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CONCENTRATION POLARIZATION: EARLY THEORIES

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OVERVIEW

Two types of transport phenomena dictate membrane separation processes. The first is transport of species across the membrane material (the permeation process), and the second is the transport of species from the bulk of the feed to the membrane surface. The material provided here will focus on the transport mechanisms outside the membrane, which carry various constituents of a feed solution or dispersion from the bulk to the membrane surface. Consideration of these so-called "external" transport phenomena will allow us to assess how the membrane separation and permeation characteristics are limited by mass transfer in a layer adjacent to the membrane, leading to the phenomenon of flux decline. The material will describe the primary reasons for flux decline, which are generally bracketed under a common terminology – concentration polarization. The outline of this document will be as follows:

1. Flux decline and its manifestations; causes of flux decline; types of flux decline.
2. Concentration polarization: description and definition; consequences and minimization of concentration polarization; crossflow filtration.
4. Traditional theories: Film theory; Osmotic pressure, gel layer, and boundary layer resistance models.

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1. FLUX DECLINE IN MEMBRANE SEPARATION PROCESSES

1.1 Flux Decline

Flux decline is associated with every pressure driven membrane separation process. In a membrane separation process using a given feed solution, the initial permeate flux is quite high and corresponds nearly to the flux obtained using the pure solvent. However, within a few minutes, the flux rapidly drops to a value much lower than the initial flux. This rapid initial decline is followed by a more gradual lowering of the permeate flux. The second gradual decline can occur over a period of days. The permeate flux thus appears to be quite steady after the rapid initial decline. This steady state flux is generally known as the “pseudo steady state flux”. The entire phenomenon of permeate flux reduction with time is generally regarded as flux decline (Fig. 1a).

Flux decline manifests itself during a membrane separation process in another way. If we compare the pseudo steady state permeate fluxes obtained for different operating pressures, and compare these with the corresponding pure solvent fluxes at the same pressures, we can see a considerable difference between the two (Fig. 1b). While the pure solvent flux increases linearly with operating pressure, the corresponding permeate flux shows a curvilinear behavior. At higher pressures, the increase in permeate flux with pressure is more gradual. This phenomenon is known as the *limiting flux behavior*. Physically, above a critical pressure (shown by the vertical dotted line in Fig. 1b), the flux cannot be varied appreciably by varying pressure. Filtration processes operating above this critical pressure are generally regarded as operating in the *pressure independent filtration regime*.

![Figure 1](image)

**Figure 1:** (a) Transient flux decline. (b) Steady-state flux behavior depicting the pressure dependent and independent regimes.

1.2. Causes of flux decline

The permeate flux is related to the effective pressure difference (driving force) and the resistance to flow by a *Darcy type equation*

\[ J_v = \frac{(\text{Driving Force})}{(\text{Total Resistance})} \equiv \frac{\Delta P_{\text{eff}}}{\eta_s R_{\text{tot}}} \quad (1) \]

An inspection of Eq. (1) shows that flux decline can occur if the driving force decreases with time or if the total resistance to permeate flow increases with time.

Let us physically inspect these two scenarios.

Increase in Resistance: The total resistance to permeate flow comprises several resistances in series. In a given membrane separation process, several (if not all) of the following resistances act in concert.

1. **Resistance of Membrane**: The membrane resistance is the hydraulic resistance offered by the membrane to both pure solvent and the permeate. This resistance is usually an intrinsic property of the membrane reflecting the pore structure and its interaction with the solvent as the solvent seeps through membrane. Barring some increase in this resistance owing to physical compaction during the initial deployment of a membrane, this hydraulic resistance varies very little during a membrane separation process. We denote this resistance as \( R_m \). This resistance cannot possibly be predominantly responsible for the transient flux decline observed in Fig. (1a).

2. **Resistance due to a cake or a gel layer**: Like traditional filtration processes, a cake type deposit may form on the membrane (particularly during microfiltration, or during ultrafiltration of large macromolecules). Buildup of this resistance with time may be responsible for the transient flux decline. *Gel layer* is the term generally used to describe a cake type deposit obtained during ultrafiltration. Its slightly different appearance from a traditional filter cake led to this nomenclature. A gel is a highly concentrated viscous layer of long chain polymeric or other macromolecular entities. In this study, we will use the symbol \( R_c \) to denote either the cake layer or the gel layer. In other words, we will not distinguish between a cake and a gel.

3. **Scaling**: Fouling can occur at the membrane surface due to scale formation, where the surface of the membrane is coated by a thin non-removable deposit of chemicals. A common type of scale formation mechanism is through precipitation of inorganic material like calcium sulfate or silica when their solubility limits are exceeded. This layer can only be removed from the membrane surface by chemical cleaning. This resistance is denoted by \( R_s \).

4. **Pore blocking**: Pore blocking is another form of membrane fouling where the membrane pores get clogged by the entrapment of particles. A particle entering the pore may get wedged in the tortuous pore, and stop further flow of solute and solvent through that pore. This results in a buildup of an additional resistance to permeate transport. We denote this resistance by \( R_p \).

1. We use the term pure solvent flux when we consider the permeation of pure solvent through the membrane. This type of operation is generally performed only to determine the membrane hydraulic resistance. The permeate flux is the flux observed when a feed solution (containing solutes) is subjected to membrane filtration. Note that when the membrane rejection is 1 the permeate also comprises pure solvent (that is, there is no solute). However, the permeate flux in this case is different from the pure solvent flux. Thus, it should be borne in mind that the pure solvent flux and permeate flux represent the flux under completely different circumstances.
5. **Adsorption**: Solutes and macromolecules may chemically interact with the pore wall. Such interactions can result in adsorption of solutes on the pore wall, thus constricting the pore. While the outcome of adsorption is similar to the physical pore blocking described above, the method of attachment is more chemical than physical. We term the resistance due to adsorption as $R_a$.

6. **Concentration Polarization**: All membrane separation processes encounter concentration polarization. We will devote the entire lecture to understand and explain this phenomenon. At this point, let us describe concentration polarization simply as the buildup of a concentrated layer of rejected solutes near the membrane surface. The resistance of this layer is denoted by $R_{CP}$.

If we now consider the total resistance buildup,

$$R_{Tot} = R_m + R_c + R_f + R_p + R_a + R_{CP}$$

we note that all the resistances except $R_m$ (if the membrane does not get compacted by pressure) have possibilities of increasing with time. Thus, buildup of these resistances can result in permeate flux decline over time. The buildup of these resistances is schematically depicted in Fig. 2.

### 1.3. Types of flux decline

Two types of flux decline are commonly encountered in a membrane separation process, **reversible** and **irreversible** (or permanent). Reversible decline is the decline that can be recovered on restarting the process, while irreversible flux decline is a result of permanent membrane fouling and cannot be recovered easily. At times, chemical cleaning or back flushing can result in recovery of some of the irreversible flux. While reversible flux decline can be attributed to cake formation or concentration polarization, the irreversible decline is attributed to fouling by scaling, pore blocking or adsorption.

The flux decline behavior during the life cycle of a membrane is schematically depicted in the Fig. 3. The pure solvent flux at a given pressure $\Delta P$ does not vary with time (uppermost blue horizontal line). During an actual separation process involving a solution, however, the permeate flux (corresponding to the applied pressure $\Delta P$) decreases with time. The first arc on the left depicts this decline. At time $T_1$, the filtration process is stopped by discontinuing the applied pressure. When the filtration process is started again by applying the same pressure $\Delta P$, the initial flux is observed to be lower than the pure water flux. Repeating this cycle, we observe that after each cycle there is a small permanent loss in the initial permeate flux, shown by the red line. This represents the irreversible flux decline due to membrane fouling. During each filtration cycle (black arcs), majority of the flux decline is reversible and only a small amount of permanent (irreversible) flux decline is manifested. The reversible flux decline is caused by concentration polarization or cake formation. Each time the filtration process is stopped, the permeate flux decline due to these phenomena is almost completely recovered. Irreversible flux decline is generally much gradual compared to the reversible decline, and is typically caused by scaling, pore blocking, compaction, and adsorption. Typically, any permanent loss in permeability of a membrane over its lifetime is attributed to irreversible fouling.

**Figure 2**: Mechanisms and consequences of Concentration Polarization.

**Figure 3**: Schematic representation of typical flux decline behavior during the lifetime of a membrane depicting reversible and irreversible flux decline.

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Decrease in Driving Force: The driving force or effective pressure difference across the membrane (referred to as transmembrane pressure or TMP) is given by

$$\Delta P_{eff} = \Delta P - \Delta \Pi$$

where $\Delta \Pi$ is the osmotic pressure difference between the solutions at the two sides of the membrane. The osmotic pressure difference is caused by the concentration difference between the feed side and permeate side solutions adjacent to the membrane surface. If there is solute accumulation due to any reason (like concentration polarization) near the membrane surface, then the osmotic pressure difference across the membrane will be higher. Consequently, the flux will be lowered as the effective driving force decreases. Thus, permeate flux decline can also be an outcome of the reduction in driving force.
2. CONCENTRATION POLARIZATION

2.1. What is concentration polarization?

Concentration polarization is broadly described as the accumulation of solutes near the membrane surface.

2.2. Description of CP phenomenon

The following steps lead to concentration polarization:

1. Convective transport of solute towards the membrane.
2. Rejection of solute by the membrane, leading to solute accumulation at the membrane surface. This raises the solute concentration near the membrane surface.
3. Diffusion of solute from the membrane surface towards the feed solution owing to the concentration difference (or concentration gradient) between membrane surface and the feed bulk.
4. At steady state, a region near the membrane with spatially varying concentration is formed, which is the outcome of the competition between the convective transport towards membrane and diffusive transport away from the membrane.
5. The mechanism of concentration polarization is depicted in Fig. 4.

2.3. Definition of CP

A competition between oppositely directed convective solute flux towards the membrane and a diffusive flux of rejected solutes away from the membrane causes a buildup of solute concentration near the membrane surface. This phenomenon is known as concentration polarization. The thin region near the membrane where the solute concentration varies spatially due to concentration polarization is known as the polarized layer.

3. CONSEQUENCES & MINIMIZATION OF CP

3.1. Consequences of CP

- Concentration polarization causes flux decline by increasing the osmotic pressure of the solution near the membrane surface. Osmotic pressure buildup results in a loss of driving force (applied pressure difference) which causes the flux decline [See Eqs. (1) and (3)].
- CP changes the observed solute rejection of a membrane separation process.
- Higher solute concentration near the membrane may result in the formation of a cake or a gel layer. This layer, if formed, causes an additional reduction in permeate flux.
- CP is a fouling precursor. Increased concentration of solutes near the membrane surface increases the tendency of fouling due to scaling, pore blocking and solute adsorption.

Let us consider how CP affects the solute rejection. Solute rejection is an intrinsic property of a membrane, which, along with feed side solute concentration at the membrane surface (at membrane pore inlet) dictates the permeate concentration. The expression for intrinsic or real solute rejection of a membrane is

\[
R_r = 1 - \frac{c_p}{c_m}
\]  

(4)

where \(c_p\) is the permeate concentration and \(c_m\) is the feed side solute concentration at the membrane surface. If the solute concentration at the membrane surface \(c_m\) increases due to concentration polarization, the permeate concentration will also increase according to Eq. (4) (for a fixed intrinsic rejection of a given membrane). The observed rejection of a membrane is defined using the feed bulk concentration \(c_b\) as

\[
R_o = 1 - \frac{c_p}{c_b}
\]  

(5)

During concentration polarization, the membrane surface concentration becomes greater than the feed bulk concentration. The higher membrane surface concentration increases the permeate concentration (according to Eq. 4).

Any increase in \(c_p\) will decrease the rejection \(R_o\) according to Eq. (5). We note that the rejection defined by Eq. (5) is the one we can measure in an actual membrane separation process as the feed and permeate concentrations can be
measured in the bulk. From the above discussion, it emerges that the observed rejection will be lower than the intrinsic rejection in a membrane filtration process owing to concentration polarization.

Therefore, CP decreases the efficiency of a membrane filtration process by decreasing the permeate flux and the observed solute rejection. Furthermore, CP is detrimental to a membrane as it increases the possibility of membrane fouling.

3.2. Minimization of CP

Concentration polarization can be significantly reduced (but never completely eliminated) by employing crossflow. In a crossflow membrane filtration process, the feed solution is made to flow tangentially (parallel) to the membrane. The typical advantage of this type of flow is shown in Fig. 5. A flow parallel to the membrane will sweep the solute molecules downstream along the filtration channel. This will result in a lower buildup of solute concentration near the membrane. By restricting the concentration buildup, crossflow effectively minimizes flux decline.

The flow configuration in a crossflow system is two-dimensional. There is an axial flow $u$ of the solution parallel to the membrane and a transverse (normal to the membrane) flow of permeate $v$ toward the membrane. Generally, the crossflow velocity $u$ is several orders of magnitude larger than the permeate velocity across the membrane $v$.

The overall picture of a crossflow filtration process is depicted in Fig. 6a. In this figure, the development of a steady state concentration profile during crossflow filtration is shown. The axial velocity "washes" away the accumulated solutes downstream, causing a lower buildup of solute concentration near the channel entrance. The low concentration buildup results in a higher permeate flux across the membrane in this region. Further downstream, the solute concentration buildup is more severe, giving rise to a thicker polarized layer. In this region, the permeate flux is also lower. Commensurate with the extent of CP at different axial positions in the filtration channel, the permeate flux changes along the channel.

4. MATHEMATICAL MODELING OF CP

In this section, we will derive the fundamental equations describing concentration polarization. The most fundamental equation describing solute accumulation in the polarized layer is the differential solute mass balance equation. This equation is more popular as the Convective Diffusion equation. We will start with a generalized derivation of the convective diffusion equation in the polarized layer formed in a two-dimensional crossflow channel shown in Fig. 6a. Following this, we will obtain various simplifications of this general equation.

4.1. Assumptions

1. Axial concentration gradients are negligible compared to concentration gradients perpendicular to the membrane.
2. The polarized layer is thin compared to the height of the filtration channel.
3. Diffusion in axial direction is negligible (this follows from assumption 1).
4. Permeate velocity $v$ remains constant in transverse direction (normal to membrane). It only varies parallel to the membrane.
5. Axial velocity $u$ is only a function of the transverse position in the channel. It does not change with the axial position.

4.2. Solute material balance

As mentioned earlier, two types of solute flux, convective and diffusive, result in the solute concentration buildup in the polarized layer. The concentration buildup can be determined by a solute material balance performed over an arbitrary cross section of the polarized layer as shown in Fig. 6. Following the symbols and notations shown in Fig. 6b, we can separately account for the different components of the material balance over the hatched region in the polarized layer. Note particularly the use of the coordinate system, where $y = 0$ represents the membrane surface.
Convective Flux:
Convective flux of solutes entering the element
\[ wc_{y+\Delta y} \Delta x + uc_{y} \Delta y \]
Convective flux of solutes exiting the element
\[ wc_{y} \Delta x + yc_{y+\Delta y} \Delta y \]

Diffusive Flux:
Diffusive solute flux entering the element
\[ \left[-D \frac{\partial c}{\partial y}\right] y \Delta x \]
Diffusive flux exiting the element
\[ \left[-D \frac{\partial c}{\partial y}\right] y+\Delta y \Delta x \]

Accumulation:
Solute accumulation rate in the element
\[ \frac{\partial c}{\partial t} \Delta x \Delta y \]
We can now obtain the solute material balance as

\[ \text{Accumulation} = \text{Input} - \text{Output} \]
which gives
\[ \frac{\partial c}{\partial t} \Delta x \Delta y = \left[ wc_{y+\Delta y} - wc_{y} \right] \Delta x - \left[ uc_{y+\Delta y} - uc_{y} \right] \Delta y + \left[ D \frac{\partial c}{\partial y} \right]_{y+\Delta y} - \left[ D \frac{\partial c}{\partial y} \right]_{y} \Delta x \]
Dividing Eq. (7) by \( \Delta x \Delta y \) and using \( \Delta x, \Delta y \to 0 \), we obtain
\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial y} \left( wc \right) - \frac{\partial}{\partial x} \left( uc \right) + \frac{\partial}{\partial y} \left( D \frac{\partial c}{\partial y} \right) \]
Equation (8) is the unsteady state (or transient) solute material balance equation in polarized layer. This partial differential equation is known as the convective diffusion equation.

The steady state counterpart of Eq. (8) is
\[ 0 = \frac{\partial}{\partial y} \left( wc \right) - \frac{\partial}{\partial x} \left( uc \right) + \frac{\partial}{\partial y} \left( D \frac{\partial c}{\partial y} \right) \]
Equation (9) describes the steady state differential solute material balance in a polarized layer.

Equations (8) and (9) are the generalized two-dimensional transport equations in the polarized layer formed during a crossflow filtration process. These partial differential equations are quite general. These equations do not impose any restriction on the terms \( u, v \) and \( D \). These can be functions of both axial and transverse coordinates. In this context, the above equations are particularly useful when the solute diffusion coefficient \( D \) is concentration dependent.

4.3. Initial and Boundary Conditions
The above partial differential equations can be solved subject to appropriate boundary conditions. Equation (8) also requires the specification of an initial condition (at time \( t = 0 \)). The necessary initial and boundary conditions for solving the convective diffusion equation are

**Initial condition:**
\[ c = c_{i} \text{ at all } (x,y) \text{ for } t = 0 \text{ (for time dependent equations)} \]
\[ c = c_{i} \text{ at all } y \text{ when } x = 0^{*} \]

**Boundary conditions**
Equations (10) – (12) are needed to solve Eq. (8), while only Eqs. (10b) to (12) are required to solve the steady state equation (9).

A further point worth noting is that we do not really know the concentration at the membrane surface \( c_{m} \). The boundary condition (12) is quite arbitrary. Thus the convective diffusion equation with the above set of boundary conditions is not sufficient to know both the permeate flux \( v \) and the membrane surface concentration \( c_{m} \). However, both the permeate flux and the membrane surface concentration can be determined if we have another independent equation. Finding this second equation is the main issue in the research leading to prediction of flux decline.

4.4. One dimensional convective diffusion equation
The two dimensional convective diffusion equation can be simplified considerably if we consider the particular case when the axial concentration gradients are negligible. This implies that in Eqs. (8) and (9), the term
\[ \frac{\partial}{\partial x} \left( wc \right) = 0 \]

\* It is more appropriate to treat Eq. (10b) as a boundary condition. Similarity between Eqs. (9) and (14) (both parabolic partial differential equations) implies that Eq. (10b) may be treated as an initial condition mathematically.
The convective diffusion equation in such cases can be simplified as

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial y} \left( \nu c \right) + \frac{\partial}{\partial y} \left[ D \frac{\partial c}{\partial y} \right] \]  

(14)

for the transient case, and

\[ \frac{d}{dy} \left( \nu c \right) + D \frac{dc}{dy} = 0 \]  

(15)

at steady state. Equation (15) becomes an ordinary differential equation as the solute concentration is now solely a function of the transverse distance from the membrane surface.

4.5. Solution of the one dimensional steady state convective diffusion equation

Equation (15) can be solved analytically subject to the boundary conditions (11) and (12). The solution is

\[ \frac{c - c_h}{c_m - c_h} = \exp \left[ -\frac{\nu y}{D} \right] \]  

(16)

Equation (16) gives the solute concentration profile in the polarized layer.

The integration of Eq. (15) is quite straightforward. Note that Eq. (15) can be simplified further by writing

\[ \frac{d}{dy} \left( \nu c + D \frac{dc}{dy} \right) = 0 \]

OR

\[ \nu c + D \frac{dc}{dy} = \text{constant} \]  

(17)

Note, however, that the expression for the concentration profile Eq. (16) is not informative because we do not know the solute concentration at the membrane surface. If the solute concentration \( c_m \) is known by some other means, we can determine the concentration at any distance from the membrane surface employing Eq. (16).

5. FILM THEORY

We now turn our attention to a traditional theory of concentration polarization. Anyone familiar with mass transfer operations (generally chemical and environmental engineers) is bound to know about film theory. This theory is the earliest and most extensively used theory of membrane filtration. It is based on analogies of membrane separations with traditional mass transfer operations.

At the outset, it is worth mentioning that the film theory is an approximate theory. A major assumption of the theory is that the mass transfer phenomenon at the membrane solution interface governs the solute transport across the entire polarized layer.

What the above assumption implies is explained in Fig. 7. The figure shows a polarized layer adjacent to a membrane. The actual concentration profile is shown by the solid curve. The curvature of the concentration profile implies that the rate of mass transfer varies with \( y \). Film theory, however, assumes that the mass transfer phenomenon remains same everywhere in a hypothetical “thin film” of thickness \( \delta \). Furthermore, it is assumed that the constant mass transfer rate in the film is obtained from a mass balance at the membrane surface (the membrane solution interface). Clearly, the above assumptions are reasonably valid only when the concentration polarization layer is very thin, a condition achieved when concentration polarization effects are very small.

5.1. Solute mass balance at membrane surface

The enlarged portion of Fig. 7 depicts the solute mass balance at the membrane surface. The only input to the membrane surface is the convective solute flux \( v c_m \). The outputs are the diffusive solute flux directed towards the feed bulk and the solute emerging from the permeate side of the membrane. Thus, a steady state mass balance for the solute at the membrane surface yields

\[ v c_m = -D \frac{dc_m}{dy} + v c_p \]

Now, using the assumption of the film theory, the concentration gradient obtained from this mass balance equation is valid everywhere in the hypothetical thin film. Thus, we can drop the subscript from Eq. (18) and write

\[ D \frac{dc}{dy} = -v(c - c_p) \]  

(19)

Note the similarity and difference between Eqs. (17) and (19). Actually, Eq. (19) can be directly derived from Eq. (17) using Eq. (18) as a boundary condition at the membrane surface. If we introduce Eq. (18) in Eq. (17) at \( y = 0 \), the constant
term in Eq. (17) becomes \(v_c\). Thus, the basic steady state mass balance in film theory is the same as the rigorous mass balance derived in Section 4. The only difference is that the membrane surface condition is given by Eq. (18) in this theory.

The boundary conditions required to solve Eq. (19) are

\[
c = c_b \quad \text{at} \quad y = \delta_f \quad \text{(bulk solution)} \tag{20}
\]

where \(\delta_f\) is the hypothetical film thickness, and

\[
c = c_m \quad \text{at} \quad y = 0 \quad \text{(membrane surface)} \tag{21}
\]

5.2. The film theory equation

Solving Eq. (19) subject to Eqs. (20) and (21) results in

\[
\int_{c_m}^{c_p} \frac{dc}{c-c_p} = -\int_0^{\delta_f} \frac{v}{D} \, dy
\]

OR

\[
\frac{c_m - c_p}{c_b - c_p} = \exp \left[ \frac{v \delta_f}{D} \right] = \exp \left[ \frac{v}{k_f} \right] \tag{22a}
\]

An analogous form of the equation is

\[
v = k_f \ln \left[ \frac{c_m - c_p}{c_b - c_p} \right] \tag{22b}
\]

If the solute rejection is 1, that is, the permeate concentration \(c_p\) is zero, then Eq. (22) simplifies to

\[
\frac{c_m}{c_b} = \exp \left[ \frac{v}{k_f} \right] \tag{23a}
\]

OR

\[
v = k_f \ln \frac{c_m}{c_b} \tag{23b}
\]

From Eqs. (22) and (23), we note that the membrane surface concentration can be determined if \(v\), \(c_m\), \(c_p\), and \(k_f\) are known. The term \(k_f (= D/\delta_f)\) is known as the mass transfer coefficient. The mass transfer coefficient is determined from various mass transfer correlations, which have a general form

\[
Sh = \alpha \, \text{Re}^\beta \, \text{Sc}^\mu \left( \frac{d_h}{L} \right)^\delta \tag{24}
\]

where \(Sh\) stands for the Sherwood number, \(\text{Re}\) is the Reynolds number, and \(Sc\) is the Schmidt number. The term \(d_h\) represents the hydraulic diameter of the filtration channel. It is defined in terms of the ratio of the wetted cross-sectional area to the wetted perimeter of the filtration channel. The constants \(\alpha, \beta, \mu, \) and \(\delta\) are different for different channel geometries and flow conditions. Table 1 lists some common forms of mass transfer coefficients used in practice.

<table>
<thead>
<tr>
<th>(Sh)</th>
<th>Condition</th>
<th>Flow Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.62(ReSc(\frac{d_h}{L}))^{0.33}</td>
<td>Laminar flow in a tube</td>
<td>(24a)</td>
</tr>
<tr>
<td>0.04Re^{0.75}Sc^{0.33}</td>
<td>Turbulent flow in a tube</td>
<td>(24b)</td>
</tr>
<tr>
<td>1.85(ReSc(\frac{d_h}{L}))^{0.33}</td>
<td>Laminar flow in a rectangular channel</td>
<td>(24c)</td>
</tr>
<tr>
<td>0.04Re^{0.75}Sc^{0.33}</td>
<td>Turbulent flow in a rectangular channel</td>
<td>(24d)</td>
</tr>
<tr>
<td>(kr)</td>
<td>Laminar (8000&lt;Re&lt;32000) flow in a stirred batch cell</td>
<td>(24e)</td>
</tr>
<tr>
<td>0.04Re^{0.75}Sc^{0.33}</td>
<td>Turbulent flow in a stirred batch cell (Re&gt;32000)</td>
<td>(24f)</td>
</tr>
</tbody>
</table>

The film theory is a simple approach for determination of the extent of concentration polarization. Its main limitation, however, lies in the use of an empirical mass transfer coefficient that needs to be determined specifically for a given channel geometry and flow condition. Furthermore, the film theory also suffers from the limitation that the permeate flux needs to be known if the membrane surface concentration has to be determined and vice versa. Thus, the theory cannot predict the permeate flux.

All the theoretical constructs described above (including the basic governing equations of concentration polarization derived in section 4) suffer from similar limitations. First, the membrane surface concentration cannot be known a priori, and secondly, the permeate flux cannot be determined directly from the theory. This implies that we must perform experiments to use the theory. However, performing experiments beats the purpose entirely, as we intend to use the theories to predict the permeate flux. This brings us to a search for other governing equations for permeate transport that can be coupled to the above theories so that the permeate flux and the membrane surface concentration can be predicted simultaneously using these theories.

3. Please refer to the textbook by Marcel Mulder for the mathematical expression for \(d_h\).
4. There are other problems with the mass transfer coefficient. The mass transfer correlations are generally based on analogies with heat or mass transfer operations in other types of systems. The major difference between membrane processes and such other processes is the absence of a porous interface (the membrane) in the latter ones. Such correlations are therefore not exact for membrane separation processes.
6. COUPLED PROTECTION OF FLUX & MEMBRANE SURFACE CONCENTRATION

6.1. Models of permeate transport across membrane

An independent expression that relates the membrane surface concentration with the permeate flux can solve the problem discussed above in Section 5. This additional independent relationship is obtained from various models for permeate transport across membranes. The commonly used theories that provide such an expression are the Osmotic Pressure Model, the Gel Layer Model, and the Boundary Layer Resistance Model.

Before describing these models, however, it is necessary to first modify the basic governing model for concentration polarization. In Section 4, we used Eq. (12) to describe the boundary condition at the membrane surface arbitrarily. The solute mass balance at the membrane surface, Eq. (18), provides a more rigorous boundary condition suitable for membrane separation processes where the membrane surface concentration is unknown. Thus, in most modern studies, Eq. (12) is replaced by Eq. (18), which is rewritten here as Solution of Eqs. (8) or (9) using Eq. (25) as a membrane surface boundary condition instead of Eq. (12) provides a solution more appropriate for membrane separation processes. This is because the membrane surface concentration is used as a variable in Eq. (25). Secondly, this boundary condition also accounts for the solute rejection by the membrane (as \( c_m - c_p = R c_m \)).

Solution of the partial differential equations (8) and (9) become feasible when we provide an additional relationship between the permeate flux and the membrane surface concentration. Various models that provide this relationship are briefly described below.

6.2. Osmotic pressure model

The osmotic pressure model is based on the concept that the concentration buildup at the membrane surface results in a corresponding buildup of osmotic pressure, which causes a loss of driving force (pressure). Physically, this approach is quite realistic when the solute concentration near the membrane surface is not high enough to form a cake (or gel) layer. The only requirement of this approach is an independent relationship for the concentration dependence of osmotic pressure.

The osmotic pressure model uses the phenomenological equation for permeate flux across the membrane as an additional equation to couple the membrane surface concentration to the permeate velocity \( v \). As we know, the equation for permeate flux is

\[
v \equiv J_v = A (\Delta P - \sigma_o \Delta \Pi )
\]

where the term \( \Delta \Pi \) is a function of the solute concentration difference across the membrane.

Consider a general expression for the concentration dependence of osmotic pressure

This general expression is known as the virial equation. The

\[
\Pi = a_1 c + a_2 c^2 + a_3 c^3 + \cdots
\]

constant coefficients \( a_i \) are known as virial coefficients. As Eq. (27) suggests, the osmotic pressure is a complex non-linear function of solute concentration. This is particularly true for macromolecular solutions or even electrolytes at high concentration. Only for dilute ideal solutions can the osmotic pressure be expressed by the vant Hoff equation. For most real solutions, the virial equation is perhaps a more appropriate way of expressing the concentration dependence of osmotic pressure. We note that the first virial coefficient \( a_1 \) is given by

\[
a_1 = kT \quad \text{(when } c \text{ is expressed in number density)}
\]

\[
= RT/M \quad \text{(when } c \text{ is in moles/lit)}
\]

This means that we recover the vant Hoff equation when we drop the higher order concentration terms in Eq. (27).

Now, noting that the solute concentration at the two sides of a membrane are \( c_m \) and \( c_p \), the osmotic pressure difference will be

\[
\Delta \Pi = a_1 (c_m - c_p) + a_2 (c_m^2 - c_p^2) + a_3 (c_m^3 - c_p^3) + \cdots
\]

Equation (29) can be substituted in Eq. (26) to yield which is

\[
v = \frac{A}{\sigma_o} \left[ a_1 (c_m - c_p) + a_2 (c_m^2 - c_p^2) + a_3 (c_m^3 - c_p^3) + \cdots \right]
\]

the additional relationship between the permeate flux and the membrane surface concentration we were looking for. For a perfectly rejecting membrane \( \sigma_o = 1 \) and \( c_p = 0 \). We can now solve Eqs. (22) and (30) simultaneously to obtain the permeate velocity \( v \) and the membrane surface concentration \( c_m \) based on the film theory. We can also relate the membrane surface concentration and the permeate flux in the convective diffusion equation (8) or (9) and its boundary condition, Eq. (25). This yields a self-consistent set of equations where the number of equations equals the number of unknowns. Equation (26), or more specifically Eq. (30), constitutes the osmotic pressure model for permeate transport across a porous barrier.

If a cake layer is formed on the membrane surface, which is usually the case in microfiltration and some ultrafiltration processes, the limiting resistance to permeate flow is offered by the gel layer. In that case, we consider the gel layer model.
6.3. Gel layer model

When a cake or gel layer is formed on the membrane, the concentration of the gel layer (denoted by $c_g$) remains constant. In this case, the membrane surface concentration becomes constant,

$$c_m = c_g \text{ (constant) at } y = 0$$

The gel layers formed by specific solutes have specific concentrations, which depend on the properties of the particular solute. If the gel concentration can be determined independently from experiments, the flux corresponding to the gel-concentration can also be determined using film theory. This approach was used to describe the limiting flux phenomenon (or the pressure independent flux) observed during ultrafiltration or microfiltration processes.

6.4. Boundary layer resistance model

This is another empirical model for permeate transport across the membrane which utilizes Eqs. (1) and (2) to express the flux decline in terms of different resistances. The resulting expression for the permeate flux becomes

$$y = \frac{\Delta P}{\eta_w (R_m + R_{cp} + R_c + R_a + \cdots)}$$

The obvious limitation of Eq. (32) is that each resistance in this equation must be separately determined experimentally. There are several semi-empirical approaches to model these resistances. Coupled with the film theory, the boundary layer resistance or resistance in series model serves as a simple approach to correlate or fit experimental flux data. An advantage of this approach is that unlike osmotic pressure model for permeate flux, the model allows the consideration of other resistances like those due to adsorption or fouling. Hence, it is an attractive model for correlating flux decline due to several factors acting in concert.

7. CLOSING REMARKS

This chapter covered the early historical developments of modeling the membrane mass transfer processes. Relating the concentration polarization phenomenon with the permeate flux decline is achieved using multiple somewhat approximate approaches. First, the traditional film theory is approximate and relies on an empirical mass transfer coefficient that needs to be determined for different channel geometries and flow conditions. Secondly, there is no single universal model to relate the permeate flux decline to concentration polarization. While the osmotic pressure model appears to be quite fundamental (being based on the phenomenological equation), its application is limited to situations when there is no cake formation or fouling of any type. The gel layer model is appropriate only for prediction of the limiting or pressure independent flux, and fails to predict the permeate flux in other situations. Finally, the boundary layer resistance model is empirical and requires experiments to empirically determine the individual resistances in Eq. (32).

Until late 1980s, these techniques were the most common tools for predicting the flux. The use of these techniques led to a lot of confusion regarding the actual causes of flux decline. None of these models could be used to accurately predict the permeate flux over the entire gamut of pressure driven membrane filtration processes. The use of these models were restricted to narrow domains of filtration operations. While they provided reasonably good results for a handful of closely related solutes, they completely failed (qualitatively as well as quantitatively) to predict permeate fluxes for other solutes. This was a reason that led to the belief that the four pressure driven membrane separation processes (RO, NF, UF and MF) are governed by vastly different mechanisms of transport, and any attempt towards unified treatment of all the membrane filtration processes was even "scoffed at" by some.

The picture has changed considerably since 1990s. The present rendering of unified transport models for membrane processes where we can model flux decline during RO, NF, UF, and MF in the framework of the same mathematical construct is the outcome of a more formal approach towards membrane separation processes.
APPENDIX

Nomenclature

A  Membrane permeability
a1,a2,a3  Virial coefficients for osmotic pressure
b  Solute concentration
c  Solute concentration in feed solution (bulk concentration)
cb  Solute concentration in feed solution (bulk concentration)
cg  Gel concentration
cm  Solute concentration at membrane surface (feed side)
cp  Solute concentration in the permeate solution at pore exit
D  Diffusion coefficient
dh  Hydraulic diameter of a filtration channel
k  Boltzmann constant (1.38x10^{-23}J/K)
kf  Mass transfer coefficient used in film theory
L  Channel length
M  Molecular weight of a solute
R  Universal gas constant
Re  Reynolds number (duh/v)
r  Resistance due to solute adsorption
RCP  Resistance of polarized layer
Rc  Resistance of a cake or gel layer
Rf  Resistance due to fouling
Robs  Observed rejection (1-cp/cb)
Rpa  Resistance due to pore blocking
Ri  Intrinsic or real rejection of a membrane (1-cp/cm)
Rtot  Total resistance to permeate flow
Rm  Resistance of membrane
r  Radius of a cylindrical batch cell
Sc  Schmidt Number (v/D)
Sh  Sherwood number (kf dh/D)
t  Time
u  Axial velocity in a crossflow system
v  Permeate velocity
x,y  Coordinate axes in a rectangular crossflow geometry

Greek symbols

α,β,µ,δ  Constants used in mass transfer correlations
ΔP  Applied pressure difference across the pore
ΔPeff  Effective pressure difference across a membrane
ΔΠ  Osmotic pressure difference across membrane
δf  Film thickness
ηw  Solvent viscosity
ν  Kinematic viscosity
σo  Osmotic reflection coefficient
ω  Stirrer speed in radians per second

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Dr. Subir Bhattacharjee possesses over 25 years of experience in water treatment research, consulting, commercialization and engineering. He previously served for 12 years as Professor of Chemical and Mechanical Engineering at the University of Alberta, Canada, ran an industry funded Canadian national research center in oil & gas water treatment, and was the founder and CEO of EnVivAqua a water technology startup in Canada.

SUGGESTED READING

1.  The text book by Marcel Mulder. **