

**Introduction to Process Modeling in Membrane Separation Process**  
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**Lecture – 19**  
**Modeling of Dialysis**

Welcome to this session. So, as you have we are discussing that we are looking into the batch cell dialysis system and we are trying to model the batch cell system. The purpose was to evaluate a parameter; there is the solid diffusivity in the dialysis membrane  $D_{IM}$ . Once that will be evaluated then you are in a position to obtain all the coefficients of all the components of the overall mass transfer coefficients. Because from the definition of mass transfer coefficients in the channel, you will be evaluating the resistances of mass transfer coefficient in the feed side will be evaluating the mass transfer coefficient in the dialysis side. So, if we can well can evaluate the member resistance that  $D_{IM}$  by  $L$  inverse of that then you will be in a position to find out all the three components of overall resistance and overall. Therefore, will be evaluating the able to find out the, what is the overall mass transfer coefficient.

So, in order to do that we have conducted an experiment in a small batch cell where we are putting the chamber in the feed on the dialysis side will be separated by a semi permeable barrier. And in the fixed side will be putting the solution side. In the dialysate side, we are putting the dialysate solution and the solute will be being transported from fixed side to the dialysate side. And what will be doing, we will be taking up samples periodically from the dialysate side and then will be measuring its concentration. Once that is done then will be comparing the profile with the theoretically calculated profile of called the dialysate side solute concentration in the dialysate side. And then will be evaluating the value of diffusivity across the in the membrane matrix by the solute of I.

So, we have written down the mass balance in the equation in the dialysate side.

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Batch Dialysis Analysis

$\begin{array}{|c|c|} \hline V_F & V_D \\ \hline \leftarrow & \rightarrow \\ \hline \end{array}$

$V_F$  &  $V_D$  are volumes of  
Feed & dialysate Chambers

Continuous & efficient stirring  $\rightarrow$  Prevention of  
formation of any film over membrane surface  
in feed & dialysate side.

$R_s = R_D = 0 \Rightarrow \frac{Dm}{L} \rightarrow$  Resistance  
due to membrane

Solute mass balance in Feed & Dialysate chamber

At  $t=0$   $\left\{ \begin{array}{l} C_{DF} = C_{F0} \\ C_{D0} = 0 \end{array} \right. \left\{ \begin{array}{l} \frac{d}{dt} (C_D V_D) = \frac{A_m D m}{L} (C_F - C_D) \rightarrow \text{Dialysate side } \checkmark \\ \frac{d}{dt} (C_F V_F) = - \frac{A_m D m}{L} (C_F - C_D) \rightarrow \text{Feed side } \checkmark \end{array} \right.$

We have written down the mass balance in the feed side and we have set the boundary condition initial condition for the both the equations. And  $V_D$  and  $V_F$  were the volume of the feed side and dialysate side respectively and they treated as constant.

So, these two equations can be solved in many ways. One of the methods is using the Laplace transform.

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Laplace Transform:  
 Apply Transform to gov eqn in Dialysate side:  
 Dialysate  $\rightarrow$   $S \bar{C}_{iD} = \frac{Am \cdot Dim}{L \cdot V_D} (\bar{C}_{iF} - \bar{C}_{iD})$   
 Feed  $\rightarrow$   $S \bar{C}_{iF} - C_{iF}^0 = - \frac{Am \cdot Dim}{L \cdot V_F} (\bar{C}_{iF} - \bar{C}_{iD})$   
 $\frac{Am \cdot Dim}{L} = K$   
 $\left\{ \begin{array}{l} S \bar{C}_{iD} = \frac{K}{V_D} (\bar{C}_{iF} - \bar{C}_{iD}) \\ S \bar{C}_{iF} - C_{iF}^0 = - \frac{K}{V_F} (\bar{C}_{iF} - \bar{C}_{iD}) \end{array} \right.$   
 $\bar{C}_{iD} = \frac{(K/V_D) C_{iF}^0}{S^2 + SK \left( \frac{1}{V_F} + \frac{1}{V_D} \right)}$

Then these two equations ordinary differential equations will be boiled down to algebra equation and it will be easier to solve. If you use a Laplace transform, apply this transform to governing equation in dialysate side. If you do that will be getting  $S \bar{C}_{iD}$  will be nothing, but  $\frac{Am \cdot Dim}{L \cdot V_D} (\bar{C}_{iF} - \bar{C}_{iD})$ . And if you apply the transform to the feed side, this is the dialysate side. We apply the same equation in the feed side will be getting  $S \bar{C}_{iF} - C_{iF}^0$  is equal to minus  $\frac{Am \cdot Dim}{L \cdot V_F} (\bar{C}_{iF} - \bar{C}_{iD})$ . Now we can take  $\frac{Am \cdot Dim}{L}$  is equal constant  $K$ .  $Am$  is the membrane area,  $Dim$  is the diffusivity of solute to the membrane matrix,  $L$  is the membrane thickness. So, the first equation becomes  $s \bar{C}_{iD}$  is equal to  $\frac{K}{V_D} (\bar{C}_{iF} - \bar{C}_{iD})$  and second one will be  $s \bar{C}_{iF} - C_{iF}^0$  is equal to minus  $\frac{K}{V_F} (\bar{C}_{iF} - \bar{C}_{iD})$ .

Now, these two equations can be solved and you can get the expression of  $\bar{C}_{iD}$ . We can just replace  $\bar{C}_{iF}$  from one equation into the other. And by putting by putting the values of this, then we can get the expression of  $\bar{C}_{iD}$ . I am just omitting two steps. They are very simple, two equations and two unknown system. So,  $\bar{C}_{iD}$  will become  $\frac{K}{V_D} C_{iF}^0$  divided by  $s^2 + SK \left( \frac{1}{V_F} + \frac{1}{V_D} \right)$ . So, that becomes the governing equation of dialysate concentration solid concentration dialysate side in the Laplace transformed coordinate. You know transform parameter or variable.

So, once we do that then we will be putting we will be doing a further simplification. Will write a is equal to K times 1 over VF plus 1 over VD.

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$$a = K \left( \frac{1}{V_F} + \frac{1}{V_D} \right)$$

$$\bar{C}_{iD} = \left( \frac{K}{V_D} \right) \frac{C_{iF}^0}{a} \left( \frac{1}{s} - \frac{1}{s+a} \right)$$

Taking Inverse Laplace Xform:

$$C_{iD}(t) = \left( \frac{K}{V_D} \right) \frac{C_{iF}^0}{a} (1 - e^{-at})$$

$$C_{iD}(t) = C_{iF}^0 \left( \frac{V_F V_D}{V_F + V_D} \right) \left[ 1 - e^{-K \left( \frac{1}{V_F} + \frac{1}{V_D} \right) t} \right]$$

$$K = \frac{Am \ Dim}{L}$$

The graph shows  $C_{iD}$  on the vertical axis and  $t$  on the horizontal axis. The curve starts at the origin (0,0) and rises exponentially, asymptotically approaching a horizontal line representing a constant value.

And these becomes  $\bar{C}_{iD}$  is equal to  $K$  over  $V_D$   $C_{iF}$  naught divided by a  $1$  over  $S$  minus  $1$  over  $S$  plus  $a$ . And one can get a inverse Laplace transform. Taking inverse Laplace transform, one can get  $C_{iD}$  as a function of time as  $K$  over  $V_D$   $C_{iF}$  naught divided by a  $1$  minus  $e$  to the power minus  $a$   $t$ . And if you put all the constants etcetera. So, you will be getting the expression of  $C_{iD}$  is a function of  $t$  is equal to  $C_{iF}$  naught  $V_F$   $V_D$  divided by  $V_F$  plus  $V_D$   $1$  minus  $e$  to the power minus  $K$   $1$  over  $V_F$  plus  $1$  over  $V_D$  times  $t$  ok.

So, essentially these will give a curve something like this,  $C_{iD}$  as a function of time. The curve will be starting from zero then it will be increasing and ultimately it will be reaching at higher value of  $t$  it will be reaching a constant value  $C_{iF}$  naught by this one. So, now if you look into this expression, everything is known to us and what is  $K$ ?  $K$  is nothing, but  $Am \ Dim$  over  $L$  ok. So, we can fit a curve or we can put a log linearized version. So, if you can do that this becomes  $C_{iD}$  is equal to  $C_{iF}$  naught  $V_F$   $V_D$  divided by  $V_F$  plus  $V_D$   $1$  minus exponential minus  $K$   $1$  over  $V_F$  plus  $1$   $V_D$  times  $t$ .

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$$C_{iD} = C_{iF} \left( \frac{V_F V_D}{V_F + V_D} \right) \left[ 1 - e^{-K \left( \frac{1}{V_F} + \frac{1}{V_D} \right) t} \right]$$

$$1 - e^{-K \left( \frac{1}{V_F} + \frac{1}{V_D} \right) t} = \left( \frac{V_F + V_D}{V_F V_D} \right) \frac{1}{C_{iF}} C_{iD}(t)$$

$$\Rightarrow e^{-K \left( \frac{1}{V_F} + \frac{1}{V_D} \right) t} = 1 - \left( \frac{V_F + V_D}{V_F V_D} \right) \frac{C_{iD}(t)}{C_{iF}}$$

$$\Rightarrow \ln \left[ 1 - \left( \frac{V_F + V_D}{V_F V_D} \right) \frac{C_{iD}(t)}{C_{iF}} \right] = -K \left( \frac{1}{V_F} + \frac{1}{V_D} \right) t$$

Graph showing  $\ln(\quad)$  vs  $t$ . Slope =  $K \left( \frac{1}{V_F} + \frac{1}{V_D} \right)$   
 $K = v \Rightarrow K = \frac{A_m D_m}{L}$   
Dim =  $K \cdot \text{hr/ml}$

So, we can rearrange it, this becomes 1 minus e to the power minus K 1 over VF plus 1 over VD times t is equal to VF plus VD divided by VF VD 1 over CiF naught CiD as a function of time. So, this becomes e to the power minus K 1 over VF plus 1 over VD times t is equal to 1 minus VF plus VD divided by VF VD 1 over CiF naught CiD times t. So, we can take the log on both sides. So, if you get log on both sides 1 minus VF plus VD divided by VF VD CiD t CiF naught is equal to minus K 1 over VF plus 1 over VD times t.

So, if we so as time progresses as we have discussed earlier will be measuring the solute concentration in the dialysate side. So, CiD will be known to us. We know it feed concentration of consulate in the feed side. We have volume of the feed and volumes of the dialysate are known to us. So, whole lot of left hand side will be known to us, if you can result the dialysate concentration every at different point of time.

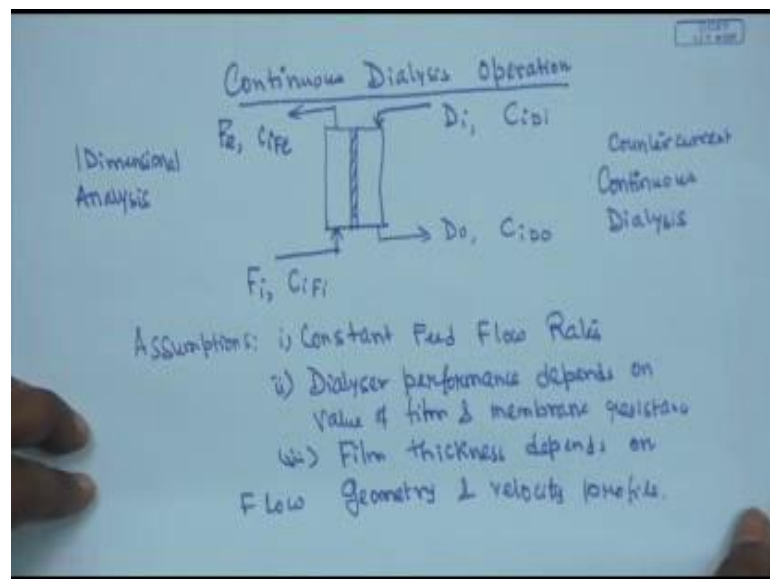
Then if you plot these ln is verses t, it will be a straight line with a negative slope and from the slope what is the slope? the slope will be K times 1 over VF plus 1 over VD and we know the volume of the feed and volume the dialysate. So, we can we will be able to estimate the value of K and what is K? K is nothing but Am Dim over L. So, once you know the value of K, we know the membrane thickness from a SEM photograph and

Dim will be nothing, and Am will be nothing, but the membrane area. So, you know the dimension of the two channels. So, the membrane area will known to us. So, we can calculate the estimate the value of Dim.

So, from this relationship will be able to estimate the Dim. So, this is the procedure to obtain the solute diffusivity in the membrane matrix. So, we will what will be a essentially will be conducting a small batch cell experiment as separate part and measuring its concentration in the measuring the solute concentration in the dialysate side at different point of time. Then will be plotting the quantity that we have already discussed in the o axis and then time in the x axis. From the slop will be getting the value of Dim. So, once Dim will be known to us, then we will able to estimate all the three components of overall mass transfer coefficient and will be find able to find out the overall mass transfer coefficient, then from the overall mass transfer coefficient will be able to find out the system performance.

Next, we will be looking into the design of the will where in a position to design the continuous dialysis process.

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So, we will be looking into the continuous dialysis operation. So, in a continuous system, first we level all the stream and their concentration. So, this is the feed going into this system  $F_i$   $C_i$ ,  $i$ 'th component in the going into the feed system  $F_e$   $C_e$ . So,  $i$ 'th component there is at existing at from the feed, then dialysate going into the system.  $D_i$  is the volumetric flow rate or the mass flow rate. Its concentration is  $C_i$  and this is  $D$  out is the flow rate. So, this will be  $C_i$  out. Ok this is a counter current, Continuous dialysis operation. So, let us let us do the analysis and the assumptions involved are is basically one dimensional analysis.

The assumptions involved are constant feed flow rates one. Two is the dialyser performance depends on value of film and membrane resistance and then film thickness of course, that is true. Film thickness depends on geometry and flow velocity. Channel geometry or flow geometry and velocity profile. So, with these assumptions let us write down the various design equations.

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Design Equations:

Transmembrane mass flux: of  $i$ 'th species  
 $m_i = \bar{k}_0 A_m (\Delta C_i)_{LMTD}$

Mass Flux:  $m_i = \dot{V}_F (C_{Fi} - C_{Fe})$   
 $\text{kg/hr} \quad = \dot{V}_D (C_{De} - C_{Di})$

$\dot{V}_F \rightarrow$  Volumetric flow rate of feed  
 $\dot{V}_D \rightarrow$  Volumetric flow rate of dialysate

Dialyzer efficiency:  
 $\eta = \frac{\text{Actual amount of Solute depletion in Feed}}{\text{Maxm amount Separated in a Dialyzer}}$

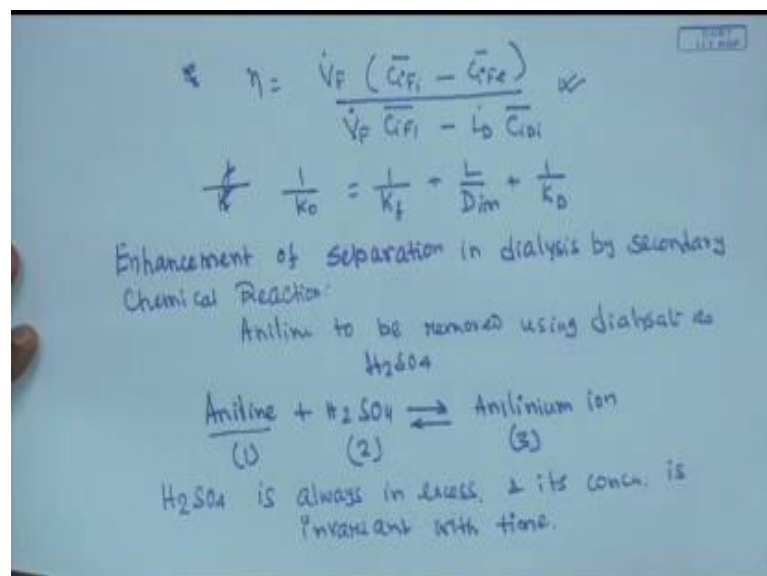
So, design equation for a continuous counter current dialyser will be the trans membrane mass flux of the species will be  $m_i$   $k_0$  overall  $A_m$  is the membrane area  $\Delta C_i$  LMTD. We are writing the mass flux of  $i$ th species. Then mass flux can also be presented as

whatever the mass that has been gone from the feed side to the dialysate side, the dialysate side will be getting that amount.

So, at the steady state  $\dot{m}_i$  will be nothing, but  $\dot{V}_F \bar{C}_{Fi}$  minus  $\bar{C}_{Fe}$  is equal to  $\dot{V}_D$  dot, we will call it  $\dot{V}_D \bar{C}_{De}$  out minus  $\bar{C}_{Di}$  in. So, this is basically the mass flux kg per unit, time, hour or minute.  $\dot{V}_F$  dot is volumetric flow rate of feed  $\dot{V}_D$  dot is nothing, but the volumetric flow rate of dialysate.  $\bar{C}_{Fi}$  is the  $i$ th for the  $i$ th specifies the concentration that is going into the system by the feed stream. The concentration of the solute that is going out of the feed stream So,  $\bar{C}_{De}$  is the concentration of  $i$ th solute that is going out of the dialysate side and this is going into the dialysate side. Typically this will be equal zero. And the amount of solute that will be lost by the feed side will be the amount of solute that has been gained by the dialysate side. So, these two will be equal.

So, next we define the dialyzer efficiency. Dialyzer efficiency is actual amount of solute depletion in feed divided by the maximum amount separated in a dialyzer. So, that is the definition of dialyzer efficiency. And if you really do that so, one can get that  $\dot{V}_F \dot{\eta}$  is equal to  $\dot{V}_F \bar{C}_{Fi}$  bar minus  $\bar{C}_{Fe}$  bar is the actual amount of solute that has been separated and these is the maximum amount of solute  $\dot{V}_F \bar{C}_{Fi}$  that is going into the system minus  $\dot{V}_D \bar{C}_{Di}$  that is going into the system through the dialyzer system.

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But typically in the dialysate stream, the concentration of solute that is going into the dialysate side will be equal to zero and this probably equal to zero in most of the cases. And if there is some amount of solute that is going into the system, this is the maximum amount of solute that can be separated and this is the actual separation that is being occurring. So, that will be defining; I know efficiency of the dialyzer.

So, using this equation, one can get the expression of the one can design the dialyzer. So, also if you remember that one the overall mass transfer coefficient can be defined as overall mass transfer coefficient that feed side  $L$  by  $Dim$  plus 1 over mass transfer coefficient in the dialysate side. We know the flow domain, flow regime and the geometry in the feed side. We can calculate the mass transfer coefficient the feed side. Similarly the flow regime and the geometry in the dialyzer chamber are also known. So, we can calculate  $kD$   $Dim$  for  $Dim$  will be conducting a separate set of experiment in a batch dialysate side under continuous high turning or turbulence, so that we will able to estimate the diffusivity of the solute in the membrane matrix only. So, once we know that than will be able to find out the overall mass transfer coefficient and will be able to design a continuous dialyzer.

So, once we do that, next item that will be looking into a system were the enhancements of separation in dialysis can be obtain by doing associating a secondary chemical reaction. So that means, in a batch system what is happening is that the solute will be transferring from the feed side to the dialysate side and therefore, enhancing the solute concentration in the dialysate side. I am talking about a batch operation process. So, therefore, in a batch operation process the solute concentration will be continuously decreasing in the feed side and it will be continuously increasing in the dialysate side.

But in the dialyzer feed, if we can put a chemical which will be reacting immediately with the solute that is arriving there from the feed side, we can maintain the concentration of the particulars solute to be zero at all the points. There why we can maximizing the concentration of gradient, the driving force across the membrane. Therefore the solute concentration in the dialysate side we can be maintain at zero concentration there why maximizing the driving force of the solute across the membrane.

Once that we can do that, then the dialysis will be much faster and it has look into the modeling of the batch dialysis which will be added by a secondary reaction.

So, next will be look into a modeling of enhancement of separation in dialysis by secondary chemical reaction. So, we select, we put let us say we given example that Aniline is removed is to be removed. Aniline to be removed using from feed side using dialysate as  $\text{H}_2\text{SO}_4$ . So, it reacts with Aniline reacts with sulfuric acid to form Anilinium ion. These anilinium ion being larger in size, they cannot get back into the feed side. So, therefore, in the dialysate side Aniline concentration will be always maintained to be zero. So, we so this is governing process. So, we call this components as one, this is two and Anilinium ion is three and components sulfuric acid will be always excess in the dialysate side. Sulfuric acid or component two is always in excess; that means, concentration of sulfuric acid is constant and its concentration is invariant with time.

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Handwritten notes on a blue background showing mass balance equations for a dialysis system with a chemical reaction. The text is as follows:

Mass Balance

Solute balance in Feed:

Component 1:  $V_F \frac{dC_{1F}}{dt} = -A_m D_{12} (C_{1F} - C_{1D})$

$\hookrightarrow \frac{dC_{1F}}{dt} = \frac{A_m D_{12}}{L V_F} (C_{1D} - C_{1F})$

Comp 1 balance in Dialysate side:

$\frac{dC_{1D}}{dt} = \frac{A_m D_{12}}{L V_D} (C_{1F} - C_{1D}) - \frac{dC_{2D}}{dt}$

$\frac{A_m D_{12}}{L} = k$

Final boxed equations:

$$\frac{dC_{1F}}{dt} = \frac{k}{V_F} (C_{1D} - C_{1F})$$

$$\frac{dC_{2D}}{dt} + \frac{dC_{1D}}{dt} = \frac{k}{V_D} (C_{1F} - C_{1D})$$

So, let us write down the mass balances then. So, solute balances in the feed as you have done earlier. We write down the mass balance in the feed chamber in the dialysate side, solute balance in the feed. So,  $V_F \frac{dC_{1F}}{dt}$  will be nothing, but minus  $A_m D_{12}$  divided by  $L C_{1F}$  minus  $C_{1D}$ . And the system is under continuous studying. So, under continuous study, so this is the solute balance of component one.

This is one, for component one. So, these equations can be rearranged as  $\frac{dC_{1F}}{dt}$  will be nothing, but  $\frac{A_m}{L} (C_{1d} - C_{1F})$ . And now we write down the solute balance that is the component one balance in dialysate side. So, that will give you  $\frac{dC_{1D}}{dt}$  will be nothing, but  $\frac{A_m}{L} (C_{1F} - C_{1D}) - k C_{1D}$ . These will be basically the rate of consumption the first one term will be the amount of solute that will be arriving in dialysate side and the second term is basically the amount of solute that will be consumed because of the reaction chemical reaction that is going on. So, we consider  $\frac{A_m}{L} (C_{1F} - C_{1D})$  should be equal to  $k C_{1D}$ .

So, if I write it that then we can shortly, we can write the governing equation in short  $\frac{dC_{1F}}{dt}$  will be nothing, but  $k C_{1D} - \frac{A_m}{L} (C_{1F} - C_{1D})$ . And the other one is  $\frac{dC_{3D}}{dt} + \frac{dC_{1D}}{dt}$  is equal to  $\frac{k}{V_D} (C_{1F} - C_{1D})$ . So, this will be the final transformed equations. So, I stop in this class, in the next class what I will do? I will find an expression of  $\frac{dC_{3D}}{dt}$  and then will be trying to solving this set of equations and see what you get. So, we I will stop here and we continue this problem in the next class. I will finish it up.

Thank you very much.