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Internal concentration polarization in forward osmosis: role of membrane orientation

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Abstract

The mechanisms governing internal concentration polarization (ICP) were studied using well-controlled forward osmosis experiments. The relationship between osmotic pressure and water flux was observed across a range of solute concentrations and molecular weights. The effect of membrane orientation on ICP was also studied. Two regimes of ICP — dilutive and concentrative — were described and characterized, and their governing equations were tested. Resistances to solute diffusion within the membrane porous support layer were calculated under each regime and found to be consistent across a wide variety of experimental parameters.

Keywords: Forward osmosis; Direct osmosis; Internal concentration polarization; Osmosis; Desalination; Draw solution

1. Introduction

While pressure-driven membrane processes such as reverse osmosis (RO) have dominated for several decades, new processes are now emerging that are driven by forward osmosis (FO). Several nascent applications based on FO could be of strategic importance in the coming decades. Foremost among these is a novel process for saline water desalination, which may outperform reverse osmosis (RO) both economically and environ-

mentally [1,2]. Additionally, pressure-retarded osmosis (PRO), a derivative process of FO, has been proposed as a clean and renewable source of energy [3].

Forward osmosis is similar to RO in that water transports across a semi-permeable membrane that obstructs transport of the solute. But instead of the hydraulic pressure difference by which RO is driven, FO uses an osmotic pressure gradient to drive water transport through the membrane. The “draw” solution, which is on the permeate side of the membrane, has a significantly higher osmotic

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pressure than the feed solution on the opposite side. Water naturally transports from the feed to the draw solution by osmosis.

Both FO and RO are accompanied by external concentration polarization (CP) at the surface of the active layer of the membrane. The concentration of the solution at the membrane surface differs from that of the bulk solution, such that water flux is reduced. This phenomenon is well understood and has been extensively modeled [4], and its effects can be largely mitigated by increasing the shear rate and turbulence of flow across the membrane.

Internal concentration polarization (ICP) is a closely-related phenomenon, but is exclusive to FO. ICP occurs within the support layer of the membrane, and is characterized by differing solute concentrations at the transverse boundaries of that layer. The result is a reduction in the osmotic pressure gradient across the active layer of the membrane and a corresponding reduction in water flux. The earliest FO studies identified ICP as a key performance-limiting phenomenon, capable of reducing water flux by more than 80% [5]. Critically, because ICP occurs within the membrane, water flux decline cannot be mitigated by altering hydrodynamic conditions.

This intractability of ICP intensifies the need to better understand the phenomenon. Due to the historical preeminence of RO, ICP has received far less scrutiny than external CP. Lee et al. [6] developed the basic governing equations of ICP, in the context of pressure-retarded osmosis. These equations were later adapted and applied to FO by Loeb et al. [7].

The objective of this paper is to further develop this understanding of ICP through well-controlled experiments involving an FO-designed membrane and solutes of varying molecular weights. The mechanisms governing ICP are illuminated and previously developed governing equations are tested.

2. Materials and methods

2.1. FO membrane

The FO membrane used for all experiments was provided by Hydration Technologies (Albany, OR). The membrane chemistry and synthesis are proprietary, but the membrane is believed to be made of cellulose acetate [2]. A woven fabric mesh appears to be embedded within the porous support portion of the membrane. Other properties of the membrane as well as areal and cross sectional SEM images verifying the asymmetric structure of the membrane are provided in our recent publications [1,2].

2.2. Feed and draw solutions

Deionized water was used to prepare the sodium chloride, dextrose, and sucrose solutions. These solutes were used as draw solutions for the FO experiments with deionized water being used as a feed. In one set of experiments, 0.5 M NaCl was used as a draw solution while the feed solution varied from deionized water to 0.375 M NaCl. All solutions used were at ambient pH (5.6–5.8). The osmotic pressures of the various solutions were calculated using software from OLI Systems, Inc. (Morris Plains, NJ) and Aspen HYSYS® (Cambridge, MA).

2.3. FO test unit and procedures

The membrane unit is a SEPA cell from GE Osmonics (Trevose, PA), which accepts flat sheet membranes. It has been modified to have symmetric channels on both sides of the membrane [1,2]. Plastic mesh spacers in both channels support the membrane, and also serve to increase turbulence and reduce external concentration polarization on both sides of the membrane. The draw solution is flowing on the permeate side and feed solution (deionized water in most experiments) is flowing cocurrently on the feed side. Both solutions flow in closed circuits via plastic tubing. Two types of pumps were used for moving

the solution through the system: peristaltic pumps from Manostat (Barrington, IL) and gear pumps from Cole-Parmer (Vernon Hills, IL). Flowmeters measured the volumetric flow rates, which were fixed at 1.5 liter per minute (corresponding to a crossflow velocity of 30 cm/s) for the feed and draw solution sides. Both the draw and feed solutions flow through the same constant temperature water bath (Neslab, Newington, NH) in order to control the temperature of both solutions at $22.5 \pm 1.5^\circ\text{C}$. The draw solution reservoir rests upon a balance from Ohaus (Pine Brook, NJ). A more detailed description of the membrane test unit and experimental methods is given by McCutcheon et al. [1,2].

Water flux is determined by measuring the rate at which the weight of the draw solution increases. Because the apparatus operates in a closed loop, the draw solution concentration and therefore the water flux decrease throughout the experiment. This is mitigated by taking data before dilution becomes significant.

3. Results and discussion

3.1. Effect of solute type against the active layer

The performance of forward osmosis in the absence of internal concentration polarization can be observed by placing the draw solution against the active layer of the membrane and using a deionized water feed solution. FO experiments were conducted under these conditions for three solutes of varying molecular weight — sodium chloride (58 g/mol), dextrose (180 g/mol), and sucrose (342 g/mol). Additionally, hydraulic permeability experiments with the FO membrane and DI water feed were conducted using a crossflow RO configuration under varying hydraulic pressures. The results are shown in Fig. 1.

It is evident that in the absence of ICP, the molecular weight of the solute has a negligible impact on performance. Furthermore, flux varies linearly with osmotic pressure. Both of these ob-

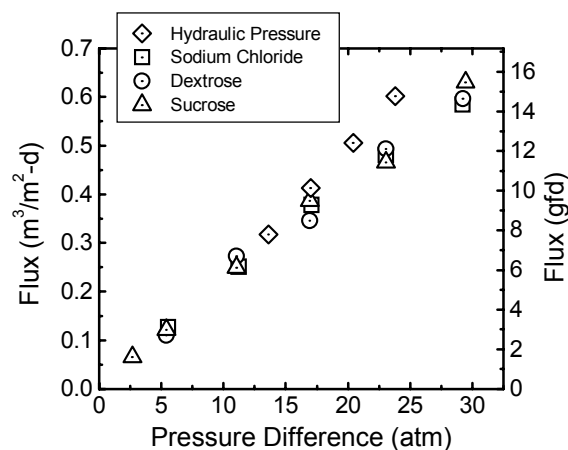


Fig. 1. Water flux as a function of driving force (pressure difference). For the FO runs with the three draw solutions, the osmotic pressure difference is generated by varying the draw solution concentrations. Draw solution is placed against the membrane active layer while the feed (deionized water) is placed against the support layer. Also presented are data points (open diamonds) for pure water flux against pressure (hydraulic) difference obtained in an RO type experiment with the same membrane. Experimental conditions: crossflow velocity and temperature of both feed and draw solutions of 30 cm/s and $22.5 \pm 1.5^\circ\text{C}$, respectively. Note that a water flux of $1 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ corresponds to $24.5 \text{ gal ft}^{-2} \text{ d}^{-1}$ (gfd) or $41.7 \text{ l m}^{-2} \text{ h}^{-1}$.

servations indicate that while external concentration polarization does occur in these FO experiments, its effect is very small because the permeate water fluxes are relatively low [2]. Note that in this case, external concentration polarization refers to the dilution of the draw solution against the active layer surface on the permeate side of the membrane. Calculation of external CP for such FO experiments has been described in McCutcheon et al. [2]. Another indication that ICP is absent in the FO runs shown in Fig. 1 is that the RO pure water permeability data has nearly the same slope as the FO data, except at higher water fluxes where the slight deviation is attributed to the external CP.

3.2. Effect of solute type against the support layer

By reversing the membrane orientation in the above experiments, internal concentration polarization becomes substantial. The solute in the draw solution must penetrate the porous support layer to the interior surface of the active layer before flux can occur. As water flux crosses the active layer into the support layer, the solute is diluted due to convection. The solute diffuses back to the interior surface. A steady-state is quickly reached, but the concentration at the interior surface of the active layer is far lower than in the bulk draw solution, as schematically shown in Fig. 2a. This will be referred to as “dilutive ICP”.

Therefore, both the draw solution concentration and the molecular weight (or diffusivity) of the solute should affect the water flux. Larger molecular weight solutes cannot diffuse as quickly through the porous support of the membrane, and dilutive ICP will be more severe, resulting in lower flux. This is confirmed experimentally, as shown

in Fig. 3. Indeed, sodium chloride (molecular weight 58 g/mol) generates far more flux than dextrose (molecular weight 180 g/mol) at the same bulk osmotic pressure, which in turn generates more than sucrose (342 g/mol). Furthermore, the relationship between concentration and water flux is now logarithmic, rather than linear. In this configuration, ICP becomes more severe as concentration and flux increase.

Both external and internal CP could be responsible for the trends observed in Fig. 3, but external CP was already shown to be relatively minimal in Fig. 1 as well as in other FO studies [2]. Therefore, it is certain that ICP is dominant when the draw solution is against the support layer, and solely responsible for the observations in Fig. 3. The effect of ICP is indeed very detrimental: a 1.02 M sucrose draw solution (or 29.4 atm bulk osmotic pressure) against the support layer generates just 23% of the flux it would generate against the active layer.

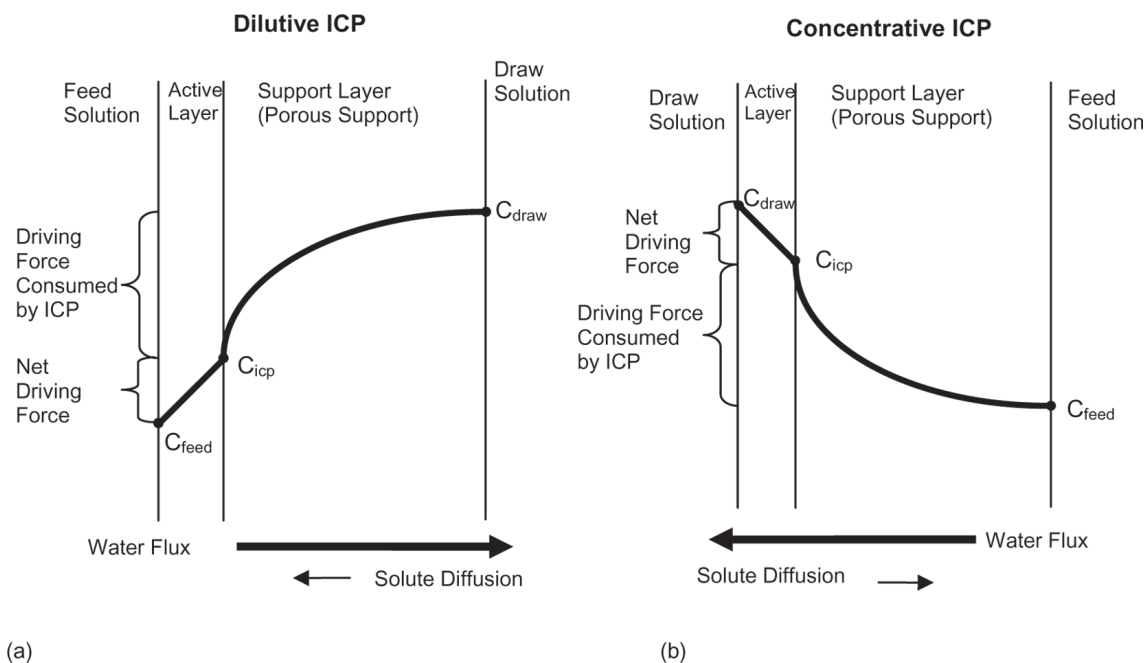


Fig. 2. Schematic representation of (a) dilutive internal concentration polarization (ICP) and (b) concentrative internal concentration polarization (ICP).

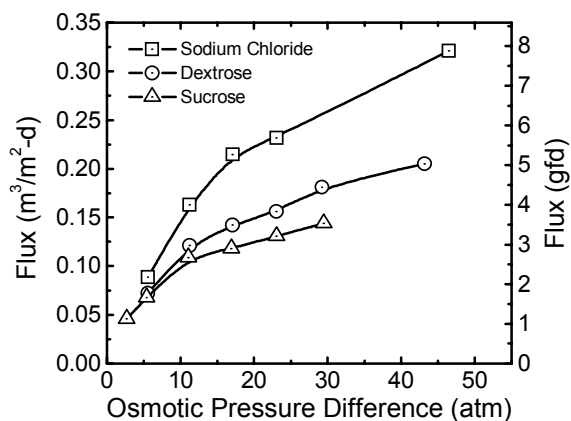


Fig. 3. Flux data for a variety of draw solution concentrations. Draw solution is placed against the support layer of the membrane and feed (deionized water) is placed against the active layer. The water flux is presented as a function of the difference in bulk osmotic pressures generated by the respective draw solutions. Experimental conditions: crossflow velocity and temperature of both feed and draw solutions of 30 cm/s and $22.5 \pm 1.5^\circ\text{C}$, respectively. Note that a water flux of $1 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ corresponds to $24.5 \text{ gal ft}^{-2} \text{ d}^{-1}$ (gfd) or $41.7 \text{ l m}^{-2} \text{ h}^{-1}$.

3.3. Effect of membrane orientation for NaCl feed and draw solutions

Internal concentration polarization can also arise when the draw solution is placed against the active layer and a feed solution (not deionized water) against the porous support layer. In contrast to the previous case, the water flux crossing from the support layer through the active layer causes the solutes against the interior surface of the active layer to become more concentrated. This is counteracted by back-diffusion away from the active layer, but the steady state concentration is much higher than in the bulk feed solution, as shown in Fig. 2b. This will be referred to as “concentrative ICP”. It is this type of internal concentration polarization that has received the most attention in literature, especially studies on pressure retarded osmosis [3,5,6].

The difference between the two types of internal concentration polarization can be seen in

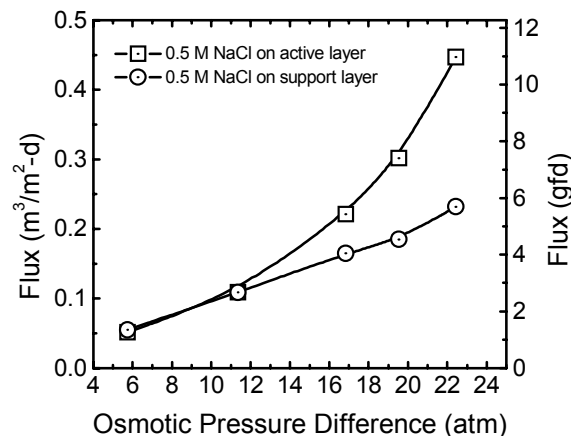


Fig. 4. Water flux data for 0.5 M NaCl draw solution and a variety of NaCl feed solutions ranging from deionized water to 0.375 M. In one set of experiments (open squares) the 0.5 M NaCl draw solution is placed against the active layer of the membrane while in another set of experiments (open circles) the 0.5 M NaCl draw solution is placed against the support layer of the membrane. The water flux is presented as a function of the difference in bulk osmotic pressures of the draw and feed solutions. Experimental conditions: crossflow velocity and temperature of both feed and draw solution of 30 cm/s and $22.5 \pm 1.5^\circ\text{C}$, respectively. Note that a water flux of $1 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ corresponds to $24.5 \text{ gal ft}^{-2} \text{ d}^{-1}$ (gfd) or $41.7 \text{ l m}^{-2} \text{ h}^{-1}$.

Fig. 4. For both sets of experiments, the draw solution was held at a constant concentration of 0.5 M NaCl. Feed solution concentrations varied from 0.375 M NaCl to deionized water, corresponding to net bulk osmotic pressure differences of 6 and of 23 atm, respectively.

When the draw solution is against the support layer, dilutive ICP occurs. Varying the concentration of the feed solution produces a linear relationship between net osmotic pressure and flux. Note that this is in contrast to the previous section, in which varying the draw solution produced a non-linear relationship. In this case, the dilutive ICP acts to reduce the slope of this line.

When the draw solution is against the active layer, concentrative ICP occurs. Now, a non-linear relationship between bulk osmotic pressure

difference and flux exists. Note that at a net osmotic pressure of 23 atm (corresponding to DI water as feed), no ICP of any kind is occurring, and the flux is very high. As concentration in the feed increases, concentrative ICP occurs, causing flux to decrease rapidly and nonlinearly.

3.4. Quantitative analysis of internal CP

It is clear that the orientation of the membrane can have a significant influence on water flux. Loeb et al. [7] observed the opposite, showing the same relationship between flux and osmotic pressure driving force exists, regardless of orientation:

$$J_w = K \ln \frac{\pi_{\text{Hi}}}{\pi_{\text{Low}}} \quad (1)$$

where J_w is the water flux, π_{Hi} and π_{Low} are the osmotic pressures of the draw and feed solutions, respectively, and K is the resistance to solute diffusion within the membrane porous support layer. The equation is a simplified form derived from an earlier work by Lee et al. [6] for concentrative ICP. This equation is valid when water flux is very small, but this was not so for the membrane we tested. Thus, for the wider range of the water fluxes described in our results, the more complete forms of the governing equations are required.

Here we use the following equations presented by Loeb et al. [7] for dilutive and concentrative ICP, respectively:

$$K = \left(\frac{1}{J_w} \right) \ln \left(\frac{B + A\pi_{\text{Hi}}}{B + J_w + A\pi_{\text{Low}}} \right) \quad (2)$$

$$K = \left(\frac{1}{J_w} \right) \ln \left(\frac{B + A\pi_{\text{Hi}} - J_w}{B + A\pi_{\text{Low}}} \right) \quad (3)$$

where A and B are the water and solute permeability coefficients of the active layer of the mem-

brane, respectively. To use these equations, separate RO experiments were used with our FO membrane to calculate the constants A (0.027 m/atm-d) and B (0.011 m/d).

We use Eqs. (2) and (3) to determine the K values — that is, the resistances to diffusion within the membrane porous support layer — for the various solutes (NaCl, dextrose, and sucrose) using the experimental data presented earlier in Figs. 3 and 4. Applying these equations to NaCl yields an average K value of 4.14 d/m, with a standard deviation of 0.56 d/m, as summarized in Table 1. The relatively small standard deviation of K indicates that Eqs. (2) and (3) adequately characterize this system. Similarly, the K values for dextrose and sucrose were determined from the data shown in Fig. 3 and Eq. (2) for dilutive ICP, yielding values of 8.98 and 12.13 d/m, respectively. For these calculations, B was assumed to be negligible due to the near complete membrane rejection of sugars.

For a given solute, the determined K values for the various water fluxes and osmotic pressure driving forces were comparable. Furthermore, for the case of NaCl, similar K values were obtained for dilutive and concentrative ICP. These results confirm that Eqs. (2) and (3) can adequately describe our FO experiments. Lastly, when examining the K values for the various solutes we see that they are inversely proportional to the diffusion coefficient of the solutes as summarized in Table 2. This is in accord with the definition of K [6]:

$$K = \frac{t\tau}{\epsilon D_s} \quad (4)$$

where t is the membrane thickness, τ is the tortuosity of the membrane porous support layer, ϵ is porosity of the porous support layer, and D_s is the diffusion coefficient of the solute. Because t , τ , and ϵ are fixed for our FO membrane, K is dependent only on D_s .

Table 1

Summary of experimental flux data, corresponding bulk osmotic pressures (π), and calculated K values for the experiments with NaCl depicted in Figs. 1, 3, and 4. Note that “AL” refers to the membrane active layer while “SL” refers to the membrane support layer.

Experimental description	π at AL atm (psi)	π at SL atm (psi)	J_w m/d (gfd)	K (d/m)
Draw solution (NaCl) varies from 0.125 to 1.0 M and is against the support layer. Feed solution is deionized water.	0 (0)	46.62 (684.84)	0.321 (7.88)	4.26
	0 (0)	22.44 (329.60)	0.232 (5.69)	4.15
	0 (0)	16.70 (245.31)	0.215 (5.27)	3.47
	0 (0)	11.08 (162.77)	0.163 (4.01)	3.72
	0 (0)	5.58 (82.02)	0.089 (2.18)	5.37
Draw solution is a constant 0.5 M NaCl against the active layer. Feed solution varies from 0.0625 to 0.375 M NaCl.	22.43 (329.6)	2.88 (42.32)	0.302 (7.41)	4.52
	22.43 (329.6)	5.58 (82.02)	0.221 (5.42)	4.25
	22.43 (329.6)	11.08 (162.77)	0.109 (2.68)	4.65
	22.43 (329.6)	16.70 (245.31)	0.051 (1.26)	4.04
Draw solution is a constant 0.5 M NaCl against the support layer. Feed solution varies from 0.0625 to 0.375 M NaCl.	2.88 (42.32)	22.43 (329.6)	0.185 (4.54)	4.53
	5.58 (82.02)	22.43 (329.6)	0.165 (4.05)	3.96
	11.08 (162.77)	22.43 (329.6)	0.109 (2.68)	3.62
	16.70 (245.31)	22.43 (329.6)	0.055 (1.34)	3.32

Table 2

Calculated K values for the three solutes based on the experimental data presented in Figs. 3 and 4 and Table 1. The diffusion coefficients for sucrose and dextrose are from [8] and for NaCl from [9].

Solute	Molecular weight (g/mol)	Diffusivity (m ² /s)	K (d/m)
NaCl	58	1.61×10^{-9}	4.14
Dextrose	180	0.67×10^{-9}	8.98
Sucrose	342	0.52×10^{-9}	12.13

4. Conclusion

The two regimes in which internal concentration polarization can occur were defined: dilutive and concentrative. Membrane orientation was shown to have a significant impact on performance due to the differences in these regimes. Because the optimal membrane orientation in forward osmosis depends on the application, it is

important to understand the difference between the two types of ICP.

The simplified governing equations presented in this paper were found to adequately model ICP. Having calculated the K value for a membrane and solute, the equations can predict performance across a broad range of experimental conditions. Furthermore, the increase in calculated K values for larger molecular weight solutes accounts for the observed decrease in water flux. Minimizing this K value is critical to improving the performance of forward osmosis processes, and this should be a primary objective for FO membrane manufacturers.

Acknowledgments

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