Transport and Removal Mechanisms of Trace Organic Pollutants by Nanofiltration and Reverse Osmosis Membranes

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Civil Engineering

by

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ABSTRACT OF THE DISSERTATION

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Nanofiltration (NF) and reverse osmosis (RO) membrane processes have been proved to be promising advanced treatment technologies for purifying water from trace organic pollutants. In order to accurately predict trace organic pollutants rejection by NF/RO membranes, a fully picture of membrane transport mechanism and how membrane intrinsic properties (i.e. membrane structure and chemistry) and surrounding environment (i.e. water chemistry) affect membrane performance should be fully explored.

The objective and focus of this study is to fully understand trace organic pollutant transport through NF/RO membranes. A comprehensive review on the mechanisms and models of solute transport relevant to osmosis membrane separation processes was presented. Classical models (i.e., pore flow, solution-diffusion, and Nernst-Planck) and
discuss the shortcomings of each, particularly focusing on their inability to explain fundamental relationships between water/solute transport and membrane properties, such as free volume, crystallinity, extent of swelling, and the presence of filler materials in mixed matrix/nanocomposite membranes were critically reviewed.

An extension of the classical solution-diffusion model had been developed that relates transport through NF/RO membranes directly to membrane structure descriptors (i.e., effective barrier layer pore size, porosity and thickness, etc.). In general, model predictions agreed well with experimental data suggesting the model captures the phenomenological behavior of commercial NF/RO membranes for separations relevant to modern water treatment objectives. The model also provides new mechanistic insights about the “effective structure” of NF/RO composite membranes and how trace organic solutes are rejected. These results suggest it is possible and important to fine-tune the surface energy of membrane and membrane structure (pore size, porosity, thickness) to achieve high membrane selectivity for certain solute.

The effects of feed solution ionic strength, pH and divalent cation content on NF/RO membrane structure and performance were elucidated experimentally and fitted with the newly developed model. All the membranes tested became more hydrophilic and swollen with increasing feed solution ionic strength, pH, and divalent cation concentrations. Generally, water permeabilities of all three membranes decreased with ionic strength and divalent cation content, but increased with pH. For RO membranes, neutral solute rejection decreased with pH and divalent cation content, but increased with ionic strength and the salt rejection remained independent with water chemistry except
for very low pH of 3; for a NF membrane, solute rejection was more sensitive to water chemistry and neutral solute rejection decreased with ionic strength, pH, but increased with divalent cation content. Ultimately, these new insights may be useful in selection of already commercial or design of new NF/RO membranes for removal of chemicals of emerging concern in water treatment.

Four different organic solute removals by six different commercial NF/RO membranes in laboratory re-created groundwater matrix were experimentally determined. In addition, membrane structural descriptors and solute-membrane interaction energies were quantified using the newly developed model. SWRO membranes exhibited excellent removal efficiency (> 90%) for both NDMA and 1,4-dioxane in groundwater, while NF membranes showed inefficient separation. Methanol could not be effectively removed by NF/RO membranes. Correlation studies suggested that both size exclusion and thermodynamic partitioning play important roles in trace organics removal and a partition coefficient, which combines both steric effects and solute-membrane interactions, can be employed to predict organic solute rejection by NF/RO membranes.
The dissertation of Jinwen Wang is approved.

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CHAPTER 1

INTRODUCTION
1.1 General Introduction

Clean water supplies are dwindling in the modern world. While the quantity of fresh water remains relatively constant, the demand of our rapidly increasing population has exploded in the last century [1]. Inefficient use of water, climate change driven water scarcity, and industrial pollution have led to the current state in which nearly 1.8 billion people live in water scarce regions and over 780 million people lack access to improved drinking water [2]. Thanks to global efforts of improved sanitation and infrastructure access to improved drinking water has been expanded significantly in the last 20 years [2]. To ensure further improvements and maintain water security into the future new freshwater sources will need to be explored further, such as reclaimed wastewater and desalinated seawater.

Aqueous trace organic pollutants are synthetic and natural organic compounds, such as industrial chemicals (e.g., solvents, intermediates, petrochemicals), industrial products (e.g., additives, lubricants), pharmaceutically active compounds (PhACs), endocrine disrupting compounds (EDC), biocides (pesticides, nonagricultural biocides), disinfection by-products, surfactants, and dyes [3, 4]. These organic chemicals are widespread in natural waters at low concentrations (µg/L or ng/L) and are considerably toxic, presenting a major environmental problem around the world [3]. Although the specific health effects of these pollutants at low concentrations are not yet fully understood, it is accepted that drinking water should free of such compounds. Thus, suitable treatment technologies are needed.
Membrane processes are now the primary separation technology used in wastewater reclamation and desalination. These technologies are efficient and effective, but there is a continued need to expand and improve their capabilities [5-9]. Improved NF membranes now enable highly energy-efficient removal of color-causing organic matter, hardness minerals, toxic metals, and chemicals of concern, from both natural and industrial waters [10]. Secondary municipal wastewater effluent, brackish groundwater, industrial wastewaters, and seawater are all purified using RO membranes to produce ultra-pure water for potable, agricultural, and industrial purposes [11]. Engineered osmosis processes, such as FO and pressure retarded osmosis (PRO), may further diversify our water future through low-energy desalination, membrane bioreactors, salinity gradient power, and osmotic energy recovery [12-14]. Membranes can be formed with a wide range of structures, chemistries, and performance characteristics by changing the material or altering the fabrication process [9]. The possibilities are seemingly endless, but effective material tailoring requires some degree of a priori knowledge. This intuition is difficult to gain due to the lack of predictive models relating membrane structure and chemistry to performance and a less efficient trial-and-error approach is often taken.

Another remaining challenge is a quantitative understanding of the relationship between NF/RO membrane structure, performance and feed solution chemistry. In a recent review, Luo and Wan comprehensively summarized the effect of solution pH and salt content on NF membrane transport [15]. Different mechanisms are proposed depending on solute type [16-22]. For charged solutes, it is thought that increasing ionic
strength, divalent cation content and lower pH all reduce Donnan exclusion, and hence, enhance ion permeation through by charged NF/RO membranes [23, 24]. However, charge interactions cannot explain changes in neutral solute rejection, which have been also observed with changes in feed water chemistry. Some researchers suggest reduction in the Stokes radius of neutral solutes due to salt ions with higher hydration energy outcompeting neutral solutes for water molecules [25, 26]. Membrane swelling and de-swelling have also been proposed to explain changes in neutral solute rejection with differences in feed water pH and ionic strength [19]. Freger and co-workers measured changes in polyamide layer thickness using atomic force microscopy (AFM) after soaking membrane in solution with different salt concentrations and pH [20]. They observed a correlation between the changes in polyamide layer thickness, permeability and solution chemistry (salinity and pH).

Historically, it has been difficult to directly characterize NF/RO membrane structure (pore size, film thickness, porosity) when exposed to different water chemistries. First, the current structure characterization techniques may not be accurate enough to resolve subtle changes [15]. Also, most structural characterization techniques are not conducted in representative filtration conditions (saturated with water and solute, wet, flowing and under positive feed pressure). Many researchers have attempted to calculated membrane structure parameters with neutral solute rejection data based on membrane transport models [15, 27, 28]. Luo and Wan fitted experimental glucose rejection data with a membrane transport model considering steric exclusion to estimate an apparent membrane pore size and structure factor (the ratio of membrane thickness to
porosity) for high salinity feeds [23]. Verliefde et al. claimed that solute transport predictions made by assuming only steric exclusion significantly overestimated solute rejection. They established a “solute-membrane affinity” model (essentially an extended solution-diffusion model), which considered both steric effect and solute-membrane interaction, to predict neutral solute rejection by NF membranes [28]. However, in these studies only one background water chemistry was evaluated. Moreover, two structure parameters (pore size and structure factor or the ratio of thickness to porosity) were estimated by one transport equation (solute rejection). With only one equation and two unknowns the structure factor was assumed to extract an apparent pore size.

Recently, nanofiltration (NF) and reverse osmosis (RO) processes have been considered for trace organic removal from ground and surface water. However, low to moderate trace organic solute, especially neutral solute (such as NDMA, 1,4-dioxane), rejection by NF/RO membranes has been reported [29-31]. As reviewed by Bellona et al. [18], solute physical-chemical properties, membrane properties and feed water chemistries were all identified to have influences on organic solute rejection by NF/RO membranes. However, solute rejections depend on the combination of all above parameters, so there is no single parameter can be used to correlate with solute rejection for prediction purpose. And it is hard to characterize some of the above key parameters, such as structural parameters of NF/RO membrane under filtration condition.

1.2 Research Hypothesis and Objectives
Based on the above background review and understanding of transport and removal mechanisms of trace organic pollutant by NF and RO membranes from literatures, the following hypotheses were developed:

1. Solute transport through NF/RO membrane is governed by structure-performance relationship.

2. Background water chemistry changes (1) membrane physical structure due to swelling caused by ions; (2) membrane chemical properties (interfacial energy).

3. Rejection of trace organic pollutants by NF/RO membranes can be correlated with solute-membrane partition coefficient, which represents both steric interaction and solute-membrane interaction.

In order to testify the above hypotheses, the present research has the following objectives:

1. Develop a structure-performance transport model with incorporating solute-membrane interaction for NF/RO membranes.

2. Investigate the effect of water chemistry on NF/RO membrane structure and performance.

3. Illustrate the mechanism of trace organic pollutant removal by NF/RO membranes and develop a feasible method to predict membrane rejection.

1.3 Overview of Dissertation

The present dissertation includes 6 Chapters and 1 Appendix. In Chapter1, the hypotheses and the objectives after a general introduction.
Chapter 2 is a critical literature review of transport models for osmotic membranes. In each model, the parameters and methods needed to effectively apply the models are laid out with paying particular attention to the inherent advantages and limitations of each.

Chapter 3 presents the mathematical derivation and experimental validation of new structure-performance transport models, including solution-diffusion-affinity model and solution-diffusion-convection-affinity model. The effects of membrane structure and operation condition on membrane transport have also been illustrated.

In Chapter 4, the newly developed transport model is used to more accurately quantify changes in membrane structure and solute-solvent-membrane interactions due to changes in feed water chemistry (ionic strength, pH and divalent cation content). The mechanism of membrane structure change salt induced membrane swelling/deswelling is also presented.

Chapter 5 discussed the removal mechanism of trace organic pollutant by NF/RO membranes. Different parameters describing solute/membrane structure and solute-membrane interaction are used to correlate with solute rejection. And a partition coefficient, which incorporates both solute-membrane structural properties and solute-membrane interaction, is proposed to predict solute rejection by NF/RO membranes.

Finally, a list of major conclusions and suggestions for future research are included in Chapter 6.
1.4 References


CHAPTER 2

TRANSPORT THROUGH OSMOTIC MEMBRANES: A CRITICAL REVIEW
2.1. Introduction

A fundamental understanding of the mechanisms at play in membrane separations is crucial to furthering the field and intelligently tuning materials to meet the presently growing needs and applications [1]. Transport models are the tools used to understand membrane transport. Two primary categories exist: phenomenological and mechanistic models [2]. Phenomenological models treat the membrane as a “black box” and describe the separation process in terms of measurable parameters, such as solute passage and water flux. Empirical coefficients are used to represent the separation performance of a membrane by relating measured concentrations in the feed and the permeate streams. While these can be used to characterize performance they offer no mechanistic explanation of separation and are, therefore, difficult to compare between materials. Mechanistic transport models have been developed to relate the separation performance observed in a membrane to the physical (e.g., pore structure, solute size) and chemical properties (e.g., energy of interaction) of the membrane and solute materials. Such structure-performance relationships allow for a more fundamental understanding of membrane transport. Herein, we review the types of membranes and relevant mechanistic transport models for osmotic membrane separations. In each model, we lay out the parameters and methods needed to effectively apply the models, paying particular attention to the inherent advantages and limitations of each.
2.2. State of the Art Osmotic Membranes

2.2.1. Integrally-skinned asymmetric membranes

The majority of membranes currently employed in industry are asymmetric porous membranes [3-5]. In asymmetric porous membranes structure and transport properties vary across the membrane thickness. An asymmetric membrane normally consists of a 0.1-1 µm thick dense layer supported by a highly porous, 100-200 µm thick support layer [3, 4]. The dense layer provides the majority of selectivity for the membrane. Separation properties are determined by the chemical nature, size of pores (0.4-1 nm), and thickness of the skin layer. The porous substructure is assumed to provide mechanical support for the thin and fragile selective layer and thought to have little effect on the separation performance of the membrane. Recently, however, the effects of the support layer chemical properties (e.g., hydrophilicity/hydrophobicity) and pore structure (i.e., pore size and porosity) on composite membrane transport have been re-evaluated [6-9].

2.2.2. Thin film composite membranes

In thin film composite membranes, the porous support layer is generally an integrally skinned membrane formed through the non-solvent induced phase separation (NIPS) process. The skin layer is typically formed through either interfacial polymerization or dip coating followed by cross-linking [4, 10]. The most common thin film chemistry for RO membranes is based on a fully aromatic polyamide (PA) formed by interfacial polymerization of meta-phenylenediamine (MDP) and trimesoyl chloride.
(TMC), while popular polyamide NF membranes are formed by interfacial polymerization of piperazine and TMC [10]. It is assumed that the dense selective layer formed by interfacial polymerization is heterogeneous throughout its thickness (20-200 nm) and highly cross-linked. The surface properties of a PA film are different from the properties within the PA dense layer because the polymer density is not uniformly distributed [11]. The PA dense layer is highly negatively charged since acyl chloride groups are not fully converted to amide in the formation process; however, it was recently reported that direct titration experiments revealed the simultaneous presence of both positive and negative fixed charges in the dense layer of composite PA NF membranes [12]. Freger and Srebnik proposed the fixed charge is not uniform and the film is actually a “sandwich” comprising two oppositely charged layers [13].

The dense coating layer has historically been treated as a non-porous film. Recently more advanced characterization techniques, such as atomic force microscopy, scanning electron microscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy, electron spin resonance, nuclear magnetic resonance (NMR), small angle X-ray scattering, and molecular dynamics simulation have been employed to reveal the dense layer structure. A highly cross-linked PA skin layer structure with sub-nanoscale pores (0.2-1 nm) and low porosity has been reported in literature [14-20].

2.2.3. Thin film nanocomposite membranes

Mixed-matrix membranes contain both organic and inorganic phases. The first mixed-matrix membranes were produced to enhance the performance of gas separation
membranes by providing interconnected flow paths of high diffusion rate materials [21].

In aqueous separations, mixed matrix membranes are generally formed from a polymer matrix with inorganic particles dispersed throughout. Classically, micron-scale inorganic fillers (e.g., zeolites and silicalite) were added to polymer membranes to form preferential flow paths for the fast transport of certain molecules [22, 23]. When nanomaterials (e.g., metal and zeolites nanoparticles) are used as the inorganic filler these membranes are referred to as nanocomposite membranes [24-27]. Inorganic particles may be present throughout the thickness of a symmetric or integrally-skinned membrane or exclusively in the coating film of a composite membrane. In theory, mixed matrices add an additional degree of freedom to membrane fabrication since the advantages of a certain filler material can be imbued into a bulk membrane material [21]. Mixed matrices have been employed to improve the overall mechanical and chemical stability of organic membranes and to add certain functionality to the interface of polymer membranes, for example targeted degradation, reduced fouling, or enhanced selectivity [27-32].

There has been a great deal of interest in using organic-inorganic hybrid membranes as next generation membrane materials for water treatment. In a quest to address low water fluxes in membranes, scientists have attempted to use nanoparticles like TiO$_2$ [33], carbon nanotubes [34], zeolites [35-37], clay [38], non-porous amorphous silica [6] and many more to enhance water flux. Jeong et al. incorporated zeolite nanoparticles in the dense layer of a polyamide membrane and increased the water permeability 1.5 times while maintaining the salt rejection [37]. The authors believed the pore in the zeolites acted as a preferential flow path for water to permeate through, while still being small
enough to reject salt ions. Pendergast et al. incorporated zeolites in both the dense layer and the support layer of composite RO membranes and found that the nanoparticles help membranes to resist compaction under hydraulic pressure [6]. Unfortunately, to this end very few scientists have studied solvent and solute transport in mixed matrix materials.

2.3. Membrane Transport Models

Numerous phenomenological and mechanistic models have been proposed to describe solute and solvent transport through porous and dense membranes. For dense membranes, perhaps most popular is the “solution-diffusion” model, in which permeants dissolve at the membrane interface and then diffuse through the membrane along the concentration gradient. In this model, separation between different permeants results from dissimilarities in the amount of mass that dissolves per membrane volume and/or the rate at which it diffuses through the membrane [5]. Pore-flow models also exist, in which different permeants are separated by size, frictional resistances, and/or charge. In addition to the solution-diffusion and pore-flow models, the Kedem-Katchalsky and Spiegler-Kedem models employ irreversible thermodynamic arguments to derive solute and solvent transport equations while treating the membrane as a “black box” [39-42]. Recently, solute/solvent-membrane affinity has also been taken into account in the convection-diffusion-affinity model [43]. Finally, mixed-matrix membranes introduce new complexities into membrane transport where multiple phases potentially containing different characteristic pore size, solubility, and diffusivity are present within a single membrane.
2.3.1 Solution-diffusion model

The solution-diffusion model applies to “non-porous” membranes in which separation is a result of differences in solubility and diffusivity of permeates. Lonsdale et al. [44] proposed the solution-diffusion model to describe transport in “non-porous” membranes based on four assumptions [44-46]: (1) the membrane morphology is homogeneous and non-porous, (2) the solvent and solute dissolve in the membrane nonporous layer and then each diffuses across it down their respective concentration gradient, (3) the solute and solvent diffuse across the membrane independently, each due to its own chemical potential, (4) the chemical gradients are the result of concentration (activity) and pressure gradients across the membrane. The chemical potential difference (Δµ) is given by

\[ \Delta \mu_i = R T \ln \Delta a_i + V_i \Delta p \]  

(2.1)

where \( a_i \) is the activity of the solute or solvent, \( V_i \) is the molar volume, and \( \Delta p \) is the pressure differential across the membrane. The variation of \( p, \mu, \) and \( a \) across the membrane are show in Fig. 2.1.

![Figure 2.1](image)

**Figure 2.1.** Depiction of the assumptions of the solution-diffusion model (adapted from Wijmans et al. [47] and Paul [48]), showing chemical potential (\( \mu \)), pressure (\( p \)), and activity (\( a \)) gradients across the membrane.
The solution-diffusion model treats permeation with a three-step mechanism: (1) the solutes partition into the polymeric membrane on the feed side, (2) the solutes diffuse through the bulk of the membrane, and (3) the solutes partition into the permeate stream. At present most solute transport studies do not take into account the rate at which the solute or solvent partition into the polymeric membrane of interest, instead they consider diffusion through the membrane as the limiting step. The solution-diffusion process is schematically shown in Fig. 2.2. Theoretically, the concentration of component $i$ at the feed side membrane surface ($C_{i,1}^f$) could be higher or lower than the solute concentration immediately inside the membrane ($C_{i,1}^m$); $C_{i,2}^m$ and $C_{i,2}^s$ are the concentrations just inside and outside the permeate side of the membrane, respectively.

![Figure 2.2. Schematic of a solution-diffusion process in a “non-porous” membrane, depicting solutes partitioning into the membrane material at the feed size and then diffusion across the membrane.](image)

There are two parameters used to characterize membrane performance: flux and rejection. Water volumetric flux ($J_w$) is derived from Henry’s law and Fick’s first law of diffusion and is related to water permeability ($A$) as follows
\[ J_w = A(\Delta p - \Delta \pi) = \frac{K_w D_w^m}{\Delta x} \frac{V_w}{R_g T} (\Delta p - \Delta \pi) \]  

(2.2)

where \( \Delta \pi \) is the osmotic pressure difference across the membrane, \( D_{wm} \) is water diffusion coefficient in membrane, \( K_w \) is water-membrane partition coefficient ([kg\textsubscript{water}·m\textsuperscript{-3}\text{membrane}]/[kg\textsubscript{water}·m\textsuperscript{-3}\text{solution}]), \( \Delta x \) is membrane thickness, and \( V_w \) is molar volume of water.

For the solute flux \((J_s)\), Henry’s law is ignored because it is assumed that chemical potential gradient due to pressure is negligible. \( J_s \) is derived from Fick's law with the assumption that the driving force is almost entirely due to concentration differences,

\[ J_s = J_w C_p = B(C_m - C_p) = \frac{K_s D_s^m}{\Delta x} (C_m - C_p) \]  

(2.3)

Here, \( D_s^m \) is the solute diffusion coefficient in the membrane, \( K_s \) is the solute-membrane partition coefficient, and \( C_p \) and \( C_m \) are the solute concentrations in the permeate bulk and at the membrane surface on the permeate side, respectively.

The definition of solute rejection by a membrane is either the observed rejection \((R_o)\) or real rejection \((R_r)\). Observed rejection is calculated from bulk feed \((C_f)\) and the permeate concentrations according to

\[ R_o = 1 - \frac{C_p}{C_f} \]  

(2.4)

while the real rejection is calculated from membrane surface and the permeate concentrations as

\[ R_r = 1 - \frac{C_p}{C_m} \]  

(2.5)
Here, the difference between $C_m$ and $C_f$ is due to rejected solute concentration polarization (see Section 2.5.1 for detailed discussion). However, from the solution-diffusion model (Eqns. 2.3-2.5), the real rejection is determined by the apparent solute permeability coefficient ($B = K_sD_s/\Delta x$ in Eqn. 2.3) and the water flux as

$$R_r = \frac{J_w}{J_w + B}$$

(2.6)

One can predict the basic performance behavior of an RO membrane based on Eqns. 2 and 6. Results for a typical seawater RO membrane are shown in Fig. 2.3. Water flux linearly increases with increasing applied pressure and salt rejection increases with both water flux and applied pressure.

**Figure 2.3.** Salt rejection and water flux as function of applied pressure ($A = 3 \times 10^{-12}$ m/Pa.s, $B = 3 \times 10^{-8}$ m/s, and $\Delta \pi = 2$ bar)
The solution-diffusion model is widely used to predict the performance of “non-porous” membranes in water treatment applications like NF and RO, as well as dialysis, gas separations, and pervaporation [49-60]. The solution-diffusion model was first used to describe the permeation of gases through a dense rubber septa membrane [61]. Most recently, Miyagi et al. [62] studied the transport mechanism of binary organic solvent system through a PDMS-based dense membrane using a regular solution model combined with a solution-diffusion model. Han et al. [63] investigated the transport of toluene through organic solvent silicone rubber membranes and concluded that the solution-diffusion model may be suitable for describing the transport of solvent through a membrane. Subramanian et al. [64] used the solution-diffusion model to investigate the separation of oil constituents by PDMS-based composite membranes. They used the following systems: triglyceride–tocopherol, triglyceride–oleic acid, and vegetable oil-hexane systems and they observed that diffusivity and solubility of the solvent depends on the molecular weight of solvents.

Despite being widely applied, there are known limitations for the solution-diffusion model. For example, Soltanieh and Gill [45] indicated that this model is limited to membranes with low water content, at which the pore flow can be neglected. Another limitation of the model was discovered by Mazid [65], where it was pointed out that it does not adequately describe $J_w$ and $J_s$ for many RO membranes. These deviations were believed to be due to imperfections in the membrane barrier layer, pore flow (convection effects), and solute-solvent-membrane interactions. To address these shortfalls, a new model was formulated: the solution-diffusion imperfection model. This model was used
by Yaroshchuk [66] to describe solute transport in NF membranes and most recently it was used by Fierro et al. [67] as a method to describe organic solvent NF of multi-component systems. Yaroshchuk [68] further revised the solution-diffusion imperfection model to account for the fact that the solute concentration at the exit of an imperfection is decreased due to solute diffusion along the membrane towards the surrounding perfect regions.

2.3.2 Pore models

2.3.2.1 Pore-flow (PF) model

Transport through porous membranes is dominated by size exclusion and can be described by the PF model [67]. This model, proposed by Okada and Matsuura [69], is relatively new. The PF model is based on three assumptions: (1) fluids on either side of membrane are in equilibrium with the membrane at the interface, meaning that there is a continuous gradient of chemical potential ($\mu$) across the membrane, (2) the solute and solvent activity gradients across the membrane are zero and the chemical potential gradient across the membrane can be expressed as a pressure gradient, and (3) straight cylindrical pores exist across the thickness of the membrane. The first two assumptions are depicted in Fig. 2.4.
Figure 2.4. Depiction of the assumptions of the pore-flow model (adapted from Wijmans et al. [47] and Paul [48]), showing chemical potential ($\mu$), pressure ($P$), and activity ($\alpha$) gradients across the membrane.

Considering the mass transport of a single component (water) system, the liquid transport in porous membranes is described by the Darcy’s equation in terms of water flux ($J_w$) as follows, [70, 71]

$$J_w = \frac{A}{\delta}(P_f - P_p) \quad (2.7)$$

Whereas the solute flux ($J_s$) is expressed as follows

$$J_s = \frac{B}{\delta}(P_f^2 - P_p^2) \quad (2.8)$$

where $A$ is the liquid (solvent) phase transport parameter, $B$ is the solid (solute) phase transport parameter, $P_f$ and $P_p$ are the pressure in the feed and permeate side of the membrane, respectively, and $\delta$ is the pore length. The PF model has not been widely used for solute transport description in membrane technology. Banerjee et al. [72] used a combination of osmotic pressure and pore flow diffusion to quantify the flux decline and solute rejection, establishing that the PF model gives an idea of the comparative fluxes of
ions within the membrane pore. The pore-flow model only considers axial solute concentration gradients. Most of the data and discussion in the literature regarding pore flow of solutes does not explain the role of pore shape relative to solute shape. In addition, the effect of tortuosity in solute rejection and transport has not been clearly stated in present PF models.

2.3.2.2 Modified surface force-pore flow model

The surface force-pore flow (SF-PF) model, which was first proposed by Matsuura and Sourirajan [73], provided a two-dimensional extension of PF model. The SF-PF model assumes: (1) the membrane is micro-porous with cylindrical pores, (2) water transports through the membrane by viscous flow, (3) solute transports through the membrane by both diffusion and convection in pores, and (4) transport through the membrane pores is determined by interaction forces, friction forces, and chemical potential gradients of the water and solute [74, 75]. Since the SF-PF model related membrane performance with both membrane structure (i.e. pore size and pore length) and membrane-solute interactions (i.e. an electrostatic or a Lennard-Jones type surface potential function), it shows potential to provide more accurate prediction results [73, 76]. However, Mehdizadeh et al. indicated that SF-PF model employed a flawed form of material balance and an inconsistent potential function in the pore with the cylindrical pore geometry. As a result, the SF-PF model predicted physically unacceptable results. They corrected the conceptual errors and proposed a modified surface force-pore flow (MD-SF-PF) model [77].
In the MD-SF-PF model, a force balance on a water element in the membrane pore (with pore radius \(r_p\)) within axial position \(z\) and \(z + dz\) and between radial position \(r\) and \(r + dr\) results in a velocity profile as follows [77],

\[
\frac{d^2 \alpha(\rho)}{d\rho^2} + \frac{1}{\rho} \frac{d \alpha(\rho)}{d\rho} + \frac{\Delta \phi - \Delta \Pi \left(1 - e^{-\alpha(\rho)}\right)}{\beta_1} - \frac{\alpha(\rho) e^{-\alpha(\rho)}}{\beta_1} \left(1 - \frac{1}{b(\rho)}\right) \left(1 + \frac{\Delta \Pi}{e^{\alpha(\rho)} - 1}\right) = 0 \tag{2.9}
\]

where \(\rho\) is dimensionless radial distance in the pore \((\rho = r/r_p)\), \(\alpha(\rho)\) is dimensionless velocity in the pore \((\alpha(\rho) = \mu_w(\rho) \delta/D_s)\), \(\beta_1\) is dimensionless water viscosity in the pore \((\beta_1 = \eta D_s w/(r_p^2 \pi_2))\), \(\Delta \phi = \Delta \rho/\pi_2\), \(\Delta \Pi = (\pi_2 - \pi_3)/\pi_2\), \(b(\rho)\) is friction parameter at position \(\rho\) \((b(\rho) = D_s w/ D_s^m(\rho))\), where \(D_s w\) is solute diffusivity in bulk solution, \(D_s^m(\rho)\) is solute diffusivity in the pore at position \(\rho\), \(\mu_w(\rho)\) is water chemical potential, \(\Phi(\rho)\) \((\Phi(\rho) = \phi(r)/R_g T)\), where \(\phi(r)\) is surface wall potential, which represents the net body force acting on the solute by membrane pore wall) is dimensionless potential function, \(\eta\) is water viscosity, \(\pi_i\) is osmotic pressure at location \(i\). The subscripts 1, 2 and 3 refer to feed solution, boundary layer solution and permeate solution, respectively. The boundary conditions for Eqn. 2.9 are

\[\alpha(\rho) = 0 \quad \text{at } \rho = 1 \quad \text{(at the pore wall, } \mu_w \text{ is zero)}\]

and

\[\frac{d \alpha(\rho)}{d\rho} = 0 \quad \text{at } \rho = 0 \quad \text{(at the center of pore, } \mu_w \text{ is constant)}\]

The average solute (with solute radius \(r_s\)) flux and water flux can be found by integrating the velocity profile equation over the cross-sectional area as

\[
\overline{J}_w = 2 \left(\frac{R T}{\delta X_{sw}}\right) \int_0^1 \alpha(\rho) d\rho \tag{2.10}
\]
and

$$\bar{J}_s = 2 \left( \frac{1}{\delta X_{sw}} \right) \int_0^1 \frac{\alpha(\rho)}{b(\rho)} \left( \pi_2 + \frac{\pi_3 - \pi_1}{e^{\alpha(\rho)} - 1} \right) e^{-\Phi(\rho)} \rho \, d\rho \quad (2.11)$$

where $X_{sw}$ is the friction constant between solute and water ($X_{sw} = F_{sw}/\Delta u_{sw}$, where $F_{sw}$ is friction force between solute and water and $\Delta u_{sw}$ is difference in velocity of solute and water in pore). With the solute flux and water flux, permeate solute concentration ($C_p$) can be calculated by

$$C_p = \frac{\bar{J}_s}{\bar{J}_w} \quad (2.12)$$

Mehdizadeh et al. found that the simulation results from MD-SF-PF model were consistent with RO membrane performance [77, 78]. Jain and Gupta [76] incorporated concentration polarization into the MD-SF-PF model and reported that the model predictions of rejection were similar to those simulated by the Spiegler-Kedem model (See Section 2.3.3). However, the model failed to provide accurate prediction when some dilute organics, which caused substantial decreases in water flux, were present in solution [79]. The dimensionless transport equations in the MD-SF-PF model can be solved by computational fluid dynamics [80] and Monte Carlo simulations [81].

### 2.3.3 Irreversible thermodynamics model

Early membrane transport models based on the principle of irreversible thermodynamics correlate transport with mechanical and osmotic pressure gradients. These models assume that the membrane near to equilibrium and the system can be
divided into small sub-systems in which local equilibrium exists. Fluxes are derived from phenomenological thermodynamic relationships [82, 83]. These models do not, however, provide insights into mechanistic transport. The Kedem-Katchalsky model is one such model. This model defines \( J_w \) as a function of the trans-membrane pressure gradient driving force,

\[
J_w = A(\Delta p - \sigma \Delta \pi)
\]  

(2.13)

The reflection coefficient (\( \sigma \)) was introduced to characterize flux interactions when water and solute cross the membrane through a common channel. According to Wijmans et al. [47], \( \sigma < 1 \) indicates a semi-permeable solute, while \( \sigma = 1 \) indicates an impermeable solute (complete rejection). In the case of binary solutions, the transport of solutes can be described by

\[
J_s = B\Delta \pi + (1 - \sigma)C_{avg}J_w
\]  

(2.14)

where \( C_{avg} \) is the average concentration in the membrane pores. A number of researchers have pointed out that the application of the classical Kedem-Katchalsky model is limited to sufficiently dilute and well-stirred membrane systems with two component solutions [84-87]. The key phenomenological parameters of the Kedem-Katchalsky model are defined as

\[
A = \left( \frac{J_w}{\Delta p} \right)_{\Delta \pi = 0}
\]  

(2.15)

\[
\sigma = \left( \frac{\Delta p}{\Delta \pi} \right)_{J_w = 0}
\]  

(2.16)
\[ B = \left( \frac{J_s}{\Delta \pi} \right)_{J_w=0} \]  \hspace{1cm} (2.17)

and

\[ \Delta \pi = R \cdot \frac{T \Delta C}{g} \]  \hspace{1cm} (2.18)

The real rejection can be expressed as

\[ R_r = \frac{C_{\text{avg}} J_w + \omega \Delta \pi}{\sigma C_{\text{avg}} J_w} \]  \hspace{1cm} (2.19)

Because the Kedem-Katchalsky model treats the membrane as a black box, it can be used to describe transport through all types of membranes. Kargol et al. [88] investigated RO membrane performance with this model and mechanistic transport equations. Kovácsa et al. [89] used the Kedem-Katchalsky model to interpret the performance of an NF membrane in amino acid rejection. Fukuda et al. [90] applied the Kedem-Katchalsky model in envisaging a dual solute (KCl-sucrose) system when an impermeable ion is present in the salt-water solution. Paynter et al. [91] investigated the dependence of membrane transport properties on temperature using the Kedem–Katchalsky model. Jarzyńska and Pietruszka [92] found that the solvent permeability (A) of an aqueous solution of ethyl alcohol depends on the concentration of the solution flowing through the membrane. The dependence of the Kedem–Katchalsky model coefficients on concentration is one of its major disadvantages [45] and the significant difference in concentration across the membrane invalidates the linear irreversible thermodynamics relationships [93]. The model was modified by Spiegler and Kedem [94] to avoid concentration dependence of the transport parameters.
As with Kedem-Katchalsky, the Spiegler-Kedem model is based on irreversible thermodynamics. The major difference between the two models is that the Spiegler-Kedem characterizes membranes in terms of two parameters: solute permeability, $B$, and reflection coefficient, $\sigma$, and these parameters have no dependence on concentration [95]. Therefore, the Spiegler-Kedem model defines $J_w$ the same way as the Kedem-Katchalsky model, but defines $J_s$ as

$$J_s = B \Delta x \frac{dc}{dx} + \left(1 - \sigma\right) J_w C$$

(Eqn. 2.20) can be integrated across the membrane to yield [76, 83]

$$R_o = 1 - \frac{C_p}{C_m} = \sigma \left(\frac{1 - Y}{1 - \sigma Y}\right)$$

(2.21)

where

$$Y = \exp \left[-\frac{J_w \left(1 - \sigma\right)}{B}\right]$$

(2.22)

Due to the difficulty in estimating the characteristic membrane parameters in Eqns. 2.21 and 2.22, the Spiegler-Kedem model is usually coupled with liquid film theory (Section 2.5.1) to yield [76, 83, 96]

$$\frac{R_o}{1 - R_o} = \frac{\sigma}{1 - \sigma} \left[1 - \exp \left(-\frac{J_w \left(1 - \sigma\right)}{B}\right)\right] \exp \left(-\frac{J_w}{k_f}\right)$$

(2.23)

Observed solute rejection increases with permeate water flux and reflection coefficient, but decreases with solute permeability (Fig. 2.5). By using a non-linear parameter estimation technique, the unknown membrane characteristic parameters ($B, \sigma,$
$k_j$ can be determined from the given experimental data of $R_o$ and $J_w$. The solution-diffusion, solution-diffusion imperfection, Kedem-Katchalsky, and Spiegler-Kedem models are frequently used to describe solute transport in NF and RO membranes at laboratory scale [97-100].

![Graph showing observed rejection vs water flux for different reflective coefficients](image-url)

(a)
Figure 2.5. Effect of (a) reflection coefficient \((k_f = 10 \ \mu\text{m/s}, B = 0.05 \ \mu\text{m/s})\) and (b) solute permeability \((k_f = 10 \ \mu\text{m/s}, \sigma = 0.95)\) on solute observed rejection based on the Spiegler-Kedem model.

2.3.4. Electrolyte transport and electrokinetic models

For charged solutes \((e.g.,\ \text{salt, organic acid})\) electrokinetic models can be used to describe membrane separations. If the solute concentration within the pore and the concentration gradient along the pore are assumed to be very small the transport modeling in the membrane is based on the extended Nernst-Planck (ENP) equation, which describes solute transport as a combination of diffusion, convection, and electromigration [101-104]. The governing equation for the steady-state flux, \(J_i\), of a charged solute \(i\) with charge \(z_i\) through membrane pore is
\[ J_i = J_w C_{i,p} = -K_{i,d} \frac{dC_i}{dx} + K_{i,c} J_w - \frac{z_i c_i D_i F}{R_T} d\psi \]  \hfill (2.24)

where \( D_i^\infty \) is the solute diffusion coefficient at infinite dilution, \( K_{i,d} \) and \( K_{i,c} \) are the diffusive and convective hindrance factors accounting for the effect of finite pore size [105], \( F \) is the Faraday constant, and \( \psi \) is the electrical potential within the pore length, due to charge accumulation close to the pore wall [102]. In some cases, the membrane zeta-potential is taken as an approximation of \( \psi \).

The concentration gradient of an ion \( i \) through the membrane can be described as

\[ \frac{dC_i}{dx} = \frac{J_w}{K_{i,d} D_i^\infty} \left( K_{i,c} c_i - C_{i,p} \right) - \frac{z_i c_i F}{R_T} \frac{d\psi}{dx} \]  \hfill (2.25)

Here, \( d\psi/dx \) is the electrical potential gradient along the membrane pore length, which is the driving force for the electrical mobility of the ions. The electrical mobility contribution assumes a constant electric field within the membrane pore and, thus, requires invoking a zero current condition,

\[ I = \sum_i F z_i J_i = 0 \]  \hfill (2.26)

and a local electro-neutrality in the membrane,

\[ \sum_i z_i c_i + X = 0 \]  \hfill (2.27)

where \( X \) is the charge density (charge/volume) in the membrane pore [106]. Combining \textbf{Eqns. 2.25} – \textbf{2.27}, yields [101]
\[
\frac{d\psi}{dx} = \frac{J_{wi} \sum_i \frac{z_i}{K_{id} D_i^m} \left( K_{ic_i} - C_{i,p} \right)}{F R T \sum_i z_i^2 c_i}
\]  
(2.28)

Substituting Eqn. 2.28 into Eqn. 2.24 yields

\[
\frac{dc_i}{dx} = \frac{J_{wi} \sum_i \frac{z_i}{K_{id} D_i^m} \left( K_{ic_i} - C_{i,p} \right)}{K_{id} D_i^m} - \frac{z_i c_i J_{wi} \sum_i \frac{z_i}{K_{id} D_i^m} \left( K_{ic_i} - C_{i,p} \right)}{\sum_i z_i^2 c_i} \]  
(2.29)

The boundary conditions for Eqn. 2.29 are [107]

\[c_i = c_{i,m} \quad \text{at} \quad x = 0\]

and

\[c_i = c_{i,p} \quad \text{at} \quad x = \Delta x.\]

Combining Eqns. 2.24 and 2.29, ionic fluxes and permeate concentrations corresponding to a given feed side membrane surface concentration and permeate flux can be solved. A more detailed procedure could be found in Bowen et al. [14, 108, 109] and Bhattacharjee et al. [101].

The above ENP equations combined with the electroneutrality condition require accurate values of certain model parameters, such as membrane effective fixed charge density and membrane thickness, which are difficult to characterize [108]. The non-linear differential equations in the model may also be difficult to solve analytically and fit to experimental data for more than three ionic species in the system [104, 110, 111]. Nevertheless, ENP provides a complete formal framework for describing ionic transport through membranes [108, 110, 112-115]. The only essential assumption is the ideal linear
relations hold for each term in Eqn. 2.24, (e.g., linearity is assumed between the ion diffusion flux and its activity gradient) [116].

To successfully implement the ENP model two additional models are required: (1) a thermodynamic model of ion exclusion to calculate local concentrations, \(c_i\), (usually within the boundary conditions at membrane-solution interfaces) and (2) a kinetic model to calculate ion hindrance factors \(K_{d,i}\) and \(K_{c,i}\) [58, 117]. At present, theoretical relations derived for motion of spherical or ellipsoid particles within cylindrical channels are commonly used to calculate hindrance factors [118, 119]. The validity of these macroscopic relations derived for continuous fluids and ideal cylindrical pores when applied to NF and RO membranes – which have irregular pores of molecular dimensions – has not been seriously questioned so far. Presumably, with a proper choice of an effective pore radius they provide a reasonable approximation for the dependence of hindrance factors on the solute radius. However, the distributions of effective pore sizes may lead to rejections lower than 100% for solutes slightly larger than the average effective pore radius.

The ion exclusion relations present the most significant challenge in developing an adequate description of NF membranes. The approach widely used at present views the exclusion mechanism as a combination of Donnan, dielectric, and steric exclusion, which yields the following relation [117, 120-125],

\[
\frac{c_i}{C_i} = (1 - \lambda)^2 \exp \left( - \frac{Fz \Delta \psi_d + \Delta W_i}{RT} \right)
\]  

(2.30)
where $\Delta \Psi_D$ and $\Delta W_i$ are the electric (Donnan) potential difference and solvation energy difference, respectively, of the ion between membrane and solution. $\Delta W_i$ is usually calculated using the Born equation with an appropriately chosen radius of the ion [120]. For known solution composition at the interfaces ($c_i$) and fixed charge of the membrane ($X$) the value of Donnan potential $\Delta \Psi_D$ is found by substituting Eqn. 2.30 for all mobile ions into Eqn. 2.27.

Eqn. 2.30 embeds a few critical assumptions, namely: (1) the membrane and/or pore interior are continuous and uniform dielectric media, (2) the ionic species in the membrane are fully dissociated and retain full translational freedom, and (3) ions in the membrane interact with each other and with fixed charges only via a uniform Donnan potential and any pair-wise interactions are negligible. A certain controversy is yet unresolved as to which values of ionic radii are to be used, however, this model or its more sophisticated versions have been widely applied to modeling ion transport in NF and RO [126]. They usually yield good fits for single salts and, using Born or Pauling (bare) radii of the ions, qualitatively agree with the observed effects of ion size on rejection; however, several recent studies demonstrate important discrepancies.

(1) The model fails to consistently describe both single salts and salt mixtures using the same set of parameters [121, 125, 127].

(2) The fitted values of membrane characteristics, such as $\varepsilon_m$ or $X$, significantly vary with feed solution composition [124].

(3) The values of $\varepsilon_m$ or $X$ fitted to filtration data strongly disagree with independently measured physical characteristics of the active layer, in particular,
fixed charge measured by Rutherford backscattering spectrometry (RBS) [12, 127-129] and known dielectric characteristics of polymer films swollen in water [130, 131].

(4) The model entirely fails to explain observed dependence of rejection on salt concentration, in particular, for divalent cations [57, 117, 132];

(5) Measurements of salt partitioning by RBS show that the model greatly underestimates salt partitioning and the strength of salt exclusion within RO membranes [133].

These results indicate some fundamental flaws of the physical mechanism assumed in Eqn. 2.30. It was recently suggested that one possible reason for the failure is disregard of ion association [117], which should be addressed in future model development [134, 135].

2.4. Additional Transport Considerations

2.4.1. Mixed-matrix membrane models

Studies of transport through mixed-matrix membranes have been conducted experimentally and theoretically since the 1960s [136]. In order to obtain an equation to relate composite membrane permeability to the both matrix phase and the filler phase permeability, and the concentration of the fillers, an analog of transport in mixed matrix membranes in dielectrics (Maxwell model) has been studied comprehensively [136-139]. In the case of a dilute dispersion of spherical fillers, fully oriented along the axis of the
applied pressure difference, the effective composite membrane permeability is determined as

$$P_{\text{eff}} = P_m \left[ \frac{P_d + 2P_m - 2\theta_d (P_m - P_d)}{P_d + 2P_m + \theta_d (P_m - P_d)} \right]$$

(2.31)

where $P$ is the single component permeability, $\theta_d$ is the fraction of dispersed filler material in the membrane, and the subscripts $d$ and $m$ refer to the dispersed and continuous phases, respectively [139]. **Eqn. 2.31** can be rewritten in the form of relative permeability as [137]

$$\frac{P_{\text{eff}}}{P_m} = \frac{P_d (1 + 2\theta_d) + (2 - 2\theta_d)}{P_d (1 - \theta_d) + (2 + \theta_d)}$$

(2.32)

**Figure 2.6.** Effect of filler volume fraction, $\theta_d$, on the ratio of composite to polymer matrix permeability. Lines drawn represent constant ratio of pure dispersed and continuous phase permeabilities.
Based on Eqn. 2.32, a plot of the ratio of effective composite membrane permeability to polymer matrix permeability versus volume fraction of the dispersed fillers can be drawn to indicate the effect the dispersed filler material (Fig. 2.6). At extreme ratios of filler permeability to matrix permeability (greater than 100 or less than 0.1) the permeability of the composite becomes less sensitive to the presence of the filler. In the case of high dispersed phase permeability the local direction of the permeate flux is towards the filler particle, while in case of a low dispersed phase permeability the local fluxes preferentially go around the filler particle. Furthermore, if an impermeable or less permeable filler material is used there will be no increase in the effective permeability of the material, in fact it there will be a decrease, unless defects are formed at the dispersed-continuous phase interface [8]. A more detailed explanation can be found in the report published by Bouma et al. [137].

2.4.2. Composite membrane transport

The support layer of a composite membrane has long been thought to contribute only mechanical stability and to play no significant role in transport. Until recently, limited information existed in literature about the impacts of support membrane physical–chemical properties on composite membrane formation and resulting performance. One exception is FO membranes, where the support structure determines the extent of internal concentration polarization, reduces the osmotic driving force, and thereby hinders performance (Section 2.5.2). It is now thought that the surface chemistry and pore structure of the support membrane may influence the thickness, roughness, and cross-
linked structure of NF and RO films, especially those formed by interfacial polymerization. Furthermore, the pore size and porosity of the underlying support may contribute significantly to the diffusive transport through the composite structure. The support membrane material is typically considered an impermeable barrier to species diffusing across the coating film. This means that diffusing species will follow preferential flow paths through the coating film to reach open pores in the underlying support structure. This results in an increase in the effective diffusive path length for water and salt, which impacts water and salt flux (Fig. 2.7) [6].

**Figure 2.7.** Schematic depictions of the effective diffusive path length for different composite membrane structures, such as a) a membrane with a thin coating film and large underlying pores, *versus* b) a membrane with smaller pores and a larger effective path length. c) Finally, an aerial view of the support membrane structure and the effect of pore size and porosity on diffusive path length. Adapted from Pendergast *et al.* [6].
Based on Fick’s law, the ratio of the “real” flux \( J_{\text{real}} \) or permeability \( P_{\text{real}} \) to “ideal” flux \( J_{\text{ideal}} \) or permeability \( P_{\text{ideal}} \) will be identical to the inverse ratio of “real (effective)” diffusive path length \( \Delta x_{\text{eff}} \) to “ideal” diffusive path length \( \Delta x \) by assuming diffusivity and concentration gradient are identical. (Note that this is only valid when the permeate concentration is much smaller than the feed concentration.) Symbolically,

\[
\frac{J_{\text{real}}}{J_{\text{ideal}}} = \frac{\Delta x}{\Delta x_{\text{eff}}} = \frac{P_{\text{real}}}{P_{\text{ideal}}} 
\]  

(2.33)

where \( \Delta x_{\text{eff}} \) can be derived geometrically from Fig. 2.7 as

\[
\Delta x_{\text{eff}} = \varepsilon \Delta x + \left(1 - \varepsilon\right) \left(\Delta x + \frac{\pi r_1^2}{2 \varepsilon} - r_1\right) 
\]  

(2.34)

Following Eqns. 2.33 and 2.34, permeability ratio is plotted in Fig. 2.8 over a range of coating film thicknesses \( \Delta x \), support membrane porosities \( \varepsilon \), and support membrane pore radii \( r_1 \). For a fixed \( r_1 \), membranes with smaller \( \Delta x \) are intrinsically more permeable (Fig. 2.8a); however, composite membrane permeability also depends on \( \varepsilon \) of the support membrane skin layer. Ultimately, a thinner coating film requires a more porous support membrane skin layer. Fig. 2.8b indicates that for a fixed \( \Delta x \), support membrane skin layer \( \varepsilon \) must increase as \( r_1 \) increases.
Figure 2.8. Permeability ratio as a function of the porosity for (a) a fixed support membrane pore size ($r_1 = 50$ nm) and a (b) fixed coating layer thickness ($\Delta x = 100$ nm).
The effect of support membrane skin layer porosity and \( r_1 \) on membrane water flux and observed salt rejection is shown in Fig. 2.9. As indicated in Fig. 2.9(a), for a fixed \( \Delta x \), water flux increases as support membrane skin layer porosity increases and as skin layer pore size decreases. For a fixed coating film structure, the maximum water flux is most easily achieved by decreasing pore size and increasing porosity. Fig. 2.9(b) suggests, for a fixed \( \Delta x \), salt rejection increases as support membrane skin layer \( \varepsilon \) decreases and as \( r_1 \) increases. It is also important to point out that for a fixed membrane coating film structure, a minimum salt rejection is fixed (determined by coating film selectivity), but the maximum salt rejection is achieved by decreasing support membrane skin layer porosity and increasing the pore size of the support membrane.

(a)
Figure 2.9. (a) Membrane water flux and (b) observed rejection shown as a function of support membrane porosity and pore size. Calculations made using transport coefficients characteristic of SWRO membrane ($\Delta p = 55$ bar, $C_f = 32 g/L$, $A = 4 \times 10^{-12}$ m/Pa.s, $B = 2 \times 10^{-8}$ m/s, $T = 298$ K, $k_f = 1 \times 10^{-5}$ m/s).

Lonsdale et al. [140] experimentally demonstrate differences in water permeability of cellulosic composite membranes by tailoring the pore structure of the support membrane. When the distance between the pores is comparable to the thickness of the thin film, significant decline in water permeability is observed. Ramon et al. [9, 141] theoretically investigate the effect of support membrane pore size and porosity on diffusive transport through composite membranes. Based on their study, support membranes with high porosity and small skin layer pores result in high water and salt permeability because the effective diffusive path length for water and salt is shorter. They
also find that a water flux distribution exists for composite membranes governed by the interplay between the active layer thickness and support membrane pore structure.

2.5. Solute Mass Transfer Limitations

2.5.1. External concentration polarization

In a NF or RO process, one of the main hindrances to transport through the membrane is the phenomenon known as external concentration polarization (ECP) (Fig. 2.10). Water and solutes are transported towards the membrane by permeate convection; water permeates, while rejected solutes can either diffuse through the membrane or back away from the membrane through the hydrodynamic boundary layer into the bulk of the feed. A buildup of rejected solutes occurs at the membrane surface, and hence, ECP increases the feed side salt concentration right at the membrane-feed solution interface, which influences both salt passage and trans-membrane osmotic pressure. With high salinity waters and significant ECP, sparingly soluble salts and organics may exceed their solubility limit and precipitate on the membrane leading to even higher hydraulic pressure requirement for permeation. Furthermore, ECP effects solute rejection. Recall that the real solute rejection \((R_r)\) of a membrane is an intrinsic property of a membrane (Eqn. 2.5), whereas the observed rejection \((R_o)\) will be much lower with significant ECP (Eqn. 2.4). Fortunately, the detrimental effects of ECP can be reduced by increasing cross-flow velocity to sweep solute molecules flowing parallel to the membrane downstream in the filtration channel and decrease the concentration near the surface of the membrane.
Figure 2.10. Schematic depicting external concentration polarization (ECP) buildup of salt on membrane surface during operation in NF or RO [141].

The ECP can be related to mass transfer by looking at solute rejection. To relate the $C_m$ to $C_f$ we define a parameter called the concentration polarization modulus or the CP modulus,

$$CP = \frac{C_m}{C_f} = (1 - R_e) + R_e \exp \left( \frac{J_w}{k_f} \right)$$  \hspace{1cm} (2.35)

When $k_f$ increases, which can be achieved by increasing the cross-flow rate across the membrane surface, $C_m$ will decrease and thereby decrease the effect of ECP. Many
correlations have been derived to determine $k_f$ either by computational efforts or by experimental results and are available in many handbooks. Several examples of correlations under various flow geometries are given in Table 2.1.

<table>
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<tr>
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<tbody>
<tr>
<td>Thin Rectangular channels without spacers</td>
<td>$Sh = 1.85 \left( \text{ReSc} \frac{d_H}{L} \right)^{0.33}$</td>
<td>$Sh = 0.04 \text{Re}^{0.75} \text{Sc}^{0.33}$</td>
<td>[142]</td>
</tr>
<tr>
<td>In a tube</td>
<td>$Sh = 1.62 \left( \text{ReSc} \frac{d_H}{L} \right)^{0.33}$</td>
<td>$Sh = 0.023 \text{Re}^{0.82} \text{Sc}^{0.33}$</td>
<td>[143]</td>
</tr>
<tr>
<td>Radial cross flow system</td>
<td>$Sh = 1.05 \left( \text{ReSc} \frac{h}{R_c} \right)^{0.38}$</td>
<td>$Sh = 0.275 \left( \text{Re}^{1.75} \text{Sc} \frac{2H}{L} \right)^{0.33}$</td>
<td>[144]-[146]</td>
</tr>
<tr>
<td>Stirred Cell</td>
<td>$Sh = 0.23 \text{Re}^{0.567} \text{Sc}^{0.33}$</td>
<td>$Sh = 0.03 \text{Re}^{0.66} \text{Sc}^{0.33} \text{Pe}_{\text{test}}^{0.16}$</td>
<td>[144], [147], [148]</td>
</tr>
<tr>
<td>Rectangular channels with spacers</td>
<td>$Sh = 0.46 \left( \text{ReSc} \right)^{0.36}$</td>
<td>$Sh = 0.0096 \text{Re}^{0.5} \text{Sc}^{0.6}$</td>
<td>[149], [150]</td>
</tr>
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*Where $Sh = k_f/d_H/D$ is the dimensionless Sherwood number that represents the ratio of convective to diffusive mass transport. The Reynolds number ($\text{Re} = u_0d_H/\eta$) represents the ratio of inertial to viscous forces for given flow conditions. The Schmidt number ($\text{Sc} = \eta/\rho D$) represents the ratio of contributions of viscosity to mass diffusivity. The Péclet number ($\text{Pe}$) represents the ratio of advective to diffusive transport. $\text{Pe}_{\text{test}}$ is the test Péclet number ($= J_w h/D$) that accounts for deviations from non-porous conduits in the system. Additionally, $d_H$ is the hydraulic diameter calculated by ($= 2wh/(w+h)$), $w$ is the width of the channel, $h$ is the height of the channel, $L$ is length of channel, $R_c$ is the radius of the flow channel, $r_c$ is the radius of the stirred cell, $u_0$ is the cross-flow velocity, $\eta$ is the dynamic viscosity of the solution, $\rho$ is the density of the solution, and $D$ is the diffusion coefficient of the solute in water.*

Based on the van ’t Hoff equation, the effective osmotic pressure difference ($\Delta \pi_{\text{eff}}$) across the membrane for can be calculated as
\[ \Delta \pi_{\text{eff}} = nC_f R \frac{T \exp \left( \frac{J_w}{k_f} \right)}{x_w} \]  

(2.36)

where \( n \) is the sum of the charges of the cations and anions in the electrolyte. For example, in a 1:1 electrolyte, such as sodium chloride, \( n = 2 \). The equation above is only valid for dilute solutions where the mole fraction of water, \( x_w \), is approximately unity. Otherwise, the osmotic pressure (\( \pi \)) is more accurately defined by the Gibbs’ equation \[151\],

\[ \pi = - \frac{R T}{V_w} \ln x_w \]  

(2.37)

Most NF and RO membrane surfaces have charged functional groups, which causes solute rejection and in effect, concentration polarization, to change in response to feed solution pH. A study from Childress \textit{et al.} \[152\] found that polyamide NF membranes with amphoteric surfaces are positively charged below its isoelectric point (pH ~ 5) due to protonation of the amino groups and negatively charged above its isoelectric point due to deprotonation of the carboxyl groups. It was also found that at the membrane isoelectric point, water flux and NaCl rejection were maximal due to decreased electrostatic repulsion and increased pore size. Bellona \textit{et al.} studied the rejection of organic compounds by NF membranes with negative surface charge at neutral solution pH. The rejection of negatively charged organic acids increased with feed water pH (below pK\(_a\)) due to an increase in the negative surface charge of the membrane resulting in higher electrostatic repulsion before reaching a plateau in rejection \[153\]. This plateau is attributed to a trade-off between membrane pore expansion and
swelling as a result of functional group deprotonation and increase in rejection from solute deprotonation. A similar study was done by Verliefde et al. in which they concluded that neutral and positively charged organic solutes can approach negatively charged NF membrane surfaces close enough to establish hydrophobic interactions [154]. This causes a buildup of neutral and positively charged solutes near the membrane surface, or external concentration polarization. The researchers further attributed the lower rejection of acidic pharmaceuticals by NF membranes to the hydrophobic interactions that help the solutes partition into the membrane. Fig. 2.11 depicts that at neutral solution pH, RO and NF membrane surfaces typically exhibit negative surface charge, which causes a rejection of negatively charged solutes and an interaction of neutral and positively charged solutes. These electrokinetic characteristics play an important role in how the membrane rejects charged solutes and causes a concentration polarization at the membrane surface, especially with varying solution pH.
Figure 2.11. Conceptual illustration depicting the difference in external mass transfer between positively charged, negatively charged and neutral solutes.

2.5.2. Internal concentration polarization

The phenomenon of internal concentration polarization is based on the concept of hindered diffusion, which describes solute particles accumulating in a layer of the membrane (e.g. Support layer, fouling layer etc.). Several factors contribute to the accumulation of solute particles in the membrane layer, including the tortuosity, porosity,
and thickness, which consequently hinders the diffusion of solute from the membrane layer.

A simple analytical expression for estimating the dependence of the hindered diffusion coefficient \( D^* \) on porosity in the membrane layer is given by

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

(2.38)

where \( D \) is the solute diffusivity in the bulk, \( \varepsilon \) is the membrane porosity, and \( \tau \approx 1 - \ln e^2 \) is the diffusive tortuosity [155]. Recent investigations have shown that fouling or “cake” layer porosities for silica colloids filtered under similar physical and chemical conditions were in the range of 0.3 to 0.7 [156-158]. The ratio of the effective diffusion coefficient to the bulk diffusion coefficient is plotted against cake layer porosity in Fig. 2.12. Over the range of typical porosity values the effective diffusion coefficient may be reduced to between 10 and 40 percent of the bulk diffusion coefficient, which results in significantly enhanced salt concentration at the membrane surface.
In FO processes, the transport of water naturally occurs due to a difference in solute concentration across the membrane, which changes the thermodynamic activity of water. Due to minimal hydraulic pressure, hindered diffusion causes accumulation of solute in the support layer of the membrane, a phenomenon called internal concentration polarization (ICP). When the dense layer of the membrane faces the high concentration draw solution (PRO-mode), concentrative ICP occurs where the solute from the feed solution becomes concentrated in the porous support membrane due to hindered diffusion, decreasing the effective osmotic pressure across the membrane (Fig. 2.13a). When the dense layer of the membrane faces the dilute feed solution (FO-mode), dilutive ICP occurs as the draw solution concentration is diminished by the incoming water flux across the membrane (Fig. 2.13b). In both cases there is a substantial reduction in the
effective osmotic pressure difference, which is the driving force for water flux in FO [159].

\[ J_w = A \left( \Delta \pi_{\text{eff}} - \Delta p \right) \]  \hspace{1cm} (2.39)

Similarly, the salt flux across the active layer, \( J_s^a \), is determined using the solute concentration at the membrane surface, after accounting for ECP and ICP [160],

\[ J_s^a = B \left( C_{\text{dm}} - C_{\text{fm}} \right) \]  \hspace{1cm} (2.40)

The concentration at the membrane surface is not a measureable quantity, but it can be related to salt flux across the support membrane,
\[ J^s_s = -D^s \frac{dC(x)}{dx} - J_w C(x) \]  
(2.41)

where \( D^s \) is the diffusivity of the solute in the porous support layer of the composite membrane. At steady-state conditions, the \( J^s_s \) must be equal to \( J^a_s \) on the basis of mass continuity,

\[ -D^s \frac{dC(x)}{dx} - J_w C(x) = B(C_{dm} - C_{Fm}) \]  
(2.42)

By integrating across the support membrane using the boundary conditions, assuming ICP dominates and ECP is negligible,

\[ C(0) = C_{Fm} \text{ at } x = 0 \]

\[ C(\Delta x_{sup}) = C_F \text{ at } x = \Delta x_{sup}, \]

an expression for \( C_{Fm} \) can be derived. Using a similar process, an expression for \( C_{Dm} \) is also derived by recognizing that at steady-state, \( J^a_s \) must equal the salt flux through the boundary layer near the membrane, which is also described with convective and diffusive components,

\[ J^BL_s = D \frac{dC(z)}{dz} - J_w C(z) \]  
(2.43)

and the boundary conditions

\[ C(0) = C_{Db} \text{ at } z = 0 \]

\[ C(\delta) = C_{Dm} \text{ at } z = \delta. \]

Assuming the van’t Hoff equation applies and osmotic pressure is proportional to the solution concentration, the expressions for \( C_{Fm} \) and \( C_{Dm} \) are substituted into Eqn. 2.43 for \( J_w \) to obtain an equation that depends only on measureable quantities [160, 161],

53
\[ J_w = A \frac{\pi_D \exp\left(-\frac{J_w}{k_f}\right) - \pi_F \exp\left(J_w K\right)}{1 + \frac{B}{J_w} \exp\left(J_w K\right) - \exp\left(-\frac{J_w}{k_f}\right)} - \Delta p \]  

(2.44)

Similarly, for the salt flux in the active layer,

\[ J_s^a = B \frac{\pi_D \exp\left(-\frac{J_w}{k}\right) - \pi_F \exp\left(J_w K\right)}{1 + \frac{B}{J_w} \exp\left(J_w K\right) - \exp\left(-\frac{J_w}{k}\right)} \]  

(2.45)

where \( K \) is a parameter to quantify the extent of ICP called resistance to solute diffusion by the porous substructure, which depends on the orientation of the membrane. For PRO-mode and deionized water as the feed solution (\( \pi_F = 0 \)) \[161, 162\]

\[ K = \left(\frac{1}{J_w}\right) \ln\left(\frac{B + A\pi_D - J_w}{B + A\pi_F}\right) \]  

(2.46)

For FO-mode

\[ K = \left(\frac{1}{J_w}\right) \ln\left(\frac{B + A\pi_D}{B + A\pi_F + J_w}\right) \]  

(2.47)

where \( \pi_D \) and \( \pi_F \) are the osmotic pressures of the draw and feed solutions, respectively.

To characterize the porous support, it is necessary to uncouple the solute resistance from the draw solution by defining a membrane structural parameter, \( S \), as

\[ S = KD = \frac{\Delta x_{\text{eff}} \tau}{\varepsilon} \]  

(2.48)

where \( \Delta x_{\text{sup}}, \tau, \) and \( \varepsilon \) are the support membrane thickness, tortuosity, and porosity, respectively \[160\].
Fig. 2.14 shows a plot of water flux as a function of either water permeability \((A)\), salt permeability \((B)\) or resistance to solute diffusion \((K)\) as presented by Eqn. 2.44 using experimental data obtained for commercial CTA membrane [141]. When deriving this plot, it is assumed that when parameter \(A\) is changing, for example, both parameter \(B\) and \(K\) are held constant. Fig. 2.14 shows that as \(A\) increases, the water flux increases, which is as expected since more water is allowed to permeated through the membrane. However, as \(B\) or \(K\) increases, the water flux decreases. As the salt permeability increases, more salt is allowed to diffuse into the support layer, exacerbating ICP, and thereby decreasing the driving force for water flux across the membrane. As \(K\) increases, the solute in the support layer has difficulty in diffusing out, which again decreases the effective osmotic pressure and the water flux across the membrane. The plot shows that water flux is more sensitive to changes with \(A\) than with \(B\) and \(K\) for the values chosen. This may be because \(A\) directly affects the water flux, while parameters \(B\) and \(K\) affects solute flux, which affects the osmotic pressure and indirectly affects the water flux.
Figure 2.14. Effect of water permeability, salt permeability and resistance to solution diffusion coefficient on FO water flux for a CTA membrane using 32g/L NaCl as draw and deionized water as feed solution.

The water and salt permeability ($A$ and $B$) used in calculating $K$ and, subsequently, $S$ are determined by RO experiments, with the membrane under hydraulic pressure, and do not reflect the accurate transport conditions in FO operation. Recently, Tiraferri et al. developed a protocol to determine the transport and structural parameters of FO membranes by conducting only FO experiments. Through a set of experiments of increasing draw solution concentration to determine the water and salt flux and by minimizing the coefficient of variation of the ratio of $J_w$ to $J_s$, the authors determine $A$, $B$, and $S$ without conducting any RO experiments [163].

According to Eqn. 2.48, the lowest hindrance to diffusion, or the lowest amount of ICP, is achieved when the FO support membrane is thin, non-tortuous, hydrophilic,
and has high porosity [164]. Although thin support membranes may be ideal, FO membranes must still be mechanically robust enough to withstand backwashes in operation and ease in handling. According to a recent study by Widjojo et al., the most permeable and selective FO membranes were formed from a composite membrane of a 50% sulphonated polyethersulfone UF membrane with a dense selective polyamide film formed on top [171]. The composite membrane had a spongy morphology, but had the highest flux and lowest salt passage (using deionized water as the feed solution and 2M NaCl as the draw solution) compared to others reported in literature. The authors conclude that the hydrophilicity of the support membrane has a greater impact on water permeability than the morphology [164]. This highlights that hydrophilicity, or the chemistry of the support membrane, is not incorporated in the membrane structural parameter. Furthermore, Wong et al. found that by changing the solution temperature, concentration, and salt composition S can change significantly when testing a commercial cellulose triacetate FO membrane [141]. This reiterates the fact that the solution chemistry affects the structure of the membrane and determines the transport of solutes, which may not be accurately reflected in the structural parameter, probing further consideration and investigation.

2.5.3. Fouling-enhanced external concentration polarization

Membrane fouling in NF/RO applications is another example of hindered diffusion as colloidal deposits also provide the tortuous path that aids in accumulation of solute particles as the support layer in FO membranes. Contrary to FO/PRO operation, in
NF/RO, water flux and salt flux are in the same direction, which offers a more simplified model construction. A fouling layer in NF/RO processes will enhance ECP by a combination of hindered back-diffusion of salt ions and averted cross-flow hydrodynamics within the fouling layer (Fig. 2.15). With no particles deposited on the membrane surface, the solute concentration profile quickly reaches steady-state, where solute transport by convection towards the membrane is balanced by solute back-transport from the polarized layer near the membrane surface by diffusion (Fig. 2.15a). As colloidal particles accumulate and form a thin cake layer over the surface of the membrane the diffusion of salt ions back into the bulk is hindered because of the tortuous path the ions must travel through in the deposited layer (Fig. 2.15b) [165]. Hindered back-diffusion of salt ions trapped in the cake layer leads to an enhanced membrane surface salt concentration ($C_{m}^*$) and, thus, enhanced osmotic pressure drop across the membrane ($D_{p_{eff}}^*$).
Figure 2.15. Schematic depicting ECP concentration profiles during (a) steady-state and (b) cake layer formation, causing cake-enhanced osmotic pressure.

To describe the transient membrane flux through a fouling layer, the flux is defined as

\[ J(t) = \frac{\Delta p}{R_m + R_c(t)} \]  

(2.49)

In the standard cake filtration model, flux decline (or decline in trans-membrane pressure) is assumed to arise solely from the added hydraulic resistance of the cake layer. However, it was previously demonstrated that this is an unreasonable assumption for salt rejecting membranes because the primary mechanism of the flux decline is a transient, cake-enhanced osmotic pressure [165, 166]. The cake-enhanced osmotic pressure model begins by rearranging the cake filtration equation into a series of pressure drops.
\[ \Delta p_m(t) = \Delta p - \Delta \pi_{\text{eff}}^*(t) - \Delta p_c(t) \]  

where the cake-enhanced osmotic pressure is described by,

\[ \Delta \pi_{\text{eff}}^*(t) = \Delta p - J(t)R_m - J(t)R_c \]  

\[ R_c(t) = \left[ \frac{45\eta(1 - \varepsilon_c)}{\rho_p a_p^2 \varepsilon_c^3} \right] M_d(t) \]

where \( \varepsilon_c \) is the cake layer porosity, \( a_p \) is the particle radius, \( \rho_p \) is the particle density and \( M_d \) is transient deposit layer mass per unit membrane area, \( R_m \) is membrane resistance and \( R_c \) is cake layer resistance. The transient driving force for permeation, the trans-membrane pressure \( (\Delta p_m = J(t)R_m) \), is a function of the constant applied pressure \( (\Delta p) \), the transient cake-enhanced osmotic pressure \( (\Delta \pi_{\text{eff}}^*) \), and the transient trans-cake hydraulic pressure \( (\Delta p_c = J(t)R_c) \).

The mathematical model that follows is based on three important assumptions. First, the cake layer is thin compared to the salt film-layer thickness. Past investigations have shown that the tangential flow field is relatively unaffected when the cake layer is thin with respect to the channel height [157] because the cake layer does not occupy a significant fraction of the channel cross section [167]. Cross-flow shear rate is relatively unaffected by the presence of the cake layer, and thus the CP layer thickness remains at the film thickness determined prior to particle deposition. Second, the colloid deposit layer does not reject salt ions, so the profile of salt concentration above the colloid deposit layer is unchanged from that prior to cake formation. Third, the effective
diffusion coefficient for salt ions trapped within the colloid deposit layer can be estimated with knowledge of the cake layer porosity.

From the previous section, it was described that $D^* = (\varepsilon/\tau) D$. Next, the effective mass transfer coefficient is broken down into two parts – one describing mass transfer through the colloid deposit layer and one describing mass transfer from the interface of the colloid layer back into the bulk. The resulting “hindered” mass transfer coefficient ($k^*$) is estimated from

$$\frac{1}{k^*} = \frac{\delta_c}{D^*} + \frac{\delta_s}{D} \quad (2.53)$$

where $\delta_c$ is the colloid deposit layer thickness and $\delta_s$ is the difference between the film ($\delta_f$) and cake layer thicknesses. Eqn. 2.53 comes directly from integrating Eqn. 2.43 separately across the cake and CP layers. Even if the cake layer is very thin ($\delta_c << \delta_s$) the cake-enhanced osmotic pressure may be significant because the hindered diffusion coefficient can be an order of magnitude smaller than the bulk diffusion coefficient.

Note that the cake layer thickness can be written in terms of cake mass per unit membrane area as $\delta_c = M_d / r_p (1-\varepsilon)$ [157]. Rewriting Eqn. 2.53, the hindered mass transfer coefficient expression, in terms of $\delta_f$ and $\delta_c$ and substituting into Eqn. 2.36, results in the following expression for the cake-enhanced osmotic pressure:

$$\Delta \pi^*_{eff}(t) = 2C_f R_g T \exp \left[ \frac{J(t)}{k_f} + \frac{J(t)M_d(t)}{\rho_p (1-\varepsilon_c)} \left( \frac{1-\ln(\varepsilon_c^2)}{D \varepsilon_c - 1} \right) \right] \quad (2.54)$$

All parameters in this equation are constant or experimentally measurable, except cake porosity ($\varepsilon_c$) and cake-enhanced osmotic pressure ($\Delta \pi^*_{eff}$). Setting Eqn. 2.54 equal to
\textbf{Eqn. 2.51} allows direct calculation of the cake layer porosity, and thus, cake-enhanced osmotic pressure.

Using the models described above, the effects of membrane fouling are demonstrated for a high flux RO membrane ($A = 9.0 \times 10^{-12}$ m/s-Pa, $B = 6.0 \times 10^{-8}$ m/s) using different sized colloidal particles under constant flux (Figs. 2.16-2.17) and constant pressure (Figs. 2.18-2.19) operations. Under constant pressure operation, the cake layer growth of particles with any size will cause membrane flux and rejection decline and CP modulus increase (Fig. 2.16) due to increasing cake enhanced osmotic pressure and trans-cake layer pressure. However, the 5 nm particle causes more flux and rejection decline than the 80 nm particle after 10 days of operation, although it produced thinner cake layer and CP modulus. This is due to the ability for smaller particles to pack into a tighter layer with higher hydraulic resistance, thereby significantly enhancing the pressure drop in the cake layer and reducing the trans-membrane pressure (water flux) at constant applied pressure (Fig. 2.17).
Figure 2.16. (a) Membrane flux, (b) cake layer thickness and (c) CP modulus for a high flux RO membrane fouled by particles with different size under constant applied pressure operation ($\Delta p = 5.7$ bar, $D_s = 1.6 \times 10^{-9}$ m$^2$/s, $\varepsilon_c = 0.46$, $k_f = 6.1 \times 10^{-5}$ m/s, $C_f = 1.0$ g/L)
Figure 2.17. Pressure drop and cake-enhanced osmotic pressure for membranes fouled by (a) 5 nm, (b) 20 nm and (c) 80 nm particles under constant applied pressure operation ($\Delta p = 5.7$ bar, $D_s = 1.6 \times 10^{-9}$ m$^2$/s, $\varepsilon_c = 0.46$, $k_f = 6.1 \times 10^{-5}$ m/s, $C_f = 1.0$ g/L)

At constant flux operation, membrane rejection, water flux, cake layer thickness and CP modulus are independent with fouling particle size (Fig. 2.18). As cake layer continuing to growth, membrane rejection decreases and CP modulus increases. Applied pressure increases with increasing cake enhanced osmotic pressure and trans-cake layer pressure. However, 5nm particle causes the applied pressure to increase dramatically compared to the 80nm particle due to increasing trans-cake layer pressure caused by increased packing of smaller particles (Fig. 2.19).
Figure 2.18. (a) Membrane flux, (b) cake layer thickness and (c) CP modulus for a high flux RO membrane fouled by particles with different size under constant flux operation ($J = 8.7 \times 10^{-6} \text{ m/s}, D_s = 1.6 \times 10^{-9} \text{ m}^2/\text{s}, \varepsilon_c = 0.46, k_f = 6.1 \times 10^{-5} \text{ m/s}, C_f = 1.0 \text{ g/L}$)
Figure 2.19. Pressure drop and cake-enhanced osmotic pressure for membranes fouled by (a) 5 nm, (b) 20 nm and (c) 80 nm particles under constant applied pressure operation ($J = 8.7 \times 10^{-6} \text{ m/s}, D_s = 1.6 \times 10^{-9} \text{ m}^2/\text{s}, \varepsilon_c = 0.46, k_f = 6.1 \times 10^{-5} \text{ m/s}, C_f = 1.0 \text{ g/L}$)

2.6. Conclusions

An impressive amount of work has been done to model solvent and solute transport in osmotic membranes. Phenomenological models based on thermodynamics and mechanistic models based on structure-performance relationships have been proposed and applied widely. Advanced structural characterization techniques provide the ability to measure pore size, porosity, pore length, and tortuosity of both the thin active layer and support structure in osmotic membranes. These membrane structural characteristics should be included in transport models to help mechanistically explain
membrane transport and to enable predictions of membrane performance. Transport models can also be used to design “ideal” membranes for targeted applications.

In addition to modeling transport in the membrane active layer, as is typically done, a close look at the support membrane structure is necessary. State-of-the-art osmotic membranes are primarily thin film composite membranes. Support membrane structure needs to be incorporated into composite membrane transport models since skin layer pore size and porosity significantly impact composite membrane permeability and rejection, as shown in modeling studies. Mixed matrix membrane transport models may also be relevant to describe transport through thin film nanocomposite NF, RO, and FO membranes. For example, the impact of filler concentration on composite membrane permeability can be calculated from mixed matrix models to offer insight into nanocomposite membrane design.

Solute gradients across the entire membrane thickness must also be considered. During separation processes solute concentrations may build up at the membrane surface or diminish in the support membrane having serious impacts on overall transport. Both external (ECP) and internal concentration polarization (ICP) play crucial roles in membrane transport. ECP not only raises energy consumption in osmotic membrane processes by increasing osmotic pressure differences across the membrane that need to be overcome, but it also reduces observed membrane rejection. ICP reduces the driving force in FO processes, thereby reducing the process productivity. Understanding and modeling concentration polarization is critical for membrane applications. Operation conditions, such as flux and cross-flow rate, can be optimized to minimize ECP based on
ECP models. To minimize ICP, the support membrane structure model is a powerful tool to design “ideal” support membrane structure.

The pore-flow model, based on size exclusion, incorporates membrane pore size into model equations; however, no other pore structural characteristics (e.g., pore shape, tortuosity) are accounted for. The solution-diffusion model, which assumes thermodynamic equilibrium exists at the membrane interface and both solvent and solute transport through the membrane are driven by chemical potential gradients, has been successfully employed due to its straightforward format. There is no structural information included in the solution-diffusion model and both pore structure and membrane-solute/solvent energetic interactions are excluded. Although Kedem-Katchalsky and Spiegler-Kedem models can be used to describe solute transport of NF and RO membranes, these models treat the membrane as a “black box” and provide no information on the transport mechanism. On the other hand, both the modified solution-diffusion and modified solution-diffusion-convection models provide insight into structure-performance relationships in osmotic membrane transport. Such models will be beneficial in allowing for fine-tuning of future materials for specific separation applications.

The major drawback of all of these models is that they do not consider interactions with charged solutes. Electrokinetic models, such as the extended Nernst-Planck model, provide complete descriptions of ionic species transport through membranes, but these models are impractical for salt mixtures. Future work should seek a combined solution-diffusion, convection, and electro-migration transport model
incorporating membrane structural characteristics and solute/solvent membrane interactions should be investigated for both normal and mixed matrix osmotic membranes. The extension of such a unified model to multi-component mixtures should also be explored. For thin film composite membranes, the effects of both support membrane structure and chemistry (e.g., hydrophilicity) on composite membrane transport should be evaluated.
2.7 List of Symbols

\( a \) activity
\( A \) solvent permeability
\( A_s \) contact area between solute molecule and membrane
\( A_w \) contact area between water molecule and membrane
\( B \) solute permeability
\( c \) concentration within membrane
\( C_{D} \) FO draw solution concentration
\( C_f \) concentration of feed solution
\( C_F \) FO feed solution concentration
\( C_m \) concentration at membrane surface
\( C_p \) permeate solute concentration
\( CP \) concentration polarization modulus
\( D \) diffusion coefficient
\( D^* \) hindered diffusion coefficient
\( d_H \) hydraulic diameter
\( d_p \) deposit particle diameter
\( F \) Faraday constant
\( h \) feed channel height
\( J_s \) solute flux
\( J_w \) solvent flux
\( K \) resistance to solute diffusion
\( k^* \) hindered mass transfer coefficient
\( k_B \) Boltzmann constant
\( K_c \) convective hindrance factor
\( K_d \) diffusive hindrance factor
\( k_f \) mass transfer coefficient of feed channel
\( K_s \) solute-membrane partition coefficient
\( K_w \) solvent-membrane partition coefficient
\( L \) feed channel length
\( M_\infty \) mass of membrane with maximum
\( M_0 \) initial mass of membrane
\( M_f \) cake layer mass pre membrane unit area
\( n \) sum of the charge of cations and anions in electrolyte
\( p \) pressure
\( P_d \) permeability of dispersed phase of composite membrane
\( P_{e f f} \) effective composite membrane permeability
\( P_{e test} \) test Peclet number
\( p_f \) feed pressure
\( P_m \) permeability of continuous phase of composite membrane
\( p_p \) permeate pressure
\( r \) radius
\( R_c \) radius of the flow channel
\( r_c \) radius of the stirred cell

\( \text{Re} \) Reynolds number

\( R_f \) fouling layer resistance

\( R_g \) gas constant

\( R_w \) membrane resistance

\( R_{fo} \) observed rejection

\( r_p \) pore radius

\( R_r \) real rejection

\( r_s \) solute Stokes radius

\( r_w \) water Stokes radius

\( S \) structure factor

\( \text{Sc} \) Schmidt number

\( \text{Sh} \) Sherwood number

\( T \) temperature

\( u_0 \) cross-flow velocity

\( V_i \) molar volume of species \( i \)

\( W \) solvation energy

\( w \) feed channel width

\( x \) axial coordinate

\( X \) charge density

\( X_{svw} \) friction constant between solute and water

\( x_w \) mole fraction of water

\( z \) number of charge

\( \alpha(\rho) \) dimensionless solute velocity in the pore

\( \beta \) concentration polarization factor

\( \beta_1 \) dimensionless solvent viscosity in the pore

\( \gamma^- \) electron-donor surface tension component

\( \gamma^+ \) electron-acceptor surface tension component

\( \gamma^{LW} \) Lifshitz-van der Waals surface tension component

\( \delta \) pore length

\( \delta_c \) colloid deposit layer thickness

\( \Delta G_s \) solute-membrane interaction energy

\( \Delta G_w \) solvent-membrane interaction energy

\( \Delta p \) pressure drop across the membrane

\( \delta_s \) difference between film and cake layer thickness

\( \Delta x \) membrane thickness

\( \Delta x_{sup} \) support layer thickness

\( \Delta \pi \) osmotic pressure difference across the membrane

\( \Delta \pi_{eff} \) effective osmotic pressure difference across the membrane

\( \Delta \pi_s \) osmotic pressure difference across the membrane during NaCl spike

\( \varepsilon \) porosity

\( \varepsilon_c \) cake layer porosity

\( \varepsilon_f \) fouling layer porosity

\( \eta \) solvent viscosity
\( \theta_a \)  amorphous volume fraction
\( \theta_d \)  volume fraction of dispersed fillers
\( \lambda \)  sieving factor
\( \mu \)  chemical potential
\( \pi \)  osmotic pressure
\( \rho \)  radical position
\( \rho_p \)  deposit particle density
\( \rho_w \)  water density
\( \sigma \)  reflection coefficient
\( \tau \)  tortuosity
\( \phi_s \)  solute-membrane pore partition coefficient
\( \phi_w \)  solvent-membrane pore partition coefficient
\( \psi \)  electrical potential
2.8. References


CHAPTER 3

STRUCTURE-PERFORMANCE MODEL TO UNDERSTAND AND IMPROVE NEUTRAL SOLUTE REMOVAL BY RO/NF MEMBRANES
3.1 Introduction

Many researchers have tried to tackle the challenge of enhancing the removal efficiency of micropollutants by NF and RO [1-6]. These studies investigate operational parameters and removal of different organic solutes, and contribute to better understanding membrane retention mechanisms by developing various solute transport models. Numerous mechanistic and mathematical models have been proposed to describe membrane transport [7-12]. Depending on the membrane, diffusion, pore flow, and Donnan exclusion may all be important mechanisms controlling solute transport.

One of the earliest models proposed for NF and RO transport is the solution-diffusion (SD) model [13]. This model is based on the principle of dissolution of water and solute molecules into membranes with a dense “nonporous” layer, followed by diffusion through the membrane due to the chemical potential gradient across the membrane [14]. The SD model simplifies the whole membrane system a black box, with no consideration of structural parameters. This means the solubility (or partition coefficient) and diffusivity of species in the membrane are not related to physical properties, such as pore structure or charge density [15].

Another model describing NF and RO membrane transport includes pore flow, in addition to the SD model [10, 11, 16]. Dissolution of water and solute molecules is proposed to be governed by steric interactions (i.e., size exclusion) and water/solute-membrane chemical interactions (i.e., affinity). When solute size is larger than membrane characteristic pore size, solute will be 100% excluded by the membrane, such that the solute partition coefficient is effectively zero. If solute size is smaller than membrane
characteristic pore size, solute partition coefficient is function of solute size/pore size ratio and solute-membrane interaction energy. After dissolution, water and solute will diffuse through membrane independently. This diffusion is hindered by both steric interactions and affinity.

Another approach for porous membrane model based on Spiegler–Kedem transport equations describes flux of uncharged organics through membranes as a combination of hindered diffusive transport and hindered convective transport [9].

Each model can be applied with some degree of success to predict mass transfer of solutes through certain membranes, but selecting the appropriate approach and determining the model parameters are not easy tasks. For example, the solubility and diffusivity of a particular solute in a given membrane material are hard to reliably measure. Although solubility and diffusivity can be related to membrane characteristic pore size, if pore model is applied, the characteristic pore sizes in NF and RO membrane are too small to characterize by conventional characterization techniques. More advanced technologies, such as atomic force microscopy (AFM) [17] and nuclear magnetic resonance (NMR) [18] need to be employed.

In this study, we developed two water/solute pore-flow transport models, each based on different transport mechanisms. One includes mechanisms of solution-diffusion (SD) and the second includes mechanisms of solution-diffusion-convection (SDC). Characteristic structural properties (i.e., characteristic pore radius and thickness-to-porosity ratio) can be determined from the models by relating the experimental results of water permeability and solute rejection. Rejection of ideal solutes (e.g., ethylene glycol
and tetrahydrofuran) were measured with three commercial membranes (NF 270, NF 90 and XLE, Dow Filmtec). Model predictions can then be made for rejection of other solutes. These predicted results can then be compared to experimental rejection statistically in order to validate the models. After model validation, the model could illustrate the effects of membrane structure properties, solute properties, solute-membrane interactions, and operation conditions on selected micropollutants rejection by commercial polyimide NF/RO membranes and lab synthesized PVA membranes.

3.2 Model Development

In the classical solution-diffusion transport model, water and solute are understood to permeate through a “nonporous” membrane skin layer. However, according to molecular dynamic simulations and advanced characterization techniques (e.g., AFM, TEM, NMR, PALS) the free volume throughout the dense polyamide layer contains interconnected pore-like voids with characteristic dimensions in the size range of 0.2 to 0.6 nm [19-22]. Herein, we model dense polymer film fractional free volume (FFV) with a hypothetical cylindrical capillary pore size \( r_p \), porosity \( \varepsilon \) and pore length \( \Delta x = \tau l \) (\( \tau \) is tortuosity and \( l \) is membrane thickness). Among a number of possible errors introduced by such simplified free volume geometry, one of the more obvious issues is that this model ignores the possibility of having free volume spaces that are partially or wholly inaccessible by either solvent or solute. This model also ignores the well known rugose morphology of polyamide RO membranes, the effects of which are only beginning to be studied theoretically and quantitatively [23, 24].
3.2.1 Extended solution-diffusion model

In the solution-diffusion model, the membrane is treated as a “non-porous” film with thickness $\Delta x$. Wang et al. modified the solution-diffusion model for NF/RO membranes assuming a porous structure [25]. Based on the classic solution-diffusion model, (volumetric) water flux, $J_w$, can be expressed as

$$J_w = A \left( \Delta p - \Delta \pi \right) = \frac{K_w D_w}{\Delta x} \frac{V_w}{R_g T} \left( \Delta p - \Delta \pi \right)$$

(3.1)

and the water solubility ($K_w$) in membrane is defined as [12]

$$K_w = \frac{\text{mass of water in the membrane}}{\text{volume of membrane}} \times \frac{\text{mass of water in the feed}}{\text{mass of water in the feed}} = \frac{c^m_w}{C^f_w}$$

(3.2)

where $c^m_w$ is the equilibrium water concentration in the membrane (kg$_{\text{water}}$·m$^{-3}$$_{\text{membrane}}$) and $C^f_w$ is the equilibrium water concentration in the bulk feed solution (kg$_{\text{water}}$·m$^{-3}$$_{\text{solution}}$).

$c^m_w$ can be defined as

$$c^m_w = \frac{\text{mass of water in the membrane}}{\text{volume of membrane}} = \frac{\text{mass of water in the membrane}}{\text{volume of membrane pores} \times \frac{1}{\text{membrane porosity}}}$$

$$= c^p_w \varepsilon$$

(3.3)

where $c^p_w$ is the equilibrium water mass concentration in membrane pore (kg$_{\text{water}}$·m$^{-3}$$_{\text{pore}}$) and $\varepsilon$ is the membrane porosity. The ratio of $c^p_w$ to $C^f_w$ can be defined as the water-membrane pore partition coefficient ($\phi_w$) [11]

$$\phi_w = \frac{\text{mass of water in the membrane}}{\text{volume of membrane pore}} \times \frac{\text{mass of water in the feed}}{\text{volume of water in the feed}} = \frac{c^p_w}{C^f_w}$$

(3.4)
Combining Eqns. 3.2-3.4 yields

\[ K_w = \phi_w \varepsilon \]  

(3.5)

According to the water-membrane partition model [10, 11]

\[ \phi_w = \left(1 - \lambda_w\right)^2 \exp \left(-\frac{\Delta G_w}{k_B T}\right) \]  

(3.6)

where \(\Delta G_w\) is water-membrane interaction energy, \(k_B\) is Boltzmann constant, and \(\lambda_w\) is the ratio of the Stokes radius of water, \(r_w\), to the membrane pore radius, \(r_p\). The diffusion coefficient of water in the membrane \((D_{w}^m)\) can be related to water diffusivity in bulk \((D_{w}^\infty)\) by the diffusive hindrance factor \((K_d)\) [16]

\[ D_w^m = K_d D_w^\infty \]  

(3.7)

Combining Eqn. 3.1-3.7 yields

\[ J_w = \frac{K_d D_w^\infty \varepsilon}{\Delta x} \left(1 - \lambda_w\right)^2 \exp \left(-\frac{\Delta G_w}{k_B T}\right) \frac{V_w}{R T} (\Delta p - \Delta \pi) \]  

(3.8)

and

\[ A = \frac{K_d D_w^\infty \varepsilon}{\Delta x} \left(1 - \lambda_w\right)^2 \exp \left(-\frac{\Delta G_w}{k_B T}\right) \frac{V_w}{R T} \]  

(3.9)

Eqn. 3.8 describes membrane water flux as a function of the pressure drop across the membrane and structural factors \((i.e.,\) characteristic pore radius, \(r_p\), and thickness-to-porosity ratio, \(\Delta x/\varepsilon\)).

Water-membrane interaction energy \((\Delta G_w)\) can be related to the interfacial surface tension of water and the membrane [26]
\[ \Delta G_w = -2A_w \left( \sqrt{\gamma_{lw}^{lw}} + \sqrt{\gamma_w^+} + \sqrt{\gamma_m^-} \right) \]  

(3.10)

where \( \gamma_{lw}^{lw} \) is the apolar Lifshitz-van der Waals component of the surface tension and \( \gamma_i^+ \) and \( \gamma_i^- \) are the polar electron-acceptor and electron-donor components of the surface tension. Subscripts \( w \) and \( m \) refer to water and membrane, respectively. \( A_w (= \pi r_w^2 / 2) \) is the area of contact between a water molecule and the membrane pore wall.

According to solution-diffusion theory [12, 14], \( J_s \) is described by the equation

\[ J_s = B \left( C_m - C_p \right) = \frac{K_s D_s^m}{\Delta x} \left( C_m - C_p \right) = \frac{K_s D_s^m}{\Delta x} \left( \beta C_f - C_p \right) \]  

(3.11)

where \( \beta \) is the concentration polarization factor and \( D_s^m \) is the average solute diffusion coefficient in membrane. The solute solubility coefficient in membrane (\( K_s \)) is defined as [12]

\[ K_s = \frac{\text{mass of solute in the membrane}}{\text{volume of membrane} \times \text{mass of solute in the feed}} = \frac{c_s^m}{C_f} \]

\[ = \frac{c_s^p}{C_f} \varepsilon \]  

(3.12)

where \( c_s^m \) is the equilibrium solute concentration within membrane (kg solute·m\(^{-3}\) membrane), \( c_s^p \) is the equilibrium solute concentration in membrane pore (kg solute·m\(^{-3}\) membrane pore), and \( \varepsilon \) is the membrane porosity. Solute-membrane partition coefficient \( (\phi_s) \) can be defined as [11]
\[ \phi_s = \frac{\text{mass of solute in the membrane}}{\text{volume of membrane pore}} = \frac{c_s^p}{C_s^f} \quad (3.13) \]

Combining Eqns. 3.11-3.13 yields

\[ J_s = \frac{\phi_s eD_s^m}{\Delta x} \left( \beta C_f - C_p \right) \quad (3.14) \]

The average solute diffusion coefficient in membrane \((D_s^m)\) can be related to solute diffusion coefficient in infinity water \((D_s^\infty)\) by hindrance factor \((K_d)\) [16]

\[ D_s^\infty = K_d D_s^m \quad (3.15) \]

According to solute-membrane partition model [10, 11]

\[ \phi_s = (1 - \lambda_s)^2 \exp \left( \frac{-\Delta G_s}{k_B T} \right) \quad (3.16) \]

where \(\Delta G_s\) is solute-membrane interaction energy and \(\lambda_s\) is the ratio of Stokes radius \((r_s)\) to membrane pore radius \((r_p)\). Combining Eqns. 3.14-3.16 yields

\[ J_s = B \left( \beta C_f - C_p \right) - \frac{K_d D_s^\infty e}{\Delta x} \left( 1 - \lambda_s \right)^2 \exp \left( \frac{-\Delta G_s}{k_B T} \right) \left( \beta C_f - C_p \right) \quad (3.17) \]

Combing Eqns. 2.4 and 3.17 yields

\[ R_o = 1 - \frac{C_p}{C_f} = 1 - \frac{\beta B}{J_w + B} = 1 - \frac{\beta K_d D_s^\infty e}{J_w + \frac{K_d D_s^\infty e}{\Delta x} \left( 1 - \lambda_s \right)^2 \exp \left( \frac{-\Delta G_s}{k_B T} \right)} \quad (3.18) \]

Eqn. 3.18 describes the observed rejection of a solute as a function of water flux and membrane structural factors. It is important to notice here that if the water flux and
solute-membrane interaction energy are known, the solute rejection becomes solely dependent on $r_p$ and $\Delta \chi/\varepsilon$. When experimentally measured ideal solute rejection and membrane water permeability are fit into **Eqns. 3.9 and 3.18**, the values of $r_p$ and $\Delta \chi/\varepsilon$ can be determined. Then, **Eqn. 3.18** becomes a predictive model for rejection of other solutes.

The free energy of interaction between solute and membrane immersed in water can be determined from [26]

$$
\Delta G_s = 2A_s \left[ \sqrt{\gamma_s^{LW} \gamma_w^{LW}} + \sqrt{\gamma_m^{LW} \gamma_w^{LW}} - \gamma_m^{LW} \gamma_s^{LW} - \gamma_s^{LW} \gamma_w^{LW} \right] + \sqrt{\gamma_w^{LW} \gamma_s^{LW}} \left( \gamma_m^{LW} \gamma_s^{LW} - \gamma_w^{LW} \gamma_m^{LW} \right)
$$

(3.19)

where $\gamma_i^{LW}$ is the apolar Lifshitz-van der Waals component of the surface tension and $\gamma_i^+$ and $\gamma_i^-$ are the polar electron-acceptor and electron-donor components of the surface tension. Subscripts $s$, $w$, and $m$ refer to solute, water and membrane, respectively. $A_s (= \pi r_s^2/2)$ is the contact area between a solute molecule and the membrane.

### 3.2.2. Modified solution-diffusion-convection model

Solute transport can also be described as a combination of diffusive and convective transport through the model structure of capillary pores [9]. $J_s$ across the membrane can be described as [11]

$$
J_s = J_s^D + J_s^C = -K_d D_s \frac{dc}{dx} + \frac{J_w}{\varepsilon} K_c c
$$

(3.20)

where $J_s^D$ is diffusive solute flux, $J_s^C$ is convective solute flux, $c$ is solute concentration within membrane pore, and $K_c$ is convective hindrance factor. Observed rejection can be
obtained by integrating Eqn. 3.20 across the membrane thickness using the boundary conditions

\[ c = \phi_0 \beta C_f \quad \text{at } x = 0 \]

\[ c = \phi_0 C_p \quad \text{at } x = \Delta x \]

resulting in

\[
R_o = 1 - \frac{C_p}{C_f} = 1 - \frac{\beta \left( 1 - \lambda_s \right)^2 \exp \left( - \frac{\Delta G_s}{k_B T} \right) K_c}{1 - \left( 1 - \lambda_s \right)^2 \exp \left( - \frac{\Delta G_s}{k_B T} \right) K_c} \exp \left( - \frac{J_w K_c \Delta x}{K_d D_s \varepsilon} \right) \]  

(3.21)

If \( J_w \) and \( \Delta G_s \) are known the \( R_o \) is solely dependent on membrane characterized pore size \( (r_p) \) and thickness-to-porosity ratio \( (\Delta x/\varepsilon) \), which are also the governing parameters in determining membrane water permeability (Eqn. 3.8) and as with the modified solution diffusion model, experimentally obtained \( R_o \) and \( J_w \) can be used to characterize \( r_p \) and \( \Delta x/\varepsilon \). Further, Eqn. 3.21 can be used to predict rejection of other solutes.

The hindrance coefficients \( (K_d \text{ and } K_c) \) are difficult to accurately determine, however, various estimations have been proposed in literature. Bungay and Brenner \[27\] proposed expressions for \( K_d \) and \( K_c \) as a function of \( \lambda = r_s/r_p \), \( 0 < \lambda < 1 \) and water/solute partition coefficients, \( \phi \),

\[
K_d = \frac{6\pi}{K_t} \]  

(3.22)

\[
K_c = \left( 2 - \phi \right) \frac{K_t}{2K_t} \]  

(3.23)
\[ K_i = \frac{9}{4} \pi^2 \sqrt{2} (1 - \lambda)^{\frac{3}{2}} \left[ 1 + \sum_{n=1}^{3} a_n (1 - \lambda)^n \right] + \sum_{n=0}^{4} a_{n+3} \lambda^n \]  

(3.24)

and

\[ K_i = \frac{9}{4} \pi^2 \sqrt{2} (1 - \lambda)^{\frac{3}{2}} \left[ 1 + \sum_{n=1}^{3} b_n (1 - \lambda)^n \right] + \sum_{n=0}^{4} b_{n+3} \lambda^n \]  

(3.25)

The constants in Eqns. 3.24 and 3.25 are listed in Table 3.1 [28].

<table>
<thead>
<tr>
<th></th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>(a_4)</th>
<th>(a_5)</th>
<th>(a_6)</th>
<th>(a_7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b_1)</td>
<td>-1.22</td>
<td>1.53</td>
<td>22.51</td>
<td>-5.61</td>
<td>-0.34</td>
<td>-1.22</td>
<td>1.65</td>
</tr>
<tr>
<td>(b_2)</td>
<td>0.12</td>
<td>-0.044</td>
<td>4.02</td>
<td>-3.98</td>
<td>-1.92</td>
<td>4.39</td>
<td>5.01</td>
</tr>
</tbody>
</table>

3.3 Materials and Methods

3.3.1 Solutes

The solutes used in this modeling study were selected based on their different physicochemical properties (polarity and aromaticity). Six different model solutes (ethylene glycol (EG), tetrahydrofuran (THF), diethylphthalate (DEP), benzene, glycerol and hexane), which were divided into four categories (aromatic polar, aromatic apolar, aliphatic polar and aliphatic apolar), were chosen. The solutes and their physicochemical properties were listed in Table 1. The solutes radius used in the modeling were Stokes radius, which were calculated by

\[ r_s = \frac{kT}{6\pi \eta D} \]  

(3.26)

where \(\eta\) is the water dynamic viscosity (\(\eta = 1.002 \times 10^{-3}\) Pa.s, at 293 K).
Table 3.2. Physicochemical characteristics for selected organic solutes.

<table>
<thead>
<tr>
<th></th>
<th>MW (g/mol)</th>
<th>$r_s$ [29]</th>
<th>$D_{∞}$ ($\times 10^{-5}$ cm$^2$/s)</th>
<th>log $K_{ow}$</th>
<th>$\gamma^{LW}$ (mJ/m$^2$)</th>
<th>$\gamma^+$ (mJ/m$^2$)</th>
<th>$\gamma^-$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>92</td>
<td>0.19</td>
<td>1.10</td>
<td>-1.76</td>
<td>34.0</td>
<td>3.92</td>
<td>57.4</td>
</tr>
<tr>
<td>EG</td>
<td>62</td>
<td>0.18</td>
<td>1.16</td>
<td>-1.36</td>
<td>29.0</td>
<td>1.92</td>
<td>47.0</td>
</tr>
<tr>
<td>THF</td>
<td>72</td>
<td>0.21</td>
<td>0.99</td>
<td>1.94</td>
<td>27.4</td>
<td>0</td>
<td>15.0</td>
</tr>
<tr>
<td>Hexane</td>
<td>78</td>
<td>0.26</td>
<td>0.85</td>
<td>3.90</td>
<td>18.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DEP</td>
<td>222</td>
<td>0.32</td>
<td>0.61</td>
<td>2.42</td>
<td>36.5</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td>Benzene</td>
<td>78</td>
<td>0.19</td>
<td>1.1</td>
<td>2.13</td>
<td>28.9</td>
<td>0</td>
<td>2.7</td>
</tr>
</tbody>
</table>

3.3.2 Membranes

The membranes used in this modeling study were both commercially available and laboratory hand-casting NF/RO membranes for different applications: water softening NF membranes: HL (GE Osmonics, Fairfield CT, USA), NF90 and NF270 (Dow Filmtec, Midland MI, USA); brackish water RO membrane: XLE (Dow Filmtec, Midland MI, USA); seawater RO membrane: SWC3+ (Hydranautics, Oceanside CA, USA); and laboratory hand-casting membrane PVAm. All the commercially available membranes are polyamide thin film composite membranes. The PVAm membrane is a malic acid cross-linked Poly(vinyl alcohol)-Polysulfone composite NF membrane. The details of the PVAm membrane synthesis and characterization can be found in a previous publication [30].

3.3.3 Solute and membrane surface tensions

In order to calculate solute-membrane interaction energy ($\Delta G_i$) by using Eq. (11), membrane, solute, solvent (water) surface tension components need to be characterized. The surface tension components of solutes and water can be found in literatures. The membrane surface tension components can be evaluated by Young-Dupré equation [31, 32]:
\[ \gamma_w^2 (1 + \cos \theta) = 2 \left( \sqrt{\gamma_{LW}^m \gamma_{LW}^w} + \sqrt{\gamma_{m}^r \gamma_{w}^r} + \sqrt{\gamma_{m}^r \gamma_{w}^r} \right) \] (3.27)

where \( \theta \) is the contact angle formed between a droplet of liquid L and the tested membrane surface. Three Young-Dupré equations can be set up by performing three times contact angle measurements using three different liquids (water, ethylene glycol and diiodomethane). The three unknown variables of membrane surface tension components can be solved from these three equations.

All contact angle measurements were conducted using an automatic contact angle goniometer (DSA10 KRÜSS GmbH, Hamburg, Germany) equipped with commercial contact angle calculation software (Drop Shape Analysis, KRÜSS GmbH). At least twelve equilibrium contact angles were measured for each sample at different locations. The highest and lowest values were discarded before calculating the average contact angle.

3.3.4 Rejection evaluation

The separation performance of NF and RO membranes (NF270, NF90, XLE) was evaluated in a bench scale cross-flow membrane filtration system equipped with six parallel membrane cells (effective membrane area is 19.4 cm\(^2\), with width of 2.54 cm, length of 7.62 cm and channel height of 0.10 cm, for each membrane cell). Pure water permeability was determined using 18 MΩ laboratory deionized water at 25 °C and applied pressures between 0.69 – 2.76 MPa (100 – 400 psi). The cross-flow rate was set at 0.55 Gal·min\(^{-1}\) (3.46×10\(^{-5}\) m\(^3\)·s\(^{-1}\)). Flow conditions were controlled so that the Reynolds number was maintained at 1900 with a mesh spacer in the feed channel. This ensured that the external mass transfer coefficient was 2.42×10\(^{-4}\) m·s\(^{-1}\), producing a
concentration polarization modulus in the range of 1.04 – 1.26 for permeate fluxes in the range of $1 \times 10^{-6} - 55 \times 10^{-6}$ m·s$^{-1}$. Flux was measured by a digital flow meter. Before testing, all the membranes were compacted with deionized water at 3.10 MPa (450 psi) and 25 °C for 16 hours. After permeability measurements, the same membranes were used to characterize the selectivity of selected solutes. Both ethylene glycol and tetrahydrofuran were spiked into deionized water at 30 mg carbon·L$^{-1}$. Solute rejection was found by measuring total organic carbon in feed and permeate solutions. During the rejection experiments, feed pressure was varied (0.69 – 2.76 MPa), while temperature (25 °C) and external mass transfer coefficient (2.42×10$^{-4}$ m/s) were kept constant. In order to eliminate the effect of adsorption of solute onto the membrane surface and into membrane inner structure, feed solution was filtered through all the membranes at 2.76 MPa (400 psi) and 25 °C for 24 hours prior to rejection tests.

3.4 Results and Discussion

3.4.1 Model validation

The surface tension parameters of membrane and solute, determined from contact angle test or adapted from literatures, are shown in Table 3.3. These values are combined with Eqn. 3.10 and 3.19, and the solute-membrane interaction energy is calculated (Table 3.4).
Table 3.3. Membrane surface contact angle and surface tension components.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle (°)</th>
<th>$\gamma^W$ (mJ/m$^2$)</th>
<th>$\gamma^+$ (mJ/m$^2$)</th>
<th>$\gamma^-$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Glycerol</td>
<td>Diiodomethane</td>
<td></td>
</tr>
<tr>
<td>NF 270</td>
<td>39.7</td>
<td>27.6</td>
<td>31.6</td>
<td>43.4</td>
</tr>
<tr>
<td>NF 90</td>
<td>67.5</td>
<td>53.4</td>
<td>33.9</td>
<td>36.6</td>
</tr>
<tr>
<td>XLE</td>
<td>67.6</td>
<td>50.1</td>
<td>18.2</td>
<td>37.2</td>
</tr>
<tr>
<td>HL</td>
<td>41.2</td>
<td>34.6</td>
<td>23.1</td>
<td>44.7</td>
</tr>
<tr>
<td>SWC3+</td>
<td>58.3</td>
<td>7.0</td>
<td>11.6</td>
<td>49.8</td>
</tr>
<tr>
<td>PVAm</td>
<td>21.6</td>
<td>48.9</td>
<td>35.5</td>
<td>41.8</td>
</tr>
</tbody>
</table>

Table 3.4. Water/solute-membrane interaction energy.

<table>
<thead>
<tr>
<th>$\Delta G$ ($\times 10^{-21}$ J)</th>
<th>NF 270</th>
<th>NF 90</th>
<th>XLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-2.62</td>
<td>-2.44</td>
<td>-1.78</td>
</tr>
<tr>
<td>EG</td>
<td>0.58</td>
<td>-0.09</td>
<td>-0.18</td>
</tr>
<tr>
<td>THF</td>
<td>-0.76</td>
<td>-2.40</td>
<td>-2.60</td>
</tr>
</tbody>
</table>

Experimentally obtained membrane water permeability and EG rejection data were fitted into SD model (Equations (1) and (3)) and SDC model (Equations (1) and (5)), independently. The experimental and model fitted EG rejection curves were plotted in Figure 3.1. The values of membrane characterized pore size ($r_p$) and porosity to thickness ratio ($\epsilon/\Delta x$), obtained by model fitting as well as from literature [19], are shown in Table 3.5.
Among the three membranes tested, NF270 membrane has largest characteristic pore radius and thickness/porosity ratio (Table 3.5). The NF90 and XLE membranes have very similar structural characteristics and separation performance. The membrane characteristic pore radius and thickness-to-porosity ratio obtained by fitting experimental data to the SDC model are larger than these obtained by the SD model.
With membrane characterized pore size \( (r_p) \) and porosity to thickness ratio \( (\varepsilon/\Delta x) \) known (Table 3.5), both the SD and SDC transport models can be used to predict the rejection of other solutes by NF270, NF90 and XLE membranes. The experimental and model fitted THF rejection curves were plotted in Figure 3.2, regression analysis was used to evaluate the model fitting. For NF90 and XLE membranes, the SD model prediction fitted experimental rejection data better than SDC model. However, the SDC model fits data better than the SD model for the NF270 membrane. The results suggest for tight NF (e.g., NF90) and brackish water RO (e.g., XLE) membranes solution-diffusion mechanism should be employed to explain membrane transport. For NF membranes with large characteristic pore radius, the mechanism of convection must be included.

3.4.2 Solute/membrane surface tension and interaction energy
ΔGs (Table 3.6) can be used to quantify the interaction (either attractive or repulsive) between solute and membrane. If ΔGs > 0, repulsive interaction exists between organic solute and membrane. The transport of solute molecules through membrane pore will be denied. A high solute rejection of membrane can be expected. If ΔGs < 0, there will be attractive force between solute and membrane. Meanwhile, the solute transport through membrane pore will be favored. The membrane will have low rejection to solute. Due to the organic nature of polymeric membrane, organic solutes tend to partition into membrane (organic) phase from water phase. This tendency can be explained by hydrophobicity of organic solute. Octanol-water partitioning coefficient (Kow) is normally used by environmental scientists to quantify the hydrophobicity of organics. In this study, except the aliphatic polar solute glycerol, all other solutes exhibited negative interaction free energy with all the polymeric membranes. The transport of these organic solutes through polymeric membranes is favored.

<table>
<thead>
<tr>
<th>Solute</th>
<th>PVAm</th>
<th>NF270</th>
<th>HL</th>
<th>SWC3+</th>
<th>XLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>2.24</td>
<td>1.44</td>
<td>1.49</td>
<td>0.51</td>
<td>0.36</td>
</tr>
<tr>
<td>Hexane</td>
<td>-2.11</td>
<td>-3.56</td>
<td>-4.02</td>
<td>-5.84</td>
<td>-6.82</td>
</tr>
<tr>
<td>DEP</td>
<td>-2.59</td>
<td>-5.01</td>
<td>-5.65</td>
<td>-8.78</td>
<td>-9.73</td>
</tr>
<tr>
<td>Benzene</td>
<td>-0.41</td>
<td>-1.29</td>
<td>-1.48</td>
<td>-2.59</td>
<td>-3.00</td>
</tr>
</tbody>
</table>

Based on the data shown in Table 3.6, glycerol has positive interaction free energy with all membranes, because it is a very hydrophilic organic solute (logKow = -1.76). Among the three solutes showed negative ΔGs, DEP has the largest negative ΔGs and benzene has the smallest negative ΔGs with all the membranes. DEP is an aromatic polar organic molecule, which is more likely to partition into aromatic or polar organic phase due to the similarity of the structure. All the membranes used in this study contain
either aromatic (polyamide) or polar (PVA) structure. Also, the Stokes radius of DEP is the highest among all the solutes in this study, so the contact area between DEP and membrane is the largest. As a result, DEP has the highest attractive interaction with membranes. The reason for why aliphatic apolar solute hexane has higher attractive interaction with membranes is that hexane has larger Stokes radius (contact area) than benzene.

For all the membranes in this study, commercial available polyamide membranes show either less positive (glycerol) $\Delta G_s$ or more negative (hexane, benzene, DEP) $\Delta G_s$ values than laboratory hand-casting PVA membrane. This can be explained by the difference in hydrophobicity/hydrophilicity of membrane surface. Polyamide membranes, which has large amount of aromatic structure, are usually considered as relatively hydrophobic membrane with water contact angle in the range of 60 – 70°. However, the water contact angle of PVAm membrane is 22°, which suggests a relatively hydrophilic surface. Hydrophobic organic solutes (hexane benzene and DEP) are more easily attracted by relative hydrophobic polyamide membranes than hydrophilic PVAm membrane, which result in more negative value for solute-membrane interaction energy.

Polyamide NF membranes (HL, NF270) have less negative $\Delta G_s$ values than polyamide RO membranes (SWC3+, XLE). The cross-linking degree in polyamide NF membrane is lower than that in polyamide RO membrane. Consequently, there will be more free carboxylic functional groups available in membrane structure. So, the surface hydrophilicity of NF membrane is higher than RO membrane.

3.4.3 Prediction of solute rejection
In order to predict solute rejection using Eqn. 3.21, operation parameters \( (J_w, k_f) \), solute property parameters \((r_s, D_s)\), membrane structure property parameters \((r_p, \Delta x \text{ and } \epsilon)\), solute-membrane interaction parameter \((\Delta G_s)\) are required (assume the temperature is constant at 293 K). In this study, values of solute property parameters and \(\Delta G_s\) were fixed in all model simulations. Other parameters will use the default values if not defined, which are shown in Table 3.7. The default values of model fitting parameters were chosen based on normal industrial operation conditions and typical membrane properties. Also, the values of fitting parameters will be optimized according to the model prediction results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Default value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size</td>
<td>(r_p)</td>
<td>0.40</td>
</tr>
<tr>
<td>Solvent flux</td>
<td>(J_v)</td>
<td>20</td>
</tr>
<tr>
<td>Mass transfer coefficient</td>
<td>(k_f)</td>
<td>300</td>
</tr>
<tr>
<td>Concentration polarization</td>
<td>(\beta)</td>
<td>1.07</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>(k)</td>
<td>(10^{-23}) J/K</td>
</tr>
<tr>
<td>Temperature</td>
<td>(T)</td>
<td>K</td>
</tr>
<tr>
<td>Coating film thickness</td>
<td>(\Delta x)</td>
<td>nm</td>
</tr>
<tr>
<td>Surface porosity</td>
<td>(\epsilon)</td>
<td></td>
</tr>
</tbody>
</table>

### 3.4.3.1 Effect of operation parameters

#### 3.4.3.1.1 Effect of permeate flux

The prediction of solutes rejection by membranes as a function of permeate flux was shown in Figure 3.3. Based on the results, within the practical permeate flux range (0 – 30 \(\mu m/s\)), solute rejection by membrane increased as membrane permeate flux increased. However, the increasing in solute rejection became slow when the permeate flux was relatively high, which is corresponded to salt rejection study in other research.
work [33]. As the permeate flux increases, progressively more solvent (water) passes through membrane relative to solute. This leads to the concentration of solute in permeate side decreases with increasing permeate flux. According to Eq. (5), as the concentration of solute in permeate going down, the solute rejection should increase. The results here suggest that operating NF/RO process at high membrane throughput (permeate flux) will also benefit the solute rejection. So, the following modeling investigation will be performed with high permeate flux (20 µm/s).

**Figure 3.3.** Predicted rejection of benzene (a), DEP (b), hexane (c) and glycerol (d) as a function of permeate flux.

### 3.4.3.1.2 Effect of external mass transfer

**Figure 3.4** presents the prediction of solute rejection as a function of external mass transfer coefficient. Similar behavior was observed with the effect of permeate flux.
on solute rejection. Large external mass transfer coefficient is required to obtain high solute rejection, especially for benzene rejection by commercial RO membranes. During the NF/RO process, concentration polarization will reduce the difference of solute concentration across the membrane, thereby lowering the solute rejection by membrane. One of the effective ways to reduce concentration polarization is to enhance external mass transfer to avoid solute accumulation at the membrane surface. As a result, the NF/RO process should be operated with high external mass transfer coefficient. Based on the rejection prediction in this study, the external mass transfer coefficient should be set at 300 µm/s. Then the concentration polarization factor $\beta$ will be 1.07 (Re = 1,900), which can meet the recommendation requirement (1.2 - 1.3) for different water qualities [34].

**Figure 3.4.** Predicted rejection of benzene (a), DEP (b), hexane (c) and glycerol (d) as a function of external mass transfer coefficient.
3.4.3.2 Effect of membrane structural properties

3.4.3.2.1 Membrane thickness

The membrane thickness here is defined as membrane selective layer (polyamide or PVA) effective thickness. The assumption is that the support layer (usually is made of polysulfone) of NF/RO membrane has no contribution to organic solute rejection in this study. To investigate the effect of membrane thickness on solute rejection, various membrane selective layer thickness values, which are range from 40 nm to 300 nm [33, 34], were fitted into the transport model. The solute prediction results were shown in Figure 3.5. When the membrane film thickness is substantially increased, the solute rejection increases as well. It is important to notice that the solute rejection dependence on film thickness becomes less significant after the film thickness reaches certain value (critical thickness). The prediction trend here is similar as some experimental study [35]. The explanation for this trend is the solute molecule will experience longer diffusion pass length when it travels through a thicker film. At the same time, the solute internal mass transfer resistance also increases. So the solute rejection will increase as the film thickness increases. For all the solutes used in this study, membrane with a 200 nm thick selective layer is preferred for solute rejection.
Figure 3.5. Predicted rejection of benzene (a), DEP (b), hexane (c) and glycerol (d) as a function of membrane thickness.

3.4.3.2.2 Membrane pore size

The solute-membrane partition coefficient is dependent on the ratio ($\lambda$) of solute size to membrane pore size, which represents the size exclusion effects. NF/RO membranes, which are used for separation at molecule level, are usually called as non-porous membranes. However, the void phase or free volume of NF/RO membranes can be regarded as cylindrical pores whose radius will be in the range of 0.2 – 1.0 nm [36-38]. The membrane pore size can be characterized by fitting the experimental solute rejection data to transport model. In this study, the solutes rejection by the membranes was predicted by varying the membrane pore size.
Figure 3.6. Predicted rejection of benzene (a), DEP (b), hexane (c) and glycerol (d) as a function of membrane pore size.

As the results shown in Figure 3.6, the effect of membrane pore size on solute rejection is dramatic, especially for the cases when solute-membrane interaction free energy is negative (benzene, DEP and Hexane). The solute rejection drops because the solutes travel more easily through the pore when the pore is more open (larger pore size). The area of membrane pore wall will also increase as pore size increases. The attractive interaction ($\Delta G_s < 0$) between solute and membrane pore wall will further enhance the decrease of solute rejection. The results suggest that in order to achieve higher solute rejection, the membrane should be engineered with small pore.

3.4.3.2.3 Membrane porosity

Polymeric membranes are composites of two phases: a solid polymer phase occupied by the polymer chains and branches, and a void phase (free volume). As indicated previously, the membrane free volume provides a route for molecule to diffuse through the membrane. The fraction of free volume is referred to membrane porosity. For dense membrane (NF/RO), the membrane porosity is usually in the range of 0.01 – 0.10. Solutes rejection as a function of membrane porosity was shown in Figure 3.7. The solute rejection decreased as the membrane porosity decreased, especially there would be
almost no rejection for benzene by RO membrane if the membrane porosity was as high as 0.06. However, the DEP rejection by membrane is almost constant when the membrane porosity is the only variable. When the membrane porosity increased, the fraction of membrane free volume also increased. According to the free volume theory, the mobility of solute in polymeric membrane, \( M_s \) is defined as [30]:

\[
M_s = A \exp\left(-\frac{B}{\varepsilon}\right)
\]  \hspace{1cm} (3.28)

where A and B are constants, which are independent of the solute concentration and temperature, but dependent only on the solute size. Eqn. 3.27 indicates that solute mobility will increase as the membrane porosity increases. The increase in solute mobility will also reduce the solute rejection by membrane. Based on the results shown in this study, a dense (low porosity) membrane is favored for solute rejection.

**Figure 3.7.** Predicted rejection of benzene (a), DEP (b), hexane (c) and glycerol (d) as a function of membrane porosity.
3.4.4 Implications on membrane development

Both specific water flux and solute rejection vary dramatically with $\lambda$, $\Delta x/\varepsilon$, and $\Delta G$ (Fig. 3.8). Variations in $\lambda$ and $\Delta x/\varepsilon$ produce opposite trends for specific $J_w$ and $R_o$. If one wants to maximize $J_w$, a membrane should have small $\Delta x/\varepsilon$ and large $r_p$; however, $R_o$ will be sacrificed. The only option to optimize both specific $J_w$ and $R_o$ is to select a membrane material that exhibits large positive $\Delta G_s$ and large negative $\Delta G_w$. For apolar solutes removal, this can be achieved by selecting a hydrophilic (polar) membrane. However, to remove a hydrophilic solute, it is hard to find a membrane material with both large positive $\Delta G_s$ and large negative $\Delta G_w$, because solid materials are predominantly monopolar electron-donors [39]. These results demonstrate how understanding the role of structural and chemical properties of the membrane on its performance can help inform the materials engineering process.
\( h = r_s / r_p \)

\( \Delta G_s = -5 \times 10^{-21} \text{ J} \)

\( \Delta G_s = 0 \text{ J} \)

\( \Delta G_s = 5 \times 10^{-21} \text{ J} \)
Figure 3.8. Illustration of effect of physical parameters ($\lambda$ and $\Delta x/\varepsilon$) and energetic interactions ($\Delta G$) on (a) membrane specific water flux (Eqn. 3.8) and solute rejection based on (b) the improved solution-diffusion model (Eqn. 3.18) and (c) the convection-diffusion-affinity model (Eqn. 3.21). ($D_w = 2.2 \times 10^{-9} \text{ m}^2/\text{s}$, $D_\varepsilon = 1.2 \times 10^{-9} \text{ m}^2/\text{s}$, $k_f = 1 \times 10^{-4} \text{ m/s}$, $T = 293 \text{ K}$, $J_w = 1 \times 10^{-5} \text{ m/s}$).

3.5 Conclusions

In general, model predictions agree well with experimental data suggesting the model captures the phenomenological behavior of commercial NF/RO membranes for separations. The model suggests the “effective pore size” may be on the order of 0.24 to 0.35 nm and the “effective diffusion path length” (i.e., barrier layer thickness) may be on the order of 10 to 20 nm; model-derived pore sizes are consistent with literature reported values for the same membranes, but thicknesses are an order of magnitude less than what is historically related to polyamide coating film thickness. These new insights provide a framework for the creation of next-generation NF/RO membrane structures specifically targeting emerging trace organic contaminants of concern for human health and environmental protection.

The model was employed to predict uncharged organic solutes rejection by commercial available polyamide membranes and laboratory hand-casting PVA membranes. The results reported here confirmed previous studies that the membrane solute rejection strongly depends on the ratio of solute size to membrane pore size and solute-membrane interaction free energy. Moreover, the dependences of operation parameters, membrane structure parameters and solute properties were also clearly presented by the modeling prediction. With given membranes, applying optimal operation condition (permeate flux, mass transfer coefficient) can enhance the solute
rejection. These results suggest it is possible and important to fine-tune the surface tension of membrane and membrane structure (pore size, porosity, thickness) to achieve high selectivity for certain solute.
3.6 References


[38] K. Kosutic, B. Kunst, Removal of organics from aqueous solutions by commercial RO and NF membranes of characterized porosities, Desalination, 142 (2002) 47-56.

CHAPTER 4

EFFECTS OF WATER CHEMISTRY ON STRUCTURE AND PERFORMANCE OF POLYAMIDE COMPOSITE MEMBRANES
4.1 Introduction

The main goal of this chapter was to expand upon the extended solution-diffusion model of Verliefde et al. [1] to more accurately quantify changes in membrane structure and solute-solvent-membrane interactions due to changes in feed water chemistry (ionic strength, pH and divalent cation content). Ultimately, this work provides new structure-performance insights into polyamide NF/RO membrane separation performance. Herein, the extended solution-diffusion model accounts for both water flux and (neutral) solute rejection. Therefore, we provide two equations that allow one to directly solve for the two membrane structural descriptors (i.e., effective pore radius and structure factor) by properly fitting to experimentally observed flux and rejection data.

4.2 Materials and Methods

4.2.1. Membranes and chemicals

Representative polyamide NF and RO membranes (NF90, NF270, BW-XLE; Dow Film Tec Corp., Minneapolis, Minnesota, USA) were received as flat sheet samples and stored in laboratory deionized water at 4 °C upon receipt. Chemical agents used to adjust feed water chemistry were all analytical grade (Fisher Scientific, Pittsburgh, Pennsylvania, USA). Ethylene glycol (EG, Sigma-Aldrich, St. Louis, MO) was used as a model neutral solute in performance tests. Key physical-chemical properties of EG are provided in Table 4.1.
### Table 4.1 Physic-chemical properties of ethylene glycol.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Molecular weight (g/mol)</th>
<th>Stokes radius (nm)</th>
<th>Diffusivity (cm²/s)</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₆O₂</td>
<td>62</td>
<td>0.18₄</td>
<td>1.16 × 10⁻⁵ [2]</td>
<td>14.2 [3]</td>
</tr>
</tbody>
</table>

Calculated by Stokes-Einstein equation in [4]

### 4.2.2. Membrane performance experiments

The separation performance of NF and RO membranes was evaluated in a bench scale cross-flow membrane filtration system equipped with six parallel membrane cells, each with an effective membrane area of 19.4 cm² (2.54 cm width, 7.62 cm length) and cross-flow channel height of 1 mm. A detailed description of the test apparatus is previously published [5]. Water flux was determined at 20 °C and applied pressures between 0.21 to 1.72 MPa (30 to 250 psi). The cross-flow rate was set at 3.46 × 10⁻⁵ m³·s⁻¹ (0.55 Gal·min⁻¹) in all experiments providing a cross-flow Reynolds number of 1,900 accounting for a mesh feed spacer placed in the feed channel. The external mass transfer coefficient was 2.42 × 10⁻⁴ m·s⁻¹, producing a concentration polarization factor in the range of 1.04 – 1.13 for permeate fluxes in the range of 1 to 30 μm·s⁻¹. Permeate flux was measured by a digital flow meter (Optiflow 1000, Agilent Technology, Forster City, CA) placed on the permeate line from each cross-flow membrane module.

Prior to testing, all the membranes were compacted with 0.056 μS/cm deionized water at 2.76 MPa (400 psi) and 20 °C for 18 hours. After water flux measurements, the same membranes were used to characterize solute rejection under various water chemistries. Feed water ionic strength was adjusted by adding various amounts of NaCl. Feed water pH was adjusted with 1M NaOH and 1M HCl solutions. CaCl₂ and MgCl₂...
was added to provide divalent cation content. New sets of membranes were used for each series of experiments. EG was spiked into deionized water at 20 mg carbon·L⁻¹. EG rejection was found by measuring total organic carbon in feed and permeate solutions. Salt rejection was evaluated by measuring conductivities of feed and permeates solution. The addition of osmotic pressure due to salt rejection had been taken into account when calculating membrane water permeability. During the rejection experiments, feed pressure was varied from 0.21 to 1.72 MPa, while temperature (20 °C) and external mass transfer coefficient (2.42×10⁻⁴ m/s) were kept constant. In order to eliminate the effects of initial adsorption of solute onto the membrane surface and into membrane inner structure, feed solution was filtered through all the membranes for 24 hours before rejection measurements were obtained.

4.2.3. Membrane and solute surface tension characterization

The membrane and solute interfacial tensions and water/solute-membrane interaction energies were determined from measured contact angles using an automated contact angle goniometer (DSA10, Krüss GmbH, Hamburg, Germany). At least twelve equilibrium contact angles at different locations were measured for each sample. The details of contact angle measurements were described in previous publication [6]. Contact angles measurement for different water chemistries (polar liquid), diiodomethane (apolar liquid) and EG (polar liquid) enables determination of surface tension components for membranes using the extended Young-Dupré equation [6]
\[
\gamma_w^T \left( 1 + \frac{\cos \theta}{r} \right) = 2 \left( \sqrt{\gamma_m^{LW} \gamma_w^{LW}} + \sqrt{\gamma_m^T \gamma_w^T} + \sqrt{\gamma_m^- \gamma_w^-} \right)
\]  

(4.1)

where \( \theta \) is the contact angle formed between the droplet of liquid and membrane surface, 
\( r \) is the roughness area ratio (i.e. the ratio of actual surface area for a rough surface to the planar area) [7]. The membrane surface roughness was analyzed form atomic force microscopy (AFM) measurement and an average of six measurements were used to produce the final roughness data (Table 4.2).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( R_a ) (nm)</th>
<th>( R_q ) (nm)</th>
<th>( R_m ) (nm)</th>
<th>( SAD ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF270</td>
<td>3.2 ± 1.6</td>
<td>4.0 ± 1.6</td>
<td>54 ± 20</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>NF90</td>
<td>31.2 ± 5.4</td>
<td>40.5 ± 7.0</td>
<td>401 ± 75</td>
<td>19.1 ± 5.0</td>
</tr>
<tr>
<td>XLE</td>
<td>44.1 ± 10.3</td>
<td>58.2 ± 14.6</td>
<td>580 ± 88</td>
<td>33.6 ± 5.7</td>
</tr>
</tbody>
</table>

\( R_a \): average deviation (above or below) the mean plane. 
\( R_q \): RMS deviation or z-data standard deviation. 
\( R_m \): maximum deviation between largest + and - z-values, spread of distribution. 
\( SAD \): surface area difference, increase in surface area over projected flat plate area \((r = 1 + SAD)\).

The surface tension components for EG and the liquids are given in Table 4.3 [8].

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>( \gamma_s^T ) (mJ/m(^2))</th>
<th>( \gamma_s^{LW} ) (mJ/m(^2))</th>
<th>( \gamma_s^+ ) (mJ/m(^2))</th>
<th>( \gamma_s^- ) (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>48</td>
<td>29</td>
<td>1.92</td>
<td>47</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>50.8</td>
<td>50.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>25.5</td>
<td>25.5</td>
</tr>
</tbody>
</table>

### 4.3 Results and Discussion

#### 4.3.1 Effects of water chemistry on membrane performance

#### 4.3.1.1. Feed ionic strength
Membrane water permeability and solute rejection (salt and EG) was evaluated while changing the ionic strength of feed water. Membrane water permeability was measured at the same operation conditions and normalized to water permeability measured with DI water as feed. And all solute rejections were measured at the same permeate water flux (~13 µm/s). As shown in Figure 4.1a, for all the membranes, membrane water permeability decreased as ionic strength in feed water increased. The trend here was the same as the experimental results published by Freger [9] and Braghetta et al. [10]. Among the three commercial membranes, the loss of water permeability for NF270 (up to 33 %) was less significant than for NF90 (up to 46 %) and XLE (up to 47 %). It is important to notice that, for all three membranes, their initial pure water permeability was almost fully recovered within experimental error, so the effect of solution water chemistry on these membranes appeared fully reversible.

<table>
<thead>
<tr>
<th></th>
<th>DI before</th>
<th>5 mM</th>
<th>50 mM</th>
<th>500 mM</th>
<th>DI after</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF270</td>
<td>1.0</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>NF90</td>
<td>1.0</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>XLE</td>
<td>1.0</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 4.1. Experimental data illustrating the effects of ionic strength on (a) water permeability normalized against measured with deionized water and (b) solute (NaCl and EG) rejection. Experimental conditions: cross-flow Re 1,900, feed temperature 20 °C, and pH 6.0±0.2. Solute rejection data reported for water flux about 13 µm/s.

Figure 4.1b shows the salt rejection for the three membranes at feed concentrations ranging from 5 mM to 500 mM. For NF90 and XLE membranes, there is no significant difference in salt rejection while varying feed salt concentration. However, NaCl retention by NF270 decreased with increasing NaCl concentration in the feed. Mazzoni et al. reported salt rejection decreases as the salt concentration increases for Desal-5 DK membranes [11]. The charge screening effect of the counter-ions on the membrane charge sites is stronger when the feed salt concentration increases. Meanwhile, the electrostatic repulsive interaction between membrane and salt ion will decrease, which will cause the decrease of salt retention [12]. The results in this study suggest that,
for dense membrane NF90 and XLE, the charge screening effect in salt rejection
deduction is less significant as for NF270 membrane.

For NF90 and XLE membranes, EG rejection increased with increasing solution
ionic strength from 5 mM to 500 mM. Similar results have been reported by Braghetta et al., in which increased PEG rejection by NF membrane at high ionic strength was observed [10]. However, for NF270, EG rejection decreased with ionic strength from 5 mM to 500 mM. These results were consistent with results of studies on N-Nitrosodimethylamine (NDMA) rejection by ESPA3 membrane conducted by Steinle-Darling et al. [13]. Luo et al. also found that glucose retention for NF270 membrane decreased with increasing salt concentration [14].

4.3.1.2 Feed pH

Membrane water permeability was tested with different feed solution pH and
normalized to water permeability measured with DI water as feed, as shown in Figure 4.2a. For NF270, membrane water permeability increased with pH from 3 to 9 and
decreased from pH 9 to 11. For NF90 and XLE, membrane water permeability increased with pH from 3 to 7, then decreased with pH from 7 to 11. However, membrane water permeability of NF 90 and XLE were less sensitive to solution pH than NF 270. As same as varying solution ionic strength, membrane water permeability of all three membranes could also be recovered.

Figure 2b shows the effect of feed solution pH on salt rejection for the tested
membranes. NF90 and XLE membrane are less pH sensitive in salt retention when pH is
varied from 5 to 11. However, when solution pH decreased to 3, NF90 and XLE
membrane salt rejection also decreased. For NF270, salt rejection first decreased with feed pH and then increased, which is similar with results in Kim et al. [15] and Xu et al. [16]. When feed solution pH was further increased to 11, the salt rejection deceased.

The effect of feed solution pH on EG rejection was also illustrated in Figure 4.2b. For all three membranes, the decrease in EG rejection was observed at a pH between 3 and 9. When the solution pH was further increased to 11, the EG rejection also increased. The trend observed here is similar with Schäfer et al., as they found the rejection of the steroid estrone by NF (TFC-SR1) and RO (TFC-S) membranes decreased when solution pH approached the pKa of estrone [17]. Also, Bellona et al. also reported their findings that rejection of ibuprofen by NF90 and NF200 membranes was the highest at pH 3, then the rejection slightly decreased at pH 5 before it increased again beyond a pH 7 [18].
Figure 4.2. Experimental data illustrating the effects of pH on (a) water permeability normalized against measured with deionized water and (b) solute (NaCl and EG) rejection. Experimental conditions: cross-flow Re 1,900, feed temperature 20 °C, and ionic strength 50 mM. Solute rejection data reported for water flux about 13 µm/s.

4.3.1.3 Presence of divalent cations in feed

Divalent ions (e.g. Ca$^{2+}$, Mg$^{2+}$) are ubiquitous in natural waters and wastewaters. So membrane water permeability was characterized in their presence (Figure 4.3a) and normalized to water permeability measured with DI water as feed. For all three membranes, membrane water permeability decreased with Ca$^{2+}$ or Mg$^{2+}$ in the feed water. And the loss of membrane water permeability (30 to 40 %) was more than that when the same ionic strength of NaCl existing in the feed (20 to 30 %). Membrane water permeability reduction percentage of three tested membranes were almost the same for each cation. However, the membrane water permeability under MgCl$_2$ feed solution was
lower than membrane water permeability under CaCl$_2$ feed for all membranes. It is interesting to point out that the DI water permeability could not fully recovered for NF90 and XLE membranes (80 to 95%). Based on the results, magnesium ion appeared to cause more water flux loss for all membranes than calcium ion at the same ionic strength. As shown in Figure 3b, there is no noteworthy difference in CaCl$_2$ and MgCl$_2$ rejection for NF90 and XLE membranes. MgCl$_2$ rejection is slightly higher than CaCl$_2$ rejection for NF270 due to the larger hydrated radius of Mg$^{2+}$ ion [19].

EG rejection was also decreased with divalent cation content in the feed water (Figure 4.3b). Also, EG rejection by all three membranes was slightly higher for Mg$^{2+}$ than Ca$^{2+}$, although the differences were not significant. For comparison, the results of EG rejection with 50 mM NaCl as feed solution were replotted here. It should be noted that, for NF90 and XLE membranes, divalent cations in feed solution caused more reduction in EG rejection than monovalent cations. Verliefde et al. studied the influence of addition of Ca$^{2+}$ into feed solution on neutral pharmaceutical compounds rejection by Desal HL and Trisep TS80 membranes. Compared to the solute rejection in NaCl electrolytes, both membranes showed lower rejection for most of the neutral solute after adding 10 mM Ca$^{2+}$ into feed solution [20]. However, for NF270 membrane, the EG rejection was smaller in feed solution with monovalent cations compared to with divalent cations.
Figure 4.3. Experimental data illustrating the effects of divalent cations on (a) water permeability normalized against measured with deionized water and (b) solute rejection.
(CaCl$_2$, MgCl$_2$ and EG, NaCl rejection was plotted for comparison). Experimental conditions: cross-flow Re 1,900, feed temperature 20 °C, pH 6.0±0.2 and ionic strength 50 mM. Solute rejection data reported for water flux of about 13 µm/s.

### 4.3.2 Effects of water chemistry on solute-water-membrane interaction energy

Based on the contact angle data shown in Table 4.4, the electrolyte solution contact angles of all three membranes decreased with increasing ionic strength, increasing solution pH and with divalent cations (Mg$^{2+}$, Ca$^{2+}$) presenting. Solute and membrane interfacial tensions and free energies were calculated from contact angles data in Table 4.4 using previously published methods [21]. The membrane (1)-liquid media (3) interfacial free energy, $-\Delta G_{13}$, fundamentally describes membrane surface wettability. The cohesive free energy, $\Delta G_{131}$, which describes energetic favorability of membrane (1) interacting through a liquid media (3) (solution with various water chemistries) with itself (1), offers a quantitative description of membrane surface hydrophilicity [5]. $\Delta G_{13}$ and $\Delta G_{131}$ can be calculated according to [21]

\[
\Delta G_{13} = -2 \left( \sqrt{\gamma_m^{LW} \gamma_w^{LW}} + \sqrt{\gamma_m^+ \gamma_w^-} + \sqrt{\gamma_m^- \gamma_w^+} \right)
\]

(4.2)

\[
\Delta G_{131} = -2 \left( \sqrt{\gamma_m^{LW}} - \sqrt{\gamma_w^{LW}} \right)^2 - 4 \left( \sqrt{\gamma_m^+ \gamma_w^-} + \sqrt{\gamma_w^+ \gamma_m^-} - \sqrt{\gamma_m^{LW}} - \sqrt{\gamma_w^{LW}} \right)
\]

(4.3)

Hydrophilic membranes produce positive $\Delta G_{131}$, while hydrophobic membranes exhibit a negative $\Delta G_{131}$ [5]. NF270 membrane was hydrophilic, while NF90 and XLE membranes were hydrophobic under the water chemistries tested in this study; all three membranes became more hydrophilic with increasing ionic strength, pH and divalent cation content increased. These results are consistent with those of Hurwitz et al. [6]
published several years ago using different samples of solvents, salts and the XLE membrane.

Water/solute-membrane interaction energy ($\Delta G_{mw}$ or $\Delta G_{mws}$), which is the free energy difference associated with interaction of water or solute molecule in the bulk water phase compared to in the membrane phase [22], indicates the attractive or repulsive water/solute membrane interactions. If $\Delta G_{mw}$ or $\Delta G_{mws}$ is positive, a repulsive interaction between water/solute and membrane is expected. The partitioning of water/solute from water phase into membrane phase will not be favored. When $\Delta G_{mw}$ or $\Delta G_{mws}$ is negative, this suggests that there are attractive interactions between water/solute and membrane, which will result in a higher concentration of water/solute in membrane phase. The water/solute membrane interaction energies calculated based on Eqns. 3.10 and 3.19 are plotted in Figure 4.4.
Table 4.4 Membrane contact angles, surface tensions and interfacial energies.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>θ (°)</th>
<th>$\gamma^L_{m}$ (mJ/m$^2$)</th>
<th>$\gamma^S_{m}$ (mJ/m$^2$)</th>
<th>$\gamma^-_{m}$ (mJ/m$^2$)</th>
<th>$\gamma^{AB}_{m}$ (mJ/m$^2$)</th>
<th>$\Delta G_{13}$ (mJ/m$^2$)</th>
<th>$\Delta G_{131}$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI</td>
<td>69.89</td>
<td>35.87</td>
<td>0.77</td>
<td>8.25</td>
<td>5.04</td>
<td>91.50</td>
<td>28.42</td>
</tr>
<tr>
<td>NaCl 5mM</td>
<td>65.52</td>
<td>35.87</td>
<td>0.59</td>
<td>11.61</td>
<td>5.25</td>
<td>95.54</td>
<td>20.73</td>
</tr>
<tr>
<td>NaCl 50mM</td>
<td>62.97</td>
<td>35.87</td>
<td>0.50</td>
<td>13.77</td>
<td>5.26</td>
<td>97.84</td>
<td>16.16</td>
</tr>
<tr>
<td>NaCl 500mM</td>
<td>61.00</td>
<td>35.87</td>
<td>0.44</td>
<td>15.53</td>
<td>5.22</td>
<td>99.61</td>
<td>12.58</td>
</tr>
<tr>
<td>NaCl 500mM, pH=3</td>
<td>67.66</td>
<td>35.87</td>
<td>0.68</td>
<td>9.90</td>
<td>5.18</td>
<td>93.60</td>
<td>24.52</td>
</tr>
<tr>
<td>NaCl 50mM, pH=5</td>
<td>64.67</td>
<td>35.87</td>
<td>0.56</td>
<td>12.31</td>
<td>5.26</td>
<td>96.31</td>
<td>19.22</td>
</tr>
<tr>
<td>NaCl 50mM, pH=7</td>
<td>62.19</td>
<td>35.87</td>
<td>0.48</td>
<td>14.46</td>
<td>5.25</td>
<td>98.57</td>
<td>14.73</td>
</tr>
<tr>
<td>NaCl 50mM, pH=9</td>
<td>60.93</td>
<td>35.87</td>
<td>0.44</td>
<td>15.60</td>
<td>5.22</td>
<td>99.69</td>
<td>12.44</td>
</tr>
<tr>
<td>NaCl 50mM, pH=11</td>
<td>56.26</td>
<td>35.87</td>
<td>0.31</td>
<td>20.04</td>
<td>4.96</td>
<td>103.68</td>
<td>3.95</td>
</tr>
<tr>
<td>MgCl$_2$ 50mM</td>
<td>61.44</td>
<td>35.87</td>
<td>0.45</td>
<td>15.13</td>
<td>5.23</td>
<td>99.19</td>
<td>13.39</td>
</tr>
<tr>
<td>CaCl$_2$ 50mM</td>
<td>64.04</td>
<td>35.87</td>
<td>0.54</td>
<td>12.85</td>
<td>5.26</td>
<td>96.91</td>
<td>18.06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>θ (°)</th>
<th>$\gamma^L_{m}$ (mJ/m$^2$)</th>
<th>$\gamma^S_{m}$ (mJ/m$^2$)</th>
<th>$\gamma^-_{m}$ (mJ/m$^2$)</th>
<th>$\gamma^{AB}_{m}$ (mJ/m$^2$)</th>
<th>$\Delta G_{13}$ (mJ/m$^2$)</th>
<th>$\Delta G_{131}$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI</td>
<td>28.25</td>
<td>38.94</td>
<td>0.20</td>
<td>50.28</td>
<td>6.41</td>
<td>129.78</td>
<td>-39.40</td>
</tr>
<tr>
<td>NaCl 5mM</td>
<td>30.96</td>
<td>38.94</td>
<td>0.24</td>
<td>47.45</td>
<td>6.79</td>
<td>128.27</td>
<td>-35.56</td>
</tr>
<tr>
<td>NaCl 50mM</td>
<td>26.38</td>
<td>38.94</td>
<td>0.18</td>
<td>52.14</td>
<td>6.14</td>
<td>130.80</td>
<td>-41.86</td>
</tr>
<tr>
<td>NaCl 500mM</td>
<td>22.80</td>
<td>38.94</td>
<td>0.14</td>
<td>55.45</td>
<td>5.66</td>
<td>132.46</td>
<td>-46.30</td>
</tr>
<tr>
<td>NaCl 500mM, pH=3</td>
<td>27.47</td>
<td>38.94</td>
<td>0.19</td>
<td>51.07</td>
<td>6.30</td>
<td>130.20</td>
<td>-40.47</td>
</tr>
<tr>
<td>NaCl 50mM, pH=5</td>
<td>24.46</td>
<td>38.94</td>
<td>0.16</td>
<td>53.97</td>
<td>5.88</td>
<td>131.76</td>
<td>-44.29</td>
</tr>
<tr>
<td>NaCl 50mM, pH=7</td>
<td>23.91</td>
<td>38.94</td>
<td>0.15</td>
<td>54.46</td>
<td>5.81</td>
<td>131.96</td>
<td>-45.00</td>
</tr>
<tr>
<td>NaCl 50mM, pH=9</td>
<td>20.04</td>
<td>38.94</td>
<td>0.12</td>
<td>57.75</td>
<td>5.30</td>
<td>133.65</td>
<td>-49.29</td>
</tr>
<tr>
<td>NaCl 50mM, pH=11</td>
<td>17.15</td>
<td>38.94</td>
<td>0.10</td>
<td>59.9</td>
<td>4.96</td>
<td>134.69</td>
<td>-52.12</td>
</tr>
<tr>
<td>MgCl$_2$ 50mM</td>
<td>21.13</td>
<td>38.94</td>
<td>0.13</td>
<td>56.87</td>
<td>5.44</td>
<td>133.23</td>
<td>-48.11</td>
</tr>
<tr>
<td>CaCl$_2$ 50mM</td>
<td>25.71</td>
<td>38.94</td>
<td>0.17</td>
<td>52.79</td>
<td>6.05</td>
<td>131.11</td>
<td>-42.76</td>
</tr>
</tbody>
</table>

Average contact angle of EG and diiodomethane were 25.1° and 35.9° for NF 90, respectively; 12.6° and 38.7° for NF 270, respectively; 26.7° and 38.2° for XLE, respectively.
Figure 4.4. Calculated data illustrating the effect of water chemistry on water-membrane interaction energy ($\Delta G_{mw}$) and solute-membrane interaction energy ($\Delta G_{mws}$).

Based on the results, water–membrane interaction energy ($\Delta G_{mw}$) became more negative (hydrophilic), which indicated the partition of water into membrane phase is favored, with increasing ionic strength, pH and presence of divalent cations for all three membranes. The trend is the same as with contact angle, surface tension and interfacial free energy. As the membrane becomes more hydrophilic, the partition of water into membrane phase will be enhanced.

Solute (EG)–membrane interaction energy ($\Delta G_{mws}$) became more positive with increasing ionic strength, increasing pH and presence of divalent cations for all three membranes. This can be explained by the higher uptake of water, which excludes solute-electron donor interaction between solute and membrane. When the ionic strength or pH
of water phase increases, or divalent cations were added into water phase, the electron donor component of membrane surface tension increased (Table 4.4). As the electron donor component of EG (Lewis-base) surface tension is relatively high (47 mJ/m$^2$), the repulsive acid-base interaction (hydrophilic repulsion) between EG and membrane is enhanced [21]. As a result, there will be resistance against partitioning of EG into membrane phase.

### 4.3.3 Effect of water chemistry on membrane structure

As indicated in transport model (Eqns. 3.8 and 3.21), increasing in pore radius ($r_p$) will lower solute rejection and enhances water flux, however, increasing in structural factor ($S = \Delta x/\varepsilon$) will greater solute retention and result in decline in water flux. Calculated membrane characteristic $r_p$ and $S$ from fitting experimental EG rejection and water flux data into Eqns. 8 and 12 were calculated and plotted in Figure 4.5. The details of model fitting were shown in support information. The membrane pore radiiuses calculated by model fitting are close to AFM measurement by Hilal et al. [23] and in the range proposed by Kim et al. [24] and Jean et al. [25]. It is important to note that the model fitted structural factor ranged from 30 to 250 nm. As reported from positron annihilation lifetime spectroscopy (PALS) measurements by Chen et al. [26] and Jean et al. [25], the free volume fraction (FFV) of dried polyamide films under vacuum is ~1.5 %. Assuming effective porosity $\varepsilon$ is the FFV, then the effective membrane thickness determined from this study’s structure factors would range from 0.45 to 3.75 nm. These thickness seem unreasonably small; hence, the accuracy of ex situ techniques like PALS could be questioned. That said, it is well know that polyamide composite membranes
have very rough coating films; recent numerical simulations suggest permeation occurs predominantly through thinner regions (“valleys”) at very high local fluxes (“hot spots”) [27]. If that model of rough membrane transport holds up it would suggest that our model fitting approach herein predominantly estimates the structural descriptors for the “hot spots” rather than the area average values such as would be the case for PALS or other *ex situ* characterization methods. Nevertheless, the results here suggest the effective membrane thickness is much smaller than the apparent thicknesses (50 to 200 nm) typically measured by AFM analyses or TEM images.

Figure 4.5. Membrane structural descriptors illustrating the apparent effects of water chemistry on membrane pore radius ($r_p$) and structure factor ($S$).

As shown in Figure 4.5, $r_p$ increased while $S$ decreased with increasing ionic strength from 5 mM to 500 mM for all three membranes. The changes in $r_p$ were relatively less significant than in $S$. The trend is the same as reported by Luo et al. [14].
The ionic strength effect could be explained by salt induced membrane swelling or de-swelling. The mechanism for membrane swelling by salt is still controversial [12]. Some researchers have attributed it to the electrostatic repulsion between specific sorbed ions on the membrane pore wall or dissociation of polymer structure [9, 28-33]. Others claimed that the salt reduced the electrostatic interaction in the membrane and the hydration layer on membrane pore wall became thinner [14]. As reported by Coronell et al., the pKa values for carboxylic groups in polyamide membranes are 5.23 and 8.97, which suggest membranes contain negative charges in natural water (pH ~ 5 to 10) [34]. When salt ions were added into feed water, cations were sorbed onto the negative charged sites in membranes. The strong repulsion of cations would cause swelling of membrane polymer as illustrated in Figure 4.6a. “Dense” membranes (e.g. NF90 and XLE) swell less than “loose” membranes (e.g. NF270) due to fewer ions could enter into relatively small membrane pores than relatively large pores. The changing in repulsion of membrane polymer due to sorbed cations corresponded well with variations in cohesive energy ($\Delta G_{131}$). As discussed previously, $\Delta G_{131}$ became more positive when solution ionic strength increased (Table 4.4) and more positive $\Delta G_{131}$ implies stronger repulsive interactions between membrane polymers. As a result, membrane pore swelled because of stronger repulsion force by sorbed salt ions. On the other hand, increase in $S$ could be explained by increasing in membrane physical thickness (swelling of polymer across the membrane) and increasing in water/solute diffusive path length (higher probability of collisions between water/EG molecules and salt ions when solution ionic strength increased [14]). For NF90 and XLE membranes with relatively small pores, the relatively
large increase in $S$ was the main reason for the changes in EG rejection and water permeability in response to changes in solution ionic strength. For NF270 membrane with relatively large pores, the increase in $r_p$ mostly accounted for the decrease of EG retention.

![Diagram](image)

**Figure 4.6.** Illustration the effect of (a) salt or H$^+$ and (b) pH on membrane swelling state.

Solution pH also influenced the membrane structure properties. Both $r_p$ and $S$ increased with increasing solution pH. The reason for the enhanced membrane swelling at basic condition (high pH) may due to the increased repulsion interactions between the
enhanced dissociation of carboxylic groups. According to Bandini et al., membrane charge concentration increased with increasing pH [30, 35], as a result, the electrostatic repulsion between membrane pore walls will be enhanced and membranes will swell (Figure 4.6b). The rise in repulsive interaction between membranes was also represented by more positive $\Delta G_{131}$ values (Table 4.4). Due to the increase in $r_p$ with increasing pH, water flux increased and EG retention decreased. When the solution pH continued to grow, the water flux declined and EG rejection (except for NF 270) was enhanced because of the further increasing of $S$.

Divalent cations (Ca$^{2+}$ and Mg$^{2+}$) in feed solution also swelled the membranes as indicated in Figure 4.5 that both $r_p$ and $S$ of membranes are larger than with DI water as feed. Compared with monovalent cation (Na$^+$) with same solution ionic strength, NF90 and XLE membranes were swelled more by divalent cations (greater $r_p$) because divalent cations have greater electrostatic repulsion [36]. As a result, EG rejection was lower when Ca$^{2+}$ and Mg$^{2+}$ was presenting in feed solution than Na$^+$ for NF90 and XLE membranes. For NF270 membrane, divalent cations swelled membrane less than monovalent cation as smaller $r_p$ and $S$ were calculated from EG rejection and water permeability data. The results could be explained by the lower positive charge concentration (33 mM) in Ca/MgCl$_2$ solution than positive charge concentration in NaCl solution (50 mM) with same ionic strength. The positive charge provided by divalent cations was not enough to neutralize the negative charged NF270 membrane, which has more unreacted carboxyl groups and higher charge density than NF90 and XLE membranes [37, 38].
4.4 Conclusions

This work presented a feasible method for characterization of apparent structural descriptors of NF/RO membranes by fitting straightforward water and solute permeation experiments with an extended solution-diffusion transport model. The results obtained in this study provide new insights about the impacts of feed water chemistry on membrane transport, interfacial and structural properties for three commercial polyamide composite membranes. All polyamide composite membranes swell with different extents while changing feed water chemistry due to repulsions between sorbed cations or increasing membrane charge density. Water flux, salt rejection and neutral solute rejection changed dramatically with water chemistry, but all were largely reversible further supporting salt induced swelling and de-swelling phenomena. Model derived structural descriptors (i.e., $r_p$ and $S$) should be considered semi-quantitative representations of the free volume of the membrane in a given water chemistry under realistic filtration conditions; the numbers obtained in this study fell well within the ranges previously reported using independent characterization methods [23, 39]. These results offer powerful new insights into polyamide NF/RO membrane performance suggesting we are inching closer to predictive capabilities. However, further model development and study is needed to elucidate the effects of feed water chemistry on membrane structure and charged solute transport.
4.5 List of Symbols

\[ A \] water permeability
\[ A_s \] solute-membrane contact area
\[ A_w \] water-membrane contact area
\[ c \] concentration within membrane
\[ C_f \] solute concentration of feed solution
\[ C_p \] solute concentration of permeate solution
\[ C_{w,f} \] water concentration at feed side of membrane
\[ C_{w,m} \] water concentration in membrane
\[ C_{w,p} \] water concentration in membrane pore
\[ D_{w,m} \] water diffusion coefficient in membrane
\[ D_{w,\infty} \] water diffusion coefficient in the bulk
\[ D_{s,\infty} \] solute diffusion coefficient in the bulk
\[ J_s \] solute flux
\[ J_w \] water flux
\[ k_B \] Boltzmann constant
\[ K_c \] convective hindrance factor
\[ K_d \] diffusive hindrance factor
\[ K_w \] water-membrane partition coefficient
\[ l \] membrane thickness
\[ Re \] Reynolds number
\[ R_g \] gas constant
\[ R_o \] observed solute rejection
\[ r \] roughness area ratio
\[ r_p \] pore radius
\[ r_s \] solute Stokes radius
\[ r_w \] water Stokes radius
\[ S \] structure factor
\[ T \] temperature
\[ V_w \] molar volume of water
\[ \beta \] concentration polarization factor
\[ \gamma^+ \] electron-donor surface tension component
\[ \gamma^- \] electron-acceptor surface tension component
\[ \gamma_{\text{LW}} \] Lifshitz-van der Waals surface tension component
\[ \gamma_{\text{AB}} \] acid-base surface tension component
\[ \gamma^T \] total surface tension
\[ \Delta G_{13} \] membrane-liquid interfacial free energy
\[ \Delta G_{13l} \] cohesive free energy
\[ \Delta G_{mw} \] membrane-liquid interaction energy
\[ \Delta G_{mws} \] membrane-solute interaction energy
\[ \Delta p \] applied pressure
\[ \Delta x \] effective pore length
\[ \Delta \pi \] osmotic pressure difference across the membrane
\( \varepsilon \)  porosity
\( \lambda_s \)  solute-membrane sieving factor
\( \lambda_w \)  water-membrane sieving factor
\( \tau \)  tortuosity
\( \phi_s \)  solute-membrane pore partition coefficient
\( \phi_w \)  water-membrane pore partition coefficient
\( \theta \)  contact angle
4.6 References


CHAPTER 5

MECHANISMS OF UNCHARGED TRACE ORGANICS REMOVAL FROM GROUNDWATER BY NF AND RO MEMBRANES
5.1 Introduction

Trace organic pollutants, such as pesticides, hormones and sterols, pharmaceuticals and personal care products, industrial chemicals and by-products, food additives and water treatment by-products, have been detected and reported in all 50 states and 80% analyzed water steams in the U.S. [1-3]. Hence, the importance of advanced water treatment technologies to convert contaminated sources into potable water has increased dramatically in recent years [4]. For example, N-Nitrosodimethylamine (NDMA) can be formed as a disinfection by-product and is often present in water above the detection limit at concentrations below 10 ng/L [5]. In toxicity studies, NDMA has been found to cause cancer through methylation of DNA [6], and hence, is identified as probable human carcinogen. The USEPA has classified 1,4-dioxane as a probable human carcinogen. The concentration level of 1,4-dioxane detected in river, ocean and groundwater samples ranges from 1 to 200 µg/L [7]. Methanol is listed as a reproductive toxicant by the State of California. Methanol also serves as precursor of methyl tert-butyl ether (MTBE), which is a well-known groundwater contaminant [8]. The human toxicity of methanol is associated with formate production from metabolism of methanol, which occurs faster than formate can be metabolized [9]. Methanol was detected in drinking waters in at least 6 of 10 U.S. cities [10].

Recently, nanofiltration (NF) and reverse osmosis (RO) processes have been considered for trace organic removal from ground and surface water. However, low to moderate trace organic solute, especially neutral solute (such as NDMA, 1,4-dioxane), rejection by NF/RO membranes has been reported [11-13]. As reviewed by Bellona et al.
[14], solute physical-chemical properties, membrane properties and feed water chemistries were all identified to have influences on organic solute rejection by NF/RO membranes. However, solute rejections depend on the combination of all above parameters, so there is no single parameter can be used to correlate with solute rejection for prediction purpose. And it is hard to characterize some of the above key parameters, such as structural parameters of NF/RO membrane under filtration condition.

In this study, we experimentally study the rejections of six commercial NF/RO membranes for one model organic solute (ethylene glycol) and three trace organic pollutants (NDMA, 1,4-dioxane, methanol) in simulated groundwater. We present a new approach to characterize the membrane structural properties based on simple filtration experiments and mathematical fitting with transport model. Different parameters describing solute/membrane structure and solute-membrane interaction are used to correlate with solute rejection. And a partition coefficient, which incorporates both solute-membrane structural properties and solute-membrane interaction, is proposed to predict solute rejection by NF/RO membranes.

5.2 Materials and Methods

5.2.1 Membranes and solutes

Representative polyamide NF (NF 90 and NF 270), brackish water RO (BWRO) (XLE), seawater RO (SWRO) (SW30HR, SW30HRLE, SWC3+) membranes were used in all experiments. These membranes were kindly provided by manufacture (Dow Film Tec Corp., Minneapolis, MN and Hydranautics, Oceanside, CA) as flat-sheet samples and
were stored in Nanopure deionized water at 4 °C prior to use. Chemical agents used to simulate groundwater chemistry (Table 5.1) were analytical grade and purchased from Fisher Scientific (Pittsburgh, PA). The organic solutes used in the rejection test were purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO) and their properties are summarized in Table 5.2. Separation performance of NF and RO membranes was evaluated in a bench scale cross-flow membrane filtration system [15, 16].

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>7.00</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>1.78</td>
</tr>
<tr>
<td>Na⁺</td>
<td>mg/L</td>
<td>207</td>
</tr>
<tr>
<td>K⁺</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>mg/L</td>
<td>124</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>mg/L</td>
<td>216</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td></td>
<td>250</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td></td>
<td>366</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>TDS</td>
<td></td>
<td>1197</td>
</tr>
</tbody>
</table>

Table 5.2. Physical-chemical properties of tested solutes.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Molecular weight (g/mol)</th>
<th>Stokes radius (nm)</th>
<th>Diffusivity ($\times 10^{-5}$ cm$^2$/s)</th>
<th>$K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG (C2H6O2)</td>
<td>62</td>
<td>0.184</td>
<td>1.16</td>
<td>0.044</td>
</tr>
<tr>
<td>1,4-Dioxane (C4H8O2)</td>
<td>88</td>
<td>0.223</td>
<td>0.95</td>
<td>0.537</td>
</tr>
<tr>
<td>NDMA (C2H6N2O)</td>
<td>74</td>
<td>0.201</td>
<td>1.06</td>
<td>0.269</td>
</tr>
<tr>
<td>Methanol (CH4O)</td>
<td>32</td>
<td>0.130</td>
<td>1.64</td>
<td>0.170</td>
</tr>
</tbody>
</table>

5.2.2 Membrane performance experiment procedures

The separation performance of NF and RO membranes was evaluated in a bench
scale cross-flow membrane filtration system equipped with six parallel membrane cells (effective membrane area is 19.4 cm², with width of 2.54 cm, length of 7.62 cm and channel height of 0.10 cm, for each membrane cell). The detail of the description of the membrane testing system can be found in elsewhere [15]. Water permeability was determined using simulated groundwater (Table 5.1) at 20 °C and applied pressures between 0.48 – 3.10 MPa (70 – 450 psi). The cross-flow rate was set at 0.55 Gal·min⁻¹ (3.46×10⁻⁵ m³·s⁻¹). Flow conditions were controlled, so that the Reynolds number was maintained at 1900 with a mesh spacer in the feed channel. This ensured that the external mass transfer coefficient was 2.42×10⁻⁴ m·s⁻¹, producing a concentration polarization factor in the range of 1.004 – 1.08 for permeate fluxes in the range of 1×10⁻⁶ – 20×10⁻⁶ m·s⁻¹. Permeate flux was measured by a digital flow meter (Optiflow 1000, Agilent Technology, Forster City, CA).

Prior to testing, all the membranes were compacted with deionized water at 3.10 MPa (450 psi) and 20 °C for 18 hours. After permeability measurements, the same membranes were used to characterize the selectivity of selected solute. Organic solutes were spiked into deionized water at 10 mg carbon·L⁻¹. The concentration was chosen to be able to measure at least 99 % rejection. Solute rejection was found by measuring total organic carbon in feed and permeate solutions. During the rejection experiments, feed pressure was varied (0.48 – 3.10 MPa), while temperature (20 °C) and external mass transfer coefficient (2.42×10⁻⁴ m/s) were kept constant. In order to eliminate the effect of adsorption of solute onto the membrane surface and into membrane inner structure, feed solution was filtered through all the membranes at 3.10 MPa (450 psi) and 25 °C for 24
hours before rejection tests.

5.2.3 Membrane and solute surface tension and interfacial energy characterization

The membrane and solute surface tensions and water/solute-membrane interaction energies were determined from measured contact angles using an automated contact angle goniometer (DSA10, Krüss GmbH, Hamburg, Germany). At least twelve equilibrium contact angles at different locations were measured for each sample. Contact angles measurement for simulated groundwater (GW, polar liquid), diiodomethane (DM, apolar liquid) and ethylene glycol (EG, polar liquid) enables determination of surface tension components ($\gamma_i^{\text{LW}}$, $\gamma_i^+$ and $\gamma_i^-$) for membranes using the extended Young-Dupré equation [17]

$$\gamma_w^T \left(1 + \frac{\cos \theta}{r}\right) = 2 \left(\sqrt{\gamma_m^{\text{LW}} \gamma_w^{\text{LW}}} + \sqrt{\gamma_m^{+} \gamma_w^{-}} + \sqrt{\gamma_m^{-} \gamma_w^{+}}\right)$$ (5.1)

where $\theta$ is the contact angle, $r$ is the roughness area ratio (i.e. the ratio of actual surface area for a rough surface to the planar area) [18].

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$R_q$ (nm)</th>
<th>$SAD$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF270</td>
<td>4.0 ± 1.6</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>NF90</td>
<td>40.5 ± 7.0</td>
<td>19.1 ± 5.0</td>
</tr>
<tr>
<td>XLE</td>
<td>58.2 ± 14.6</td>
<td>33.6 ± 5.7</td>
</tr>
<tr>
<td>SW30HR</td>
<td>71.0 ± 8.7</td>
<td>42.5 ± 2.7</td>
</tr>
<tr>
<td>SW30HRLE</td>
<td>108.0 ± 12.0</td>
<td>32.4 ± 7.4</td>
</tr>
<tr>
<td>SWC3+</td>
<td>140 ± 21.6</td>
<td>45.3 ± 9.1</td>
</tr>
</tbody>
</table>

$R_q$: RMS deviation or z-data standard deviation.  
$SAD$: surface area difference, increase in surface area over projected flat plate area ($r = 1 + SAD$).

The membrane surface roughness was analyzed form atomic force microscopy (AFM) measurement (Table 5.3). The surface tension components for probe liquids were
obtained from literature [19, 20]. The surface tension components of liquids are given in Table 5.4. The details of calculation can be found in previous publications [21]

Water-membrane interaction energy ($\Delta G_{mw}$) can be related to the contact area ($A_w = \pi r_w^2/2$) between water molecule and membrane and interfacial surface tension of water and the membrane [22]

$$\Delta G_{mw} = -2A_w\left(\sqrt{\gamma_{w}^{LW}\gamma_{m}^{LW}} + \sqrt{\gamma_{w}^{+}\gamma_{m}^{-}} + \sqrt{\gamma_{w}^{-}\gamma_{m}^{+}}\right) \tag{5.2}$$

The free energy of interaction between solute and membrane immersed in water can be determined from the Dupré equation [22]

$$\Delta G_{smw} = 2A_s\left[\sqrt{\gamma_{s}^{LW}\gamma_{w}^{LW}} + \sqrt{\gamma_{m}^{LW}\gamma_{w}^{LW}} - \sqrt{\gamma_{m}^{LW}\gamma_{s}^{LW}} - \sqrt{\gamma_{w}^{LW}\gamma_{m}^{LW}} - \sqrt{\gamma_{m}^{+}\gamma_{s}^{+}} - \sqrt{\gamma_{s}^{+}\gamma_{m}^{+}} - \sqrt{\gamma_{m}^{+}\gamma_{w}^{+}} + \sqrt{\gamma_{w}^{+}\gamma_{m}^{+}} + \gamma_{m}^{-}\gamma_{s}^{-} - \gamma_{m}^{+}\gamma_{s}^{+} + \gamma_{m}^{+}\gamma_{w}^{+}\right] \tag{5.3}$$

where $A_s$ ($A_s = \pi r_s^2/2$) is the contact area between solute molecule and membrane.

<table>
<thead>
<tr>
<th>Liquid/membrane</th>
<th>Contact angle (°)</th>
<th>$\gamma^{LW}$</th>
<th>$\gamma^{+}$</th>
<th>$\gamma^{-}$</th>
<th>$\gamma^{AB}$</th>
<th>$\gamma^{TOT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GW</td>
<td>DM</td>
<td>EG</td>
<td>(mJ/m²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DM</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>50.8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>EG</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>29.0</td>
<td>1.9</td>
<td>47.0</td>
</tr>
<tr>
<td>GW</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>21.8</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>NF270</td>
<td>15.4</td>
<td>38.7</td>
<td>12.6</td>
<td>40.1</td>
<td>0.1</td>
<td>63.2</td>
</tr>
<tr>
<td>NF90</td>
<td>73.1</td>
<td>35.9</td>
<td>25.1</td>
<td>35.9</td>
<td>0.9</td>
<td>6.1</td>
</tr>
<tr>
<td>XLE</td>
<td>67.5</td>
<td>38.2</td>
<td>26.7</td>
<td>32.1</td>
<td>0.5</td>
<td>11.0</td>
</tr>
<tr>
<td>SW30HR</td>
<td>28.8</td>
<td>27.9</td>
<td>4.0</td>
<td>33.4</td>
<td>0.03</td>
<td>37.5</td>
</tr>
<tr>
<td>SW30HRLE</td>
<td>38.4</td>
<td>39.9</td>
<td>6.1</td>
<td>31.7</td>
<td>0.3</td>
<td>32.7</td>
</tr>
<tr>
<td>SWC3+</td>
<td>50.3</td>
<td>25.3</td>
<td>9.6</td>
<td>33.4</td>
<td>0.2</td>
<td>21.4</td>
</tr>
</tbody>
</table>

5.3 Theory
Water/solute-membrane partition coefficient \((\phi_i)\), which related water/solute concentration in membrane pore and in the bulk, is defined as \([21, 23]\)

\[
\phi_{w/s} = \left(1 - \lambda_{w/s}\right)^2 \exp\left(-\frac{\Delta G_{mw/sm}}{kT}\right)
\]

(5.4)

where \(\lambda_i\) is sieving factor \((\lambda_i = r_i/r_p)\), \(r_p\) is the membrane pore radius, \(r_p\) is the solute radius, \(k\) is Boltzmann constant and \(T\) is temperature. Structure factor, defined as the ratio of membrane thickness to porosity, was characterized by fitting experimentally measured water flux \((J_w)\) and solute rejection \((R)\) with the following equations.

\[
J_w = \frac{\phi_w K_d D_{w,m}^\infty V_w}{S} \frac{R_g T}{\Delta p - \Delta \pi}
\]

(5.5)

\[
R = 1 - \frac{\beta \phi_s K_c}{1 - (1 - \phi_s K_c) \exp\left(-\frac{J_w K S}{K_d D_{s,m}^\infty}\right)}
\]

(5.6)

Here, \(\Delta p\) is applied pressure, \(\Delta \pi\) is osmotic pressure difference across membrane, \(D_{w,m}\) and \(D_{s,m}\) is water and solute diffusivity in membrane, respectively, \(V_w\) is water molar volume, \(R_g\) is gas constant, \(\beta\) is concentration polarization factor, while \(K_d\) and \(K_c\) are the diffusive and convective hindrance factors for solutes in a confined pore \([24]\).

**5.4 Results**

The free energy difference associated with interaction of water and solute molecules with the membrane material indicates the affinity (attraction or repulsion) of water and solute molecules with membrane polymers \([25]\). Generally, the sign and magnitude of \(\Delta G_{mw}\) and \(\Delta G_{smw}\) are subject to the membrane polymer chemistry and
structure, the feed side water chemistry, and (for $\Delta G_{swm}$) the solute chemistry and size (Table 5.5). For example, if $\Delta G_{swm}$ is positive, the solute is intrinsically repelled by the membrane leading to a smaller partition coefficient, $f_i$; a negative $\Delta G_{swm}$ indicates it is thermodynamically favorable for the solute to be drawn into the membrane matrix and a higher partition coefficient results.

Table 5.5 Membrane structural descriptors and solute/water-membrane interaction energies.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$r_p$ (nm)</th>
<th>$S$ (nm)</th>
<th>GW</th>
<th>EG</th>
<th>1,4-Dioxane</th>
<th>NDMA</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF270</td>
<td>0.303</td>
<td>117</td>
<td>-2.71</td>
<td>1.91</td>
<td>4.60</td>
<td>-1.15</td>
<td>1.71</td>
</tr>
<tr>
<td>NF90</td>
<td>0.237</td>
<td>71</td>
<td>-1.72</td>
<td>-0.32</td>
<td>0.17</td>
<td>-5.45</td>
<td>0.18</td>
</tr>
<tr>
<td>XLE</td>
<td>0.246</td>
<td>96</td>
<td>-1.78</td>
<td>0.08</td>
<td>0.75</td>
<td>-5.76</td>
<td>0.44</td>
</tr>
<tr>
<td>SW30HR</td>
<td>0.230</td>
<td>304</td>
<td>-2.23</td>
<td>1.27</td>
<td>3.94</td>
<td>1.50</td>
<td>1.26</td>
</tr>
<tr>
<td>SW30HRLE</td>
<td>0.232</td>
<td>336</td>
<td>-2.20</td>
<td>1.05</td>
<td>3.17</td>
<td>0.40</td>
<td>1.08</td>
</tr>
<tr>
<td>SWC3+</td>
<td>0.227</td>
<td>295</td>
<td>-2.00</td>
<td>0.63</td>
<td>2.24</td>
<td>3.02</td>
<td>0.83</td>
</tr>
</tbody>
</table>

$\Delta G_{swm}$ for GW, EG and methanol were calculated using Eqs. 5.2 and 5.3, while $\Delta G_{swm}$ for 1,4-dioxane and NDMA were obtained from fitting rejection data and membrane structural parameters into Eqn. 5.6.

For all membranes, in groundwater NF270 exhibited the most negative $\Delta G_{swm}$ value followed by all three SWRO membranes and then NF90 and XLE; this is the order of decreasing hydrophilicity. All membranes except NF90 repelled EG. All the membranes except SWC3+ and SW30HR/HRLE attracted NDMA, while all membranes repelled both 1,4-dioxane and methanol. Also, in Table 2, apparent pore radii ranged from about 0.2 nm to about 0.3 nm, which generally agrees with AFM measurements by Hilal et al. [26] and in the range proposed by Kim et al. [27] and Jean et al. [28] for similar NF/RO membranes. All RO membranes had smaller pores than NF270 as expected, but they all shared very close to the same pore size. The structure factor was
distinctly larger for all three SWRO membranes suggesting that while they exhibited similar apparent pore size their porosity was lower and/or their polyamide film was thicker [29, 30].

Methanol was poorly rejected by all membranes (Figure 5.1). Methanol in simulated groundwater was rejected less than 10% by NF and BWRO membranes and about 20-30% by SWRO membranes, which is consistent with other work [31]. The free energy data above suggest membrane polymers repelled methanol; hence, the low rejection must be attributed to its small size (0.130 nm). Rejection of EG was low for NF270 (18%), which has the largest pore size, and increased for BWRO (50-60%) and further for SWRO membranes (>90%). Fairly low rejection of NDMA was observed for NF270 (11%), NF90 (22%) and XLE membranes (22%), which is similar to other reports [13]; however, SWRO membranes provided 85-90% rejection of NDMA. In this study, 1,4-dioxane had the largest hydrodynamic radius among all tested solutes and was rejected well by all membranes (80-99%) except NF270 (30%). It is important to point out that SWRO membranes offer very high removal of trace organics from this simulated groundwater, which may prove interesting as a new approach to achieving better performance in groundwater remediation albeit at higher energy and operating costs.
Figure 5.1. Membrane groundwater permeability and solute observed rejection. Solute rejection data were determined at a water flux of 13 µm/s, cross-flow Reynolds number of 1,900 and feed water temperature of 20±2 °C.

5.5 Discussion

Solute rejection by membranes is determined by solute properties, membrane properties, solute-membrane-water interactions and operation conditions that affect water permeation and cross-flow mass transfer [14]. This makes prediction of trace organic removal challenging as there is not a traditional measureable solute parameter (like log\textit{K}_{ow} for bioaccumulation) that correlates well with observed rejection. In order to predict uncharged trace organics rejection by NF/RO membranes, size exclusion (sieving) factors and thermodynamic (partitioning) factors are often been considered [23,
In this study, linear correlation study was performed between solute rejection and various sieving and partitioning factors. Solute-membrane pore partition coefficient, $\phi_s$, which accounts for both steric effects and solute-membrane-water interactions, was used in the correlation study first. Re-arranging Eqn. 5.6 yields

$$
1 - \exp\left(-\frac{J_w K S}{D_{\infty} K_d}\right) \frac{1}{\beta} + \exp\left(-\frac{J_w K S}{D_{\infty} K_d}\right) \frac{1}{\beta} = \frac{1}{1 - R}
$$

(5.7)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>EG</th>
<th>1,4-Dioxane</th>
<th>NDMA</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF270</td>
<td>0.998</td>
<td>0.998</td>
<td>0.994</td>
<td>0.999</td>
</tr>
<tr>
<td>NF90</td>
<td>0.997</td>
<td>1.000</td>
<td>0.995</td>
<td>0.999</td>
</tr>
<tr>
<td>XLE</td>
<td>0.996</td>
<td>1.000</td>
<td>0.986</td>
<td>0.999</td>
</tr>
<tr>
<td>SW30 HR</td>
<td>0.991</td>
<td>1.000</td>
<td>0.998</td>
<td>0.996</td>
</tr>
<tr>
<td>SWHR LE</td>
<td>0.989</td>
<td>1.000</td>
<td>0.996</td>
<td>0.995</td>
</tr>
<tr>
<td>SWC3+</td>
<td>0.991</td>
<td>1.000</td>
<td>0.999</td>
<td>0.996</td>
</tr>
</tbody>
</table>

For constant operation conditions, $J_w$, $\beta$ and all parameters in the exponential term should remain constant (as indicated in support information Table 5.6); hence, $1/(1-R)$ should scale with $1/\phi_s$. The correlation coefficient between $1/(1-R)$ and $1/\phi_s$ was 0.933 (Figure 5.2a), so it appears one could predict uncharged organic solute rejection by NF/RO membranes using simply $1/\phi_s$. 

Table 5.6. Summary of values of $\exp(-J_w K_c S/D_{s,m})$ (T = 298 K).
(a) 

Correlation $= -0.899$

Correlation $= 0.933$

(b) 

Correlation $= 0.339$

Correlation $= -0.291$
Figure 5.2. Correlation coefficient between partition coefficient and rejection.
Other partition coefficients were also investigated here. Traditionally, \(\log K_{ow}\) is an important and meaningful parameter in assessing environmental behavior of organic pollutants \([39]\); many researchers have attempted to correlate \(R\) with \(K_{ow}\) of solute \([34-38]\). However, the results here (Figure 5.2b) suggested \(K_{ow}\) was not a good predictor of organic solute rejection. The specific interfacial interaction energy between solute and membrane in water (\(\Delta G_{smw}\)) has also been taken into consideration in other studies \([40]\). The correlation between \(\exp(-\Delta G_{smw}/kT)\) and \(R\) was weak (Figure 5.2c). Some debate remains about the role of steric exclusion in NF/RO membrane transport \([41]\), but here the steric factor, \((1-\lambda)^2\), correlated moderately well with \(R\) (Figure 5.2d), which suggested steric effect might be significant in uncharged trace organics transport through NF/RO membranes.

![Figure 5.3](image)

**Figure 5.3.** Illustration of effect of physical parameters \((\lambda\) and \(S\)) and energetic interactions \((\Delta G)\) on (a) NDMA rejection based on Eqn. 5.6 and (b) specific water flux based on Eqn. 3.8. \((D_w = 2.20 \times 10^{-9} \text{ m}^2/\text{s}, D_s = 1.06 \times 10^{-9} \text{ m}^2/\text{s}, k_f = 9 \times 10^{-5} \text{ m/s}, T = 293 \text{ K}, J_w = 5 \times 10^{-6} \text{ m/s}).

The results presented herein suggest seawater RO membranes could provide very high removal of some trace organic groundwater pollutants, which is not a common
application of these membranes. Further, we now have a mechanistic framework for understanding why a given NF/RO membrane rejects a given trace organic pollutant more or less. This mechanistic framework is not yet fully predictive as rejection can change dramatically with different background electrolyte concentrations [16]. Perhaps most interesting and practical is that this new mechanistic framework may shed new light on membrane design for trace organics removal. For example, as shown in Figure 5.3, if one could develop a membrane with very positive $\Delta G_{sw}$ (e.g. $20 \times 10^{-21}$ J) and very negative $\Delta G_{mw}$ (e.g. $-20 \times 10^{-21}$ J) to improved organic solute rejection while retaining high flux. However, further studies are needed to understand the rejection of charged solutes by NF/RO membranes in combination with different water chemistries.
5.6 List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>water permeability</td>
</tr>
<tr>
<td>$A_s$</td>
<td>solute-membrane contact area</td>
</tr>
<tr>
<td>$A_w$</td>
<td>water-membrane contact area</td>
</tr>
<tr>
<td>$c$</td>
<td>concentration within membrane</td>
</tr>
<tr>
<td>$C_f$</td>
<td>solute concentration of feed solution</td>
</tr>
<tr>
<td>$C_p$</td>
<td>solute concentration of permeate solution</td>
</tr>
<tr>
<td>$C_{w,f}$</td>
<td>water concentration at feed side of membrane</td>
</tr>
<tr>
<td>$C_{w,m}$</td>
<td>water concentration in membrane</td>
</tr>
<tr>
<td>$C_{w,p}$</td>
<td>water concentration in membrane pore</td>
</tr>
<tr>
<td>$D_{w,m}$</td>
<td>water diffusion coefficient in membrane</td>
</tr>
<tr>
<td>$D_{w,\infty}$</td>
<td>water diffusion coefficient in the bulk</td>
</tr>
<tr>
<td>$D_{s,m}$</td>
<td>solute diffusion coefficient in membrane</td>
</tr>
<tr>
<td>$D_{s,\infty}$</td>
<td>solute diffusion coefficient in the bulk</td>
</tr>
<tr>
<td>$J_s$</td>
<td>solute flux</td>
</tr>
<tr>
<td>$J_w$</td>
<td>water flux</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$K_c$</td>
<td>convective hindrance factor</td>
</tr>
<tr>
<td>$K_d$</td>
<td>diffusive hindrance factor</td>
</tr>
<tr>
<td>$K_w$</td>
<td>water-membrane partition coefficient</td>
</tr>
<tr>
<td>$l$</td>
<td>membrane thickness</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$R_g$</td>
<td>observed solute rejection</td>
</tr>
<tr>
<td>$r$</td>
<td>roughness area ratio</td>
</tr>
<tr>
<td>$r_p$</td>
<td>pore radius</td>
</tr>
<tr>
<td>$r_s$</td>
<td>solute Stokes radius</td>
</tr>
<tr>
<td>$r_w$</td>
<td>water Stokes radius</td>
</tr>
<tr>
<td>$S$</td>
<td>structure factor</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$V_w$</td>
<td>molar volume of water</td>
</tr>
<tr>
<td>$\beta$</td>
<td>concentration polarization factor</td>
</tr>
<tr>
<td>$\gamma_e$</td>
<td>electron-donor surface tension component</td>
</tr>
<tr>
<td>$\gamma_a$</td>
<td>electron-acceptor surface tension component</td>
</tr>
<tr>
<td>$\gamma_{LW}$</td>
<td>Lifshitz-van der Waals surface tension component</td>
</tr>
<tr>
<td>$\gamma_{AB}$</td>
<td>acid-base surface tension component</td>
</tr>
<tr>
<td>$\gamma^T$</td>
<td>total surface tension</td>
</tr>
<tr>
<td>$\Delta G_{mw}$</td>
<td>membrane-liquid interaction energy</td>
</tr>
<tr>
<td>$\Delta G_{mws}$</td>
<td>membrane-solute interaction energy</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>applied pressure</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>effective pore length</td>
</tr>
<tr>
<td>$\Delta \pi$</td>
<td>osmotic pressure difference across the membrane</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>porosity</td>
</tr>
</tbody>
</table>
\( \lambda_s \)  
\text{solute-membrane sieving factor}

\( \lambda_w \)  
\text{water-membrane sieving factor}

\( \tau \)  
\text{tortuosity}

\( \phi_s \)  
\text{solute-membrane pore partition coefficient}

\( \phi_w \)  
\text{water-membrane pore partition coefficient}

\( \theta \)  
\text{contact angle}
5.7 References


CHAPTER 6

CONCLUSIONS AND FUTURE WORK
6.1 Major Conclusions

An impressive amount of work regarding modeling solvent and solute transport in osmotic membranes has been reviewed and summarized as follows:

1. Membrane structural characteristics (\textit{i.e.} pore size, porosity, pore length, and tortuosity) should be included in transport models to help mechanistically explain membrane transport and to enable predictions of membrane performance.

2. Support membrane structure needs to be incorporated into composite membrane transport models since skin layer pore size and porosity significantly impact composite membrane permeability and rejection.

3. Both external (ECP) and internal concentration polarization (ICP) play crucial roles in membrane transport. Understanding and modeling concentration polarization is critical for membrane applications.

An extension of the classical solution-diffusion model for NF/RO membranes has been developed and validated.

1. In general, model predictions agree well with experimental data suggesting the model captures the phenomenological behavior of commercial NF/RO membranes for separations.

2. The model suggests the “effective pore size” may be on the order of 0.24 to 0.35 nm and the “effective diffusion path length” (\textit{i.e.}, barrier layer thickness) may be on the order of 10 to 20 nm; model-derived pore sizes are consistent with literature reported values for the same membranes, but thicknesses are an order of magnitude less than what is historically related to polyamide coating film thickness. These new insights provide a
framework for the creation of next-generation NF/RO membrane structures specifically targeting emerging trace organic contaminants of concern for human health and environmental protection.

3. The dependences of operation parameters, membrane structure parameters and solute properties were also clearly presented by the modeling prediction. With given membranes, applying optimal operation condition (permeate flux, mass transfer coefficient) can enhance the solute rejection. These results suggest it is possible and important to fine-tune the surface tension of membrane and membrane structure (pore size, porosity, thickness) to achieve high selectivity for certain solute.

A feasible method for characterization of apparent structural descriptors of NF/RO membranes by fitting straightforward water and solute permeation experiments with an extended solution-diffusion transport model has been developed. The effects of water chemistry on membrane structure, transport and interfacial properties were explored.

1. All polyamide composite membranes swell with different extents while changing feed water chemistry due to repulsions between sorbed cations or increasing membrane charge density.

2. Water flux, salt rejection and neutral solute rejection changed dramatically with water chemistry, but all were largely reversible further supporting salt induced swelling and de-swelling phenomena.

3. These results offer powerful new insights into polyamide NF/RO membrane performance suggesting we are inching closer to predictive capabilities.
The removal mechanisms of trace organic pollutant by NF/RO membranes were studied.

1. Seawater RO membranes could provide very high removal of some trace organic groundwater pollutants, which is not a common application of these membranes.

2. A mechanistic framework for understanding why a given NF/RO membrane rejects a given trace organic pollutant more or less has been presented. Perhaps most interesting and practical is that a partition coefficient can be used to predict trace organics rejection by NF/RO membranes.

3. This new mechanistic framework may shed new light on membrane design for trace organics removal.

6.2 Future Research

The results and conclusions summarized from this dissertation have provided insights and tools to understand trace organic pollutants transport through and removal mechanisms of NF/RO membranes. Also, questions regarding the limitation of this study open new angles for future research.

1. How to accurately model charged solute transport through NF/RO membrane? Classical models regarding charged solute are mainly based on Donnan exclusion mechanism, which is developed for ion exchange process. Charged solute-membrane interaction (affinity) should be included into the transport equation. Some researchers tried to use electrical potential to describe the interactions between membrane and charged solute (Chapter 2). However, it is hard to directly or indirectly characterize the electrical potential.
2. How to compare membrane structure parameter calculated from transport model with independent physical characterization? This study has provided a feasible way to characterize membrane structure and the obtained values are close to the values reported in the literatures (Chapter 3 and 4). However, independent physical characterization evidences are still required to validate the method proposed in this study.

3. Can the membrane be tailored to maximize rejection to certain solute while maintaining reasonable water flux? According to the model simulation results (Chapter 3), membrane structure has the same effect on solute and water flux. So, there is no optimal membrane structure for increasing solute rejection without sacrificing water permeability. As discussed in Chapter 2 and 5, if one could develop a membrane with very positive $\Delta G_{s,mw}$ and very negative $\Delta G_{m,w}$ to improved organic solute rejection while retaining high flux. For apolar solutes removal, this can be achieved by selecting a hydrophilic (polar) membrane. However, to remove a hydrophilic solute, it is hard to find a membrane material with both large positive $\Delta G_s$ and large negative $\Delta G_w$, because solid materials are predominantly monopolar electron-donors.
## APPENDIX

### APPENDICES FOR CHAPTER 4

**Table A4.1**  
Water-membrane and solute (EG)-membrane interaction energies. (Corresponding to Figure 4.4)

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>NF90</th>
<th>NF270</th>
<th>XLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta G_{swm}$ ($10^{-21}$J)</td>
<td>$\Delta G_{swm}$ ($10^{-21}$J)</td>
<td>$\Delta G_{swm}$ ($10^{-21}$J)</td>
</tr>
<tr>
<td>DI</td>
<td>-0.15</td>
<td>1.56</td>
<td>-2.55</td>
</tr>
<tr>
<td>NaCl 5mM</td>
<td>0.08</td>
<td>1.47</td>
<td>-2.52</td>
</tr>
<tr>
<td>NaCl 50mM</td>
<td>0.21</td>
<td>1.61</td>
<td>-2.57</td>
</tr>
<tr>
<td>NaCl 500mM</td>
<td>0.31</td>
<td>1.71</td>
<td>-2.61</td>
</tr>
<tr>
<td>NaCl 50mM, pH=3</td>
<td>-0.03</td>
<td>1.58</td>
<td>-2.56</td>
</tr>
<tr>
<td>NaCl 50mM, pH=5</td>
<td>0.12</td>
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<tr>
<td>NaCl 50mM, pH=7</td>
<td>0.25</td>
<td>1.68</td>
<td>-2.60</td>
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<tr>
<td>NaCl 50mM, pH=9</td>
<td>0.31</td>
<td>1.78</td>
<td>-2.63</td>
</tr>
<tr>
<td>NaCl 50mM, pH=11</td>
<td>0.54</td>
<td>1.84</td>
<td>-2.65</td>
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<tr>
<td>MgCl$_2$ 50mM</td>
<td>0.29</td>
<td>1.75</td>
<td>-2.62</td>
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<tr>
<td>CaCl$_2$ 50mM</td>
<td>0.16</td>
<td>1.63</td>
<td>-2.58</td>
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176
Table A4.2
Membrane structural parameters. (Corresponding to Figure 4.5)

<table>
<thead>
<tr>
<th>Solutions</th>
<th>NF90</th>
<th></th>
<th>XLE</th>
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<th>NF270</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( r_p ) (nm)</td>
<td>( S ) (nm)</td>
<td>( r_p ) (nm)</td>
<td>( S ) (nm)</td>
<td>( r_p ) (nm)</td>
<td>( S ) (nm)</td>
</tr>
<tr>
<td>DI</td>
<td>0.219</td>
<td>46</td>
<td>0.224</td>
<td>52</td>
<td>0.286</td>
<td>91</td>
</tr>
<tr>
<td>NaCl 5mM</td>
<td>0.237</td>
<td>70</td>
<td>0.241</td>
<td>83</td>
<td>0.300</td>
<td>120</td>
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<tr>
<td>NaCl 50mM</td>
<td>0.242</td>
<td>95</td>
<td>0.245</td>
<td>108</td>
<td>0.318</td>
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</tr>
<tr>
<td>NaCl 500mM</td>
<td>0.246</td>
<td>145</td>
<td>0.247</td>
<td>148</td>
<td>0.333</td>
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<tr>
<td>NaCl 50mM, pH=3</td>
<td>0.237</td>
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<td>0.238</td>
<td>107</td>
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<td>NaCl 50mM, pH=5</td>
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<td>0.316</td>
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<td>NaCl 50mM, pH=7</td>
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<td>NaCl 50mM, pH=9</td>
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<td>123</td>
<td>0.250</td>
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<td>NaCl 50mM, pH=11</td>
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<td>112</td>
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<tr>
<td>CaCl(_2) 50mM</td>
<td>0.240</td>
<td>65</td>
<td>0.244</td>
<td>77</td>
<td>0.307</td>
<td>120</td>
</tr>
<tr>
<td>MgCl(_2) 50mM</td>
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<td>105</td>
<td>0.250</td>
<td>118</td>
<td>0.307</td>
<td>123</td>
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</tbody>
</table>
Figure A4.1. Experimental data and model fits illustrating the effects of ionic strength and water flux on EG rejection for (a) NF90, (b) XLE and (c) NF270 membranes.
Figure A4.2. Experimental data and model fits illustrating the effects of pH and water flux on EG rejection for (a) NF90, (b) XLE and (c) NF270 membranes.
Figure A4.3. Experimental data and model fits illustrating the effects of divalent cations and water flux on EG rejection for (a) NF90, (b) XLE and (c) NF270 membranes.