Introduction to Process Modeling in Membrane Separation Process

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Lecture – 08
Osmotic Pressure Controlling Filtration (Contd.)

Welcome to this session. Now as we have seen in the last class that you are basically we are trying to predict the system performance that is the permeate flux and permeate concentration for an osmotic pressure control filtration using the one dimensional model in your mass transfer boundary layer. And the one dimensional model is also commonly and popularly known as the film theory model.

So, we have seen that ultimately we have written down the film theory model and we got the one equation Vw is equal to K ln Cm minus Cp divided by C naught minus Cp and the solvent flux to the porous membrane that is the osmotic pressure model Vw is equal to delta P minus delta pi.

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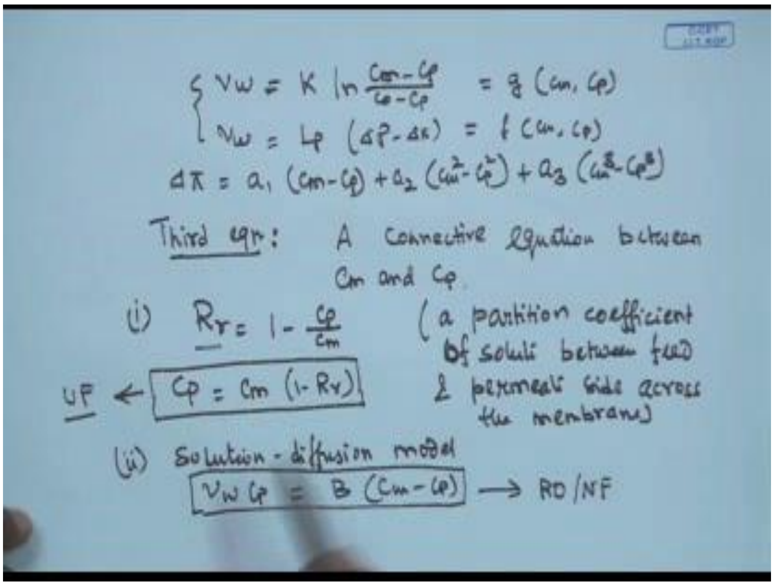

$$\begin{cases} V_w = K \ln \dfrac{C_m - C_p}{C_0 - C_p} = g(C_m, C_p) \\ V_w = L_p(\Delta P - \Delta\pi) = f(C_m, C_p) \end{cases}$$

$$\Delta\pi = a_1(C_m - C_p) + a_2(C_m^2 - C_p^2) + a_3(C_m^3 - C_p^3)$$

Third eqn: A connective equation between C_m and C_p

(i) $R_r = 1 - \frac{C_p}{C_m}$ (a partition coefficient of solute between feed & permeate side across the membrane)

$$UF \leftarrow \boxed{C_p = C_m(1 - R_r)}$$

(ii) Solution - diffusion model

$$\boxed{V_w C_p = B(C_m - C_p)} \longrightarrow RO/NF$$

And we have also seen, let me write down these two equations Vw equal to K ln Cm minus Cp divided by C naught minus Cp and Vw is equal to Lp del P minus del pi. And we have also seen that how delta pi is related to Cm minus Cp as a 1 Cm minus Cp plus a 2 Cm square minus Cp square plus a 3 Cm cube minus Cp cube.

So therefore, these equations can be expressed in terms of Cm and Cp and these equations are also expressed in another function of Cm and Cp. But there are three unknown; Cm, Cp and Vw and we have two equations so we need to have one more equation. So, let us look what is the third equation. Third equation is basically a connective equation between Cm and Cp. So, what are the connective equations? If you look into the definition of real retention; definition of real retention is 1 minus Cp by Cm, so this is one route how to connect Cp and Cm solute concentration at the permeate and solute concentration on the membrane surface.

So, as we have discussed already that real retention is nothing but a intrinsic parameter of the membrane which connects the concentration of solute on the membrane surface and concentration of solute on the permeate side, and it is constant for a particular membrane solute solvent system. And we have also seen how independently the real retention of a solute solvent and membrane system can be estimated by conducting a separate set of experiment.

Therefore, real retention can be treated as constant. If you look at into the expression of real retention it can also be interpreted as a partition coefficient of solute between feed and permeate side across the membrane. It can be interpreted that by that as well. So, if you estimate real retention form a separate set of experiment we can connect Cp in favors of Cm and real retention. So, Cp can be written as Cm into 1 minus R r. That is how we get a third equation or extra equation for Cp as a function of Cm. What is the second idea? The second idea is one can instead of real retention one can really use the solution diffusion model that we have already derived earlier.

So, if you are talking about a nano filtration system or a reverse osmosis system we are going to use the solution diffusion model in order to invoke the third equation. If you are talking about the ultra filtration or various lower cut off ultra filtration or higher cut off ultra filtration then will be invoking the definition of real retention in order to connect the Cp and Cm as a third equation.

Let us write down the solution diffusion model or there are other variants of solution diffusion model that you can also look into. So, this will be Vw Cp is equal to B times Cm minus Cp, so this is the solution diffusion model this can be utilized as a third equation in case of reverse osmosis and nano filtration. And in case of ultra filtration we can use the definition of real retention to connect Cp and Cm as a third equation. So, let us look into the case of ultra filtration first, because that will be given the easy way of handling the system. Then will be looking into the solution diffusion model and after that will be examining the various cases of various other cases of variants of solution diffusion model.

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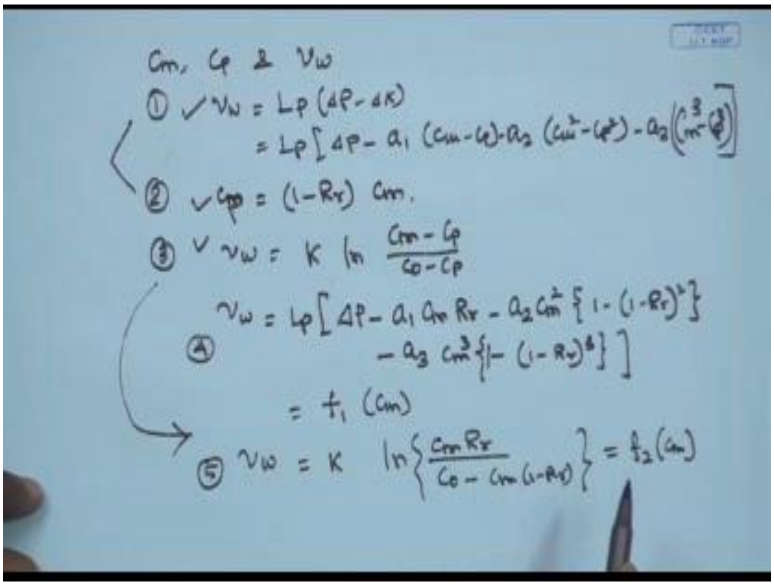

C_m, C_p & v_w

① ✓ $v_w = L_p(\Delta P - \Delta\pi)$

$= L_p\left[\Delta P - a_1(C_m - C_p) - a_2(C_m^2 - C_p^2) - a_3(C_m^3 - C_p^3)\right]$

② ✓ $C_p = (1 - R_r)\,C_m$

③ ✓ $v_w = k \ln \frac{C_m - C_p}{C_0 - C_p}$

④ $v_w = L_p\left[\Delta P - a_1 C_m R_r - a_2 C_m^2\{1 - (1 - R_r)^2\} - a_3 C_m^3\{1 - (1 - R_r)^3\}\right]$

$= f_1(C_m)$

⑤ $v_w = k \ln\left\{\frac{C_m R_r}{C_0 - C_m(1 - R_r)}\right\} = f_2(C_m)$

So, let us continue with the osmotic pressure model, the third equation that we have already found out. Now let us write down the equation to solve. We have three unknowns; Cm, Cp and permeate flux Vw and three equations now Vw is equal to Lp del P minus del pi which will be essentially Lp del P minus a 1 Cm minus Cp plus minus a 2 Cm square minus Cp square minus a 3 Cm cube minus Cp cube.

You have the definition of real retention Cp is equal to 1 minus Rr time Cm there is the connection. And we have the film theory model Vw is equal to K ln Cm minus Cp divided by C naught minus Cp. So, we have three equations and three unknown Cm Cp and Vw. Next what I am going to write; I am replacing Cp is as a function of Cm in equation 1. Suppose this equation number 1, this equation 2, this equation 3. If we combine this two will getting Vw is equal to Lp del P minus a 1 Cm Rr minus a 2 Cm square 1 minus 1 minus Rr square of that minus a 3 Cm cube 1 minus 1 minus Rr whole cube.

Since Rr is constant a 1, a 2, a 3 coefficients are osmotic pressure coefficients constant delta P is constant for a particular operating condition Lp is constant, so Vw will be some function of Cm. And you can write down the third equation the film theory model as Vw equal to K ln Cm minus c p; so ln Cm times Rr and this will be C naught minus Cm 1 minus Rr. Now this will be another function of Cm. So, this equation number 4 and this equation number 5.

Now, will be having two equations and two unknown only because we have eliminated Cp in favor of Cm in both the equations; and equation number 4 and equation number 5 at the two resultant equations. Now what are these two equations are algebraic equations which can be algebraic equations and they are basically connected a coupled non-linear algebraic equation and therefore these two equations can be solved using Newton-Raphson method by a guess value of Cm. So, we use a guess value Cm and then we will basically be equating equation 4 and 5. So, if we equate the equation 4 and 5 will be landing up only one equation in c m.

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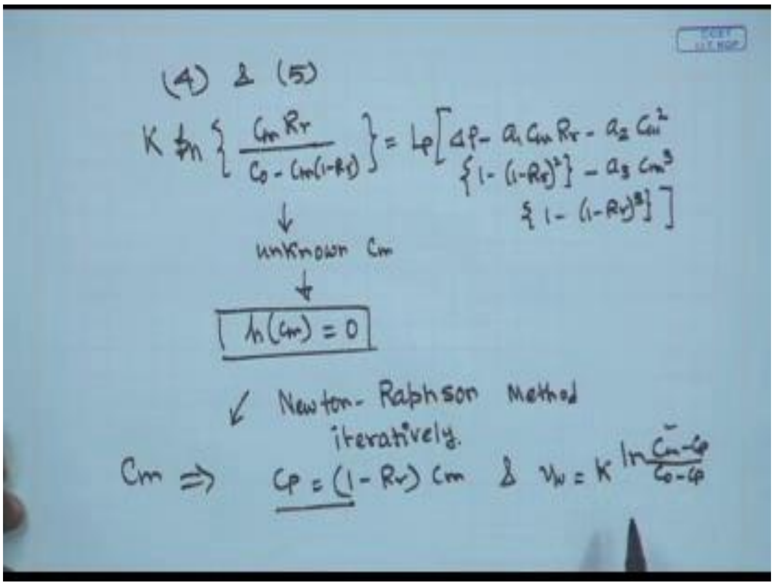

(4) & (5)

$$K \ln \left\{ \frac{C_m R_r}{C_0 - C_m(1-R_r)} \right\} = L_p \left[\Delta P - a_1 C_m R_r - a_2 C_m^2 \{1-(1-R_r)^2\} - a_3 C_m^3 \{1-(1-R_r)^3\} \right]$$

↓

unknown C_m

↓

$$\boxed{h(C_m) = 0}$$

↙ Newton-Raphson method iteratively.

$C_m \Rightarrow$ $C_p = (1-R_r) C_m$ & $v_w = K \ln \frac{C_m - C_p}{C_0 - C_p}$

So, comparing equations 4 and 5 we can equate them out so these becomes K ln Cm Rr divided by C naught minus Cm 1 minus Rr is equal to Lp del P minus a 1 Cm Rr minus a 2 Cm square 1 minus 1 minus Rr square of that minus a 3 Cm cube 1 minus 1 minus Rr cube bracket close.

So, this will be a non-linear equation in Cm only; only known is Cm. We can cast it in the form of h times Cm some function is equal to 0. So, if you take the right side on the left hand side then we can write it in the form of some function of Cm a non-linear function of Cm algebraic equation. So therefore, this can be solved using Newton-Raphson method iteratively. So, once we get the value Cm, what will be the output of this; output will be the Cm once you get the value of Cm you can get the value of Cp as 1 minus Rr times Cm and one can get the value of permeates flux as K ln Cm minus Cp divided C naught minus Cp. We know the value of Cp now we have already estimated; we know the value of Cm estimated from this C naught is known K is known Vw can be estimated.

So therefore, this is a predictive method of calculation of permeate flux and permeate concentration as a system performance for one dimensional modeling of mass transfer boundary layer and hooking it up with the flow through the porous media for a cross flow filtration system. This will be giving you a very brief very very good idea about the as a first hand calculation for having a system performance and these can really done we done in an internally predictive mode, because you have not there is no adjustable parameter if you really know the solute diffusivity. So what are the input parameters this problem? The input parameters of these problems are the operating conditions. What are the operating conditions? The operating conditions are delta P the trans membrane pressure drop feed concentration and cross flow velocity that is u naught. These three values are operating conditions we are already setting them so you know their values.

Another important operating condition is ph of the solution and the how the p h solution will be affecting. P h of the solution will be affecting the osmotic pressure of the solution. So, osmotic solution relationship is known to us pi is equal to a 1 c plus a 2 c square plus a 3 c cube. These osmotic coefficients a 1 a 2 and a 3 they are known to us. So, one of the other transport coefficients you require; the other transport coefficient you require density, viscosity and diffusivity, we are assuming them to be constant and they values are known to us.

What are the others; the other two parameters should be known to us these are basically the membrane performance parameters. One indicates how porous my membrane is that is permeability of the membrane another was the how selectively my membrane is, that is the real retention of the membrane. So, in the earlier classes we have already seen how to estimate membrane permeability and the selectivity of the membrane independently. And therefore using these values only one can really solve permeate flux and permeate concentration in a predictive mode. There is no adjustable parameter in this model and a prediction can be really done.

And in the process and another parameter the membrane surface concentration, solute concentration of the membrane surface can be estimated as well. So therefore, one can really estimate what is the extent of concentration polarization. This is also known as polarization modulus. So, what is the polarization modulus?

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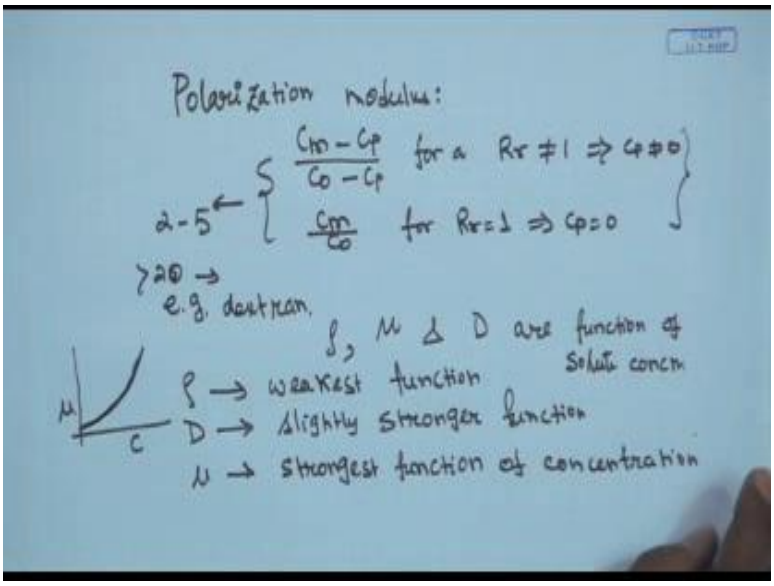

Polarization modulus:

$$2\text{-}5 \leftarrow \left\{ \begin{array}{ll} \frac{C_m - C_p}{C_0 - C_p} & \text{for a } R_r \neq 1 \Rightarrow C_p \neq 0 \\ \frac{C_m}{C_0} & \text{for } R_r = 1 \Rightarrow C_p = 0 \end{array} \right\}$$

$> 20 \rightarrow$
e.g. dextran.

ρ, μ & D are function of solute concn

$\rho \rightarrow$ weakest function
$D \rightarrow$ slightly stronger function
$\mu \rightarrow$ strongest function of concentration

Polarization modulus is known as by this ratio Cm by Cp divided by C naught minus Cp or for a partially retentive membrane that is Rr is not equal to 1. For a completely retentive membrane Cm divided by C naught for Rr is equal 1. Where, Cp is equal to 0 and in this case Cp is not equal to 0. So, typically the polarization module as for the osmotic pressure control filtration will be around 2 to 5 most of the cases and it can be as 24 or greater than 20 in case of solutes like dextran. So, this polarization modular will indicate the extent of concentration polarization that will be occurring within the mass transfer boundary layer or the polarization the concentration of solute will suffer within the mass transfer boundary layer.

In the next will be seen as how we can overcome the assumption that the solute constancy of transport coefficients. Now as we have discussed earlier the various transport coefficients those are involving the system are density, viscosity and solute diffusivity; now all of them are functions of concentrations. Out of these 3 rho is the weakest function of concentration followed by the diffusivity, diffusivity is a slightly stronger function of concentration in some cases and viscosity is the strongest function of concentration. In fact, viscosity is an exponential function of concentration. Viscosity increases exponentially with the concentration. So, from the values of polarization modulus we can see that the concentration polarization becomes very very dominant in some cases, in some in case of some solutes. Therefore, the solute concentration may suffer a 4 folds up to 30 fold to 20 folds of feed concentration.

So therefore, the some of the transport coefficients or transport properties will be suffering the most and out of these transport coefficients the viscosity suffers the most. Therefore, one has to invoke the viscosity correction factor in order to rectify the mass transfer coefficient so that the property variation with respect to concentration is taken care off. How that is done? That is done by; all of us know probably about the selected correction factor.

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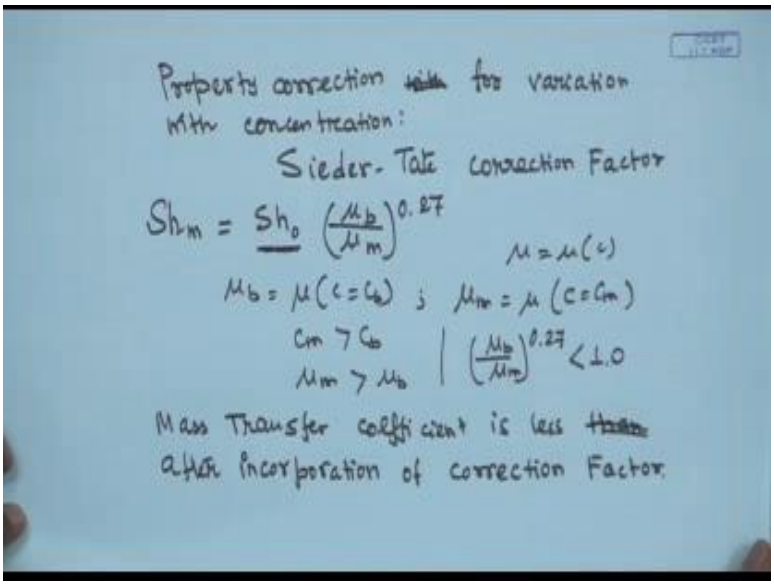

Property correction for variation with concentration:

Sieder-Tate correction Factor

$$Sh_m = \underline{Sh_0} \left(\frac{\mu_b}{\mu_m}\right)^{0.27}$$

$$\mu = \mu(c)$$

$$\mu_b = \mu(c = C_b) \; ; \; \mu_m = \mu(c = C_m)$$

$$C_m > C_b \qquad \left(\frac{\mu_b}{\mu_m}\right)^{0.27} < 1.0$$

$$\mu_m > \mu_b$$

Mass Transfer coefficient is less after incorporation of correction Factor.

So, property correction for variation with concentration, this is known as the famous Sieder Tate correction factor. And these are included in the Sherwood number relationship, Sherwood modified is Sherwood 0 mu bulk divided by mu at membrane surface raise to the power 0.27. What is Sherwood naught? Sherwood naught is basically the basic Sherwood relationship that we have already discussed for the living equation for the laminar flow through a rectangular channel Sherwood naught will be 1.85 Reynold Schmidt d l y raise to the power 1 upon 3. What is the Sherwood naught for the tubular flow 1.62 Reynold Schmidt d by l raise to the power 1 upon 2 for the laminar flow. For the turbulent flow Sherwood naught will be 0.023 Reynolds Schmidt to the power 0.88 Schmidt to the power 0.33. Those are the basic Sherwood number relation relations without any correction factor.

So, what is the modified version of Sherwood number? The original Sherwood number will be multiplied by the viscosity at the bulk concentration divided by the viscosity at the solute concentration at the membrane surface raise to the 0.27. Since we have already talked about that viscosity is an increasing function of concentration, then since mu b is equal to mu evaluated at C is equal to Cb and mu m is evaluated is equal to mu evaluated at C is equal to Cm. We all know that Cm is much greater then Cb so therefore mu m has to be greater than mu bulk. Therefore, factor mu b by mu m raise to the power 0.27 is less than 1.

So therefore, this modified Sherwood number after viscosity Sieder Tate correction factor will be less than the value without it. So, modified Sherwood number will be less compare to the Sherwood number without Sieder Tate correction factor. Therefore, the mass transfer coefficient will be decreased; mass transfer coefficient is less after incorporation of correction factor. So, that is how the system performance can be predicted in terms of taking care of property variation within the mass transfer boundary layer.

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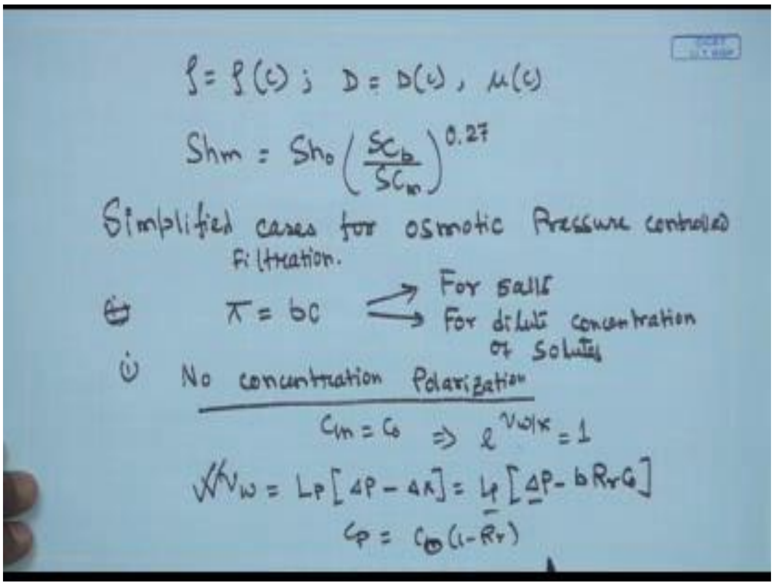

$\rho = \rho(c)$; $D = D(c)$, $\mu(c)$

$$Sh_m = Sh_0 \left(\frac{Sc_b}{Sc_m}\right)^{0.27}$$

Simplified cases for osmotic Pressure controlled filtration.

$\pi = bc$ → For salts
→ For dilute concentration of solutes

(i) No concentration Polarization

$C_m = C_0 \Rightarrow e^{v_w/k} = 1$

$v_w = L_p[\Delta P - \Delta\pi] = L_p[\Delta P - b R_r C_0]$

$C_p = C_0(1 - R_r)$

Now I would like to say one more thing is that if one tries to encounter the concentration variation on the properties like density as well as the diffusivity and then viscosity all if their quite important then one can write the Sieder Tate correction factor as Sh modified is equal to Sh naught. One can combine there is a non-dimensional number that will combining all this three properties and there what is that number the number is schmidt number. So, schmidt evaluated at bulk divided by schmidt evaluated membrane surface raise to the power 0.27. So, if one wants to now consider the property variation of all density diffusivity and viscosity then one can include the schmidt number your at bulk concentration divided by schmidt number at membrane surface concentration raise to the 0.27 as a sieder correction factor.

After this, what will be looking into; we will be looking into some simplified cases for osmotic pressure control filtration, because we have already seen that in an actual case the solution has to be an alternative one through Newton-Raphson technique. Now let us look into some of the simplified cases. Controlled filtration; so the first case is do we consider for all the cases osmotic pressure is a linear function of concentration. So, when the osmotic pressure is linear function of concentration actually if you considered osmotic pressure as a polynomial of concentration that will include the non-linearity in the governing in the system and that will be leading to, that will (Refer Time: 24:18) to obtain then analytical solution.

So, let us look into some simplified cases where an analytical solution is possible and things will be in the functional verification of the independent variable with respect to the dependent will be cleared in front of the eyes of the readers. Let us consider osmotic pressure is a linear function of concentration or one this can arise in two cases for the salts and for dilute concentration of solutes. So, if that is the case then we consider the case number 1; first no concentration polarization. When the concentration polarization can be neglected if someone has very high turbulence in the system, if the turbulence in the system is very high then the mass transfer boundary layer thickness will be gone and the whole mass transfer boundary layer will be properly mixed up, it is a throw mixed up system. And there is no polarization of concentration from the bulk to the membrane surface, so there exists no concentration polarization everywhere is the bulk concentration.

So, how will you module in that system. In that case Cm is equal to C naught and one will be having exponential Vw by K is equal to 1. So, permeate flux can be represented as Lp del P minus del pi and if you write del pi del pi will be pi m minus pi so it will be b Cm minus Cp and Cm is equal to C naught in this case, so Lp del P minus b real retention times C naught. We know all the values, we know the Lp, we know delta P, there is transfer membrane pressure drop, we know the b there is a osmotic coefficient, real retention is known to us, fit concentration is known to us; so we can get what is the value of Vw.

So, once we know value of Vw and since Cm is equal to C naught from the definition of real retention one can get the value of Cp as Cp is equal to Cm into 1 minus real retention, and Cm is equal to C naught in this case. So therefore, one can get a system prediction quite easily in the case when no concentration polarization at the turbulence is very very high in the system.

I stop here in this class and then will be going to the next session looking into some more simplifications. And then will be moving over to various other formulations for reverse osmotic nano filtration system, where the definition of real retention will be replaced by the solution diffusion models and various variants of solution diffusion model in order to get a more realistic situation.

Thank you very much.