# THE PENNSYLVANIA STATE UNIVERSITY MILLENNIUM SCHOLARS PROGRAM

# DEPARTMENT OF BIOLOGY

# MODELING NON-IDEAL FORWARD OSMOSIS PROCESSES WITH NOVEL DRAW SOLUTES

# SACHIRA DENAGAMAGE SPRING 2017

A thesis submitted in partial fulfillment of the requirements for a baccalaureate degree in Biology

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#### ABSTRACT

Forward osmosis desalination is a promising technology for tackling the lack of access to freshwater that much of the world population faces. However, there is a significant need for new low-cost, non-toxic draw solutes that can generate large osmotic pressures. An accurate computational model would be indispensable in the development of such draw solutes, as it would shed insight into how best to optimize their structure. Here, a computational model is proposed that accounts for both aspects of draw solute surface chemistry and concentration polarization gradients. Osmotic pressure and flux predictions generated with this model indicate that maximizing interaction between the draw solute surfaces and the water molecules of the draw solution is essential for optimizing water flux. These results are then discussed within the context of future endeavors aiming to develop novel draw solutes.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Forward Osmosis.

Access to freshwater is emerging as the most critical resource limitation facing humanity. An ever-rising population, poor resource management, and pollution have left approximately 40 percent of the current global population, or 2.3 billion people, facing serious water shortages.<sup>1</sup> This number is expected to rise to 3.5 billion within ten years.<sup>1</sup> The problems associated with this lack of clean, fresh water are well known: 3.4 million people, most of them children, die annually from diseases related to a lack of clean water.<sup>2,3</sup> In response to this looming water crisis, increased focus has been placed on measures such as resource management, infrastructure repair, improved distribution systems, and conservation.<sup>4,5</sup> However, these approaches can only improve the efficient use of existing freshwater resources, but do little to expand them.<sup>4</sup> The only existing methods for expanding this supply are the re-use of wastewater and the desalination of saltwater.<sup>5</sup> As a result of the extensive chemical treatments involved in the re-use of wastewater, potentially leading to hazardous contamination, the focus here will instead be on saltwater desalination for a more environmentally friendly approach to expanding the existing freshwater supply.<sup>5,6</sup>

Current commercial desalination technologies rely on multi-stage flash (MSF) distillation, which rapidly evaporates water at low pressures and high temperatures, or reverse osmosis (RO), which forces water through a membrane against an osmotic gradient using high pressures (Fig 1b).<sup>7</sup> However, because of the pressures and temperatures involved, these methods are associated with a high energy and monetary cost.<sup>8</sup> While more efficient processes and novel materials have continued to lower energy consumption, the cost of large-scale plants utilizing

these technologies is expected to remain high.<sup>4</sup> As a result, forward osmosis (FO) represents a more energy efficient option for saltwater desalination. Instead of relying on the use of energy-intensive high pressure pumps to force water *against* the osmotic gradient, forward osmosis desalination pulls water across a semipermeable membrane *along* the osmotic gradient through the use of a high concentration draw solution, resulting in significantly decreased energy consumption (Fig 1a).<sup>9</sup>

# **1.2 Magnetic Nanoparticle Draw Solutes.**

An ideal draw solute for forward osmosis applications has three key characteristics: (1) high solubility in water in order to generate a sufficiently high osmotic pressure, (2) easy separation from water, and (3) lack of toxicity.<sup>10</sup> To meet these criteria, researchers are increasingly turning to magnetic nanoparticles as FO draw solutes.<sup>11,12</sup> These nanoparticles can be made hydrophilic via various surface coating techniques, and have been shown to form a highly monodisperse solution.<sup>13</sup> The use of magnetic nanoparticles also allows for easy separation from desalinated water through the use of an induced magnetic field. Furthermore, many nanoparticles are sufficiently nontoxic to be used in desalination, especially if they avoid the use of common chemical cross-linkers such as glutaraldehyde, which can be shed over time into the surrounding solution.<sup>13,14</sup>

Several past studies have attempted to evaluate the potential of magnetic nanoparticles as draw solutes. For example, Ling et al prepared magnetic nanoparticles with surface coatings and compared of 2-pyrollidine, triethylene glycol, and polyacrylic acid before comparing their efficacies as FO draw solutes.<sup>11</sup> Nonetheless, substantial work still needs to be done to identify

surface coatings are both sufficiently durable over long periods of time and capable of preventing agglomeration.<sup>11,12</sup>

### **1.3 Osmotic Pressure and Flux.**

In order to evaluate the scalability, productivity, and efficiency of a potential FO system, an accurate computational model must be developed to identify good candidate systems and eliminate poor ones. The theoretical basis for most FO models originates with the calculation of osmotic pressure, which is defined as the pressure needed to prevent the flow of water across a membrane. The osmotic pressure  $\pi$  can be calculated with the van't Hoff equation:

$$\pi = \frac{n}{V}RT$$
[1]

Here, *n* is the number of moles of solute, *V* is the volume of the solution, *R* is the ideal gas constant, and *T* is the temperature. Note that the proportionality of  $\pi$  with concentration  $(\frac{n}{V})$  makes osmotic pressure a colligative property.

The ultimate goal of all desalination modeling endeavors is to better approximate the flux of the system, or the flow rate across the membrane per unit area. Typically, the flux J is represented as a function of the membrane-specific hydraulic permeability coefficient A and the difference in osmotic pressure between the draw and feed solutions.<sup>15</sup>

$$J = A(\pi_D - \pi_F)$$
<sup>[2]</sup>

# **1.4 Concentration Polarization.**

Previous experimental studies using only the above equations for flux predictions have reported lower than expected levels of water flow, indicating the inadequacy of those equations in accurately representing the reality of osmotic systems.<sup>15–17</sup> This is largely due to a

phenomenon known as concentration polarization, wherein the concentration of the solution directly adjacent the membrane changes over time as a consequence of solvent flux.<sup>15–17</sup> As water flows across the membrane from the feed solution to the draw solution, the loss of water molecules along the feed solution side of the membrane results in an increase in concentration. Correspondingly, the gain of water molecules along the draw solution side of the membrane results in a decrease in concentration. This leads to a net reduction in the difference between the osmotic pressure of the feed and draw solutions, gradually lowering the flux as time progresses. As such, considering concentration polarization is critical for accurate predictions of flux, and extensive efforts have been made to modify the standard osmotic pressure equation to account for its effects.<sup>15,16,18</sup> To counteract concentration polarization in experimental settings, spacers have been used to induce turbulence adjacent to the membrane and thus promote mixing.<sup>19</sup> Although modeling the effects of such spacer geometries is outside of the scope of this study, an optimized forward osmosis system in the real world will almost certainly need to utilize them.

In the case of a symmetric membrane that rejects salt at both surfaces, concentration polarization occurs outside the confines of the membrane itself and results in osmotic pressure gradients at the membrane-solution boundary (Fig. 2a). This is referred to as external concentration polarization (ECP). However, conventional forward osmosis membranes consist of a dense active layer alongside a porous support layer, with the active layer rejecting salt and the support layer allowing its passage. This results in osmotic pressure gradients developing adjacent to the active layer, both inside the porous support layer and at the active layer-solution boundary (Fig. 2b,c). The concentration polarization occurring within the support layer is referred to as internal concentration polarization (ICP). Because forward osmosis systems typically orient the membrane such that the active layer faces the feed solution and the support layer faces the draw solution, they experience both concentrative ECP and dilutive ICP (Fig. 2c).

# 1.4.1 Concentrative External Concentration Polarization.

As water passes from the feed solution to the draw solution across the active layer of the membrane, the loss of water molecules from the feed solution generates a localized increase in concentration at the feed solution-active layer boundary, which in turn raises the osmotic pressure. To determine this altered concentration of the feed solution-active layer boundary, the mass transfer coefficient k, which quantitatively represents the movement of particles along the concentration gradient, must be calculated.

$$k = \frac{Sh D}{d}$$
[3]

Note that *Sh* is the Sherwood number, *D* is the solute diffusion coefficient (approximated as 2 x  $10^{-5}$  cm<sup>2</sup>/s)<sup>15</sup>, and *d* is the hydraulic diameter.

The Sherwood number used in Eq. 3 can be calculated as follows.<sup>15</sup> Laminar flow is assumed.

$$Sh = 1.85 \left( Re \ Sc \ \frac{d}{l} \right)$$
[4]

Here, Re is the Reynold's number, Sc is the Schimdt number (340 for water), d is the hydraulic diameter, and l is the channel length.

The Reynold's number used above is a function of the density of the fluid  $\rho$  (~1g/cm<sup>3</sup> for water), velocity of the liquid *V*, the length or diameter of the liquid *L*, and the viscosity of the liquid  $\mu$  (8.90 × 10<sup>-4</sup> Pa).

$$Re = \frac{\rho VL}{\mu}$$
[5]

With the mass transfer coefficient (Eq. 3), a modulus can be calculated for concentrative ECP as follows:

$$\frac{\pi_{F,m}}{\pi_{F,b}} = e^{\frac{J}{k}}$$
[6]

Here,  $\pi_{F,m}$  is the osmotic pressure of the feed solution at the active layer surface and  $\pi_{F,b}$  is the osmotic pressure of the feed solution in bulk.<sup>15</sup>

# 1.4.2 Dilutive Internal Concentration Polarization.

Loeb et al. developed a model for ICP in an asymmetric membrane which can be used to calculate a dilutive ICP modulus similar to the one shown above for concentrative ECP.<sup>20</sup> In their model, the solute resistivity to diffusion within the support layer *K* is defined as a function of the membrane salt permeability coefficient *B*, flux *J*, hydraulic permeability coefficient *A*, and the osmotic pressures.<sup>20</sup>

$$K = \left(\frac{1}{J}\right) ln \frac{B + A\pi_{D,b}}{B + J + A\pi_{F,m}}$$
[7]

An ideal forward osmosis membrane will reject nearly all salt, so *B* can be approximated as zero. *K* can be calculated as follows:

$$K = \frac{t\tau}{D\varepsilon}$$
[8]

Here, t is thickness of the support layer,  $\tau$  is the tortuosity of the support layer, D is the diffusion coefficient of the solute, and  $\varepsilon$  is the porosity of the support layer.

Rearranging Eq. 7 yields the following, which can then be used to determine the dilutive ICP modulus (Eq. 10).<sup>15</sup>

$$J = A(\pi_{D,b}e^{-JK} - \pi_{F,m})$$
[9]

$$\frac{\pi_{D,i}}{\pi_{D,b}} = e^{-JK}$$
[10]

Note that  $\pi_{D,i}$  is the osmotic pressure at the active layer-support layer boundary.

# 1.4.3 Modified Flux Equation.

Solving the concentrative ECP modulus (Eq. 6) and dilutive ICP modulus (Eq. 10) for the osmotic pressure at the active layer surfaces and then substituting into the standard equation for flux (Eq. 2) yields a modified equation that accounts for the effects of concentration polarization on an asymmetric membrane during forward osmosis.<sup>15</sup>

$$J = A\left(\pi_{D,b}e^{-JK} - \pi_{F,b}e^{\frac{J}{k}}\right)$$
[11]

## 1.5 Hydration Force.

While substantial progress has been made in modeling FO systems, no previous work has looked specifically at modeling a FO system utilizing a magnetic nanoparticle draw solute. Due to the size of magnetic nanoparticles, which are substantially larger than the compounds typically found dissolved in water, the interaction of the solute particles with the surrounding water becomes increasingly important. This concern is highlighted by previous work in biochemistry, which has shown that macromolecules in solution strongly repel one another, with the force needed to bring the molecules closer together increasing exponentially with decreasing distance.<sup>21,22</sup> The repulsion is believed to be a consequence of the thin and highly ordered sheet of water that surrounds a dissolved macromolecule; as the macromolecules are brought closer together, work must be done to push aside the sheet of water. This has been termed the "hydration force" and is described mathematically as follows:

$$F = F_0 e^{\frac{-d}{\lambda}}$$
[12]

In other words, the hydration force *F* has a value of  $F_0$  at a distance of zero (molecular contact) and then decays exponentially as a function of the distance *d* and decay constant  $\lambda$ . Experimental results have demonstrated that  $\lambda$  is approximately the diameter of a water molecule (~ 2.75 Angstroms).<sup>22</sup>

The hydration force equation can be integrated to calculate the minimum distance of separation beyond which two molecules cannot be brought closer. Thus, when temperature and solute identity remain constant, there exists a thin layer of water surrounding each dissolved molecule (a "hydration sphere"). As such, the parameters of the osmotic pressure equation can be modified to account for this unresponsive volume of water.

The mass of the "bound" water  $m_h$  can be related to the mass of the solute  $m_s$  by a constant *I*, which reflects the ability of that solute to maintain a hydration sphere:

$$m_h = Im_s \tag{13}$$

Similarly, the mass of free water  $m_{fw}$  can be expressed in terms of the total water  $m_w$  and bound water:

$$m_{fw} = m_w - m_h = m_w - Im_s \tag{14}$$

The equation for osmotic pressure (Eq. 1) can be rewritten in terms of the masses of solute and solvent, and then these new expressions can be substituted to yield a non-ideal equation for osmotic pressure.<sup>22</sup>

$$\pi = \frac{m_s}{a_s m_w} RT$$
[15]

$$\pi = \frac{m_s}{m_w - Im_s} \frac{RT}{a_s}$$
[16]

Note that  $a_s$  is the molecular weight of the solute.

While the impact of hydration forces has been examined primarily in the context of biological macromolecules, the same principles can be extended to all large hydrophilic compounds, including nanoparticles that have been modified with hydrophilic surfaces. As previously mentioned, no existing models of forward osmosis account for the effects of hydration forces, which will become increasingly impactful when relatively large compounds (i.e. nanoparticles) are used at high concentrations (i.e. as draw solutes). Here, the influence of hydration forces on the use of magnetic nanoparticles as draw solutes is explored extensively through computational means.



Figure 1. Forward and Reverse Osmosis

(a) Forward osmosis draws water along its concentration gradient, from a region of low osmotic pressure to a region of high osmotic pressure, to generate flux. (b) Reverse osmosis uses artificially applied pressure to force water against its concentration gradient from a region of high osmotic pressure to a region of low osmotic pressure.



Figure 2. Internal and External Concentration Polarization

Redrawn from McCutcheon 2006.<sup>15</sup> (a) Symmetrical forward osmosis membranes experience external concentration polarization at both membrane-solution interfaces. (b), (c) Membranes with a dense active layer supported by a porous support layer experience both external and internal concentration polarization, with the location of the two polarization gradients depending on the orientation of the membrane. Note that  $\Delta \pi$ , the effective osmotic driving force, is smaller than the difference bulk solution osmotic pressures in all three scenarios.

# CHAPTER 2 METHODS

Matlab R2016b was used for all modeling and simulations. First, the influence of hydration force coefficients on non-ideal osmotic pressures was investigated by simulating a number of hypothetical draw solutes. These draw solutes were artificially given a molecular weight identical to that of NaCl (MW = 58.44 g/mol) but were given variable hydration force coefficients *I*. The osmotic pressures generated by these hypothetical draw solutes were simulated for a range of concentrations, ranging from 0 to 10 M.

Next, flux predictions were made for the same hypothetical draw solutes when paired with a 0 M DI water feed solution. Concentrative external concentration polarization and dilutive internal concentration polarization were also considered (Eq. 11), with the active layer of the membrane facing the feed solution and the porous support layer facing the draw solution. The draw solution was again given a variable concentration ranging from 0 to 10 M.

Parameter	Symbol	Value					
Ideal Gas Constant	R	0.082057 L atm/K mol					
Temperature	Т	20 °C (293.15 K)					
Water permeability coefficient	Α	$3.11 \times 10^{-7} \text{ m/s atm}$					
Mass Transfer Coefficient	k	1.74 x 10 <sup>-5</sup> m/s					
Solute resistance to diffusion	K	$2.67 \times 10^5 $ s/m					

 Table 1. Constants and Parameters Used During Modeling

#### CHAPTER 3





Figure 3. Ideal and Non-Ideal Osmotic Pressures

Ideal and non-ideal osmotic pressures were calculated for hypothetical draw solutes with a mass equal to that of NaCl (MW = 58.44 g/mol). The non-ideal variations utilized two different values for *I*, one representing a small molecule (I = 0.25) and the other representing a large macromolecule (I = 1.5). At all non-zero concentrations up to 10 M, the I = 1.5 curve generated a greater osmotic pressure than the I = 0.25 curve, which likewise generated higher osmotic pressures than the ideal (I = 0) curve. Interestingly, the difference between the individual curves began to increase as the concentration of the solution increased. This corresponds closely with experimental results utilizing compounds with known values of *I*.



**Figure 4. Flux Prediction with Variable Concentration and Hydration Force Coefficients** Next, flux predictions were made for hypothetical draw solutes with a mass equal to that of NaCl (MW = 58.44 g/mol). These calculations consider both the influence of variable hydration force coefficients (Eq. 16) and external/internal concentration polarization (Eq. 11). The feed solution was given a constant concentration of 0 M to represent DI water. Similar to the calculations of osmotic pressure alone, the curves with higher *I* values generated a greater flux, with the difference between the individual curves increasing as the concentration increased. Notably, the I = 1.5 curve appears to have an inflection point around an x value of 6 M and then begins to generate flux at a rapidly increasing rate. This is not expected, as experimental results indicate

that the most rapid payoffs between an increase in concentration and an increase in flux are found between 0-1 M.<sup>15</sup>

# **CHAPTER 4**

# DISCUSSION

## 4.1 Maximizing Non-Ideal Osmotic Pressure.

In order to optimize flux across any given forward osmosis membrane, it is essential that the draw solute generate as high an osmotic pressure as possible. This ensures that the osmotic pressure differential between the draw and feed solutions is maximized, thus producing the largest possible flux (Eq. 2). By simulating the non-ideal osmotic pressures generated by hypothetical draw solutes with a constant molecular weight but varying hydration force coefficients I (Fig. 3), the relationship between hydration force and osmotic pressure is revealed. Thus, it is revealed that by increasing I, we can generate a significantly greater osmotic pressure without having to increase the draw solute concentration. Because I represents the level of interaction between the solute and solvent, modifying the draw solute particles to maximize Iwill generate the greatest possible flux.

The flux prediction results (Fig. 4) demonstrate these payoffs, which become substantially greater at higher concentrations. Between 5-6 M, the difference between an I = 0 draw solute and an I = 1.5 draw solute starts to account for a 25% increase in flux, which is sufficiently large that it could determine the viability of forward osmosis as a long-term potable water production technology.

An obvious route for increasing *I* is to increase the size of the draw solute particles, thereby increasing their surface area and contact with the solvent. This approach is made particularly promising by the fact that a doubling of the particle diameter will result in a fourfold increase in the surface area. Despite this, the draw solute particles cannot be made so large that they result in a very viscous draw solution, which would both exacerbate the problem of concentration polarization as mixing of the fluid becomes more difficult while also making subsequent removal of the draw solute to yield pure water more troublesome.

Thus, a more appealing method for maximizing *I* lies not with altering particle size but with modifying the surface chemistry of the draw solute particles to optimize surface to water interaction. This could be accomplished in either of two ways. First, highly hydrophilic groups can be added to magnetic nanoparticles surfaces to increase their affinity to water. Second, these surfaces groups can be composed of long, highly chained molecules, thereby allowing water to interact not only at the outermost surface but also along the entire length of the chain. These approaches have the substantial advantage of increasing solute-water interaction without decreasing the maximum usable draw solute concentration as increasing the particle diameter would do.

Maximization of *I*, however, comes with one significant drawback: as interaction between the draw solute particles and water increases, it becomes more difficult to pull the particles out of solution to produce potable water. Therefore, if nanoparticles are to be used as draw solvents, they not only need the appropriate surface chemistry for generating a large hydration force, but must also be nontoxic and capable of generating a sufficiently strong response in the presence of a magnet. The synthesis of such a particle remains a significant challenge as forward osmosis technologies continue to develop.

# 4.2 Limitations

While the hydration force model for osmotic pressure seems to be accurate at low concentrations, as corroborated by experimental evidence<sup>21,22</sup>, its behavior begins to diverge from expectation at higher concentrations (Fig. 5). The beginnings of this trend can also be seen

in Fig. 4, as the I = 1.5 curve begins to increase at an unreasonable rate at around 7-8 M. The concentration at which this divergence occurs varies with the hydration force coefficient of the draw solute in question (Fig. 5), with higher *I* values leading to greater inaccuracy at lower concentrations. Examination of the non-ideal osmotic pressure equation (Eq. 16 – reproduced below) makes it clear why this occurs.

$$\pi = \frac{m_s}{m_w - Im_s} \frac{RT}{a_s}$$
[16]

The factor  $m_w - Im_s$  in the denominator indicates the presence of a vertical asymptote when that factor equals zero.  $m_w$  and I are specific to the draw solute in question, but  $m_s$  varies with concentration; thus, when the concentration becomes sufficiently large, the denominator will become zero and a vertical asymptote is present at that point. Compounds with greater values of I require a lower concentration for that asymptote to appear. Nonetheless, this model should still remain useful for forward osmosis applications, which currently rely on large draw solutes that cannot be used at high concentrations without the solution becoming too viscous for practical applications.

# **4.3 Future Directions**

These results emphasize the importance of developing new surface coatings for magnetic nanoparticles if they are to serve as draw solutes for forward osmosis technologies. This has been a developing area of research<sup>10, 11, 12</sup>, but substantial work still needs to be done to optimize these particles so that they are nontoxic, easily removable from water, and generate high osmotic pressures. Future modeling efforts could also incorporate fluid dynamics simulations in the feed and draw solutions with varying spacer geometries to identify flow patterns that maximally

disrupt concentration polarization and improve water flux. Lastly, the development of efficient, symmetrical, and low-cost membranes would substantially improve the feasibility of forward osmosis as a desalination technology. The need for symmetrical membranes is of unique importance, as they isolate the concentration polarization gradients outside the confines of the membrane itself (Fig. 3), making it easier to disrupt those gradients with spacers and turbulent flow.



**Figure 5. Model Limitations** 

Vertical asymptotes appear at higher concentrations, indicating that the model becomes increasingly inaccurate past a certain point. Note that a larger *I* results in the model becomes inaccurate at lower concentrations.

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