ChE *laboratory*

SIMPLE MASS TRANSFER EXPERIMENT USING NANOFILTRATION MEMBRANES

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Membrane technology is increasingly recognized as an important separation process with a wide range of applications in biotechnology, food processing, water and wastewater treatment, and gas separations. But at the undergraduate level, laboratory experiments involving membrane technology have been lacking. This is probably due to the fact that the preparations involved in setting up an experiment using a membrane are quite difficult. For example, in reverse osmosis the applied pressure needed is very high, whereas for ultrafiltration, the sample preparation and analysis is quite laborious.

This paper will describe a simple experiment using a nanofiltration (NF) membrane for determination of mass transfer correlations at the feed side of the membrane cell. Conceptually, this experiment will introduce the students to the concept of concentration polarization, separation due to charge of ions, and overall performance of an NF membrane. Experimentally, the students will be able to determine the mass-transfer correlations, which will involve dimensionless numbers such as Reynolds, Sherwood, and Schmidt—the "classical" chemical engineering numbers.

THEORY

A nanofiltration membrane is a type of membrane that has properties in between ultrafiltration membranes and reverse osmosis membranes. It is usually identified as having a negative charge and pore size of approximately 1 nm. The charge and small pore size mean it can provide separation based on the Donnan effect for charged molecules and ions and sieving effect for neutral molecules. As such, it offers a wide range of separation capabilities in many areas of interest.[1]

One of the major problems with any membrane operation is the occurrence of concentration polarization at the membrane surface. The solutes that are rejected are held back in a layer next to the membrane surface. This solute buildup is called concentration polarization.

Observed rejection is defined as

$$R_{obs} = 1 - \frac{C_p}{C_b} \tag{1}$$

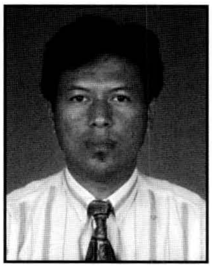
where C_p is the permeate concentration and C_b is the bulk solution concentration. It is an experimentally obtained measurement of the degree of rejection of the solute by the membrane. Due to concentration polarization, however, this definition of rejection is not accurate. The real concentration at the membrane interface is higher than the bulk concentration. Thus, the real rejection is defined as

$$R_{real} = 1 - \frac{C_p}{C_w} \tag{2}$$

The problem now is in determining the value of C_w, which is the concentration at the membrane wall. Figure 1 shows a schematic diagram of the interface between the bulk solution and the membrane surface for a three-component system. Concentration polarization close to the membrane surface is assumed to occur within a boundary film layer of thickness, δ. For a system containing charged ions, a mass balance for the film layer yields

$$j_i = -D_{i,\infty}\frac{dC_i}{dx} - \frac{z_i F}{RT}C_i D_{i,\infty}\frac{d\psi_f}{dx} + C_i J_v \tag{3}$$

where $D_{i,\infty}$ is the bulk diffusivity of ion i in the solution. The equation can be solved using the boundary conditions



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$$\text{at} \quad x = -\delta, \quad c = C_{i,b}$$
$$\text{at} \quad x = 0, \quad c = C_{i,w}$$

For a binary salt, the cation and anion will move together due to the requirement of electroneutrality. Equation (3) can be solved for both ions and the flux expressed as

$$j_+ = j_- = -D_{eff,\infty}\frac{dC_\pm}{dx} + C_\pm J_v \tag{4}$$

where $D_{eff,\infty}$ is the effective diffusivity of the salt defined as[2]

$$D_{eff,\infty} = \frac{D_{+,\infty}D_{-,\infty}(z_+ - z_-)}{z_+D_{+,\infty} - z_-D_{-,\infty}} \tag{5}$$

Using the boundary condition defined above, the wall concentration, C_w, can be correlated to other measurable parameters as

$$\frac{J_v}{k} = \ell n\frac{(C_w - C_p)}{(C_b - C_p)} = \ell n\frac{\left(\frac{1-R_{real}}{R_{real}}\right)}{\left(\frac{1-R_{obs}}{R_{obs}}\right)} \tag{6}$$

where k is the mass-transfer coefficient in the polarized boundary layer and is defined as

$$k = \frac{D_{eff,\infty}}{\delta} \tag{7}$$

This result is equally applicable to a system of neutral solutes. The mass-transfer coefficient is often characterized by a Sherwood number (N_{Sh}) correlation that is expressed as a function of Reynolds number (N_{Re}) and Schmidt number (N_{Sc}). For a laminar flow ($N_{Re}<32000$) in a stirred cell, the correlation is given as[3,4]

$$N_{Sh} = \phi(N_{Re})^n(N_{Sc})^{0.33} \tag{8}$$

$$N_{Sh} = \frac{kr}{D_{eff,\infty}} \qquad N_{Re} = \frac{\omega r^2}{\nu} \qquad N_{Sc} = \frac{\nu}{D_{eff,\infty}} \tag{9}$$

where r is the radius of the stirred cell, ω is the angular velocity of the stirrer in radians per second, ν is the kinematic viscosity defined as η/ρ, where η and ρ are the viscosity and the density of the fluid, respectively.

Another method of obtaining k is by extrapolating Eq. (6).[5] When written in linear form, Eq. (6) becomes

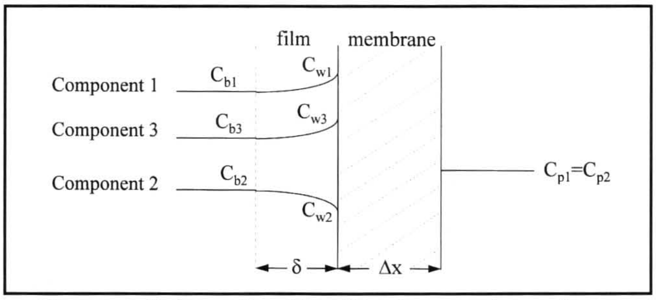

Figure 1. *Schematic of the film layer and membrane for three-component system.*

$$\ell n\left(\frac{1-R_{obs}}{R_{obs}}\right) = \ell n\left(\frac{1-R_{real}}{R_{real}}\right) + \frac{J_v}{k} \tag{10}$$

k was found to be a function of the stirring speed, and thus from Eq. (8), k can be written as a function of ω as

$$k = k'\,\omega^n \tag{11}$$

where

$$k' = \left[\phi\left(\frac{r^2}{\nu}\right)^n\left(\frac{\nu}{D_{eff,\infty}}\right)^{0.33}\frac{D_{eff,\infty}}{r}\right] \tag{12}$$

Thus, a plot of $\ell n(1 - R_{obs}/R_{obs})$ vs J_v/ω^n will give a slope of 1/k' and intercept of $\ell n(1 - R_{real} \setminus R_{real})$. The value of R_{real} obtained is the real rejection at infinite stirring speed. The most suitable values for n and ϕ have been determined by other workers using extensive sets of data and were found to be 0.567 and 0.23, respectively.[3,4] These values were used in this work.

MATERIALS AND METHODS

The experiment can be carried out either in a stirred cell or a cross-flow cell. In this work, the experiments were carried out using a stirred cell with an effective membrane area of 28.7 cm^2. The setup of the whole experiment is shown in Figure 2. A simpler setup involving only the stirred cell, the magnetic stirrer, the nitrogen flask, and a pressure gauge is also feasible. The pressure is varied from 100 to 500 kN m^{-2}. The membrane used was NF-PES5, obtained from Hoechst. The membrane has a pore radius of about 1.2 nm.[6] The concentration of NaCl used for the feed is 1 mM. The diffusivity values for $Na^+\left(D_\infty = 1.33\times10^{-9}m^2s^{-1}\right)$ and $Cl^-\left(D_\infty = 2.03\times10^{-9}m^2s^{-1}\right)$ were obtained from published work.[7]

The membrane should be soaked overnight in the pure water solution. For the experiments, the following procedure was used:

1. In each run, 180 ml of fresh solution was used as the feed solution. The stirring speed was set initially at 20 rpm and the solution was left for 2 to 3 minutes to equilibrate in the cell. The operating pressure was started at 100 kN m^{-2}.
2. After 20 grams (ml) of permeate was collected, the experiment was stopped. Then the conductivities of the fresh

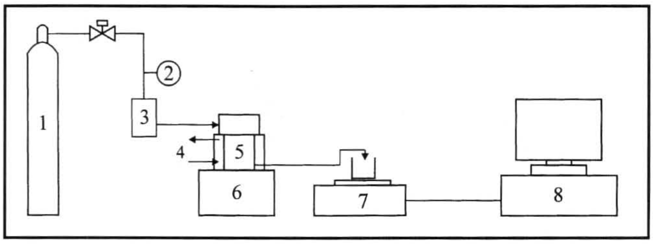

Figure 2. *Schematic diagram of dead-end filtration system. (1) nitrogen flask; (2) pressure transducer; (3) 250 mL reservoir; (4) water jacket; (5) filtration cell; (6) magnetic stirrer; (7) electronic balance; (8) personal computer*

solution, the retentate, and the permeate were recorded.

3. The conductivities of the feed solution, the retentate, and the permeate were converted into concentration using the conductivity calibration curve. The average bulk concentration in the feed was calculated as

$$C_b = \frac{C_{feed} + C_{retentate}}{2}$$

where C_{feed} and $C_{retentate}$ are the concentrations in the cell before and after the experiments, respectively. The observed rejection can be determined from Eq. (1).

4. The experiment was then repeated at the same operating pressure for the stirring speed of between 30, 50, 100, 200, 300, and 350 rpm.
5. The experiments were then repeated for operating pressures of 300 and 500 kN m^{-2}.
6. The weight of permeate collected against time was plotted and the data analyzed using linear regression. The slope of the plot represented the permeate flux in g/s or cm^3/s.

For a loose membrane such as NS-PES5, the flux is relatively large, and thus the experiments can be completed with three hours. But some membranes can be very "tight," and the fluxes are very low. Thus, careful consideration should be given in choosing which membrane to use.

RESULTS AND DISCUSSION

The experimental data were analyzed using the calculated k' obtained from the slope of Eq. (10). The data were then compared to the theoretical values obtained by using the calculated values of k' from Eq. (12).

Figure 3a shows the observed rejection of NaCl at three different pressures as a function of stirring speed for NF-PES5. It can be seen that R_{obs} changed considerably with stirring speed. The large changes were caused by the concentration polarization effect.

The data were then used to obtain k' using Eq. (10). Figure 3b shows the plot of $\ell n\left[(1-R_{obs})/R_{obs}\right]$ vs $J_V / \omega^{0.567}$. The lines are very linear, the calculated values of k' obtained by using Eqs. (10) and (12) are tabulated in Table 1 together with the values for $\exp(J_V / k' \omega^{0.657})$. This value is essentially the measure of the degree of concentration polarization. It can be seen that the error obtained when k' calculated by using Eqs. (10) and (12) is less than 5%.

The k' values were then used to calculate the experimental real rejection of NaCl. Figure 4 shows the real rejection as a function of the stirring speed. The filled points are those calculated using k' from Eq. (10), while the blank points are those calculated theoretically using Eq. (12). It can be seen that the effect of stirring speed has diminished, especially at larger stirring speeds. This means that the concentration polarization effect has been corrected. Agreement in the calculated real rejection using k' from Eqs. (10) and (12) are reasonably good, which means that the calculated k' from Eq. (12) can be used to estimate the mass transfer coefficient of the feed side.

An interesting observation is that the real rejection, R_{real}, was found to be dependent on the pressure drop. For nanofiltration membranes, this dependence is due to the fact that the rejection mechanism is not only determined by its intrinsic pore size, but also by the charge of the membrane (through the Donnan effect).[6,8] Furthermore, the transmembrane pressures used in this work produced fluxes in the range where the transport mechanisms of diffusion convection and electromigration are equally important, and thus the real rejection varied as a function of the applied pressure.[9] This behavior is different from the "standard" ultrafiltration or microfiltration membranes that show no dependence of

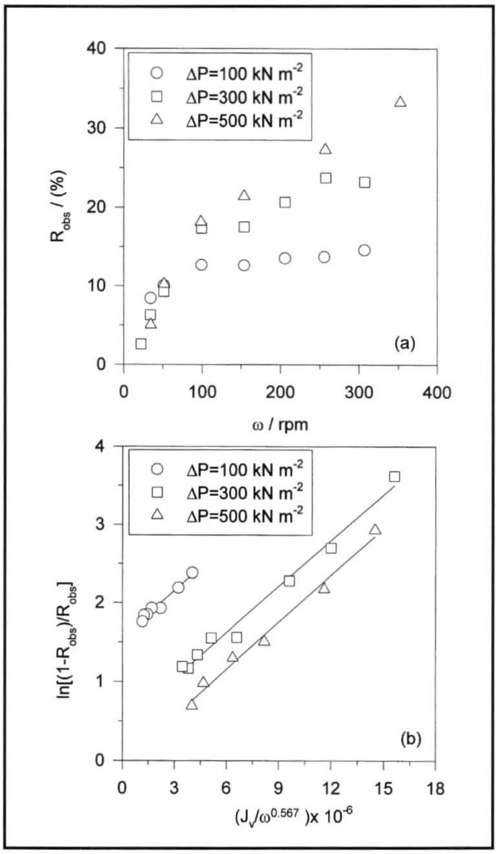

Figure 3. *Result for NF-PES5. a) Observed rejection as a function of stirring speed; b) linearization of the data to obtain k'.*

TABLE 1
Calculated Values for k'
and the Exponential of the Peclet Number

Pressure	k'		$\exp(J_V / k' \omega^{0.567})$		
	Eq. (10)	Eq. (12)	Eq. (10)	Eq. (12)	% error
100 kN m^{-2}	5.02 x 10^{-6}	4.859 x 10^{-6}	1.26	1.27	0.8
300 kN m^{-2}	5.10 x 10^{-6}	4.859 x 10^{-6}	1.98	2.05	3.4
500 kN m^{-2}	5.02 x 10^{-6}	4.859 x 10^{-6}	2.58	2.66	3.0

R_{real} on transmembrane pressure at high fluxes where the transport of solutes is only through convection.

CONCLUSIONS

In conclusion, the experiments described here are very suitable for showing the concept of concentration polarization in membrane operations and how the "classical" mass transfer correlations are used to describe it. The equipment needed to run the experiments is quite easy to set up, and the experiment can be completed within the three-hour period normally reserved for the junior/senior laboratory.

The students should be able to make the following inferences/observations:

- *Concentration polarization is an important phenomenon in membrane filtration.*
- *A simple mass balance of the system allows one to deduce the mass transfer coefficient, which relates the solvent flux to the boundary concentrations.*
- *The mass transfer coefficient, k, can be calculated through an equation involving dimensionless numbers such as the Sherwood number, Reynolds number, and Schmidt number.*
- *The dimensionless equation can be confirmed through a simple experiment involving the measurement of rejection of a binary salt.*

For additional experiments, the correlations can be used to determine the diffusivity (by reversing the calculation method used here) value for another salt, such as KCl or LiCl (the student should not be told what salt they are using). The calculated diffusivity value can then be compared to the published data. This will be a good check on whether or not the students did the experiments correctly.

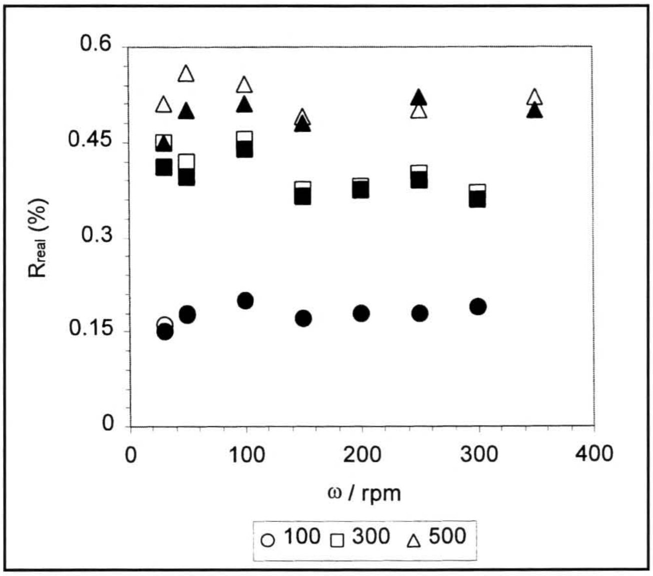

Figure 4. *Real rejection as a function of stirring speed. The darkened points show those calculated using k' from Eq. (10), while the clear points are those calculated using Eq. (12) The legend shows pressure drop in units of kN* m^{-2}.

NOTATION

C_b	bulk concentration on the feed side of membrane (mol m^{-3})
C_i	local concentration on the feed side of membrane (mol m^{-3})
C_p	concentration in permeate (mol m^{-3})
C_w	wall concentration on the feed side of membrane (mol m^{-3})
$D_{i,\infty}$	bulk diffusivity (m^2s^{-1})
$D_{eff,\infty}$	effective bulk diffusivity (m^2s^{-1})
F	Faraday constant (C mol^{-1})
j_i	ion flux (based on membrane area)(mol $m^{-2}s^{-1}$)
J_V	volume flux (based on membrane area)(m s^{-1})
k	mass transfer constant (m s^{-1})
k'	mass transfer constant defined by Eq. (8)
n	constant defined in Eq. (8)
ΔP	applied pressure drop (kN m^{-2})
r	radius of stirrer (m)
R	gas constant (J $mol^{-1}K^{-1}$)
R_{real}	real rejection
R_{obs}	observed rejection
T	absolute temperature (K)
x	distance normal to membrane (m)
z_i	valence of ion
δ	thickness of film layer (m)
ϕ	constant defined in Eq. (8)
η	viscosity of solution (Pa s)
ν	kinematic viscosity (m^2s^{-1})
ω	stirring speed (rad s^{-1})
ψ_f	potential in bulk solution (V)

subscripts

+	referring to cation
-	referring to anion

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