Modeling of external and internal concentration polarization effect on flux behaviour of forward osmosis
C. H. Tan and H. Y. Ng

ABSTRACT
The forward osmosis process has recently gained more interest from researchers and is being viewed as an alternative to various membrane processes. The primary challenge in developing the process is the severity of both external and internal concentration polarizations, which significantly reduce the water flux across the highly selective membrane. This study investigates the impact of concentration polarization on flux behaviour. A model adopted from the boundary layer concept was used to describe the external concentration polarization effect. A previously developed model for the internal concentration polarization was further improved from the governing convective-diffusion equations, to achieve a better transport model that was in excellent agreement with experimental flux data. Laboratory experiments were carried out to account for both the external and internal concentration polarization and the associated water flux was verified with the improved models. Results showed excellent agreement for both models, which were used to describe external and internal concentration polarization, and these modified models were more accurate than previously used models.

Key words | concentration polarization, forward osmosis, modeling

INTRODUCTION
While the demand for fresh water increases globally, the supply of fresh drinking water is limited. Water scarcity has led to many countries turning to water reclamation and seawater desalination. Membrane processes, particularly reverse osmosis (RO) is currently the most cost effective technology for seawater desalination. However, with the growing cost for energy, further reduction in energy is necessary to tap treated used water and seawater as a source of drinking water.

Recently, forward osmosis (FO) has been studied for seawater desalination. The low energy cost and high recovery of this process is remarkable as demonstrated by McCutcheon & Elimelech (2006). The FO process utilizes a draw solution that has a higher osmotic pressure than the feed solution and this osmotic pressure gradient across a highly-selective membrane results in water flux across the membrane. Various draw solution at high concentration can have exceedingly large osmotic pressure, potentially leading to a much high water flux and recoveries compared to the more expensive RO process.

Recently, McCutcheon et al. (2005) presented a novel ammonia-carbon dioxide FO process for seawater desalination and a pilot plant was set up (Elimelech 2007). FO process had also been developed by Holloway et al. (2007) for the concentration of anaerobic digester concentrate with much success. It is also currently being used for landfill leachate treatment and is also being actively used as a direct osmotic concentration of liquid food (Cath et al. 2006). More recently, Tang & Ng (2007) proposed to use the FO process for brine concentration for brine disposal.

Just like all other membrane technologies, the FO process suffers from concentration polarization. This is due to the FO process requiring two solutions on both sides of the membrane for osmosis to take place. With existing FO
membrane, the FO process suffers from severe internal concentration polarization. The above mentioned effect cannot be mitigated by adjustments to process operation external of the membrane as its impact is inherent to the membrane itself. McCutcheon et al. (2006) suggested using the Film Theory to model the external concentration polarization for the FO process, and Gray et al. (2006) and McCutcheon & Elimelech (2006) had also suggested using a previously developed model to describe the internal concentration polarization for the FO process. However, at higher water flux and higher concentration for the draw solution, there is a need to develop a more robust and accurate model for both the internal and external concentration polarization layer. It is essential to have a more accurate model for flux prediction for process optimization, fouling studies, determining possible draw solutes with high osmotic pressure, treating potential feed streams, etc.

The objectives of this study are to investigate the effect of external and internal concentration polarization on the FO process. By using the boundary layer concept, the external concentration polarization (ECP) layer can be analyzed under different flow regimes. Governing equations for the internal concentration polarization (ICP) layer are extended to include the variation of the diffusion coefficient for the feed/draw solute within the ICP layer. Water fluxes are then predicted, with both ECP and ICP correction, and then tested against experimental results.

MATERIALS AND METHODS

Feed and draw solutions

The feed and draw solutions with different NaCl concentrations were prepared using deionized water. The feed solution used in the experiments is either deionized water or 0.5 M NaCl, which simulates seawater. The draw solution concentration used in all the experiments ranged from 0.1 to 2 M NaCl. Solution properties, particularly osmotic pressure, viscosity, density and diffusion coefficient, were calculated using the software, StreamAnalyzer 2.0 (OLI systems Inc., Morris Plains, NJ). NaCl was the only solute used in this investigation since its properties are well characterized by the software.

FO membrane and membrane orientation

The FO membrane (Hydration Technologies Inc., Albany, OR) used is made from cellulose acetate and is highly hydrophilic. It consisted of a porous support mesh embedded within the membrane. The detailed description and SEM images of the membrane are provided elsewhere (Ng et al. 2006). The transport phenomenon for the FO process is shown in Figure 1. From Ng et al. (2006), Figure 1 shows the membrane orientation for the FO process. The first mode (Figure 1a) is the normal mode for FO operations, whereby the

![Figure 1](https://iwaponline.com/ies/article-pdf/8/5/533/418987/533.pdf)
active layer of the membrane faces the draw solution while the porous layer faces the feed solution. The second mode (Figure 1b) is subsequently named the reverse mode.

**Experimental setup**

Figure 2 shows a schematic diagram of the laboratory-scale unit used in this study. Two specially designed cross-flow membrane cell has a symmetric channel on each side of the membrane. For each channel, the dimensions are 2, 250, and 30 mm for channel height, length and width, respectively. The draw and feed solutions flowed on the permeate side and co-currently on the feed side, respectively, both of which were controlled independently by a centrifugal pump (Cole-Parmer, Barrington, IL) and a flow-meter (Blue-white Industries Ltd, USA) and the volumetric flow-rates for the experiments varies from 1.0–4.4 L/min. Both the feed and draw solutions were kept homogenous by 2 independent mechanical stirrers. A weighing scale (SB16001, Mettler Toledo, Germany) connected to a computer with a recording software was used to monitor the weight changes of the draw solution due to the water flux across the membrane.

**Modeling concentration polarization and flux prediction**

The water flux, \( J_w \) in the FO process is based on the differential flux across the membrane and is typically represented by the osmotic-pressure model, given as

\[
J_w = A(\pi_{db} - \pi_{fb})
\]

where \( A \) is the pure water permeability coefficient, and \( \pi_{db} \) and \( \pi_{fb} \) are the bulk osmotic pressures for the draw and the feed solution, respectively. Both ECP and ICP have significant impacts on the FO process as they extensively reduce the effective osmotic pressure across the membrane (Figure 1).

**The external concentration polarization layer**

The ECP layer had been well characterized by various researchers. However, no one Sherwood relationship used for the calculation of the mass transfer coefficient of the ECP layer could accurately describe for all systems (Gekas & Hallström 1987). The boundary layer concept and the appropriate Sherwood relationships are used to account for this phenomenon in the FO process.

For fluid flow through a rectangular channel, whereby the hydrodynamic boundary-layer thickness is significantly smaller than the height of the flow channel, it is appropriate to adopt the boundary layer concept for the prediction of the mass transfer coefficient within the concentration boundary layer (Welty et al. 2000). The local mass-transfer coefficient for a concentration boundary layer formed over a flat plate channel has been correlated in terms of a local Sherwood number, \( Sh \), by

Laminar boundary layer (\( Re_y \leq 2 \times 10^5 \))

\[
Sh = 0.332 Re_y^{1/2} Sc^{1/5}
\]  
(2)

Turbulent boundary layer (\( Re_y > 2 \times 10^5 \))

\[
Sh = 0.0292 Re_y^{4/5} Sc^{1/3}
\]  
(3)

where \( Re_y \) is the local Reynolds number at \( y \) distance downstream of the leading edge of the channel head and \( Sc \) is the Schmidt number. The mass transfer coefficient, \( k \), is related to \( Sh \), by

\[
k = \frac{ShD}{d_b}
\]  
(4)

where \( D \) is the solute diffusion coefficient and \( d_b \) is the hydraulic diameter. The mean mass transfer coefficient, \( k_c \), which applies over a plate of width \( W \) and length \( L \), may be obtained by integrating both Equations 2 and 3 to give Equation 5.

\[
k_c = \frac{0.664D(Re_t)^{1/2}(Sc)^{1/3} + 0.0365D(Sc)^{1/3}[((Re_t)^{4/5} - (Re_t)^{4/5})]}{L}
\]  
(5)

where \( Re_t \) corresponds to the transition from laminar to turbulent flow. With the mass transfer coefficient, \( k_c \), the
dilutive ECP modulus can be calculated for a given permeate flux, \( J_w \), using
\[
\frac{C_{d,w}}{C_{d,b}} = \exp\left( \frac{J_w}{K_t} \right)
\]  
(6)
For concentrative ECP modulus, it will be defined as
\[
\frac{C_{d,w}}{C_{d,b}} = \exp\left( \frac{J_w}{K_t} \right)
\]  
(7)

Osmotic pressure and diffusion coefficient as a function of NaCl concentration

At higher solute concentrations, osmotic pressures do not vary linearly with concentrations. The diffusion coefficients of Na\(^+\) and Cl\(^-\) ions, calculated using the OLI software, are obtained and the average salt diffusivity is calculated as follows (Cussler 1997):
\[
D_{\text{avg}} = \frac{\left( |Z_i| + |Z_j| \right)}{\left( |Z_i| + |Z_j| \right)}
\]  
(8)
where \( D_{\text{avg}} \) is the overall diffusion coefficient for the electrolyte in water, \( Z_i \) is the cation/anion charge, and \( D_i \) is the cation/anion diffusion coefficient in water. These empirical correlations for diffusivities at 30°C are then used to facilitate the modeling of the concentration polarization layer and the prediction of flux as shown below:

For \( 0 \leq C < 0.5 \),
\[
D_{\text{avg}} = -6.73e^{-8}C^5 + 9.84e^{-8}C^4 - 5.40e^{-8}C^3
\]
\[+ 1.39e^{-8}C^2 - 1.88e^{-9}C + 1.71e^{-9} \]  
(9)
For \( 0.5 \leq C \leq 2 \),
\[
D_{\text{avg}} = 6.67e^{-12}C^2 - 1.33e^{-10}C + 1.71e^{-9}
\]  
(10)

The internal concentration polarization layer

When either the feed or the draw solution is placed against the porous layer of the FO membrane, the solute can enter and exit the porous layer of the membrane via convective water flux and direct diffusion. Since the solute cannot penetrate the selective layer of the membrane easily, it will result in a concentration polarization layer within the internal structure of the porous layer of the membrane.

An earlier work by Lee et al. (1981) derived an equation for the calculation of the concentrative ICP modulus in the pressure-retarded osmosis (PRO). Subsequently, Loeb et al. (1997) used the modified form of the equations for dilutive and concentrative ICP, which McCutcheon et al. (2006) used to describe for the FO process. \( K \), the solute resistivity for diffusion within the porous support layer, is given as
\[
K = \frac{t \tau}{D_e}
\]  
(11)
where \( t \) is the thickness, \( \tau \) is the tortuosity of the porous layer, and \( e \) is the porosity of the porous layer. However, \( K \) might not be a constant, due to the fact that the diffusion coefficient is not a constant at a large solute concentration difference. An expression for the ICP modulus has been developed from the governing equations in this study.

The solute flux, \( J_s \), across the porous support layer for dilutive ICP can be written as
\[
-J_s = B(C_{d,w} - C_{l,w})
\]  
(12)
where \( B \) is the salt permeability constant of the membrane. Using the governing convective-diffusion equation, the solute flux can also be written as
\[
-J_s = \varepsilon \frac{dD_{C(x)}C(x)}{dx} - J_wC(x)
\]  
(13)
It is noted that the diffusion coefficient for the solute is a function of concentration of solute at distance \( x \). The distance \( x \) is measured from the membrane active layer to the porous layer interface with the bulk solution. Combining Equations 12 and 13 yield
\[
B(C_{d,w} - C_{l,w}) = \varepsilon \frac{dD_{C(x)}C(x)}{dx} - J_wC(x)
\]  
(14)
The appropriate boundary conditions are
\[
C(x) = C_{d,w} \quad \text{at} \quad x = 0
\]
\[
C(x) = C_{d,b} \quad \text{at} \quad x = \tau
\]
Under the boundary conditions and at negligible salt flux across the membrane, i.e. \( B = 0 \), the separable differential
equation can be solved to give

For \(0 \leq C < 0.5\),

\[
K^* = \frac{G_1}{f_w}(C_{d.b} - C_{d.w}) + \frac{G_2}{f_w}(C_{d.b}^2 - C_{d.w}^2) + \ldots + \frac{G_5}{f_w}(C_{d.b}^5 - C_{d.w}^5) + \frac{G_6}{f_w} \ln \left( \frac{C_{d.b}}{C_{d.w}} \right)
\]

For \(0.5 \leq C \leq 2\),

\[
K^* = \frac{H_1}{f_w}(C_{d.b} - C_{d.w}) + \frac{H_2}{f_w}(C_{d.b}^2 - C_{d.w}^2) + \frac{H_3}{f_w} \ln \left( \frac{C_{d.b}}{C_{d.w}} \right)
\]

where \(K^* = (t/\eta)\), and \(G_n\) and \(H_n\) are constants associated with the diffusivity coefficients. We can observed that \(K^*\) is a constant of the ICP modulus for this membrane, independent of the diffusion coefficients. In an analogous manner, the equations for concentrative ICP can also be developed.

Flux prediction for the FO process

Following the derivation of both the ECP and ICP modulus, \(f_w\) across the membrane can be predicted with known values of the concentrations for both the bulk feed and draw solutions, temperature associated solutions constants and cross-flow flow-rates. The \(K^*\) of the ICP modulus and \(A\) of the membrane have to be determined experimentally. Thereafter, Eq. 1, 7, 15 and 16 can be combined, and then to be solved for the FO operation in normal mode using an iterative software. Fluxes calculated are then compared with experimental results.

RESULTS AND DISCUSSION

Effects of external concentration polarization on flux behaviour

Experiments are conducted in the normal mode and deionized water is used as the feed solution. Figure 3 presents the flux data plotted against the bulk osmotic pressure difference between the feed and draw solutions at 30°C. As expected, water flux increased at increasing osmotic pressure difference. However, the effect of ECP at higher concentration of the draw solution is more severe.

Equations 5 and 6 are applied to calculate the concentration of NaCl at the wall of the active layer on the draw side of the membrane, \(C_{d.w}\). Figure 4 is the revised data corrected for dilutive ECP. The slopes of these lines matched the pure water permeability, \(A\), of the membrane at 30°C. Modeling of the flows in both laminar and turbulent regimes is necessary to test the robustness of the equations developed for the ECP modulus. By the boundary layer concept, the flux data after ECP correction matched the pure water permeability data closely at both lower and higher cross-flow velocities. Therefore, it is appropriate to use the equations developed from the boundary layer concept for subsequent ECP modeling.
Effects of internal concentration polarization on flux behaviour

Firstly, the membrane permeability constant can be found using the RO experiment and the water permeability constant, A, at 30°C was found to be 4.00 \times 10^{-7}. Figure 5 shows the flux data for experiments carried out in the reverse mode, which facilitated the investigation of the dilutive ICP modulus. It can be observed that changes in the cross-flow velocities did not affect the water flux across the membrane. By using Equations 15 and 16, the average $K_p$ was found to be $2.75 \times 10^{-4}$ m.

With the average $K_p$ value, water fluxes at varying draw solution concentration were predicted using Equations 1 and either 15 or 16, via a regression method. The predicted fluxes are compared with the experimental water fluxes at a volumetric cross-flow rate of 1.5 L/min. An excellent agreement was observed in the results obtained from theoretical prediction and the experimental runs. This suggests that the $K_p$ value found had allowed an excellent prediction of water flux at different draw concentrations. Hence the effect of the ICP modulus is well accounted for.

In order to demonstrate that the modified model for ICP developed in this study was a significant improvement over the model developed previously, a comparison of the flux data was made using both the ICP models. The flux data predicted from the old model was also plotted in Figure 6. The results showed that the old model had overestimated the corresponding water flux at each osmotic pressure due to the fact that a fixed constant for the diffusivity coefficient was used for the constant $K$.

Modeling the effects of external and internal concentration polarization and flux prediction

The effects of both the ECP and ICP were investigated concurrently by simulating seawater as the feed water using 0.5 M NaCl and increasing NaCl concentrations on the draw side in normal mode. With this, concentrative ICP and dilutive ECP would occur. Results of the flux data are plotted in Figure 7. A comparison was made between the experimental data and the predicted flux. The predicted fluxes were the iterative solutions of Equations 1, 7, 15 and 16 concurrently. The comparison shows that mathematical modeling of the water flux at various feed/draw concentrations and cross-flow velocities had provided an almost exact replication of the experimental flux.
CONCLUSION

In this paper, both the effects of ECP and ICP were investigated separately for the FO process. Together with experimental results, it had been shown that the boundary layer concept as opposed to film theory could be used to model the ECP effects in both laminar and turbulent boundary layer regimes. New equations were developed from the convective-diffusion governing equations to account for the changes in diffusion coefficient of the solute. The equations were then used to describe the ICP layer with a constant $K^+$, which is unique for each type of membrane. Experiments were carried out to account for both ECP and ICP modulus in tandem and the developed equations were used for flux predictions. The predicted fluxes were then compared with the experimental flux data and the results showed that the predicted fluxes were in excellent agreement with the experimental data. This implies that the modified models developed for both ECP and ICP can be used to predict accurately the actual water flux data for the FO process and have significant improvements over previous models used in FO modeling.

REFERENCES


