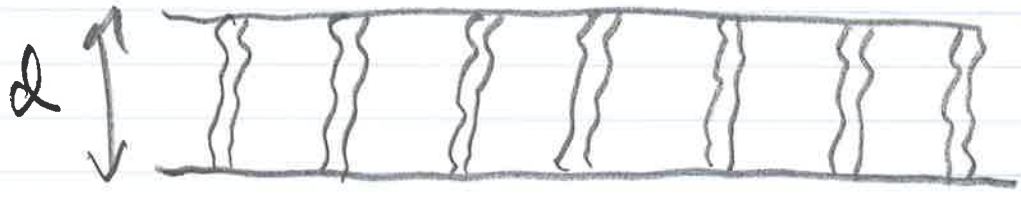


In FFF concentration polarization is good: it's what leads to separation!
 In filtration it's bad because it reduces the permeate flux through the membrane. Let's look at this!

What is a membrane? Simplistically, it is a solid layer with pores:



$\epsilon \equiv$ open area

$a \equiv$ pore radius

$d \equiv$ membrane thickness

$\tau \equiv$ tortuosity

pores are usually small, so inertial effects are negligible.

We can approximate the flow through a single pore w/ Poiseuille's Law:

$$Q_{\text{pore}} = \frac{1}{8} \frac{\Delta P}{\mu} \frac{\pi a^4}{\lambda d}$$

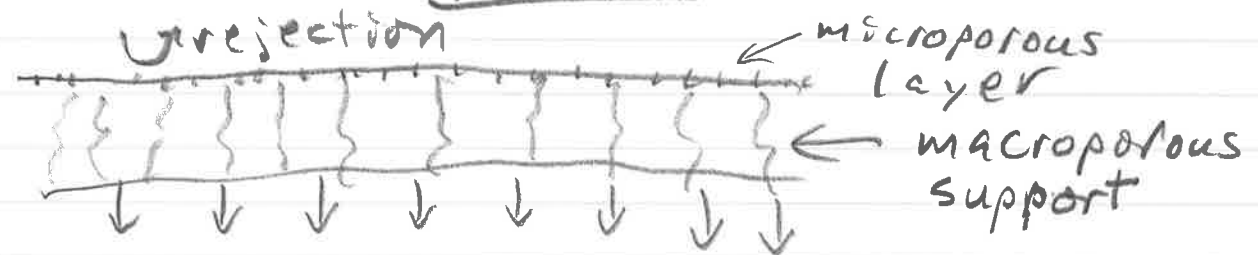
← pore radius
 ← effective length
 pressure drop fluid viscosity

We have n pores/area = $\frac{\epsilon}{\pi a^2}$

∴ trans-membrane flux = $u_0 = n Q_{\text{pore}} = \frac{\Delta P}{\mu} \left(\frac{\epsilon a^2}{8 \lambda d} \right)$

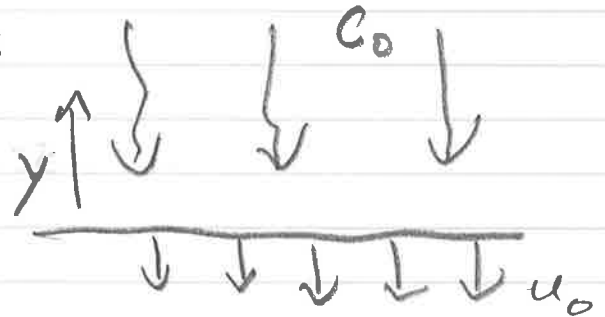
the quantity $K_H = \frac{\epsilon a^2}{8 \lambda d}$ is the hydraulic permeability of the membrane! For tract etched membranes (nuclepore) where pores are circular & straight this works ($w/\lambda = 1$). For more complicated membranes it is just a scaling and K_H is determined empirically.

Because of the strong dep. on pore size, for rejecting small species you want to use asymmetric membranes:



Most of the hydrodynamic resistance is in the thin microporous layer.

OK, so what happens in dead end filtration:



We have one-D diffusion:

$$\frac{\partial c}{\partial t} - u_0 \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}$$

$$c|_{y \rightarrow \infty} = c_0 \quad u_0 c|_{y=0} + D \frac{\partial c}{\partial y}|_{y=0} = 0$$

Let's scale:

$$c^* = c/c_0, \quad y^* = y/y_c, \quad t^* = t/t_c$$

$$\therefore \frac{c_0}{t_c} \frac{\partial c^*}{\partial t^*} - \frac{u_0 c_0}{y_c} \frac{\partial c^*}{\partial y^*} = D \frac{c_0}{y_c^2} \frac{\partial^2 c^*}{\partial y^{*2}}$$

$$\text{So } \left[\frac{y_c^2}{Dt_c} \right] \frac{\partial c^*}{\partial t^*} - \left[\frac{u_0 y_c}{D} \right] \frac{\partial c^*}{\partial y^*} = \frac{\partial^2 c^*}{\partial y^{*2}}$$

$$\text{So } y_c = D/u_0, \quad t_c = \frac{y_c^2}{D} = \frac{D}{u_0^2}$$

$$\therefore \frac{\partial c^*}{\partial t^*} - \frac{\partial c^*}{\partial y^*} = \frac{\partial^2 c^*}{\partial y^{*2}}$$

$$c^* \Big|_{y^* \rightarrow \infty} = 1 \quad c^* \Big|_{y^*=0} + \frac{\partial c^*}{\partial y^*} \Big|_{y^*=0} = 0$$

Ignoring the IC, this has the solution:

$$c^* = 1 + t^* e^{-y^*} + (1 - y^*) e^{-y^*}$$

The problem is that the conc. at the membrane grows linearly in time! This has three primary effects:

1) For dilute small molecules (e.g., salt) you will have more unwanted solute flux (e.g., the rejection ratio of, say, Li^+/K^+ will go down due to buildup of K^+)

2) For more conc. small molecules you will increase the osmotic pressure

$$\pi = i C R T$$

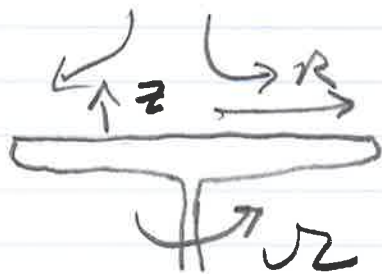
\leftarrow molar conc
 \leftarrow temp in $^{\circ}K$
 \leftarrow Ideal gas const
 i van't Hoff Index
 (* dissociated ions/mol)

This reduces the permeate flux by effectively reducing the driving force (e.g., $u_0 = K_H (\Delta P - \pi)$)

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3) For larger species you may exceed the solubility limit, or simply build up a cake layer! This would plug the holes, or otherwise reduce K_H .
How do we control the buildup?
Introduce a cross-flow! This would sweep away the concentration polarization layer and permit steady operation!

A classic approach used for study of membranes is a rotating filter:



The rotation introduces a centrifugal force which causes fluid to sweep the membrane surface. The

reason why this works so well is
the mass transfer BL is uniform
over the whole surface. Let's look
at this!

First, we need the velocity profile!
we have an axi-sym. problem: no θ
variation!

\therefore CE:

$$\frac{1}{r} \frac{\partial}{\partial r} (r u_r) + \frac{\partial u_z}{\partial z} = 0$$

θ mom:

$$\rho \left(u_r \frac{\partial u_\theta}{\partial r} + u_z \frac{\partial u_\theta}{\partial z} + \frac{u_r u_\theta}{r} \right) \\ = \mu \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r u_\theta) \right) + \frac{\partial^2 u_\theta}{\partial z^2} \right]$$

r -mom:

$$\rho \left(u_r \frac{\partial u_r}{\partial r} + u_z \frac{\partial u_r}{\partial z} - \frac{u_\theta^2}{r} \right) \\ = -\frac{\partial p}{\partial r} + \mu \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r u_r) \right) + \frac{\partial^2 u_r}{\partial z^2} \right]$$

We have BCs:

$$u_\theta \Big|_{z=0} = \Omega r \quad (\text{rotation})$$

$$u_\theta \Big|_{z \rightarrow \infty} = 0$$

$$u_r \Big|_{z=0, \infty} = 0$$

$$u_z \Big|_{z=0} = -u_0 \quad (\text{permeate flux!})$$

We are interested in the boundary layer limit. We anticipate that $z_c \ll R$! Recall that in this limit the pressure gradient outside the BL is impressed on the BL. Thus,

$$\frac{\partial P}{\partial r} = 0$$

Let's scale this!

$$\text{From BC } u_\theta^* = \frac{u_\theta}{\Omega R}, \quad r^* = r/R$$

We take $u_r^* = u_r / U_{rc}$, $u_z^* = u_z / U_{zc}$

$$z^* = z / z_c$$

From the CE:

$$\frac{U_{rc}}{R} \frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* u_r^*) + \frac{U_{zc}}{z_c} \frac{\partial u_z^*}{\partial z^*} = 0$$

$$\therefore U_{zc} = \frac{z_c}{R} U_{rc}$$

⊖ mom:

$$\begin{aligned} & \rho \frac{U_{rc} \sqrt{2} R}{R} \left(u_r^* \frac{\partial u_\theta^*}{\partial r^*} + u_z^* \frac{\partial u_\theta^*}{\partial z^*} + \frac{u_r^* u_\theta^*}{r^*} \right) \\ &= \rho \frac{\sqrt{2} R}{z_c^2} \left(\frac{\partial^2 u_\theta^*}{\partial z^{*2}} + \frac{z_c^2}{R^2} \frac{\partial}{\partial r^*} \left(\frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* u_\theta^*) \right) \right) \end{aligned}$$

small

$$\text{So } \frac{U_{rc} z_c^2}{\nu R} = 1$$

r mom:

$$\begin{aligned} & \rho \frac{U_{rc}^2}{R} \left(u_r^* \frac{\partial u_r^*}{\partial r^*} + u_z^* \frac{\partial u_r^*}{\partial z^*} \right) - \rho \sqrt{2} R \frac{U_\theta^{*2}}{r^*} \\ &= \rho \frac{U_{rc}}{z_c^2} \left[\frac{\partial^2 u_r^*}{\partial z^{*2}} + \frac{z_c^2}{R^2} \frac{\partial}{\partial r^*} \left(\frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* u_r^*) \right) \right] \end{aligned}$$

small

$$\text{so: } \frac{U_{rc} z_c^2}{\Omega R} = 1 \quad (\text{as before})$$

$$\underline{\text{and}} \quad \frac{\Omega^2 R z_c^2}{U_{rc} \Omega} = 1 \quad (\text{balancing centrifugal force w/ dof}^n \text{ of radial mom in } z\text{-dir})$$

This has the solution:

$$U_{rc} = \Omega R \quad ; \quad z_c = \left(\frac{\Omega}{\Omega} \right)^{1/2}$$

$$\text{and } U_{zc} = \Omega \left(\frac{\Omega}{\Omega} \right)^{1/2}$$

We have the dimensionless eq'n's:

$$\frac{\partial u_z^*}{\partial z^*} = - \frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* u_r^*)$$

$$\frac{\partial^2 u_\theta^*}{\partial z^{*2}} = u_r^* \frac{\partial u_\theta^*}{\partial r^*} + u_z^* \frac{\partial u_\theta^*}{\partial z^*} + \frac{u_r^* u_\theta^*}{r^*}$$

$$\frac{\partial^2 u_r^*}{\partial z^{*2}} = u_r^* \frac{\partial u_r^*}{\partial r^*} + u_z^* \frac{\partial u_r^*}{\partial z^*} - \frac{u_\theta^{*2}}{r^*}$$

$$\text{w/ BC's } u_\theta^* \Big|_{z^*=0} = r^*, \quad u_z^* \Big|_{z^*=0} = - \frac{u_0}{(\Omega \Omega)^{1/2}} = -u_0^*$$

$$\text{and } u_\theta^* \Big|_{z^* \rightarrow \infty} = u_r^* \Big|_{z^* \rightarrow \infty} = 0$$

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OK, now for the concentration:

$$u_r \frac{\partial C}{\partial r} + u_z \frac{\partial C}{\partial z} = D \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial z^2} \right]$$

or, w/ $C^* = C/C_0$:

$$u_r^* \frac{\partial C^*}{\partial r^*} + u_z^* \frac{\partial C^*}{\partial z^*} = \frac{D}{\nu} \frac{\partial^2 C^*}{\partial z^{*2}} \quad \hookrightarrow 1/Sc$$

Recall for liquids $Sc \gg 1$

$$\text{BC's: } C^* \Big|_{z^* \rightarrow \infty} = 1$$

$$\text{and at } z=0: \quad -u_0 C \Big|_{z=0} - D \frac{\partial C}{\partial z} \Big|_{z=0} = 0$$

(this is for complete rejection - if some solute gets through, it would be equal to the solute flux)

$$\text{This yields } u_0^* C^* \Big|_{z^*=0} + \frac{1}{Sc} \frac{\partial C^*}{\partial z^*} \Big|_{z^*=0} = 0$$

These equations are non-linear, but they admit a similarity solution!

$$u_\theta^* = r^* f(z^*)$$

$$u_r^* = r^* g(z^*)$$

$$u_z^* = h(z^*)$$

and $c^* = f''(z^*)$ alone!

So:

$$f'' = fg + hf' + fg \equiv 2fg + hf'$$

$$g'' = g^2 + hg' - f^2$$

$$h' = -2g$$

w/ $f(0) = 1, f(\infty) = 0$

$$g(0) = g(\infty) = 0$$

$$h(0) = -u_0^*$$

and $c^{*''} = Sc^*h c^{*'}$

$$c^*(\infty) = 1 \quad c^{*'}(0) + Sc^*u_0^*c^*(0) = 0$$

So our dimensionless conc. at $z=0$ is a function of $u_0^* = \frac{u_0}{(\nu z)^{1/2}}$ and Sc . We can solve these for arbitrary u_0^* and Sc , but since $Sc \gg 1$ we can get at the scaling another way. We want to remove the concentration polarization layer via radial convection. If our polarization layer is thin, the excess concentration needs to balance the inward flux:

$$(2\pi R) \left(\frac{\nu R}{\nu} \right)^{1/2} g'(0) \left(\frac{D}{u_0} \right)^2 (C^*|_{z=0} - 1) = u_0 \pi R^2$$

↑ circumference
 ↑ shear rate at membrane
 ↑ length scale of polarization layer
 ↑ excess conc.
 ↑ flux in from outside

$$\therefore C^*|_{z=0} - 1 \sim \frac{1}{2g'(0)} \left(\frac{\nu^2}{D^2} \right) \frac{u_0^3}{(\nu z)^{3/2}}$$

$$= \frac{1}{2g'(0)} Sc^2 u_0^*{}^3$$

Let's see how this works! In the Bruening lab they are using a track etched membrane (30 nm pores) to separate Li^+ and K^+ . They get great selectivity (RR 150) at 1000 RPM rotation, but at 100 RPM it drops to 2! (K^+ gets through) The hydraulic permeability is 22.5 LMH (liters/ $m^2 \cdot hr$ at 1 bar) and the ΔP is about 6 bar. The radius $R = 1.45 \text{ cm}$, and the diffusivity of K^+ in solution is about $1.8 \times 10^{-5} \text{ cm}^2/\text{s}$. So:

$$u_0 = (6 \text{ bar}) \left(22.5 \times \frac{1000}{10^4} \frac{1}{3600} \right) = 0.0038 \text{ cm/s}$$

$$(\Omega R)^{1/2} = \left(1000 \times \frac{2\pi}{60} \times 0.01 \right)^{1/2} = 1.02 \text{ cm/s}$$

$$\text{so } u_0^* = 0.0038 \text{ at } 1000 \text{ RPM}$$

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$$Sc = \frac{\nu}{\Delta} = \frac{0.01}{1.8 \times 10^{-5}} = 555$$

$$\therefore Sc^2 u_0^{*3} = 0.016$$

A numerical solution shows $g'(0) \sim \frac{1}{2}$ (not exact), so from scaling

$$C^* \Big|_{z^*=0} \sim 1 + 0.016 \quad \text{at this rotation rate.}$$

At 100 RPM, however, $(\sqrt{2}\nu)^{1/2} \sim 0.32 \text{ cm/s}$

and thus:

$$C^* \Big|_{z^*=0} \sim 1 + 0.5$$

so we are starting to see buildup of K^+