UNDERSTANDING INORGANIC SALT ION FLUXES IN FORWARD OSMOSIS EXPERIMENTS

A Thesis

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To the people who believed in me when I did not.
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Rhyme or reason in ion transport remains a fastidious task. We cannot probe coupled diffusion mechanisms in their active state, but instead must settle for analyzing the results. We can, however, change the experimental parameters in the hope that they affect the mechanism. The relationship between the experimental parameters and the mechanism is the key to solving the phenomenon explored in this thesis.
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1.1 Forward Osmosis: An Introduction

The growing demand for fresh water is an important issue faced by the modern world. *World Resources Institute* predicts that two thirds of the world’s population will live in water stressed regions by 2025.¹ Some relief to water stressed regions can come through improvement of infrastructure and water reclamation. However, the use of new water supplies (i.e., seawater desalination and reuse of nontraditional sources) is required to meet the increasing demand.² Desalination by reverse osmosis (RO) is a popular choice for regions with abundant saline water sources. RO creates potable water by applying a hydraulic pressure greater than the osmotic pressure of the salt water to force water across a semipermeable membrane. Since the first application of RO in the 1960s, RO technology has progressed to the point of almost reaching the thermodynamic limitation of the separation (the minimum energy is $\Delta G_{\text{mix}}$).² The remaining options on improving the performance of RO promise only small improvements. Accordingly, researchers are looking for techniques that are capable of treating non-traditional water sources such as reclaimed waste and process waters. One class of techniques that has proved promising is osmotically-driven membrane processes (ODMP).
Osmosis is the process of allowing water to flow down its chemical potential gradient. Hence, osmosis does not require an applied hydraulic pressure. The process results in a diluted draw stream (the solution of lower chemical potential), requiring reconcentration at the end of a run. Thus, the draw solute should be easily removed from the permeate stream. Consideration must also be given to the retentate, as the feed stream will be concentrated by the same process. However, these issues are minor, and it is believed that the process can be energetically favorable over RO.\(^3\)

One class, known as Forward Osmosis (FO), has looked to apply this phenomenon to specialized separations such as desalination of sea and brackish waters, wastewater treatment, and food processes.\(^4-10\) One clear advantage of FO is that it shows low fouling propensity.\(^11,12\) However, some have expressed skepticism based off current mass transport limitations.\(^13\)

![Figure 1.1.1: The Different Osmotic Processes.](image)

The graph shows water flux as a function of hydraulic pressure. When \(\Delta P=0\), then a systems is a forward osmosis process. If \(\Delta P < \Delta \Pi\), then the system is a pressure retarded osmosis process. Finally, when \(\Delta P > \Delta \Pi\), then the system is a reverse osmosis process.
Another osmotic process is Pressure Retarded Osmosis (PRO). PRO is suggested as possible power producing technology. The process utilizes the difference in osmotic pressure between fresh and seawater to turn a turbine and provide power.\textsuperscript{14-18} Figure 1.1.1 shows the differences between FO, PRO, and RO. In order to improve on applicability of FO and PRO, an understanding how analytes permeate across the membrane is required.

In real systems, the membrane is not semipermeable, and thus allows for a small flux of the feed and draw solutes. Several previous studies have looked into developing models that would predict the permeation of solutes during FO processes.\textsuperscript{19-21}

The studies on solute permeation in ODMP have utilized the same commercial Hydration Technology Innovations cellulose tri-acetate membrane, which has an asymmetric structure typical of membranes made by the Loeb-Sourirajan phase inversion process (see Figure 1.1.2).\textsuperscript{3,22,23} The asymmetric structure consists of a dense active layer that is approximately 5 microns thick embedded into woven porous support layer (~50 microns).\textsuperscript{20}

![Figure 1.1.2: A represents the dense active layer that ranges from 5 to 10 microns. B is the porous support layer which varies from 50-30 microns. The figure to the right is a cross-sectional SEM of HTI FO membrane.\textsuperscript{7}}
In the paper *Bidirectional Permeation of Electrolytes* the researchers attempted to systematically quantify solute interactions between draw and feed solute. As Figure 1.1.3 demonstrates, the researchers found an almost perfect agreement between salt fluxes in bidirectional systems and a simple Fickian model that accounted for no solute-solute interactions.

However, the same researchers noticed that nitrate containing systems did not conform to the simple model (as shown in Figure 1.1.4). The work presented here in attempts to address this deviatory behavior. Attention is given to the possibility of increased hydrolysis of the membrane in the presence of nitrate being the mechanism. Furthermore, many aspects of the system were changed in order to tease out the mechanism including, non-nitrate salt anion and cation identity, nitrate salt cation identity, and quaternary data sets (all four ion fluxes quantified).
Figure 1.1.3: Previous literature results comparing predicted values from a simple Fickian model to experimentally measured results. The systems show close agreement between the model and experimental results. For each system there are three points corresponding to the two cation fluxes and the common anion flux. The first salt in the legend is the draw salt at a concentration of 1.0M. The second salt is the feed salt at a concentration of 0.05M.

Figure 1.1.4: Previous literature results comparing predicted values from a simple Fickian model to experimentally measured results. There are four points for each system cooresponding to the four ion fluxes. The first salt in the legend is the draw salt at a concentration of 1.0M. The second salt is the feed salt at a concentration of 0.05M.
THEORY

2.1 Active Layer Permeation

The model used to predict salt fluxes in Figure 1.1.4 and 1.1.5 is essentially Fickian in nature. Specifically, it relies on the solution diffusion mechanism to explain solute permeation through the dense active layer of the asymmetric membrane. The solution diffusion mechanism theorizes that the thermal motion of the polymer chains results in free volume elements in the membrane that the solute and solvent can jump between to progress across the membrane. A simple steady state mass balance on the active layer yields Equation 1. Note that the mass balance does not contain a convective flux term because the model theorizes that there are no permanent pores within the active layer.

\[ 0 = -D_a \frac{d^2 C}{dz^2} \]  

(1)

with boundary conditions:

\[ C(z) = H C_i^P \quad @ \quad z = 0 \]

\[ C(z) = H C_i^F \quad @ \quad z = \delta_a \]

\( D_a \) is the diffusion coefficient through the active layer. For a dissolved salt, it can be calculated by taking the harmonic average of the ionic diffusion coefficients. \( H \) is the partition coefficient and is calculated by taking the geometric average of the partition coefficients of individual ions. \( C_i^P \) is the surface concentration external to the active
layer, and \( C_i^F \) is the surface concentration external to the active layer on the feed side. 

\( \delta_a \) is the thickness of the active layer.

### 2.1.1 Partition Coefficients

Partition coefficients become important when dealing with the transport of solute across phase interfaces. The assumption is made that rate of adsorption/desorption at the active layer-solution interface is fast compared to the diffusion of the solute across the active layer. Hence, the solute in solution and the solute in the active layer are in equilibrium at the interface. Therefore, the concentrations on each side of the interface can be related with a Henry’s law type coefficient. \(^{26}\)

\[
C_{i,D}^A = HC_i^D  \tag{2}
\]

\( C_{i,D}^A \) is the interface concentration internal to the membrane on the draw side. Hence, \( H \) relates an internal concentration to an external concentration.

### 2.1.2 Permeability Coefficient (B)

Integrating Equation 1 twice, and applying the boundary conditions yields the following equation

\[
C(z) = \frac{-H}{\delta_a} (C_i^D - C_i^F) z + HC_i^D  \tag{3}
\]

Now, substituting Equation 3 into the definition of Fickian diffusion yields an expression for the solute flux across the dense layer of the asymmetric membrane.
\[ J_s = -D_a \frac{dC}{dz} = \frac{HD_a}{\delta_a} (C_i^D - C_i^F) \]  

Equation 4 shows that the flux across the active layer of the membrane depends on the differences in the surface concentrations external to the membrane and a combination of terms known as the solute permeability coefficient \( B \). The downstream concentration can be assumed to be zero under certain circumstances that are covered in the experimental section.

\[ B = \frac{HD_a}{\delta_a} \]  

2.2 Concentration Polarization

Osmotically driven processes produce water fluxes which result in the interfacial concentrations, \( C_i^D \) and \( C_i^F \), often being different from the concentration of solute in the bulk solution, \( C_B^D \) and \( C_B^F \). Unfortunately, the interfacial concentrations are experimentally immeasurable quantities. Accordingly, if the goal is to develop a model that predicts the solute flux based on experimentally measurable quantities, the two interfacial concentrations need to be related to the bulk concentrations. This can be done by accounting for a phenomenon known as concentration polarization (CP).

CP is the result of multiple mass transport mechanisms being active in a region. In the case of the membrane system studied here, the two mechanisms are the convective and diffusive flux of solute. CP is akin to boundary layer formation at interfaces in momentum and heat transfer processes. In mathematical form, CP is represented by the following differential equation:
\[ \frac{dJ_s}{dx} = 0 = -D^* \frac{d^2C}{dx^2} + J_w \frac{dC}{dx} \]  

(6)

with boundary conditions

\[ C(x) = C_i^D \quad \text{at } x = 0 \]
\[ C(x) = C_B^D \quad \text{at } x = \delta^* \]

where \( C_i^D \) is the bulk draw concentration, \( \delta^* \) is the boundary layer thickness, \( J_s \) is the solute flux, and \( J_w \) is the water flux. For the dilute systems studied here, the water flux is approximately equal to the superficial convective velocity. \( \delta \) depends upon which CP is being analyzed. As shown in Figure 2.1.1, CP can occur inside the support layer, and external to the active layer. By solving the differential given in Equation 6 and applying the appropriate boundary conditions, \( C_B^D \) can be related to \( C_i^D \).

2.2.1 Internal Concentration Polarization

Internal concentration polarization (ICP) occurs in the support layer. Referencing Equation 6, \( D^* \) is replaced by \( D^e \), an effective diffusion coefficient that accounts for the porous structure of the support layer.

\[ D^e = \frac{D\varepsilon}{\tau} \]  

(7)

\( D \) is the diffusion coefficient in the bulk aqueous solution; \( \tau \) and \( \varepsilon \) are the tortuosity and porosity of the support layer respectively. The boundary layer thickness \( \delta^* \) is replaced with \( \delta_s \) (the support layer thickness). The solution to Equation 6 for the support layer (Equation 8) yields several pertinent parameter groupings.
Figure 2.1.1: Internal and external concentration polarization are shown in the above two diagrams. ICP and ECP are the result of multiple mass transport mechanism being active in a region, e.g. diffusion, and convection. The draw solution is in contact with the support layer on the left (FO mode), and with the active layer on the right (PRO). \( J_s \) and \( J_w \) are the salt and water fluxes respectively. The concentration nomenclature is defined in the following way: the superscript denotes the draw or feed side of the active layer; a \( B \) in the subscript denotes bulk, and an \( i \) denotes interfacial. \( \delta \) is the particular regions thickness, with the subscript denoting which region: \( a \) for active, \( s \) for support, and \( e \) for external. \( x \) and \( z \) are the coordinate systems used in solving the differentials of this chapter.

\[
C(z) = \frac{(C_B^D - C_i^D) \exp\left( \frac{J_w \delta_s \tau X}{\varepsilon D} \right) + C_i^D \exp\left( \frac{J_w \delta_s \tau}{\varepsilon D} \right) - C_B^D}{\exp\left( \frac{J_w \delta_s \tau}{\varepsilon D} \right) - 1}
\]  

(8)

The first is known as the structural parameter, \( S \), which is the effective boundary layer thickness of the support layer.\(^{27,28}\)

\[
S = \frac{\delta_s \tau}{\varepsilon}
\]  

(9)
Note that $D$ is purposefully left out of this definition so that $S$ is solely a membrane property, and independent of solute identity. When $S$ is substituted into Equation 8 the result is Equation 10.

\[
C(z) = \frac{(c_B^D - c_i^D) \exp\left(\frac{lwS_x}{D}\right) + c_i^D \exp\left(\frac{lwS}{D}\right) - c_B^D}{\exp\left(\frac{lwS}{D}\right) - 1}
\]  

(10)

Taking advantage of the new groupings, Equation 10 can be simplified further. The exponentials in Equation 10 contain a dimensionless number known as the Péclet number ($P_e$). The Péclet number is the ratio of convective to diffusive flux, normalized by a characteristic length (mass transfer analogue of the Reynolds number). The number is a quick reference to determine which type of flux dominates a system. In the experiments covered by this thesis, $P_e$ is order 1 in the support layer, implying that both diffusive and convective flux influence the gradient of the solute. Equation 11 gives the $P_e$ number for the support layer.

\[
P_e^S = \frac{lwS_S}{D_e} = \frac{lwS}{D}
\]  

(11)

The concentration profile, with the $P_e$ number substituted in, is plugged into the total flux equation given by Equation 12.

\[
J_s = -D \frac{dC}{dx} + JwC(x)
\]  

(12)

The resulting flux equation can be set equal to the flux across the active layer as a result of the assumption of no accumulation. The resulting equation produces a relationship between $C_B^D$ and $C_i^D$. By substituting this relationship into Equation 4, the flux can be expressed without $C_i^D$. 

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2.2.2 External Concentration Polarization

External concentration polarization (ECP) is identical in nature to ICP, except that ECP occurs in the region adjacent to the active layer on the feed side of the membrane (see Figure 2.1.1). Equation 6 still applies with the same boundary conditions; however $D^*$ is replaced by the aqueous diffusion coefficient, and $\delta^*$ from the boundary conditions is replaced by $\delta_e$ (external boundary layer thickness). Therefore Equation 8 becomes

$$C(z) = \frac{(c_B^D - c_i^D) \exp\left(\frac{Jw \delta_e}{D}\right) + c_i^D \exp\left(\frac{Jw \delta_e}{D}\right) - c_B^D}{\exp\left(\frac{Jw \delta_e}{D}\right) - 1}$$  \hspace{1cm} (13)

Equation 13, unsurprisingly, also contains an order 1 Péclet number.

$$Pe_E = \frac{Jw \delta_e}{D} = \frac{Jw}{\kappa}$$  \hspace{1cm} (14)

$\kappa$ is the mass transfer coefficient of the external boundary layer. In order to quantify $\kappa$ the boundary layer thickness must be determined. $\delta_e$ can be calculated using the Sherwood number ($Sh$). The Sherwood number relates the transverse liquid flow through the FO cell to the flow through the membrane. The transverse flow causes several boundary layers to form between the membrane and the flowing solution. The Reynolds number, $Re$, (ratio of convective to diffusive momentum transfer) defines the momentum boundary layer between the solution and the membrane. The Schmidt number ($Sc$) is used to relate the momentum boundary layer thickness to $\delta_e$. The relationship between the two dimensionless numbers depends on the geometry of the cell. In this case a circular conduit relationship was used, with the exception the $d_h$ (hydrodynamic diameter) was used instead of radius.\textsuperscript{29}
\[ Sh = \kappa \frac{d_h}{D} = 1.62 \left( Re \frac{Sc \frac{d_h}{L_c}}{L_c} \right)^{1/3} \]  \hspace{1cm} (15)

With a little rearranging:

\[ \kappa = 1.62 \left( \frac{u D^2}{2H_c L_c} \right)^{1/3} \]  \hspace{1cm} (16)

Where \( u \) is the flow velocity, \( H_c \) is the height of the channel, and \( L_c \) is the length of the channel. Clearly, ECP is affected by cell geometry and flow rate. However, ICP is only a function of the membrane and \( J_w \).

2.3 Bidirectional Permeation

If an assumption of no solute–solute interaction is made, then the mathematical model above does not change. The only difference between the model above and the model found in a recent paper is that the authors take the development a step further and express the downstream external active layer concentration, \( C_i^F \), in terms of the downstream bulk concentration, \( C_i^B \). The utility of this additional feature is lost for the experimental setup used for this thesis as the assumption that the downstream concentration is equivalent to zero is sufficient (the actual concentration in a typical experiment is \( \sim 4 \) magnitudes lower the bulk solution). An excellent step by step development of this theory is available in the supplemental information of the paper.\(^{20}\)

The governing equation is given in Equation 17.\(^{30}\)

\[ J_k = J_w B_k \left( c_k^{F,b} \exp(p_{E_k}^E + p_{E_k}^S) - c_k^{D,b} \right) \left( B_k \exp(p_{E_k}^E + J_w) \exp(p_{E_k}^S) - B_k \right) \]  \hspace{1cm} (17)
Note that $k$ in this equation is an index denoting which solute the equation is expressing the flux of (e.g. $k=1$ for draw solute, and $k=2$ for feed solute). The beauty of Equation 17 is that it predicts both draw and feed solute flux for non-interacting solutes.

The model assumes electrolyte permeation (EP) meaning that when a salt is dissolved in the feed or draw, the individual ions will permeate across the membrane in a stoichiometric ratio according to the parent salt. This assumption is necessary in keeping with electroneutrality in light of the model’s other assumption (non-interaction). These assumptions seem to work well with many salt systems as shown in Figure 1.1.4. However, when dealing with systems that are not accurately predicted by the Fickian model, these assumptions are the first thing to consider.
3.1 FO Cell Specifications and Setup

The cell geometry has been stated in previously published papers. A clear diagram of the cell setup is given in Figure 3.1.1. The cell is operated in crossflow. Two gear pumps are used to flow solutions through the cell. The flow rate on both sides of the membrane is set to 0.6 L/min using Gilmont Instruments® flow meters. 1 gallon Nalgene bottles serve as reservoirs for both feed and draw. The draw reservoir is placed on a scale that is interfaced with a computer. This setup allows for the measurement of mass change over time. The feed reservoir is placed on a magnetic stir plate.

Figure 3.1.1: FO Flow Cell: This figure represents the experimental apparatus used in the Water purification and Advanced Transport Engineering Research (WATER) laboratory to measure water and salt fluxes. Between the dashed lines under ‘Membrane Cell’ is where the membrane sits. The draw solution reservoir rests on a scale that is connect to a computer for mass data logging. The flow meters verify that the flow rate is set to 0.6 L/min.
3.1.1 Measuring the Water Flux

The Denver® scale used in the setup interfaces with a computer via USB. Using software provided with the scale, mass reading are recorded at a rate of 1 mass reading per minute. Mass data is collected from the beginning to the end of an experiment. The resulting data is plotted in excel (mass versus time), and a linear regression least-squares model is used to fit the data. In bidirectional tests, the slopes are weight-averaged by their time span. The resulting mean slope value is then converted into a water flux using the following simple mass balance on the draw solution.

\[ j_w \rho = \frac{\partial M}{\partial t} \frac{1}{A_m} \]  

(18)

The differential in Equation 18 is the slope discussed previously. \( A_m \) is the membrane area (20.02 cm\(^2\)), and \( \rho \) is the density of water (which is assumed constant at 997 g/L). An example water flux is shown in Figure 3.1.2. Clearly, the water flux is independent of time, and dependent on draw concentration.

3.1.2 Single Salt Calculations

Single salt experiments are used to quantify many different variables of the membrane in relationship to either the system or particular salts. First the method by which a salt flux is calculated for a single salt is presented. Next, the different operating modes, and how they allow for the calculation of different pertinent parameters that are needed to predict bidirectional salt fluxes using the simple Fickian model, are discussed.
Figure 3.1.2: Mass versus time for various NaCl draw concentrations. A linear fit slope divided by density and the membrane area yielded 5.76, 9.75, and 18.5 L m\(^{-2}\) hr\(^{-1}\) respectively. As expected the result shows that \(J_w\) is independent of time.

The salt flux for a single salt experiment is determined by a mass balance on both solute and solvent on the feed side of the membrane.

\[
\frac{d(C_f V_f)}{dt} = J_s A_m \quad (19)
\]

\[
\frac{dV_f}{dt} = J_w A_m \quad (20)
\]

Equation 19 gives concentration as a function of time, and Equation 20 gives volume as a function of time. Together, they result in an Equation 21, which expresses moles as a function of time. The reader is warned that the \(J_w\) is a vector taken to be positive in the direction of the draw.

\[
C_f (V^0 + J_w A_m t) = J_s A_m t \quad (21)
\]

\(V^0\) is the starting water volume of the feed, which in all experiments was set to 2 L. \(C_f\) is the feed permeate concentration. Accordingly, the product on the left side of the equation is the moles of the permeating species. A plot of time versus moles yields \(J_s\)
multiplied by $A_m$. An example plot is given in Figure 3.1.3. The next step is to relate the measured $J_w$ and $J_s$ to important experimental parameters such as $B$, $S$, and $A$ (water permeation coefficient).

![Figure 3.1.3: The moles of ammonium for a single experiment were quantified using Equation 21. The resulting fluxes were 0.054, and 0.053 mol m$^{-2}$ hr$^{-1}$ respectively. The $R^2$ values were 0.9976 and 0.9986 respectively. The IC and Phenate method are discussed in section 3.5.2 and section 3.5.3 respectively.](image)

Depending upon the orientation of the membrane in relationship to the draw solution, the system is said to be operating in one of two modes. The existence of the two modes is a direct result of the asymmetry of the membrane. The two modes are Pressure Retarded Osmosis mode (PRO) and Forward Osmosis mode (FO). The distinction between the two modes arises out of the different membrane orientation used in PRO versus FO. In PRO it is necessary to have the support layer face the draw solution because the draw is pressurized in order that it may turn a turbine. 

\[32\]
3.2 Pressured Retarded Osmosis (PRO)

PRO is primarily used to quantify $B$ for salts. The utility of PRO in single salt tests is a direct result of ECP; in ECP the mass transfer coefficient is defined as a result of the cell geometry, and therefore can be very accurately estimated a priori. Hence, the surface concentration is easily calculated using $\kappa$ and the measured $J_w$. With $C_i^D$ in hand (which is assumed constant over the length of the experiment) and the assumption that the downstream concentration is zero, Equation 3 is used in conjunction with the measured $J_s$ to quantify $B$. Conversely, $C_i^D$ can be related to $C_B^D$ (essentially the opposite process) resulting in Equation 22.

\[
B = \frac{J_s}{C_B^D \exp\left(-\frac{J_w S}{\kappa}\right)}
\]  
(22)

A number of PRO experiments are run for each salt at various concentrations.

3.3 Forward Osmosis (FO)

The $A$ and $S$ are quantified via FO tests. The van ’t Hoff equation relates $J_w$ to $A$ and $C_i^D$ via a simple equation. By taking into account ICP, $C_i^D$ can be related to $C_B^D$.

\[
J_w = AnRT C_B^D \exp\left(-\frac{J_w S}{D}\right)
\]  
(23)

$R$ is the ideal gas constant, $T$ is temperature, and $n$ is the sum of the stoichiometry for the salt (e.g. 2 for a 1:1 salt). In order to solve for both unknowns in Equation 23, another equation is required. The relationship via ICP between the surface and bulk concentrations is taken advantage of again to express the salt flux as a function of the bulk concentration.

19
\[ J_s = \frac{J_w C_B^D}{1 - (1 + \frac{J_w}{B}) \exp\left(\frac{J_w S}{D}\right)} \]  

The ratio of Equation 23 and Equation 24 yields an equation with two contributing parts.

\[ \frac{J_w}{J_s} = \frac{A n RT}{J_w} \left[ \exp \left( - \frac{J_w S}{D} \right) - \left( 1 + \frac{J_w}{B} \right) \right] \]  

Simple mathematical analysis shows that in Equation 25 one part dominates over the other. The exponential minus one term varies between 0 and -1. \( \frac{J_w}{B} \) is order one and dominates at the concentration ranges used in these experiments. Thus the ratio simplifies significantly giving a convenient relationship between \( B \) of a salt and \( A \).\(^{21}\)

\[ \frac{J_w}{J_s} = \frac{A}{B} n RT \]  

Hence, measured \( J_w \) and \( J_s \) in FO, in conjunction with \( B \), yield \( A \). The final variable required before the predicted flux values for non-interacting salts can be produced is the previously mentioned \( S \) parameter. \( S \) is given by \(^{21}\)

\[ S = \left( \frac{D}{J_w} \right) \ln \frac{B + A \pi_{D_B}}{B + J_w} \]  

\( \pi_{D_B} \) is the bulk osmotic pressure.

\[ \pi_{D_B} = n R T C_B^D \]  

3.4 Bidirectional Salt Test Calculations

In bidirectional tests everything is the same as single salt except now the feed also contains a salt instead of DI water. Depending upon the exact experiment, the concentration of the feed varies from 0.5 to 1.5 magnitudes lower than that of the
draw. However, typically the feed concentration is set to 0.05M at the beginning of the experiment. Samples (2.5 mL) of the feed and draw are drawn every half hour for the duration of the two hour experiment and stored in 15 mL Falcon™ tubes. The concentrations in the drawn samples are quantified via IC. The concentrations of the permeating ions are then plugged into a modified Equation 21 (to account for the withdraw of the 2.5 mL every half hour). As mentioned before, watch the sign of $J_w$, it should be positive when calculating the flux of a feed salt into the draw ($J_f$), and negative in the other case ($J_d$).

3.5 Ion Detection Methods

There are several techniques employed to quantify the concentration of the permeating ions. A conductivity probe is used to measure concentration changes in single salt tests. Ion Chromatography is the work horse of the lab, doing nearly 95% of the quantification work for bidirectional experiments. IC is also used to quantify single salt experiment concentrations when the concentrations of the permeating species are too low to be measured accurately by the conductivity probe. Inductively Coupled Plasma analysis and an UV-Vis analysis for ammonium are primarily used to verify the concentrations computed using IC analysis.\textsuperscript{33}
3.5.1 Conductivity Probe

Conductivity (the inverse of resistance) is a property of salts that depends simultaneously on the diffusivity and the charge carrying capacity of the ion pair. Accordingly, different salts will have different coefficients relating concentration to conductivity. An Oakton® conductivity probe was used to measure conductivity. For each salt a calibration curve was made up relating conductivity to concentration in the range of interest (~$10^{-5}$ molarity). A generic conductivity calibration curve is given in Figure 3.5.1. The probe is used to measure concentration every 10 to 15 minutes. In order to verify that the conductivity probe provided accurate readings of salt concentration, several experiments were ran where the concentration was determined by IC, as well as with the conductivity probe. This method of measuring salt flux is valid in both PRO and FO modes.

Figure 3.5.1: A conductivity probe calibration curve for the salt sodium chlorate (NaClO₃). The $R^2$ value was 1.000. Credit: Trenton Jackson
3.5.2 Ion Chromatography

The CEST A64 Thermo Dionex® ICS-5000 system serves as the basic instrument used for quantitative ion analysis. An AS23 column is employed to separate anions in samples, whereas an AS16 column is used for cations. After samples are withdrawn during experiment described previously, they are diluted 1:5 (100 μL to 500 μL). Note that the dilution of 1:5 is only a minimum requirement for bidirectional tests, as it is not the permeating ion that needs to be diluted, but rather the bulk salt ions so that they will not overload the column. The prepared samples are placed in the auto-sampler along with 5 standards with dilution ratios of 1:160, 1:200, 1:285, 1:500, and 1:2500 of a 10 mM stock solution. These dilutions are picked based on the range expected from the data. A calibration curve for the IC is given in Figure 3.5.2.

IC separates the ions based on their affinity for the mobile phase versus the stationary phase. When the ions elute from the analytical column they flow into a cell that has a potential applied across it. The ions flow in opposite directions determined by the sign of their charge. Depending upon the analysis, an ion exchange membrane trades proton or hydroxyl groups for the ions. When the ions reach the other side of the membrane they change the conductivity reading which is recorded against time via computer. The result is a chromatographic peak (μS min). The peak areas can be related to concentration via the standards.
3.5.2 IC calibration curve for chloride. A 10 mM stock solution was used to prepare the standards. Dilution ratios of 1:160, 1:200, 1:285, 1:500, and 1:2500 are used.

3.5.3 UV-Vis Spectra Analysis for Ammonium

This method is employed specifically to ammonium containing samples. Via an organic reaction, all ammonium in a sample can be linked to phenol forming indophenol, which has a characteristic adsorption at 640 nm. Thus by preparing standards, the concentration of ammonium can be quantified in samples collected during single, and bi-directional tests. The experimental procedure from the literature was modified by reducing all reagents by 1/5. For example, 1 mL was withdrawn from the samples collected during the bidirectional tests and diluted 1:5 resulting in a 5 mL solution; whereas the original protocol called for a 25 mL sample, which is unrealistic for the experimental setup. A comparison between this method and IC is shown in Figure 3.1.3.
3.5.4 Inductively Coupled Plasma Analysis

ICP experiments were used as another check for the reported IC values. Solutions were prepared from samples at 1:10 dilution with .2 v/v nitric acid. Standards were created in the same way as described in the IC section. ICP is an elemental analysis technique, which is powerful and limiting at the same time (e.g. ICP will not distinguish between an elements’ source).

3.6 Partition Experiments

Membranes supplied by HTI were cut into 1 inch diameter circles. Twenty samples were prepared and stored in DI. Each sample was removed and pat dried with a Kimwipe™. The mass was then measured. This procedure was repeated for all twenty samples to get an average mass to diameter.

In 40 mL Falcon™ tubes salt solutions with varying concentration between 0.25 M and 1.0 M with and without nitrate at 0.05 M were prepared. Solutions of pure nitrate were also prepared at 0.1 M, 0.05 M, 0.01 M and 1 M. Dab dried circle-cut membranes were placed in the solutions (three per solution) and allowed to equilibrate over 24-hours. After 24-hours the samples were removed, dab dried, and placed in 40 mL of DI water. These samples were also allowed to equilibrate with the DI water for at least 24 hours. Finally, 1 mL samples were withdrawn from the DI vials and ran in the IC. The reported partition coefficients are calculated with the assumption that all adsorbed salt in the membrane was desorbed when the membrane was placed in the DI solution.
The partition coefficient is given as the ratio of calculated $C_{\text{mem}}$ to the original salt concentration, $C_{\text{salt}}$.

$$H = \frac{C_{\text{mem}}}{C_{\text{salt}}}$$ (29)

with $C_{\text{mem}}$ given by

$$C_{\text{mem}} = \frac{C_{\text{DI}}V_{\text{DI}}}{M_{\text{ave}}^{\text{mem}}}$$ (30)

where $M_{\text{ave}}^{\text{mem}}$ is the average mass of the membrane section.
RESULTS

4.1 Single Salt Experiments

As mentioned before, single salt experiments are important part of establishing the Fickian model. Without these measurements there is no ability to predict non-interacting salt permeations for bidirectional experiments.

4.1.1 PRO and FO Experiment Results

For the establishment of the $B$ parameter, PRO experiments were run at 0.05, 0.25M, 0.5M and 1.0M. Thus, this experiment not only allowed for the establishment of $B$, but verifies that the mechanism by which the solute permeates is indeed a solution diffusion mechanism, as compared to pore diffusion.$^{24,35}$ The difference between the two being that in pore diffusion the salt flux would be proportional to the water flux. Chloride PRO results are presented in Figure 4.1.1.
Figure 4.1.1: Permeability coefficient ($B$) versus concentration, and observed water flux. The data shows that $B$ is not dependent on concentration nor water flux, which is evidence for the solution diffusion model used by previous works to develop the Fickian model.\textsuperscript{20,21,24,35}

If the orientation of the membrane is flipped then the $S$ parameter can be quantified. Instead of quantifying the $S$ parameter for each membrane as had been in previous papers, the average $S$ parameter over many membranes was quantified.\textsuperscript{20} The value of $S$ calculated was 498.1±0.6 μm. $A$ was also calculated from the same FO data and resulted in a value of 0.48±0.05 L m$^{-2}$ h$^{-1}$ bar$^{-1}$, as compared to 0.44±0.12 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ from previous papers.\textsuperscript{21}

Furthermore, single salt tests were used to check that the transport properties of the membranes had not changed over the course of several tests and weeks of use in the FO cell. Table 4.1.1 contains the calculated B-values from the PRO results.
4.1.2 Single Salt Partitioning Experiments

In these experiments membrane samples were soaked in solutions containing only one salt. The goal was to establish a baseline result to which to compare the multiple salt partitioning experiments. These experiments are important because coupled diffusion coefficients are typically 10% of the individual ion diffusivity. Hence, in systems that show multi-component behavior, quantifying the change in a partition coefficient can potentially explain deviatory behavior. The results are summarized in Table 4.1.2.

### Table 4.1.2

<table>
<thead>
<tr>
<th>Salt:</th>
<th>NaCl</th>
<th>KCl</th>
<th>NH₄Cl</th>
<th>Mg₂Cl</th>
<th>NaBr</th>
<th>KBr</th>
<th>NaClO₃</th>
<th>NaNO₃</th>
<th>KNO₃</th>
<th>NH₄NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{app} \times 10^9$ (m$^2$/s)</td>
<td>1.61</td>
<td>1.99</td>
<td>2.00</td>
<td><strong>1.61</strong></td>
<td>1.62</td>
<td>1.95</td>
<td>1.67</td>
<td>1.56</td>
<td>1.91</td>
<td>1.91</td>
</tr>
<tr>
<td>$K \times 10^9$ (m/s)$^a$</td>
<td>1.25</td>
<td>1.40</td>
<td>1.45</td>
<td>1.45</td>
<td>1.22</td>
<td>1.41</td>
<td>1.45</td>
<td>1.51</td>
<td>1.45</td>
<td>1.45</td>
</tr>
<tr>
<td>$B \times 10^8$ (m/s)</td>
<td>4.72</td>
<td>5.92</td>
<td>7.68</td>
<td>1.61</td>
<td>8.53</td>
<td>13.6</td>
<td>10.6</td>
<td>12.8</td>
<td>18.1</td>
<td>36.2</td>
</tr>
</tbody>
</table>

Note: $\kappa$ and $D_{app}$ were taken from the literature.$^{20,36}$
4.2 Multicomponent Bidirectional Experiments

The results contained within this section look to establish how, and why nitrate systems are deviating from the Fickian model, with emphasis on the assumptions inherent to the model.

4.2.1 Deviation of Nitrate

The results definitively show that not only does nitrate deviate but so does the draw anion. Figure 4.2.1 shows that even by doing an error propagation calculation for $B$, and the surface concentration, the result still does not account for the deviation of

---

TABLE 4.1.2

PARTITION COEFFICIENTS

OF SINGLE SALTS

IN A HTI FO MEMBRANE

<table>
<thead>
<tr>
<th>Salt: System</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NaClO$_3$</th>
<th>NaNO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol/L)</td>
<td>Anion</td>
<td>Cation</td>
<td>Anion</td>
<td>Cation</td>
</tr>
<tr>
<td>1.0</td>
<td>$8.56E-04$</td>
<td>$3.64E-04$</td>
<td>$6.83E-04$</td>
<td>$2.95E-04$</td>
</tr>
<tr>
<td>0.5</td>
<td>$5.92E-04$</td>
<td>$3.70E-04$</td>
<td>$6.22E-04$</td>
<td>$3.38E-04$</td>
</tr>
<tr>
<td>0.25</td>
<td>$5.60E-04$</td>
<td>$6.70E-04$</td>
<td>$5.66E-04$</td>
<td>$6.08E-04$</td>
</tr>
</tbody>
</table>
nitrate from the Fickian prediction. The dashed green lines represent 1 standard deviation from the predicted value (solid green line).

Figure 4.2.1: The nitrate concentration was held constant for all draw concentrations as 0.05M. Samples were withdrawn every half hour over a two hour experiment. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The solid lines represent the predicted flux produced by the Fickian model. The dotted line is a rough error calculation produced by assuming 100% error in the surface concentration of nitrate, and the standard deviation of the B coefficient of nitrate according to the rules of error propagation.

4.2.2 Effect of Hydrolysis

One of the original proposed mechanism was that nitrate, in the presence of the draw solute, caused a higher than normal rate of hydrolysis. Hydrolysis is the process of cleaving the ester bond between the acetate group and the gluconic repeat unit. Previous published results suggest that the rate of hydrolysis of cellulose acetate increases at high and low pH. Furthermore, very early research suggested that the presence of salts also affected the rate of hydrolysis.
Accordingly, a selection of Good’s Buffers (large organic buffers) were chosen based on a desired buffering range. Large buffers were wanted to prevent their permeation across the membrane. Experiments were run with both draw and feed buffered, along with experiments where only one side or the other was buffered. Figure 4.2.2 shows that the pH of solution had no effect on the anion fluxes during the relatively short duration of the experiments.

Figure 4.2.2: Buffering the draw and feed showed no effect on chloride or nitrate flux. All system were NaCl (draw) – 0.05M NaNO3 (feed). The buffers used were citric acid, 2-(N-morpholino)ethanesulfonic acid (MES), and tris(hydroxymethyl)aminomethane (TRIS); citric acid for pH 3, MES for pH 4, and TRIS for pH 8. Error bars represent one standard deviation. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The dotted lines represent predicted fluxes based on the Fickian model.

4.2.3 Effect of Draw and Feed Cation Identity

The permeability coefficient is dependent on the salt. As stated previously, the diffusion coefficient for a strong electrolyte is calculated by taking the harmonic average of the diffusion coefficients of the individual ions. Hence, a reasonable assumption is that by pairing chloride with a more mobile cation, higher draw fluxes would be
observed. Chloride was paired with potassium, ammonium, and magnesium, and these salts were run as the draw. Figure 4.2.3 shows the result of the 1:1 electrolytes. The effect of the mobility of the draw cation seems to be only on the draw anion. Furthermore, as clear from Figure 4.2.3, $B$ is less of a predictor of the chloride flux than the diffusion coefficient of the cation in an aqueous solution. The diffusion coefficient is the same for both $K^+$ and $NH_4^+$ in an aqueous solution.\textsuperscript{36}

![Figure 4.2.3: The mobility of the draw cation affects the permeation of draw anion. The increase is directly correlated to the diffusional coefficient of the cation. KCl and NH$_4$Cl have different B-values, as is clear from the predicted fluxes. However, K$^+$ and NH$_4^+$ have the same diffusion coefficient in solution. Error bars represent one standard deviation. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The dotted lines represent predicted fluxes based on the Fickian model.](image)

The feed cation data is a comparison between potassium and sodium containing nitrate salts. The results are plotted in Figure 4.2.4. The results demonstrate the identity of the feed cation plays no role in the flux of the nitrate, suggesting that nitrate containing systems violate one of the main assumptions of the Fickian model: electrolyte permeation. As stated before, EP is a direct result of the assumptions of non-
interacting feed and draw fluxes and the necessity to maintain electroneutrality. Clearly from the graph, the model predicts that when coupled with a more mobile cation (K⁺), nitrate will permeate quicker. However, Figure 4.2.4 shows that KNO₃ and NaNO₃ result in the same nitrate flux.

![Graph showing chloride and nitrate fluxes](image1)

Figure 4.2.4: Changing the feed cation does not affect the nitrate flux. Error bars represent one standard deviation. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The dotted lines represent predicted fluxes based on the Fickian model.

4.2.4 Effect of Draw Anion Identity

Thus far, the data has established that the cation identity (feed or draw) does not affect the deviatory behavior of nitrate. Accordingly, the next step was to elucidate the effect of draw anion. Systems of bromide or chlorate coupled to sodium were run. The results are plotted in Figure 4.2.5. The data shows that a more mobile draw anion (based on the diffusivity of the salt in an aqueous solution) increases the nitrate flux. Thus, having shown that the draw cation has no effect, and that the anion does, strongly
suggests decoupling behavior. In other words, the permeation of a draw anion is semi-independent from the permeation of the draw cation.

![Graphs showing ion permeation](image)

Figure 4.2.5: The salts in the legend were the draw salts, and the feed salt was 0.05 M NaNO₃. Error bars represent one standard deviation. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The dotted lines represent predicted fluxes based on the Fickian model.

4.2.5 Behavior of Non-Nitrate Containing Systems

The interest in these experiments arises from the need to quantify random error in the study. Although a rough estimate of experimental error was given earlier, by running other salts in the feed and showing that the fluxes agree with the non-interacting model, the deviation of nitrate can be shown to be a real phenomenon. Accordingly, a system of NaCl – NaBr was run. The results show that within a reasonable doubt, both the draw and feed anions are predicted by the $B$ values calculated in the single salt tests. A set of Chlorate containing feed solutions was also run. Strangely enough, this data also showed deviatory behavior from the predicted values, although of a lesser degree than nitrate. The results are plotted in Figure 4.2.6.
Figure 4.2.6: Chlorate containing systems also deviated from the Fickian model, while bromide systems did not. All systems were run with NaCl as the draw salt, and with the feed salt at 0.05 M. Error bars represent one standard deviation. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The dotted lines represent predicted fluxes based on the Fickian model.

4.2.6 Multi-Component Partition Behavior

In these experiments, nitrate containing salts at feed concentrations (~0.05 M) were mixed with non-nitrate salts at draw concentrations (1.0 M, 0.5 M, and 0.25 M). The goal was to observe a change in the nitrate partition coefficient due to the presence of the counter salt as compared to the single salt partition. The Table 4.2.1 shows that the nitrate partition coefficient is unaffected by the presence of any of the salts tested. The values of the table are averages of 3 data point. Some points were omitted as the standard deviations were on the same order as the mean. The data clearly shows that the deviatory behavior of nitrate is not due to a change in the partition coefficient.
### TABLE 4.2.1

**PARTITION COEFFICIENTS**

**OF IONS**

**IN MULTIPLE COMPONENT SOLUTIONS**

---

#### Single Salt Test

<table>
<thead>
<tr>
<th>Salt:</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NaClO₃</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NaClO₃</th>
<th>NaNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conc. (mol/L)</td>
<td>K-value x 10⁴ [(mol/g\text{mem})/C\text{sol}]</td>
<td>Conc.</td>
<td>K-value x 10⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>8.6</td>
<td>6.8</td>
<td>8.5</td>
<td>3.6</td>
<td>2.9</td>
<td>6.7</td>
<td>0.1</td>
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<tr>
<td>0.5</td>
<td>5.9</td>
<td>6.2</td>
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<td>3.7</td>
<td>3.4</td>
<td>6.3</td>
<td>0.05</td>
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<tr>
<td>0.25</td>
<td>5.6</td>
<td>5.7</td>
<td>7.1</td>
<td>6.7</td>
<td>6.1</td>
<td>6.5</td>
<td>0.01</td>
</tr>
</tbody>
</table>

#### Mixed Salt Tests

<table>
<thead>
<tr>
<th>Salt:</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NaClO₃</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NaClO₃</th>
<th>NaNO₃ at 0.05 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other Salt:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05M NaNO₃</td>
</tr>
<tr>
<td>Ion:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anion</td>
</tr>
<tr>
<td>Salt Conc.*</td>
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<td></td>
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<tr>
<td>K-value x 10⁴</td>
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<td></td>
</tr>
<tr>
<td>0.75</td>
<td>6.9</td>
<td>7.1</td>
<td>-</td>
<td>6.7</td>
<td>6.7</td>
<td>6.9</td>
<td>6.0</td>
</tr>
<tr>
<td>0.5</td>
<td>6.7</td>
<td>6.7</td>
<td>7.3</td>
<td>6.0</td>
<td>6.7</td>
<td>4.7</td>
<td>6.2</td>
</tr>
<tr>
<td>0.25</td>
<td>6.0</td>
<td>6.0</td>
<td>7.1</td>
<td>6.4</td>
<td>6.4</td>
<td>6.4</td>
<td>5.9</td>
</tr>
</tbody>
</table>

**NOTE:** A clear description of how the partition experiments were conducted and the coefficients calculated is given in section 3.6. A dash denotes excluded data. Data was excluded when the standard deviation of the set was of the same order as the mean. * for the nitrate mixed salt tests, salt concentration applies to *Other Salt*. + the cation partition for mixed salts is calculated for the total concentration of sodium ions, e.g. for a 0.5 M NaCl mixed with a 0.05 M NaNO₃, the total concentration of sodium is 0.55 M.
4.3 Weak Anionic Exchange Membrane Behavior

A weak ion exchange membrane is defined as barrier that allows for a higher permeation of one type of ion (i.e. cation or anion) over the other. There are a few membranes known to behave in this way. Normally, they have a weakly disassociated substitutonal group.41,42

4.3.1 Quaternary Nitrate Systems

The literature shows that cellulose-acetate membranes often act as weak ionic exchange membranes, specifically, cationic exchange.42,43 However, there is some precedence for switching the membranes characteristics to an anionic exchange membrane. To test the ion-exchange behavior of the HTI membranes, quaternary experiments were ran, similarly to the results from 4.2.4, except now both the cationic and anionic fluxes were quantified. A quick look at Figure 4.3.1 shows that clearly the cations are moving across the membrane at slower rates than the anions. This is the exact behavior expected of anionic exchange membrane, and donnan dialysis.3 This is an odd result, considering that in previously published results, the researchers had to soak a cellulose acetate membrane in a magnesium salt for a day to observe this type of behavior.42 Table 4.3.1 summarizes the data in Figure 4.3.1. Here the draw cation has been taken to be in the positive direction. Hence a sum of the draw flux that results in a negative number demonstrates a dominance of anionic flux. The opposite is true for the feed side, where the anion flux is now positive due to the sign of the charge carried and the direction of travel.
TABLE 4.3.1

ELECTRONEUTRALITY

OF QUATERNARY EXPERIMENTS

CONTAINING NITRATE

<table>
<thead>
<tr>
<th>Conc (mol/L)</th>
<th>NaCl - KNO₃</th>
<th>KCl - NH₄NO₃</th>
<th>KCl - NH₄NO₃</th>
<th>NH₄Cl - KNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KCl - NH₄NO₃</td>
<td></td>
<td>NH₄Cl - KNO₃</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>-28.4</td>
<td>29.3</td>
<td>0.9</td>
<td>-54.8</td>
</tr>
<tr>
<td>0.5</td>
<td>-76.6</td>
<td>56.6</td>
<td>-20.0</td>
<td>-80.2</td>
</tr>
<tr>
<td>1</td>
<td>-27.7</td>
<td>57.4</td>
<td>29.7</td>
<td>-128.0</td>
</tr>
</tbody>
</table>
Finally, Table 4.3.1 demonstrates, within reasonable experimental error, that the complete sum of the vector results in electroneutrality, which is expected from a system in the absence of an applied current.

Figure 4.3.1: Monovalent Quaternary Systems. The feed concentration for all experiments was 0.05 M. Error bars represent one standard deviation. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The dotted lines represent predicted fluxes based on the Fickian model.
4.3.2 Monovalent versus Divalent Cationic Effect

From the results above, an interest was taken in divalent cation effect on the permeation of the salts. Accordingly, MgCl$_2$ was run against NaNO$_3$. The results are plotted in Figure 4.3.2. Once, again, it was shown that the identity of the cation does not play a role in the permeation of the anions, although now it has been shown for divalent cations too. This data set also demonstrates a more extreme example of the decoupling of anion and cation fluxes.

![Figure 4.3.2: Mono versus Divalent draw cation. The introduction of a divalent cation did not affect the nitrate and draw anion permeations, providing more evidence for a decoupled mechanism. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The dotted lines represent predicted fluxes based on the Fickian model.](image-url)
4.3.3 Quaternary Results of Systems Not Containing Nitrate

Having earlier observed that chlorate systems also deviate from the values predicted by the Fickian model, and that the bromide systems did follow the predicted values, experiments were ran to quantify the cation fluxes in systems similar to those reported in section 4.2.5. Accordingly, a system of KCl draw and NaClO₃, and a system of NaCl drawn and KBr were ran. The results, with a comparison to the ternary systems, are plotted together in Figure 4.3.3. The data shows that unlike nitrate feed systems, the chloride draw flux is almost exactly as it is predicted by the Fickian model. Interestingly, the bromide system, which has the characteristic of following the Fickian model for both the feed and draw anions, shows a deviation for the feed cation. Whether this is a real phenomenon, or a result of experimental error should be resolved by further experimentation. Table 4.3.2 contains the electroneutrality calculations.
TABLE 4.3.2

ELECTRONEUTRALITY

OF QUATERNARY EXPERIMENTS

NOT CONTAINING NITRATE

| Conc (mol/L) | KCl - NaClO3 | | | NaCl-KBr |
|--------------|--------------|| | | |
| | Draw (meq/m²/hr) | Feed | Sum (meq/m²/hr) | Draw | Feed | Sum |
| 0.25 | -1.77 | 14.6 | -16.4 | 14.0 | -12.0 | 26.1 |
| 0.5 | 10.4 | -33.8 | 44.1 | -6.68 | -15.0 | 8.30 |
| 1 | 2.81 | - | - | 7.52 | -11.3 | 18.8 |

NOTE: - 1 molar chlorate flux was excluded from the set as the IC analysis gave nonsensical concentrations
Figure 4.3.3: Quaternary Systems that do not contain nitrate. The ion concentrations were determined in the drawn samples via IC analysis. Salt flux determination was carried out as described in the experimental section 3.1.3. The dotted lines represent predicted fluxes based on the Fickian model.
CONCLUSIONS/FUTURE WORK

The data clearly shows that in the presence of nitrate the membrane acts as an anionic exchange membrane. The behavior might also be compared to donnan dialysis, with the exception that it seems to be selective towards nitrate, and to a lesser extent chlorate; whereas a true donnan dialysis mechanism would not be selective. The fact that both nitrate and chlorate deviate is a good place to start when attempting to solve the riddle of the data. What do these two ions have in common with one another and to the membrane? There is also some possibility that the crystalline structure of the membrane is somehow contributing to the observed behavior.\textsuperscript{44,45} Data currently being collected by Dr. Rajesh Sahadevan suggests that the super structure of the casted membrane has a significant effect on its ability to transport ions. Even though these are the type of questions that the project in the future aims to answer, there are still some glaring holes in the data presented in this thesis.

To start, much of the quaternary data should be replicated several times. Furthermore, there is much work that can be done to investigate the effect of valency. Experiments should be conducted were nitrate is coupled with a divalent cation. Furthermore, the effect of a divalent draw anion might yield interesting results. Beyond nitrate containing systems, there are still unanswered questions. More systems that do not contain nitrate should be run. A good place to start would be with perchlorate,
which showed very predictable behavior in a previously published paper.\textsuperscript{20} Finally, a question of interest to this researcher is whether or not specific cationic systems will show similar discrepancies to the predicted values. Accordingly, an interesting experiment to conduct would pair chloride containing salts. Ammonium has been observed in this lab and in literature, to have anomalous behavior when interacting with cellulose-acetate membranes. Hence, a system of NaCl draw to a NH\textsubscript{4}Cl feed should be run.

In conclusion, it has been shown definitively that the HTI CTA membrane in the presence of nitrate behaves in a manner reminiscent of a weak ion exchange membrane. The exact transport mechanism that is responsible for this behavior is still unclear. The future applicability of this phenomenon to separation processes depends on the ability to decipher the mechanism. For, if the mechanism is understood, then perhaps the chemistry can be tuned to more selectively transport nitrate and retard water flux.


