

Module :
3

Membrane based separation processes

Dr. Sirshendu De
Professor, Department of Chemical Engineering
Indian Institute of Technology, Kharagpur
e-mail: sde@che.iitkgp.ernet.in

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Membrane Based Separation Processes

3.1 Definition of a membrane:

It is an interface that separates the two phases and restricts the transport of various chemical species through it. Membrane can be homogeneous, heterogeneous, symmetric, asymmetric, charged, neutral.

3.2 Membrane Casting:

Common polymeric membrane material is Cellulose Acetate. Various steps of a typical casting process are:

1. Solvent (acetone) is added to polymer. A viscous solution is prepared.
2. It is put on a plate. Place another plate on top of it. The gap is of the order of ~ 0.25mm
3. Give a one directional motion to the top plate. A thin film is produced on the bottom plate.
4. Take out bottom plate and place it in ice-water bath, which releases the film.
5. Heat treat the film in hot water.

Typical casting conditions are:

Casting solution : CA 25%, Formamide 30% and Acetone 45%.

Casting temperature : 25⁰C

Evaporation time : 1 minute

3.3 Types of barrier:

Homogeneous barrier:

- Pore size is 2-10 \AA
- Diffusion is controlling mechanism.
- Typical RO membrane

Microporous Barrier:

- Pore size is 10-1000 \AA
- Both convection and diffusion are dominant mechanism.

Asymmetric Barrier:

In this case, a thin polymeric skin is cast on another polymeric support. It is shown schematically in Fig. 3.1. The skin acts like a membrane. Since the thickness of the skin is really small, the resistance offered is less and one can expect a higher flux compared to homogeneous membranes.

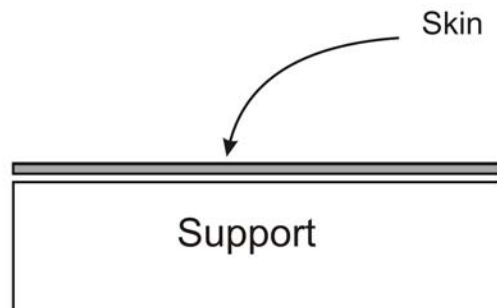


Fig. 3.1: Schematic of an asymmetric membrane

Trans membrane permeate flux is inversely proportional to the membrane thickness.

If homogeneous barrier is the skin, micro porous barrier may be the support.

3.4 Types of motion of molecules through barrier:

1) Permeation:

- a) Dissolution of permeating molecules in the membrane
- b) Diffusion of dissolved molecules
- c) Desorption of penetrant molecules to the downstream side.

2) Knudsen diffusion ($d/\lambda < 0.2$):

Single gaseous molecules diffuse under rarefied conditions so that the mean free path is longer than the pore diameter.

3) Convection ($d/\lambda > 20$):

Viscous flow through the pores of ultrafiltration and microfiltration.

3.5 Categorization of such processes:

Reverse Osmosis:

Small solute particles to be separated.

Molecular weight < 100

Pore size: $2 - 10 \text{ \AA}$

Pressure: $> 25 \text{ atm}$.

Permeation is main transport mechanism

Example: Filtration of salt solution

Nanofiltration:

Particles to be separated with Molecular weight: $200 - 1000$

Pore size: $5 - 20 \text{ \AA}$

Pressure: $15 - 25 \text{ atm}$.

Particle retention of salts.

Example: Filtration of dyes, small molecular weight organics, etc.

Ultrafiltration:

Molecular weight of particles : $10^3 - 10^5$

Pore size: $20 - 1000 \text{ \AA}$

Pressure: $6 - 8 \text{ atm}$.

Transport Mechanism: Convection (main) + diffusion

Example: Filtration of protein, Red blood cells, polymers, etc.

Microfiltration:

Molecular weight $> 1 \text{ lakh}$

Pore size: more than 1000 \AA

Pressure: $2 - 4 \text{ atm}$.

Example: Filtration of clay solution, latex, paint, etc.

3.6 Useful definitions:

Some useful definitions are presented below.

(1) Osmotic Pressure:

Osmosis means craving for water.

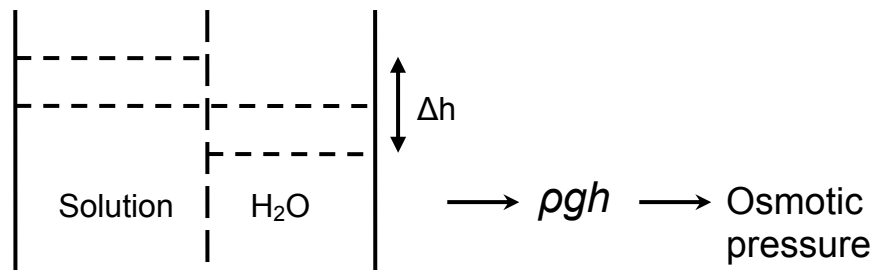


Fig.3.2: A schematic presentation of the osmosis process

Fig. 3.2 shows that a semipermeable barrier separates a solution having some solute in one side and pure solvent (water in this case) at the other side. Due to presence of difference in concentration of solvent in both sides, water from solution side permeate through the membrane to the solvent side. Therefore, the level of water in solvent side goes down and that in the solution side goes up. At equilibrium, there exists a difference in hydrostatic pressure in both the chambers, although the chemical potential of the solvent is equal across the membrane. The developed hydrostatic head is called osmotic pressure. If the solute concentration in the solution is more, the solution is more “thirsty” of water and equilibrium hydrostatic pressure head is more.

When water is forced through a concentrated solution (by applying pressure), the osmotic pressure resists. The energy required to overcome this resistance is called osmotic energy.

As discussed above, osmotic pressure is a colligative property, directly proportional to concentration.

$$\pi \propto \frac{1}{M_w} \quad \text{and} \quad \pi \propto C$$
$$\text{and hence, } \pi = \frac{RTC}{M_w} \quad (3.1)$$

The above equation is vant hoff's equation for dilute solutions.

It may be mentioned that any solution has its own osmotic pressure, but it can only be realized in presence of a semipermeable barrier or membrane. For example, a glass of saline water has its own osmotic pressure but it can only be realized, if we place it across a semi-permeable barrier.

(2) Observed retention: (Selectivity of membrane)

This property indicates the extent of separation of a membrane can produce with respect to the solute concentration in the feed. Thus, observed retention is defined as,

$$R_o = 1 - \frac{C_p}{C_o} \quad (3.2)$$

where, C_p = Solute concentration in permeate

C_o = Solute concentration in feed

If $R_o \rightarrow 1.0$, solute is completely retained by the membrane.

(3) Real retention:

Real retention is a constant that defines the partition of the solute concentration across the membrane, i.e., between the the membrane-solution interface and the permeate side. Since, this definition is not masked by any physical phenomenon like concentration polarization, (defined later) etc., this definition indicates the true separation efficiency of the solute by the membrane.

$$R_r = 1 - \frac{C_p}{C_m} \quad (3.3)$$

Here, C_m = Solute concentration in membrane solution interface . It may be mentioned here that since, membrane surface concentration of solute is always greater than the bulk concentration, real retention is always greater than observed retention. For complete solute retention, $R_r = 1.0$.

(4) Molecular Weight Cut-Off (MWCO):

Molecular weight cut off is another concept to characterize a membrane. In this case, generally neutral solutes of various molecular weights are considered to conduct experiments. The operating conditions of these experiments are low transmembrane pressure drop, high turbulence and low feed concentration. Experiments are conducted using each of these solutes and the observed retention values at the steady state are measured. The observed retention values are then plotted against the molecular weight of the solutes in a semi-log plot. The typical solutes are glucose (molecular weight 180), sucrose (molecular weight 342), various fractions of polyethylene glycol (molecular weights: 200, 400, 600, 1000, 1500, 2000, 4000, 60000, 10000, 30000), dextran (molecular weight 40000, 1,50,000), etc. The molecular weight at 90% solute retention indicates roughly the molecular weight cut off of the membrane. The molecular weight cut off curves are shown in Figs. 3.3 and 3.4

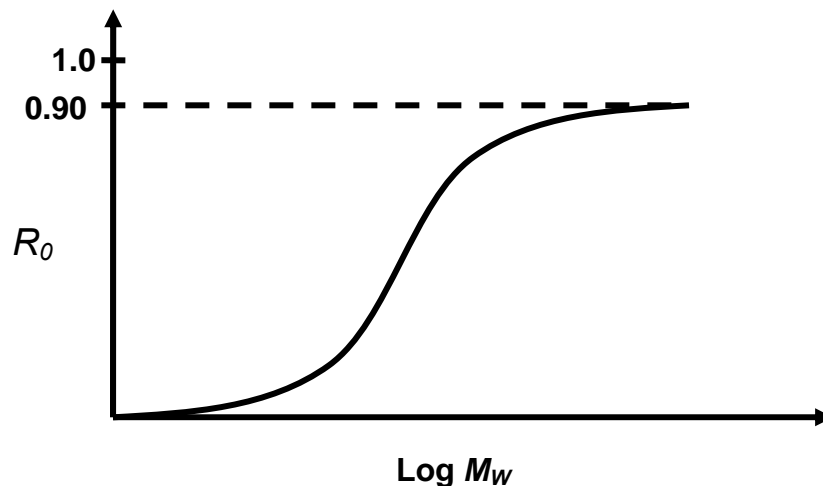


Fig.3.3: Typical molecular cut off curve of a membrane

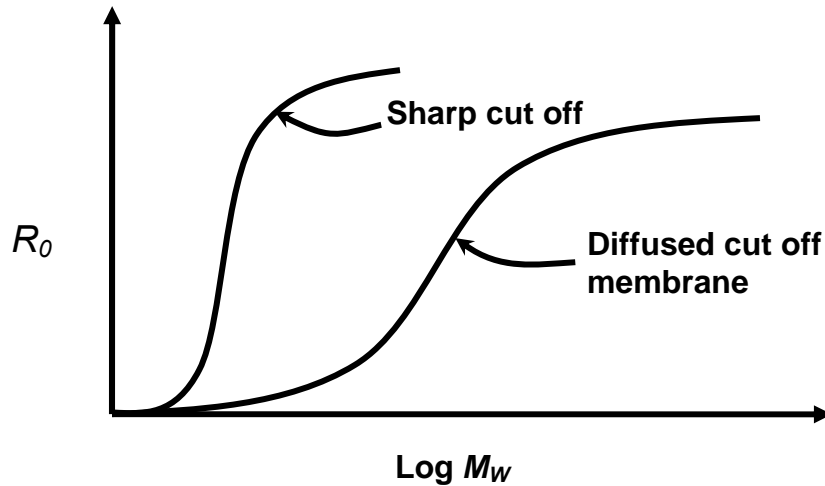


Fig.3.4: Sharp and diffused molecular cut off curves

Molecular weight cut off curves may be a sharp cut off or a diffused cut off. If the retention curve raises sharply to 90% level over a small span of molecular weight regime, then the cut off curve is called a sharp cut off curve. If the retention curve rises over a wide span of molecular weight region, it is a diffused cut off curve. One has to have an accurate control over the operating conditions to achieve the sharp cut off membranes. In fact, most of the commercial membranes are diffused type.

(5) Membrane Permeability (L_p):

This parameter shows how porous the membrane is. If L_p is more, then the membrane is more porous. Mathematically, L_p is defined as, $L_p = \frac{J^0}{\Delta P}$, where, J^0 is the pure water flux and ΔP is transmembrane pressure drop. This concept is elaborated in detail in the subsequent sections.

(6) Estimation of retention & permeability:

Retention:

Observed retention (R_o): Estimate by direct experimental measurement

Real retention (R_r): One has to conduct batch experiments at high stirring speed, low feed concentration and low operating pressure. In that case, it is assumed that there is no formation of concentrated solute layer over the membrane surface and in absence of polarized layer, observed retention is almost same as retention retention.

Permeability:

Membrane permeability is measured by distilled water runs. Experiments are conducted using distilled water at various transmembrane pressure drops values. At various pressure drops, the water flux is measured. A plot of permeate flux versus operating pressure would be a straight line through the origin, as shown in Fig. 3.5. The slope of this curve indicates the permeability (L_p) of the membrane. It may be noted here that the permeability of a membrane is its pressure history only. In other words, permeability of the membrane is independent of turbulence (stirring speed or cross flow velocity) in the

flow channel. The unit of permeability is $\frac{m^3}{m^2 \cdot Pa \cdot s}$ or $\frac{m}{Pa \cdot s}$.

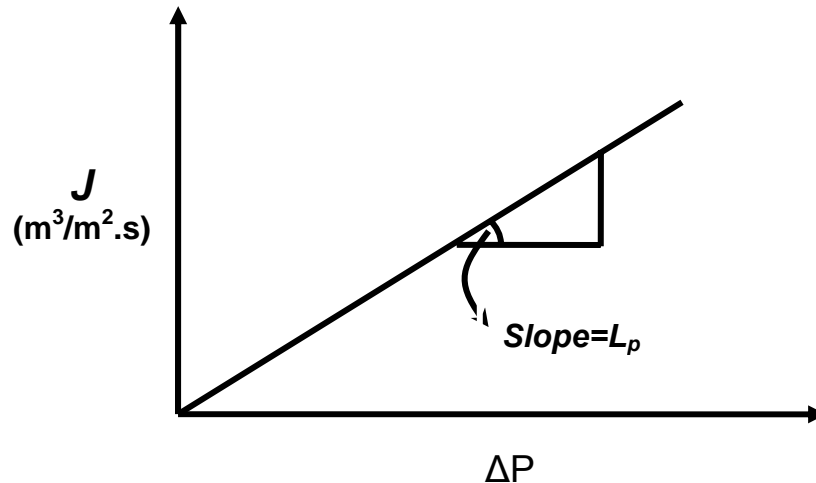


Fig.3.5: A typical flux versus pressure plot for distilled water as feed

Membrane modules:

The practical equipment where the actual membrane based separation occurs is known as membrane modules. The basic aim of development of these modules is to provide maximum membrane area in relatively smaller volume, so that the permeate flux i.e., the productivity of the system is maximum. These membrane modules are of four types, (i) plate and frame module, (ii) hollow fiber module, (iii) spiral wound and (iv) tubular modules. Each of these modules is described below:

Plate and frame modules

The heart of plate-frame module is the support plate that is sandwiched between two flat sheet membranes. The membranes are sealed to the plate, either gaskets with locking devices, glue or directly bonded. The plate is internally porous and provides a flow channel for the permeate which is collected from a tube on the side of the plate. Ribs or grooves on the face of the plate provide a feed side flow channel. The feed channel can be a clear path with channel heights from 0.3 to 0.75 mm. The higher channel

heights are necessary for high viscosity feeds; reduction in power consumption of 20 to 40% can be achieved by using a 0.6 mm channel compared to a 0.3 mm channel. Alternatively, retentate separator screens (20 or 50 mesh polypropylene) can be used. Commercial plate-frame units are usually horizontal with the membrane plates mounted vertically. They can be run with each plate in parallel plates in two or three series. Laboratory are also available as preformed stacks up to 10 plates. A typical plate and frame module is shown in Fig. 3.5a.

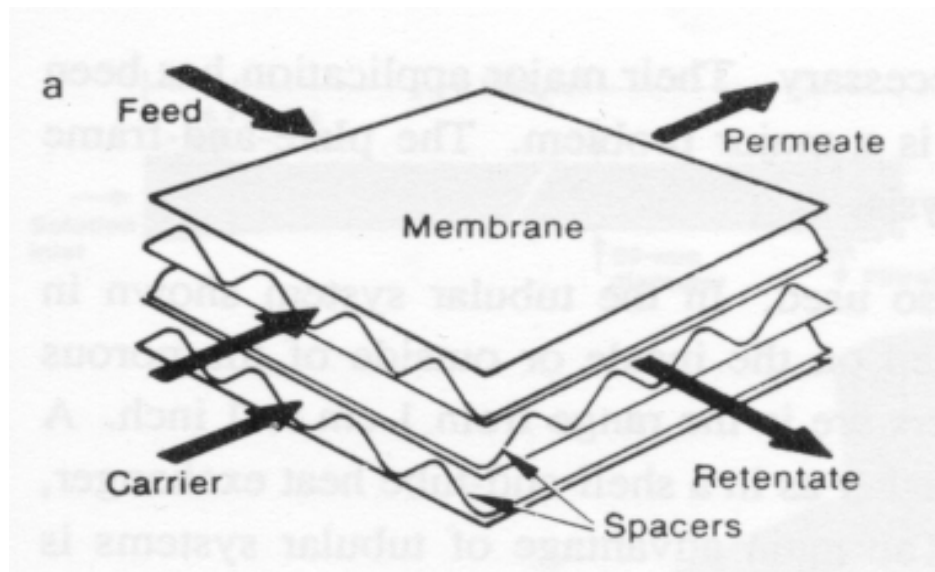


Fig.3.5a: A plate and frame module

Tubular modules

In such modules, the membrane is cast on the inside surface of a porous tube. Tubular membranes operate in tangential, or cross-flow, design where process fluid is pumped along the membrane surface in a sweeping type action. The feed solution is pumped through the center of the tube at velocities as high as 6 m/s. These cross-flow velocities minimize the formation of a concentration polarization layer on the

membrane surface, promoting high and stable flux and easy cleaning, especially when the objective is to achieve high suspended solids in the MF, UF or NF concentrate. Permeate is driven through the membrane to be directed out of the system or back into the process depending on the application. There are many advantages in tubular membrane configurations. Besides their rugged construction, they have a distinct advantage of being able to process high suspended solids, and concentrate product successfully and repeatedly to relatively high end point concentration levels without plugging. A common objective of an end-of-pipe waste treatment UF system is to reduce waste volume as much as possible to reduce concentrate hauling costs. For juice clarification applications, tubular membrane systems produce the greatest yields and the highest final suspended solids concentration levels. Tubular MF, UF and NF systems do not require significant prefiltration. Some tubular products have the ability to be mechanically cleaned with spongeballs. Spongeballs can be used in process, and are also used to enhance chemical cleaning by reducing time and cleaning chemicals. Tubular membranes are ideally suited to treatment of metalworking oily waste, wastewater minimization and recovery from industrial processes, juice clarification, treatment of pulp and paper industry waste, etc. Tubular membranes typically have life upto 2 to 10 years. The following figure (Fig. 3.5 b) shows some tubular membranes.

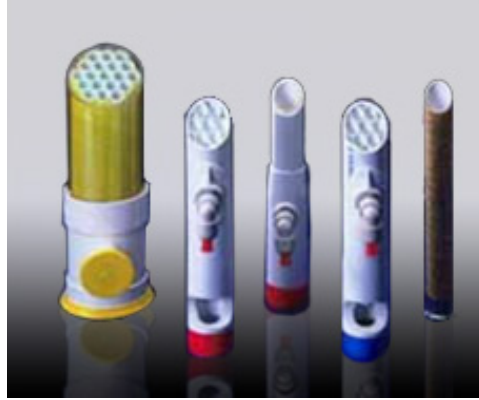


Fig.3.5b: Pictures of tubular modules

Hollow fiber module

In hollow fiber module, lots of hollow fibers (each fiber is a tubular module) are kept in a large pipe. Geometry allows a high membrane surface area to be contained in a compact module. This means large volumes can be filtered, while utilizing minimal space, with low power consumption. Hollow fiber membranes can be designed for circulation, dead end and single pass operation. Some of the many hollow fiber membrane filtration applications include, potable water treatment, juice clarification, wine filtration, dairy processing, etc. The advantages of such modules include reduction in space requirement, lowering in labor cost, lowering in chemical cost, delivery of high quality product water, etc. Hollow fiber membranes offer the unique benefits of high membrane packing densities, sanitary designs and, due to their structural integrity and construction, can withstand permeate back pressure thus allowing flexibility in system design and operation. Most KMS hollow fiber products are available in (i) 1" diameter laboratory test cartridges ranging up to 10" diameter for commercial products, (ii) Standard commercial cartridge lengths of 25", 43", 48", 60" and 72", (iii) Nominal separation ranges from 0.2 micron down to 1,000 MWCO, (iv)

Fiber inside diameters from 0.02"(.5mm) up to 0.106"(2.7mm), (v) Various materials of construction including polysulfone and polyacrylonitrile.

The following figure (Fig. 3.5c) shows some hollow fiber cartridges of 5, 8 and 10" diameter with endcaps.



Fig.3.5c: Pictures of hollow fiber modules with end cap

Benefits of hollow fiber membranes include (i) controlled flow hydraulics, (ii) tangential flow along the membrane surface limits membrane fouling, (iii) membranes can be backflushed to remove solids from the membrane inside surface, thus extending the time between two chemical cleaning cycles, (iv) high membrane packing density resulting in high throughput, (v) modular in structure so that future extension of the plant becomes easier. The flow pattern in a typical hollow fiber module takes place as shown in Fig. 3.5d.

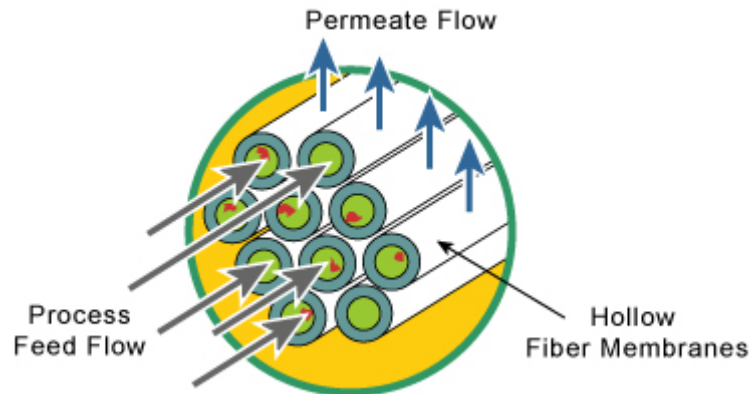


Fig.3.5d: Flow pattern in hollow fiber module

Spiral wound module

In spiral wound membrane, membrane is cast as a film onto flat sheet. Membranes are sandwiched together with feed spacers (typical thickness 0.03 to 0.1 inch) and permeate carrier. They are sealed at each edge and wound up around a perforated tube. The module diameter ranges from 2.5 to 18 inch and length varies from 30 to 60 inch. The typical cross section of the spiral wound module is shown below:

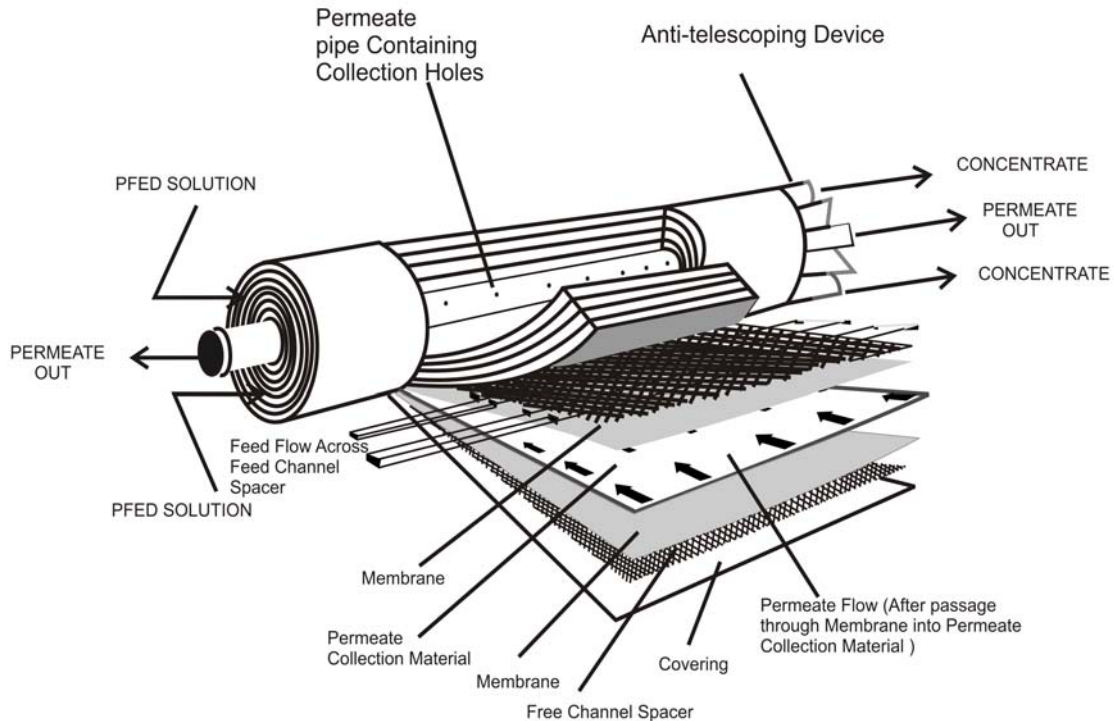


Fig.3.5e: Flow pattern in spiral wound module

The application of spiral wound module includes, seawater desalination, brackish water treatment, potable water treatment, dairy processing, electrocoat paint recovery, protein separation, whey protein concentration, etc.

Therefore, it can be identified that the modeling of plate and frame and spiral wound module can be done by considering the flow through a rectangular channel. On the other hand, that for a tubular and hollow fiber module are done by considering flow through a tube.

3.7 Driving forces in membrane separation processes:

Separation in membrane is the result of differences in the transport rates of chemical species through it.

Transport rate is determined by the driving force acting on individual components, their mobility, concentration of solute in membrane phase, etc..

Mobility : Depending on solute size and structure of membrane.

Concentration : Chemical compatibility of solute & interface material.

3.8 Basic forces of transport:

Driving forces for transport:

Gradient of electro chemical potential of species is the driving force of transport of species. This gradient may be caused by pressure difference, concentration, temperature or electrical potential between two phases separated by the membrane.

(a) Passive Transport:

As described in Fig. 3.6, in such cases, the upstream chemical potential of a component is more than that in the downstream.

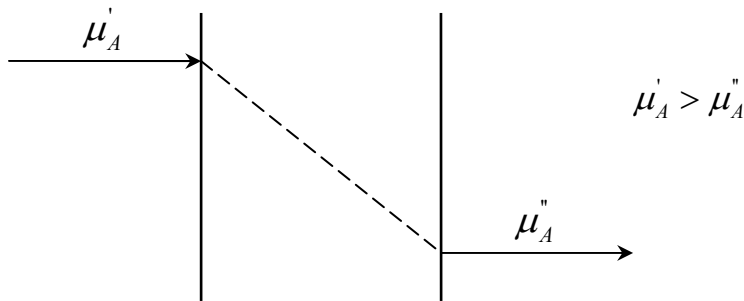


Fig.3.6: Passive transport

(b) Facilitated transport:

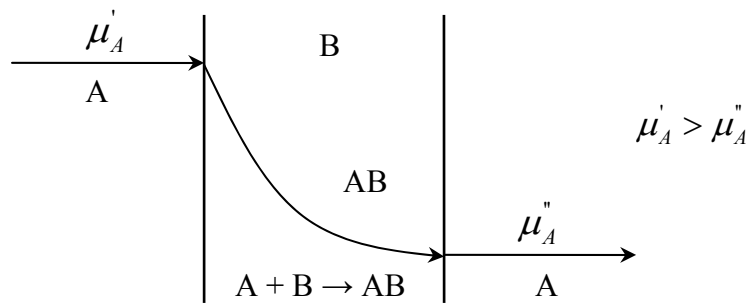


Fig.3.7: Facilitated transport

In this case also the chemical potential of a species in upstream is more than that in the downstream. However, as shown in Fig. 3.7, components to be transported are coupled with a carrier in the membrane phase. So, it is a special form of passive transport and very selective and at the same time, the transport is facilitated by the carrier component.

(c) Active transport:

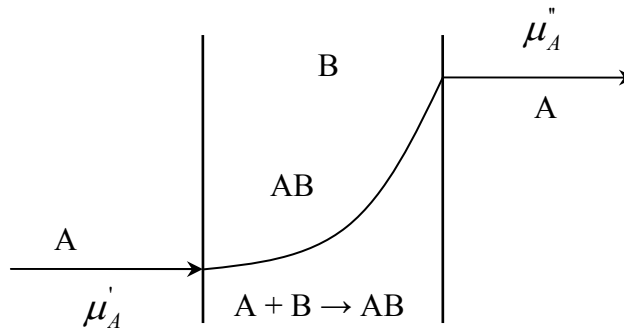


Fig.3.8: Active transport

As shown in Fig. 3.8, components are transported against driving force. Driving force for transport is provided by the activation energy of chemical reaction in the membrane phase (Living Cell). In this case, the upstream chemical potential is higher than that of downstream potential.

3.9 Description of transport process by phenomenological equation

The transport processes are generally described by the phenomenological equations. Such equation describes “cause-effect” relationship. It presents flux of anything is proportional to the driving force. The proportionality constant is the transport property specific to the system. Table 3.1 presents various phenomenological equations common in chemical engineering applications.

Table 3.1: Examples of phenomenological equations

Phenomenon relation	Flux	Driving force	Constant of property
Fick's Law	Mass	Concentration difference	D
Ohm's Law	Electricity	Electric potential difference	R
Fourier's Law	Heat	Temperature difference	K

In membrane separation process, driving forces may be interdependent. Thus, a concentration gradient across a membrane not only leads to flow of matter, can also cause build up of pressure. An example is osmosis.

A pressure difference leads to volumetric flow as well concentration difference. An example is reverse osmosis.

Temperature difference across the membrane leads to heat flow associated with flow of matter. An example is Thermo diffusion/ Soret effect.

Concentration difference across the membrane causes mass flux as well as temperature gradient. An example is Dufour effect.

3.10 Osmotic pressure: A thermodynamic point of view

Let us consider an experiment, where, a solvent and a solution are separated by a semi-permeable membrane as shown in fig. 3.9.

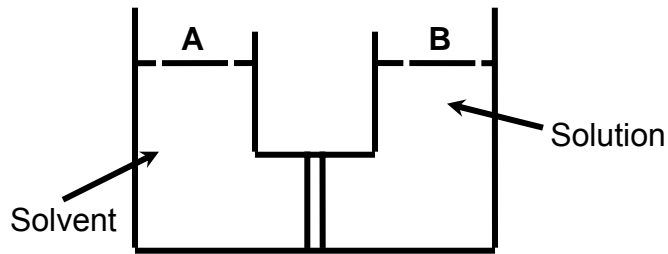


Fig. 3.9: Solution and solvent are separated by a semi-permeable barrier

Osmotic equilibrium means chemical potential of solvent at both chambers are equal.

Let us use the notation, '2' is for solvent and '1' is for solute. P_1 is pressure in chamber A and P_2 is pressure in chamber B.

At osmotic equilibrium:

$$\mu_2(\text{at } P_1) = \mu_2(\text{at } P_2) \quad (3.4)$$

The above equation can be written as,

$$\mu_2 = \mu_2^0 + RT \ln a_2 \quad (3.5)$$

Where, μ_2^0 is for pure solvent and a_2 is solvent activity.

Following hypothetical experiment is conducted.

Hypothetical Experiment:

Both chambers have pure water and initially at pressure P_1 , μ_2 is same at both chambers.

Now small amount of solute is added in chamber B.

Then, $\mu_2^0(P_1)$ becomes $\mu_2(P_1)$ in B

$$\mu_2(P_1) = \mu_2^0(P_1) + RT \ln a_2 \quad (3.6)$$

In B, apply pressure and so that P_1 becomes P_2 and osmotic equilibrium is restored.

At osmotic equilibrium,

$$\mu_2(\text{at } P_1) \text{ in 'B'} = \mu_2(\text{at } P_2) \text{ in 'A'} \quad (3.7)$$

The above equation can be written as,

$$\mu_2^0(P_2) + RT \ln a_2 = \mu_2^0(P_1) \quad (3.8)$$

Rearrangement of above equation leads to

$$\mu_2^0(P_2) - \mu_2^0(P_1) = -RT \ln a_2 \quad (3.9)$$

From the definition of partial molar volume, we get,

$$\bar{V}_i = \text{Partial molar volume of } i^{\text{th}} \text{ species} = \left(\frac{\partial \mu_i^0}{\partial P} \right)_{T,n}. \text{ Thus, Eq.(3.9) is written as,}$$

$$\mu_2^0(P_2) - \mu_2^0(P_1) = \int_{P_1}^{P_2} \bar{V}_2 dP \quad (3.10)$$

Assuming, $\bar{V}_2 \neq \bar{V}_2(P)$, Eq.(3.10) is expressed as,

$$\bar{V}_2(P_2 - P_1) = -RT \ln a_2 \quad (3.11)$$

We, thus, obtain an expression of osmotic pressure,

$$\bar{V}_2 \pi = -RT \ln a_2 \quad (3.12)$$

Here, $a_2 =$ Solvent activity

$$= \frac{\text{Solvent vapour pressure in presence of solute}}{\text{Pure solvent vapour pressure}}$$

$$= \frac{P_S}{P_S^*}$$

$$\text{So, } \pi = \frac{RT}{\bar{V}_2} \ln \left(\frac{P_S^*}{P_S} \right) \quad (3.13a)$$

The above equation is presented in the following more amenable forms:

$$\text{Vant-Hoff equation} \quad : \quad \pi = CRT \quad \text{for dilute solutions} \quad (3.13b)$$

$$\text{Virial Type equations} \quad : \quad \pi = B_1C + B_2C^2 + B_3C^3 \quad \text{for concentrated solution.}$$

$$(3.13c)$$

3.11 Transports in Reverse Osmosis (RO):

Transport equation for the solute and solvent through reverse osmosis membrane is derived from irreversible thermodynamics.

The assumptions involved are,

- (a) Flux of i^{th} species may be a function of every force that exists in the system.
- (b) Under conditions not too far from equilibrium the flux-force relation is linear.

$$\vec{N}_i = \sum_{j=1}^{n_f} L_{ij} \vec{F}_j \quad (3.14)$$

Here, $N_i =$ Molar flux of i^{th} species in a stationary frame of reference

$\vec{F}_j = j^{\text{th}}$ driving force

$L_{ij} =$ Phenomenological coefficient

(c) No other external/mechanical force is applied on any of the species

The notations are, '1' is for solute and '2' is for solvent. Thus, the fluxes for the solvent and the solute are expressed as,

$$\vec{N}_2 = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 \quad (3.15)$$

$$\vec{N}_1 = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 \quad (3.16)$$

Onsager's reciprocating relationship:

If fluxes & forces are properly selected, then, $L_{ij} = L_{ji}$

Coupling:

The addition to the flux of one species due to the existence of force acting on another species is termed as coupling. For RO, it is assumed that no coupling takes place between solute and solvent flow.

Therefore, $L_{12} = L_{21} = 0$. Therefore, the solvent and solute fluxes are expressed as,

$$\vec{N}_2 = -L_{22}\nabla\mu_2; \quad (3.17)$$

$$\vec{N}_1 = -L_{11}\nabla\mu_1 \quad (3.18)$$

The gradient of chemical potential in absence of any electric potential gradient is expressed as,

$$\nabla\mu_i = \left(\frac{\partial\mu_i}{\partial P}\right)_{T,n} \nabla P + \left(\frac{\partial\mu_i}{\partial C_i}\right)_{P,T} \nabla C_i \quad (3.19)$$

Therefore, the solvent flux is expressed as,

$$\vec{N}_2 = -L_{22} \left[\left(\frac{\partial\mu_2}{\partial P}\right)_{T,n} \nabla P + \left(\frac{\partial\mu_2}{\partial C_{2m}}\right)_{P,T} \nabla C_{2m} \right] \quad (3.20)$$

Where, C_{2m} is molar concentration of solvent in membrane .

At the steady state, one dimensional transport across the membrane of thickness “ l ” is shown in Fig. 3.10.

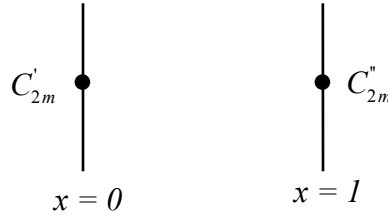


Fig. 3.10: Steady state, one dimensional transport across the membrane.

Integrating Eq.(3.20) across the membrane thickness, the following expression is obtained.

$$\int_0^l N_2 dx = -L_{22} \left[\int_{C'_{2m}}^{C''_{2m}} \left(\frac{\partial \mu_2}{\partial C_{2m}} \right)_{P,T} dC_{2m} + \int_{P_2}^{P_1} \left(\frac{\partial \mu_2}{\partial P} \right)_{n,T} dP \right] \quad (3.21)$$

Where, P_2 is higher, upstream pressure and P_1 is lower, downstream pressure. At steady state, N_2 is constant. The definition of partial molar volume is,

$$\bar{V}_i = \text{Partial molar volume of } i^{\text{th}} \text{ species} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T,n}$$

Using this definition of partial molar volume, the integration of above equation results,

$$\text{So, } N_2 l = -L_{22} \left[\int_{C'_{2m}}^{C''_{2m}} \left(\frac{\partial \mu_2}{\partial C_{2m}} \right)_{P,T} dC_{2m} + \int_{P_2}^{P_1} \left(\frac{\partial \mu_2}{\partial P} \right)_{n,T} dP \right] \quad (3.22)$$

At osmotic equilibrium, $N_2 = 0$ (from closure equation). Assuming, $\bar{V}_2 \neq f(P)$ over the range of pressure, the following expression is obtained.

$$\bar{V}_2 (P_2 - P_1) = \int_{C'_{2m}}^{C''_{2m}} \left(\frac{\partial \mu_2}{\partial C_{2m}} \right)_{P,T} dC_{2m}$$

$$= \bar{V}_2 \Delta \pi \quad (3.23)$$

Combining Eqs.(3.22) and (3.23), the following equation of the solvent flux is obtained.

$$\begin{aligned} N_2 l &= -L_{22} \left[\bar{V}_2 \Delta \pi - \int_{P_1}^{P_2} \bar{V}_2 dP \right] \\ &= -L_{22} [\bar{V}_2 \Delta \pi - \bar{V}_2 \Delta P] = \frac{L_{22} \bar{V}_2}{l} [\Delta P - \Delta \pi] \end{aligned} \quad (3.24)$$

The above equation is re-written as,

$$N_2 = k_{sol} [\Delta P - \Delta \pi] \quad (3.25)$$

Where, k_{sol} is a constant related to membrane permeability.

Thus, the phenomenological equation of the solvent flux through reverse osmosis membrane is derived.

Solute flux through the membrane:

The assumptions involved are:

- (a) Steady state
- (b) One dimensional
- (c) No coupling

Therefore, integration of Eq.(3.16) results into,

$$\begin{aligned} \int_0^l N_1 dx &= -L_{11} \left[\int_{C_{1m}}^{C_{1m}^*} \left(\frac{\partial \mu_1}{\partial C_{1m}} \right)_{P,T} dC_{1m} + \int_{P_2}^{P_1} \left(\frac{\partial \mu_1}{\partial P} \right)_{n,T} dP \right] \\ &= L_{11} \int_{C_{1m}}^{C_{1m}^*} \left(\frac{\partial \mu_1}{\partial C_{1m}} \right)_{P,T} dC_{1m} + \bar{V}_1 L_{11} \Delta P \end{aligned} \quad (3.26)$$

For dilute solution, $a_{1m} \approx C_{1m}$ and the expression of chemical potential is,

$$\mu = \mu^0 + RT \ln a_{1m}$$

$$= \mu^0 + RT \ln C_{1m} \quad (3.27)$$

The derivative of chemical potential with concentration becomes,

$$\left(\frac{\partial \mu}{\partial C_{1m}} \right)_T = RT \frac{\partial \ln C_{1m}}{\partial C_{1m}} \quad (3.28)$$

Combination of Eqs.(3.26) to (3.28) results into following expression of solute flux, through the membrane,

$$N_1 l = L_{11} RT \ln \frac{C'_{1m}}{C_{1m}} + \bar{V}_1 L_{11} \Delta P$$

$$N_1 = \frac{L_{11} RT}{l} \ln \frac{C'_{1m}}{C_{1m}} + \frac{\bar{V}_1 L_{11}}{l} \Delta P \quad (3.29)$$

In most of the cases, $\frac{\bar{V}_1 L_{11}}{l} \Delta P \sim 0$

Thus, expression of solute flux becomes,

$$N_1 = \frac{L_{11} RT}{l} \ln \frac{C'_{1m}}{C_{1m}} \quad (3.30)$$

For dilute solution, $L_{11} \approx D_{1m} \times C_{1m,avg}$. Thus, solute flux expression becomes,

$$N_1 = -L_{11} \left(\frac{\partial \mu_1}{\partial C_{1m}} \right) \nabla C_{1m}$$

$$= -D_{1m} \left(\frac{\partial \mu_1}{\partial C_{1m}} \right) C_{1m} \nabla C_{1m}$$

$$= -D_{1m} \left[RT \frac{d \ln C_{1m}}{d C_{1m}} \right] C_{1m} \frac{d C_{1m}}{d x}$$

$$= -D_{1m} R T C_{1m} \frac{d \ln C_{1m}}{d x} \quad (3.31)$$

The final expression of solute flux hence becomes,

$$N_1 l = -D_{1m} RT \int_{C'_{1m}}^{C''_{1m}} dC_{1m} = D_{1m} RT (C''_{1m} - C'_{1m})$$

$$N_1 = \frac{D_{1m} RT}{l} (C'_{1m} - C''_{1m})$$

$$N_1 = K_S (C'_{1m} - C''_{1m}) \quad (3.32)$$

Where, K_S = solute permeability, which is depending on solute diffusivity in membrane matrix. The model of solute flux through the membrane presented by Eq.(3.32) is known as **solution-diffusion model**.

It may be noted that the solvent flux N_2 presented above is molar flux with the unit $\frac{\text{moles}}{\text{m}^2 \cdot \text{s}}$. This can be converted to volumetric flux (J), $\text{m}^3/\text{m}^2 \cdot \text{s}$. Following equation presents the conversion.

$$J = \frac{N_2 M_{2W} \times 10^{-3}}{\rho_{\text{solution}}} \quad (3.33)$$

The solute flux in Eq. (3.32), is therefore presented as,

$$J C''_{1m} = K_S (C'_{1m} - C''_{1m}) \quad (3.34)$$

Combining the above equation with the definition of observed retention, the permeate flux can be expressed in terms of retention.

$$J = B \left(\frac{1}{1 - R_0} - 1 \right) \quad (3.35)$$

The solvent flux, in terms of volumetric flux and membrane permeability (L_p), can be expressed from Eq.(3.25),

$$J = L_p (\Delta P - \Delta \pi) \quad (3.36)$$

Combining the above two equations, the observed retention can be expressed in terms of operating pressure.

$$R_0 = \frac{L_p (\Delta P - \Delta \pi)}{L_p (\Delta P - \Delta \pi) + B} \quad (3.37)$$

For high values of ΔP , R_0 approaches to one. ($R_0 \rightarrow 1.0$). Physically, as ΔP increases, solvent flux will increase due to increase in driving force. So, solute becomes diluted and permeate concentration becomes extremely small and observed retention tends to 1.

3.11.1 Solution-diffusion imperfection model

In case of solution diffusion imperfection model, the solution diffusion model is modified to incorporate the convective effects, i.e., the effects due to pressure drop across the membrane. Therefore, the solute and solvent flux through the membrane are written as,

$$N_2 = k_1 (\Delta P - \Delta \pi) + k_2 \Delta P \quad (3.38)$$

$$N_1 = k_3 (C_1' - C_1'') + k_4 \Delta P \quad (3.39)$$

3.12 Concept of concentration polarization and membrane fouling

3.12.1 Concentration polarization

Accumulation of solute particles as shown in Fig. 3.11 over the membrane surface is defined as concentration polarization. It has the following effects

- (i) Increase in osmotic pressure of the solution.
- (ii) Formation of gel over the membrane surface.
- (iii) Increases the viscosity of the solution.
- (iv) Solute enters into the pores and pores are blocked partially or completely.

First phenomena decrease in driving force. Second and third increases the resistance against flux. Fourth decreases the membrane permeability. All these effects lead to decrease in permeate flux.

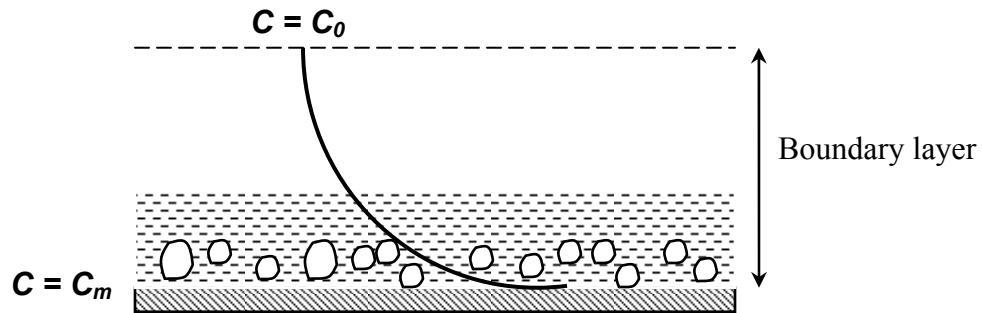


Fig. 3.11: Schematic of concentration polarization

Concentration polarization cannot be avoided, it can only be minimized.

3.12.2 Fouling of membrane:

Fouling of membrane is of two types reversible and irreversible.

Reversible fouling:

It can be washed away by adopting an appropriate cleaning protocol, like membrane washing. After cleaning, membrane permeability is restored. Concentration polarization is reversible fouling.

Irreversible fouling:

In this case, membrane pores are blocked permanently and they cannot be removed, even after proper washing. Permeability is lost permanently.

3.13 Film theory

It must be clear by now that in any membrane separation process, there exists a concentration boundary layer between the bulk of the solution and the membrane surface,

that is termed as concentration polarization as discussed in the preceding section. Film theory is used to quantify this concentration polarization or expresses the permeate flux in terms of solute concentration at the membrane surface, bulk and the permeate stream. At the membrane surface, three solute fluxes can appear. Convective flux towards the membrane ($J C$); diffusive flux away from the membrane ($-D \frac{dC}{dy}$) and convective flux away from the membrane ($J C_p$). A solute mass balance at the steady state results,

$$J(C - C_p) + D \frac{dC}{dy} = 0 \quad (3.40)$$

The main assumption in film theory is consideration of constant thickness or film of the mass transfer boundary layer. The above equation must satisfy the conditions at $y=0$ (at the membrane surface), $C=C_m$. At the edge of mass transfer boundary layer, i.e., at $y=\delta$, $C=C_0$. The solution of Eq.(3.40) is given as,

$$\frac{C_m - C_p}{C_0 - C_p} = \exp\left(\frac{J}{k}\right) \quad (3.41)$$

In the above equation, k is mass transfer coefficient and is expressed as $k = D / \delta$.

Mass transfer coefficient

We can find out the mass transfer coefficient (k), from the appropriate Sherwood number relation. Leveque relation is valid for the laminar flow through a conduit.

For tube,

$$Sh = \frac{kd}{D} = 1.62 \left(Re Sc \frac{d}{l} \right)^{\frac{1}{3}} \quad \text{for } Re < 2100 \quad (3.42)$$

$$\text{Where, } Re = \frac{\rho u_0 d}{\mu}; \quad Sc = \frac{\mu}{\rho D}$$

For flow through rectangular conduit, (3.43)

$$Sh = \frac{kd_e}{D} = 1.85 \left(Re Sc \frac{d_e}{l} \right)^{\frac{1}{3}} \quad \text{for } Re < 2100$$

$$\text{Where, } Re = \frac{\rho u_0 d_e}{\mu}; \quad Sc = \frac{\mu}{\rho D}$$

For turbulent flow, Dittus – Boelter relation is used.

$$Sh = 0.023 (Re)^{0.8} (Sc)^{0.33} \quad (3.44)$$

In case of stirred cell,

$$Sh = \frac{kr}{D} = 0.285 (Re)^{0.55} (Sc)^{0.33} \quad (3.45a)$$

In the above relation, Reynolds number is defined on stirrer speed (ω) in rad/s as,

$Re = \frac{\rho \omega r^2}{\mu}$. The above relation is valid when $Re < 32000$. For $Re > 32,000$, the following

relation is used.

$$Sh = \frac{kr}{D} = 0.0443 (Re)^{0.8} (Sc)^{0.33} \quad (3.45b)$$

In the above equation, r is the radius of the stirred cell.

3.14 Cross flow filtration

It may be noted here that the concentration polarization cannot be avoided altogether. It can only be minimized. The popular way to reduce concentration polarization is imparting more turbulence in the flow channel or filtration unit. In a

stirred cell, this can easily be done by increasing stirring. For a continuous system, the feed is allowed to flow tangentially over the membrane surface and the growth of concentration boundary layer is arrested. Since the direction of feed flow is normal to the direction of the permeate flow, the system is defined as a cross flow system.

3.15 Prediction of system performance

Prediction of membrane system performance includes prediction of permeate flux (J), i.e., throughput of the process and the permeate quality (permeate concentration or observed retention).

3.15.1 Osmotic pressure model

For membrane separation systems, where, osmotic pressure plays important and limiting role, osmotic pressure model is used to predict the system performance. Eq. (3.36) represents the flux as a function of operating pressure and osmotic pressure difference across the membrane. The osmotic pressure across the membrane is expressed as,

$$\Delta\pi = \pi_m - \pi_p \quad (3.46)$$

Using the osmotic pressure relation for concentrated solution Eq.(3.13c), Eq.(3.46) can be expressed as,

$$\Delta\pi = B_1(C_m - C_p) + B_2(C_m^2 - C_p^2) + B_3(C_m^3 - C_p^3) \quad (3.47)$$

Since real retention is constant for a membrane – solute system, using Eq.(3.3), permeate concentration can be expressed in terms of membrane surface concentration as,

$$C_p = C_m(1 - R_r) \quad (3.48)$$

Combining Eqs.(3.47) and (3.48), the osmotic pressure difference can be expressed in terms of C_m only.

$$\Delta\pi = B_1 C_m R_r + B_2 C_m^2 [1 - (1 - R_r)^2] + B_3 C_m^3 [1 - (1 - R_r)^3] \quad (3.49)$$

Eq.(3.41) can also be expressed in terms of C_m only as,

$$J = k \ln \left(\frac{C_m R_r}{C_0 - C_m (1 - R_r)} \right) \quad (3.50)$$

Therefore, Eqs. (3.36) and (3.50) can be solved simultaneously with two unknowns J and C_m . An iterative algorithm like Newton-Raphson technique may be used. Once C_m is determined, the permeate concentration is calculated from Eq.(3.48).

It may be mentioned that osmotic pressure model can be used for reverse osmosis, nanofiltration and some of the ultrafiltration processes for prediction of system performance.

Some simplified cases for osmotic pressure $\pi = bC$:

- (i) No concentration polarization, $C_m = C_0$

$$e^{\frac{J}{k}} = 1 \quad (3.51)$$

Thus the permeate flux becomes from Eq.(3.36),

$$J = L_p [\Delta P - b R_r C_0] \quad (3.52)$$

- (ii) Low polarization: $J/k \ll 1$

$$e^{\frac{J}{k}} = 1 + \frac{J}{k} + \dots \quad (3.53)$$

Combining Eqs.(3.53), (3.50) and (3.36), the following expression of permeate flux is resulted.

$$J = L_p \left[\frac{\Delta P - bR_r C_0 \left(1 + \frac{J}{k}\right)}{R_r + (1 - R_r) \left(1 + \frac{J}{k}\right)} \right] \quad (3.54)$$

The above solution results into a quadratic in J and can be solved, explicitly.

- (iii) Low polarization and $C_p=0$ i.e. perfectly rejecting membrane.

$$J = L_p \left[\Delta P - bC_0 \left(1 + \frac{J}{k}\right) \right] \quad (3.55)$$

By simplifying this we get,

$$J = \frac{L_p (\Delta P - bC_0)}{1 + \frac{bC_0 L_p}{k}} \quad (3.56)$$

$$L_p = \frac{1}{\mu R_m}$$

Here, R_m is membrane resistance. Thus, the above expression can be written as,

$$J = \frac{\Delta P - bC_0}{\mu R_m + \frac{bC_0}{k}} \quad (3.57)$$

Here, the first term in denominator represents the membrane resistance and the second term in the denominator represents the mass transfer resistance and both are in series.

Another method for determination of real retention using film theory:

This is another experimental method and is known as velocity variation technique.

Recall the film theory equation as,

$$\frac{C_m - C_p}{C_0 - C_p} = \exp\left(\frac{J}{k}\right) \quad (3.58)$$

Using the definition of real retention, $R_r = 1 - \frac{C_p}{C_m}$, one can write $C_p = C_m(1 - R_r)$.

Using the definition of observed retention, $R_o = 1 - \frac{C_p}{C_o}$, one can write, $C_p = C_o(1 - R_o)$.

Thus, C_m and C_p in Eq.(3.58) can be replaced and that equation can be expressed as,

$$\frac{\frac{C_p}{1 - R_r} - C_p}{\frac{C_p}{1 - R_o} - C_p} = e^{\frac{J}{k}} \quad (3.59)$$

The above expression can be simplified as,

$$R_r = \frac{R_o e^{\frac{J}{k}}}{R_o e^{\frac{J}{k}} + (1 - R_o)} \quad (3.60)$$

The above equation can be rearranged as,

$$\ln\left(\frac{R_o}{1 - R_o}\right) = \ln\left(\frac{R_r}{1 - R_r}\right) - \frac{J}{k} \quad (3.61)$$

Now, at various operating conditions, experiments are conducted. The corresponding steady state values of the permeate flux and observed retention are noted. A plot of

$\ln\left(\frac{R_o}{1 - R_o}\right)$ versus $\frac{J}{k}$ would be a straight line, as shown in Fig. 3.12. From the intercept

of the plot, the value of real retention, R_r is estimated.

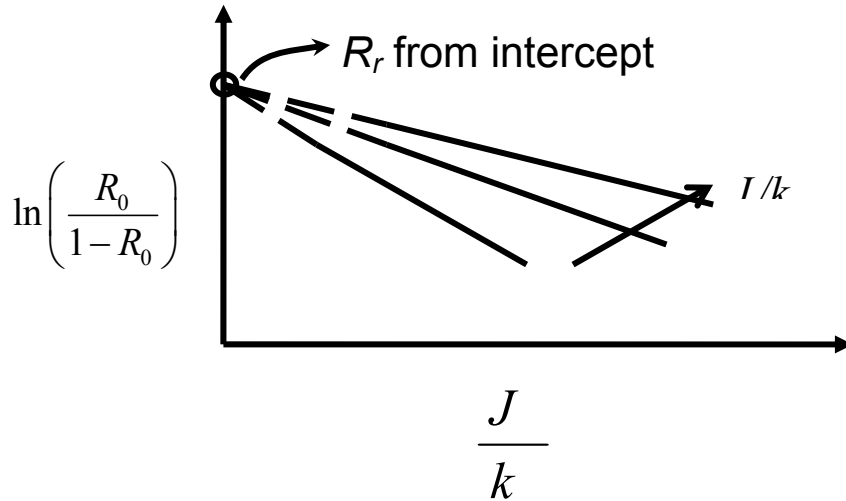


Fig. 3.12: Schematic of velocity variation technique

3.15.2 Solution diffusion model for RO/NF:

It can be identified that the concept of real retention is nothing but a partition coefficient between the solute concentration in the permeate and that at the membrane surface. Hence for a more realistic situation, the solute flux through the membrane is considered using solution diffusion model described earlier. The osmotic pressure is considered here as linear with concentration as occurs generally in case of salt solution, $\pi = aC$. The starting equations are osmotic pressure equation Eq.(3.36) and the film theory equation, Eq.(3.41). The osmotic pressure model can be written by inserting the expression of the osmotic pressure difference,

$$J = J^0 \left[1 - \alpha (C_m - C_p) \right] \quad (3.62)$$

Where, $\alpha = \frac{a}{\Delta P}$, $J^0 = L_p \Delta P$ is the pure water flux. The above equation can be equated with the film theory equation and the following equation is resulted.

$$J^0 \left[1 - \alpha (C_m - C_p) \right] = k \ln \frac{C_m - C_p}{C_0 - C_p} \quad (3.63)$$

From the solution-diffusion model, the solute flux is written as,

$$J C_p = B (C_m - C_p) \quad (3.64)$$

Combining Eqs. (3.62) and (3.64), the following equation is obtained.

$$J^0 \left[1 - \alpha (C_m - C_p) \right] = B \left(\frac{C_m - C_p}{C_p} \right) \quad (3.65)$$

The above equation can be simplified as,

$$1 - \alpha C_m + \alpha C_p = \beta \frac{C_m - C_p}{C_p} \quad (3.66)$$

Where, $\beta = \frac{B}{v_w^0}$. From above equation, the membrane surface concentration is obtained

as,

$$C_m = C_p \left[1 + \frac{1}{\beta + \alpha C_p} \right] \quad (3.67)$$

Put C_m from above equation in Eq.(3.63) we get,

$$\frac{\beta v_w^0}{\alpha C_p + \beta} - k \ln \left[\frac{C_p}{(\alpha C_p + \beta)(C_0 - C_p)} \right] = 0 \quad (3.68)$$

Again, a trail and error solution for C_p is sought using some standard iterative technique.

3.15.3 Kedem-Katchalsky equation for RO/NF/UF:

Another variant of osmotic pressure model is Kedem-Katchalsky equation. In this case, the imperfect retention of the solutes by the membrane is incorporated by a reflection coefficient in the expression of permeate flux.

$$J = L_p (\Delta P - \sigma \Delta \pi); \quad (3.69)$$

σ = Reflection coefficient. Incorporating the expression of osmotic pressure in the above expression leads to the following expression of flux.

$$J = L_p [\Delta P - a\sigma(C_m - C_p)] \quad (3.70)$$

From the film theory equation, the membrane surface concentration can be expressed as,

$$C_m = C_p + (C_0 - C_p) e^{\frac{J}{k}} \quad (3.71)$$

Combining Eqs. (3.70) and (3.71), the following equation is resulted

$$J = L_p \left[\Delta P - a\sigma \left\{ (C_0 - C_p) e^{\frac{J}{k}} \right\} \right] \quad (3.72)$$

The permeate concentration, C_p can be expressed in terms of C_m by either using the definition of real retention or solution diffusion model, Eq.(3.64). After that, Eq.(3.72) has to be solved by adopting some iterative scheme.

3.15.4 Modified solution diffusion model for RO/NF/UF:

In this case, the solute transport through the membrane is modified by incorporating the convective transport of the solutes through the pores, in addition to the diffusive transport. Thus, this model is more applicable for more porous membrane. The solute flux is written as,

$$JC_p = \beta(C_m - C_p) + (1 - \sigma)JC_{avg} \quad (3.73)$$

Where,

$$C_{avg} = \frac{C_m - C_p}{\ln\left(\frac{C_m}{C_p}\right)}$$

By combining the equations (3.69), (3.71) and (3.73) we get,

$$C_p = \frac{\beta}{J} \left[(C_0 - C_p) e^{\frac{J}{k}} \right] + \frac{(1 - \sigma)(C_0 - C_p) e^{\frac{J}{k}}}{\ln \left[1 + \frac{C_0 - C_p}{C_p} e^{\frac{J}{k}} \right]} \quad (3.74)$$

We have 3 equations (3.69), (3.71) and (3.3) and 3 unknowns in C_m , C_p and J . We can solve the above problem iteratively, to have a system prediction.

3.16 Limitation of film theory:

The description of existence of concentration profile across the mass transfer boundary layer outside the membrane in the flow channel by film theory has certain shortcomings. These are,

- Constant thickness of mass transfer boundary layer underpredicts the permeate flux. Mass transfer boundary layer is actually developing.
- No effect of suction in Shrewood number is taken directly from Heat-mass transfer analogy.
- Physical properties are constant.

These effects are more prominent for ultrafiltration. As, for RO, permeate flux is less and the effects of suction are less prominent.

3.17 Developing mass transfer boundary layer and relevant mass transfer coefficient

Rectangular thin channel

The schematic of the flow geometry and flow pattern in a rectangular thin channel is shown in Fig. 3.13.

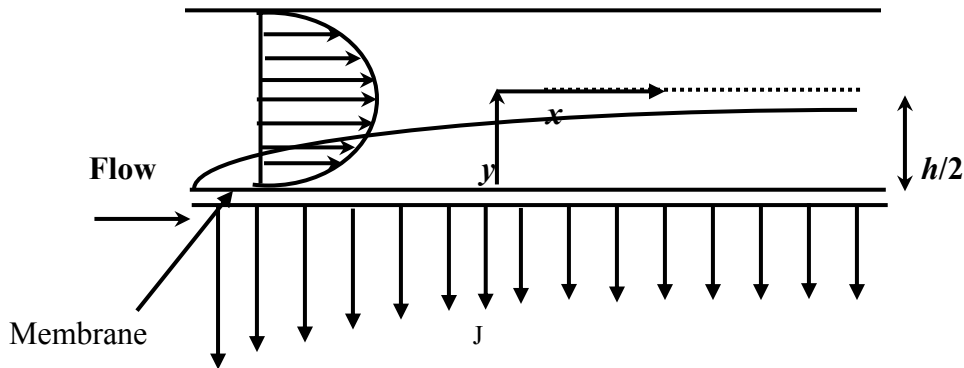


Fig. 3.13: Flow geometry in a rectangular channel

The following assumptions are made: (i) steady state, fully developed, laminar flow; (ii) permeation rate is negligible compared to cross flow rate and hence the parabolic velocity profile remains intact; (iii) there is no adsorption of solute on the membrane surface. Under these assumptions, the solute balance equation in the thin concentration boundary layer becomes,

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \quad (3.75)$$

The above equation is coupled with the momentum balance equations in x and y directions and the coupling points are the velocity components in x and y direction. This complicates the calculation procedure. To overcome this, the velocity fields can be decoupled without compromising the physical understanding of the system using the

assumption (i) and (ii). By virtue of this, it is safely assumed that the x-component velocity remains a parabolic one, given by the following expression,

$$u(y) = \frac{3}{2}u_0 \left[1 - \left(\frac{y-h}{h} \right)^2 \right] \quad (3.76)$$

Therefore, we are dealing with a problem where the hydrodynamic boundary layer is completely developed and the mass transfer boundary layer is still developing. Assuming the mass transfer boundary layer is very thin, the domain of applicability of the velocity profile given by Eq.(3.76) becomes negligible compared to the physical dimension of the channel. In other words, within thin concentration boundary layer where, Eq.(3.76) is valid, the dimension y is much less than channel half height h . This further simplifies Eq.(3.77) by opening up the square and neglecting the term y^2/h^2 . Therefore, the x-component velocity profile becomes,

$$u(y) = \frac{3u_0y}{h} \quad (3.77)$$

Within the thin concentration boundary layer, it is further assumed that the y-component velocity remains constant and is,

$$v = -J(x) \quad (3.78)$$

Inserting these velocity profiles in Eq.(3.75), the governing equation of the solute becomes,

$$\frac{3u_0y}{h} \frac{\partial c}{\partial x} - J \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \quad (3.79)$$

The above equation is a parabolic partial differential equation. We require one condition on x and two conditions on y . These are, at the channel inlet,

$$\text{At } x=0, \quad c=c_0 \quad (3.80)$$

At the edge of the concentration boundary layer, the concentration is almost the feed concentration. Therefore,

$$\text{At } y=\delta, \quad c=c_0 \quad (3.81)$$

The above boundary condition requires some discussion. Since, the thickness of the mass transfer boundary is very small compared to the channel height, therefore, concentration remains almost unchanged in the channel, beyond the boundary layer. Thus, any location in the channel cross section can be assumed to be located at infinity. Hence, the boundary condition, Eq.(3.81) can be replaced as,

$$\text{At } y = \infty, \quad c=c_0 \quad (3.82)$$

This enables Eq.(3.79) to be eligible for having a similarity solution. The other boundary condition at the membrane surface is that at the steady state all fluxes towards the membrane is zero.

$$JC + D \frac{\partial C}{\partial y} = JC_p \quad (3.83)$$

Now, let us find out the similarity parameter for this system of equations. The similarity parameter is obtained by evaluating the governing equation (Eq. 3.79) at the edge of the mass transfer boundary layer, recognizing the fact that at this location the term $\frac{\partial c}{\partial y} = 0$.

$$\frac{3u_0 y}{h} \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2} \quad (3.84)$$

Now, doing an order of magnitude analysis between $x = 0$, $y = 0$ and any x, y , we obtain,

$$\frac{3u_0 \delta}{h} \frac{\Delta c}{x} \approx D \frac{\Delta c}{\delta^2} \quad (3.85)$$

From the above equation, the spatial variation of the concentration boundary layer is obtained.

$$\delta = \left(\frac{hDx}{3u_0} \right)^{\frac{1}{3}} \quad (3.86)$$

Thus, the similarity parameter is selected as

$$\eta_1 = \frac{y}{\delta} = \left(\frac{u_0}{hD} \right)^{\frac{1}{3}} \frac{y}{x^{\frac{1}{3}}} \quad (3.87)$$

We have carried out the above analysis in the dimensional form to show that ultimately the similarity parameter turns out to be non-dimensional. Now, the partial derivatives in Eq.(3.79) can be expressed in terms of the similarity parameter.

$$\frac{\partial c}{\partial x} = \frac{dc}{d\eta_1} \left(-\frac{1}{3} \right) \left(\frac{u_0}{hD} \right)^{\frac{1}{3}} \frac{y}{x^{\frac{1}{3}}} \frac{1}{x} = \left(-\frac{\eta_1}{3x} \right) \frac{dc}{d\eta_1} \quad (3.88)$$

$$\frac{\partial c}{\partial y} = \left(\frac{u_0}{hD} \right)^{\frac{1}{3}} \frac{1}{x^{\frac{1}{3}}} \frac{dc}{d\eta_1} \quad (3.89)$$

$$\frac{\partial^2 c}{\partial y^2} = \left(\frac{u_0}{hD} \right)^{\frac{2}{3}} \frac{1}{x^{\frac{2}{3}}} \frac{d^2 c}{d\eta_1^2} \quad (3.90)$$

Substituting the above derivatives in Eq.(3.79), the following equation is obtained after simplification.

$$\left[-\eta_1^2 - J \left(\frac{hx}{u_0 D^2} \right)^{\frac{1}{3}} \right] \frac{dc}{d\eta_1} = \frac{d^2 c}{d\eta_1^2} \quad (3.91)$$

Since mass transfer boundary layer varies directly as one third power with x, the permeate flux inversely varies with x.

$$J \propto \frac{1}{x^3} \quad (3.92)$$

In other words, $Jx^3 = \text{constant}$. Therefore, the following equation can be written,

$$J \left(\frac{hx}{u_0 D^2} \right)^3 = \text{const} \tan t = A_1 \quad (3.93)$$

Therefore, Eq.(3.91) now becomes,

$$\frac{d^2 c}{d\eta_1^2} = [-\eta_1^2 - A_1] \frac{dc}{d\eta_1} \quad (3.94)$$

In the above equation, all the quantities except c is non-dimensional. Therefore, the concentration is made non-dimensional using the bulk concentration c_0 as,

$$\frac{d^2 c^*}{d\eta_1^2} = [-\eta_1^2 - A_1] \frac{dc^*}{d\eta_1} \quad (3.95)$$

The above equation can be integrated once to result,

$$\frac{dc^*}{d\eta_1} = K_3 \exp\left(-\frac{\eta_1^3}{3} - A_1 \eta_1\right) \quad (3.96)$$

One more integration leads to the solution of the concentration field.

$$c^*(\eta_1) = K_3 \int_0^{\eta_1} \exp\left(-\frac{\eta_1^3}{3} - A_1 \eta_1\right) d\eta_1 + K_4 \quad (3.97)$$

The non-dimensional boundary conditions in terms of the similarity parameter become,

$$\text{at } \eta_1 = 0, \quad \frac{dc^*}{d\eta_1} + A_1 c_m^* R_r = 0 \quad (3.98)$$

$$\text{at } \eta_1 = \infty, \quad c^* = 1 \quad (3.99)$$

From Eq.(3.97), it may be observed that the membrane surface concentration is evaluated at $\eta_1 = 0$, i.e., $c_m^* = K_4$. Applying the boundary conditions, Eqs.(3.98) and (3.99), the constants of integration can be obtained,

$$K_3 = -\frac{A_1 R_r}{1 - A_1 R_r I_1} \quad (3.100)$$

$$K_4 = c_m^* = \frac{1}{1 - A_1 R_r I_1} \quad (3.101)$$

$$\text{and, } I_1 = \int_0^{\infty} \exp\left(-\frac{\eta_1^3}{3} - A\eta_1\right) d\eta_1 \quad (3.102)$$

The non-dimensional form of the osmotic pressure relation (Eq. 3.36) in this case becomes,

$$Pe_w(x^*) = B \left(1 - \frac{\Delta\pi}{\Delta P}\right) \quad (3.103)$$

Where, $B_1 = L_p d_e \Delta P / D$ and the expression of $\Delta\pi$ in terms of dimensionless concentration remains as Eq.(3.47). By defining the equivalent diameter of the thin channel as $d_e = 4h$, Eq.(3.93) can be made dimensionless

$$Pe_w = \frac{Jd_e}{D} = 4^{\frac{1}{3}} A_1 \left(\text{Re} \text{Sc} \frac{d_e}{L}\right)^{\frac{1}{3}} x^{*\frac{-1}{3}} \quad (3.104)$$

The constant can be expressed now as,

$$A_1 = \frac{Pe_w}{4^{\frac{1}{3}} \left(\text{Re} \text{Sc} \frac{d_e}{L}\right)^{\frac{1}{3}}} x^{*\frac{1}{3}} \quad (3.105)$$

With the above formulation, it is possible to calculate the permeate flux profile along the channel length, using the following algorithm:

At a particular x^* location,

- (i) the value of c_m^* is guessed.
- (ii) Pe_w is calculated from Eq.(3.103)
- (iii) A_1 is evaluated from Eq.(3.105)
- (iv) I is evaluated from Eq.(3.102)
- (v) c_m^* is evaluated from Eq.(3.101)
- (vi) Convergence between calculated c_m^* from Eq.(3.101) with guessed valued at the step (i) is checked.
- (vii) If convergence is achieved in the previous step, calculation for the next axial location is done until the end of the channel is reached ($x^*=1$).

Length averaged permeate flux and the mass transfer coefficient

The length averaged permeate flux is obtained by integrating Eq.(3.83)

$$\overline{Pe_w} = \int_0^1 Pe_w(x^*) dx^* = 4^{\frac{1}{3}} A_1 \left(\text{Re} Sc \frac{d_e}{L} \right)^{\frac{1}{3}} \int_0^1 x^{*-3} dx^* = 2.38 A_1 \left(\text{Re} Sc \frac{d_e}{L} \right)^{\frac{1}{3}} \quad (3.106)$$

The above equation is rearranged to express the constant A_1 in terms of length averaged permeate flux.

$$A_1 = 0.42 \lambda_1 \quad (3.107)$$

Where, the suction parameter is expressed,

$$\lambda_1 = \frac{\overline{Pe_w}}{\left(\text{Re} Sc \frac{d_e}{L} \right)^{\frac{1}{3}}} \quad (3.108)$$

The definite integral I_1 is expressed in terms of the suction parameter as,

$$I_1 = \int_0^{\infty} \exp\left(-\frac{\eta_1^3}{3} - 0.42\lambda_1\eta_1\right) d\eta_1 \quad (3.109)$$

The mass transfer coefficient is defined by

$$k = \frac{-\left(\frac{\partial C}{\partial y}\right)_{y=0}}{C_m - C_0} \quad (3.110)$$

Eq.(3.110). In terms of non-dimensional concentration and similarity variable, the following expression is obtained.

$$k(C_m^* - 1) = -D \left(\frac{u_0}{hxD}\right)^{\frac{1}{3}} \left(\frac{dC^*}{d\eta_1}\right)_{\eta_1=0} \quad (3.111)$$

Substituting the values of c_m^* and $dc^*/d\eta_1$ at $\eta_1 = 0$ from Eqs.(3.96) and (3.97), the expression of mass transfer coefficient becomes,

$$k = -\frac{K_3}{K_4 - 1} \left(\frac{u_0 D^2}{hx}\right)^{\frac{1}{3}} \quad (3.112)$$

Combining Eqs.(3.100), (3.101) and (3.112) and after simplification, the following equation is obtained.

$$k(x) = \frac{1}{I_1} \left(\frac{u_0 D^2}{hx}\right)^{\frac{1}{3}} \quad (3.113)$$

Expressing the mass transfer coefficient in terms of Sherwood number (kd_e / D) as a function of dimensionless channel length, one can write,

$$Sh(x^*) = \frac{4^{\frac{1}{3}}}{I_1} \left(\text{Re Sc} \frac{d_e}{L}\right)^{\frac{1}{3}} (x^*)^{-\frac{1}{3}} \quad (3.114)$$

The average Sherwood number over length is thus obtained.

$$\overline{Sh} = \int_0^1 Sh(x^*) dx^* = \frac{2.381}{I_1} \left(\text{Re} Sc \frac{d_e}{L} \right)^{\frac{1}{3}} \quad (3.115)$$

Case 1: For no wall suction: $Pe_w=0$

The integral given by Eq.(3.109) becomes,

$$I_1 = \int_0^{\infty} \exp\left(-\frac{\eta_1^3}{3}\right) d\eta_1 = 1.288 \quad (3.116)$$

The corresponding equation for Sherwood number becomes,

$$\overline{Sh} = 1.85 \left(\text{Re} Sc \frac{d_e}{L} \right)^{\frac{1}{3}} \quad (3.117)$$

The above equation is same as the Leveque solution for flow through a thin channel.

Case 2: For wall suction: $Pe_w \neq 0$

For a typical reverse osmosis and ultrafiltration system, the suction parameter λ_1 vary from low value to upto about 10. The variation of $1/I_1$ with λ_1 is shown in Fig. 3.**, and the results are fitted in the form of a third degree polynomial and the final expression of Sherwood number becomes,

$$\overline{Sh} = 1.85 \left(\text{Re} Sc \frac{d_e}{L} \right)^{\frac{1}{3}} \left[1 + 0.32\lambda_1 + 0.02\lambda_1^2 - 8.05 \times 10^{-4} \lambda_1^3 \right] \quad (3.118)$$

Tubular Module

The detailed derivation of Sherwood number for such a case is available in literature. The corresponding equation for Sherwood number becomes,

$$\overline{Sh} = 1.62 (R_e Sc d_e / L)^{1/3} \left[1.0 + 0.37\lambda_2 + 0.03\lambda_2^2 - 1.05 \times 10^{-4} \lambda_2^3 \right] \quad (3.119)$$

Where, $\lambda_2 = \frac{Pe_w}{\left(\text{Re} Sc \frac{d}{L}\right)^{\frac{1}{3}}}$.

3.18 Faster Procedure/algorithm for calculation of length averaged permeate flux, membrane surface concentration, etc., in case of cross flow filtration

Rectangular cross flow geometry

The convective-diffusive boundary condition (known as Robin mixed boundary condition), presented by Eq.(3.83) holds good at the membrane surface ($y=0$), over the element of length Δx , between x and $x+\Delta x$ (i.e., at every x -location on the membrane surface). Now, if the element Δx is considered as the membrane length itself, then all the dependent can be represented as the length averaged values, as shown below.

$$\bar{J}(C_m - C_p) = -D \left(\frac{\partial C}{\partial y} \right)_{y=0} \quad (3.120)$$

In the above equation, v_w , c_m , c_p , etc., all are length averaged values. This equation can be combined with Eq.(3.110), definition of mass transfer coefficient as,

$$\bar{J}(C_m - C_p) = \bar{k}_L (C_m - C_0) \quad (3.121)$$

In the above equation, all the quantities are length averaged. The non-dimensional form of the above equation is,

$$\overline{Pe_w} = \frac{\overline{Sh}_L}{R_r} \left(1 - \frac{1}{C_m^*} \right) \quad (3.122)$$

Where, $\overline{Pe_w} = \frac{\bar{J}d_e}{D}$ and $\overline{Sh}_L = \frac{\bar{k}_L d_e}{D}$.

The non-dimensional form of the Darcy's law or osmotic pressure relationship (Eq. 3.36) over the membrane length becomes,

$$\overline{Pe_w} = B_1 \left(1 - \frac{\Delta\pi}{\Delta P} \right) \quad (3.123)$$

The expression of length averaged Sherwood number is derived for different geometries, flow regimes and rheologies, which are essentially functions of length averaged permeate flux ($\overline{Pe_w}$). For example, Eq.(3.118) for Newtonian fluid, laminar flow. The appropriate expression of average Sherwood number may be inserted in Eq.(3.122). Eqs. (3.122) and (3.123) are then solved by simultaneously using trial and error. Therefore, it is noted that using similarity solution method, the governing partial differential equation along with its boundary conditions and osmotic pressure relationship finally boil down to two non-linear algebraic equations to be solved simultaneously to predict the system performance. It may be emphasized that the permeate flux, membrane surface concentration, etc., obtained by this method are all length averaged quantities and profiles of these are not possible to be obtained by this method. Therefore, similarity solution method is a powerful tool to estimate quickly the behavior of the state variables of the systems.

3.19 Unstirred Batch systems:

In case of the filtration in an unstirred batch cell, we assume that the permeate volume is much less than the feed volume. Therefore, the feed volume remains almost constant leading to the unchanged concentration of the feed. The species mass balance equation within the concentration boundary layer is,

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} \quad (3.124)$$

In the above equation, it may be assumed that within thin concentration boundary layer,

$$v = -J \quad (3.125)$$

Thus, the species balance equation becomes,

$$\frac{\partial C}{\partial t} - J \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} \quad (3.126)$$

The above equation is a parabolic partial differential equation. The pertinent initial condition is

$$\text{at } t=0, C=C_0 \quad (3.127)$$

At the membrane surface, assuming no adsorption of solutes, total flux towards the membrane surface becomes zero. This results in the following boundary condition at the membrane surface,

$$\text{at } y=0, J(C_m - C_p) + D \frac{\partial C}{\partial y} = 0 \quad (3.128)$$

We require one more boundary condition on y as Eq.(3.3) is second order with respect to y . The other boundary condition will be,

$$\text{at } y=\delta, C=C_0 \quad (3.129)$$

Since, the thickness of concentration boundary layer is in the order of micron and the solute concentration is at c_0 from the edge of the boundary layer to the bulk of the feed solution, Eq.(3.129) can be written as,

$$\text{at } y=\infty, C=C_0 \quad (3.130)$$

Eq.(3.124) can be made non-dimensional, using the following non-dimensional variables, $c^* = c/c_0$ and $y^* = y/R$, where, R is the cell radius. If these two non-dimensional quantities are inserted in Eq.(3.124), the following equation is emerged.

$$\frac{R^2}{D} \frac{\partial C^*}{\partial t} - Pe_w \frac{\partial C^*}{\partial y^*} = \frac{\partial^2 C^*}{\partial y^{*2}} \quad (3.131)$$

In the above equation, Pe_w is non-dimensional permeate flux (JR/D) which is a function of time. It may be noted that using the above analysis, the non-dimensional form of time is emerged as $\tau = tD/R^2$. Therefore, the solute balance equation in non-dimensional form becomes,

$$\frac{\partial C^*}{\partial \tau} - Pe_w \frac{\partial C^*}{\partial y^*} = \frac{\partial^2 C^*}{\partial y^{*2}} \quad (3.132)$$

The non-dimensional forms of the initial and boundary conditions become,

$$\text{at } \tau = 0, \quad C^* = 1 \quad (3.133)$$

$$\text{at } y^* = 0, \quad \frac{\partial C^*}{\partial y^*} + Pe_w C_m^* R_r = 0 \quad (3.134)$$

$$\text{at } y^* = \infty, \quad C^* = 1 \quad (3.135)$$

Any governing equation is valid inside as well as on the boundary of the control volume.

Thus evaluating Eq.(3.132) at the edge of the boundary layer and recognizing the fact that

at the edge of boundary layer $\frac{\partial C^*}{\partial y^*} = 0$, the following equation is evolved:

$$\frac{\partial C^*}{\partial \tau} = \frac{\partial^2 C^*}{\partial y^{*2}} \quad (3.136)$$

Now, doing an order of magnitude analysis between $\tau = 0, y^* = 0$ and any τ, y^* , we obtain,

$$\frac{\Delta C^*}{\tau} \approx \frac{\Delta C^*}{\delta^2} \quad (3.137)$$

From the above equation, the time variation of the concentration boundary layer is obtained.

$$\delta = \sqrt{\tau} \quad (3.138)$$

Thus, the similarity parameter is obtained as

$$\eta = \frac{y}{\delta} = \frac{y}{\sqrt{\tau}} \quad (3.139)$$

Now, the partial derivatives in Eq.(3.9) can be expressed in terms of the similarity parameter,

$$\frac{\partial C^*}{\partial \tau} = \frac{dC^*}{d\eta} \frac{\partial \eta}{\partial \tau} = -\frac{1}{2} \frac{y^*}{\tau \sqrt{\tau}} \frac{dC^*}{d\eta} \quad (3.140)$$

$$\frac{\partial C^*}{\partial y^*} = \frac{dC^*}{d\eta} \frac{\partial \eta}{\partial y^*} = \frac{1}{\sqrt{\tau}} \frac{dC^*}{d\eta} \quad (3.141)$$

$$\frac{\partial^2 C^*}{\partial y^{*2}} = \frac{\partial}{\partial y^*} \left(\frac{1}{\sqrt{\tau}} \frac{dC^*}{d\eta} \right) = \frac{\partial}{\partial \eta} \left(\frac{1}{\sqrt{\tau}} \frac{dC^*}{d\eta} \right) \frac{\partial \eta}{\partial y^*} = \frac{1}{\tau} \frac{d^2 C^*}{d\eta^2} \quad (3.142)$$

Substituting these partial derivatives in Eq.(3.132), the following second order ordinary differential equation is obtained,

$$\frac{d^2 C^*}{d\eta^2} = -\left(\frac{\eta}{2} + J\sqrt{\tau} \right) \frac{dC^*}{d\eta} \quad (3.143)$$

The permeate flux is inversely proportional to the thickness of the concentration boundary layer,

$$J \propto \frac{1}{\delta} \quad (3.144)$$

Combining Eqs.(3.138) and (3.144), it can be written as,

$$J\sqrt{\tau} = \text{constant} = A \quad (3.145)$$

Thus, the governing equation becomes,

$$\frac{d^2 C^*}{d\eta^2} = -\left(\frac{\eta}{2} + A\right) \frac{dC^*}{d\eta} \quad (3.146)$$

The boundary conditions in terms of the similarity parameters now become,

$$\text{at } \eta = 0, \quad \frac{dC^*}{d\eta} + AC_m^* R_r = 0 \quad (3.147)$$

where, R_r is the real retention defined by Eq. (3.3) and

$$\text{at } \eta = \infty, \quad C^* = 1 \quad (3.148)$$

Integrating Eq.(3.146) once, the following expression is obtained,

$$\frac{dC^*}{d\eta} = K_1 \exp\left(-\frac{\eta^2}{4} - A\eta\right) \quad (3.149)$$

One more integration of the above equation results the profile of the concentration,

$$c^*(\eta) = K_1 \int_0^\eta \exp\left(-\frac{\eta^2}{4} - A\eta\right) d\eta + K_2 \quad (3.150)$$

Use of boundary condition given by Eq.(3.147) results

$$K_1 + AR_r K_2 = 0 \quad (3.151)$$

Use of boundary condition given by Eq.(3.148) results

$$K_1 I_1 + K_2 = 1 \quad (3.152)$$

where, the parameter I_1 is,

$$I_1 = \int_0^\infty \exp\left(-\frac{\eta^2}{4} - A\eta\right) \quad (3.153)$$

Solving Eqs.(3.151) and (3.152), the integration constants are obtained,

$$K_1 = -\frac{AR_r}{1 - AR_r I} \quad (3.154)$$

$$\text{and } K_2 = C_m^* = \frac{1}{1 - AR_r I} \quad (3.155)$$

It may be noted that K_2 is identical with the membrane surface concentration.

The above formulation must be coupled with the osmotic pressure model, assuming there is no solute adsorption. The non-dimensional form of Darcy's law (Eq.3.36) becomes,

$$Pe_w(\tau) = B \left(1 - \frac{\Delta\pi}{\Delta P} \right) \quad (3.156)$$

where, $B = L_p R \Delta P / D$ and the expression of $\Delta\pi$ in terms of dimensionless concentration becomes,

$$\Delta\pi = b_1 c^* + b_2 c_m^{*2} + b_3 c_m^{*3} \quad (3.157)$$

Where, $b_1 = a_1 c_0 R_r$; $b_2 = a_2 c_0^2 [1 - (1 - R_r)^2]$; $b_3 = a_3 c_0^3 [1 - (1 - R_r^3)]$.

The solution algorithm is as follows:

At a particular operating time τ ,

- (i) a value of C_m^* is guessed.
- (ii) Pe_w is calculated from Eq.(3.156).
- (iii) A is calculated from Eq.(3.145).
- (iv) Definite integral I is evaluated from Eq.(3.153) (the upper limit of this integral can be taken safely as 10).
- (v) C_m^* is calculated from Eq.(3.155).

- (vi) The values of C_m^* from steps (i) and (v) are compared and if they are sufficiently close, the iteration is stopped and convergence is achieved at that time point.
- (vii) The whole calculation is proceeded for next time point.

It may be noted that the convergence is faster if the guess value of membrane surface concentration at $\tau + d\tau$ is taken as the converged value at τ .

Mass transfer coefficient

Mass transfer coefficient is a vital design parameter for the design of membrane modules. The definition of mass transfer coefficient is,

$$k(C_m - C_0) = -D \left(\frac{\partial C}{\partial y} \right)_{y=0} \quad (3.158)$$

In terms of similarity parameter, the non-dimensional form of the above equation becomes,

$$Sh = \frac{kR}{D} = \frac{-\left(\frac{\partial C^*}{\partial y^*}\right)_{y^*=0}}{(C_m^* - 1)} = \frac{-\frac{1}{\sqrt{\tau}} \left(\frac{dC^*}{d\eta}\right)_{\eta=0}}{(C_m^* - 1)} = \frac{-\frac{K_1}{\sqrt{\tau}}}{K_2 - 1} \quad (3.159)$$

By substituting the expressions of K_1 and K_2 from Eqs.(3.154) and (3.155) in the above equation, the following equation is obtained,

$$Sh = \frac{1}{I\sqrt{\tau}} \quad (3.160)$$

3.20 Gel layer controlled filtration:

A gel can be formed over the membrane surface due to two ways,

- (i) Membrane surface concentration increases with pressure or along the length or a channel and it can exceed the solubility limit of the solutes at that temperature. Thus, the solid particles settle over the membrane surface as a gel.
- (ii) Some solutes form a thick viscous layer of constant concentration over the membrane surface from the very beginning of the filtration. For example, PVA (poly vinyl alcohol), pectin etc. It is assumed that solute concentration in the gel layer is constant. Theory for the gel layer controlling filtration is presented below for viscous cases.

(i) Steady state:

The steady state permeate flux is obtained from film theory as,

$$J = k \ln \frac{C_g}{C_0} \quad (3.161)$$

(ii) Most likely gel polarized filtration:

In most of the realistic cases, gel layer grows with time and then attain a steady state, as shown in Fig. 3.14.

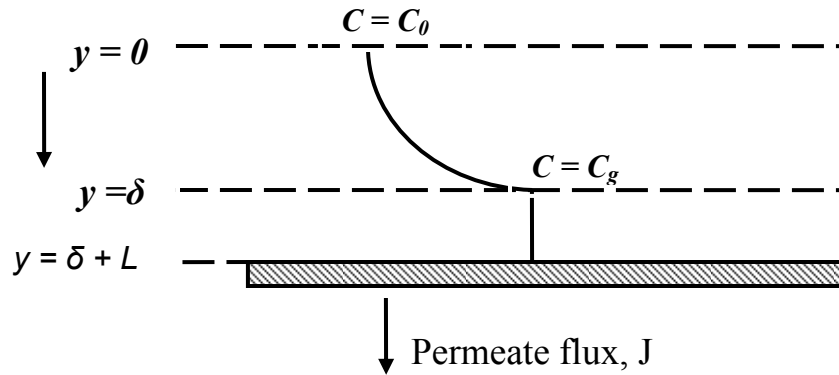


Fig. 3.14: Formation of gel layer and mass transfer boundary layer over the membrane

There exists a concentration boundary layer beyond gel layer. Where the concentration varies from C_0 to C_g . Within the gel layer, C_g remains constant. Solute balances at various domains of flow regime are presented below:

For $0 < y < \delta$

$$\text{Solute balance} = \rho_g \frac{dL}{dt} = JC - D \frac{dC}{dy} \quad (3.162)$$

The boundary conditions on concentration should be,

$$\text{At } y=0, \quad C=C_0 \quad (3.163)$$

$$\text{and at } y=\delta, \quad C=C_g \quad (3.164)$$

The above equation is a non-homogeneous ordinary differential equation. Solution of above equation is given as,

$$\rho_g \frac{dL}{dt} = J \frac{C_g - C_0 \exp\left(\frac{J}{k}\right)}{1 - \exp\left(\frac{J}{k}\right)} \quad (3.165)$$

Please note that the Eq. (3.165) at steady state is reduced to film theory equation.

The phenomenological equation of flux can be written as,

$$J = \frac{\Delta P}{\mu(R_m + R_g)} \quad (3.166)$$

Where, R_m = Membrane resistance; R_g = Gel layer resistance

Gel layer resistance can be written as,

$$R_g = \alpha(1 - \varepsilon_g)\rho_g L \quad (3.167)$$

Where, α = specific gel layer resistance; ε_g = gel porosity; ρ_g = gel layer density and L = gel layer thickness.

α can be obtained by from Kozney-carman equation as,

$$\alpha = \frac{180(1 - \varepsilon_g)}{\varepsilon_g^3 \rho_g d_p^2} \quad (3.168)$$

Eq. (3.165) to (3.168) can be solved simultaneously and numerically to obtain L and J as a function of time.

Estimation of various parameters in the above model:

Estimation of specific cake layer resistance (α):

This can be estimated from the experiments conducted in unstirred batch cell. The filtration flux for such a system is given as,

$$J = \frac{1}{A} \frac{dV}{dt} \quad (3.169)$$

Where, A = filtration area

V = cumulative volume

By combining the Eq. (3.166) and (3.169), we get

$$\begin{aligned}\frac{1}{A} \frac{dV}{dt} &= \frac{\Delta P}{\mu(R_m + R_g)} \\ &= \frac{\Delta P}{\mu R_m \left(1 + \frac{R_g}{R_m}\right)}\end{aligned}\quad (3.170)$$

Noting, $J_w^0 = \text{pure water flux} = \frac{\Delta P}{\mu R_m}$

Eq. (3.170) can be written as,

$$\frac{1}{A} \frac{dV}{dt} = \frac{J_w^0}{1 + \frac{R_g}{R_m}} \quad (3.171)$$

A solute mass balance in gel layer leads to,

$$LA(1 - \varepsilon_g) \rho_g = C_0 V \quad (3.172)$$

Combining Eq. (3.166) and (3.172) we get,

$$R_g = \frac{\alpha C_0 V}{A} \quad (3.173)$$

Inserting Eq. (3.173) in Eq. (3.170) one gets,

$$\frac{1}{A} \frac{dV}{dt} = \frac{J_w^0}{1 + \left(\frac{\alpha C_0}{AR_m}\right)V} \quad (3.174)$$

An integration of above equation between the limits 0 to t results in,

$$V + \left(\frac{\alpha C_0}{2AR_m}\right)V^2 = AJ_w^0 t \quad (3.175)$$

A rearrangement of Eq. (3.175) results,

$$\frac{t}{V} = \frac{1}{AJ_w^0} + \left(\frac{\alpha C_0}{2A^2 J_w^0 R_m}\right)V \quad (3.176)$$

A plot of t/V vs V would result in a straight line. The slope can give an estimate α as other parameters of the slope are known.

Since, an unstirred batch experiment can be conducted at various transmembrane pressure drops, α can be obtained as a function of ΔP as,

$$\alpha = \alpha_0 (\Delta P)^n \quad (3.177)$$

If $n = 0$, gel layer is incompressible

If $n < 1$, gel layer is compressible

Estimation of ε_g , d_p :

If d_p is particle molecular diameter then volume of one molecule is

$$V_0 = \frac{\pi}{6} d_p^3 \quad (3.178)$$

$$\text{Volume of 1 mole} = N_A \frac{\pi}{6} d_p^3, \quad N_A = \text{Avagadro number}$$

$$\text{Number of moles in } 1 \text{ m}^3 \text{ solution} = 10^3 \frac{C_g}{M_w}$$

Where, $C_g =$ gel layer concentration in kg/m^3

$M_w =$ molecular weight of solutes

$$\text{Thus, volume of gel in } 1 \text{ m}^3 \text{ solution is} = 10^3 \frac{C_g}{M_w} N_A \frac{\pi}{6} d_p^3$$

The gel layer porosity is thus given as,

$$\varepsilon_g = 1 - 10^3 \frac{C_g}{M_w} N_A \frac{\pi}{6} d_p^3 \quad (3.179)$$

Combining Eq. (3.168) and (3.177),

$$\alpha_0 (\Delta P)^n = \left(\frac{1 - \varepsilon_g}{\varepsilon_g^3 d_p^2 \rho_g} \right) 180 \quad (3.180)$$

Eq. (3.180) has only one variable d_p on the right hand side as ε_g can be expressed in terms of d_p by Eq. (3.179).

Eq. (3.180) can be solved using Newton-Raphson technique to obtain d_p and ε_g at various values of ΔP .

It may be mentioned that above method is for malleable particles like polymeric and polysaccharide solutes. For proteins and colloids, hard sphere diameter is considered as d_p .

Estimation of gel layer concentration (C_g):

Steady state experiments are conducted at various degrees of turbulence or mass transfer coefficient, at various feed concentration. A plot of steady state concentration vs $\ln C_0$ is done, as shown in Fig. 3.15.

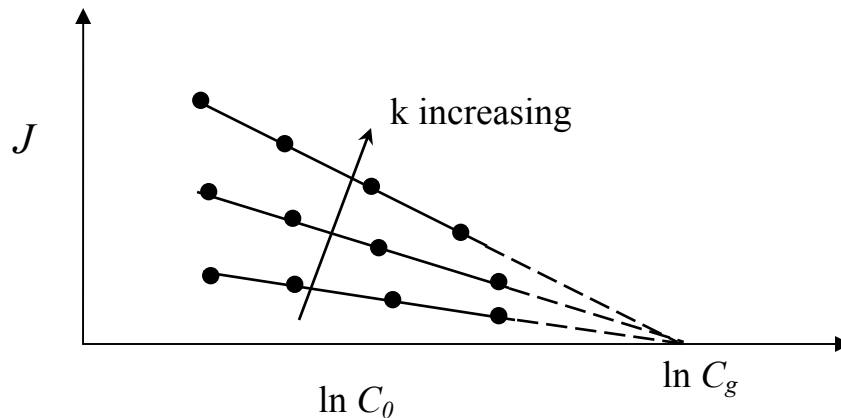


Fig. 3.15: Estimation of gel concentration

All the curves are extrapolated and they cut at $\ln C_g$ on the axis.

Thus, experimentally gel layer concentration is determined.

3.21 Resistance in series model

It is a black box approach. Various resistances are presented in series and flux is proposed as,

$$J = \frac{\Delta P}{\mu(R_m + R_g + R_{bl} + R_{irr})} \quad (3.181)$$

Where, R_m is membrane resistance, R_g is gel layer resistance, R_{bl} is boundary layer resistance and R_{irr} is irreversible membrane resistance. These resistances are related to the operating conditions.

3.22 Modeling of Membrane Modules

In this section, design equations of various modules under various flow regimes have been developed. A one-dimensional analysis is mainly considered. The development of the equations for membrane module is carried out in step by step manner, with increasing order of complexity. First, the case is considered when the permeate flux is constant. Next, the permeate flux is considered as proportional to transmembrane pressure drop and negligible osmotic pressure build up across the membrane. Finally, the inclusion of osmotic pressure is considered.

Simplified models (Newtonian fluid and laminar flow)

3.22.1: Permeate flux is constant

Spiral wound module

The flow through a spiral wound module can be reasonably approximated as the flow through a rectangular channel when the module is opened up. In this case, we consider the permeate flux is constant. This situation corresponds to the case, where, very dilute solution is filtered. The assumptions involved are: (i) the flow is steady; (ii) no concentration build up over the membrane surface, leading to almost constant permeate flux; (iii) permeation rate is negligible compared to bulk cross flow; (iv) the flow regime is laminar. The flow geometry is presented in Fig.3.16.

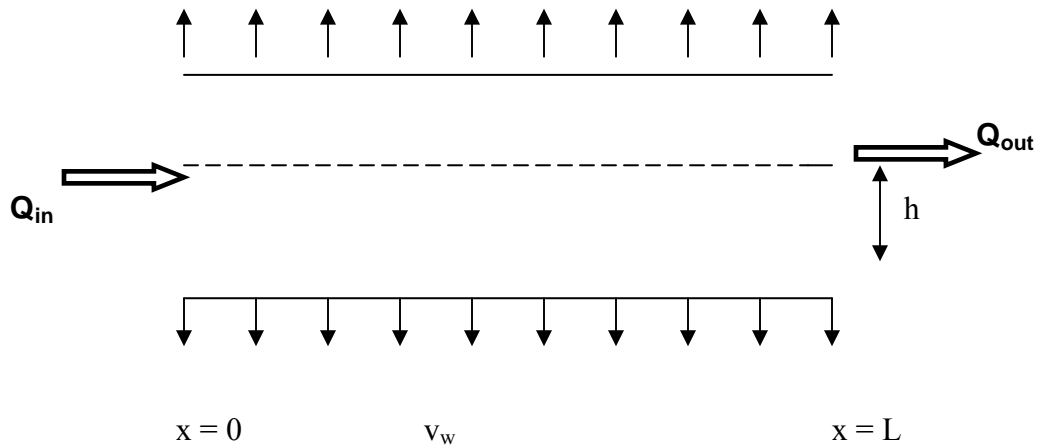


Fig. 3.16: Flow through a rectangular channel

For slit flow with impermeable wall, the volumetric flow rate at any axial x -location can be calculated by solving equations of motion and is expressed as,

$$Q = \frac{2h^3 w}{3\mu} \left(-\frac{dP}{dx} \right) \quad (3.182)$$

For impermeable channel, the volumetric flow rate is constant and therefore pressure is a linear function of axial location. At this point the definition of pressure needs to be clarified. P in Eq.(3.182) is absolute value of pressure at any axial location. The term $\frac{dP}{dx}$ represents the axial pressure drop. It may be noted here that the pressure in the permeate side is near atmospheric pressure. Therefore, transmembrane pressure difference at any axial location is defined as,

$$\Delta P(x) = P(x) - P_{atm} \quad (3.183)$$

Differentiating Eq.(3.183) with respect to x , one obtains,

$$\frac{dP}{dx} = \frac{d\Delta P}{dx} \quad (3.184)$$

Therefore, variation of pressure inside the channel along the axial direction is equivalent to variation of transmembrane pressure drop along same direction.

The volumetric flow rate (Q) is not constant for membrane channel. In case of membrane channel, permeation occurs through the walls of the channel. Therefore, the volumetric flow rate is a decreasing function of x due to loss of the materials. Now, consider, a differential element of the membrane channel. The overall material balance over the differential element leads to the governing equation of change of volumetric flow rate at the steady,

Rate of material in – Rate of material out = Rate of accumulation

$$\rho Q|_x - \rho Q|_{x+\Delta x} - \rho_p J(2w dx) = 0 \quad (3.185)$$

The factor 2 appears in Eq.(3.185), because of there is suction across the membrane wall from both sides of the channel. Assuming, the density of the feed and permeate are same, the governing equation of the flow rate in the channel is obtained.

$$-\frac{dQ}{dx} = 2wJ \quad (3.186)$$

Differentiating Eq.(3.182) with respect to x , the following equation is obtained,

$$\frac{2}{3} \frac{h^3 w}{\mu} \left(-\frac{d^2 \Delta P}{dx^2} \right) = \frac{dQ}{dx} \quad (3.187)$$

Combining Eqs.(3.186) and (3.187), the explicit expression for profile of transmembrane pressure drop is obtained.

$$\frac{d^2 \Delta P}{dx^2} = \frac{3\mu}{h^3} J \quad (3.188)$$

Since, the above equation is a second order ordinary differential equation, two boundary conditions are required to solve the same. It may be remembered that only the inlet conditions are specified for this problem. Therefore, we have to formulate two distinct boundary conditions from the inlet conditions (at $x=0$). The first one is that the transmembrane pressure drop is known at the inlet.

$$\Delta P = \Delta P_i \quad (3.189)$$

The second inlet information that is known to us is the flow rate. This is directly obtained from Eq.(3.182),

$$\frac{d\Delta P}{dx} = -\frac{3\mu}{2h^3 w} Q_i \quad (3.190)$$

It is interesting to note that this problem is a typical example where both the boundaries are specified at the same location and one is dirichlet (value of dependent variable specified) and the other one is neumann (derivative of the dependent variable is specified). Thus, this problem is truly an initial value problem. Eq.(3.188) is now solved using the boundary conditions given by Eqs.(3.189) and (3.190) and the solution is given below,

$$\Delta P_i - \Delta P(x) = \frac{3}{2} \frac{\mu}{h^3 w} Q_i x \left(1 - \frac{2Jwx}{2Q_i} \right) \quad (3.191)$$

The total pressure drop in the full channel is given as,

$$\begin{aligned} \Delta P_i - \Delta P(L) &= \frac{3}{2} \frac{\mu}{h^3 w} Q_i L \left(1 - \frac{2JwL}{2Q_i} \right) \\ &= (\Delta P)_{v_w=0} \left(1 - \frac{f}{2} \right) \end{aligned} \quad (3.192)$$

In the above equation, f is the fractional permeate recovery which is the ratio of total permeate flow rate to total inlet flow rate. Physically, f indicates the fraction of the net material entering into the system is recovered in the permeate stream. Higher be the value of f , better is the throughput of the system.

Tubular module

The above analysis is carried out for tubular module as described below.

For tubular flow with impermeable wall, the volumetric flow rate at any axial x -location can be calculated by solving equations of motion and is expressed as,

$$Q = \frac{\pi R^4}{8\mu} \left(-\frac{dP}{dx} \right) \quad (3.193)$$

Overall material balance over a differential element located between x and $x+\Delta x$, at the steady state results,

$$\rho \left(Q|_x - Q|_{x+\Delta x} \right) - \rho_p J (2\pi R \Delta x) = 0 \quad (3.194)$$

The above equation is simplified to,

$$-\frac{dQ}{dx} = 2\pi R J \quad (3.195)$$

Differentiating Eq.(3.193) with respect to x , the following expression is obtained,

$$\frac{dQ}{dx} = \frac{\pi R^4}{8\mu} \left(-\frac{d^2 \Delta P}{dx^2} \right) \quad (3.196)$$

Equating Eqs. (3.195) and (3.196), the governing equation of transmembrane pressure drop is obtained,

$$\frac{d^2 \Delta P}{dx^2} = \frac{16\mu}{R^3} J \quad (3.197)$$

Eqs.(3.189) and (3.190) present the boundary conditions for the above equation. The solution is as follows,

$$\Delta P_i - \Delta P(x) = \frac{8}{\pi} \frac{\mu}{R^4} Q_i x \left(1 - \frac{JRx}{Q_i} \right) \quad (3.198)$$

The axial pressure drop over the module length L is given as,

$$\Delta P_i - \Delta P_L = \frac{8}{\pi} \frac{\mu}{R^4} Q_i L \left(1 - \frac{f}{2\pi} \right) \quad (3.199)$$

Where, the fractional recovery of feed f is expressed as,

$$f = \frac{2\pi RLv_w}{Q_i} \quad (3.200)$$

3.22.2: Permeate flux is proportional to transmembrane pressure difference, completely retentive membrane and osmotic pressure is negligible

Spiral wound module

In this case, the concentration polarization is assumed to be negligible. This indicates, the osmotic pressure generated in the feed channel is small compared to the transmembrane pressure difference and the feed channel has uniform solute concentration at the entry level. Therefore, the permeate flux at any x-location of the module is proportional to the transmembrane pressure difference at that location.

$$J = L_p \Delta P \quad (3.201)$$

As shown earlier, the governing equation of transmembrane pressure drop is obtained by Eq.(3.188):

$$\frac{d^2 \Delta P}{dx^2} = \frac{3\mu L_p}{h^3} \Delta P \quad (3.202)$$

Using the boundary conditions presented by Eqs. (3.189) and (3.190), the profile of pressure drop is,

$$\frac{\Delta P(x)}{\Delta P_i} = \cosh(\lambda x) - \frac{3}{2} \frac{\mu Q_i}{h^3 w \lambda \Delta P_i} \sinh(\lambda x) \quad (3.203)$$

The profile of axial pressure drop becomes,

$$\Delta P_i - \Delta P(x) = \Delta P_i [1 - \cosh(\lambda x)] + \frac{3}{2} \frac{\mu Q_i}{h^3 w \lambda} \sinh(\lambda x) \quad (3.204)$$

Where, the parameter λ is given as, $\lambda = \sqrt{\frac{3\mu L_p}{h^3}}$.

The axial pressure drop over the full length of the module is obtained by substituting “x” by “L”.

$$\Delta P_i - \Delta P(L) = \Delta P_i [1 - \cosh(\lambda L)] + \frac{3}{2} \frac{\mu Q_i}{h^3 w \lambda} \sinh(\lambda L) \quad (3.205)$$

The fractional recovery of the feed over the complete module is given as,

$$f = \frac{Q_p}{Q_i} = \frac{2wL_p \int_0^L \Delta P(x) dx}{Q_i} = \frac{2wL_p \Delta P_i}{\lambda Q_i} \left[\sinh(\lambda L) - \frac{3\mu Q_i}{2h^3 w \lambda \Delta P_i} \{ \cosh(\lambda L) - 1 \} \right] \quad (3.206)$$

The profile of permeate flux is obtained from Eq.(3.201) as,

$$J(x) = L_p \Delta P_i \left[\cosh(\lambda x) - \frac{3\mu Q_i}{2h^3 w \lambda \Delta P_i} \sinh(\lambda x) \right] \quad (3.207)$$

The profile of cross flow velocity is obtained by substituting flow rate $Q = 2xhu$ in Eq.(3.186).

$$\frac{du}{dx} = -\frac{J}{h} \quad (3.208)$$

Expression of permeate flux is then substituted in Eq.(3.208) from (3.207) and integration is carried out from inlet to any location in the module,

$$\int_{u_i}^u du = \frac{L_p \Delta P_i}{h} \int_0^x \left[\frac{3\mu Q_i}{2h^3 w \lambda \Delta P_i} \sinh(\lambda x) - \cosh(\lambda x) \right] dx \quad (3.209)$$

Carrying out the above integration, the profile of cross flow velocity along the module length is obtained.

$$\frac{u(x)}{u_i} = 1 - \frac{L_p \Delta P_i}{h \lambda u_i} \left[\sinh(\lambda x) - \frac{3 \mu Q_i}{2 h^3 w \lambda \Delta P_i} \{ \cosh(\lambda x) - 1 \} \right] \quad (3.210)$$

The cross flow velocity at the channel outlet is obtained by substituting x by L in the above equation. Since, the membrane is completely retentive membrane, the species balance over the differential element results,

$$d(uC_2wh) = 0 \quad (3.211)$$

The channel dimensions remain constant, the above expression reduces to the following equation,

$$u(x)C(x) = u_i C_i \quad (3.212)$$

Combining Eq.(3.212) and (3.210), the profile of bulk concentration is obtained as,

$$\frac{C(x)}{C_i} = \frac{u_i}{u(x)} = \frac{1}{1 - \frac{L_p \Delta P_i}{h \lambda u_i} \left[\sinh(\lambda x) - \frac{3 \mu Q_i}{2 h^3 w \lambda \Delta P_i} \{ \cosh(\lambda x) - 1 \} \right]} \quad (3.213)$$

The bulk concentration at the module outlet is obtained by putting L in place of x in the above equation.

Tubular module

In case of tubular module, the cross sectional averaged velocity is obtained from Eq.(3.193),

$$u = \frac{R^2}{8\mu} \left(- \frac{d\Delta P}{dx} \right) \quad (3.214)$$

The above equation is valid assuming that the permeation velocity is so less, it does not affect magnitude of cross flow velocity, keeping its parabolic profile intact. Eq.(3.214) presents the governing equation of transmembrane pressure drop,

$$\frac{d\Delta P}{dx} = -\frac{8\mu}{R^2}u \quad (3.215)$$

Writing down the material balance over a differential element, the governing equation of cross flow velocity is obtained at steady state.

$$\rho[u - (u + du)]\pi R^2 - \rho_p J 2\pi R dx = 0 \quad (3.216)$$

Assuming the feed and permeate density do not vary much, the governing equation of cross flow is becomes,

$$\frac{du}{dx} = -\frac{2J}{R} \quad (3.217)$$

Since, the osmotic pressure is negligible compared to transmembrane pressure drop, utilizing Eq.(3.201), the following equation is resulted.

$$\frac{du}{dx} = -\frac{2L_p \Delta P}{R} \quad (3.218)$$

Differentiating Eq.(3.215) with respect to x and combining Eq.(3.217), the governing equation of pressure drop is obtained

$$\frac{d^2 \Delta P}{dx^2} = \frac{16\mu L_p}{R^3} \Delta P \quad (3.219)$$

Eqs(3.189) and (3.190) are the boundary condition of the above equation. Therefore, the profile of trans membrane pressure drop becomes,

$$\Delta P(x) = \Delta P_i \cosh(mx) - \beta \sinh(mx) \quad (3.220)$$

where, $m = \sqrt{\frac{16\mu L_p}{R^3}}$ and $\beta = \frac{8\mu u_i}{mR^2}$. The profile of axial pressure drop along the module becomes,

$$\Delta P_i - \Delta P(x) = \Delta P_i [1 - \cosh(mx)] + \beta \sinh(mx) \quad (3.221)$$

the total axial pressure drop across the module becomes,

$$\Delta P_i - \Delta P(L) = \Delta P_i [1 - \cosh(mL)] + \beta \sinh(mL) \quad (3.222)$$

The permeate flux is obtained from Eq.(3.201),

$$J(x) = L_p [\Delta P_i \cosh(mx) - \beta \sinh(mx)] \quad (3.223)$$

Substituting profile of trans membrane pressure in Eq.(3.218) and integrating between $x=0$ and any location in the module, the profile of cross section averaged velocity is obtained,

$$\frac{u}{u_i} = 1 - \frac{2L_p}{mR} [\Delta P_i \sinh(mx) + \beta \{1 - \cosh(mx)\}] \quad (3.224)$$

As formulated in Eq.(3.212), the bulk concentration of the solute at any x -location is given as,

$$\frac{C(x)}{C_i} = \frac{u_i}{u(x)} = \frac{1}{1 - \frac{2L_p}{mR} [\Delta P_i \sinh(\lambda x) - \beta \{ \cosh(\lambda x) - 1 \}]} \quad (3.225)$$

3.22.3 Osmotic pressure is not negligible and partially retentive membrane

In this section, we have developed the one dimensional design equations for membrane modules. The model is fairly detailed. The osmotic pressure and effects of concentration polarization are included. The membrane is considered as partially retentive. The effects of suction on the mass transfer coefficient are also included. The section is divided into several subsections, each elaborates calculation procedure for various types of fluids, flow regime and geometry of flow.

Newtonian fluids – Laminar flow

Spiral wound module:

In this case, the governing equation of transmembrane pressure drop is obtained from Eq.(3.182) as

$$\frac{d\Delta P}{dx} = -\frac{3\mu Q}{2h^3 w} \quad (3.226)$$

By substituting the flow rate as $Q = 2whu$ in above equation, the governing equation of pressure drop is obtained.

$$\frac{d\Delta P}{dx} = -\frac{3\mu u}{h^2} \quad (3.227)$$

The governing equation for cross flow velocity is subsequently obtained from Eq.(3.208) which is directly derived from Eq.(3.186). Osmotic pressure across the membrane is not neglected in this case. The permeate flux through the membrane is expressed by Darcy's law for the porous medium,

$$J = L_p (\Delta P - \Delta \pi) \quad (3.228)$$

Using Eqs. (3.3), (3.47) and (3.228), the permeate flux can be expressed as a function of membrane surface concentration,

$$J = L_p \left\{ \Delta P - B_1 c_m R_r - B_2 c_m^2 \left(1 - (1 - R_r)^2 \right) + B_3 c_m^3 \left(1 - (1 - R_r)^3 \right) \right\} \quad (3.229)$$

A solute mass balance in the differential element results,

$$\frac{d(uC)}{dx} = -\frac{J.C_p}{h} \quad (3.230)$$

Using Eq. (3.208), Eq. (3.230) is simplified to,

$$u \cdot \frac{dC}{dx} = \frac{J}{h} \cdot (C - C_p) \quad (3.231)$$

Where, C_p is the permeate concentration.

Thus, three ordinary differential equations are arrived at for three independent variables transmembrane pressure drop, cross flow velocity and bulk concentration.

The membrane surface concentration, c_m is related to the bulk concentration c by the definition of mass transfer coefficient at any x ,

$$k(C_m - C) = -D \left(\frac{\partial C}{\partial y} \right)_{y=0} \quad (3.232)$$

At the steady state, summation all the fluxes towards the membrane surface is zero. This leads to the following condition,

$$J(C_m - C_p) = -D \left(\frac{\partial C}{\partial y} \right)_{y=0} \quad (3.233)$$

Combining Eqs. (3.3), (3.232) and (3.233), the following expression is obtained,

$$k(C_m - C) = J C_m R_r \quad (3.234)$$

Combining Eqs.(3.229) and (3.234), the following algebraic equation for membrane surface concentration with the bulk concentration is obtained,

$$\frac{k(C_m - C)}{C_m R_r L_p} = \left[\Delta P - (A_1 C_m + A_2 C_m^2 + A_3 C_m^3) \right] \quad (3.235)$$

Where, $A_1 = B_1 R_r$; $A_2 = B_2 [I - (I - R_r)^2]$; $A_3 = B_3 [I - (I - R_r)^3]$. The mass transfer coefficient can be expressed as function of x and u as,

$$k(x) = \frac{1}{I} \left(\frac{u D^2}{h x} \right)^{1/3} \quad (3.236)$$

Where, I can be calculated by evaluating the following definite integral

$$I = \int_0^{\infty} \exp\left[-\frac{\eta^3}{3} - 0.42 \lambda \eta\right] d\eta \quad (3.237)$$

In the above equation, λ is the suction parameter and is defined as,

$$\lambda = \bar{J} \left(\frac{d_e L}{uD^2} \right)^{1/3} \quad (3.238)$$

Where, \bar{J} is the length averaged permeate flux represented as,

$$\bar{J} = \frac{1}{L} \int_0^L J(x) dx \quad (3.239)$$

For impervious conduit (no suction), the value of λ is zero and the value of I becomes, $I = 1.2879$.

Tubular module:

The governing equation of transmembrane pressure drop in terms of tube diameter is obtained from Eq.(3.215)

$$\frac{d\Delta P}{dx} = -\frac{32 \mu u}{d^2} \quad (3.240)$$

The governing equation of cross flow velocity is obtained from Eq.(3.217),

$$\frac{du}{dx} = -\frac{4J}{d} \quad (3.241)$$

and that for the solute concentration is obtained by carrying out a solute mass balance in the differential element,

$$u \frac{dC}{dx} = \frac{4J}{d} (C - C_p) \quad (3.242)$$

The expression of permeate flux remains same as Eq. (3.229). The equation relating the membrane surface concentration with the bulk concentration through mass

transfer coefficient remains as Eq.(3.234). The mass transfer coefficient for the tubular module is derived as a function of x and u as,

$$k = \frac{1}{I_1} \left(\frac{uD^2}{dx} \right)^{1/3} \quad (3.243)$$

Where, I_1 can be calculated by evaluating the following definite integral,

$$I_1 = \int_0^{\infty} \exp\left(-\frac{8\phi^3}{9} - \frac{2}{3}\lambda\phi\right) d\phi \quad (3.244)$$

λ is defined as in Eq.(3.238) replacing d_e by d . \bar{J} is the length averaged permeate flux represented as in Eq.(3.239). For impervious conduit (without suction, $\lambda=0$), the value of the integral I_1 is 0.926.

Newtonian fluids – turbulent flow

Spiral wound module:

In case of turbulent flow regime, the governing equations of cross flow velocity and solute concentration remain same as Eqs.(3.208) and (3.231). The governing equation of transmembrane pressure drop is obtained by carrying out an overall energy balance over the differential element. The energy balance equation in the differential element becomes,

$$P - (P + dP) + \frac{\rho u^2}{2} - \frac{\rho(u + du)^2}{2} + \frac{A_m J}{Q} \frac{\rho}{2} (u^2 - v_w^2) = \frac{4\rho f dx u^2}{2d_e} \quad (3.245)$$

where, A_m is the area of the permeation. In the differential element, $A_m = 2w dx$. It may be noted here that P in Eq.(3.245) is the gauge pressure and since the permeate is collected at near atmospheric pressure, P in Eq.(3.245) is equivalent to ΔP , the transmembrane pressure drop. Inserting the definition of A_m in Eq.(3.245), the following equation is obtained,

$$-d\Delta P - \rho(u du) + \frac{wJ}{Q} \rho u^2 dx - \frac{wv_w}{Q} \rho J^2 dx = \frac{4\rho fu^2}{2d_e} dx \quad (3.246)$$

The equivalent diameter is defined as $d_e \approx 4h$ for a thin channel. Using the definition of equivalent diameter, Eq.(3.246) can be simplified to the following equation,

$$\frac{d\Delta P}{dx} = -\rho u \frac{du}{dx} + \frac{wJ}{Q} \rho u^2 - \frac{wJ}{Q} \rho J^2 - \frac{\rho fu^2}{2h} \quad (3.247)$$

Replacing the flow rate, $Q=2xhu$ and $\frac{du}{dx}$ from Eq.(3.208), the governing equation of the transmembrane pressure drop across the module length is obtained as,

$$\frac{d\Delta P}{dx} = \frac{\rho}{2h} \left[3uJ - \frac{J^3}{u} - fu^2 \right] \quad (3.248)$$

The fanning friction factor, f for the turbulent flow in a smooth pipe is given by Blasius formula,

$$f = \frac{0.079}{\text{Re}^{0.25}} \quad (3.249)$$

In Eq.(3.249), Reynolds number is defined based on the equivalent diameter. The expression of permeate flux remains same as Eq.(3.229). The equation relating the membrane surface concentration with the bulk concentration through mass transfer coefficient remains as Eq.(3.232). The mass transfer coefficient for the turbulent flow can be expressed as function of x and u as,

$$k(x) = \frac{0.236D}{I} \left[\frac{\text{Re}^{1.75} \text{Sc}}{xd_e^2} \right]^{\frac{1}{3}} \quad (3.250)$$

Where, the integral I is calculated as,

$$I = \int_0^\infty \exp\left(\frac{\eta^3}{3} - 2.82\lambda\eta\right) d\eta \quad (3.251)$$

In the above equation, λ is the suction parameter and is defined as,

$$\lambda = \frac{\bar{v}_w}{D \left[\frac{\text{Re}^{1.75} \text{Sc}}{d_e^2 L} \right]^{\frac{1}{3}}} \quad (3.252)$$

Where, \bar{J} is the length averaged permeate flux defined as Eq.(3.239). For impervious conduit, the value of λ is zero and the value of I becomes 1.29.

Flow through a tubular module:

For flow through a tubular module of diameter “ d ”, Eqs.(3.241) and (3.242) present the governing equations of cross flow and solute concentration. An energy balance over the differential element like the spiral wound module, the following equation for the transmembrane pressure drop is obtained.

$$\frac{d\Delta P}{dx} = \frac{2\rho}{d} \left[3u v_w - \frac{v_w^3}{u} - fu^2 \right] \quad (3.253)$$

The mass transfer coefficient for the tubular module is derived by Minnikanti et al. and Eqs. (3.250) to (3.252) remain in the same form; only d_e is replaced by the tube diameter d .

3.23 Dialysis

In dialysis system the transportation of solute is takes place due to concentration gradient. The schematic of a batch and continuous dilayzer are shown in Figs. 3.17 a and 3.17 b.

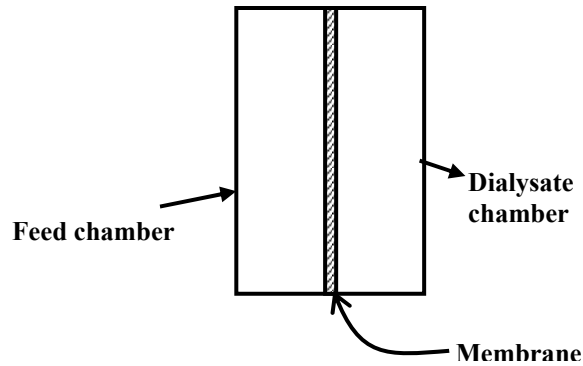


Fig. 3.17 (a): Schematic of a batch dialyzer

In a batch system there is a level difference after some time as both solute and solvent move together.

Continuous System:

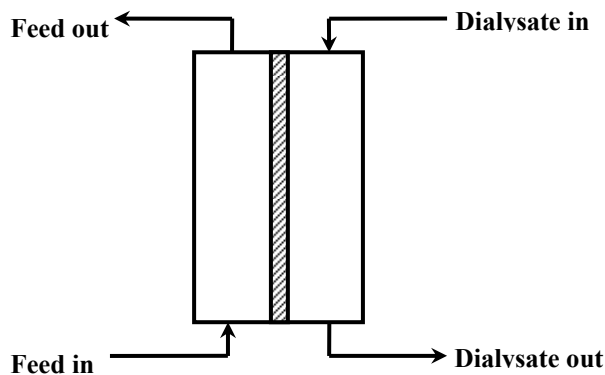


Fig. 3.17 (b): Schematic of a continuous dialyzer

Transport mechanism across the membrane:

Diffusion is the main mechanism.

N_i = Mass flux of i^{th} species

$$= D_{im} \frac{dC_{im}}{dx} = D_{im} \frac{\Delta C_{im}}{L} \quad (3.254)$$

Here, D_{im} = Diffusivity through the membrane; L = membrane thickness

$$N_i = \frac{D_{im}}{L} (C_{im}^F - C_{im}^D) \quad (3.255)$$

It is assumed that,

$$\frac{C_{im}^F}{C_i^F} = m_i = \frac{C_{im}^D}{C_i^D} \quad (3.256)$$

Where, C_i^F, C_i^D = bulk concentration of Feed and Dialysate and

m_i = distribution coefficient . Thus, the solute flux across the membrane becomes

$$N_i = \frac{D_{im}}{L} m_i (C_i^F - C_i^D) \quad (3.257)$$

Here, $m_i = 0.5$ for urea in water and regenerated cellulose and $D_{im} \approx 10^{-11} \text{ m}^2/\text{s}$.

For phenol, $m_i = 0.01$ (for a polyethylene film)

$= 17.5$ (for an Ethyl cellulose film)

Determination of D_{im} :

Diffusivity of solute through the membrane phase can be determined as,

$$D_{im} = \frac{D_{iB} \varepsilon}{\tau} F_{drag} \quad (3.258)$$

Where, D_{iB} = bulk diffusivity ; ε = membrane porosity ; τ = tortuosity

and F_{drag} = drag coefficient on the particle of radius r_i in a pore of radius r_s

$$= 1 - 2.1 \left(\frac{r_i}{r_s} \right) + 2.09 \left(\frac{r_i}{r_s} \right)^3 - 0.95 \left(\frac{r_i}{r_s} \right)^5 \quad (3.259)$$

Various resistive films of liquids across the membrane is shown in Fig. 3.18 (a) and 3.18

(b).

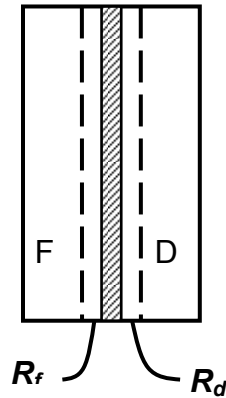


Fig. 3.18 (a): Schematic of various films across the membrane

R_f = liquid film in feed side

R_d = liquid film in dialysate side

\overline{C}_{iF} = bulk concentration of feed at steady state

C_{iF} = bulk interface concentration of membrane solution

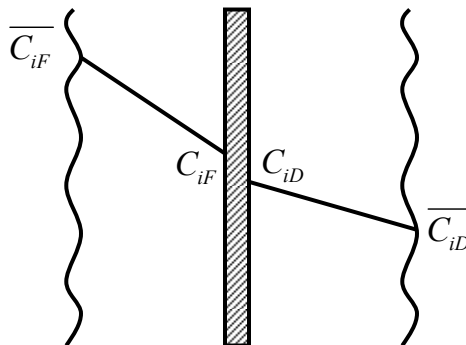


Fig. 3.18 (b): Concentration gradient across the membrane

The solute flux across the membrane in the various flow domains are presented below:

$$N_i = \frac{\overline{C}_{iF} - C_{iF}}{R_f} \quad (\text{Across liquid film in feed})$$

$$= \frac{D_{im}}{L} (C_{iF} - C_{iD}) \quad (\text{Across membrane})$$

$$= \frac{\overline{C_{iD}} - \overline{C_{iD}}}{R_d} \quad (\text{Across dialysate side}) \quad (3.260)$$

Thus, the overall solute flux becomes,

$$N_i = \frac{\overline{C_{iF}} - \overline{C_{iD}}}{R_0} \quad (3.261)$$

Where, overall resistance is given as,

$$R_0 = R_f + \frac{L}{D_{im}} + R_d \quad (3.262)$$

In terms of overall mass transfer coefficient, the overall mass transfer coefficient is expressed as,

$$\frac{1}{k_{overall}} = \frac{1}{k_f} + \frac{L}{D_{im}} + \frac{1}{k_d}$$
$$k_{overall} = \frac{1}{\frac{1}{k_f} + \frac{L}{D_{im}} + \frac{1}{k_d}} \quad (3.263)$$

The above equation is valid for every location, along the length of the dialyzer.

Calculation of net mass flow rate across the membrane in a dialysate unit:

The concentration gradient in a counter current dialyzer is presented in Fig. 3.19.

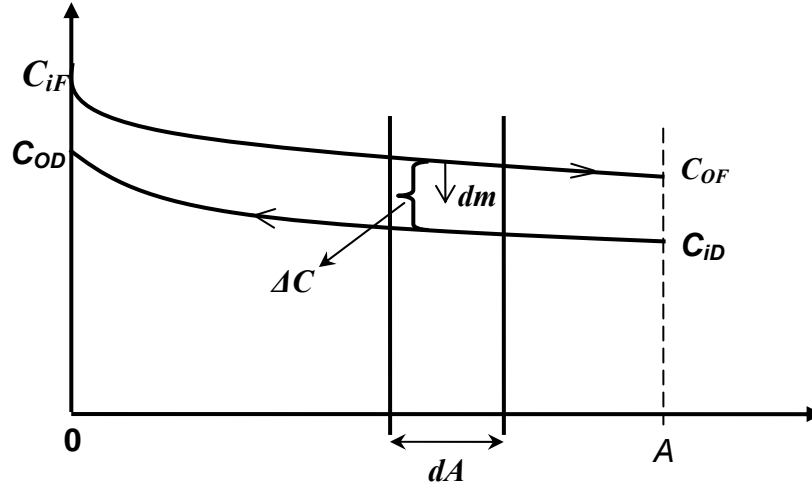


Fig. 3.19: Concentration gradient across a counter current dialyzer

dm = Mass flow rate across dA

$$= k_0 \Delta C dA \quad (3.264)$$

\dot{V}_F = volumetric flow rate of feed and \dot{V}_D = volumetric flow rate of dialysate . Mass

balance over differential element becomes,

$$d\dot{m} = -\dot{V}_F dC_F = \dot{V}_D dC_D \quad (3.265)$$

Rearrangement of above equations leads to the following,

$$dC_F = -\frac{d\dot{m}}{\dot{V}_F}; \quad dC_D = \frac{d\dot{m}}{\dot{V}_D} \quad (3.266)$$

$$\Delta C = C_F - C_D \quad (3.267)$$

$$d(\Delta C) = dC_F - dC_D \quad (3.268)$$

$$d(\Delta C) = -\left(\frac{1}{\dot{V}_F} + \frac{1}{\dot{V}_D}\right) d\dot{m} \quad (3.269)$$

From Eq. (3.264), the following equation is resulted.

$$d(\Delta C) = -\left(\frac{1}{\dot{V}_F} + \frac{1}{\dot{V}_D}\right)(k_0 dA) \Delta C \quad (3.270)$$

Integration of above equation is carried out between the inlet and exit of the channel,

$$\int_i^0 \frac{d\Delta C}{\Delta C} = -\left(\frac{1}{\dot{V}_F} + \frac{1}{\dot{V}_D}\right) \int_0^A k_0 dA \quad (3.271)$$

The final result becomes,

$$\ln \frac{\Delta C|_0}{\Delta C|_i} = -\left(\frac{1}{\dot{V}_F} + \frac{1}{\dot{V}_D}\right) \int_0^A k_0 dA \quad (3.272)$$

Integration of Eq.(3.269) results,

$$\int_i^0 d(\Delta C) = -\left(\frac{1}{\dot{V}_F} + \frac{1}{\dot{V}_D}\right) \int_0^{\dot{m}} d\dot{m}$$

$$\Delta C|_0 - \Delta C|_i = -\left(\frac{1}{\dot{V}_F} + \frac{1}{\dot{V}_D}\right) \dot{m} \quad (3.273)$$

Combining Eqs. (3.272) and (3.273), the following is the expression of mass transported across the membrane per unit time.

$$\dot{m} \text{ (Kg/s)} = k_0 A \frac{[(\Delta C)_0 - (\Delta C)_i]}{\ln \frac{(\Delta C)_0}{(\Delta C)_i}} \quad (3.274)$$

Thus, the mass transported can be expressed in terms of overall mass transfer coefficient and Log mean temperature difference.

$$\dot{m} = k_0 A (\Delta C)_{LMTD} \quad (3.275)$$

$$k_0 = \frac{1}{\frac{1}{k_f} + \frac{L}{D_{im}} + \frac{1}{k_d}} \quad (3.276)$$

Batch dialysis analysis:

A typical batch dialyzer is shown in Fig. 3.20.

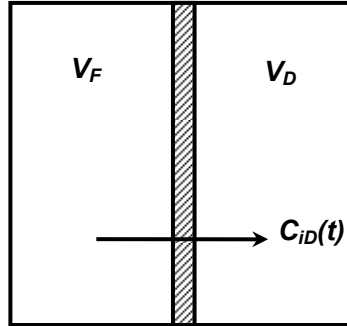


Fig. 3.20: A typical batch dialyzer

V_F, V_D = volumes of feed and dialysate chambers (fixed)

Assume the both chambers are well stirred, so that, the concentration is uniform throughout the chambers.

Mass balance in dialysate and feed side are written as,

$$\frac{d}{dt}(C_{iD}V_D) = \frac{A_m D_{im}}{L}(C_{iF} - C_{iD}) \quad (3.277)$$

$$\frac{d}{dt}(C_{iF}V_F) = -\frac{A_m D_{im}}{L}(C_{iF} - C_{iD}) \quad (3.278)$$

The initial conditions are: at $t=0$, $C_{iF} = C_{iF}^0$ and $C_{iD} = 0$.

Applying Laplace transform to equations (3.277) and (3.278), the following equations are resulted.

$$s\overline{C_{iD}} = \frac{A_m D_{im}}{LV_D}(\overline{C_{iF}} - \overline{C_{iD}}) \quad (3.279)$$

$$s\overline{C_{iF}} - C_{iF}^0 = -\frac{A_m D_{im}}{LV_F}(\overline{C_{iF}} - \overline{C_{iD}}) \quad (3.280)$$

Let us take, $\frac{A_m D_{im}}{L} = K$ and the above equations become

$$S\bar{C}_{iD} = \frac{K}{V_D} (\bar{C}_{iF} - \bar{C}_{iD}) \quad (3.281)$$

$$S\bar{C}_{iF} - C_{iF}^0 = -\frac{K}{V_F} (\bar{C}_{iF} - \bar{C}_{iD}) \quad (3.282)$$

The above two equations can be solved as,

$$\bar{C}_{iD} = \frac{\left(\frac{K}{V_D}\right) C_{iF}^0}{S^2 + SK \left(\frac{1}{V_F} + \frac{1}{V_D}\right)} \quad (3.283)$$

Considering, $a = K \left(\frac{1}{V_F} + \frac{1}{V_D}\right)$, the above equation becomes,

$$\bar{C}_{iD} = \left(\frac{K}{V_D}\right) \frac{C_{iF}^0}{a} \left(\frac{1}{S} - \frac{1}{S+a}\right) \quad (3.284)$$

Taking inverse laplace, the solution becomes,

$$\begin{aligned} C_{iD}(t) &= \left(\frac{K}{V_D}\right) \frac{C_{iF}^0}{a} (1 - e^{-at}) \\ &= C_{iF}^0 \left(\frac{V_F}{V_F + V_D}\right) \left[1 - e^{-K \left(\frac{1}{V_F} + \frac{1}{V_D}\right) t}\right] \end{aligned} \quad (3.285)$$

Now, with measured values of C_{iD} at different time, a plot of C_{iD} with time is shown in Fig. 3.21.

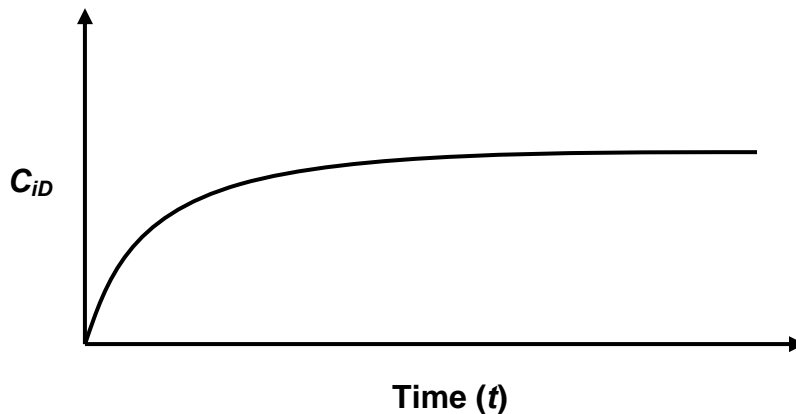


Fig. 3.21: Typical variation of C_{iD} with time in a batch dialyzer

A rearrangement of Eq.(3.285) becomes,

$$\ln\left(1 - \frac{C_{iD}}{R_1}\right) = -KR_2t \quad (3.286)$$

Thus, a plot of time vs $\ln\left(1 - \frac{C_{iD}}{R_1}\right)$, is a straight line as shown in Fig. 3.22.

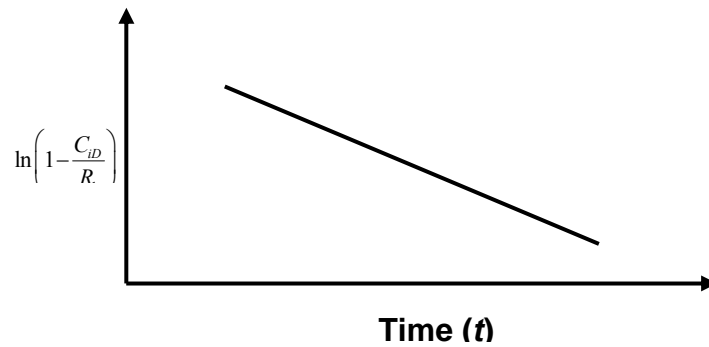


Fig. 3.22: Typical variation of time vs $\ln\left(1 - \frac{C_{iD}}{R_1}\right)$ in a batch dialyzer

We get a straight line with a negative slope of KR_2 , where, $K = \frac{A_m D_{im}}{L}$

and $R_2 = \frac{1}{V_F} + \frac{1}{V_D}$. Therefore, $\frac{D_{im}}{L}$ can be estimated.

Continuous Dialysis:

A continuous counter current dialysis system is shown in Fig. 3.23.

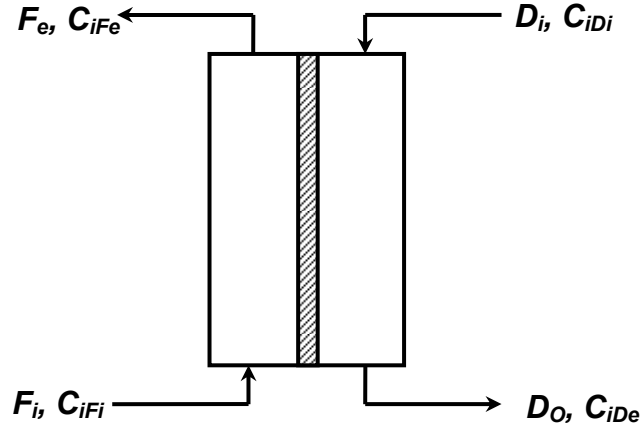


Fig. 3.23: Typical schematic of a counter current dialyzer

The assumptions involved in the analysis are listed below:

- 1) Constant feed flow rates
- 2) Dialyser performance depends on the value of film and membrane resistance
- 3) Film thickness depend upon the geometry and velocity profiles in channel

Design Equations:

Transmembrane molar flow rate (mole/sec):

$$m_i = \bar{k}_0 A_m (\Delta C_i)_{LMTD} \quad (3.287)$$

Molar Flux can also be presented as:

$$\begin{aligned} m_i &= \dot{V}_F (\bar{C}_{iFi} - \bar{C}_{iFe}) \\ &= \dot{V}_D (\bar{C}_{iDe} - \bar{C}_{iDi}) \end{aligned} \quad (3.288)$$

Using above equations, one can design membrane area for a given separation.

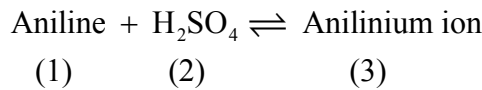
Dialyzer efficiency (η), can be defined as:

$$\eta = \frac{\text{Actual amount of solute depletion in feed}}{\text{Maximum amount separated portion in a dialyzer}}$$

$$= \frac{\dot{V}_F (\overline{C}_{iF_i} - \overline{C}_{iF_0})}{\dot{V}_F \overline{C}_{iF_i} - \dot{L}_D \overline{C}_{iD_i}} \quad (3.289)$$

Enhancement of separation in dialysis by secondary chemical reaction:

In a dialyzer chamber, select a dialyzer such that diffused components react and product ions cannot diffuse back and therefore, a maximum concentration gradient is always maintained. For example, Aniline is to be removed, using dialysate as H₂SO₄.



Component 2 is in excess such that reaction is always complete.

Mass balance:

Solute balance in the feed chamber becomes,

$$V_F \frac{dC_{1F}}{dt} = -A_m \frac{D_{im}}{L} (C_{1F} - C_{1D}) \quad (3.290)$$

The above equation is rearranged as,

$$\frac{dC_{1F}}{dt} = \frac{A_m D_{im}}{L V_F} (C_{1D} - C_{1F}) \quad (3.291)$$

Solute balance in the dialysis chamber becomes,

$$\frac{dC_{1D}}{dt} = \frac{A_m D_{im}}{L V_D} (C_{1F} - C_{1D}) - \frac{dC_{3D}}{dt} \quad (3.292)$$

Considering $\frac{A_m D_{im}}{L} = K$, the above equations become,

$$\frac{dC_{1F}}{dt} = \frac{K}{V_F} (C_{1D} - C_{1F}) \quad (3.293)$$

$$\frac{dC_{3D}}{dt} + \frac{dC_{1D}}{dt} = \frac{K}{V_D}(C_{1F} - C_{1D}) \quad (3.294)$$

Initial conditions are: at $t=0$, $C_{1F} = C_{1F}^0$

$$C_{1D} = 0$$

$$C_{3D} = 0$$

At any time 't', C_{3D} is in equilibrium. So that,

$$K_{eq} = \frac{C_{3D}}{C_{1D}C_{2D}} \quad (3.295)$$

Here, C_{2D} is constant because it is in excess.

Take laplace transform to equations (3.293) and (3.294), the following equations are obtained.

$$\frac{K}{V_F}(\overline{C_{1D}} - \overline{C_{1F}}) = S\overline{C_{1F}} - C_{1F}^0 \quad (3.296)$$

$$\frac{K}{V_D}(\overline{C_{1F}} - \overline{C_{1D}}) = S\overline{C_{1D}} - C_{1D}^0 + S\overline{C_{3D}} - C_{3D}^0 \quad (3.297)$$

From above two equations, the following equation is resulted.

$$\frac{K}{V_F}\overline{C_{1D}} = \left(\frac{K}{V_F} + S\right)\left[1 + \frac{V_D}{K}(1 + C_{2D})S\right]\overline{C_{1D}} - C_{1F}^0 \quad (3.298)$$

By simplifying the above equation finally we get it as,

$$\overline{C_{1D}} = \frac{C_{1F}^0}{AS + BS^2} \quad (3.299)$$

Where, $A = \frac{V_D}{V_F}(1 + C_{2D})$; $B = \frac{V_D}{K}(1 + C_{2D})$

Laplace inverse can be taken of Eq.(3.299) to obtain the variation of C_{1D} as a function of time.

$$\overline{C_{1D}} = f(t) \quad (3.300)$$

Detailed two dimensional analysis of Dialysis:

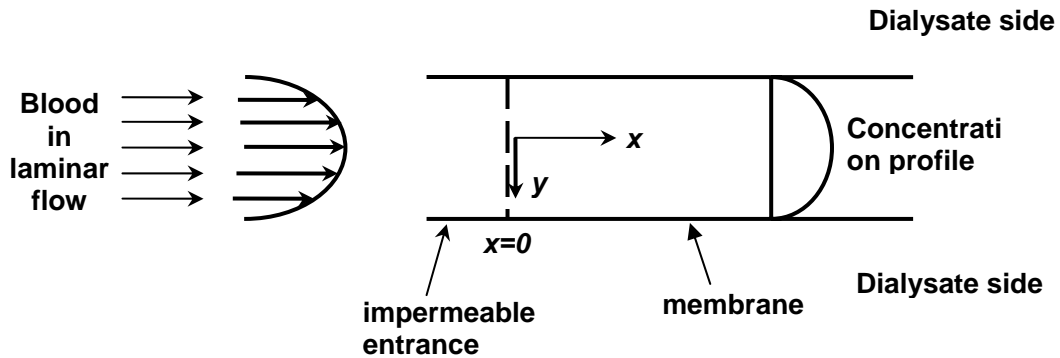


Fig. 3.24: A typical dialysis channel.

A typical dialysis channel with the coordinate system is shown in Fig. 3.24. The origin is at the center-line of channel. We consider a Newtonian-laminar flow in a rectangular channel with the velocity profile,

$$u(y) = \frac{3}{2} u_0 \left(1 - \frac{y^2}{h^2} \right) \quad (3.301)$$

y is at mid plane and h is channel half height

$$Q = 2u_0WH = \text{flow rate} .$$

The various assumptions involved are channel is very wide compared to channel height H and flow and mass transport is two dimensional

At steady state, for $-H \leq y \leq H$, the solute mass balance becomes,

$$u \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial y^2} \quad (3.302)$$

$$\text{At } x = 0, \quad C = C_0 \quad (3.303)$$

Symmetry at mid plane provides another boundary condition:

$$\frac{\partial C}{\partial y} = 0 \quad \text{at } y = 0 \quad (3.304)$$

at $y = h$; molar flux = PC

Where, P is membrane permeability.

- (i) Flux is positive if it is from blood to dialysate side.
- (ii) P includes a partition coefficient for species between blood and membrane phase as well as diffusivity of toxic species through the membrane.
- (iii) C is concentration of species in feed side and species on dialysate side is extremely dilute.

Therefore, the third boundary condition is

$$-D \frac{\partial C}{\partial y} = PC \quad \text{at } y = h \quad (3.305)$$

Here both terms in the above equation are positive. This is a standard eigen value problem or Sturm-Liouville problem.

We define non-dimensional forms as:

$$C^* = \frac{C}{C_0}; \quad y^* = \frac{y}{h}; \quad x^* = x \frac{D}{u_0 h^2}; \quad P^* = \frac{Ph}{D} = \text{Membrane Biot number}$$

If we substitute the above non-dimensional numbers in the above equation we get

$$\frac{3}{2} (1 - y^{*2}) \frac{\partial C^*}{\partial x^*} = \frac{\partial^2 C^*}{\partial y^{*2}} \quad (3.306)$$

Boundary conditions are:

$$C^* = 1 \quad \text{at } x^* = 0, \quad \forall y^* \quad (3.307a)$$

$$\frac{\partial C^*}{\partial y^*} = 0 \quad \text{at } y^* = 0, \quad \forall x^* \quad (3.307b)$$

$$\frac{\partial C^*}{\partial y^*} + P^* C^* = 0 \quad \text{at } y^* = 1, \quad \forall x^* \quad (3.307c)$$

Analytical solution of the above equation is:

$$C^* = \sum_{m=1}^{\infty} A_m \exp\left(-\frac{2}{3} \lambda_m^2 x^*\right) \sum_{n=0}^{\infty} a_{nm} y^{*n} \quad (3.308)$$

It is a series solution where, eigen values = λ_m .

Rate of removal of pollutants is given as,

$$M = 2u_0 h W (C_0 - C_{cm}) \quad (\text{in Kg/s}) \quad (3.309)$$

Here, C_{cm} = cup-mixing concentration and is given as,

$$C_{cm} = \frac{\int_0^H \frac{3}{2} u_0 \left(1 - \frac{y^2}{h^2}\right) C(x, y) dy}{\int_0^H \frac{3}{2} u_0 \left(1 - \frac{y^2}{h^2}\right) dy} \quad (3.310)$$

The non-dimensional cup-mixing concentration becomes,

$$\begin{aligned} C_{cm}^* &= \frac{C_{cm}}{C_0} \\ &= 3 \left[\sum_{m=1}^{\infty} A_m \exp\left(-\frac{2\lambda_m^2 x^*}{3}\right) \sum_{n=0}^{\infty} \frac{a_{nm}}{(n+1)(n+3)} \right] \end{aligned} \quad (3.310)$$

Here eigen values (λ_m) are roots of polynomial of the form,

$$0 = P^* - \left(\frac{2}{3} + \frac{5}{12} P^*\right) \lambda_m^2 + \left(\frac{1}{20} + \frac{1}{45} P^*\right) \lambda_m^4 \quad (3.311)$$

Here, $a_{0m} = 1$; $a_{1m} = 0$; $a_{2m} = -\frac{\lambda_m^2}{2}$; $a_{3m} = 0$

$$a_{4m} = \frac{\lambda_m^2 (2 + \lambda_m^2)}{24}; \quad a_{5m} = 0; \quad a_{6m} = -\frac{\lambda_m^4}{720} (14 + \lambda_m^2); \quad a_{7m} = 0$$

$$A_m = \frac{\sum_{n=0}^{\infty} \frac{a_{nm}}{(n+1)(n+3)}}{\sum_{n=0}^{\infty} \sum_{p=0}^{p=n} \frac{a_{pm} a_{(n-p)m}}{(n+1)(n+3)}}$$

Simplifications:

Exponential terms decay rapidly and so, use first eigen value,

$$\lambda_1^2 = \frac{P^*}{\frac{2}{3} + \frac{5}{12}P^*} \quad (3.312)$$

and consider first term of series. A typical plot of cupmixing concentration with axial distance according to Eq.(3.310) is shown in Fig. 3.25.

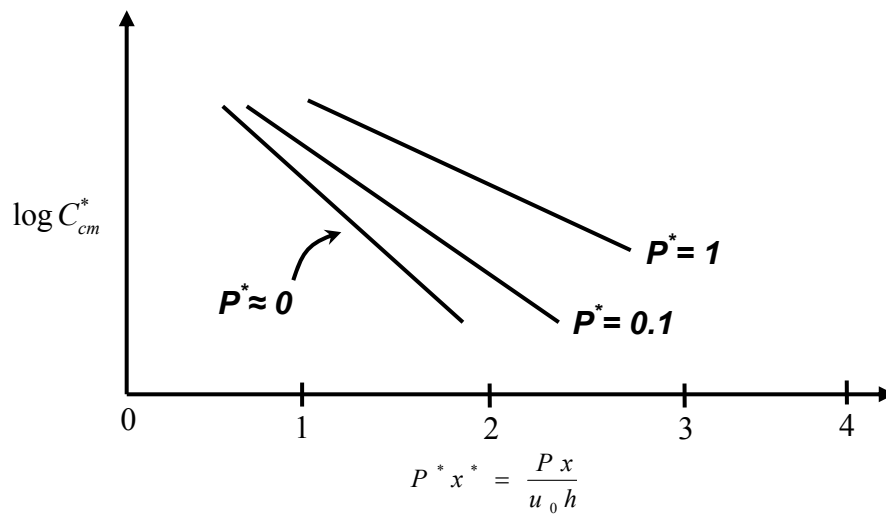


Fig. 3.25: Variation of cupmixing concentration with axial distance

Simplistic approach:

Take the flow as plug flow. This can be realized at higher flow rate of blood in the feed chamber. Therefore, the assumptions are:

1. Plug flow
2. dialysate is dilute
3. steady state

The solute mass balance in the feed chamber is given as,

$$u_0 \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial y^2} \quad (3.313)$$

Take, $C^* = \frac{C}{C_0}$; $y^* = \frac{y}{h}$, $x^* = x/L$, the above equation is made non-dimensional.

$$A \frac{\partial C^*}{\partial x^*} = \frac{\partial^2 C^*}{\partial y^{*2}} \quad (3.314)$$

Where, $A = \frac{u_0 h^2}{DL} = \frac{1}{4} \text{ReSc} \frac{d_e}{L}$.

The nondimensional boundary conditions become,

$$\text{At } y^* = 0; \quad \frac{\partial C^*}{\partial y^*} = 0 \quad (3.315a)$$

$$\text{At } y = h; \quad D \frac{\partial C}{\partial y} + PC = 0 \quad (3.315b)$$

$$\text{At } y^* = 1; \quad \frac{\partial C^*}{\partial y^*} + P_{em} C^* = 0 \quad (3.315c)$$

$$\text{Where, } P_{em} = \frac{Ph}{D}$$

$$\text{At } x^* = 0; \quad C^* = 1 \quad (3.315d)$$

Using a separation of variable type solution, $C^* = X(x^*) Y(y^*)$

$$\frac{A}{X} \frac{dX}{dx^*} = \frac{1}{Y} \frac{d^2 Y}{dy^{*2}} = -\lambda_n^2 \quad (3.316)$$

$$\text{Therefore, the X varying part is } \frac{dX}{X} = -\frac{\lambda_n^2}{A} dx^* \quad (3.317)$$

$$\text{The solution is } X = c_1 \exp\left(-\frac{\lambda_n^2 x^*}{A}\right) \quad (3.318)$$

$$\text{The y-varying part is, } \frac{d^2 Y}{dy^{*2}} + \lambda_n^2 Y = 0 \quad (3.319)$$

The solution is
$$Y = c_3 \sin(\lambda_n y^*) + c_4 \cos(\lambda_n y^*) \quad (3.320)$$

Boundary conditions are

At $y^* = 0$;
$$\frac{dY}{dy^*} = 0 \quad (3.321a)$$

At $y^* = 1$;
$$\frac{dY}{dy^*} + P_{em} Y = 0 \quad (3.321b)$$

So after applying boundary condition we get

$$Y = c_4 \cos(\lambda_n y^*) \quad (3.322)$$

And for λ_n we get,

$$\lambda_n \tan \lambda_n = P_{em} \quad (3.323)$$

The above equation is called “Transcendental equation”.

The final solution is

$$C^*(x^*, y^*) = \sum_{n=1}^{\infty} c_n \cos(\lambda_n y^*) \exp\left(-\frac{\lambda_n^2 x^*}{A}\right) \quad (3.324)$$

Initial condition is At $x^* = 0$; $C^* = 1$

$$1 = \sum_{n=0}^{\infty} c_n \cos(\lambda_n y^*) \quad (3.325)$$

The constant c_n can be evaluated using the orthogonal properties of cosine functions.

$$c_n = \frac{\int_0^1 \cos(\lambda_n y^*) dy^*}{\int_0^1 \cos^2(\lambda_n y^*) dy^*} \quad (3.326)$$

$$\text{Numerator} = \int_0^1 \cos(\lambda_n y^*) dy^* = \frac{\sin \lambda_n y^*}{\lambda_n} \Big|_0^1 = \frac{\sin \lambda_n}{\lambda_n}$$

$$\begin{aligned}\text{Denominator} &= \frac{1}{2} \int_0^1 (1 + \cos 2\lambda_n y^*) dy^* \\ &= \frac{1}{2} \left[1 + \frac{\sin 2\lambda_n}{2\lambda_n} \right]\end{aligned}$$

But from the transcendental equation we finally get

$$\text{Denominator} = \frac{1}{2} \left[\frac{P_{em}^2 + P_{em} + \lambda_n^2}{P_{em} + \lambda_n^2} \right]$$

$$\text{So, } c_n = \frac{2 \sin \lambda_n}{\lambda_n} \frac{P_{em}^2 + \lambda_n^2}{P_{em}^2 + P_{em} + \lambda_n^2} \quad (3.327)$$

$$C^*(x^*, y^*) = \sum_{n=1}^{\infty} c_n \cos(\lambda_n y^*) \exp\left(-\frac{\lambda_n^2 x^*}{A}\right)$$

Thus, the cupmixing concentration becomes,

$$C_{cm}^*(x^*) = \sum_{n=1}^{\infty} c_n \exp\left(-\frac{\lambda_n^2 x^*}{A}\right) \cos(\lambda_n)$$

$$\begin{aligned}C_{cm} &= \frac{\int V_x(y) C(x, y) dA}{\int V_x(y) dA} \\ &= \frac{\int \mu_0 C(x, y) dy \cdot \mathcal{W}}{\mu_0 \cdot \mathcal{W}h}\end{aligned}$$

$$C_{cm} = \frac{1}{h} \int_0^h C(x, y) dy$$

$$\begin{aligned}C_{cm}^* &= \int_0^1 C^*(x^*, y^*) dy^* \\ &= \sum c_n \exp\left(-\frac{\lambda_n^2 x^*}{A}\right) \int_0^1 \cos(\lambda_n y^*)\end{aligned}$$

By simplifying the above equation we get,

$$C_{cm}^*(x^*) = \sum c_n \frac{\sin \lambda_n}{\lambda_n} \exp\left(-\frac{\lambda_n^2 x^*}{A}\right) \quad (3.328)$$

$$\begin{aligned}
 M(x^*) &= \text{Rate of removal of pollutant} \\
 &= 2u_0 h W (C_0 - C_{cm}) \\
 &= 2u_0 h W C_0 \left[1 - \sum c_n \frac{\sin \lambda_n}{\lambda_n} \exp\left(-\frac{\lambda_n^2 x^*}{A}\right) \right]
 \end{aligned} \tag{3.329}$$

Mass Transfer Coefficient (MTC):

$$k(-C_{cm} + C_m) = -D \frac{\partial C}{\partial y} \Big|_{y^*=h} \tag{3.330}$$

$$k(-C_{cm}^* + C_m^*) = -\frac{D}{h} \frac{\partial C^*}{\partial y^*} \Big|_{y^*=h}$$

$$Sh = \frac{kh}{D} = \frac{-\frac{\partial C^*}{\partial y^*} \Big|_{y^*=h}}{-C_{cm}^* + C_m^*}$$

$$\frac{\partial C^*}{\partial y^*} = \sum c_n (-\lambda_n) \sin(\lambda_n y^*) \exp\left(-\frac{\lambda_n^2 x^*}{A}\right)$$

$$-\frac{\partial C^*}{\partial y^*} \Big|_{y^*=1} = \sum c_n \lambda_n \sin \lambda_n \exp\left(-\frac{\lambda_n^2 x^*}{A}\right)$$

For n=1 (first eigen value):

$$-\frac{\partial C^*}{\partial y^*} \Big|_{y^*=1} = c_1 \lambda_1 \sin \lambda_1 \exp\left(-\frac{\lambda_1^2 x^*}{A}\right)$$

$$C_{cm}^* = c_1 \frac{\sin \lambda_1}{\lambda_1} \exp\left(-\frac{\lambda_1^2 x^*}{A}\right)$$

$$C_m^*(x^*) = c_1 \exp\left(-\frac{\lambda_1^2 x^*}{A}\right) \cos \lambda_1$$

$$C_m^* - C_{cm}^* = c_1 \exp\left(-\frac{\lambda_1^2 x^*}{A}\right) \left[\cos \lambda_1 - \frac{\sin \lambda_1}{\lambda_1} \right]$$

$$Sh = \frac{\cancel{\lambda_1} \sin \lambda_1 \exp\left(\frac{\cancel{\lambda_1^2 x^*}}{A}\right)}{\cancel{\lambda_1} \exp\left(\frac{\cancel{\lambda_1^2 x^*}}{A}\right) \left[\cos \lambda_n - \frac{\sin \lambda_n}{\lambda_n} \right]}$$

$$Sh = \frac{\lambda_1 \sin \lambda_1}{\cos \lambda_n - \frac{\sin \lambda_n}{\lambda_n}} \quad (3.331)$$

Solved Problems

- The performance of an osmotic pressure controlled ultrafiltration is investigated. The pure distilled water flux is found to be $4.14 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$ at 276 kPa and $8.28 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$ at 552 kPa pressure. Under high stirring speed and at 138 kPa pressure and for 0.5 kg/m^3 solute concentration, the permeate concentration is obtained as 0.04 kg/m^3 . The osmotic pressure of the solute is given as, $\pi = 37.5 \times 10^2 c + 10c^2$, where, π is in Pa and c is in kg/m^3 .

Steady state cross flow UF of the solute is now conducted in a rectangular cell with length 1 m, equivalent diameter 1 mm, feed concentration 10 kg/m^3 , transmembrane pressure drop 345 kPa, cross flow velocity 0.5 m/s and solute diffusivity $10^{-11} \text{ m}^2/\text{s}$. Find out the permeate flux and permeate concentration. How much membrane area is required to produce 500 L/hr of filtrate under the same operating conditions with this solute? Assume validity of the film theory and the solute concentration in the permeate and the membrane surface can be related through real retention. Assume viscosity and density are those of water. Use: $Sh = 1.85(\text{ReSc}_e/D)^{1/3}$

Solution:

- Pure water flux data:

Membrane permeability (L_p) is determined,

$$J_w = L_p \Delta P$$

$$L_p = \frac{J_w}{\Delta P}$$

$$\therefore L_p = \frac{1}{2} \left[\frac{4.14 \times 10^{-6}}{276 \times 10^3} + \frac{8.28 \times 10^{-6}}{552 \times 10^3} \right] = 0.015 \times 10^{-9}$$

$$L_p = 1.5 \times 10^{-11} \frac{m}{pa.s}$$

$$R_r \approx R_0 \quad (\text{at high stirring speed})$$

$$R_r = 1 - \frac{0.04}{0.5} = 0.92$$

$$\pi = 37.5 \times 10^2 C + 10C^2 = B_1 C + B_2 C^2$$

$$L = 1 \text{ m}; \quad d_e = 10^{-3} \text{ m}; \quad C_0 = 10 \text{ kg/m}^3; \quad \Delta P = 3.45 \times 10^5 \text{ pa.}$$

$$u_0 = 0.5 \text{ m/s}; \quad D = 10^{-11} \text{ m}^2/\text{s}$$

Mass transfer coefficient:

$$Sh = \frac{k d_e}{D} = 1.85 \left(\text{Re} Sc \frac{d_e}{L} \right)^{1/3}$$

$$k = 1.85 \left(\frac{D}{d_e} \right) \left(\frac{u_0 d_e}{\nu} \cdot \frac{\nu}{D} \cdot \frac{d_e}{L} \right)^{1/3}$$

$$= 1.85 \left(\frac{D}{d_e} \right) \left(\frac{u_0 d_e^2}{DL} \right)^{1/3}$$

$$k = 1.85 \left(\frac{u_0 D^2}{d_e L} \right)^{1/3}$$

$$= 1.85 \left(\frac{0.5 \times 10^{-22}}{10^{-3} \times 1} \right)^{1/3} = 6.82 \times 10^{-7} \text{ m/s}$$

$$J = K \ln \frac{C_m - C_p}{C_0 - C_p} = L_p (\Delta P - \Delta \pi)$$

$$K \ln \frac{C_m R_r}{C_0 - C_m (1 - R_r)} = L_p (\Delta P - \Delta \pi)$$

$$\Delta\pi = B_1(C_m - C_p) + B_2(C_m^2 - C_p^2)$$

$$= B_1 C_m R_r + B_2 C_m^2 [1 - (1 - R_r)^2]$$

$$6.82 \times 10^{-7} \ln \frac{0.92 C_m}{10 - 0.08 C_m} = 1.5 \times 10^{-11} [3.45 \times 10^5 - 3450 C_m - 9.94 C_m^2]$$

$$\ln \frac{0.92 C_m}{10 - 0.08 C_m} = 7.6 [1 - 0.01 C_m - 2.88 \times 10^{-5} C_m^2]$$

C_m	11	20	50	60
LHS	0.104	0.784	2.036	2.36
RHS	6.7	6	3.25	2.25

$$C_m \approx 58 \text{ kg} / \text{m}^3$$

$$C_p = \text{Permeate concentration} = C_m (1 - R_r)$$

$$= 0.08 \times 58 = 4.64 \text{ kg} / \text{m}^3$$

$$J = K \ln \frac{C_m R_r}{C_0 - C_p} = 6.82 \times 10^{-7} \ln \frac{58 \times 0.92}{10 - 4.64}$$

$$= 1.57 \times 10^{-6} \text{ m}^3 / \text{m}^2 \cdot \text{s}$$

$$\text{Productivity} = 500 \text{ L/hr}$$

$$= \frac{500 \times 10^{-6} \times 10^3}{3600} \text{ m}^3 / \text{s} = 1.39 \times 10^{-4} \text{ m}^3 / \text{s}$$

$$\text{Area required} = \frac{1.39 \times 10^{-4}}{1.57 \times 10^{-6}} = 88.5 \text{ m}^2$$

2. Consider separation of 10 kg/m^3 concentration of a protein solution using ultrafiltration. Filtration is gel layer controlled, with gel concentration 300 kg/m^3 . Filtration takes place in a thin channel with equivalent diameter 2 mm and width 4 cm. The cross flow velocity

is 0.5 m/s and protein diffusivity is $2 \times 10^{-11} \text{ m}^2/\text{s}$. If the filtrate rate is 100 L/day, find the length required of the membrane module.

Use the following correlations to estimate mass transfer coefficient:

$$Sh = 1.86 \left(\text{Re} Sc \frac{d_e}{L} \right)^{\frac{1}{3}} \text{ for laminar flow}$$

Solution:

$$C_0 = 10 \text{ kg/m}^3; \quad C_g = 300 \text{ kg/m}^3; \quad d_e = 2 \times 10^{-3} \text{ m}; \quad W = 4 \text{ cm}$$

$$u_0 = 0.5 \text{ m/s}; \quad D = 2 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\begin{aligned} \text{Filtration rate} = 100 \text{ L/day} &= \frac{100 \times 10^3 \times 10^{-6} \text{ m}^3}{24 \times 3600 \text{ s}} \\ &= 1.157 \times 10^{-6} \text{ m}^3/\text{s} \end{aligned}$$

$$J = K \ln \frac{C_g}{C_0} = \frac{8.59 \times 10^{-7}}{L^{1/3}} \ln \frac{300}{10}$$

$$J = \frac{2.92 \times 10^{-6}}{L^{1/3}}$$

$$A = W.L = 0.04L \text{ m}^2$$

$$J.A = \text{Filtration rate}$$

$$\Rightarrow \frac{2.92 \times 10^{-6}}{L^{1/3}} \cdot 0.04L = 1.157 \times 10^{-6}$$

$$\Rightarrow L^{\frac{2}{3}} = 9.9058$$

$$L = 31 \text{ m}$$

3. Consider, a batch gel layer controlling cross flow ultrafiltration. The permeate is not recycled back. The feed is getting concentrated and the feed volume is reduced as time of operation progresses. Assume, film theory is valid in the cross flow ultrafiltration unit.

The mass transfer coefficient in the ultrafiltration unit is 2×10^{-5} m/s, initial feed concentration is 1 kg/m^3 . Effective filtration area of the membrane is 0.2 m^2 . Gel layer concentration of the solute is 500 kg/m^3 . Initial feed volume is 5 liters. Assume that in the permeate, there is no solute present and always the retentate concentration is much less than gel concentration ($c_b \ll c_g$). Find the time required concentrating the feed concentration 10 times and what is the volume remaining in the feed chamber?

Solution:

$$C_0 = 1 \text{ kg/m}^3; \quad C_g = 500 \text{ kg/m}^3; \quad K = 2 \times 10^{-5} \text{ m/s}; \quad A = 2 \text{ m}^2$$

$$V_0 = \text{initial feed volume} = 5 \text{ L.}$$

$$J = K \ln \frac{C_g}{C_b} \quad (\text{A1})$$

Overall mass balance,

$$\frac{d}{dt}(\rho V) = -JA\rho_p$$

By assuming $\rho \approx \rho_p$

$$\frac{dV}{dt} = -JA \quad (\text{A2})$$

Overall species balance,

$$\frac{d}{dt}(CV) = 0$$

$$C_0V_0 = C_bV \quad (\text{A3})$$

From equation (A2),

$$\frac{d}{dt} \left(\frac{C_0V_0}{C_b} \right) = -KA \ln \frac{C_g}{C_b}$$

$$C_0V_0 \left(\frac{1}{C_b^2} \frac{dC_b}{dt} \right) = -KA \ln \frac{C_g}{C_b}$$

$$\frac{dC_b}{dt} = \left(\frac{KA}{C_0V_0} \right) C_b^2 \ln \frac{C_g}{C_b}$$

$$\frac{dC_b}{dt} = \left(-\frac{KA}{C_0V_0} \right) C_b^2 \ln \frac{C_b}{C_g}$$

$$= \left(-\frac{KA}{C_0V_0} \right) C_b^2 \ln \left[1 - \frac{C_g - C_b}{C_g} \right]$$

$$= \left(-\frac{KA}{C_0V_0} \right) C_b^2 (-) \left[\frac{C_g - C_b}{C_g} \right]$$

$$= \left(\frac{KA}{C_0V_0} \right) \left(1 - \frac{C_b}{C_g} \right) C_b^2$$

$$= \left(\frac{KA}{C_0V_0} \right) \left(C_b^2 - \frac{C_b^3}{C_g} \right)$$

$$\frac{dC_b}{dt} = \left(\frac{KA}{C_0V_0} \right) \left(C_b^2 - \frac{C_b^3}{C_g} \right)$$

$$\frac{dC_b}{C_b^2 \left(1 - \frac{C_b}{C_g} \right)} = \left(\frac{KA}{C_0V_0} \right) dt$$

$$\because C_b \ll C_g \quad \Rightarrow 1 - \frac{C_b}{C_g} \approx 1$$

$$\int_{C_0}^{10C_0} C_b^{-2} dC_b = \left(\frac{KA}{C_0V_0} \right) t$$

$$\frac{1}{C_0} - \frac{1}{10C_0} = \frac{KA}{C_0V_0} t$$

$$t = 0.9 \left(\frac{V_0}{KA} \right)$$

$$= 0.9 \frac{5 \times 10^3 \times 10^{-6}}{2 \times 10^{-5} \times 0.2} = 1125 \text{ sec}$$

$$\approx 18.75 \text{ min}$$

$$C_0V_0 = C_bV$$

$$V = 5 \times \frac{1}{10} = 0.5 L$$

- 4: A macromolecular solution of diffusivity $D=6 \times 10^{-11} \text{ m}^2/\text{s}$ is flowing through a rectangular channel of length 1m, width 5cm, half height 1mm at a flow rate of 40L/h and transmembrane pressure drop 500kPa. Permeability of the membrane is $2.5 \times 10^{-11} \text{ N.s/m}^3$. The feed concentration of the membrane is 10 kg/m^3 and real retention $R_r=1.0$. Membrane is placed at the bottom only. $\Pi=1.5 \times 10^4 C$, Π is in Pa and C in kg/m^3 . Using the method in section 3.18, solve the problem.

Solution:

Area of cross section of channel

$$\begin{aligned} &= 2wh \\ &= 2 * 0.05 * 10^{-3} \text{ m}^2 = 10^{-4} \text{ m}^2 \end{aligned}$$

$$Q = 40L / h = 1.11 \times 10^{-5} \text{ m}^3 / \text{s}$$

$$u_o = \frac{1.11 \times 10^{-5}}{10^{-4}} \text{ m/s} = 0.11 \text{ m/s}$$

Equivalent diameter, $d_e = 4h = 4 \times 10^{-3} \text{ m}$

$$\text{Re} Sc \frac{d_e}{L} = \frac{u_o d_e}{\nu} \frac{\nu}{D} \frac{d_e}{L} = 2.93 \times 10^4$$

Osmotic pressure difference,

$$\Delta\pi = 1.5 \times 10^4 (c_m - c_p)$$

$$= 1.5 \times 10^4 c_m R_r$$

$$= 1.5 \times 10^4 c_m c_o$$

$$= 1.5 \times 10^5 c_m^*$$

$$\frac{\Delta\pi}{\Delta p} = \frac{1.5 \times 10^5}{5 \times 10^5} c_m^* = 0.3 c_m^*$$

From equation (3.123), $Pew = B_1 \left(1 - \frac{\Delta\pi}{\Delta P} \right)$

$$B_1 = \frac{L_p \Delta P d_e}{D} = \frac{2.5 \times 10^{-11} \times 5 \times 10^5 \times 4 \times 10^{-3}}{6 \times 10^{-11}} = 833.33$$

Therefore, $Pew = 833.33(1 - 0.3c_m^*)$

From equation (3.108), $\lambda_1 = \frac{\overline{Pew}}{\left(Re S_c \frac{d_e}{L} \right)^{1/3}}$

$$\lambda_1 = \frac{833.33}{(2.93 \times 10^4)^{1/3}} (1 - 0.3c_m^*)$$

Rearranging above equation, we get an expression of c_m^* with respect to suction parameter,

$$c_m^* = 3.33 - 0.123\lambda_1 \quad (A1)$$

Rearrangement of Eq(3.108) and (3.122), the following equation is obtained

$$\lambda_1 = \frac{\overline{Pew}}{\left(Re S_c \frac{d_e}{L} \right)^{1/3}} = 1.85 \left[1 + 0.32\lambda_1 + 0.02\lambda_1^2 - 8.05 \times 10^{-4} \lambda_1^3 \right] \left[1 - \frac{1}{c_m^*} \right] \quad (A2)$$

Eq(3.122) and Eq(3.123) have to be solved simultaneously.

It may be noted that, $c_m^* > 1.0$

So, from the Eq(A1),

$$\lambda_1 < 18.94$$

Combining Eq(A1) and Eq(A2) presents only non-linear equation in λ_1 ,

$$\lambda_1 = 1.85 \left[1 + 0.32\lambda_1 + 0.02\lambda_1^2 - 8.05 \times 10^{-4} \lambda_1^3 \right] \left[1 - \frac{1}{3.33 - 0.123\lambda_1} \right] \quad (A3)$$

Eq(A1), gives an idea of the guess value of λ_1 ;

$$\lambda_1 \quad \quad \quad 2 \quad 2.14 \quad 2.21 \quad 2.24$$

$$\text{RHS of Eq. (A3)} \quad 2.14 \quad 2.21 \quad 2.24 \quad 2.25$$

Therefore, $\lambda_1 = 2.24$

$$\text{So, } P_{ew} = 69.05 \text{ and } \bar{v}_w = 69.05 \times 6 \times 10^{-4} \times \frac{1}{4 \times 10^{-3}} = 1.035 \times 10^{-6} \text{ m}^3 / \text{m}^2 \cdot \text{s}$$

From Eq.(A1), $c_m^* = 3.05$

$$\text{So, } c_m = 30.5 \text{ kg/m}^3$$

Mass transfer coefficient:

$$S_{hl} = 103.1$$

$$= \frac{\bar{k}_L d_e}{D}$$

$$\text{Thus, } \bar{k}_L = 1.545 \times 10^{-6} \text{ m} / \text{s}$$

5. A mixture of two solutes, A and B is subjected to osmotic pressure controlled laminar cross flow nanofiltration in a rectangular channel at steady state. Solute A is completely and B is partially retained by the membrane. The feed mixture contains 10 ppm of A and B each. The average feed velocity in the channel is 0.3 m/s and channel geometry is 30cmx5cmx0.15cm. The membrane permeability is 2×10^{-11} Ns/m³. Real retention of the

membrane for solute B is 0.8 and the operating pressure is 300 kPa. Use stagnant film theory. Calculate the permeate flux and permeate quality. $\pi_A=6000 c_A$ and $\pi_B=6000 c_B$. Osmotic pressure is in Pa and c is in kg/m^3 . $D_A=2 \times 10^{-10} \text{m}^2/\text{s}$ and $D_B=4 \times 10^{-10} \text{m}^2/\text{s}$. Solution viscosity and density are taken to be same as those for water.

Solution:

$$C_{A0} = 10 \times 10^{-3} = 10^{-2} \text{ kg / m}^3 = C_{B0}$$

$$u_0 = 0.3 \text{ m / s}; \quad d_e \approx 4h = 4 \times \frac{0.5}{2} \times 10^{-2} \text{ m} = 3 \times 10^{-3} \text{ m}$$

$$L = 30 \text{ cm} = 0.3 \text{ m}; \quad L_p = 2 \times 10^{-11} \text{ N.s / m}^3$$

$$R_{rB} = 0.8; \quad R_{rA} = 1.0; \quad \Delta P = 300 \text{ kPa}$$

$$D_A = 2 \times 10^{-10} \text{ m}^2 / \text{s}; \quad D_B = 4 \times 10^{-10} \text{ m}^2 / \text{s}$$

$$\pi_A = 6000 C_A; \quad \pi_B = 6000 C_B$$

$$J = k_A \ln \frac{C_{mA} - C_{pA}}{C_{A0} - C_{pA}} = k_B \ln \frac{C_{mB} - C_{pB}}{C_{B0} - C_{pB}}$$

But $C_{pA} = 0$

$$\text{So, } J = k_A \ln \frac{C_{mA}}{C_{A0}} = k_B \ln \frac{C_{mB} - C_{pB}}{C_{B0} - C_{pB}}$$

$$k = 1.85 \left(\frac{u_0 D^2}{d_e L} \right)^{1/3}$$

$$k_A = 1.85 \left(\frac{0.3 \times 4 \times 10^{-20}}{3 \times 10^{-3} \times 0.3} \right)^{1/3}$$

$$= 4.387 \times 10^{-6} \text{ m / s}$$

$$k_B = 1.85 \left(\frac{0.3 \times 16 \times 10^{-20}}{3 \times 10^{-3} \times 0.3} \right)^{1/3}$$

$$= 6.96 \times 10^{-6} \text{ m / s}$$

$$4.387 \times 10^{-6} \ln \frac{C_{mA}}{10^{-2}} = 6.96 \times 10^{-6} \ln \frac{0.8 C_{mB}}{10^{-2} - 0.2 C_{mB}}$$

$$\ln(100C_{mA}) = 1.586 \ln\left(\frac{80C_{mB}}{1-20C_{mB}}\right) \quad (\text{B1})$$

$$J = L_p (\Delta P - \Delta \pi)$$

$$\begin{aligned} J &= L_p [\Delta P - 6000C_{mA} - 6000R_{rB}C_{mB}] \\ &= 2 \times 10^{-11} [3 \times 10^5 - 6000C_{mA} - 4800C_{mB}] \\ &= 6 \times 10^{-6} [1 - 0.02C_{mA} - 0.016C_{mB}] \end{aligned}$$

$$J = k_A \ln \frac{C_{mA}}{C_{A0}}$$

$$4.387 \times 10^{-6} \ln \frac{C_{mA}}{10^{-2}} = 6 \times 10^{-6} [1 - 0.02C_{mA} - 0.016C_{mB}]$$

$$\ln(100C_{mA}) = 1.37 [1 - 0.02C_{mA} - 0.016C_{mB}] \quad (\text{B2})$$

From the equation (B1),

$$\frac{80C_{mB}}{1-20C_{mB}} = \exp\left[\frac{\ln(100C_{mA})}{1.586}\right]$$

$$\frac{1-20C_{mB}}{80C_{mB}} = \exp\left[-\frac{\ln(100C_{mA})}{1.586}\right]$$

$$\frac{1}{80C_{mB}} = \frac{1}{4} + \exp\left[-\frac{\ln(100C_{mA})}{1.586}\right]$$

$$80C_{mB} = \frac{1}{0.25 + \exp\left[-\frac{\ln(100C_{mA})}{1.586}\right]}$$

$$C_{mB} = \frac{0.0125}{0.25 + \exp\left[-\frac{\ln(100C_{mA})}{1.586}\right]} \quad (\text{B3})$$

From equation (B2),

$$C_{mA} = 0.01 \exp\left[1.37(1 - 0.02C_{mA} - 0.016C_{mB})\right] \quad (\text{B4})$$

$C_{mA,guess}$	0.02	0.03	0.04
C_{mB} from B3	0.014	0.0167	0.187
C_{mA} from B4	0.039	0.039	0.039

$$C_{mA} = 0.039 \text{ kg} / \text{m}^3$$

$$C_{mB} = 0.0187 \text{ kg} / \text{m}^3$$

$$\text{In permeate} = 0.0187 \times 0.08 = 1.496 \text{ ppm}$$

$$J = 4.387 \times 10^{-6} \ln \frac{0.039}{0.01}$$

$$= 5.97 \times 10^{-6} \text{ m}^3 / \text{m}^2 \cdot \text{s}$$

6. Water is flowing through a rectangular channel of half height 1 mm and width 8 cm. The inlet flow rate is 40 L/h. Inlet transmembrane pressure of 500 kPa results in a constant permeate flux of $2 \times 10^{-5} \text{ m}^3 / \text{m}^2 \cdot \text{s}$. The length of the channel is 2m.
- Find the axial pressure drop across the module.
 - What is the transmembrane pressure drop at the module exit?
 - Find out the fractional recovery of the feed.
 - What is the flow rate at the channel exit?
 - For a fractional recovery of 0.92 what is the length of the module is required? What is the axial pressure drop and flow rate at the module exit?

Solution:

$$h=10^{-3} \text{ m}; w=0.08 \text{ m}; \Delta P_i=5 \times 10^5 \text{ N/m}^2; L=2\text{m}; v_w=2 \times 10^{-5} \text{ m}^3 / \text{m}^2 \cdot \text{s}$$

$$Q_i=40 \text{ l/h} = 1.11 \times 10^{-5} \text{ m}^3 / \text{s}.$$

- From Eq.(3.191),

$$\begin{aligned}\Delta P_{axial} &= \frac{3}{2} \frac{\mu}{h^3 w} Q_i x \left(1 - \frac{2v_w wx}{2Q_i} \right) \\ &= \frac{3 \cdot 10^{-3} \times 1.11 \times 10^{-5} \times 2}{2 \cdot (10^{-3})^3 \times 0.08} \left(1 - \frac{2 \times 10^{-5} \times 0.08 \times 2}{1.11 \times 10^{-5}} \right) \\ &= 416.25(1 - 0.29) \\ &= 296 \text{ Pa}\end{aligned}$$

(b) ΔP_L = transmembrane pressure drop at the outlet

$$= P_1 - 296 = 499.7 \text{ kPa}$$

(c) Fractional feed recovery in the permeate

$$f = \frac{2v_w wL}{Q_i} = \frac{2 \times 2 \times 10^{-5} \times 8 \times 10^{-2} \times 2}{1.11 \times 10^{-5}} = 0.576$$

(d) Flow rate at the channel exit

Differentiating Eq.(3.191) with respect to x the following expression is obtained

$$-\frac{d\Delta P}{dx} = \frac{3}{2} \frac{\mu Q_i}{h^3 w} \left(1 - \frac{2v_w wx}{2Q_i} \right)$$

Combining the above equation with respect to Eq.(3.190), the expression of cross flow rate is obtained.

$$Q = Q_i \left(1 - \frac{2v_w wx}{2Q_i} \right)$$

Substituting the values of various parameters in the above equation, at the channel exit,

i.e., at $x=L$,

$$Q = 1.11 \times 10^{-5} \left(1 - \frac{2 \times 2 \times 10^{-5} \times 0.08 \times 2}{1.11 \times 10^{-5}} \right)$$

$$= 5 \times 10^{-5} \text{ m}^3 / \text{s} = 28.5 \text{ L/h}$$

$$(e) f = 0.92 = \frac{2v_w wL}{Q_i}$$

For the same flow rate, channel width and suction rate, length required,

$$L = 0.92 \times \frac{1.11 \times 10^{-5}}{2 \times 2 \times 10^{-5} \times 0.08} = 3.19 \approx 3.2 \text{ m}$$

$$\Delta P_{axial} = \frac{3}{2} \frac{\mu}{h^3 w} Q_i x \left(1 - \frac{2v_w w x}{2Q_i} \right)$$

By putting the numbers in the above equation, axial pressure drop becomes

$$\Delta P_{axial} = 360 \text{ Pa}$$

Similarly, the new flow rate becomes, 21.6 L/h

7. In the above problem, if the half channel height of 0.5 mm. find the (a) axial pressure drop, (b) transmembrane pressure drop at the module outlet, (c) fractional recovery of the feed, and (d) flow rate at the channel outlet.

Solution:

(a) In this case, axial pressure drop will be changed.

$$\Delta P_{axial} = \frac{3}{2} \times \frac{10^{-3}}{(0.5 \times 10^{-3})^3 \times 0.08} \times 1.11 \times 10^{-5} \times 2(1 - 0.29)$$

$$= 2364.3 \text{ Pa}$$

(b) The pressure drop at the channel outlet:

$$\Delta P_L = 5 \times 10^5 - 2364.3 = 4.97 \times 10^5 \text{ Pa} = 497 \text{ kPa}$$

(c) since, in the expression of fractional feed recovery, channel height does not appear, f remains as 0.576

(d) Similarly, the flow rate at the channel outlet remains same as 28.5 L/h.

Note: The pressure drop across the module increases as the channel height decreases due to increase in the flow rate.

8. A protein solution of concentration 0.2kg/m^3 is concentrated by ultrafiltration. The operating pressure at the channel inlet is 5×10^5 Pa, width 0.08m and channel half length is 1mm. The membrane permeability is 10^{-11} N.s/m². The feed flow rate at the channel entrance is 40 L/h. The length of the channel is 2m. Find out (a) Pressure drop across the channel (b) Fractional recovery of feed (c) Velocity and (d) concentration at channel outlet.

Solution:

$\Delta P_i = 5 \times 10^5$ Pa ; $w = 0.08\text{m}$; $h = 10^{-3}\text{m}$; $L_p = 10^{-11}$ N.s/m² ; $Q = 40$ L/h = 1.11×10^{-5} m³/s ;
 $L = 2\text{m}$

$$u_o = \frac{Q}{2hw} = \frac{1.11 \times 10^{-5}}{2 \times 10^{-3} \times 0.08} = 0.07\text{m/s}$$

$$\lambda = \sqrt{\frac{3\mu L_p}{h^3}} = \sqrt{\frac{3 \times 10^{-3} \times 10^{-11}}{10^{-9}}} = 5.48 \times 10^{-3}$$

$$\beta = \frac{3}{2} \frac{\mu Q_i}{h^3 w \lambda \Delta P_i} = \frac{3}{2} \times \frac{10^{-3} \times 1.11 \times 10^{-5}}{10^{-9} \times 0.08 \times 5.48 \times 10^{-3} \times 5 \times 10^5} = 0.076$$

$$\lambda L = 0.011; \sinh(\lambda L) = 0.011; \cosh(\lambda L) = 1.0$$

(a) Pressure drop

$$\frac{\Delta P(L)}{\Delta P_i} = \cosh(\lambda L) - \beta \sinh(\lambda L) = 1 - 0.076 \times 0.011 = 0.999$$

$$\Delta P(L) = 499.50 \text{ kPa}$$

$$\text{So, } \Delta P|_{axis} = 5 \times 10^5 - 499500 = 500 \text{ Pa}$$

(b) Fractional feed recovery

$$f = \frac{2wL_p \Delta P}{Q_i \lambda} [\sinh(\lambda L) - \beta (\cosh(\lambda L) - 1)]$$

$$= \frac{2 \times 0.08 \times 10^{-11} \times 5 \times 10^5}{1.11 \times 10^{-5} \times 5.85 \times 10^{-3}} [0.011 - 0] = 0.147$$

(c) Velocity at the outlet

$$\frac{\bar{u}(L)}{u_o} = 1 - \frac{L_p \Delta P_i}{h \lambda u_o} [\sinh(\lambda L) - \beta (\cosh(\lambda L) - 1)]$$

$$= 1 - \frac{10^{-11} \times 5 \times 10^5}{10^{-3} \times 5.85 \times 10^{-3} \times 0.07} [0.011 - 0] = 0.86$$

So, velocity at the outlet is 0.06m/s

(d) Concentration at the outlet

$$\frac{C(L)}{C_o} = \frac{u_o}{u(L)} = \frac{1}{0.86} = 1.16$$

So, the concentration at the outlet is 0.232 kg/m³

9. In a gel layer controlling ultrafiltration, the specific gel layer resistance is given as, $\alpha = \alpha_0 (\Delta P)^{0.3}$, where, α is in m/kg, $\alpha_0 = 2.56 \times 10^{16}$ and ΔP is in Pa. Gel layer thickness is given as $L = L_0 (\Delta P)^{0.8}$, where, $L_0 = 5.74 \times 10^{-11}$ and ΔP is in Pa. Gel layer

density is 1050 kg/m^3 and gel layer porosity is 0.7. Membrane permeability is $5 \times 10^{-11} \text{ m/Pa.s}$.

Find the value of limiting operating pressure and what are the values of flux and gel layer resistance at this pressure?

Solution:

$$J = \frac{\Delta P}{\mu(R_m + R_g)}$$

$$\begin{aligned} R_g &= \alpha(1 - \varepsilon_g)\rho_g L \\ &= \alpha_0(\Delta P)^{0.3}(1 - \varepsilon_g)\rho_g L_0(\Delta P)^{0.8} \\ &= \alpha_0(1 - \varepsilon_g)\rho_g L_0(\Delta P)^{1.1} \\ &= 4.36 \times 10^8 (\Delta P)^{1.1} \end{aligned}$$

$$R_g = R_{g0}(\Delta P)^{1.1}, \quad \text{where } R_{g0} = 4.36 \times 10^8$$

$$J = \frac{\Delta P}{\mu(R_m + R_{g0}(\Delta P)^{1.1})}$$

$$\frac{dJ}{d\Delta P} = \frac{1}{\mu(R_m + R_{g0}(\Delta P)^{1.1})} - \frac{\Delta P R_{g0} [1.1(\Delta P)^{0.1}]}{\mu(R_m + R_{g0}(\Delta P)^{1.1})^2} = 0$$

$$R_m + R_{g0}(\Delta P)^{1.1} = 1.1 R_{g0}(\Delta P)^{0.1}$$

$$R_m = 0.1 R_{g0}(\Delta P)^{1.1}$$

$$(\Delta P)^{1.1} = \frac{10 R_m}{R_{g0}}$$

$$\begin{aligned} \Delta P &= \left(\frac{10 R_m}{R_{g0}} \right)^{\frac{1}{1.1}} = \left[\frac{10 \times 2 \times 10^{15}}{4.63 \times 10^8} \right]^{0.91} \\ &= 8.876 \times 10^6 \text{ pa} \\ &= 8876 \text{ kPa} \end{aligned}$$

$$\Delta P_{Lim} = 8876 \text{ kPa}$$

$$J = \frac{8876 \times 10^3}{\mu [2 \times 10^{15} + 4.63 \times 10^8 \times 8876^{1.1}]}$$

$$= 4.41 \times 10^{-6} \text{ m/s}$$

$$R_g = 2 \times 10^{16} \text{ m}^{-1}$$

10. In a steady state, counter current dialyzer of rectangular cross section, urea is removed by pure water as dialysate. Inlet feed concentration is 1500 mg/L. Feed and dialysate flow rates are 18 L/h and 90 L/h, respectively. D_{urea} in the membrane is $10^{-12} \text{ m}^2/\text{s}$ and in the bulk is $10^{-10} \text{ m}^2/\text{s}$. membrane thickness is 1 micron. Feed and dialysate chambers are identical in shape. Width of each channel is 5 mm and height 5 mm. In the feed side, the urea concentration has to be reduced from 1500 (inlet) to 300 mg/L (outlet).

Find the membrane area required. Neglect mass transfer resistances on both sides.

$$C_{iF_i} = 1500 \text{ mg/l}; \quad C_{iF_e} = 300 \text{ mg/l}; \quad \dot{V}_F = 18 \text{ l/h}; \quad \dot{V}_D = 90 \text{ l/h}$$

$$D_{im} = 10^{-12} \text{ m}^2/\text{s}; \quad D_i = 10^{-10} \text{ m}^2/\text{s}; \quad L = 10^{-6} \text{ m}; \quad W = 5 \text{ mm};$$

$$h = \text{height} = 5 \text{ mm}; \quad C_{iD_i} = 0$$

$$\dot{m} = \dot{V}_F (C_{iF_i} - C_{iF_e}) = \dot{V}_D (C_{iD_0} - C_{iD_i})$$

$$18(1500 - 300) = 90(C_{iD_0} - 0)$$

$$18 \times 1200 = 90 C_{iD_0}$$

$$C_{iD_0} = \frac{18 \times 1200}{90} = 240 \text{ mg/l}$$

- (i) Neglecting mass transfer resistance on both sides

k_0 = overall mass transfer coefficient

$$= \frac{D_{im}}{L} = \frac{10^{-12}}{10^{-6}} = 10^{-6} \text{ m/s}$$

$$(\Delta C)_{LMTD} = \frac{(\Delta C)_i - (\Delta C)_o}{\ln \frac{(\Delta C)_i}{(\Delta C)_o}}$$

$$(\Delta C)_{in} = C_{iF_i} - C_{iD_0} = 1500 - 240 = 1260 \text{ mg/l}$$

$$(\Delta C)_{out} = C_{iF_e} - C_{iD_i} = 300 - 0 = 300 \text{ mg/l}$$

$$(\Delta C)_{LMTD} = \frac{1260 - 300}{\ln \frac{1260}{300}} = 668.95 \text{ mg/l}$$

$$\begin{aligned} \dot{m} &= \dot{V}_F (C_{iF_i} - C_{iF_e}) = 18 \left(\frac{l}{h} \right) \times 1200 \frac{mg}{l} \\ &= 18 \times 1200 \frac{mg}{h} = 21.6 \text{ g/h} \end{aligned}$$

$$\begin{aligned} \dot{m} &= k_0 A_m (\Delta C)_{LMTD} \\ &= 10^{-6} A_m 668.5 \frac{m}{s} \cdot m^2 \cdot \frac{mg}{l} \\ &= 10^{-6} \times 668.5 A_m \cdot 10^{-3} \times 3600 \frac{g \cdot m^3}{h \cdot 10^{-3} m^3} \\ &= 10^{-6} \times 668.5 \times 3600 A_m \text{ g/h} \\ &= 2.41 A_m \text{ g/h} \end{aligned}$$

$$21.6 = 2.41 A_m$$

$$A_m = 8.96 \text{ m}^2$$

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