

Novel Separation Processes
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Lecture No. # 32
Micellar Enhanced Ultra filtration

Good morning every one. So, we are discussing about the micellar enhanced ultra filtration processes. And in the last class, we have given an over view of the micellar enhanced ultra filtration and introduction of it. And as we know that in any membrane based separation processes there are two aspects one is how good the separation is and next one is how effective the separation is in **in** terms of through put or the total volume of productivity of the system is concerned. Now, in the last class we have seen that the quantity that the quality of the product; that means, how much solute has been solubilized in the micells can be really quantified and it can be expressed as a solubilization isotherm the form of a solubilization isotherm.

So, therefore, we propose that the we have seen that this isotherms are in the if you plot this isotherm; that means, if you plot the amount solubilized per amount of surfactant versus the concentration of solute present in the free form. That will follow a langevin type of equation, and we have seen that a langevin type of fitting fits very well to the trend. So, therefore, using that isotherm one can quantify the amount of solute that has been solubilized and what is the concentration of the solute is present in the permeate stream or in the free form unbounded form. Now, in today's class we will look into the other, aspect how, what is the productivity of the system; that means, we will be trying to quantify the permeate flux and various associated phenomena that'll be arising due to the **due to the** various complications of micellar enhanced ultra filtration.

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Permeate Flux:-
2-10 nm
Micelles form a gel type of layer on the membrane surface.
Gel controlled filtration Theory

$$J_s = k \ln \frac{C_g}{C_0}$$

↑ Steady state permeate flux
k → mass transfer coeff.
C_g → gel layer concn. of surfactant micelles.

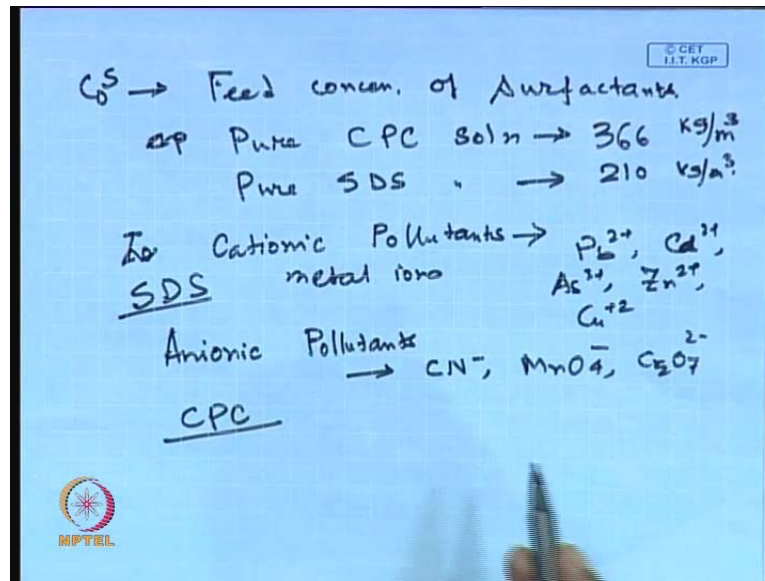
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So, let us look into the permeate flux the permeate flux in case of permeate flux it is assumed that these types these micelles they are larger in size they will be having a size average size in the range of 2 to 10 nanometer. So, they can be separated by an ultra filtration membrane these micelles form a gel type layer on the membrane surface micelles form a gel type of layer on the membrane surface therefore, they will the solutes will be passing through them and if you remember the since the outer surface of micelles are charged they will form a network a gel layer or cake type layer with a charged spheres like micelles.

So, therefore, the permeate flux can be predicted using a gel controlled filtration theory. So, permeate flux can be predicted as J steady state let us talk about the steady state $k \ln \frac{C_g}{C_0}$ and J_s is the steady state permeate flux number 1 and k is mass transfer coefficient C_g is gel layer concentration of the surfactant micelle of surfactant micelles and C_0 is the concentration of the surfactant as monomer with the feed concentration of surfactants.

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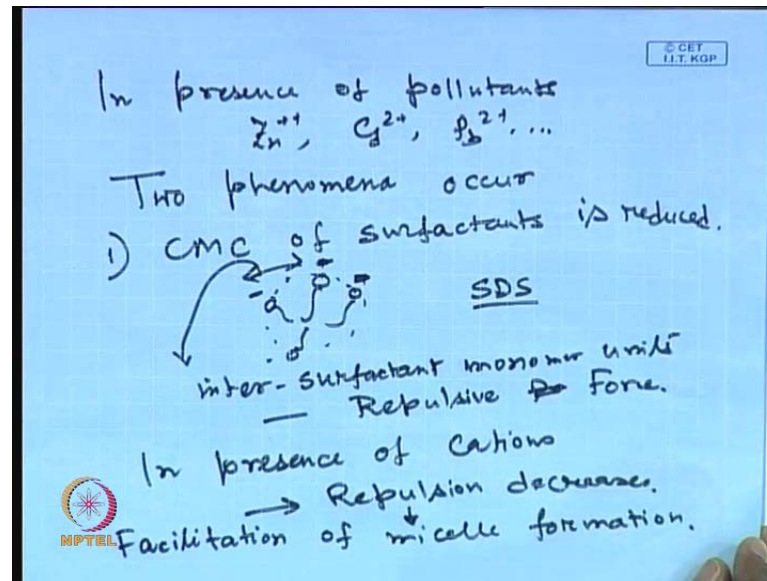


Now, the gel layer concentration of C P C is typically pure C P C solution, if you have a pure C P C chloride solution the gel layer concentration is about 366 kg per meter cube. On the other hand pure S D S solution will be having a gel layer concentration around 210 k g per meter cube.

Now, in presence of counterions; suppose you would like to would now as we have discussed in the last class there you can have **the** and ionic pollutants cationic pollutants or anionic pollutants. Cationic pollutants like metal ions they will be like lead heavy metal ions like lead cadmium arsenic then you can have a zinc copper. So, on. So, forth all these cations, **they** if they go beyond a particular limit they are in nature, you can have anionic pollutants like you know CN minus cyanide m n o 4 minus manganate dichromate C r 2 o 7 2 minus.

Now, if you would like to remove the cationic pollutants like lead cadmium etcetera then you has to use the surfactants like sodium doddery sulfate. So, that the outer surface will be negatively charged and in case of removal anionic pollutants, you must be using a using a cetyl pyridinium chloride. So, therefore, the outer surface will be positively charged that is the basic fundamentals of any micellar enhanced separation process. Now, whenever these ionic **the** in this you **you know** you know you **you** charge the ionic pollutants in a in the solution two phenomena will occurred simultaneously.

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In presence of pollutants it is a ionic pollutants we are talking about the inorganic pollutants; not organic pollutants, $z n$ plus plus or let us say cadmium plus plus 2 plus or lead two plus something like this. Then two phenomena will occur number one is that the C m C of the surfactants will be, if the presence of these cations the C m C of surfactants will be reduced why the C m C of the surfactant would reduce simply because whenever you'll be having a globule or a spherical shape micelles, **the** if you remember the outer surface will be the head groups of the surfactants will be facing the solution. And all the head groups will be; let us say similar charges, if you talk about S D S micelle the sodium will go out in the solution, and all the head groups will be negatively charged.

Now, when you are placing when they are **they are they are** arrange themselves in the form of a sphere; these head groups will be placed one after aside one after another. So, therefore, they will ripple each other and this repulsion, will cause instability in the micelle formation. So, the inter surfactant monomer units there is a strong repulsive force present, but in presence of counterions like $z n$ plus or cadmium 2 plus. This repulsion will decrease in presence of captions repulsion decreases.

Now, what is this repulsive force? This repulsive force will be manifested as an instability source of instability in the formation of the micelles. So, therefore, when this repulsive force will decrease the micelle formation will be facilitated right. So, this repulsion when this repulsion decreases; this leads to a facilitation of micelle formations.

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In presence of these cations/counterions
CMC of surfactant ↓
More micelles will form at a fixed concentration of feed surfactant.
↓
More solubilization of counterions
⇓
Enhanced separation/efficiency.

(2) Effect on gel layer concentration

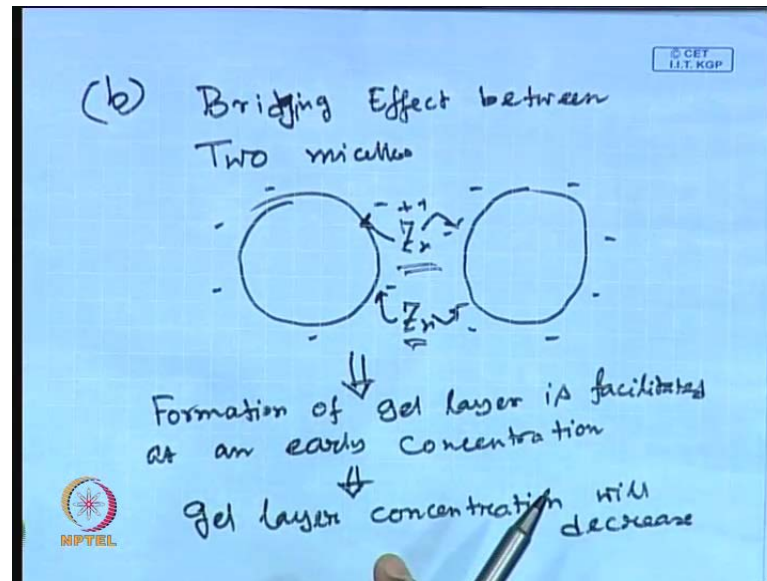
(A) - (B)

The diagram shows a circular micelle with a dashed outer boundary and a solid inner boundary. Several small circles representing Zn²⁺ ions are shown outside the micelle, with arrows pointing towards the outer surface of the micelle, indicating their attachment to the negatively charged surface.

So, in other word; what it physically do **the** in presence of these counter these counterions of the cations the critical micellar concentration will decrease **right** presence of these cations or in general it is a let us a call it counterion the C m C of surfactants decreases. What does that mean if the C m C of the surfactant decreases more? So, at a at a lower concentration of the feed surfactant more micelles will be formed **right** more micelles will form at a fixed concentration of feed surfactant **when**. So, therefore, when more micelles will be form. There will be more solubilization of the counterions **right**. So, this leads to more solubilization of the counterions and finally, this will result into enhanced separation enhanced separation; that means, enhanced efficiency of the system.

Now, the second phenomena that will occur that will **that will** directly affect the gel layer concentration. The second phenomena will lead to effect on gel layer concentration. So, when you'll be having an S D S micelle with a negatively charged negative charges residing over its surface. Now this let us say z n plus. So, the it'll be having a two valency. So, either this will be. So, this must be occurred this must be attached to the outer surface, when it'll be attached to two negatively charged ions negatively charged sides. So, that is one aspect the second aspect these **these** cations may cause a bridging of the two micelles as well.

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So, this is one second one will be I will write it in the next slide the second aspect will be it can do a bridging effect this is known as g i n g bridging effect between two micelles what is this bridging effect you have the you have one micelle you have the another micelle let us say $z n$ plus plus.

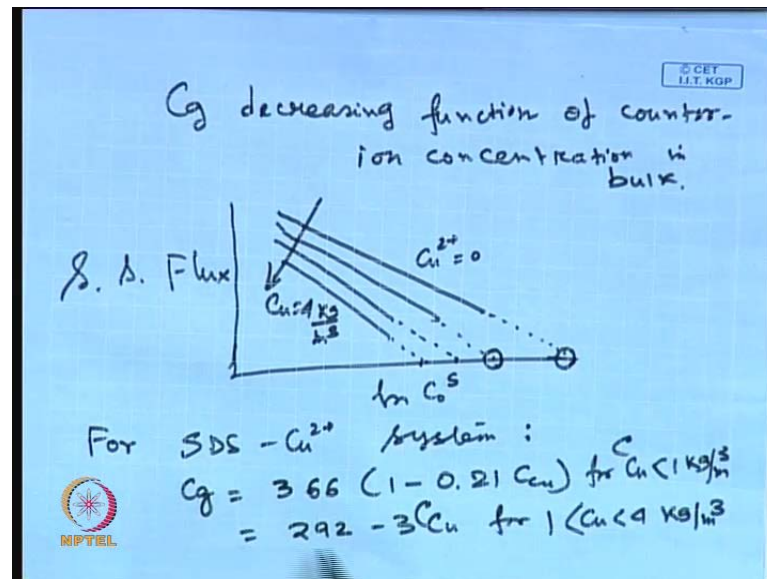
So, it can attach to this micelle also it can attach to this micelle. So, it can attach to this micelle it can attach to this micelle. So, this can, this is the second phenomena and what it what it means **it means** that all these bridging will be lead to formation of the gel layer at an early concentration. So, these leads to formation of. So, when these agglomerates of the, when this bridging effect will be there; these agglomerate we grow in size and the formation of the gel layer over the membrane surface will be facilitated.

So, gel layer is facilitated at an early stage what is the early stage at an early concentration of the at an early concentration. So, quantitatively these effects means what quantitatively these effect means that gel layer concentration will decrease **right**; that means, gel layer concentration will decrease and more be the number of free counterions or the cations available in the solution more prominent this effect will be.

So, therefore, gel layer concentration, over surfactant; decreases as concentration of the counterions in the feed solution increases. So, there are two effects, when you added the counterion of you know multivalent counterion number one it is critical micellar concentration will decrease. Secondly, the onset of the get layer will occur at an early

concentration; that means, its gel layer concentration will decrease.

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So, C_g will be a function is a decreasing function of counterion concentration in the bulk. Therefore, if you plot a flux versus steady state flux versus $\ln C_0^S$ of surfactant in the feed solution. You'll be getting a straight line for let us say counterion let us let us say zinc or copper Cu^{2+} is equal to 0, And when you go on increasing the copper solution the counterion. And concentration in the feed this line will shift towards left; that means, and this is let us say copper is equal to four kg per meter cube; that means, 4000 ppm and the shift of the curve occurs in these direction. So, what does that mean, that you'll be having you can extrapolate these lines and they will be corresponding to the gel layer concentration; corresponding to each copper concentration. And we have to conduct these experiments as a constant same mass transfer coefficient; that means, at the same starting speed or the cross flow velocity.

Now, if you have a pure copper solution the gel layer concentration will be maximum, if you increase the copper solution in the feed, then gel layer concentration will decrease, if we increase the copper solution copper concentration further the gel layer concentration will be lowest. So, therefore, the gel layer concentration will be having a decreasing trend with respect to the counterion concentration in the feed.

Now, for SDS Cu^{2+} system we conducted experiments for every copper

concentration and we have seen that gel layer concentration is really decreasing with the copper concentration. And **they are they are** they obey, you know almost straight line of relationship over a free over a particular concentration range.

Now, if you want I can give you the expressions C_g ; becomes $366 - 0.21 C_u$ concentration of copper for copper concentration, less than C_u copper concentration less than one kg per meter cube that is thousand ppm. And this becomes $200 - 92 C_u$ for a copper concentration lying between 1 and 4 kg per meter cube, when copper concentration is 0; you'll be getting the maximum gel layer concentration that is 366. When you increase the copper concentration in this range, it will decrease gel layer concentration of surfactant; will decrease as a linear function with the copper concentration in place in place of copper.

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For Ca^{2+} RA counter ion:

$$C_g = 366 (1 - 0.14 C_{Ca}) \quad \text{for } C_{Ca} < 1 \text{ kg/m}^3$$

$$= 318 - 4.37 C_{Ca} \quad \text{for } C_{Ca} < 4 \text{ kg/m}^3$$

Mass Transfer Coeffs.

Laminar: $Sh = \frac{Kd_e}{D} = 1.86 (Re Sc \frac{d_e}{L})^{1/3}$

Turb: $Sh = \frac{Kd_e}{D} = 0.023 (Re)^{0.8} (Sc)^{0.3}$

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If you have a calcium as a counterion for calcium, as counterion the gel layer concentration decreases like this $366 - 0.14 C_{Ca}$ and is equal to $318 - 4.37 C_{Ca}$. For calcium concentration this is for calcium concentration less than 1 kg per meter cube and this is for calcium concentration lying between 1 and 4 kg per meter cube.

The mass transfer coefficient can be calculated from the equations or the correlations depending upon the laminar. And the turbulent flow regime that we have already seen earlier for the laminar flow regime the Sherwood number. That is given as $K d_e$ by D is

equal to $1.86 \text{ Reynolds}^{1/3}$ and by 1 raised to the power 1 upon 3. And for the turbulent flow it will be calculated as from the relationship $0.023 \text{ Reynolds}^{0.8}$ smith raised to the power 0.3. So, that **is the**, you know the permeate flux can be predicted in terms of when there is a pure component or pure counterion is present next we will see the effect of binary mixture on C gel; that means.

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Effect of binary mixture on gel layer concentration

Reduction of gel layer concentration
is a function of composition of counter ions.

$C_{Cu^{2+}} : C_{Ca^{2+}}$ (mg/l)	C_g^{2+} (kg/m ³)
0.5 : 3.0	311
1 : 2.5	302
2 : 2	298
3 : 1	291
4 : 0.5	281

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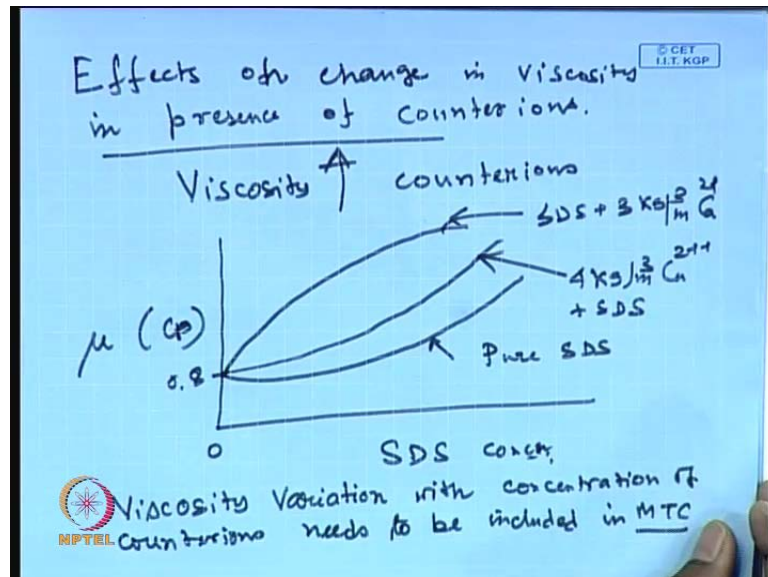
If you have a binary mixture of copper and calcium, then what will be its effect on the gel layer concentration or in presence of competitive counterions effect of binary mixture on gel layer concentration?

Now, it may **it may** have a **the** case that you may **you may** not be having a single counterion. You may be having a mixture of counterions. Now, for example, if you have a mixture of counterions for example, copper and calcium then it'll be having a prominent effect on the gel layer concentration. The reduction of the gel layer is also very important reduction of gel layer concentration of gel layer concentration; is a function is definitely is a function of composition of counterions. And, this **the** can be quantified, you had you, it is measured. And it has been found out that, if you have $C_{Cu^{2+}}$ plus is to $C_{Ca^{2+}}$ and this concentration I mean I were talking about the concentration of these. If these concentrations are **are** represented in kg per meter cube then the gel layer concentration can be experimentally, found out. And this trend will be obtained 0.5 is to if you have a ratio of copper. And that of calcium in 0.5 and 3 then mixtures

concentration becomes 311 by gel layer concentration becomes 311. And if you have a 1 is to 2.5, then it'll be 302, if you have 2 is to 2. And you will be having 298 then if you have 3 is to 2, then you'll be having 291 a 4 is to 0.5 then you'll be having 281.

So, there will be the, so, there is a competitive you know absorption of the counterions on the micelle surface. And based on the composition of the counterions, the gel layer concentration will change or will vary next, that is a very important. There is a the presence of these counterions, and the presence of the micelle formation will be having an important effect on the viscosity of the solution.

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Effects on change in viscosity, in presence of counterions is very important that the surfactant micelles; and presence of counterions change the viscosity of the solution. And it has been observed that viscosity of the surfactant solution increases in present of the in presence of the counterions. Now, viscosity increases in presence of counterions, and if you plot the variation of viscosity this is in unit of centipoise μ is in unit of centipoise and let us say this is S D S concentration obviously, the with S D S concentration the viscosity will increase it starts from point eight for zero S D S concentration; that means, for pure water and the variation of pure S D S viscosity will be in this form it increases the viscosity of the pure S D S solution increases with the S D S concentration this is for pure S D S pure S D S means there is no counterions present in the system.

Now, if you have a presence of copper the tune of 4 k g per meter cube the variation the

viscosity value will be more compared to no without presence of calcium copper 4 k g per meter cube copper plus S D S. Now if you have calcium a viscosity will be further higher. And these becomes you know S D S plus 3 k g per meter cube calcium solution. Now, **these these** this is a complex phenomena, and this viscosity variation with concentration needs to be incorporated in the mass transfer coefficient viscosity variation becomes pretty important. And this viscosity variation with concentration of counterions needs to be included in calculation of mass transfer coefficient; that means, you must be having a type of relationship to you know correct the viscosity variation by the change in concentration in the system.

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Counterion binding on micellar surface → Quant. Localized adsorption Model
Rothman & Scamhorn.

The binding ratio of counterions on micelles, → β_i

$$\beta_i = \frac{K_i C_i e^{-\frac{z_i \psi}{k_B T}}}{1 + K_i C_i e^{-\frac{z_i \psi}{k_B T}} + K_{Na} C_{Na} e^{-\frac{z_i \psi}{k_B T}}}$$

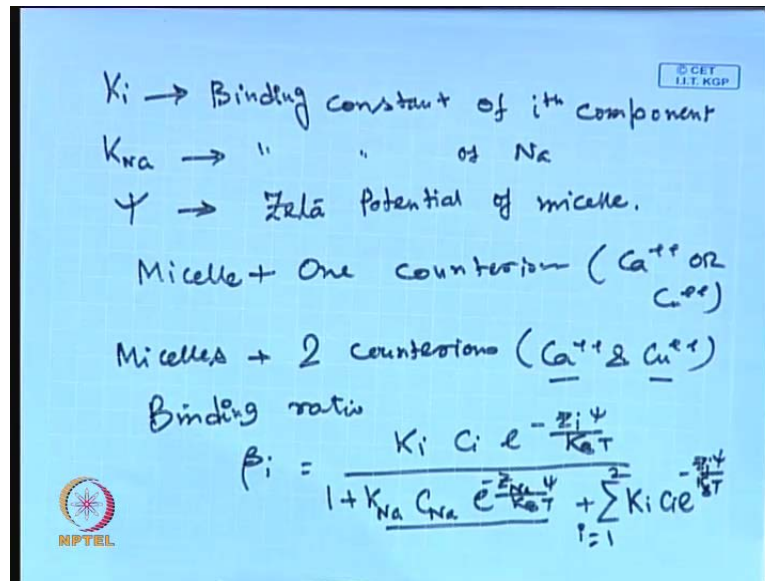
SDS & cationic system
 C_i → bulk concentration of solute

Now, in case of counterion binding counterion binding on micellar surface can be quantified by something called localized isotherm adsorption model; this quantification can be done by localized adsorption model; and this model was first proposed Rothmans, and scam horn in early 1980's; and it is it is assumed that, and these isotherm can be evaluated to calculate the amount of count the counterion that that was present in the free solution.

And the binding ratio **binding ratio** of counterions on micelles is defined by the binding constant beta, and these beta, i is defined as $K_i C_i$ exponential minus $z_i \psi$ over $k_B T$ divided by 1 plus $K_i C_i$ e the power minus $z_i \psi$ over $k_B T$ plus k of $N_a C$ of N_a e to the power minus $z_i \psi$ over $K B T$. We were talking about sodium (()) micelle, and S

D S, and counterions may be let us say, cation; in cations or metal ions there are two metal ions present. So, it is **it is** basically langevin type of isotherm talking about these K_i C_i is the bulk concentration of the solute this for the solute, **if you have a**, if you have copper, and calcium; this i is for copper in one case, in another case it will be for calcium.

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$K_i \rightarrow$ Binding constant of i^{th} component
 $K_{Na} \rightarrow$ " " of Na
 $\psi \rightarrow$ Zeta potential of micelle.

Micelle + One counterion (Ca^{++} or Cu^{++})
 Micelles + 2 counterions (Ca^{++} & Cu^{++})

Binding ratio

$$\beta_i = \frac{K_i C_i e^{-\frac{z_i \psi}{k_B T}}}{1 + K_{Na} C_{Na} e^{-\frac{z_{Na} \psi}{k_B T}} + \sum_{i=1}^2 K_i C_i e^{-\frac{z_i \psi}{k_B T}}}$$

So, C_i is the bulk concentration of solute K_i is the binding constant of i component K_{Na} will be that is the binding constant of sodium ion, and ψ is the zeta potential of the micelle. So, you can measure the zeta potential of the micelle, that be it I can be measured using a zeta meter, but in case of sodium dodecyl sulfate apart from the counterions, I mean the metal ions you will be having the sodium or an ion also present in the solution as a counterion.

So, you have to take care of that as well now, for a two this is basically a micelle the expression that, you have given is for the micelle plus 1 counterion for example, calcium plus plus or copper plus plus in sodium dodecyl micelle. Suppose, you will be having a system of micelle plus 2 counterions; that means, in effect if you have the system of micelle as 1 counterion. You will be having 2 counterions for example, copper and sodium ions will be always present in the system, because sodium will be coming out in the solution from the surfactant monomers.

So, if you have a system called micelles plus two counterions for example, if you have C

a plus plus, and copper plus plus present. So, there will be 3 counterions present at effectively. So, in these two and the sodium by default so, therefore the isotherm the extent of binding ratio. In this case is given as binding ratio is defined as beta i is nothing, but $K_i C_i e^{-z_i \psi / K_B T}$ over $K_B T$ is the boltzmann constant k_B is the temperature one plus k_B of $N_A C_i / N_A e^{-z_i \psi / K_B T}$ basically. So, it'll be one ψ over $K_B T$ plus summation of $K_i C_i e^{-z_i \psi / K_B T}$ over two species 1 to 2. So, the one for the copper another for the calcium, and you will having a term called corresponding to sodium. So, this is in the same form of extended langevin isotherm as we have discussed in the last class. So, it can be extended for multi component system.

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Experimental Evaluation of β_i

$$\beta_i^{\text{exp}} = 2 \left[\frac{C_i - C_{p_i}}{C_0^S - C_m C} \right]$$

C_i → initial concentration of cations
 C_{p_i} → concentration of i th cation in the permeate.

$K_i S$ and ψ → are unknown in the isotherm expression.
 Measurable → ψ parameter.

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Now, you can experimentally found-evaluate the value of beta experiment evaluation of beta of solubilisation constant beta i experimental can be obtained as 2 times C i minus C p i divided by C naught S minus C m C, what is this the C i is nothing, but the concentration of ith counter ion for example, zinc plus plus, that is present in the solution initial concentration C i is the initial concentration of cations, and what is C p I; C p i means of out of out of the total concentration of the cation some of them will be attached to the micelle, and rest of them in the free state. And since they are easily permeable through they are **they are** easily permeable on across the membrane. So, the concentration of the free metal ions present in the bulk will be same as the concentration of the free metal ions in the permeate.

So, if you measure the concentration of free metal ions in the permeate stream by using an either enhanced selective electrode or an atomic absorption spectrophotometer. You will be able to measure the amount of free counterions present in the solution $C_{p,i}$ is the concentration of i th cation in the permeate; and $C_{0,S}$ is the total concentration of the surfactant present in the feed solution minus $C_{m,C}$ $C_{m,C}$ is the amount of concentration the it corresponds to critical miceller concentration.

So, therefore, $C_{0,S}$ minus $C_{m,C}$ will represent the amount of the concentration of the micelle present in the system in terms of monomer. So, why this factor two will be coming this factor two will be coming, because of the valency of the counterions. Now, this is the experimental evaluation of β_i . So, you know the concentration of the counterions in the feed. You know the concentration of surfactant in the feed; you know the value of $C_{m,C}$, and you will, you can measure the concentration of the permeate for the counterions of the metal ions. So, by measuring all these, and knowing various quantities; you can define, you can measure, the experimental values of extent of solubilization or the extent of binding ratio.

Now, **the** So, therefore in the **...** if you remember in the definition of the binding ratio there are some constants have to be determined one is the is your k_i 's **k_i 's** and ψ_i ; ψ_i is unknown; they are unknown in the isotherm expression. So, in fact, these is a measurable quantity, you can use the use the zeta meter, and can measure the value of zeta potential.

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K_i 's can be evaluated

$$S = \sum_{\text{no. of exp'ts}} (\beta_{i, Cu}^{\text{exp}} - \beta_{i, Cu}^{\text{cal}})^2 + \sum_{\text{no. of exp'ts}} (\beta_{i, Ca}^{\text{exp}} - \beta_{i, Ca}^{\text{cal}})^2$$

- (1) Start with guess values of K_i .
- (2) Evaluate S .
- (3) Use an optimization technique to minimize 'S'.
- (4) result a new set of K_i 's.
- (5) Check $S < 10^{-3}$.

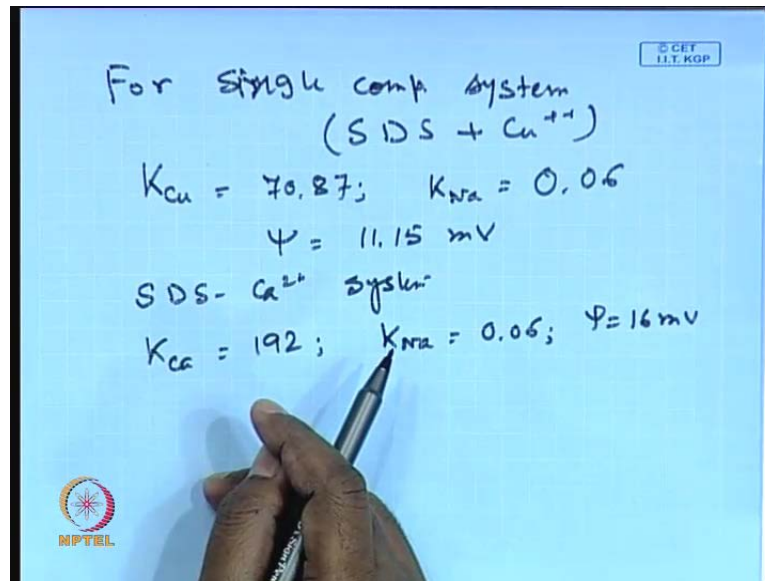
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So, what is left behind is the various values of binding constants K_i . Now, these isotherm constants can be evaluated from experimental data, how you measure the, you know, how to measure the value of beta i . You know how to measure the you know calculate the values of beta i , if you know the values of K_i S .

So, you minimize these sum this can be optimized basically, and this optimization value will be beta i copper experimental minus beta i copper calculated, square of that plus summation beta i calcium experimental minus beta i calcium calculated, square of that. So, you start with a guess values of K_i S start with guess values of k_i 's. Then you calculate-evaluate the value of beta i 's. And then evaluate, and compare with the experimental value, and evaluate this sum S over the number of experiments. This summation is over number of experiments. Then evaluate S , and then use an optimizer use an optimization technique to minimize the value of S that means, you are doing the minimization of sum of squares of the errors; the error between the maximum, I mean the measured value, and the experimental value. And the calculated value use an optimization technique to minimize the value of S . And these, optimizer will then find out it will it will result a new set of k_i 's that is the job of the optimizer you need not to worry about it once you get the new set of k_i 's evaluate the value of s again and see whether s is less than less than a particular criteria check s is less than 10 to the power minus 3 or 10 to the power minus 2. So, there is some error limit, if S is below that limit. The iteration will stop, and the corresponding values K_i will be the final net

values of K i's. Otherwise, it will be iterated once again; and they will **it will** the optimizer will again evaluate the various values of K i by technique or some other technique by itself, and evaluate the value of S again, and see whether it is minimum or not. So, that how that is how the various values of isotherm constants will be evaluated by comparing the experimental data with the measure measured with the calculated data.

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Now for single component system, I have some typical data for single component system remains for S D S, and copper system. The values of isotherm constants are given as K of C u is 70.87, that for K of N a is 0.06, the value of psi will be 11.15 milli volt on the other hand for S D S calcium system value of calcium is 192 k of sodium is 0.06 and psi will be around 16 milli volt.

Now, similar results can be obtained for S D S, and copper calcium system and so on. **So, forth.** So, that is how one can obtain the various values of isotherm constants. So, these will give you comprehensive, give an comprehensive idea, how to may, how to evaluate the counterion binding extent of counterion binding on the micelles, and **and** by using the isotherm. One can evaluate the value of the of this counterions of the metal ions present in the free form; that is number one, and using the gel layer theory. One can evaluate the amount of the quantification the permeate flux; we are going to get which is nothing, but the productivity of the system.

Now, next we will be **we will be** taking up some of the examples, how to do the

calculations of these system micellar enhanced ultra filtration system.

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Ex 1: Removal of organic pollutant using MEUF. SDS + Phenol.

C_0^S → Feed concentration of surfactant → 10 kg/m^3 .

C_0 → Feed concn. of Phenol → 20 mg/L .

Solubilization isotherm is given by

$$S = \frac{q b_1 C_p}{1 + b_1 C_p}$$

$[S]$ → mg/mg .

So, the first example, we talking about is removal of an organic using the micelles of organic pollutants using MEUF, and we the surfactant, we are talking about S D S, and the organic (()). We are talking about phenol, the feed concentration of surfactant is given this is around 10 k g per meter cube; the feed concentration of phenol is given these 20 milligram per liter; and solubilization S the value, the solubilization isotherm is given as is given as S is equal to Q times b 1 times C p divided by 1 plus b 1 times C p, and the unit of S is in milligram per milligram of the milligram of the solute, per milligram of the micelle.

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$C_g = 0.1 \text{ mg/mg.}$
 $b_1 = 9 \times 10^2 \text{ l/mg.}$
Given $S = 2.34 \times 10^{-3} \text{ mg/mg}$ SDS $\rightarrow C_g = 280 \text{ kg/m}^3.$
 $K = 2 \times 10^{-5} \text{ m/s.}$
CMC of SDS = $2.3 \text{ kg/m}^3.$
 $J = ? \rightarrow$ Permeate flux
 $C_p \rightarrow$ Permeate conc. of phenol.
Soln: $J = K \ln \frac{C_g}{C_s}$
 $= 2 \times 10^{-5} \ln \frac{280}{10} = 6.67 \times 10^{-5} \frac{\text{m}^3}{\text{m}^2 \cdot \text{s}}$

And the various values of the isotherm constants are given Q is equal to 0.01 milligram per milligram b_1 is given as 9×10^2 liter per milligram, and gel layer concentration of SDS; the gel layer concentration is given 280 kilogram per meter cube. And the mass transfer coefficient of this particular system is given as 2×10^{-5} meter per second; the CMC of SDS is also given as 2.3 kg per meter cube.

So, what you have to find out **you have to find out** the permeate flux, how much is the permeate flux of the system, and permeate concentration of phenol. So, the first **first first** question is very straight forward; the flux is given as J equal to $K \ln \frac{C_g}{C_s}$ if you just put the values of put various parameters $2 \times 10^{-5} \ln \frac{280}{10}$ that will be directly give you the value of permeate flux; it will be 6.67×10^{-5} meter cube per meter square second. The extent of solubilization is also given in this problem S is given as 2.34×10^{-3} milligram per milligram that is also given.

So, now once you get the value of permeate flux. Then you are going to find out, what is the permeate concentration for that, you are going to put the value of S in the soluble in the isotherm expression.

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$2.34 \times 10^3 = \frac{0.1 \times 9 \times 10^2 C_p}{1 + 9 \times 10^2 C_p}$
 $C_p = 0.266 \text{ mg/L.}$
Observed retention of Phenol.
 $R_o = 1 - \frac{C_p}{C_o} = 98.67\%$

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So, if you put the value of S in the isotherm expression 2.34 into 10 to the power minus 3 is equal to 0.1 into 9 into 10 to the power minus 2 times C p divided by 1 plus 9 into 10 to the minus 2 time C p. And you can find out, you can evaluate the value of C p as 0.266 milligram per liter, and the observed retention of the phenol can be easily found out 1 minus C p by C naught, and it turns out to be around 98.67 percent. So, that gives the quality of the permeate. And you can find out the... you know permeate flux from the gel layer concentration module. Now, the next problem it is a counterion ion binding on a on a micelles surface; that means, you must be having a metal ion in your system.

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Ex 2: SDS micelle $\rightarrow 4 \text{ kg/m}^3$
 $\text{Cu}^{2+} \rightarrow 4 \text{ kg/m}^3$
 $K \rightarrow 10^{-5} \text{ m/L.}$
Permeate flux? $C_o^S = 10 \text{ kg/m}^3$
 $R_o, \text{Cu}^{2+} = ?$
 $C_g = 2.92 - 3 C_{cu}$
 $\text{CMC} = 2.3 \text{ kg/m}^3$

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So, I will be just discussing one more example in this topic example two; in this case, copper is removed from a S D S micelle solution. You have the S D S micelle with the feed concentration 4 kilogram per meter cube; the copper concentration is 4 kilogram per meter cube copper present in the system is 4 kilogram per meter cube; mass transfer coefficient is also given as 10 to the power minus 5 meter per second. You have to find out the permeate flux, and observed retention of copper, and a S D S concentration is also given in the feed that is 10 k g per meter cube.

Now, in this case if we use the organic solute we can use the solubilization isotherm, if you use the, if you have the counter ions present in the system, which has to be removed by your system micelle enhanced ultra filtration. You have to use the localized isotherm localized adsorption model. So, there are two things; one is the, if you have the solubilization of the organic pollutions that we will be those will be solubilised in the hydrophobic core; you have to use the (β) term, if you have the counterions that should be bound over the outer surface of the micelles. Then you have to use the localized adsorption theory. The gel layer concentration as a function of copper concentration is given **it is given** as 292 minus 3 of concentration of copper in the bulk, and C m C of S D S is also given as 2.3 kilogram per meter cube .

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Localized adsorption model. 2 various binding constants:

$$\beta = \frac{K_{Cu} C_{Cu} \exp\left(\frac{-z_{Cu} e \psi}{k_B T}\right)}{1 + K_{Cu} C_{Cu} \exp\left(\frac{-z_{Cu} e \psi}{k_B T}\right) + K_{Na} C_{Na} \exp\left(\frac{-z_{Na} e \psi}{k_B T}\right)}$$

$K_{Cu} = 71$, $K_{Na} = 0.06$; $z_{Cu} = 2$
 $z_{Na} = 1$, $\psi = 11 \text{ mV}$; $T = 300 \text{ K}$.

Permeate flux $\rightarrow J = k \ln \frac{C_0}{C_g}$
 $C_g = 292 - 3 \times 4 = 280 \text{ kg/m}^3$

Now, localized adsorption model is also the isotherm form is given and various binding constants are also given beta is K C u C u exponential minus z C u e psi over K B T

divided by 1 plus $K C_u C_u$ you please remember in the **in the** expression in the within the exponential. There will be, it will be $z e \psi$ by $K b$ did not mention the e earlier, but it should be e included, because z being the dimensionless number the unit of $K B T$ is nothing, but the energy similarly, it should be multiplied by e that is the electronic charge 1.6×10^{-19} to be that multiplied by voltage will be give you the energy. So, this value the term within the exponential must be dimensionless.

So, it should be multiplied by the e exponential minus $z C_u e \psi$ over $K B T$ plus k of $N a C$ of $N a$ exponential minus z of $N a e \psi$ over $K B T$ various values of isothermal constants, and the data potential etcetera are known, in this particular problem $K C_u$ is $71 K$ of $N a$ is 0.06 z of copper is 2 plus 2 z of $N a$ is plus 1 ψ is given as the zeta potential; that is 11 mill volt and T is 300 Kelvin. The permit flux, you can easily obtain, if you know the gel layer concentration J is equal to the mass transfer coefficient is given the feed concentration is given of the surfactant; that is given, and gel layer concentration can be evaluated C_g can be evaluated from the relation, that is given 292 minus 3 into 4 that is around 280 kilogram per meter cube.

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The image shows a handwritten derivation on a blue background. At the top right, there is a small logo for '© CET I.I.T. KGP'. The main calculation starts with the permeate flux $J = 10^{-5} \times \ln \frac{280}{10} = 3.33 \times 10^{-5} \frac{m^3}{m^2 s}$. Below this, the reflection coefficient β is calculated as $\beta = \frac{71 \times 4 \times \exp\left[-\frac{2 \times 11 \times 10^{-3} \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300}\right]}{1 + 71 \times 4 \times \exp\left[-\frac{2 \times 11 \times 10^{-3} \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300}\right] + 0.06 \times 20 \times \exp\left[-\frac{1 \times 11 \times 10^{-3} \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300}\right]}$. The result is $\beta = 0.985$. To the right of this, a box contains the values $C_{p1} = 0.21 \times 10^{-3} \frac{kg}{m^3}$ and $R_0 = 94.75\%$. At the bottom left, there is an NPTEL logo. The final equation shown is $0.985 = 2 \left(\frac{C_{o1} - C_{p1}}{C_{o2} - C_{mc}} \right) \Rightarrow \left(\frac{C_{o1} - C_{p1}}{C_{o2} - C_{mc}} \right) = 0.4925$.

Using these value of gel layer concentration, you can find out the value of the steady state permeate flux as 10 to the power minus 5 into logarithm 280 divided by 10 . So, this turns out to be 3.33 into 10 to the power minus 5 meter cube per meter square second. So, that directly gives you the value of the permeate flux next we will be finding out

what is the value of beta a, if you **if you** put the various values in the expression of beta it turns out to be 71×10^4 I am just putting the values, in order to you can find out the, you know detail steps of the calculations 10^{-2} into 10^{11} into 10^{10} to the power minus 3 that is the psi into 1.6×10^{19} ; that is the electronic charge divided by 1.38×10^{23} that is the boltzmann constant into 300 that is the temperature in Kelvin 27 degree centigrade. So, it'll around 300 kelvin these divided by $1 + 71 \times 10^4 \times 10^{-2} \times 10^{11} \times 10^{10}$ to the minus 3 multiplied by 1.6×10^{19} divided by 1.38×10^{23} into 300 this corresponds to copper the next one will be corresponding to sodium. So, 0.06×10^{20} into exponential minus 1 into 10^{11} into 10^{10} to the power minus 3 this 20 comes from the concentration of the surfactant means, the same amount of sodium ions will be generated so, $1 \times 10^{11} \times 10^{10}$ to the power minus 3 into 1.6×10^{19} divided by 1.38×10^{23} times 300. So, all this calculation will be leading to a value 0.985.

Now, if you calculate the value of beta from the experimental conditions. So, you will be getting beta is equal to $2 \times C_{01} - C_{p1}$ divided by $C_{0S} - C_{mC}$ of the S D S solution. You know the C_{mC} of the S D S solution; you know the feed concentration of surfactants, you know the feed concentration of solute, and you know, then so you do not know the value of concentration of the **of the** countenance in the permeate, but you have already found out the value of beta from this theory that is 0.985. So, use the value of 985 here and on the right hand side. You will be having that same thing $C_{01} - C_{p1}$ $C_{0S} - C_{mC}$. So, it will be you just put the values only one unknown is there that is C_{p1} So, $4 \times 10^4 - C_{p1}$ divided by $10^{10} - 2.3$. So, this leads you to the value of C_{p1} as 0.21 kilogram per meter cube or if you would like to calculate the observed retention this turns out to be 94.75 percent.

So, that is the answer. So, what do you have seen that, if you know the experimental, you know concentrations, and if you know the ice thump values; you know constants using the isotherm of the localized adsorption model. You will be in a position to calculate the permeate quality **the** what is the permeate concentration of the copper, and what is the observed retention. So, that that **that that** will finish the micelle enhanced ultra filtration part of our course. And let us, summarize whatever we have done. So, we have looked into the fundamental principles of working principles of micelle enhanced ultra

filtrations. We have defined our critical micelle concentrations, and we have identified the region, where the organic solutes will be adsorbed or solubilized or under region, where the ionic solutes of the **of** counterions in nature of the opposite polarity will be adsorbed. The counterions will be adsorbed on the outer surface of the micelles; the ionic pollutants, and the organic pollutants, will be will be solubilized within the hydrophobic core of the micelles. And this solubilizations in the transfer of the counterions of the solutes over the micelles are almost instantaneous in nature.

Now, assuming the gel layer concentration model, the permit flux can be predicted using the gel layer concentration model assuming that the surfactants will be the micelles, will be forming a gel type layer of layer over the membrane surface, and the counterions to the to the quality of the permeate or the amount of counterions; that is present in the permeate can be obtained or can be quantified using the adsorption model, whether it will be adsorption for the solubilization isotherm using the isotherms of solubilization, isotherms of the organic or the localized absorption model **of the** for the counter ions using these isotherm models, one can easily calculate or the predict the concentration of the solutes in the permeate stream. So, in **So, in** the next class, we will move forward, and we will be looking into the principles of liquid membranes.

Thank you.