturally as we keep on adding solvent, we keep on moving towards this. So, therefore this also presents an additional challenge the ternary distribution plot.

So, naturally the calculations become much more difficult. Remember one thing. Despite all these challenges, there are situations where instead of using distillation to separate the two miscible components of a liquid solution, we have to resort to extraction.

Definitely there are applications and that is why where this particular topic is being discussed with you and this particular topic, it is getting increasingly important in industrial applications particularly with the advent of pharmaceuticals, fine chemicals food products, etc.

Definitely you have to remember that with all these challenges extraction will be opted only under conditions, where either distillation is not possible. When is it completely not possible? When suppose I have a comp I have say A and B and this from this A and B say I have started from 50 percent A and 50 percent B and this specification is that I from here I have to recover say about 90 percent B.

And we know that an azeotrope is formed say around 80 percent B. So, therefore when we start distilling, what do we get? Initially and B is the more volatile components say? So, when we start distilling, initially and the top product we start getting B, this is the more volatile component. So, we start getting the top product which has more of B as compared to A.

We can increase the number of trays and we can keep on attaining more and more enrichment of B. This continues till we reach the azeotrope composition at 80 percent B. After that we find that there is no further enrichment and we have no way of moving from a feed liquid of 50 percent B to an enriched liquid containing 90 percent B.

So, there are certain things that we can do about it which was told to you earlier. First thing is we can add a third component which breaks the azeotrope. This is known as an azeotropic or an extractive distillation. It can also happen that you can change the pressure and on changing the pressure, the azeotrope condition can be, it can be eliminated under that condition. Also we can get this there are situations where none of these are very possible.

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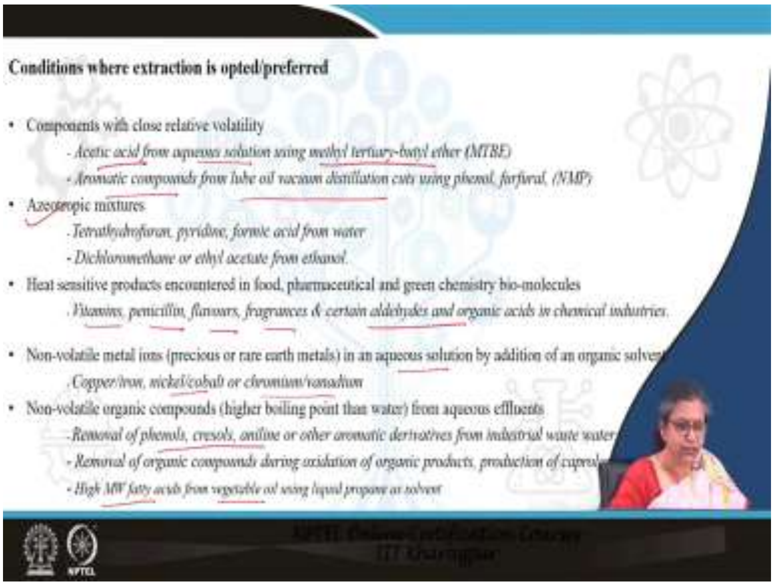

Conditions where extraction is opted/preferred

- Components with close relative volatility
  - *Acetic acid from aqueous solution using methyl tertiary-butyl ether (MTBE)*
  - *Aromatic compounds from lube oil vacuum distillation cuts using phenol, furfural, (NMP)*
- Azeotropic mixtures
  - *Tetrahydrofuran, pyridine, formic acid from water*
  - *Dichloromethane or ethyl acetate from ethanol.*
- Heat sensitive products encountered in food, pharmaceutical and green chemistry bio-molecules
  - *Vitamins, penicillin, flavours, fragrances & certain aldehydes and organic acids in chemical industries.*
- Non-volatile metal ions (precious or rare earth metals) in an aqueous solution by addition of an organic solve
  - *Copper/iron, nickel/cobalt or chromium/vanadium*
- Non-volatile organic compounds (higher boiling point than water) from aqueous effluents
  - *Removal of phenols, cresols, aniline or other aromatic derivatives from industrial waste water*
  - *Removal of organic compounds during oxidation of organic products, production of caprol*
  - *High MW fatty acids from vegetable oil using liquid propane as solvent*

So, under those particular conditions where we find that the azeotrope it cannot it is not worth changing or rather we if we change the pressure, the relative volatility between the two components, they do not change to a great extent and it is also not very feasible to use a third component to break the azeotrope. Under that conditions definitely we have to opt for Liquid-liquid extraction and some very common examples is to extract formic acid tetrahydrofuran pyridine from water or maybe to extract ethyl acetate from ethanol.

So, these for these particular situations we go for Liquid-liquid extraction. It can also happen that the components they do not form an azeotrope, but they have a very close relative volatility and therefore, in order to effect some particular separation, we have to use a very large number of trees, say, 45-50 trays which is definitely not going to be economical.

Under that conditions also possibly we can go for extraction particularly when the conditions are such that recovering the solvent from the raffinate and the x and the extract is not very difficult. A typical example is say we have an aqueous solution containing acetic acid.

Normally what we do in this particular case, we use methyl tertiary butyl ether as the solvent which can be easily evaporated away and we can recover the acetic acid from the MTBE solution. Under this condition definitely we would opt for the extraction rather than the distillation process.

The same thing a very typical example from oil refineries is that from the lube oil vacuum distillation cuts, we often have to recover the aromatic compounds and this we do very easily by using phenol furfural all in NMP such type of solvents. There can be situations where the product that we want that is very heat sensitive and therefore, we cannot go for distillation. It cannot withstand the heat film which is going to be supplied in this case.

This is more relevant for pharma companies, food industries, find chemicals particularly for the extraction of vitamins, penicillin’s flavours, fragrances, etc. also in chemical industries for recovering of certain aldehydes and organic acids.

So, for such particular cases, extraction has become increasingly important. As I have already told you that the importance of extraction has is particularly more relevant in the modern times with the importance of food industries, pharmaceutical industries etcetera etcetera.

There are certain other cases say separation of metal ions, copper from ion, nickel from cobalt, chromium from vanadium, in these particular cases suppose they are there in an aqueous solution, the conventional thing that we do is we add an organic solvent. What happens, out of the two ions one of them that forms a chelate with the organic solution or the organic solvent and the other remains in the aqueous solution.

This is a very typical way of separating the metal ions, the precious or rare earth metal ions from one another when they are there in an aqueous solution by using an organic solvent. There is one another thing also. Suppose you have got some non volatile organic compounds in an aqueous effluent, say maybe we want to remove phenol, cresol, aniline etcetera from industrial wastewater.

For such cases definitely instead of going for vacuum distillation etcetera, it is much more economic to have proper solvent which can bring about this separation. This is a standard thing which is also used in food industries. When we have to remove high molecular weight, fatty acids from vegetable oil instead of going for vacuum distillation which will be much more expensive, we prefer to use liquid propane as the solvent.

So, therefore due to these conditions despite the limitations which liquid liquid extraction has which I have already told you, the primarily challenges it has liquid liquid extraction is often opted for and therefore, we will be keeping the challenges in mind. We are going to address the design of different extractors challenges. I will repeat once more.

First thing is separation of raffinate from the extract phase. This is a unique problem which you did not face for absorption, adsorption distillation and this is naturally due to the close density of the raffinate and the extract phase.

After this once they are separated, next is the solvent recovery unit. As I have told you this is primarily done with flash distillation or and followed by maybe one or two flash followed by steam stripping or batch distillation. So, therefore this step and the cost incurred here, this has to be considered when we deal with Liquid-liquid extraction.

We cannot deal with just the extraction part alone and to make matter towards the ternary distribution plot, definitely has to be considered when we are dealing with this extraction problem.

There are situations where we can go for the xy plots, we will be discussing under what conditions we can do it. So, therefore what are the things that we have to do? Just like in the case of absorption, we had to select the proper solvent. In case of adsorption, we had to select a proper adsorbent.

In this case also, choice of solvent is the first important thing and the same second important thing is the contacting device. The first thing that we are going to discuss is the choice of solvent. In this particular case again we refer to the ternary plot in order to guide us in the choice of solvents.

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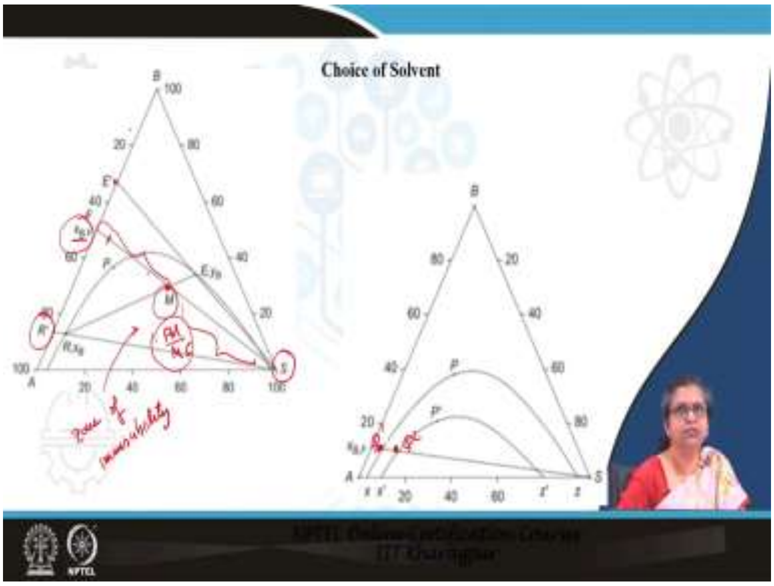

Choice of Solvent

Now there are two things also I would like to remember. When we select a solvent, it will be depending first on the solvent which will have a greater selectivity for the solute that we are going to opt and the second thing is the solvent can be recovered easily from the solute, both in the extract as well as in the raffinate phase.

We will deal first with the selectivity part, the extraction part. Now in this case as I had already mentioned that we represent the equilibrium in the case of a ternary plot as I have told you. Now as I have told you that this is the feed composition and I am using pure solvent. We assume that either we are using fresh solvent or the regenerated solvent has very less amount of A and B which can be neglected.

So, naturally what we find? That the feed composition now shifts along the line FS as I have told you. Now remember one thing. Inside the triangle, we have got the three components together. Now here if you find I have drawn a dome, this zone is the zone where the A and S, they are more or less quite immiscible from one another and therefore, within this dome, the liquid it forms two different layers.

So, this is the zone of immiscibility. So, therefore you have to remember that when we add a solvent, the quantity should be sufficient such that the point we reach after the solvent is attained that lies within the zone of immiscibility. If we add a very small amount of solvent such that the point lies here, then in that case it is going to represent a solution containing A B and S A homogeneous solution containing A B and S. Those compositions correspond to this particular point

If we have added solvent to come to this point, we cannot get the separation by means of extraction. So, we need to add solvent sufficiently such that we have entered this dome. Now what does that mean then definitely it means that if we have a solvent where the dome, these dome of immiscibility is larger, definitely we will opt for that particular solvent.

So, therefore if you observe in this case this is X B F, this is S. The feed composition is going to vary along this line when we keep on adding solvent. Now we find that the minimum amount of solvent that we need to enter the to the zone of a immiscibility, it is say Q prime in the first case and maybe for the solvent 2, it is say it is Q 2 say this is Q 1 Q 2.

Naturally we find that if you opt for the solvent which is represented by this zone of immiscibility, then we need a greater amount of solvent that has to be added here. So, naturally if we are given these two solvents, we would definitely opt for the solvent 1 with the zone of miscibility which is given here.

So, this is one comparison. The other thing also remember that this particular zone for the same solvent, it is influenced by temperature and as we increase the temperature, the liquids they get more and more miscible.

So, therefore with increase in temperature we find that this zone of miscibility shifts from the P, this zone to this zone. So, naturally what does that imply that we would always like to opt or we would always like to perform extraction with the same solvent at the lowest admissible temperature.

But at the same time you need to remember when you are going for a lower temperature, the rate of mass transfer that the rate of diffusion that decreases. So, therefore we have to optimize on such a temperature where we get a sufficient zone of immiscibility and also, keep into mind a sufficient rate of transfer, so that we can optimize a better efficiency and a better throughput and we can perform the extraction process. This is point one

The point two is that well we have added solvent, we have come into the zone of immiscibility say now we are at a point M, what is the solvent that we have added? We have added this is the ratio of the feed to the solvent is quite naturally FM by MS. Perfect after the extraction has taken place, then we go for a recovery stage.

So, from so after the once we have added solvent at, it is in this particular M point definitely this lies within the zone of immiscibility. So, therefore it separates into two liquids; the raffinate phase and the extract phase. Now if you remember both the extract phase, we had sent it to a solvent recovery unit.

When we send it to a solvent recovery unit if we assume that the entire solvent has been recovered, then after that what is remaining from the extract the E prime that I had shown you E prime means that portion of the extract from which the solvent has been completely removed.

So, naturally that lies on this particular point. From the raffinate also we remove the entire amount of solvent. When we have removed the entire amount of solvent, then in that case the raffinate point lies in at R prime. It is quite evident now that the farther away R prime is from E prime, the better is the solvent.

So, we would always like to opt for a solvent which has a greater difference between R prime and E prime. So, what do we do? For that we take different solvents. We try to plot this ternary plots, the feed composition is fixed, we take the same proportion of the solvent which is denoted by point M.

Or we take the same proportion FM by MS and then, we draw the ternary plots. We find the difference between E prime and R prime and then the solvent which gives us the greater difference between the two, we naturally opt for that particular solvent.

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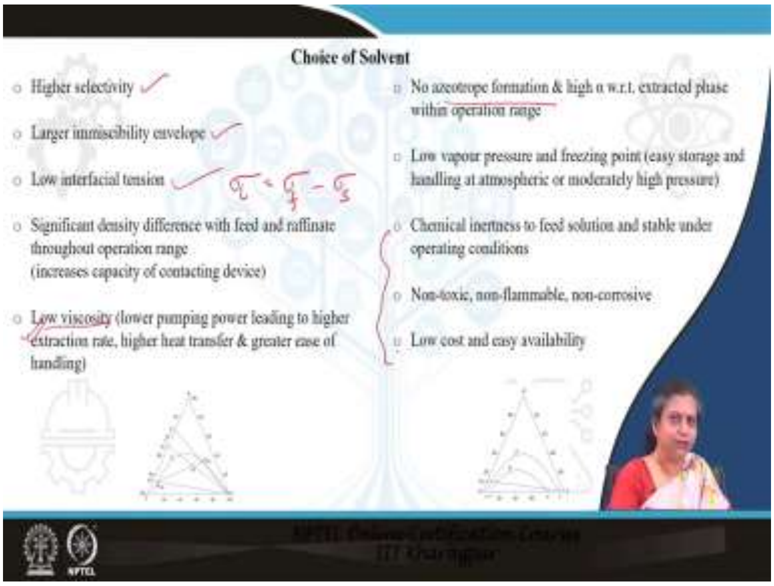

Choice of Solvent

- Higher selectivity ✓
- Larger immiscibility envelope ✓
- Low interfacial tension ✓ $\sigma_I = \sigma_f - \sigma_s$
- Significant density difference with feed and raffinate throughout operation range (increases capacity of contacting device)
- Low viscosity (lower pumping power leading to higher extraction rate, higher heat transfer & greater ease of handling)
- No azeotrope formation & high α w.r.t. extracted phase within operation range
- Low vapour pressure and freezing point (easy storage and handling at atmospheric or moderately high pressure)
- Chemical inertness to feed solution and stable under operating conditions
- Non-toxic, non-flammable, non-corrosive
- Low cost and easy availability

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There are certain additional considerations of course that is denoted by higher selectivity and larger immiscibility envelope. There are also certain other considerations that we need to consider. We will be discussing them before ending this class.

First thing is, it is very evident that there has to be significant density difference between feed and raffinate throughout the operation range, so that we can get a proper separation between the two and before the raffinate and the extract that can be sent to their respective solvent recovery units.

That is a must I have told you and often what we do, we employ centrifugal separation rather than gravity separation in order to bring an effective separation between feed and raffinate. And I have also told you that the reduced stage efficiency is also due to the inadequate separation rather than the equilibrium considerations.

Next thing is what? Low interfacial tension. Remember one thing when we are going for extraction, what do we do one of the phases that gets dispersed in the other phase. So, therefore, if you want a proper mass transfer, definitely the phase which has a higher mass transfer resistance that has to be broken down into large number of droplets. So, therefore the smaller the droplets, the better will be the mass transfer.

So, therefore lower the interfacial tension, the smaller we will be getting the droplets and better will be the mass transfer. So, we would always like to opt for a low interfacial tension. Here also I would give you some particular caution. See suppose the droplets they have become very fine very emulsified, then in that case coalescence becomes a problem, but after the extraction has occurred, we would like the droplets to coalesce and either settle or rise depending upon its density relative to the continuous phase density.

So, therefore we would not want to have very fine droplets. At the same time, we would like a proper emulsion. So, therefore a more or less lows interfacial tension is necessary. I would also like to mention normally data on interfacial tension is not available. So, therefore we often what we do we denote the interfacial tension as the difference between the surface tension of the feed solution and the solvent. Well there is one other thing, low viscosity on this.

We will be discussing much more. At this moment, it is sufficient for you to remember that naturally when we have a low viscosity, the pumping power will be less. We have to pump the solvent into the extractor. Pumping power is less, extraction rate is higher; heat transfer is higher, it is easier to handle.

So, we will always like to go for low viscosity of course and this point we will be having some discussions later. Well after this the extraction part, we go for the solvent recovery part. There what we need to remember? There should not be any azeotrope formation with respect between the solute and the extract or rather bit between the solute and the solvent and there should be a sufficient high amount of relative volatility to facilitate solvent recovery.

We would also like to have a solvent which is remains liquid over a large portion or in other words, it has a high boiling point and the low freezing point. Again when I tell you this, we have to remember definitely we will we would want a higher boiling point or a lower vapor pressure for ease of handling and storage, but at the same time we have to remember that we are going to separate it from the solute by means of distillation.

So, naturally we for that particular considerations, we would not like a solvent with a very high boiling point. So, here also there has to be a compromise and most of the cases what we do? We select a solute which has the high selectivity. So, the extract phase that we get that has a large amount of solute or lesser amount of solvent and it is easier to vaporize away the or distill away the solvent.

So, naturally there has to be a compromise such that the solvent can be distilled away. It has a sufficient alpha. The relative volatility difference with the solute at the same time you would want a solvent which remains liquid for a larger portion. The other things that they are common to all particular solvent selection for different operations. I would not like to go into the details of this.

So, once you have realized the challenges of Liquid-liquid extraction, you have realized that based on these challenges we are going to select the solvent. So, therefore after this we will be going for the contacting devices. We will take up this simplest contacting device simply a mixer while we mix the two, we agitated and then the extraction occurs and then we separate it. And once we have discussed this, we will go for continuous operation systems. So, for the moment this much only.

Thank you very much.