Modeling Water Flux in Forward Osmosis: Implications for Improved Membrane Design

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Osmotically-driven membrane processes, such as forward osmosis and pressure retarded osmosis, operate on the principle of osmotic transport of water across a semipermeable membrane from a dilute feed solution into a concentrated draw solution. The major hindrance to permeate water flux performance is the prevalence of concentration polarization on both sides of the membrane. This article evaluates the external and internal boundary layers, which decrease the effective osmotic driving force. By modeling permeate flux performance, the role that feed and draw concentrations, membrane orientation, and membrane structural properties play in overall permeate flux performance are elucidated and linked to prevalence of external and internal concentration polarization. External concentration polarization is found to play a significant role in the reduction of driving force, though internal concentration polarization has a far more pronounced effect for the chosen system conditions. Reduction of internal concentration polarization by way of membrane modification was found to improve the predicted flux performance significantly, suggesting that alteration of membrane design will lead to improved performance of osmotically driven membrane processes. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 1736–1744, 2007*
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Introduction

Recent developments in osmotic processes have prompted a flurry of research activity in the field of forward osmosis (FO). FO has recently been studied in the areas of food processing,[1–3] electricity production,[4–7] and desalination.[8–10] These processes all rely on the use of a concentrated "draw" solution to drive the transport of water from a dilute feed solution across a semipermeable membrane. In each case, process performance is evaluated based on solvent (water) recovery, permeate water flux, and solute rejection. Solute rejection is a membrane specific property and will not be discussed in detail in this article. Recovery and permeate water flux are more pertinent to evaluating FO processes, especially in comparison to pressure driven membrane processes.

Most current membrane processes, such as reverse osmosis (RO), are pressure driven such that permeate water flux and recovery are controlled by the hydraulic pressure applied to the feedwater. Concentration polarization, which results in a region of increased solute concentration at the rejecting surface of the membrane, also limits water flux and recovery. In FO, the primary factor controlling water flux and recovery is the transmembrane osmotic pressure. However, concentration polarization, now occurring on both sides of the membrane, also plays a prominent role in reducing the effective transmembrane osmotic pressure. The coupled effect of two polarized boundary layers has significant consequences on FO performance, especially when asymmetric membranes are considered.

Most membranes today are designed for pressure driven membrane processes and have an asymmetric structure, which consists of a thin selective active layer supported by thick layers of porous polymer and fabric support. It has been reported that these asymmetric polymeric membranes

perform poorly when used for osmotically driven membrane processes due to the boundary layers that occur within these supporting layers.[4,8–10] This phenomenon is called internal concentration polarization (ICP). Similar in concept to the concentration polarization discussed earlier, ICP refers to the development of a boundary layer within the protective confines of the membrane support structure.

For asymmetric membranes, two types of ICP exist depending on the membrane orientation.[11] In one orientation, referred to as the pressure retarded osmosis (PRO) mode, the feed solution is directed against the support layer. This orientation is commonly used for PRO applications when osmotic pressure gradients are used to generate electricity. The other orientation, where the draw solution is directed against the support layer, is the FO mode. This is the primary orientation considered for water treatment processes, such as FO desalination. In either case, ICP occurs within the porous support layer where, unlike concentration polarization in pressure driven membrane processes, it cannot be mitigated by hydrodynamics, such as turbulence, and hence drastically reduces the osmotic driving force.

Several previous investigations[4,12–14] found that osmosis tests, using RO membranes, yielded poor water flux performance. These results were attributed primarily to ICP while assuming external boundary layers on either side of the membrane to be negligible. This was a reasonable assumption, being that the water fluxes were often low and the solutions were well mixed. In more recent studies,[8–11] permeate fluxes have shown marked improvement and external concentration polarization (ECP) can no longer be ignored. Understanding the relative impacts of ICP and ECP on osmotic driving force would help to improve performance of osmotic processes by optimizing system parameters and membrane characteristics. Using models to predict water flux for both the PRO and FO modes under the influence of both ECP and ICP can help achieve this, though only once have existing models for ICP and ECP been combined. In this previous study, McCutcheon and Elimelech[11] showed that a combined model incorporating internal and external CP accurately described experimental data for both the PRO and FO modes and thus could work as a standalone predictor of flux under a variety of experimental conditions for either orientation.

The purpose of this study is to use this combined model to predict water flux performance of osmosis through asymmetric membranes that are oriented in both the PRO and FO modes under a range of feed and draw solution concentrations and membrane structural properties. The negative impacts on osmotic driving force caused by ICP and ECP will be quantified both for individual and coupled scenarios. Changes in membrane structural characteristics will elucidate performance improvements due to hypothetical changes in membrane design. The ramifications of tailoring membrane structural properties for both PRO and FO applications will be discussed.

Governing Equations for Permeate Flux

Two variations on the "film theory" model for concentration polarization are considered in this investigation. ECP is modeled using traditional film theory,[15] which incorporates the use of the mass transfer coefficient. ICP is modeled similarly by considering the resistance to diffusion of solute molecules within the porous support layer. Both symmetric and asymmetric membranes are considered. For the asymmetric membrane, two orientations of the membrane are studied: one with the active layer facing the feed solution (FO mode) and the other with the active layer facing the draw solution (PRO mode).[11]

External concentration polarization

Concentration polarization on the feed side of a membrane is a significant problem in pressure-driven membrane desalination processes. This phenomenon inhibits permeate flow due to an increased osmotic pressure at the membrane active layer interface on the feed side of the membrane. In an osmotic process, this phenomenon occurs on both sides of the membrane, with the effect being dilutive on the permeate side. We refer to these two phenomena collectively as ECP. Specifically, this phenomenon on the feed and permeate side will be referred to as concentrative and dilutive ECP, respectively.

To predict flux in the presence of ECP, we must determine the effective osmotic driving force at the membrane–solution interface on both the feed and permeate sides of the membrane. This is accomplished using film theory. For the purposes of this model, we will use a similar method of calculating ECP as provided in McCutcheon and Elimelech.[11]

For a pressure driven membrane process, such as RO, in the absence of ECP and salt passage, the generalized flux equation is

$$J_{\mathrm{w}} = A(\Delta P - \pi_{\mathrm{F,b}}) \tag{1}$$

where A is the pure water permeability coefficient, ΔP is the transmembrane pressure, and $\pi_{\mathrm{F,b}}$ is the osmotic pressure of the bulk feed solution. Note that we assume complete rejection of the feed solute (i.e., the reflection coefficient $\sigma = 1$). Equation 1 is valid only when the flux is low or the feed solution is very dilute. If flux becomes higher, the concentration polarization effect becomes significant. The membrane surface concentration on the feed side becomes larger than that of the bulk as solute is rejected, concentrating the feed solute. We therefore refer to this phenomenon as concentrative ECP. Using film theory, we can modify Eq. 1 to account for concentrative ECP:

$$J_{\mathrm{w}} = A\left(\Delta P - \pi_{\mathrm{F,b}} \exp\left(\frac{J_{\mathrm{w}}}{k}\right)\right) \tag{2}$$

Here, the exponential term is the concentrative ECP modulus,[11] which is a function of water flux and mass transfer coefficient, k. Mass transfer coefficient may be calculated from the appropriate Sherwood number correlations, incorporating viscosity, density, diffusion coefficient, and flow velocity, as explained in our previous investigation.[14] Even though Eq. 2 presents the water flux implicitly, it can still be solved iteratively to model flux for a given set of experimental conditions as is done later in this study. This equation, as will subsequent equations below, assumes a proportional relationship between concentration and osmotic pressure.

For osmotically driven membrane processes with a nondilute feed, a similar concentrative ECP will occur. In an

osmotically driven membrane process, however, we must also consider the dilutive effect that occurs on the permeate side of the membrane. Dilutive ECP occurs as permeate water flow displaces draw solute at the membrane–draw solution interface, reducing the effective driving force of the draw solution. These two ECP phenomena are coupled for osmotic flow when solute is present on both sides of the membrane and they must be accounted for when modeling flux behavior, as shown below.

The standard flux equation for FO is given as

$$J_w = A(\pi_{D,b} - \pi_{F,b}) \qquad (3)$$

which predicts flux as a function of the difference in bulk osmotic pressures of the draw ($\pi_{D,b}$) and feed ($\pi_{F,b}$) solutions. As earlier, this equation assumes complete rejection of the feed and draw solutes. This equation does not account for ECP, which may be valid only if the permeate flux is very low. When flux rates are higher, though, the equation must be modified to include both the concentrative and dilutive ECP moduli:

$$J_w = A\left[\pi_{D,b}\exp\left(-\frac{J_w}{k_D}\right) - \pi_{F,b}\exp\left(\frac{J_w}{k_F}\right)\right] \qquad (4)$$

Note that the dilutive effect is indicated by the negative exponential term modifying the draw solution osmotic pressure. We must also consider individual mass transfer coefficients on the feed, k_F, and permeate, k_D, sides of the membrane, though for the model parameters chosen below, k_F and k_D are essentially equal. Equation 4 represents an implicit model for osmotic flux using a dense symmetric membrane. However, no synthetic dense symmetric membranes are in use today for osmotic processes, and therefore, the usefulness of this particular flux model is limited. We must therefore consider the case where the membrane is asymmetric, for which ICP effects are most significant.

Internal concentration polarization

Asymmetric membranes, commonly used in pressure driven membrane processes, use porous layers to mechanically support a thin salt rejecting active layer. In osmotic processes, salt must pervade these porous layers, which do not reject the salt to any appreciable degree, yet still hinder its diffusion, to establish the osmotic driving force across this active layer. When water begins to permeate the membrane, concentration polarization occurs on both sides of this active layer. However, the porous layer provides a protected environment on one side of the active layer where the polarized layer can form without the mitigating effects of crossflow.[9,10] There are two types of ICP depending on the orientation of the membrane. In the PRO mode, the porous layer is against the feed solution and the feed solute will be concentrated within the membrane. In the FO mode, the porous layer is against the permeate side. The draw solute diffuses into this porous layer but becomes diluted as water permeates the membrane. We refer to these phenomena as concentrative and dilutive ICP, respectively.[10,11]

Both the structure of the membrane support layer and the solute diffusion coefficient play a significant role in deter-

mining the severity of these phenomena and must be considered when modeling flux. These characteristics affect the ability of the solute to diffuse out of (concentrative ICP) and into (dilutive ICP) the porous support layer, and in part control the magnitude of ICP. Lee et al.[4] defined a term signifying the solute resistance to diffusion within the membrane support layer, K:

$$K = \frac{t\tau}{D\varepsilon} \qquad (5)$$

where D is the bulk diffusion coefficient of the solute, and t, τ, and ε, are the thickness, tortuosity, and porosity of the support layer, respectively. Note that this term is essentially the inverse mass transfer coefficient within the support layer, where $D_{eff} = D\varepsilon/\tau$. In this case, the thickness of the effective "boundary layer" is the thickness of the support layer. We maintain the use of the K term due to convention established in previous studies on ICP.[4,10,14] This term can be incorporated into Eq. 3 to describe flux in the presence of ICP as done in McCutcheon and Elimelech.[11] The ICP modulus will modify the bulk osmotic pressure of the solution that is in contact with the porous support layer. In the case of the PRO mode, Eq. 3 is modified to yield[11,16]

$$J_w = A\left[\pi_{D,b} - \pi_{F,b}\exp(J_w K)\right] \qquad (6)$$

Note how the ICP modulus has a positive exponential term, indicating the concentrative effect. For moderate and high fluxes, dilutive ECP on the permeate (draw) side is not negligible and hence must be accounted for as well[11]:

$$J_w = A\left[\pi_{D,b}\exp\left(-\frac{J_w}{k_D}\right) - \pi_{F,b}\exp(J_w K)\right] \qquad (7)$$

All of the terms in Eq. 7 are readily determined through experiments or calculations. By solving Eq. 7 numerically, we can predict the water flux through an asymmetric membrane in the PRO mode. It is important to note that this model assumes that the support layer creates no hydraulic resistance to solvent (water) transport and that solute may freely enter the support structure at the membrane interface such that no concentrative ECP occurs on the support layer. This equation was found to accurately model flux for osmosis through an asymmetric membrane in the PRO mode.[11]

A similar approach can be taken for membranes used in the FO mode. Following the work of Loeb et al.[16] and McCutcheon and Elimelech,[11] the result is an equation resembling Eq. 7:

$$J_w = A\left[\pi_{D,b}\exp(-J_w K) - \pi_{F,b}\exp\left(\frac{J_w}{k_F}\right)\right] \qquad (8)$$

Equation 8 resembles Eq. 7 except that the ICP now occurs on the draw solution side and is dilutive, while the ECP occurs on the feed side and is concentrative. Equation 8 has been shown to accurately model water flux for an asymmetric membrane used in the FO mode.[11] Note that in the FO mode, dilutive ICP is coupled with concentrative ECP. As earlier, it is assumed that no ECP occurs on the permeate side of the membrane since the support layer is completely permeable to the draw solute.

Table 1. Parameters for Forward Osmosis Flux Modeling

Parameter	Symbol	Units	Value/Range
Bulk draw osmotic pressure*	$\pi_{D,b}$	atm (psi)	0–70 (0–1028.3)
Bulk feed osmotic pressure*	$\pi_{F,b}$	atm (psi)	0–65.4 (0–960.7)
Water permeability coefficient[†]	A	m/s atm	3.11×10^{-7}
Mass transfer coefficient[‡]	K	m/s	1.74×10^{-5}
Solute resistance to diffusion (PRO mode)[11]	K	s/m	2.24×10^5
Solute resistance to diffusion (FO mode)[11]	K	s/m	2.67×10^5
Temperature		°C	20
Crossflow velocity		cm/s	21.3

*Calculated using Hysis/OLI.
[†]Determined from RO experiments.[9]
[‡]Calculated with values from Hysys/OLI, same for feed and draw solution.

In each of these cases, the ECP and ICP moduli all contribute negatively to the overall osmotic driving force. The negative contribution of each increases with higher flux, which suggests a self limiting flux behavior. This implies that increasing osmotic driving force will provide diminishing increases in flux. Below, a quantitative analysis of the negative impact that ICP and ECP have on flux is evaluated for a variety of experimental conditions, draw and feed solution concentrations, and hypothetical symmetric and asymmetric membranes.

Model parameters

The models for the PRO and FO modes – Eqs. 7 and 8, respectively—were solved iteratively using Microsoft Excel Solver for a range of feed and draw solution concentrations to determine permeate water flux. Assumed experimental conditions are similar to those presented in McCutcheon and Elimelech[11] and are summarized in Table 1. Draw solution concentrations were limited to a range of 0.05–1.5 M NaCl. Feed solution concentrations range from 0 (deionized water) to 1.4 M NaCl. Sodium chloride is used as the model solute for the feed and draw solutions because diffusion coefficients for a wide range of salt concentrations and temperatures are readily available.[17] Viscosity, density, and osmotic pressure of each solution were calculated for the feed and draw solutions using software from OLI Systems, Inc. (Morris Plains, NJ) and Aspen HYSYS® (Cambridge, MA). For the membrane channel, a crossflow, plate and frame assembly of rectangular geometry with dimensions of 7.7 cm × 2.6 cm × 0.3 cm ($L \times W \times D$) was assumed, similar to our previous studies.[9,11] The membrane characteristics are based on those determined previously[9] for a commercially available FO membrane made by Hydration Technologies (Albany, OR). The K values were taken from a previous study using this membrane.[11]

Results and Discussion

The following results model permeate water flux behavior under a variety of experimental conditions, most of which are provided in Table 1. These results quantify the deleteri-

ous affects of internal and external CP both individually and coupled.

Dense symmetric membrane

Concentration polarization in pressure driven membrane processes occurs as convective water flux drags solute up against the dense, rejecting layer of the membrane, thereby increasing the concentration of the feed solute at the membrane surface. This increases the osmotic pressure that must be overcome before water can permeate the membrane. The severity of this concentrative ECP can be modeled based on film theory as presented earlier in Eq. 2. Shown in Figure 1, this equation was solved iteratively after accounting for all system parameters (temperature, solution characteristics, and hydrodynamics) and using the model parameters in Table 1 to predict the water flux behavior based on the net driving force, $\Delta P - \pi_{F,b}$, for feed concentrations ranging from deionized water to 1 M NaCl. A deionized water feed is indicated by the hydraulic permeability line in Figure 1. Figure 1 illustrates, as deviations from this dashed line, that higher net driving forces are needed to achieve the same flux for higher feed concentrations because of the greater prevalence of concentrative ECP. Using Figure 1, we determine the excess net driving force required to obtain a typical operating flux for RO of 10 gfd (4.71 μm/s) for each feed concentration, given in the fourth column of Table 2.

The excess pressure is indicative of the portion of the hydraulic pressure that is used to compensate for the concentrative ECP. This excess pressure exceeds 50% of the total net driving force, severely limiting flux performance and requiring higher hydraulic pressures for flux maintenance at higher feedwater concentrations (or high feedwater recoveries).

In osmosis across a dense membrane, we must consider both concentrative and dilutive ECP as described in Eq. 4. First, we consider dilutive ECP exclusively. In Figure 2, the
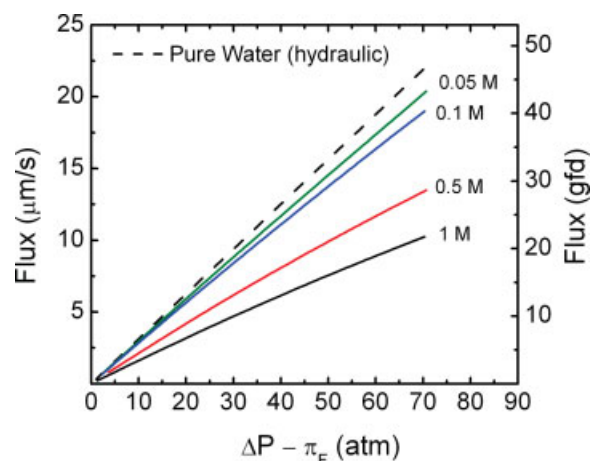

Figure 1. Effect of concentrative ECP on flux performance based on net driving force in reverse osmosis mode for various NaCl feed solutions.

Flux is driven hydraulically and is predicted based on Eq. 2. Conditions: listed in Table 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 2. Performance Data from Figure 1 for a Set Flux of 10 gfd (4.71 μm/s)

Feed Concentration (M)	$\pi_{F,b}$ atm (psi)	Required ($\Delta P - \pi_{F,b}$), atm (psi)	Excess Pressure Required for 10 gfd, atm (psi)	% of Net Driving Force
0	0.0 (0.0)	14.7 (216.1)	0.0 (0.0)	0.0
0.05	2.3 (33.8)	16 (235.2)	1.3 (14.7)	8.1
0.1	4.7 (69.1)	16.6 (244.0)	1.9 (23.5)	11.4
0.5	23.3 (342.5)	22.6 (332.2)	7.9 (111.7)	35.0
1	46.7 (686.5)	30.3 (445.4)	15.6 (224.9)	51.5

solid line is the modeled osmotically-driven flux for a symmetric membrane over a range of NaCl draw solution concentrations from 0 to 1.5 M NaCl. The deviation from the pure water hydraulic permeability line (the straight dashed line) and this solid line is caused entirely by dilutive ECP on the permeate side of the membrane. When solute is assumed to be present in the feed solution, dilutive ECP on the permeate side of the membrane is coupled with concentrative ECP on the feed side of the membrane. The dotted line in Figure 2 indicates the coupled effect of concentrative and dilutive ECP at a draw solution concentration of 1.5 M NaCl and a varying feed concentration from 0 to 1.4 M NaCl. As feed concentration is increased, flux will decrease due to a decreased osmotic driving force and concentrative ECP. Simultaneously, however, lower flux will yield a decreased severity of dilutive ECP on the permeate side. The coupling of concentrative and dilutive ECP yields a lower flux than either phenomenon alone, but the effects are not purely additive.

The scenarios described earlier take into account only external boundary layers associated with dense membranes. However, current generation membranes, especially those
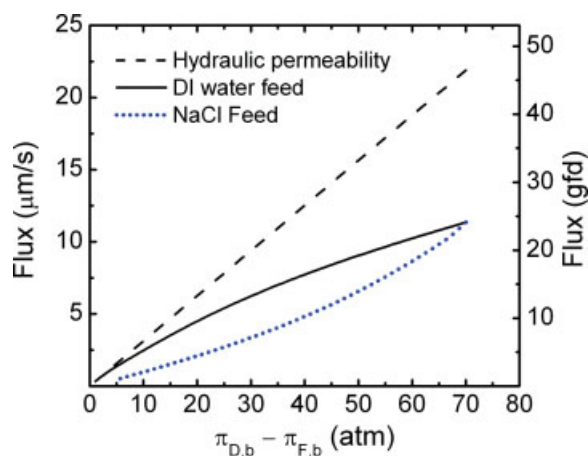

Figure 2. Effect of dilutive ECP (solid line) and coupled concentrative and dilutive ECP (dotted line) in forward osmosis as determined from Eq. 4.

The hydraulic permeability (dashed) line is indicative of pure water flux under hydraulic pressure. Model conditions were as follows. For dilutive ECP only (solid line), feed solution was deionized water and draw solution concentration ranged from 0.05 to 1.5 M NaCl. For the coupled concentrative and dilutive ECP (dotted line), draw solution was fixed at 1.5 M NaCl and feed solution ranged from 0 to 1.4 M. Other conditions are listed in Table 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
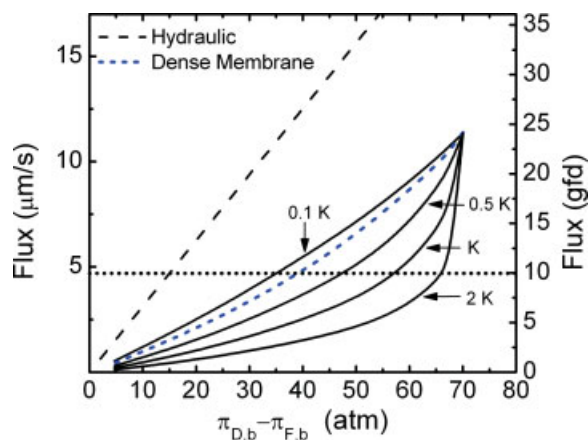
used in pressure driven membrane processes, are asymmetric with a porous layer, which provides mechanical support to a thin, dense active layer. In the following sections, flux is predicted in the presence of ECP along the active layer and ICP that occurs within this porous layer. Further analysis elucidating the impact of support layer properties on flux performance is presented.

Asymmetric membrane in PRO mode

Asymmetric membranes can be oriented in either the PRO or the FO mode, as described earlier. In the PRO mode, the draw solution is on the active layer, while the feed solution is on support layer, as is typical of PRO applications.[4,11,16] To model flux through these membranes, we use Eq. 7, again, solved iteratively as earlier. If the feed is deionized water or very dilute, concentrative ICP will not occur to a significant extent, and the modeled flux will be the same as given by the solid line in Figure 2. For a nondilute feed solution, internal CP will have a significant impact on water flux, the severity of which is determined by the value of the solute resistance to diffusion within the porous layer, K.

Flux Simulation in the PRO Mode. A simulation using a draw solution of 1.5 M NaCl and a feed solution concentration varied as high as 1.4 M under conditions specified in Table 1 is shown in Figure 3 for membranes with a variety of K values. The line labeled "K" is indicative of flux performance in the PRO mode with the K value provided in Table 1. This value was also used for comparing experimental flux behavior with model predictions in our recent publication.[11] Lines are indicative of the model flux over a range of transmembrane osmotic pressure differences using variable factors of K as indicated by the label. These different K values are representative of changes in membrane support layer structural characteristics (thickness, tortuosity, and porosity as represented in Eq. 5). For this investigation, it is assumed that D will not change since we are only examining NaCl solutions at 20°C. Diffusion coefficient is also assumed to change negligibly over the concentration range imposed by the model (no greater than 1.5 M NaCl). Higher values of K, typically associated with thicker and denser support layers, which have an increased solute diffusion resistance, resulted in lower fluxes for a given transmembrane osmotic pressure. This is due to the buildup of solute within the support layer (concentrative ICP) as the solute diffusion out into the bulk is significantly hindered. As K is lowered, flux increases because solute can diffuse out of the support layer more easily, decreasing the prevalence of concentrative ICP.

The value of K can be lowered to zero, hypothetically approaching a dense membrane. However, as K gets small, the model assumption of negligible ECP on the support layer

Figure 3. Flux modeled in the PRO mode (concentrative ICP coupled with dilutive ECP) for membranes with varying solute resistivity, *K*.

Simulations are based on Eq. 7. The hydraulic permeability (dashed) line is indicative of pure water flux under hydraulic pressure. The line labeled ''*K*'' is indicative of the performance of a membrane with the PRO value of *K* given in Table 1. The other values of *K* have been changed by the indicated factor. Model assumes that no concentrative ECP occurs at the surface of the porous support layer. The dotted line is the dotted line from Figure 2 and indicates the performance of a dense symmetric membrane under the same conditions. Conditions used in the simulations: NaCl draw solution concentration of 1.5 M (or $\pi_{D,b}$ = 70 atm), NaCl feed solution range from 0 to 1.4 M, and other conditions as summarized in Table 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

becomes invalid. Superimposed on Figure 3 is the dotted line from Figure 2, showing the dense symmetric membrane flux in the presence of concentrative and dilutive ECP. This line represents the theoretical maximum of water flux performance for any membrane with the same water permeability in a FO process in either PRO or FO mode under these conditions. Hence, this line indicates the actual performance for a membrane where $K = 0$. We therefore conclude that the flux profile labeled by 0.1 *K* as determined from our model does not actually exist for a real membrane. Hence, while improving flux performance is possible by tailoring membrane structural properties, there is a limit of performance improvement due to ECP.

Performance Assessment of the PRO Mode. For PRO applications, the salinity of the feedwater plays a major role in the performance of the process since this solution is subject to concentrative ICP. Therefore, we can more explicitly quantify the performance for different membranes used in the PRO mode by selecting a desired operating flux of 10 gfd (4.71 μm/s) as indicated by the horizontal dotted line in Figure 3, and determining the maximum feed concentration that will allow this flux to occur for a fixed draw solution concentration of 1.5 M NaCl. The comparison of the different membranes listed in Figure 3 at this flux is provided in Table 3. The required driving force ($\Delta \pi = \pi_{F,b} - \pi_{D,b}$) is given by where the 10 gfd (4.71 μm/s) line intersects each flux profile. The ideal behavior is defined by deionized water being hydraulically driven through the membrane (flux with no external or ICP).

In the presence of coupled concentrative and dilutive ECP, the dense membrane can maintain a flux of 10 gfd with a feed solution having an osmotic pressure 56.2% of a feed solution for a system experiencing no ECP. This indicates that the coupled concentrative and dilutive ECP phenomena have a significant impact on performance of this membrane in the PRO mode under these conditions at this flux. When concentrative ICP is considered, the maximum feed concentration drops even more precipitously, with the performance at the given value of *K* allowing for just 23.1% of the ideal maximum feed concentration. Doubling that *K* value reduces the concentration to 6.5% of the maximum. These values will change with a different desired flux, since the ECP and ICP moduli are both functions of flux.

Asymmetric membrane in FO mode

In the FO mode, the draw solution on the support layer will be subjected to dilutive ICP, while the feed solution on active layer will be vulnerable to concentrative ECP. This is typical orientation for FO desalination or other osmotically driven membrane processes designed for water treatment.[18,19] To model flux in this mode, we use Eq. 8. If the feed is deionized water or very dilute, concentrative ECP will be negligible. For a nondilute feed solution, ECP will impact flux performance. Both of these scenarios are discussed individually later.

Simulating Flux in the FO Mode: Deionized Water Feed. Modeling flux in the FO mode normally incorporates the coupled effects of dilutive ICP and concentrative ECP. We can, however, examine dilutive ICP independently by first considering a deionized water feed. This evaluation is also reasonable for very dilute feed solutions. Figure 4 shows the flux performance of different membranes using a deionized water feed and draw solutions ranging in concentration from 0.05 to 1.5 M NaCl. Again, we observe the effect of changing membrane structural properties on flux performance. Lower *K* values improve flux due to the increased ability of the draw solute to diffuse into the porous support layer to replenish the diluted draw solution. However, as in Figure 3, there is a limit to flux improvement. As *K* gets small, the model assumption that no dilutive ECP is occurring on the support layer begins to fail and the dense membrane model is approached (solid line from Figure 2). Therefore, as earlier, the flux profile indicating the performance of a membrane with a *K* value one-tenth of that given in Table 1 does not exist for a real membrane.

Performance Assessment of the FO Mode: Deionized Water Feed. For these experimental conditions, performance is evaluated for each type of membrane by determining the driving force required to obtain a desired water flux set at 10 gfd (4.71 μm/s) (horizontal dotted line in Figure 4). Table 4 lists the required osmotic driving force (equivalent to the osmotic pressure of the draw solution alone since $\pi_{F,b} = 0$) for each membrane and compares it to the hydraulic driving force required to obtain a permeate flux of 10 gfd (4.71 μm/s) with pure water. A dense membrane in the presence of only dilutive ECP requires 1.4 times more driving force (provided by osmotic pressure) than pure water that is hydraulically driven. In the presence of ICP, the required driving force increases substantially. The driving force must be 3.4 times greater for

Table 3. Performance Data from Figure 3 (PRO Mode) for a Flux Set at 10 gfd (4.71 μm/s)

Membrane	Required $\pi_{F,b} - \pi_{D,b}$*, atm (psi)	Max. $\pi_{F,b}$, atm (psi)	% of Ideal
Ideal[†]	14.7[†] (216.1)	55.3 (812.9)	100
Dense	38.9 (571.8)	31.1 (457.2)	56.2
0.5 K	47.4 (696.8)	22.6 (332.2)	40.9
K	57.2 (840.8)	12.8 (188.2)	23.1
2K	66.4 (976.1)	3.6 (52.9)	6.5

Draw solution is fixed at 1.5 M NaCl (or 70 atm).
*Draw solution osmotic pressure is 70 atm.
[†]Based on deionized water feed under hydraulic pressure.

Table 4. Performance Data from Figure 4 (FO Mode) for a Flux of 10 gfd (4.71 μm/s)

Membrane	Required $\pi_{F,b} - \pi_{D,b}$*, atm (psi)	Ratio of Actual:Ideal Driving Force
Ideal	14.7 (216.1)	1
Dense	20.7 (304.3)	1.41
0.5 K	28.9 (424.8)	1.97
K	50.3 (424.8)	3.42
2K	190.5 (2798.4)	12.96

*Feed solution osmotic pressure is 0 atm.

the membrane described in Table 1. Increasing K two-fold and extrapolating from Figure 4 indicates that more than 190 atm of osmotic pressure (about 13 times the ideal driving force) is required to obtain the desired flux of 10 gfd. These results show that dilutive ICP has a considerable diminishing affect on effective driving force.

Simulating Flux in the FO Mode: Nondilute Feed. When salt is assumed to be in the feed solution at an appreciable concentration, concentrative ECP occurs, further reducing driving force and hence flux. Figure 5 shows model results, based on Eq. 8, assuming the draw solution is constant at 1.5 M NaCl and the feed solution is varied from 0 to 1.4 M NaCl. As in Figure 4, the dotted line is indicative of the dense membrane flux behavior (dotted line from Figure 2). This is the theoretical limit of flux under the specified conditions. As K approaches zero, dilutive ICP no longer

solely controls flux behavior since dilutive ECP effects are no longer negligible on the support side.

It should also be noted that in the presence of a nondilute feed solute, the differences in flux behavior between the different membranes are diminished. As the osmotic pressure of the feed solution is increased, decreased osmotic driving force reduces flux. Lower flux reduces the severity of ICP and hence the impact of K on flux behavior. The presence of concentrative ECP only increases the effective osmotic pressure of the feed solution, intensifying this effect.

Performance Assessment FO Mode: Nondilute Feed. Table 5 quantifies performance at a given permeate flux of 10 gfd or 4.71 μm/s (see horizontal dotted line in Figure 5). Since the draw solution concentration is set at 1.5 M NaCl, performance will be quantified by the maximum feed osmotic pressure that can exist at 10 gfd flux for a given membrane. When the fourth column of Table 5 is compared with the fourth column of Table 3 (both sets of data taken under the same sets of conditions except that the membranes are oppositely oriented), it is clear that the effects of dilutive
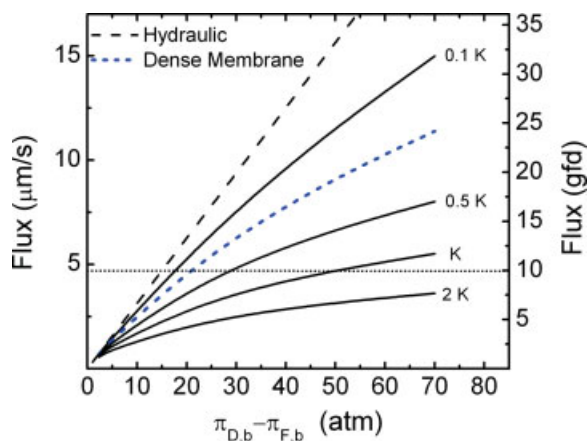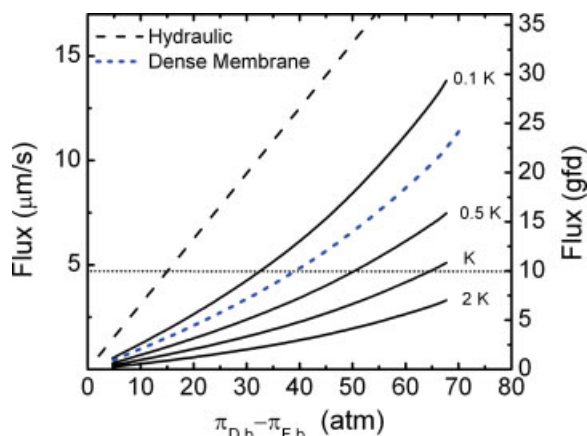

Figure 4. Flux modeled in the FO mode (dilutive ICP in the absence of concentrative ECP) for membranes with variable solute resistivity (from Eq. 8).

Some data taken from McCutcheon and Elimelech.[11] The line labeled ''K'' is indicative of the performance of a membrane with the FO value of K given in Table 1. The other values of K have been changed by the indicated factor. The dotted line is identical to the solid line from Figure 2 and indicates the performance of a dense membrane under the same conditions. Conditions: NaCl draw solution concentration ranging from 0.05 to 1.5 M, deionized water feed, and other conditions listed in Table 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5. Flux modeled in the FO mode (dilutive ICP coupled with concentrative ECP) for membranes with variable solute resistivity (from Eq. 8).

The line labeled ''K'' is indicative of the performance of a membrane with the FO value of K given in Table 1. The other values of K have been changed by the indicated factor. The dotted curved line is identical to the dotted line from Figure 2 and indicates the performance of dense membrane under the same conditions. Conditions: NaCl draw solution concentration of 1.5 M, feed concentrations ranging from 0 to 1.4 M NaCl, and other conditions listed in Table 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 5. Performance Data from Figure 5 (FO Mode) for a Flux of 10 gfd (4.71 μm/s)

Membrane	Required $\pi_{F,b} - \pi_{D,b}$*, atm (psi)	Max. $\pi_{F,b}$, atm (psi)	% of Ideal
Ideal[†]	14.7[†] (216.1)	55.3 (812.9)	100
Dense	20.7 (304.3)	31.1 (457.2)	56.2
0.5 K	28.9 (424.8)	20.2 (296.9)	36.5
K	50.3 (739.4)	5.6 (82.3)	10.1
2 K	>70 (>1029)	N/A	N/A

*Draw solution osmotic pressure is 70 atm.
[†]Based on deionized water feed under hydraulic pressure.

ICP are far more significant than the effects of concentrative ICP. At twice the provided value of K, even a deionized water feed cannot obtain 10 gfd (4.71 μm/s) under the constraints of the model for the FO mode, which is also apparent in Figure 4. This is due to the fact that dilutive ICP is impacting the concentrated draw solution, while concentrative ICP impacts the more dilute feed solution. Dilutive ICP therefore has a greater impact on overall driving force.

Implications for improved membrane design

Tailoring membranes for optimal performance in osmotic processes is critical for the future success of FO and PRO. In general, membranes used for osmotic processes should have high salt rejection, high water permeability coefficient, and lowest possible K value. If a membrane cannot be made without any support layer (i.e., $K = 0$), then the K value can be reduced by altering the membrane support layer by making it thinner and more porous (lower t and larger ε in Eq. 5). This is in contrast to RO membrane design, where the support layer has no effect on flux and can be made as thick as needed to provide mechanical strength. By designing new membranes in this fashion, osmotically driven membrane processes, such as PRO and FO, can be made more economically viable for power generation and desalination, respectively.

The use of PRO as a means of power generation near river deltas has been suggested for some time.[4,5] However, feedwater salinity significantly impacts the flux performance due to concentrative ICP as shown earlier. Any salt leakage through the membrane from the draw solution side will also contribute to ICP, further reducing flux. Tailored membranes with a thinner or more porous support layer, while maintaining a very high selectivity (or solute rejection), will reduce the prevalence of ICP and improve water flux, as suggested in Tables 4 and 5. Higher flux rates in PRO result in higher energy production per unit area of membrane. If the energy produced per unit area of membrane is increased adequately, capital expenditures for a PRO power plant will be reduced. Being economically competitive with current energy producing technologies, this renewable energy resource could produce electricity where any freshwater river or stream meets a saline water body.

Tailoring membranes for use in the FO process, such as for FO desalination, will improve the overall FO process in two ways. In FO desalination, such as that described by McCutcheon et al.,[8] the draw solute is recovered and recycled, yielding fresh water and a reconcentrated draw solution. This recovery process is where the vast majority of

the energy required for the overall FO process is consumed.[20] The concentration of this draw solution must be minimized to reduce the energy used by the solute recovery system. Unfortunately, the prevalence of dilutive ICP forces the use of highly concentrated draw solutions to obtain desired fluxes, as demonstrated by the results of this article. By reducing the prevalence of dilutive ICP, more dilute draw solutions can be used, thereby reducing the energy required to recover and reconcentrate the draw solute. This is also suggested in Table 4, where it is shown that less osmotic pressure is required for obtaining a desired flux for FO membranes tailored to have lower K. The second improvement is the increased recovery possible with tailored membranes. By reducing the prevalence of dilutive ICP, feedwaters with higher salinity can be treated with a given draw solute concentration, thereby improving the recovery of the FO desalination system. This is depicted in Table 5. Increased recoveries will reduce the volume of the brine discharge, which is the single most environmentally harmful byproduct of all desalination processes.

Concluding remarks

This investigation has quantified the impact of external and ICP on the osmotic driving force for both symmetric and asymmetric membranes. Permeate flux through both of these membranes was modeled for a variety of draw and feed concentrations at a set of specified experimental conditions. Water flux through asymmetric membranes was modeled in both the FO and PRO modes. It was determined that both ECP and ICP played major roles in the reduction of the osmotic driving force in both FO and PRO modes, though, in general, ICP impacted permeate water flux more. In the PRO mode, dilutive ECP was found to have a significant impact on the osmotic driving force when operated with a very dilute (or deionized) water feed. Water fluxes were sharply reduced for the PRO mode when the feed contained solutes. It was found that even in the presence of dilute feed solutions, concentrative ICP significantly reduced the effective osmotic driving force. In the FO mode, dilutive ICP was found to have a dramatic impact on the driving force due mostly to the fact that the phenomenon was acting on the concentrated draw solution. Concentrative ECP on the feed side was determined to have only a minor effect on driving force unless the feed concentration and/or the permeate flux was relatively high.

With asymmetric membrane flux modeling, the value of the solute resistance to diffusion, K, was varied to determine the impact of membrane design on flux performance. Smaller values of K yielded better flux performance due to reduced severity of ICP for membranes oriented in either the PRO or FO mode, though flux improvement was limited by ECP on both sides of the membrane as the value of K became small. The effect was most pronounced in the FO mode with a very dilute (or deionized water) feed, since dilutive ICP was the lone negative contributor to driving force. In both the PRO and FO modes with a nondilute feed, permeate water flux was less dependent on K since the existence of ECP reduced flux such that ICP was less severe. Overall, reducing K was found to significantly improve permeate water flux performance in either the PRO or FO mode. In both PRO and FO,

reduced K also allowed for higher salinity feedwaters to be used, indicating the possibility of higher feedwater recovery.

This study is intended to show the possible improvements in flux behavior and recovery that can be realized by designing membranes specifically for FO or PRO processes. These improvements may include making the support layer thinner or more porous. While flux is ultimately limited by ECP on either side of the membrane, there is still much room for improvement over current generation membranes used for FO in this and other studies. Improving the membrane would allow for better flux performance, higher feedwater recoveries, and lower energy use of the draw solute recovery thereby improving the economic viability and utility of a variety of osmotically driven membrane processes.

Acknowledgments

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