Novel Separation Processes
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Lecture No. # 30
Surfactant Based Separation Processes (Contd.)

Well. So, in this class, what we will be doing we will be continuing with the discussion with the cloud point extraction; and in the last example, whatever we have seen that, if we talk about we've just taken a case study of a particular dye that is the chrysoidine dye; and we are looking into the performance of extraction using cloud point extraction process by using two particular surfactants, one is Tx100 and Tx114.

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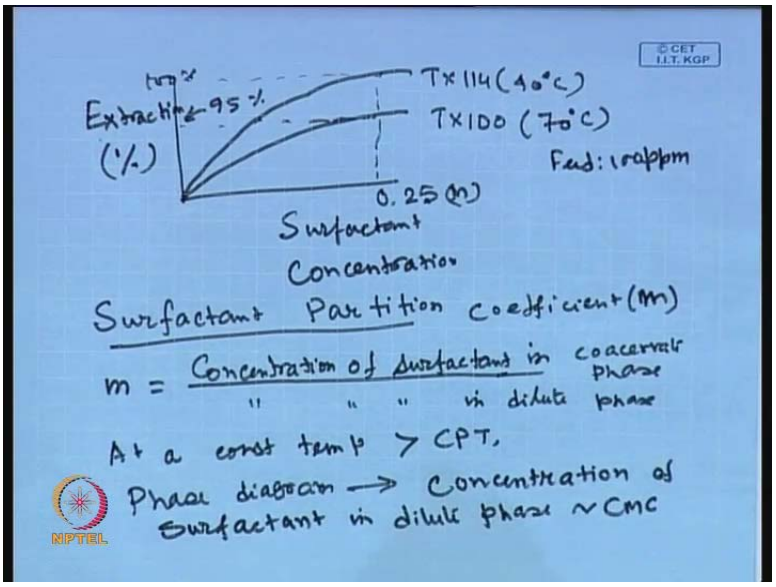

Now, if you look into the performance curve of the extraction of these two dyes, extraction in percentage and these surfactant concentration, the performance curve will look something like this; the upper one is for Tx114 that the operating temperature is around 40 degree centigrade, and the lower one is of Tx100 the operating temperature was 70 degree centigrade.

Now, if we use a surfactant concentration of 0.25 molar for a feed solute concentration of hundred p p m, one can get almost 100 percent separation using Tx114 and using Tx100, one can get around 95 percent separation, 90 to 95 percent of the separation. So, the

extraction efficiency will be more in case of Tx114 at lower temperature, but it will be costlier compared to Tx100.

So, next thing we will look around look into that is for the surfactant partition coefficient; in this is quite important because about cloud point the surfactant molecules get partitioned across coacervate phase and the dilute phase; and these partition coefficient is, there is a particular trend with that of the partition coefficient and that is very important, because it is really very very important to understand, how much surfactant will go into the coacervate phase, how much surfactant will be present in the lean phase or in the dilute phase; the definition of this patrician coefficient is defined as that concentration of surfactant in coacervate phase divided by concentration of surfactant in dilute aqueous phase.

Now, at a constant. So, this is the definition. So, it gives the concentration ratio of surfactants in the dense phase and in the lean phase; now at a constant temperature at a constant temperature above cloud point temperature, the value of the phase diagram dictates dictates that, the concentration of surfactant in the dilute phase will be around CmC, surfactant in dilute phase will remain out CmC; now, if you keep on increasing the feed surfactant concentration, now in order to maintain the material balance, more surfactant should go to the dilute to the coacervate phase, because the concentration of the surfactant in the dilute phase will be maintained around CmC.

So, now, if you would like to increase the surfactant concentration in the feed; now, you cannot increase the concentration in the dilute phase, it will be around CmC. So, what the rest surfactants will go? The rests rest surfactants molecules will be going into the coacervate phase. So, what it implies? It implies that the volume of the coacervate phase or the dense phase will be increased.

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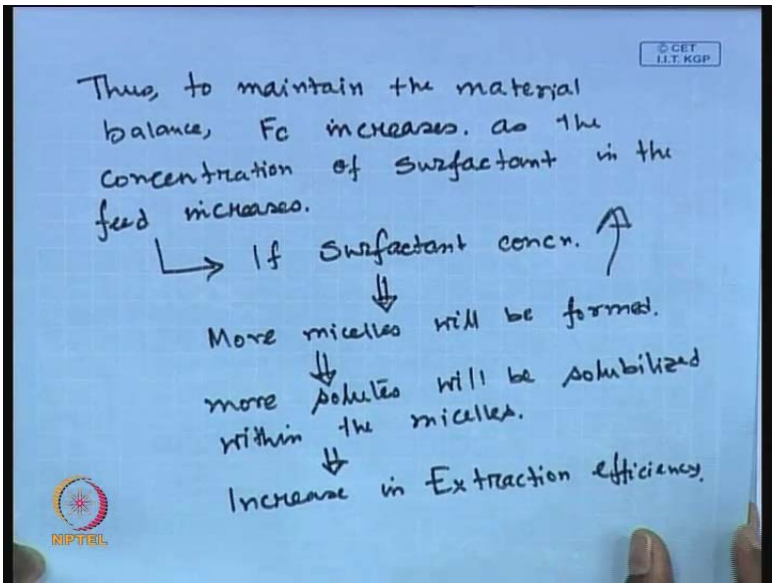

So, to maintain the material balance, F c increases; what is the F c? F c is the coacervate phase volume divided by the total volume.

Now, since more surfactant will be going into the coacervate phase, its volume will increase. So, therefore, F c increases, as the concentration of surfactants in the feed increases increases; and what what what does it implies? it implies, if you increase more surfactants, then more surfactants will be will be will be forming more micelles; if surfactant concentration increases, more micelles will be formed; if more micelles will be formed, more solutes will be solubilized within the micelles; within the micelles and the extraction efficiency increases that leads to increase in extraction efficiency.

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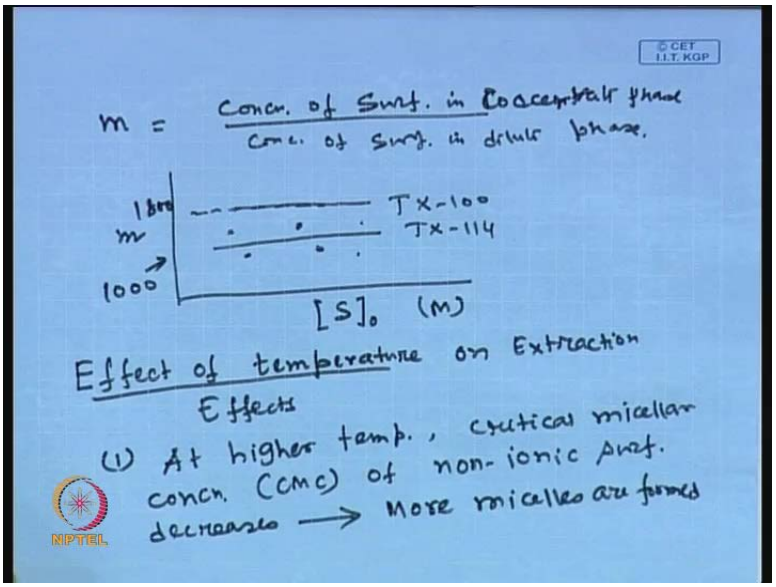

Now, what has this what does it imply in case of in the definition of the partition coefficient, if you look into the definition of partition coefficient, there is a concentration of surfactant in feed, in coacervate phase, concentration of surfactant in dilute phase . So, if you increase the surfactant concentration the dilute phase concentration will also be increasing, but it will be in the order of CmC; but concentration of coacervate phase will also increase and these two will maintain almost at the same level.

Now, if you plot m, you know, m verses concentration of surfactant in the feed in molar, then they will be almost at the same level; this for Tx100, this for Tx114; and these value will be around 1800 for 100 Tx100 and these value will be around 1000 for Tx114; and you'll be having the experimental data points scattered about these values.

Next, we talk about the effect of temperature on extraction. Now, effect of temperature has a profound effect on the extraction of solute during cloud point extraction; what are these effects? these effects are are are can can be can be discussed as follows; number 1, at high temperature, the critical micellar concentration of the non ionic surfactant decreases, at higher temperature critical micellar concentration is CmC of non ionic surfactants decreases; what does it imply? these implies, that if you increase the temperature, since critical CmC level will be decreasing, more number of micelles will be formed. So, more micelles will be formed; if more micelles are formed, their

solubilization capability of the solutes will be more; therefore, extraction efficiency will be more that is number 1 implication.

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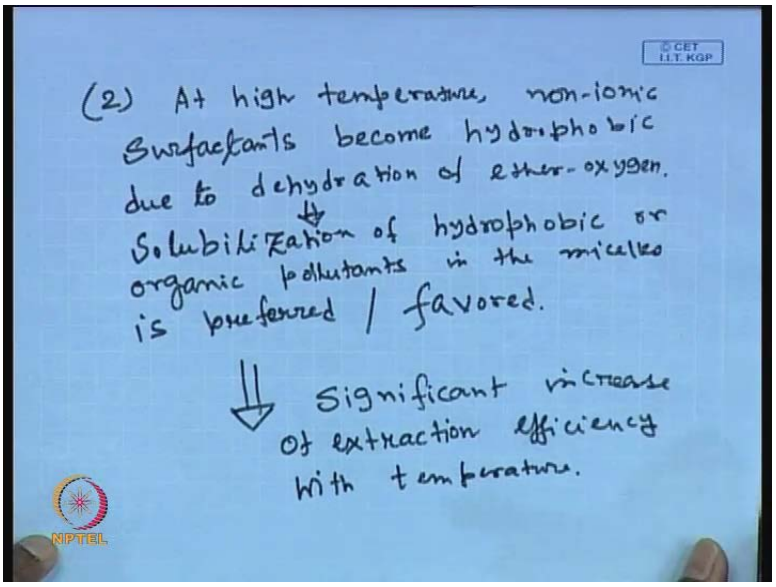

The second implication is that, at high temperature as we have discussed earlier in the earlier class, at high temperature, non ionic surfactants becomes hydrophobic, they become hydrophobic; why they become hydrophobic? because the expulsion of the water due to dehydration of ether oxygen; that means, these micelles becomes more hydrophobic in nature; if they becomes more hydrophobic in nature, their surrounding environment they will make them more hydrophobic; if they are more hydrophobic, they will solubilize more hydrophobic pollutants.

So, solubilization of these leads to solubilization of hydrophobic pollutants or organic pollutants in the micelles is preferred or they are favored. So, what does that mean? So, all these two results, all these two factors will lead to an increase of extraction efficiency with temperature; significant increase of extraction efficiency with temperature. Now, I will give some idea, how this will be you know, what are these significant increase means, you know in case of chrysoidine dye the case study we are discussing.

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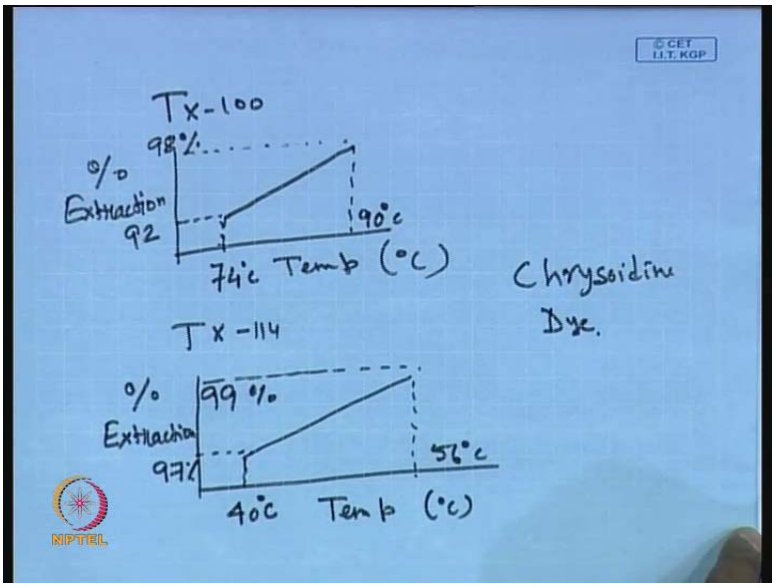

For T x 100, and this is the temperature in degree centigrade, at 74 degree centigrade, the increase is something like this; these are 74 degree centigrade, this extraction is percentage extraction the extraction is 92 percent; on the other hand, at 90 degree centigrade, if you increase the temperature, the extraction is away as 98 percent, and this increase is almost linear from 92 to 98 percent; in case of Tx114, they also again a linear variation; this is at 40 degree centigrade, the extraction is 97 percent; when you increase the temperature to 56 degree centigrade, the extraction is as I as 99 percent.

So, one can get, this is of course, in case of chrysoidine dye. So, one can get a significant enhancement in the extraction efficiency, if you increase the temperature; and the effect of this temperature is twofold that as we have discussed earlier; in one case it reduces the critical micellar concentration therefore, increases the micelle concentrations or number of micelles, and it increases the extraction efficiency that is number 1 number 2 with increase in temperature; the hydrophobicity of the micelle is increasing the increase therefore, it favors more solubilization of the pollutants and leading to the increase in extraction efficiency.

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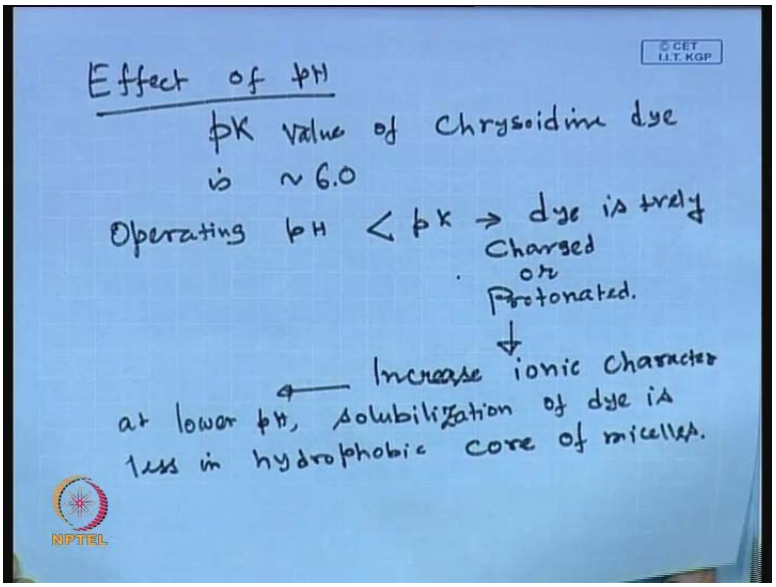

The next operating effect of operating pH will be looking into, now PK value of chrysoidine dye is about six about six. So, the any pH, which will be the any operating pH that will be kept below PK value, the that will make the chrysoidine dye, you know positively charged or protonated; on the other hand, if we increase the operating PH beyond PK value, it will make the dye molecule negatively charged.

So, operating pH less than PK dye becomes positively charged or they are protonated ; that means, you what does that imply? These implies you increase the ionic characteristic; ionic character therefore, at lower pH, these results, this means at lower PH, solubilization of dye is less in hydrophobic micelles in hydrophobic core hydrophobic core of the micelles.

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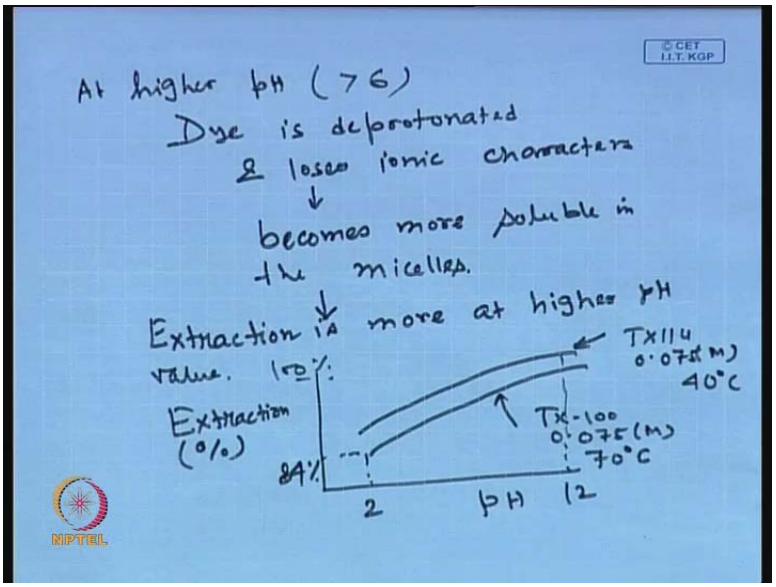

On the other hand at higher pH, at higher pH means greater than 6, the dye is deprotonated. Therefore, it loses its ionic characters and loses ionic characters and becomes more soluble in the micelles. So, therefore, at higher pH value, the extraction is more; now, if you plot the extraction efficiency and pH, then the plot look something like this; this is for Tx114.075 molar and 40 degree centigrade; this is for Tx100 at same concentration 0.075 molar and 40 degree centigrade and it is 70 degree centigrade, and is the value of pH, the value is at around pH 2, it shows a rejection of extraction of 84 percent; on the other hand, at a higher value of pH around 12, the extraction will be extremely high close to 100 percent;

That means, so, in short we can say that, if you increase the pH the dye dye loses this particular dye loses its you know ionic character, it becomes more hydrophobic and gets more solubilized in the micelles in the separation extraction percent efficiency becomes high.

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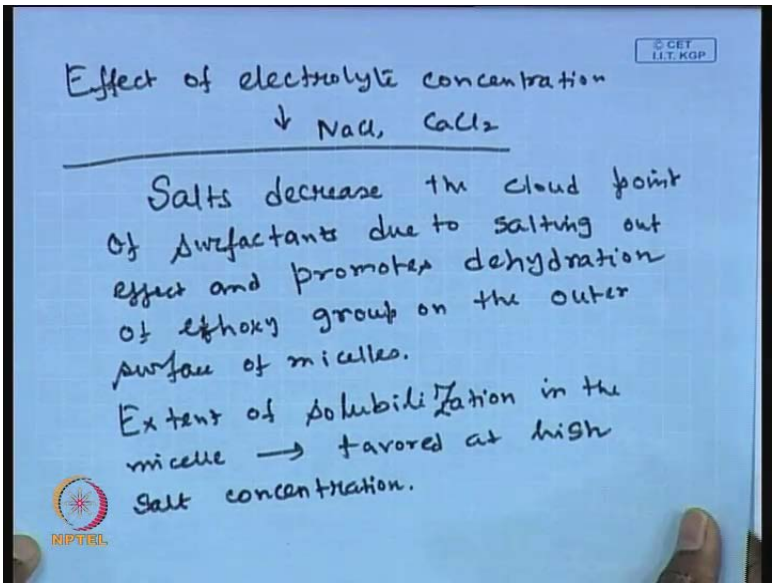

Next thing that we will be talking about effect of added salt or the electrolyte concentration; and electrolyte we are talking about sodium chloride, the electrolyte can be sodium chloride, can be calcium chloride and so on. So, forth the they will be having a profound effect on the extraction efficiency as well, because salts decease the cloud point, cloud point of surfactants due to salting out effect and it favors or promotes dehydration of ethoxy group on the outer surface of micelles .

So, therefore, what happens, if you increase the salt concentration, the cloud per itself decreases; So, the whole system becomes, so, if you increase the temperature slightly, then there will be co phase separation and more solubilization will occur in the micelles. So, extent of, So, therefore, extent of extraction or extent of solubilization in the micelle is favored at high salt concentration. So, since the extent of solubilization is more, extent of extraction is also more.

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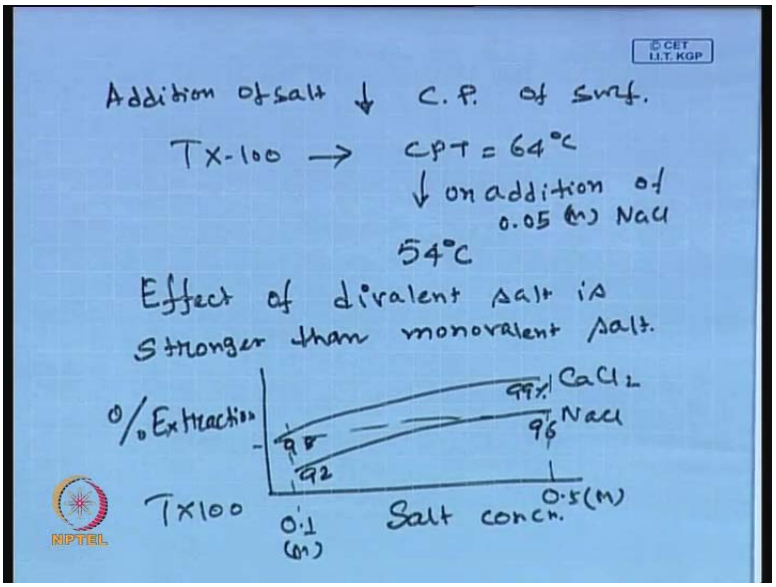

So, we said that by the addition of salt, decreases the cloud point of surfactant; now, what is that extent of decrease? for Tx100, the cloud point temperature is 64 degree centigrade; now, if you add on addition of 0.05 molar NaCl, the cloud point temperature reduces to 54 degree centigrade; similarly, and the effect of similar decrease in cloud point temperature can also be observed in case of Tx114; effect of divalent salt is stronger than monovalent salt. So, instead of, if you use if you use calcium chloride instead of sodium chloride, this effect will be more prominent.

So, we give some example these are salt concentration; these are percentage extraction, this for Tx100, this is the effect of calcium chloride, and this is the effect of sodium chloride; and if you increase the salt from 0.1 molar to 0.5 molar and the percentage increase increment is from 92 percent to 96 percent in case of sodium chloride; that means, this value is 96 percent and in case of calcium chloride it is from 98 to 99 percent almost complete removal.

So, these are the various effects of the operating conditions on cloud point extraction, and these will include the surfactant concentration, the cloud point the operating temperature, operating pH, operating electrolyte concentration, all these have all all these will have a profound effect on the extraction efficiency of the during the cloud point extraction.

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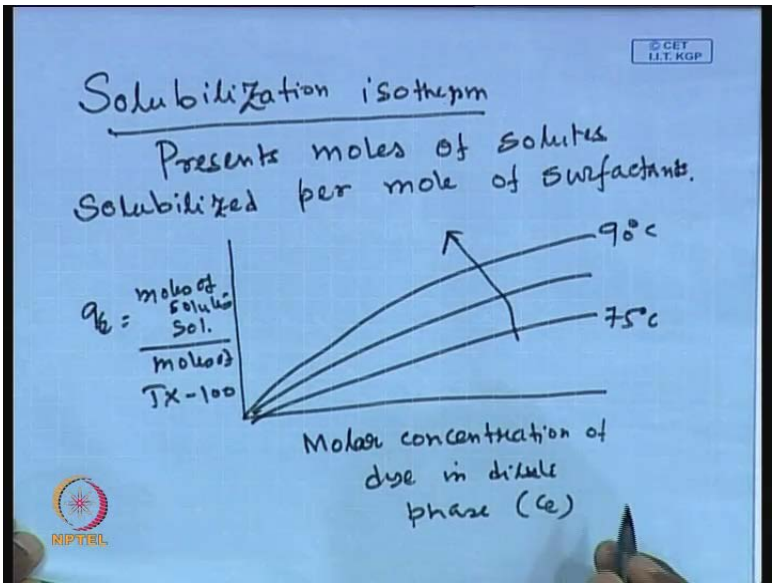

Next one, we will talk about the solubilization isotherm. Why it is important? it gives a quantitative description of how much moles of solutes are solubilized per mole of surfactant; these isotherm presents moles of solutes solubilized per mole of surfactants.

So, these quantitatively describe that solubilization capability of one mole of surfactant. So, if we plot this, this will be giving you the q e; q e is a one-dimensional number; moles of solutes solubilized divided by moles of surfactant let us say Tx100; and these are molar concentration of dye in the dilute phase, call this as C e;and these isotherms they look something like this, this is at 75 degree centigrade, this is at 90 degree centigrade and with temperature they move up; that means, with temperature the solubilization capability of the of the of the surfactant increases; and why it will increase? that we have discussed just now during the discussion of effect of temperature on the extraction efficiency.

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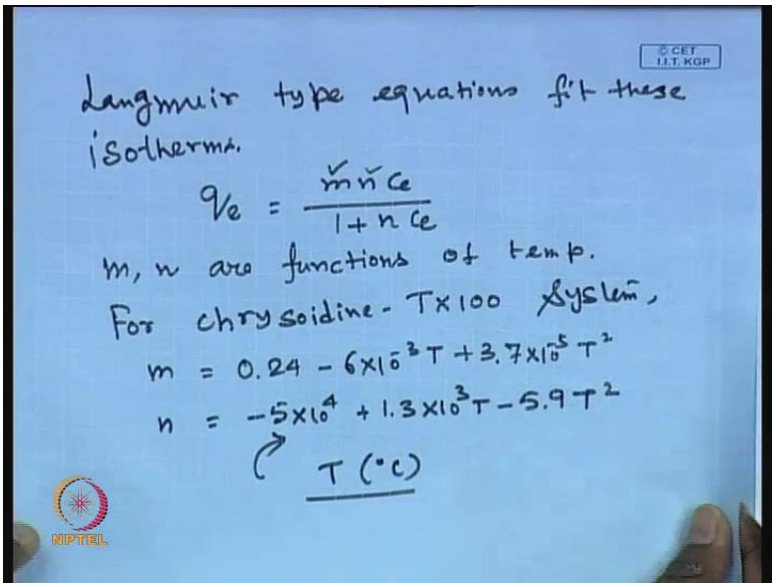

Now, if you if you look into these curves, these curves will be increasing and they are decreasing their slope, it will be decreasing later on; and they'll be described by typical langmuir type of equation, langmuir type equations fit these isotherms. So, q e will be m n C e divided by 1 plus n C e; C e is the concentration of the solute or the dye in the dilute phase; and q e is the ratio of mole the moles of solutes solubilized per mole of surfactant or the non ionic surfactant; that we are talking about

Now, these constants, the isotherm constants, m and n, as it is like absorption isotherm and they are strongly depending on the value of temperature. So, m and n are functions, reasonably strong functions of temperature; now, for chrysoidine Tx100 system, these values are m is equal to 0.24 minus 6 into 10 to the power minus 3 times T plus 3.7 into 10 to the minus 5 T square, and n is minus 5 into 10 to the power 4 plus 1.3 into 10 cube T minus 5.9 T square where T in degree centigrade in both the equations.

So, the isotherm constants are functions of temperature and for this particular system, chrysoidine takes 100, we have conducted the experiments and fitted the data; it has been found that m and n can be varied they are they are they are varying with a quadratic form of temperature.

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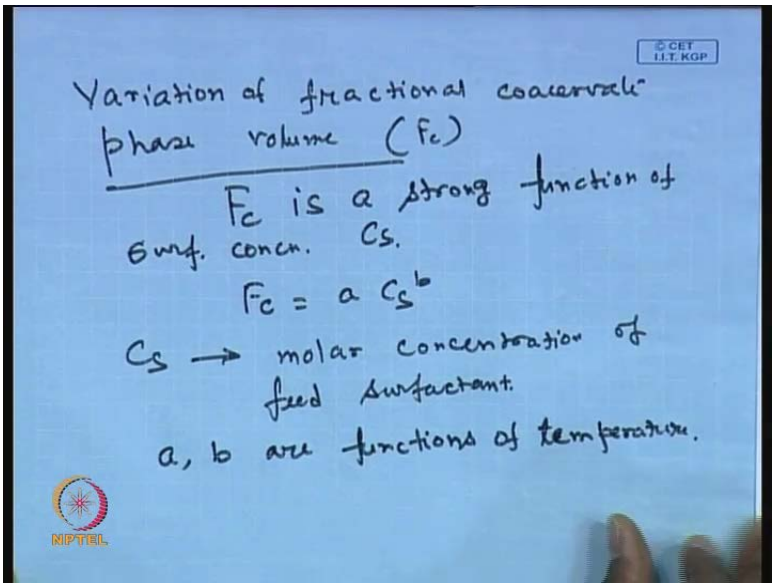

Next we consider the variation of fractional coacervate volume. The F c that we have defined earlier, volume F c.

Now, as we have discussed earlier that, it is a function of surfactant concentration; F c is a strong function of surfactant concentration; right typically, this will be an increasing function of concentration of surfactant, because as we have discussed that, dilute phase will be having a surfactant concentration around CmC, but in order to maintain the material balance, if you if you keep on increasing the concentration of surfactant, more surfactant will be going into the coacervate phase.

So, therefore, its volume or F c will be increasing. So, therefore, F c will be having increasing variations with surfactant concentration; and typically, these variation is given in the form of a C s to the power b. So, this is these will increasing and this this increase will be non-linear; and this non-linear fitting is given something like this, a C s to the power b. Now, in this correlation, C s is the molar concentration of the surfactant. Now, parameters a and b in this equation, they are strong functions of temperature; they are they are found to be functions of temperature; and we have conducted the experiments, it has been found out, they are linear function of temperature.

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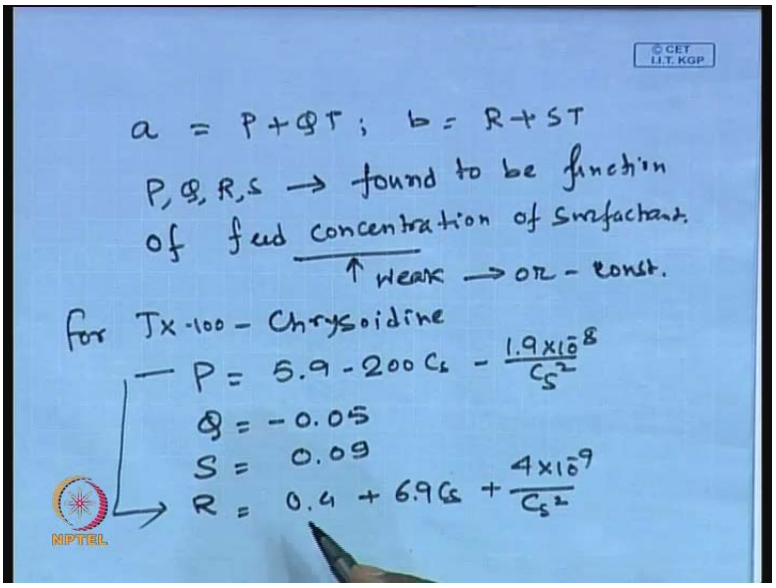

P plus Q T and b is given as R plus S T. So, they are suppose to be linear function of concentration of temperature, and the coefficients P Q R and S are are found to be function of feed concentration of surfactant; and this functionality is quite weak; this functionality is a weak function or they are constants; Now, for Tx100, and chrysoidine system, these functional variations are evaluated by experimenters experimentations and they are reported as P is equal to 5.9 minus 200 times C s minus 1.9 into 10 to the power of minus 8 C s square; Q is about it is found to be constant minus 0.05, S is found to be constant, it is 0.09 and R is found to be a weak function of concentration, it is 0.4 plus 6.9 C s plus 4 into 10 to the power minus nine C s square .

So, knowing the variation of various process parameters. So, these are the process parameters; what are the what are the main operating conditions? the process parameters are concentration of surfactant, temperature, pH, electrolytic concentration and so on. So, forth now knowing these process parameters and this type of variation by conductors. So, these these variations, functional variations that whatever, we have discussed here or the soluble isotherms, they are developed when we conducted experiments in a small scale set up; now, once these functional variations are known with the process parameters, a scaled up version of the cloud point extractor can be designed.

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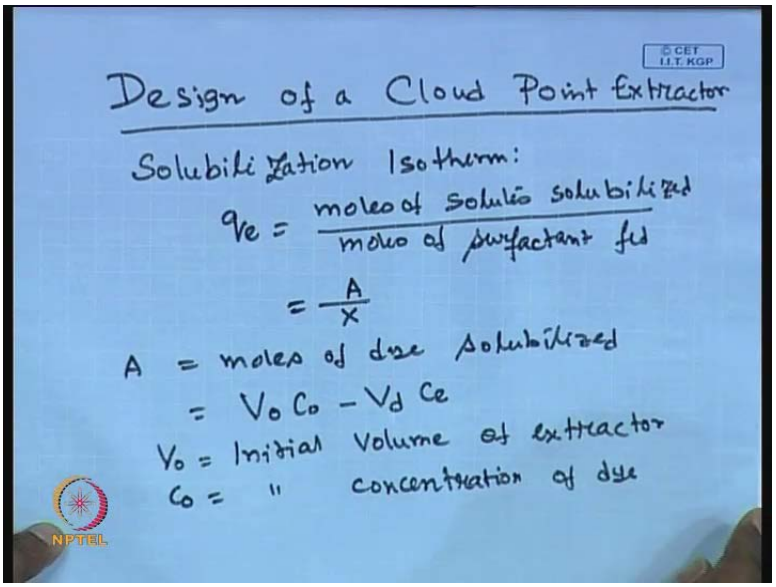

So, next, we just look into how to design a cloud point extraction. So, next we discuss the design of a cloud point extractor; that is very important, only thing is, for variation of some of the parameters with the operating conditions, we have to conduct small experiment in the test tubes; once those variations are quantified, then we will be in a position to scale it up to design a real cloud point extractor. Now, for that, we just look into the definition of solubilization isotherm; this is the first isotherm is the first design equation; q e is equal to moles of solutes solubilized moles of surfactants fed.

So, this is A divided by X. So, X is the moles of surfactant that we have used and A is the moles of solute that has been solubilized. So, A is the moles of moles of dye for this particular system, let us say let us say Tx100 chrysoidine dye; dye solubilized is given as, V naught C naught minus V d times C e. So, what is a V naught? V naught is the initial volume of the extractor; and what is C naught? C naught is the initial concentration of the dye in the system.

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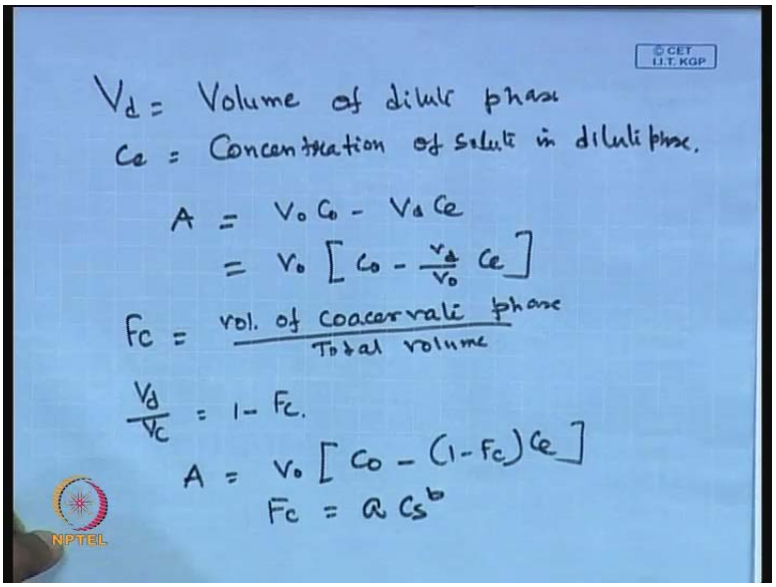

Now, what is V d? V d is the volume of the dilute phase and C e is the concentration, final concentration of solute in dilute phase.

So, rest amount V naught C naught is the total amount of dye that was present in the system; and V d C e is the total amount of dye that was present in the dilute phase. So, where is the rest amount? the rest amount has been gone in the coacervate phase. So, that that much of that that that many moles of the solutes will be solubilized in the coacervate phase or in the surfactant micelles.

Now, this will give you A, we can the So, A is given as V naught C naught minusV d times C e. So, we can rearrange this equation, and by taking V naught common. So, this becomes C naught minus V d by V naught times C e. Now, what is V d by V naught? if you remember if you remember the definition of fractional coacervate phase volume, this is the volume of coacervate phase divided by total volume; that means, this fractional volume of coacervate phase. So, V d by V naught is 1 minus F c dilute phase. So, V d by V c is nothing, but 1 minus F c. So, therefore, A can be written as V naught into C naught minus 1 minus F c multiplied by C e; and F c, the fractional coacervate phase volume that we have already seen that, it will be a function of fit surfactant concentration in the form of a C s to the power b.

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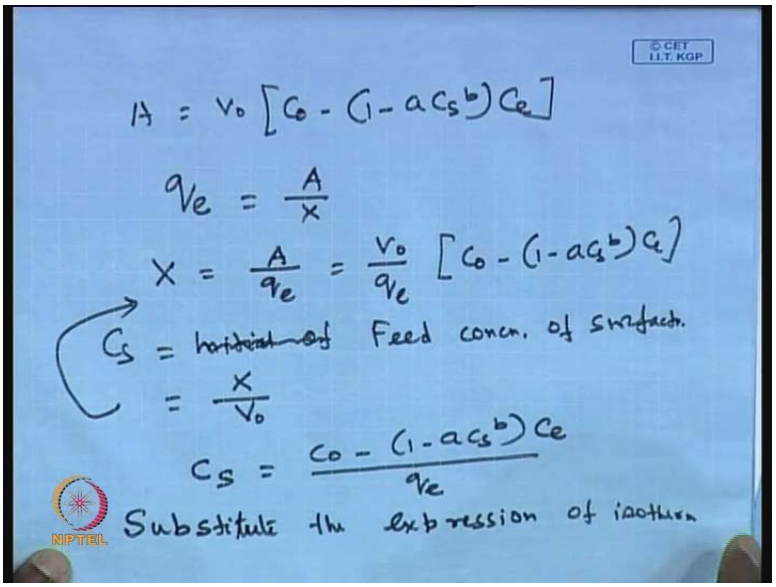

So, if you substitute that in the in this equation, what we get is that, A is nothing but V naught times C naught minus 1 minus a C s to the power b multiplied by the C e. Now, variation of F c with the surfactant concentration is given with surfactant concentration is given in terms of P Q R, so and so, forth all these are established.

So, therefore, this can be put in the definition of the isotherm. So, if you remember the definition of isotherm q e is equal to A by X. So, X is the moles of surfactant that is been used in the feed X is nothing, but A by q e and A is given as v 0 divided by q e into C naught minus one minus a C s to the power b multiplied by C e . So, therefore, if you know the C s, the initial feed concentration of the surfactant; so, what is X? X is number of moles of surfactant is used; if C s is known, what is C s? C s is initial concentration of surfactant; that means, initial means feed concentration, feed concentration of surfactant and what is the definition of it? this is the molar definition.

So, number of moles is X and divided by volume that is the V naught. So, I replace X by C s times V naught. So, therefore, C s can be, so, therefore, using the combining these two equations, we can get the value of C s, as C naught minus 1 minus a C s to the power b times C e divided by q e. Now, you can you can substitute the isotherm expression of q e in terms of C e and your C s.

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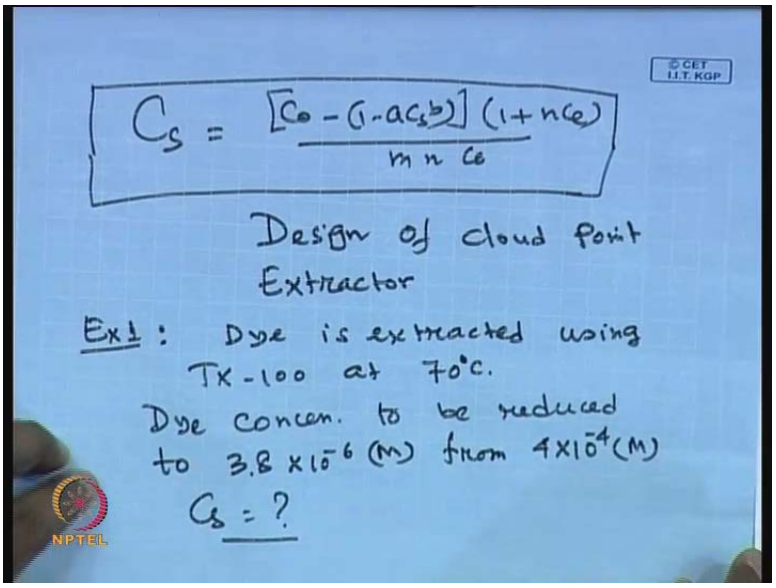

So, it turns out to in terms of C e, it turns out to be now, you substitute the expression of isotherm; it turns out to be C s is equal to C 0 minus 1 minus a C s to the power b into bracket into 1 plus n times of C e divided by m n C e.

Now, this is the design equation for any cloud point extraction extractor. So, what is, So, if you if you look into it, what is C e? C e is basically the concentration of the solute in the dilute phase. So, that is the target concentration we are looking at, I would like to reduce the concentration of the dye in the dilute phase below 2 p p m. So, 2 p p m will be the value of C e, and what is C naught? C naught is the concentration of the of the dye or the solute in the feed stream, let us let us say, we have started from hundred p b v and we our hundred p p m and our aim is to bring down the concentration of the dye to 2 p p m.

So, C e will be 2 and C naught will be 100, and what is the C s? C s will be the amount of surfactant that we are going to use to achieve this. So, you can you can calculate or design, the how much surfactant concentration that we are going to use in order to attain, in order to bring down the concentration of the solute from the level of C naught to C s. So, that gives the total design equation of the cloud point extractor; now, with this, we have come to end of that out point extractor design; now I have, I am having couple of examples to elaborate or elucidate these ideas. So, we let us look into some of the examples of design of cloud point extractor.

So, I have two examples; the first example, it deals with we we're we're since the we in in this lecture, we have given the correlations for chrysoidine dye and Tx100 system. So, we stick to that particular solute. So, that those correlations can be utilized; dye is extracted using Tx100 surfactant at 70 degree centigrade, the cloud point temperature of Tx100 is 64 degree centigrade; so, we keep the operating temperature above that. So, let us keep it at 70 degree centigrade; dye concentration has to be removed, a has to be reduced to be reduced to 3.8 into 10 to the power minus 6 molar from 4 into 10 to the power minus 4 molar. So, we have a concentration of 4 into 10 to the power minus 4 molar and we have to reduce it to 3.8 into 10 to the minus 6 molar to that extent. So, how much surfactant concentration is required for this purpose.

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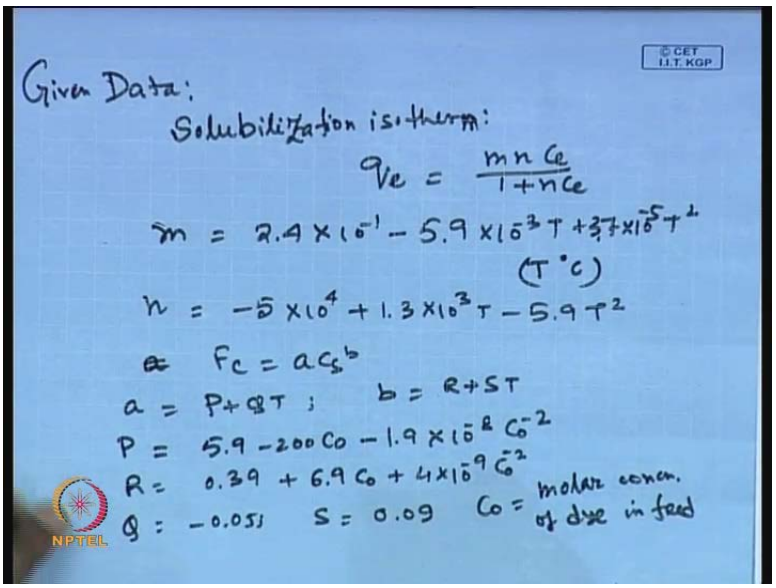

So, how much of surfactant concentration, you must be having in order to achieve this. So, that is the idea. So, various data's are given; the first data, given data are, solubilize isotherm is given; solubilization isotherm is given for this dye and the surfactant system; and this will be in the form of q e is equal m n C e divided by 1 plus n C e. So, C e is the molar concentration of the dye in the dilute phase. So, m is m is given as two point four into ten to the power minus 1. So, m n is the strong functions of temperature. So, it it will be 2.4 into 10 to the power minus 1 minus 5 point nine into 10 to the power minus 3 T plus 3.7 into 10 to the power minus 5 T square, where T in degree centigrade; and n is given as minus 5 into 10 to the power 4 plus 1.3 into 10 cube T minus 5.9 T square, again T is in degree centigrade.

So, these data are given and a and b in the in the coacervate phase volume correlation, the a and b, if you remember F c was a C s to the power b; a and b, variation of temperature etcetera are given; a is given as P plus Q T and b is given as R plus S T. So, P and P and Q P and R are weak function of concentration of surfactant. So, P is 5.9 minus 200 C naught of solute, right they are they are weak function of solute, 200 C naught minus 1.9 into 10 to the power minus 8 C naught to the power minus 2 and R is given as 0.39 plus 6.9 C naught plus 4 into 10 to the power minus 9 C naught square C naught to the power minus 2, and Q value are given minus 0.05 S is given as 0.09.

So, these data are given and what is C naught? C naught is the molar concentration of dye in feed; as we have discussed that, these the expression of P and R, they are found to be weak function of concentration, feed concentration of the dye and these expressions are given by this.

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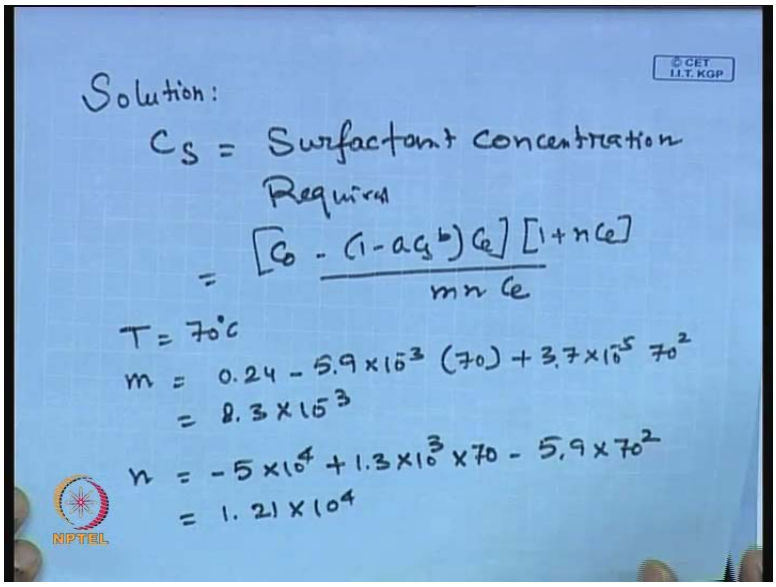

Now, let us look into the solution. The solution goes like this, the concentration of the surfactant required is C naught minus 1 minus a C s to the power b times C e 1 plus n times C e divided by m n C e; the temperature is given as 70 degree centigrade. So, you evaluate m. So, m will be 0.24 minus 5.9 into 10 to the power minus 3 times 70 plus 3.7 into 10 to power the minus 5 70 square and it turns out be 8.3 into 10 to the power minus 3; n, you can evaluate at this particular temperature minus 5 into 10 to the power of 4 plus 1.3 into ten to the power 3 into 70 minus 5.9 into 70 square ; this turns out to be

1.21 into 10 to the power 4. these are the values of m and n the isotherm constant at the temperature 70 degree centigrade.

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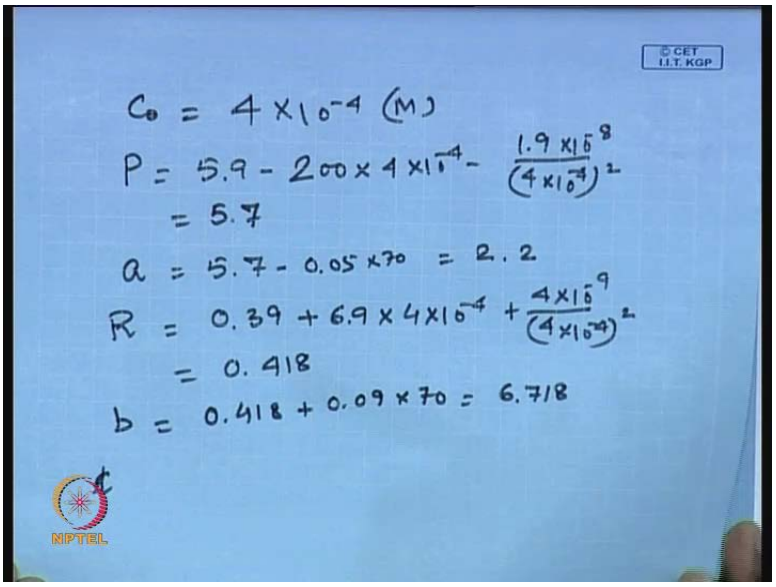

The value of C naught that is, the concentration of the dye in the feed, was given as 4 into 10 to the power minus 4 molar; and so, once it is given, you can, you will be able to calculate the parameters P and R. P is 5.9 minus 200 into 4 into 10 to the power minus 4 minus 1.9 into 10 to the power minus 8 divided by 4 into 10 to the power minus 4 square of that and it turns out to be 5.7; this a will be 5.7 minus 0.05 into 70, so this turns out to be 2.2.

Similarly, you can evaluate the value of R. The R turns out to be 0.39 plus 6.9 into 4 into 10 to the power minus 4 plus 4 into 10 to the power minus 9 divided by 4 into 10 to the power minus 4 square; so, these turns out to be 0.418. and you can once you calculate R, you will be able to calculate the parameter b as 0.428 plus 0.09 into 70 and this turns out to be 6.718; once you calculate all this parameter, then you will able to calculate the value of C s and C s expression write it neatly.

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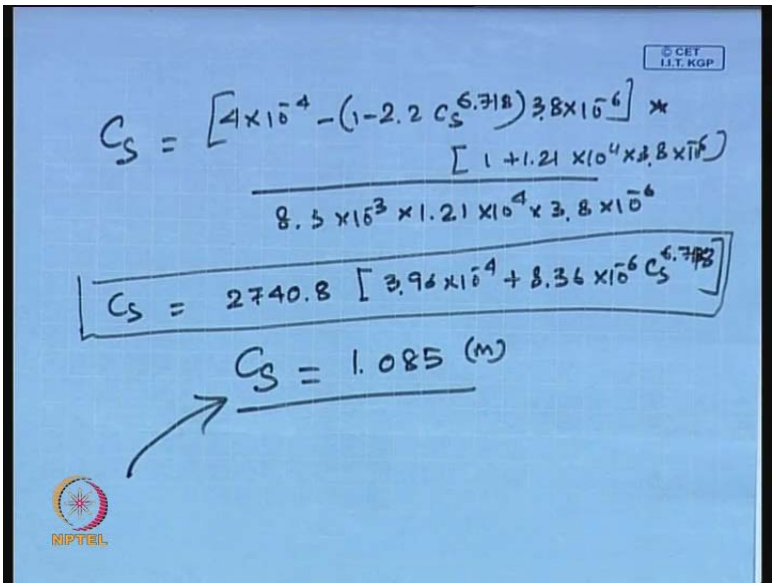

If you put all these values in the governing equation, the C s turns out to be 4 into 10 to the power minus 4 minus 1 minus 2.2 C s to the power 6.718 3.8 into 10 to the power minus 6 multiplied by 1 plus 1.21 into 10 to the power 4 into 3.8 into 10 to the power minus 6, then divided by 8.3 into 10 to the power minus 3 into 1.21 into 10 to the power 4 into 3.8 into 10 to the power minus 6; this it will be if you simplify all these values it will it will be 2740.8 into 3.96 into 10 to the power minus 4 plus 8.36 into 10 to the power minus 6 C s to the power 6.718.

So, now this 1 equation and one unknown it is a non-linear equation this can be solved iteratively; and if you solve iteratively, this C s turns out to be 1.085 molar; So that means, if you would like to reduce the dye concentration from three point from from 4 into 10 to the power minus 4 molar to 3.8 into 10 to the power minus 6 molar using Tx100 tricellar in time, you must be required to feed about 1.085 molar of surfactant, in order achieve this type of this type of these extent of separation of the dye to that particular concentration level.

So, in the next class, we will take one more example of cloud point extractor; and then we move on to the next surfactant based separation process that is, the micellar enhanced separation process.

Thank you