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Polybenzimidazole Membranes Functionalized to Increase Hydrophilicity, Increase Surface Charge, and Reduce Pore Size for Forward Osmosis Applications

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Master of Science Degree in Chemical Engineering

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An Abstract of

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Forward osmosis is the movement of water across a selectively permeable membrane. The driving force for water permeation through the membrane is the difference in osmotic pressure between the feed and draw solutions. Polybenzimidazole (PBI) is a material with excellent chemical resistance and high mechanical and thermal stability that is a promising material for forward osmosis separations. Drawbacks associated with the use of PBI as a membrane material include low hydrophilicity and surface charge neutrality at neutral pH values. These properties effect membrane wettability and solute rejection.

In this study, PBI membranes were cast using the phase-inversion technique in the form of asymmetric flat sheets, and membrane surfaces were functionalized using different modifying agents with the goal of increasing hydrophilicity, increasing surface charge, and reducing membrane pore sizes. A charge increase of the membrane surface was expected to yield an increased rejection of ions and of charged species in the feed solution. An increase in hydrophilicity was expected to reduce fouling propensity and
enhance wettability of the membrane surface. Lastly, a reduction in pore size was expected to allow for greater steric effects. In order to modify the membranes, the surfaces of the membranes were first activated with 4-(chloromethyl) benzoic acid (CMBA). The modifying agents selected for membrane functionalization included: taurine, para-phenylene diamine, ethylene diamine, and poly(acrylamide-co-acrylic acid).

Membranes were characterized using Fourier transform infrared spectroscopy in attenuated reflectance mode (FTIR-ATR), zeta potential, environmental scanning electron microscopy (ESEM), contact angle measurements, and total organic carbon (TOC). Functionalization, surface charge, increased hydrophilicity, and reduced pore size were all verified. Pure water permeability and monovalent salt rejection were tested in a pressure driven mode for comparison between both virgin and modified membranes. Salt rejection was investigated using various sodium chloride feed concentrations, and a range of pH values.

Flat sheet membranes were also tested in forward osmosis (FO) applications. The FO process involved use of an ammonium bicarbonate draw solution and a sodium chloride feed solution. All modified membranes showed enhanced water permeability and increased salt rejection over the unmodified membrane surface.
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List of Abbreviations

CP ...................... Concentration Polarization
CMBA .................. 4-(chloromethyl) benzoic acid
CFM ..................... Chemical Force Microscopy
COOH .................. Carboxylate functional group

DI ..................... Deionized/Distilled Water
DMAc .................. Dimethylacetamide

ECP .................... External Concentration Polarization
ED ...................... Ethylene diamine
EDCH ................... N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride
ESEM ................... Environmental scanning electron microscopy

FO ..................... Forward Osmosis
FTIR-ATR ............... Fourier transform infrared spectroscopy in attenuated reflection mode

ICP ..................... Internal Concentration Polarization
MES ................... 2-(N-morpholino)ethanesulfonic acid
MF ...................... Microfiltration

NF ..................... Nanofiltration
NHS ..................... N-hydroxysuccinimide

PAcA .................... Poly(acrylamide-co-acrylic acid)
PBI ...................... Polybenzimidazole
PD ...................... p-Phenylenediamine
PEG .................... poly(ethylene glycol)
pH ...................... Potential of Hydrogen
PRO .................... Pressure Retarded Osmosis
PWP .................... Pure Water Permeability

RO ..................... Reverse Osmosis

SEM .................... Scanning Electron Microscopy
TOC..............................Total Organic Carbon

UF ..............................Ultrafiltration
List of Symbols

ΔP............................Pressure differential
ζ............................Zeta
Δμw......................Effective driving force
μw......................water chemical potential
μL........................microliters
μm........................micrometers
Δπ......................Osmotic pressure gradient
π...........................Osmotic pressure
Δπbulk................Pressure difference between bulk feed and bulk draw solution
ρ........................density
σ........................reflection coefficient
Δw......................weight change

Å..........................angstroms
°C............................degrees Celsius

A............................water permeability coefficient
c_i..........................concentration of species i
CH₃..........................methyl group
cm..........................centimeter
Da..........................dalton
g............................gram
g/cm³........................gram per cubic centimeter
g/mol........................gramps per mole
M..........................molarity
min........................minutes
mL..........................milliliter
mM..........................millimolar
pKa........................negative logarithm of the acid dissociation constant
pKb........................negative logarithm of the base dissociation constant
psi..........................pounds per square inch
R.............................ideal gas constant
T.............................temperature
t...........................time
wt%........................weight percent
X_i..........................mole fraction of species i
Chapter 1

Introduction

Forward osmosis (FO) is an emerging desalination process that is gaining favor as a substitute for currently used desalination methods [1.1]. Pressure-driven processes, such as reverse osmosis (RO), have been the most common techniques for separating dissolved solutes from feed water for many decades [1.2]. Like RO, forward osmosis uses a semi-permeable membrane to allow for water separation. The water flux in a FO system varies from RO, however, in that the driving force for mass transport is the osmotic pressure gradient between the feed and draw solutions (generally a high concentration salt solution), as opposed to hydraulic pressure. The flow of water through the membrane leads to a concentration of the feed solution and a dilution of the draw solution.

FO is in the early stages of development, and there are still major obstacles that need to be overcome before FO can be utilized as a water production technology. Such obstacles include: a small number of commercially available FO membranes with proper separation performance, and a lack of economically viable and user friendly draw solutions [1.1]. The lack of commercially available FO membrane materials stems from the fact that current membrane materials were developed for pressure-driven applications. RO membranes are built on thick fabric support layers that suffer high levels of internal
concentration polarization, significantly reducing membrane flux \[1.3\]. Other obstacles include the lack of understanding of transport behavior and fouling, and the fact that ideal draw solutions are still being researched.

Ideal FO membranes should have thinner support layers, have very low transport resistance to minimize internal concentration polarization, and enhance membrane permeability. Studies on water transport through FO membranes show that internal concentration polarization within the support layer significantly reduces membrane flux [1.4-1.6]. Therefore, thickness and transport resistance of the support layer plays a critical role in FO membrane performance, although the support layer properties do not affect the performance of RO/NF membranes. Nevertheless, most of the commercially available semi-permeable membranes, such as the widely used polyamide thin-film membranes, have very thick woven fabric supports that would restrict their application as FO membranes. The thickness of successful and commercially available FO membrane support layers as reported by Saren et al. [1.7] is between 40-90 µm for woven fabric supported membranes. This is much thinner than that of conventional thin film composite (TFC) RO membranes (~150 µm).

The approach taken in this study to address these obstacles involves functionalization of existing membranes, in this case nanofiltration (NF) membranes, with the expectation of improving surface characteristics and providing more ideal operating conditions for FO. Functionalization involves chemically attaching a modifying agent to the surface of a membrane. The added functional group is hoped to result in an increased rejection of electrolytes (i.e. sodium chloride and potassium chloride) and charged particles.
Researchers in Singapore recently developed a hollow fiber nanofiltration (NF) FO membrane made of polybenzimidazole (PBI) [1.8-1.9]. PBI is a material with outstanding mechanical and thermal stability and chemical resistance. PBI membranes can generate high flux in FO processes [1.8-1.9] and thus is a very promising material for FO membrane development. The drawback with PBI, however, is the salt rejection of this membrane in the virgin stage is relatively low, and the membrane has low hydrophilicity. If the PBI membrane surfaces can be modified to address these flaws, then PBI has the potential to become an economically viable FO membrane material.

Studies by previous researchers have shown that PBI membranes can be successfully modified and their properties enhanced. Research with PBI membranes chemically modified with p-xylylene has shown that modification can successfully decrease membrane pore size in the selective layer to a molecular level [1.10]. Additionally, a recent study by Hausman et al. [1.11] focused on increasing the surface charge and hydrophilicity of PBI membranes using a very similar approach to the one presented here, with the main difference being that the functionalization of the membrane was achieved after a lengthy and expensive procedure.

PBI nanofiltration membranes from these studies showed amphoteric behavior with desirable water flux and high rejection of divalent ions [1.9]. Rejection of ionic species was found to be highly dependent on the solution pH. pH values determine the phases and sizes of the ionic species, in addition to the surface charge characteristics of the PBI membrane [1.7-1.11]. It was also shown through surface modification of the PBI membranes that the rejection of aqueous solutes was highly dependent on both the membrane pore size and electrostatic interaction between the solute and membrane.
Analysis of virgin and modified PBI membranes in pressure driven systems, with single electrolyte solutions, at various pH values, showed a decrease in solute permeability with modification at neutral pH values, with increasingly higher rejection as the pH increased and the membranes took on higher surface charges [1.10-1.11].

The focus of this study was on functionalization of PBI surfaces to impart a surface charge, increase hydrophilicity, and reduce the membrane pore size. A summary of the procedure used in this study includes: casting of asymmetric (asymmetric meaning a membrane with a dense selective layer opening up into a more porous support layer) flat sheet PBI membranes via the phase-inversion technique, chemically modifying the membrane surfaces, characterizing the virgin and modified membranes, testing the membranes in a pressure-driven process for pure water permeability and monovalent salt rejection, and testing the membranes in a FO system.

Continued exploration and development of FO membrane materials could lead to a viable and efficient replacement for current membrane desalination processes. Forward osmosis has the potential to greatly reduce the required energy input for water treatment processes. Successful modification and implementation of PBI membranes has the potential to be a significant advancement toward achievement of a viable FO membrane system.
Chapter 2

Literature Review

Water purification technologies involving traditional membrane processes are divided based on pore size and/or the size of the materials they can reject (Figure 2-1 and Table 2.1). Based on decreasing pore size, membranes are divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).

Figure 2-1. Filtration characteristics of membranes based on pore sizes. (Source: www.kochmembrane.com)
The fundamental concept of all water purification membrane processes is to allow permeation of water from a process stream while simultaneously rejecting certain contaminants. The technique and driving force for water permeation vary for each type of process. In reverse osmosis (RO), and nanofiltration (NF) membrane systems, the driving force for water permeability is hydraulic pressure. These types of processes are highly energy intensive and require that the hydraulic pressure overcome the osmotic pressure of the system. A developing membrane process called forward osmosis (FO), however, uses an osmotic pressure gradient between the feed and draw solutions to create the driving force. Water flows through the membrane, concentrating a saline feed solution, and diluting a draw solution of much higher osmotic pressure. Forward osmosis membranes are generally found in the NF/RO range.

Pressure-retarded osmosis (PRO) can be viewed as the intermediate process between FO and RO, but the goal of PRO is to generate power. In PRO the salinity gradient energy is utilized to generate power. A concentrated salt solution and a fresh water solution are passed on opposite sides of a membrane where power is generated by the difference in

<table>
<thead>
<tr>
<th>Separation Process</th>
<th>Driving Force</th>
<th>Solute Permeability</th>
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<tbody>
<tr>
<td>Microfiltration</td>
<td>Pressure</td>
<td>Size Exclusion</td>
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<tr>
<td>Ultrafiltration</td>
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<tr>
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</tr>
<tr>
<td>Reverse Osmosis</td>
<td>Pressure</td>
<td>Diffusion</td>
</tr>
</tbody>
</table>

Table 2.1. Membrane classification based on pore sizes.
salt concentration of the two solutions. Like RO processes, a hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient [2.1]. However, like FO, the net water flux is still in the direction of the concentrated draw solution. The general equation to describe water transport in all three membrane processes is:

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

(2.1)

where,

\[ \sigma = 1 - \left( \frac{c_{i_{\text{permeate}}}}{c_{i_{\text{concentrate}}}} \right) \]  

(2.2)

where \( J_w \) is the water flux (L m\(^{-2}\) hr\(^{-1}\)), \( A \) the water permeability constant of the membrane (L m\(^{-2}\) hr\(^{-1}\) bar\(^{-1}\)), \( \sigma \) is the reflection coefficient (the reflection coefficient indicates the extent to which the solute particles are reflected/rejected by the membrane in comparison with the solvent), \( \Delta \pi \) is the osmotic pressure gradient (bar), \( \Delta P \) is the applied pressure (bar), \( c_{i_{\text{permeate}}} \) is the concentration of the solute that permeates the membrane and \( c_{i_{\text{concentrate}}} \) is the concentration of the solute that is rejected by the membrane. For FO, \( \Delta \pi > \Delta P \) where \( \Delta P = 0 \); for RO, \( \Delta P > \Delta \pi \); and for PRO, \( \Delta \pi > \Delta P \). The direction of water permeation for FO, PRO, and RO are displayed in Figure 2-2.
2.1 Reverse Osmosis/Nanofiltration

Currently, RO is the most common pressure-driven water purification technology. The driving force for water permeability in RO is hydraulic pressure. Purified water is produced when the hydraulic pressure exceeds the osmotic pressure of an aqueous feed solution, and thus, facilitates mass transfer across the membrane [2.2]. A basic schematic representing water transport in a pressure driven membrane process is shown in Figure 2-3. Because the osmotic pressure of the solution must be exceeded, the concentration of the solution is directly proportional to the hydraulic pressure requirement for water permeation, and this pressure requirement accounts for the high energy input needed in RO processes.

Figure 2-2. Direction of water permeability in FO, PRO, and RO processes [2.1].
The osmotic pressure of seawater systems is roughly 25 bar [2.4]. The energy requirements reported for RO purification of seawater are typically about 15-30 KJ/Kg of fresh water [2.5], although values as high as 61 KJ/Kg have been reported [2.6]. Recent technological advancements have been made in regard to recovering lost energy and large scale RO systems are now equipped with devices to recover the mechanical compression energy from the discharged concentrated brine stream with efficiencies reported around 95%. In such systems, the energy requirements for seawater desalination have been reported to be as low as 9 KJ/Kg [2.7].

### 2.2 Types of Membranes

Several different types of membranes and membrane materials are available for various applications. Typical membrane designs include: flat sheet membranes, tubular
membranes, and hollow fiber membranes [2.8]. The flat sheet membrane design is generally used in a spiral wound element that allows for high operational pressures and a high ratio of surface area to volume [2.8]. Because of the pressure tolerance of the spiral wound membrane design, these types of membranes are almost always used in RO processes.

Tubular and hollow fiber membranes have very similar geometries, with the largest difference between the two being the size of the inner diameter of the membrane. Tubular membranes have large inner diameters and are used in applications with high solids content or colloidal particles. The drawbacks with tubular membranes are the low packing density and high unit cost [2.8].

Hollow fiber membranes have very small inner diameters and allow for very high packing densities. The high packing density allows for a very high surface area to volume ratio [2.8] within the membrane module and makes them good for microfiltration and ultrafiltration processes. A significant drawback associated with these types of modules is the occurrence of plugging due to the large number of fibers in the module and the small inner diameters of the fibers.

2.3 Forward Osmosis Processes

Forward osmosis (FO) is an emerging desalination process that is gaining favor as a substitute for currently used desalination methods. The most attractive features of a FO membrane system include lower operational costs and less energy requirement. Like RO, forward osmosis uses a semi-permeable membrane to allow for water separation. The
water flux in a FO system varies from RO, however, in that the driving force for mass transport is the osmotic pressure gradient between the feed and draw solutions (generally a high concentration salt solution), as opposed to hydraulic pressure. Water flows through the membrane, concentrating a saline feed solution, and diluting a draw solution of much higher osmotic pressure.

While emphasis has been placed on developing FO processes recently [2.1], two main drawbacks still exist. Most commercially available membranes were designed for RO processes and have proven to be less than ideal for FO systems. RO membranes are built on thick fabric support layers that suffer high levels of internal concentration polarization, significantly reducing membrane flux [2.9]. The second drawback involves finding an economically viable and easily separable draw solute. Many draw solutes have been examined as possible candidates for FO processes including: ammonium bicarbonate, calcium chloride, potassium bicarbonate, magnesium chloride, magnesium sulfate, and sodium bicarbonate [2.1, 2.10-2.11].

2.3.1 Osmosis

The driving force for water transport across a selectively permeable membrane by way of osmosis is the osmotic pressure gradient. Osmotic pressure (\( \pi \)) is the pressure which, if applied to the more concentrated solution, would prevent transport of water across the membrane. Water with a higher chemical potential flows across the membrane to water with a lower chemical potential. A solutions chemical potential is directly related to the solute concentration, and the gradient forces the passage of water through the membrane.
Depending on the membranes properties, specific solute molecules and ions are rejected by the membrane.

Osmotic pressure ($\pi$) is a thermodynamic property of a solution and is related to the mole fraction of the solvent, $X_{Bi}$, by the equation:

$$\pi_i = -\frac{RT}{V_B} \ln X_{Bi}$$  \hspace{1cm} (2.3)

where $R$ is the universal gas constant ($\text{L bar K}^{-1} \text{ mol}^{-1}$), $T$ is temperature (K), and $V_B$ is the volume of the solvent (L) [2.12]. For dilute solutions, the osmotic pressure is found to obey the ideal gas law, where $C_{Ai}$ is concentration of solute ($\text{mol L}^{-1}$), making equation 2.3 simplify to the van’t Hoff equation:

$$\pi_i = C_{Ai}RT$$  \hspace{1cm} (2.4)

FO processes result in concentration of a feed stream and dilution of a highly concentrated draw solution. A schematic of an osmotically-driven membrane processes is shown in Figure 2-4. Forward osmosis is a naturally occurring process that, unlike RO, does not require an external pressure.
2.3.2 Draw Solutions

The higher osmotic pressure of the solution of the permeate side of the membrane is the source of the driving force for FO processes (Figure 2-4a). When selecting a draw solution, the main characteristic is that it should have a higher osmotic pressure than the feed solution. Other important criterion of draw solutions for FO applications involve selection of a suitable solute and process for re-concentrating the draw solution after it has been diluted, or choosing a draw solution with an easily separable solute. Depending on the method of concentrated feed water disposal and the draw solute selected, reverse diffusion of the solute through the membrane must also be considered. In applications where low reverse diffusion is needed, multivalent ion solutions may be preferable.
Some naturally occurring candidates for FO draw solutions include: seawater [2.13], Dead Sea water [2.14], and Great Salt Lake water [2.15]. Various other chemicals have been suggested and tested as solutes for draw solutions, particularly in seawater desalination applications. Batchelder [2.16] suggested using sulfur dioxide solution as the draw solution in desalination of seawater. Glew [2.17] expanded on this idea and suggested using mixtures of water and another gas (e.g. sulfur dioxide) or liquid (e.g. aliphatic alcohols) as the draw solutions for FO. Glew also proposed the recycling of the draw solutions in conjunction with FO. Frank [2.18] used an aluminum sulfate solution, Kravath and Davis [2.19] used a glucose solution in FO desalination of seawater, Kessler and Moody [2.20] used a mixed solution of glucose and fructose for seawater desalination, and Stache [2.21] used a concentrated fructose solution to create a nutritious drink during FO of seawater. McGinnins [2.22] suggested a two-stage FO process that takes advantage of the temperature dependence of solutes’ solubilities. Specifically, McGinnis suggested solutions of potassium nitrate and sulfur dioxide as draw solutions for seawater desalination. In a later novel application of FO by McGinnis and coworkers [2.23-2.25], it was demonstrated that combining ammonia and carbon dioxide gases in specific ratios created highly concentrated draw solutions of thermally removable ammonium salts. This approach produced FO draw solutions with osmotic pressures in excess of 250 atm, allowing unprecedented high recoveries of potable water from concentrated saline feeds and substantial reductions in brine discharges from desalination.

While many of the early draw solutions were successful in creating the osmotic driving forces required for forward osmosis [2.16-2.21], low water permeability and solute
separation were found to remain to be difficulties. An ideal draw solution solute provides a high osmotic pressure difference and is easily separated from the diluted water stream. While Stache [2.21] successfully used a fructose draw solution to desalinate sea water and create sugary drinks for use at sea, the process didn’t generate high osmotic pressures and didn’t produce substantial volumes of water. Similarly, Kessler and Moody [2.20] used a mixed solution of glucose and fructose for seawater desalination but it resulted in low water fluxes. Through the use of soluble ammonia and carbon dioxide gases [2.23-2.25] high osmotic pressure gradients can be achieved and diluted draw solutions can easily be separated from their solutes through moderate heating and resultant thermal degradation of the solutes.

2.3.3 Concentration Polarization

The water flux in osmotic-driven membrane processes is described in Equation 2.1. In this equation, $\Delta \pi$ represents the osmotic pressure difference across the selective layer of the membrane. In such processes, the osmotic pressure gradient across the selective layer of the membrane is much lower than the bulk osmotic pressure gradient. The reduced osmotic pressure gradient results in much lower water flux than expected [2.26-2.30]. The lower-than-expected water flux is often primarily attributed to two types of concentration polarization (CP) phenomena – external CP and internal CP.

2.3.3.1 External Concentration Polarization

In pressure-driven membrane processes, convective permeate flow causes a buildup of solute at the surface of the membrane selective layer. Referred to as concentration
polarization (CP), the increased osmotic pressure caused by this phenomenon reduces permeate water flux and must be overcome by hydraulic pressure [2.31-2.33]. CP resultant of water permeation, is not limited to pressure-driven membrane processes, but also occurs during osmotic-driven membrane processes. Additionally, this phenomenon occurs on both the feed and permeate sides of the membrane. When the feed solution flows on the selective layer of the membrane, solutes build up at the selective layer. This may be called external CP and is similar to CP in pressure-driven membrane processes. Simultaneously, the draw solution in contact with the permeate side of the membrane is being diluted at the permeate-membrane interface by the water diffusing through the membrane. This is called dilutive external CP (Figure 2-5). Both concentrative and dilutive CP phenomena reduce the effective osmotic pressure gradient. The adverse effect of external CP on osmotic-driven membrane processes can be minimized by increasing flow velocity and turbulence at the membrane surface or by manipulating the water flux [2.34].
Figure 2-5. Schematic showing both internal concentration polarization (ICP) and external concentration polarization (ECP) through an asymmetric FO membrane [2.35].

Because of the minimal hydraulic pressure used in FO processes, membrane fouling induced by external CP has milder effects on water flux compared to pressure-driven membrane processes. It has been shown that external CP plays a minor role in osmotic-driven membrane processes and is not the main cause for the lower-than-expected water flux in such processes [2.25].
2.3.3.2 Internal Concentration Polarization

When an osmotic pressure gradient is established across a completely rejecting dense symmetric membrane, as illustrated in Figure 2-6a, the driving force is the difference in osmotic pressure of the bulk solutions in the absence of external CP. However, FO membranes are asymmetric – pore size and structure vary from one side of the membrane to the other – and thus, add more complexity to the CP phenomena. When an asymmetric membrane, consisting of a dense separating layer and a porous support layer, is used in FO, two phenomena can occur depending on the membrane orientation. If the porous support layer of the asymmetric membrane faces the feed solution, a polarized layer is established along the inside of the dense selective layer as water and solute propagate within the porous layer (Figure 2-6b). Referred to as concentrative internal CP [2.29], this phenomenon is similar to concentrative external CP, except that it takes place within the porous layer, and therefore, cannot be minimized by cross-flow.

Typically, in FO applications for desalination and water treatment, the selective layer of the membrane faces the feed solution, and the porous support layer faces the draw solution. As water permeates through the selective layer, the draw solution within the porous substructure becomes diluted. This is referred to as dilutive internal CP (Figure 2-6c) [2.29]. The result of this phenomenon is that the osmotic pressure difference between the bulk feed and bulk draw solution ($\Delta \pi_{\text{bulk}}$) becomes higher than the osmotic pressure difference across the membrane ($\Delta \pi_{\text{m}}$). The effective osmotic pressure gradient ($\Delta \pi_{\text{eff}}$) is even lower due to internal CP than external CP. Operation of FO in a counter-current flow configuration – feed and draw solutions flowing tangential to the membrane but in
opposite directions to one another – provides constant $\Delta \pi$ along the membrane module and makes the process more effective [2.36].

Figure 2.6. Driving force profiles for FO membrane systems. (a) A symmetric dense membrane. (b) Profile of concentrative internal concentration polarization for an asymmetric membrane with the feed facing the porous support layer of the membrane. (c) Profile of dilutive internal concentration polarization for an asymmetric membrane with the feed facing the selective layer of the membrane [2.1].

2.3.4 Current Forward Osmosis Membrane Materials

FO is in the early stages of application, and there are still major obstacles that need to be overcome before fully utilizing FO as a widely used water production technology. One primary obstacle involves a small number of commercially available FO membranes with
proper separation performance. The lack of commercially available FO membrane materials stems from the fact that previously developed membrane materials were developed for pressure-driven applications, there is not a full understanding of transport behavior and fouling, and ideal draw solutions are still being researched.

Ideal FO membranes should have thin support layers, have very low transport resistance to minimize internal concentration polarization, and enhance membrane permeability. Studies on water transport through FO membranes show that internal concentration polarization within the support layer significantly reduces membrane flux [2.36-2.40]. While thickness and transport resistance of the support layer plays a critical role in FO membrane performance, the support layer properties do not nearly affect the performance of RO/NF membranes. Most of the commercially available semi-permeable membranes, such as the widely used polyamide thin-film membranes, have very thick woven fabric supports that would restrict their application as FO membranes. The thickness of successful and commercially available FO membrane support layers, as reported by Saren et al. [2.41], is between 40-90 µm for woven fabric supported membranes. This is much thinner than that of conventional thin film composite (TFC) RO membranes (~150 µm).

Some work has been done in developing materials for use in FO. Hydration Technologies, Inc. (Albany, OR) produced a cellulose acetate FO membrane [2.1]. Although this membrane has relatively high flux, it finds limited applications due to high material biodegradability, severely shortening the membrane life.

Recently, researchers in Singapore have made significant developments with the design of FO membranes. Two types of TFC FO hollow fibers with an ultra-thin polyamide-
based RO-like skin layer (300–600 nm) have been developed [2.42]. The TFC layer could be fabricated on either the outer surface or inner surface of a porous hollow fiber substrate. Both membranes appeared to show excellent water fluxes and salt rejection. The membranes were found to be very hydrophilic and show very low pore size distributions. To date, the membrane with the TFC layer on the inner surface is believed to be superior to all FO and NF membranes used in FO processes which have been reported in the literature [2.42].

Also, a hollow fiber FO membrane made of polybenzimidizole (PBI) has been developed [2.43]. The PBI membrane can generate high flux in FO process and thus is very promising material for FO membrane development, even though the salt rejection of this membrane in the current stage is relatively low.

2.4 Polybenzimidazole Membranes

PBI is a class of heterocyclic polymers that were commercially developed by the Celanese Corporation in 1983 [2.44-2.45], with the chemical structure of the repeat unit shown in Figure 2-7.

![Figure 2.7. Structure of the polybenzimidazole repeat unit.](image-url)
PBI membranes have been fabricated for use in several membrane processes including reverse osmosis, nanofiltration, and as ion-exchange membranes in fuel cells because of the materials excellent chemical and thermal stability [2.46-2.49]. The heterocyclic imidazole ring makes it possible for both inter and intra-molecular hydrogen bonding to occur between PBI molecules. This mechanism allows PBI to become self-charged in aqueous environments due to the adjacent benzene ring delocalizing the proton of the imidazole group [2.50].

2.4.1 Reverse Osmosis Applications

The use of PBI as a reverse osmosis membrane material has been explored since as early as 1984 [2.46]. In these studies the microstructure of the internal membrane was studied and found to be asymmetric in cross-section but uniform along and across the casting direction. The selective layer was found to be very thin and quite dense, with the pore sizes opening up throughout the support structure. It was also estimated that annealing procedures could reduce the membrane pore sizes to roughly half the as-cast size [2.46].

2.4.2 Fuel Cell Membranes

Polybenzimidazole has been used as a high-temperature polymer electrolyte membrane for fuel cell operation [2.51]. Use of this type of membrane material allows for operation above 120 °C without humidification, and offers many benefits including increased resistance to fuel impurities, most notably carbon monoxide (CO), fast electrode kinetics, and simplified water/thermal management. For automotive applications, membranes
operable at temperatures of approximately 120 °C with long-term stability would offer the largest system efficiency enhancement and reduce the radiator size by 50% [2.51].

2.4.3 Forward Osmosis Applications

Recently, researchers in Singapore have developed novel asymmetric PBI nanofiltration hollow fiber membranes for use in FO applications [2.43, 2.52]. Hollow fiber membranes were cast with mean effective pore sizes around 0.32nm in radius. The membranes exhibited desirable water permeation flux and high rejection to divalent ions and colloidal particles. While certain forms of PBI membranes showed a much higher rejection to divalent ions, much lower rejection values were seen for monovalent ions in their as-cast state [2.53].

Studies of anions and cations removal with PBI hollow fiber membranes have shown amphoteric membrane behavior with pH values greatly impacting the membranes rejection performance. The solution pH strongly affects the rejection of ionic species in the feed solution because solution pH determines the phases and chemical compositions of the ions, the ion sizes, and also the surface charge characteristics of the PBI membranes in aqueous environments. The amphoteric imidazole groups within PBI molecules can become self-charged in aqueous environments due to the adjacent benzene ring delocalizing the proton of the imidazole group depending on solution pH values [2.43, 2.52, 2.54].
2.5 Polybenzimidazole Surface Modification

Previous research has been done focusing on the surface modification of PBI for various applications. Roziere et al. [2.55] grated (4-bromomethyl)benzenesulfonate onto PBI as a means of producing a proton exchange polymer with a variable degree of sulfonation. Staiti et al. [2.49] sulfonated PBI through sulfuric acid treatment on pre-formed membranes for use in electrodialysis. Wang et al. [2.54] functionalized PBI with p-xylylene dichloride for use as high-rejection, high-flux forward osmosis membranes for water reuse and seawater desalination. Modification with p-xylylene [2.54] involves a similar reaction to the activation step with CMBA described by researchers at the University of Toledo [2.56], but has two reactive chloride groups that result in cross-linking of the PBI chains. Additionally, PBI modified with p-xylylene has shown that modification could successfully decrease membrane pore size in the selective layer to a molecular level [2.54].

Hausman et al. [2.56] studied functionalization of PBI membranes through a two-step modification process in order to increase the surface charge and hydrophilicity of the membrane surface. This technique involved a very similar approach to the one presented in this study, with the main difference being that the functionalization of the membrane was achieved after a long and expensive procedure using carbodiimide (EDC) chemistry. The focus of the study presented here was on functionalization of PBI surfaces to impart a surface charge, increase hydrophilicity, and reduce the membrane pore size using a less expensive and faster method for the surface modification. After modification, the membranes were tested in forward osmosis applications.
Chapter 3

Research Objectives

The objectives of this research were to prepare flat sheet PBI membranes via the phase inversion technique and chemically modify their surfaces using four separate modifying agents (taurine, ethylene diamine, para-phenylene diamine, and poly(acrylamide-co-acrylic acid)). The modification agents were selected based on their potential to increase hydrophilicity and impart charges to the membrane surface. PBI membranes were prepared in house and modified using a two-step activation and modification procedure. PBI membranes were first activated using 4-(chloromethyl) benzoic acid (CMBA). The activated membranes were then modified using N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCH) and N-hydroxysuccinimide (NHS) chemistry catalysis as an intermediate for reaction of the carboxylic (-COOH) functional group, added from the CMBA activation, with the primary amine of the desired modifying agent.

Several analytical techniques were employed to verify that surface modification was successful. Environmental scanning electron microscopy (ESEM) was used to verify the asymmetric morphology of the membranes. Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR) was used to detect changes based on
specific functional groups associated with each of the modifying agents. Determination of changes in hydrophilicity was examined by contact angle measurements using a goniometer. Total organic carbon (TOC) experiments were run with uncharged solutes in single solute permeation runs to determine membrane pore sizes. Transport characteristics were evaluated for unmodified, CMBA surface activated, and all modified membranes. Dead-end flow permeability cells were used in a pressure-driven mode for pure water permeability and verification of imparted characteristics. Pure water permeability along with monovalent (sodium chloride) salt rejection was determined for all membranes. In order to detect changes in salinity, the conductance of both the feed and the resulting permeate were tested using a conductivity meter. Forward osmosis experiments were run using sodium chloride feed and ammonium bicarbonate draw solutions. The water flux and salt transport across all the membrane samples was studied.
Chapter 4

Experimental

4.1 Chemistry

Polybenzimidazole dope was supplied by PBI Performance Products, Inc. (Charlotte, NC) as a 26 wt% solution. Ammonium bicarbonate, ethylene diamine, para-phenylene diamine, poly(acrylamide-co-acrylic acid), taurine, dimethylacetamide, 4-(chloromethyl) benzoic acid, N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride, N-hydroxysuccinimide, all poly(ethylene glycol) solutes, sodium chloride, and sodium persulfate were purchased from Sigma–Aldrich (USA). Acetone, glycerol, glucose, sucrose, and raffinose were purchased from Fisher Scientific (USA). 2-mercaptoethanol was purchased from Alfa Aesar. All reagents were used as received. DI water was supplied by a continuous distillation apparatus.

4.2 Phase Inversion Technique

All PBI flat sheet membranes were prepared in house via the phase inversion technique. Polybenzimidazole dope was supplied at 26 wt% in a 72 wt% solution of dimethylacetamide (DMAc) with 2.0 wt% lithium chloride. The procedure used to prepare the membranes was adapted from Wang et al. [4.1]. A desired concentration of
20 wt% was achieved by dilution with DMAc. In order to achieve uniform flat sheet membranes, and to prevent air bubbles from being trapped in the dope, the beaker was sealed with parafilm and placed in a sonicator on degas setting for approximately two hours. The dope was then spread in an even line across a well-cleaned mirror. A doctor's blade set at a thickness of 150 μm was used to push the dope across the mirror forming a thin flat sheet. In order to reduce friction between the blade and the mirror, the rails of the doctor’s blade were lubricated with motor oil. After the flat sheet was cast, the mirror and sheet were placed in a 12-gallon DI water coagulation bath to remove the solvent by way of the phase-inversion technique [4.1]. The membrane peeled from the mirror when the phase-inversion process was complete. The membrane was thoroughly washed with DI water and either one inch circles were punched out for modification and testing or flat sheets were cut out for modification and forward osmosis experiments. All membranes were stored in a 50/50 mixture of DI water and glycerol until used. The addition of glycerol was to ensure the membranes would stay wet during storage because when they are dried, they would become brittle and susceptible to breakage.

4.3 PBI Surface Modifications

4.3.1 CMBA Activation

The initial activation using CMBA [4.2] was performed as follows: 0.5 wt% solution of CMBA was prepared in acetone and stirred until the solute was completely dissolved. A separate beaker, with 1.0 wt% sodium persulfate was prepared in DI water and stirred until the solute was completely dissolved. Sodium persulfate acted as a free radical initiator for the CMBA activation. The virgin membrane samples to be modified were
added to the sodium persulfate solution. The CMBA/acetone solution was slowly added to the aqueous sodium persulfate solution. The slow addition was necessary to prevent the CMBA from precipitating from solution, since it is insoluble in water. The reaction procedure is given in Figure 4-1.

![Reaction Diagram]

Figure 4-1 CMBA activation of the PBI virgin membrane.

There are two reactive –NH sites on the backbone of the PBI repeat unit. Both of the –NH sites are susceptible to reaction, but for simplification, reaction to one site is shown throughout this paper. The final volume was a 50/50 mixture of DI/acetone. The reaction mixture was sealed with parafilm, heated on a hot plate to 40 °C, and reacted for 24 hours. This temperature was selected to help keep the reagents in solution while minimizing acetone evaporation. No agitation was applied. After 24 hours, the sheets were removed and washed with acetone to remove any residual CMBA; then washed with copious amounts of DI water to remove any remaining sodium persulfate and acetone. Once thoroughly cleaned the sheets were stored in 50/50 DI water and glycerol solution.
4.3.2 Surface Functionalization

Hausman et al. [4.3] showed an effective technique to functionalize CMBA-activated PBI membranes using N-ethyl-N(3-dimethylaminopropyl) carbodiimide (EDC) chemistry. A simpler approach using N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCH) and N-hydroxysuccinimide (NHS) (Figure 4-2) chemistry was the focus of this study. The EDCH/NHS method was favored over the EDC method because it allowed for a reduction in the reaction time and required chemical usage. EDCH facilitated the reaction between –COOH groups bound to the CMBA activated PBI backbone and the primary amine group of the functional modifying agents [4.4]. The EDCH/NHS reaction occurred with the carboxylic acid to form an unstable ester (Figure 4-3). The modifying agents included ethylene diamine, taurine, para-phenylene diamine, and poly(acrylamide-co-acrylic acid) (bottom Figure 4-3). The amount of reagent necessary for EDCH catalyzed modification depended on the final weight of dried surface activated samples. Subsequent modifications were performed in a 2-(N-morpholino) ethanesulfonic acid (MES) buffer solution.

![EDCH and NHS molecular structures.](image)

**Figure 4-2 EDCH and NHS molecular structures.**
Figure 4-3 Two-step modification technique (a) EDCH/NHS reaction with CMBA activated PBI to form ester intermediate (b) NHS ester intermediate reacted with modifying agent to form final functionalized membrane (top) R groups for final surface functionalization (bottom)
A buffer solution composed of 0.1 M MES and 0.5 M NaCl was prepared for all EDCH/NHS reactions. A stock solution was prepared, and titrated with 1 N NaOH to a pH of 6. The pH adjusted MES buffer was used to prepare a 0.002 M EDCH and 0.005 M NHS solution for the final surface modification. After the EDCH/NHS solution was prepared, the membrane sheets were added to the solution and mixed. After 15 minutes, 2-mercaptoethanol was added to the solution to quench the reaction for modifying agent addition. To optimize the conditions for reaction, the pH was adjusted to 7-7.5 with 1N NaOH before the desired modifying agent was added. From the molecular weight of CMBA modified sheets (442 g/mol) and the final weight of the samples to be modified, the weight of the modifying agent was determined. The final step involved a 10 fold-molar addition of modifying agent to that of the CMBA modified samples. Then the reaction was stirred for two hours. Once the reaction was complete, copious amounts of DI water were used to wash the membranes. It is also important to note that amphoteric compounds, such as taurine, usually require blocking of acid functionality to prevent internal salt formation and free amino-group, which was not done since the reaction proceeded as described. Membranes were stored in a 50/50 DI water and glycerol solution.

4.4 Membrane Characterization

After the two-step modification procedure was complete it was visually obvious that the modification was successful. Figure 4-4 shows images of the support layer of a PD modified membrane next to an unmodified flat sheet membrane. The virgin membrane samples were light brown in color and each functionalized membrane showed a
noticeable color change after modification. The image of the virgin and PD modification was selected because it was the most noticeable color change of all the modifications, turning a dark purple color after the reaction.

**Figure 4-4** Support layer side of a virgin flat sheet membrane (left) and support layer side of a PD modified flat sheet membrane (right). The bright spots on the membranes are due to a light reflection when the images were taken.

Despite the noticeable color changes observed after the membrane modifications, several characterization techniques were employed to confirm the success of the modification. ESEM was used to confirm the asymmetric morphology and thickness of the membranes. FTIR-ATR was used to detect changes in the chemistry of the membrane surfaces. Contact angle measurements were taken to show changes in hydrophilicity. Zeta potential readings obtained from the modification technique reported in Hausman et al. [4.3] were used to show surface charge characteristics. Total organic carbon (TOC) experiments with uncharged solute in single solute permeation runs were used to determine membrane pore sizes.
4.4.1 Environmental Scanning Electron Microscopy (ESEM)

ESEM was used to verify the asymmetric structure of the membranes, as well as verify thickness of the cast virgin membrane. An FEI Quanta 3D FEG Dual Beam Electron Microscope (FEI, USA) was used to test the samples. By freezing small samples of the membranes in liquid nitrogen and cracking them, smooth cross-sectional areas could be observed. After the samples were frozen and cracked, they were wet using DI water, and placed vertically in carbon paste. ESEM was advantageous in this case over SEM (scanning electron microscope) because it was important to test wet samples since in aqueous environment, PBI membranes are strong and flexible but when allowed to dry, PBI becomes very brittle and susceptible to breaking.

4.4.2 FTIR-ATR

Evidence that the PBI was successfully modified was obtained using Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR). FTIR uses measurements of vibrational spectra to identify the chemical structure of materials. By monitoring the vibrational spectra changes, molecular conformation can also be observed. FTIR analysis was obtained on a Varian Excalibur Series Fourier Transform Infrared instrument, the FTS-4000 Spectrometer and the UMA-600 Microscope (Randolph, MA).

4.4.3 Contact Angle

A goniometer was used to monitor the changes in the hydrophilicity of the modified membranes over that of the virgin sample. A Tantec Model CAM-MICRO Contact Angle Meter (Tantac, Inc., USA) was used. By placing a small drop of water onto the
surface of the sample, the angle of the resulting water bead can be determined (Figure 4-5). In samples that are hydrophobic the water droplet beads up and the angle remains high. Successful functionalization of the membrane surface resulted in an increase in hydrophilicity, thus a decrease in the water bead contact angle was expected.

![Contact angle measurement diagram](image.png)

**Figure 4-5 Contact angle measurement.**

### 4.4.4 Zeta Potential

Surface charge was analyzed by measuring the zeta potential on the membrane surface. Before analysis, membranes were rinsed with copious amounts of DI water to remove any residual glycerol from the storage solution. The KCl electrolyte solution used in these measurements had an ionic strength of 1.0 mM. The pH values for the various readings were adjusted using 0.5 M NaOH and 0.5 M HCl solutions [4.5]. Zeta potential is the potential difference between a point in the bulk fluid and the interface of the stationary layer of fluid attached to a charged surface. Zeta potential measurements indicate the degree of repulsion between adjacent, similarly charged particles. Zeta
potential readubgs are widely used for quantification of the magnitude of the electrical charge of a membrane surface [4.6-4.7].

### 4.4.5 Total Organic Carbon (TOC)

Total organic carbon (TOC) analysis was used to determine the membranes rejection of several uncharged organic solutes, of varying molecular weights, to find a relationship between the % rejection of the solutes and the pore sizes of the membranes developed. Concentrations of the solute in the solutions used for pore size determination were measured with a Tekmar-Dohrmann, Phoenix 8000 UV-persulfate TOC Analyzer (Tekmar Company, OH). The approach involved introducing feed solutions containing uncharged solutes (Table 4.1) of various Stokes-Einstein radii to the selective layer of the PBI membranes in an Amicon 8010 dead-end filtration cell (Millipore, USA). The dead-end filtration cell is shown in Figure 4-6.

![Schematic of Amicon dead-end filtration cell.](image)

**Figure 4-6 Schematic of Amicon dead-end filtration cell.**
All experiments were performed as single solute permeation runs. The diluted permeate and original feed solutions were sampled in the TOC to determine solute rejection. The apparent solute rejection $R$ (%) was calculated by Equation 4.1:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad \text{(4.1)}$$

where $C_p$ and $C_f$ are the solute concentrations in the permeate and feed solutions, respectively. The uncharged solute samples are shown in Table 4.1 along with their Stokes-Einstein radii [4.6-4.7]. Nonionic molecules have been used to determine membrane pore sizes by previous researchers [4.6, 4.8-4.11] and a similar procedure was followed for this study.

**Table 4.1. Molecular weights and Stokes-Einstein radii of neutral solutes for pore size determinations.**

<table>
<thead>
<tr>
<th>Solute</th>
<th>Mw (g mol$^{-1}$)</th>
<th>Stokes radii (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>92</td>
<td>0.26</td>
</tr>
<tr>
<td>Glucose</td>
<td>180</td>
<td>0.37</td>
</tr>
<tr>
<td>Sucrose</td>
<td>342</td>
<td>0.47</td>
</tr>
<tr>
<td>Raffinose</td>
<td>504</td>
<td>0.58</td>
</tr>
<tr>
<td>PEG</td>
<td>600</td>
<td>0.61</td>
</tr>
<tr>
<td>PEG</td>
<td>1000</td>
<td>0.80</td>
</tr>
<tr>
<td>PEG</td>
<td>2000</td>
<td>1.41</td>
</tr>
<tr>
<td>PEG</td>
<td>4600</td>
<td>1.75</td>
</tr>
<tr>
<td>PEG</td>
<td>8000</td>
<td>2.31</td>
</tr>
</tbody>
</table>

200 ppm solutions were made of each individual solute in DI water. Each separation experiment involved permeation of a single solute in a pressure driven dead-end flow cell at 4.82 bar. Every membrane-solute combination was repeated three times so the average value could be calculated. The rejection values for all solutes were used to determine the
mean effective pore size and the molecular weight cut-off (MWCO) for each membrane modification. The MWCO of a membrane is the molecular weight of the solute that is 90% retained by the membrane [4.9].

4.5 Forward Osmosis Operational Set-up

For all experiments the draw solution used was a 2M ammonium bicarbonate (NH₄HCO₃) solution made by dissolving reagent grade ammonium bicarbonate in DI water. The feed solutions for all experiments consisted of a 0.1M sodium chloride (NaCl) solution. The osmotic pressure gradient across the membrane was approximately 65 bar [4.12-4.13].

The FO process used in this study is shown in Figure 4-7. The membrane filtration cell was a Sterlitech CF042 acrylic filtration cell (Sterlitech Corporation, Kent, WA) modified for forward osmosis to allow for water to flow through rectangular channels on both sides of the membrane. The channel dimensions of 8.25 cm length and 5.1 cm height provided a total membrane area of 42 cm². The 0.1M sodium chloride feed solution flowed across the selective (dense layer) side of the membrane and the 2M ammonium bicarbonate draw solution across the permeate side of the membrane. Polypropylene mesh feed spacers were used in the channels to provide membrane support and to enhance turbulence and mass transport. Variable speed peristaltic pumps (Fischer Scientific) were used to pump the liquids in co-current flow and at equal flow rates. Due to the endothermic disassociation of ammonium bicarbonate, the draw solution was allowed to equilibrate to room temperature before the FO experiments were begun.
solution was continuously mixed during the equilibration period. Both the feed and draw solutions were run at room temperature for all experiments.

**Figure 4-7. Schematic of co-current flow forward osmosis system.**

This experimental set-up allowed for minimization of strain to the membrane as a result of unequal pressure across the length of the membrane; and to reduce the effect that additional parameters (temperature gradient, different fluid velocities, counter-current flow, etc.), other than concentration gradient, would have on the transport of feed solution across the membrane.
The initial experimental approach involved testing a 2M ammonium bicarbonate draw solution against feed solutions of 0.1M sodium chloride solutions, at both pH 7 and pH 10. The pH adjustments were made with concentrated sodium hydroxide solution. The flow rates of both the feed and draw solution were approximately 65 mL/min. The osmotic pressure gradient between the bulk feed and draw solutions was approximately 65 bar [4.12-4.13].

4.6 Transport Properties

4.6.1 Pressure Driven Dead-End Filtration

4.6.1.1 Pure Water Permeability

Pure water permeability testing was performed using an Amicon 8010 dead-end flow cell (Millipore, USA) (Figure 4-6) operated as a pressure-driven process. A feed of 10 ml of DI water was used for each test. A Fisher Scientific digital conductivity meter was used to test feed solutions to check if any contamination was present. A constant pressure of 70 psi was used in all tests. Each membrane was supported on a 0.1 μm SH magna nylon filter (Osmonics, Livermore, CA). In order to determine pure water permeability, samples were collected at regular intervals over a period of 10 hours. This process was repeated for the virgin, CMBA activated, and all membrane modifications. In order to obtain a standard deviation for the above-mentioned membranes, three separate membranes were tested for the virgin and modified samples.
4.6.1.2 Monovalent Salt Rejection

Monovalent salt rejection was tested using five solutions of varying sodium chloride concentration. Using a 100 mM stock solution of NaCl in DI water, solutions of 3.4, 10, 20, 35, and 100 mM were prepared as needed. The effects of pH were of interest, and samples of the above mentioned concentrations were tested at both pH 7 and pH 10. In order to obtain samples at pH 10, titrations were performed using 0.5 M sodium hydroxide.

Solutions were run through the dead-end cell (Figure 4-6) under the same conditions as used for the pure water permeability testing. Continuous stirring was maintained inside the cell just above the membrane to prevent salt build-up on the membrane surface. 10 mL samples were used for all initial feed volumes. To determine the salt rejection, conductivity readings of each feed solution was tested before sample collection. Two mL samples were collected and the conductivity of these samples measured. The apparent solute rejection R (%) was calculated using Equation 4.1. As with pure water permeability, three separate membranes for the virgin and each of the modifications was tested. For each membrane-concentration-pH combination, three two-mL samples were collected and tested.

4.6.2 Forward Osmosis Applications

4.6.2.1 Water Flux

Mass transport across the membrane was determined by measuring the weight change of the draw solution in one hour intervals over a five hour period. The weight of the draw
solution increases as water permeates across the membrane from the feed solution by way of osmosis. The water flux was calculated according to equation 4.2:

\[
J_w = \frac{\Delta w}{\rho \cdot A \cdot t}
\]

(4.2)

where \(J_w\) is the water flux (L m\(^{-2}\) hr\(^{-1}\)), \(\Delta w\) is the weight change of the draw solution over the given time period (g), \(\rho\) is the density (g L\(^{-1}\)), \(A\) is the area of the membrane (m\(^2\)), and \(t\) is the time period (hr).

### 4.6.2.2 Salt Permeability

Sodium chloride transport was determined by taking a sample of draw solution, after a complete FO run, and boiling the solution until the solvent had completely evaporated. The boiling process resulted in the decomposition of ammonium bicarbonate into ammonia and carbon dioxide gases \([4.14-4.15]\) leaving only sodium chloride and sodium hydroxide crystals remaining. The weight of the remaining crystals was measured after boiling, and the crystals were then diluted with a known volume of DI water after which the pH and conductivity were measured. The concentrations of sodium chloride solutions were measured with a conductivity meter. All solution pH values were measured with a Corning 430 glass pH-electrode and a pH meter (Corning, NY). Pure water permeability from the pressure driven processes at 4.82 bar were used for comparison.

In order to determine the true rejection of the chloride ion by the selective layer of the PBI membranes tested, a chloride selective electrode would be needed. However, since this was not available, a second approach involving calculating the sodium hydroxide
concentration from the pH measurements of the diluted salt solutions was used. The weight of the sodium hydroxide present was subtracted from the total weight of the dried salt permeate weighed before dilution. The weight of the sodium chloride sample could then be divided by the weight of the water permeate and presented as the weight fraction to be compared against the other membranes.
Chapter 5

Surface Functionalization of Polybenzimidazole Membranes to Increase Hydrophilicity and Charge

Abstract

Forward osmosis is the movement of water across a selectively permeable membrane. The driving force for water permeation through the membrane is the difference in osmotic pressure between the feed and draw solutions. Polybenzimidazole (PBI) is a material with excellent chemical resistance and high mechanical and thermal stability that is a promising material for forward osmosis separations. Drawbacks associated with the use of PBI as a membrane material for water treatment include low hydrophilicity and surface charge neutrality. In this study, PBI membranes were cast using the phase-inversion technique in the form of flat sheets, and membrane surfaces were functionalized using different modifying agents with the goal of increasing hydrophilicity and surface charge. The negative charge on the membrane surface was expected to yield an increased rejection of ions and of negatively charged particles in the feed solution, while increased hydrophilicity decreases fouling propensity. The surfaces of the membranes were activated with 4-(chloromethyl) benzoic acid (CMBA). The modifying agents selected for membrane functionalization included: taurine, para-phenylene diamine, and ethylene diamine. These modifying agents were selected for their potential
to impart a charge on the PBI membrane when in near neutral pH environments. Membranes were characterized using Fourier transform infrared spectroscopy in attenuated reflectance mode (FTIR-ATR), ζ potential, environmental scanning electron microscopy (ESEM), and contact angle measurements. Functionalization, surface charge, and increased hydrophilicity were all verified. Pure water permeability and salt rejection were tested for comparison between both virgin and modified membranes. Monovalent salt rejection was investigated using various sodium chloride feed concentrations, and a range of pH values.

5.1 Introduction

Forward osmosis (FO) is an emerging desalination process that is gaining favor as a substitute for currently used desalination methods. Pressure-driven processes, such as reverse osmosis (RO), have been the most common techniques for separating dissolved solutes from feed water for many decades [5.1]. Like RO, forward osmosis uses a semi-permeable membrane to allow for water separation. The water flux in a FO system varies from RO, however, in that the driving force for mass transport is the osmotic pressure gradient between the feed and draw solutions (generally a high concentration salt solution), as opposed to hydraulic pressure. The net flow of water through the membrane leads to a dilution of the draw solution and a concentration of the feed stream.

FO is in the early stages of application, and there are still major obstacles that need to be overcome before fully utilizing FO as a widely used water production technology. Such obstacles include a small number of commercially available FO membranes with proper separation performance, and lack of economically viable and user friendly draw
solutions. The lack of commercially available FO membrane materials stems from the fact that previously developed membrane materials were developed for pressure-driven applications, there is not a full understanding of transport behavior and fouling in FO processes, and ideal draw solutions are still being researched. Ideal FO membranes should have thinner support layers, have very low transport resistance to minimize internal concentration polarization, and enhance membrane permeability. Studies on water transport through FO membranes show that internal concentration polarization within the support layer significantly reduces membrane [5.2-5.5]. Therefore, thickness and transport resistance of the support layer plays a critical role in FO membrane performance, although the support layer properties do not affect the performance of RO/NF membranes. Nevertheless, most of the commercially available semi-permeable membranes, such as the widely used polyamide thin-film membranes, have very thick woven fabric supports that would restrict their application as FO membranes. The thickness of successful and commercially available FO membrane support layers as reported by Saren et al. [5.6] is between 40-90 µm for woven fabric supported membranes. This is much thinner than that of conventional thin film composite (TFC) RO membranes (~150 µm). The approach taken in this study is through functionalization of existing nanofiltration (NF) membranes to provide more ideal operating conditions. Functionalization involves chemically attaching a charged modifying agent on the surface of a membrane. The added functional group is expected to result in an increased rejection of monovalent salts (i.e. sodium chloride and potassium chloride).
Researchers in Singapore recently developed a hollow fiber nanofiltration (NF) FO membrane made of polybenzimidazole (PBI) [5.7]. PBI is a material with outstanding mechanical and thermal stability and chemical resistance. PBI membranes can generate high flux in FO processes [5.7-5.8] and thus is a very promising material for FO membrane development. The drawback, however, is the salt rejection of this membrane in the virgin stage is relatively low, and the membrane has a high hydrophobicity. If the PBI membrane surfaces can be modified to improve these flaws then PBI has the potential to become an economically viable FO membrane material. A recent study by Hausman et al. [5.9] focused on increasing the negative charge and hydrophilicity of PBI membranes using a very similar approach to the one presented here, with the main difference being that the functionalization of the membrane was achieved after a long and expensive procedure.

This study focused on functionalization of PBI surfaces to impart a surface charge and an increase in hydrophilicity using a less expensive and faster method for the surface modification. The objectives of this research were to cast flat sheet PBI membranes via the phase-inversion technique and to chemically modify the membrane surfaces. PBI membranes were activated using 4-(chloromethyl) benzoic acid (CMBA). N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCH) and N-hydroxysuccinimide (NHS) chemistry catalysis was used as an intermediate for reaction of the COOH group added from the CMBA activation with the desired modifying agent. The modifying agents (taurine, ethylene diamine, and para-phenylene diamine) were chosen based on their potential to impart a charge to the membrane surface in near
neutral pH environments. It was also expected that the overall hydrophilicity would increase and the increase in surface charge would lead to an increase in salt rejection.

Several analytical techniques were employed to verify that surface modification was successful. Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR) was used to detect changes based on specific functional groups associated with each of the modifying agents. \( \zeta \) potential measurements were taken to detect changes in the membranes surface charge. Environmental scanning electron microscopy (ESEM) was used to detect any changes in morphology of the membranes during and after modification. Determination of changes in hydrophilicity was examined by contact angle measurements using a goniometer.

Transport characteristics were evaluated for unmodified, CMBA surface activated, and all modified membranes. Dead-end flow permeability cells were used in a pressure-driven mode for verification of imparted characteristics. Pure water permeability along with monovalent (sodium chloride) salt rejection was determined for all membranes. In order to detect changes in salinity, the conductance of both the feed and the resulting permeate were tested using a conductivity meter.

5.2 Experimental

5.2.1 Materials

Polybenzimidazole dope was supplied by PBI Performance Products, Inc. (Charlotte, NC) as a 26 wt% solution. The chemistry used for all membrane modifications was described in detail in Chapter 4. All reagents were used as received. DI water was supplied by a continuous distillation apparatus.
5.2.2 PBI membrane preparation

All PBI flat sheet membranes were prepared in house. Polybenzimidazole dope was supplied at 26 wt% in a 72 wt% solution of dimethylacetamide (DMAc) with 2.0 wt% lithium chloride. The procedure used to prepare the membranes was adapted from Wang and Chung [5.10]. A desired concentration of 20 wt% was achieved by dilution with DMAc. In order to achieve uniform flat sheet membranes, and to prevent air bubbles from being trapped in the dope, the beaker was sealed with parafilm and placed in a sonicator on degas setting for approximately two hours. The dope was then spread in an even line across a well-cleaned mirror. A doctor's blade set at a thickness of 150 μm was used to push the dope across the mirror forming a thin flat sheet. In order to reduce friction between the blade and the mirror, the rails of the doctor’s blade were lubricated with motor oil. After the flat sheet was cast, the mirror and sheet were placed in a 12 gallon DI water coagulation bath to remove the solvent by way of the phase-inversion technique. The membrane peeled from the mirror when the phase-inversion process was complete. The membrane was thoroughly washed with DI water and one inch circles were punched for testing and modification. All membranes were stored in a 50/50 mixture of DI water and glycerol until used. The addition of glycerol was to ensure the membranes would stay wet during storage.
5.2.3 Membrane modification

5.2.3.1 CMBA membrane activation

The initial activation using CMBA [5.11] was performed as follows: in a 50-mL beaker, a 0.5 wt% solution of CMBA was prepared in acetone and stirred until the solute was completely dissolved. A separate 50-mL beaker, with 1.0 wt% sodium persulfate was prepared in DI water and stirred until the solute was completely dissolved. Sodium persulfate acted as a free radical initiator for the CMBA activation. The virgin membrane samples to be modified were added to the sodium persulfate solution. The CMBA/acetone solution was slowly added to the aqueous sodium persulfate solution. The slow addition was necessary to prevent the CMBA from precipitating from solution, since it is insoluble in water. The reaction procedure is given in Figure 5-1.

![Reaction Diagram]

**Figure 5-1.** CMBA activation of PBI virgin membrane.

There are two reactive –NH sites on the backbone of the PBI repeat unit. Both of the –NH sites are susceptible to reaction, but for simplification, reaction to one site will be
shown throughout the figures in this paper. The final volume was a 50/50 mixture of DI/acetone. The reaction mixture was sealed with parafilm, heated on a hot plate to 40 °C, and reacted for 24 hours. This temperature was selected to help keep the reagents in solution while minimizing acetone evaporation. No agitation was applied. After 24 hours, the sheets were removed and washed with acetone to remove any residual CMBA; then washed with copious amounts of DI water to remove any remaining sodium persulfate and acetone. Once thoroughly cleaned the sheets were stored in 50/50 DI water and glycerol solution.

5.2.3.2 EDCH and NHS chemistry

Hausman et al. [5.9] showed an effective technique to functionalize CMBA activated PBI membranes using N-ethyl-N(3-dimethylaminopropyl) carbodiimide (EDC) chemistry. A simpler approach using N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCH) and N-hydroxysuccinimide (NHS) (Figure 5-2) chemistry was the focus of this study. The EDCH/NHS method was favored over the EDC method because it allowed for a reduction in the reaction time and required chemical usage. EDCH facilitates the reaction between –COOH groups bound to the CMBA activated PBI backbone and the amine group of the functional modifying agents [5.12]. The EDCH/NHS reaction occurs with the carboxylic acid to form an unstable ester (Figure 5-3). The modifying agents (R in Fig. 5-3) included ethylene diamine, para-phenylene diamine, and taurine (Figure 5-4). The amount of reagent necessary for EDCH catalyzed modification depended on the final weight of dried surface activated samples (0.30–0.33 g). Subsequent modifications were performed in a 2-(N-morpholino) ethanesulfonicacid (MES) buffer solution.
Figure 5-2. EDCH and NHS molecular structures.

Figure 5-3. Two-step modification procedure (a) EDCH/NHS reaction with CMB activated PBI to form ester intermediate. (b) NHS ester intermediate reacted with modifying agent to form final functionalized membrane.
A buffer solution composed of 0.1 M MES and 0.5 M NaCl was prepared for all EDCH/NHS reactions. A stock solution was prepared, and titrated with 1 N NaOH to a pH of 6. The pH adjusted MES buffer was used to prepare a 0.002 M EDCH and 0.005 M NHS solution for the final surface modification. After the EDCH/NHS solution was prepared, the membrane sheets were added to the solution and mixed. After 15 minutes, 2-mercaptoethanol was added to the solution to quench the reaction for modifying agent addition. To optimize the conditions for reaction, the pH was adjusted to 7-7.5 with 1N NaOH before the desired modifying agent was added. From the molecular weight of CMBA modified sheets (442 g/mol) and the final weight of the samples to be modified, the weight of the modifying agent was determined. The final step involved an equal-molar addition of modifying agent to that of the CMBA modified samples. Then the reaction was stirred for two hours. Once the reaction was complete, copious amounts of DI water were used to wash the membranes. The final products are shown in Figure 5-5. It is also important to note that amphoteric compounds, such as taurine, usually require blocking of acid functionality to prevent internal salt formation and free amino-group, which was not done since the reaction proceeded as described. Membranes were stored in a 50/50 DI water and glycerol solution.
Figure 5-5. Final membrane modifications (a) Ethylene diamine modified PBI. (b) Phenylene diamine modified PBI. (c) Taurine modified PBI.
5.2.4 Membrane characterization

5.2.4.1 Fourier transform infrared spectroscopy (FTIR-ATR)
Evidence that the PBI was successfully modified was obtained using Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR). FTIR uses measurements of vibrational spectra to identify the chemical structure of materials. By monitoring the vibrational spectra changes, molecular conformation can also be observed. FTIR analysis was obtained on a Varian Excalibur Series Fourier Transform Infrared instrument, the FTS-4000 Spectrometer and the UMA-600 Microscope (Randolph, MA).

5.2.4.2 ζ potential
Surface charge was analyzed by measuring the zeta potential on the membrane surface. Samples were measured using an electrokinetic analyzer (BI-EKA, Brookhaven Instrument Corp., Holtsville, NY) which was located at Volodymyr Tarabara's laboratories at Michigan State University, East Lansing, MI. Before analysis, membranes were rinsed with copious amounts of DI water to remove any residual glycerol from the storage solution. The KCl electrolyte solution used in these measurements had an ionic strength of 1.0 mM. The pH values for the various readings were adjusted using 0.5 M NaOH and 0.5 M HCl solutions [5.13].

5.2.4.3 Environmental scanning electron microscopy (ESEM)
ESEM was used to detect the impact of surface modification of the membranes, as well as verify thickness of the cast virgin membrane. An FEI Quanta 3D FEG Dual Beam Electron Microscope (FEI, USA) was used to test the samples. By freezing small
samples of the membranes in liquid nitrogen and cracking them, smooth cross-sectional areas could be observed. After the samples were frozen and cracked, they were wet using DI water, and placed vertically in carbon paste. ESEM was advantageous in this case over SEM (scanning electron microscope) because it was important to test wet samples. In aqueous environment, PBI membranes are strong and flexible. When allowed to dry, PBI becomes very brittle and susceptible to breaking.

5.2.4.4 Contact angle

A goniometer was used to monitor the changes in the hydrophilicity of the modified membranes over that of the virgin sample. A Tantec Model CAM-MICRO Contact Angle Meter (Tantec, Inc., USA) was used. By placing a small drop of water onto the surface of the sample, the angle of the resulting water bead can be determined. In samples that are hydrophobic the water droplet beads up and the angle remains high. Successful functionalization of the membrane surface results in an increase in hydrophilicity, thus a decrease in the water bead contact angle.

5.2.5 Transport properties

5.2.5.1 Pure water permeability

Pure water permeability testing was performed using an Amicon 8010 dead-end flow cell (Millipore, USA) run as a pressure-driven process, as shown in Figure 5-6. A feed of 10 ml of DI water was used for each test. A Fisher Scientific digital conductivity meter was used to test feed solutions to check if any contamination was present. A constant pressure of 70 psi was used in all tests. Each membrane was supported on a 0.1 μm SH
magna nylon filter (Osmonics, Livermore, CA). In order to determine pure water permeability, samples were collected at regular intervals over a period of 10 hours. This process was repeated for the virgin, CMBA activated, and all membrane modifications. In order to obtain a standard deviation for the above-mentioned membranes, three separate membranes were tested for the virgin and modified samples.

![Schematic of dead end cell.](image)

**Figure 5-6.** Schematic of dead end cell.

### 5.2.5.2 Monovalent salt solutions for testing

Monovalent salt rejection was tested using five solutions of varying sodium chloride concentration. Using a 100 mM stock solution of NaCl in DI water, solutions of 3.4, 10, 20, 35, and 100 mM were prepared as needed. The effects of pH were of interest, and samples of the above mentioned concentrations were tested at both pH 7 and pH 10. In order to obtain samples at pH 10, titrations were performed using 0.5 M sodium hydroxide.

Solutions were run through the dead-end cell (Figure 5-6) under the same conditions as used for the pure water permeability testing. Continuous stirring was maintained inside
the cell just above the membrane to prevent salt build-up on the membrane surface. 10 mL samples were used for all initial feed volumes. To determine the salt rejection, conductivity readings of each feed solution was tested before sample collection. Two mL samples were collected and the conductivity of these samples measured. As with pure water permeability, three separate membranes for the virgin and each of the modifications was tested. For each membrane-concentration-pH combination, three two-mL samples were collected and tested.

5.3 Results and Discussion

5.3.1 Membrane characterization

5.3.1.1 Fourier transform infrared spectroscopy (FTIR)

The FTIR-ATR spectrum of PBI is characterized by several typical peaks (Figure 5-7 and Table 5.1) as reported by previous researchers [5.14-5.19]. The FTIR spectrum for the virgin PBI samples and all the functionalized membrane samples is described in detail in Hausman et al [5.9]. The EDCH/NHS modification technique used in this research yielded the same quality of FTIR data as reported in [5.9], for the EDC chemistry technique used for the membrane modifications.

In summary, the most obvious verification of the success of this modification technique can be seen by the appearance of peak 1 on the CMBA curve, and then the disappearance of peak 1 for all the modified membrane curves. The presence of this peak is due to the C-O bond from the carboxylic functional group added during CMBA modification. This bond is then removed during the final modification step where the primary amine of the modifying agent is reacted with the carboxylic group of the activated surface.
Figure 5-7. FTIR results for the virgin and all modifications.

Table 5.1. FTIR functional group location (data obtained from Hausman et al. [5.9]).

<table>
<thead>
<tr>
<th>Number</th>
<th>Functional group</th>
<th>Wave number (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C–O</td>
<td>1057</td>
</tr>
<tr>
<td>2</td>
<td>C=O</td>
<td>1620–1640</td>
</tr>
<tr>
<td>3</td>
<td>OH</td>
<td>~ 2670</td>
</tr>
<tr>
<td>4</td>
<td>Secondary amine N–H</td>
<td>1645</td>
</tr>
<tr>
<td>5</td>
<td>Primary amine NH$_2$</td>
<td>1645</td>
</tr>
<tr>
<td>6</td>
<td>S=O</td>
<td>1215</td>
</tr>
<tr>
<td>7a</td>
<td>SO$_2$ (symmetrical)</td>
<td>1168</td>
</tr>
<tr>
<td>7b</td>
<td>SO$_2$ (anti-symmetrical)</td>
<td>1285</td>
</tr>
</tbody>
</table>
5.3.1.2 ζ potential

The change in surface charge was determined by finding the ζ potential of all the membranes surfaces as reported in Hausman et al. [5.9]. The virgin membrane samples were mostly comprised of neutral and slightly positive charges. ζ potential results are plotted against various pH values in Figure 5-8. All modifying agents used during the final modification step led to an overall increase in the charge of the modified membrane surfaces. These results agree with the research expectations, since all modifying agents were chosen for their ability to impart a charge on the membrane surface.

Figure 5-8. ζ potential vs. pH for virgin, CMBA activated, and all final membrane modifications (figure and data obtained from Hausman et al. [5.9]).
5.3.1.3 Environmental scanning electron microscopy (ESEM)

As shown in Figure 5-9, the cross-sectional SEM image of a fractured PBI membrane shows the overall thickness of the membranes used was actually 170 μm. From the figure, the thin selective layer (the top of the membrane) and thicker support layer were observed. This is characteristic of an asymmetric membrane, and is evidence that the phase-inversion process was successful.

![SEM image of virgin membrane](Image)

**Figure 5-9.** SEM image of virgin membrane.

5.3.1.4 Contact angle

Contact angle measurements for the virgin, CMBA activated, and all final modifications are shown in Figure 5-10. The hydrophilicity of the membrane surfaces increased for all the final modifications. The taurine functionalized PBI membranes were shown to have the largest increase in hydrophilicity. This was most likely due to its greater ability to
hydrogen bond. The sulfonic acid group associated with taurine contains three oxygen groups, two of which contain two pairs of free electrons and the third with the ability to form salts (i.e. move into an ionic state). The ethylene diamine modification was shown to have the least increase in hydrophilicity which was expected due to its structure. Ethylene diamine is an aliphatic amine, and it offers little in the ability to increase hydrogen bonding. The increased hydrophilicity was most likely due to the amine group, which contains one pair of free electrons and also has the ability to hydrogen bond.

Figure 5-10. Contact angle measurements for virgin and all modified membranes.
5.3.2 Transport properties

5.3.2.1 Pure water permeability

As shown in Figure 5-11, the pure water permeability (PWP) decreased following surface modification. After surface activation with CMBA, the average permeability decreased by approximately 33% relative to the virgin membrane samples. For each of the final membrane modifications, the permeability measurements dropped approximately 70% relative to the virgin PBI membranes. The average pure water permeability of the flat sheet virgin, CMBA activated, taurine, ethylene diamine, and p-phenylene diamine samples were 3.67, 2.59, 1.21, 1.20, and 1.16 L m$^{-2}$ bar$^{-1}$ h$^{-1}$ respectively. Lv et al. [5.8] reported PBI nanofiltration FO hollow fiber membranes can produce PWP values of 1.86 L m$^{-2}$ bar$^{-1}$ h$^{-1}$ and other studies have also reported significant losses of membrane permeability after surface modifications with modifying agent additions [5.20 –5.27].
Figure 5-11. Pure water permeability readings in an Amicon 8010 dead-end flow cell at 70 psi.

5.3.2.2 Monovalent salt rejection

Figure 5-12 shows the results for monovalent salt rejection for the virgin, CMBA activated, and all final membrane modifications. Monovalent salt rejection increased for all membrane modifications. Though taurine has a larger negative dipole moment associated with the two pi bonded oxygen groups containing free electrons, in addition to the hydroxyl group, at pH 7 (Figure 5-12 (a)), para-phenylene diamine had the highest salt rejection for lower concentrations.
As the salt concentration increased, the rejection stabilized, and there was no significant difference in the final percent rejected among the modified membranes. Salt rejection via charge exclusion is only effective at low ionic strengths where monovalent and divalent cations do not screen the negative charge of the membrane surface [5,28]. This is consistent with the results presented here. The rejection of the salts drops as a function of increasing ionic strength. Previous studies [5,29] have shown similar results where by increasing hardness, ionic strength, or hydrogen ions (pH), the surface charge of the membrane was masked.

When the pH of the feed stream was increased to 10, the salt rejection for all membranes increased (Figure 5-12 (b)). The taurine-modified membrane showed the highest rejection values at lower concentration, but the difference from the other modifications was not as significant as that seen at pH 7. Once again, as the concentration increased, the percent rejection stabilized and there was less of a difference. There was only a small increase in the percent rejection of the phenylene diamine from pH 7 to pH 10, but there was a significant increase for taurine functionalized membranes over the same pH range.
To evaluate the effects of the modifications further, the salt permeability coefficients ($B$) ($L \cdot m^{-2} \cdot hr^{-1}$) were determined during 3.4mmol salt rejection studies using equation 5.1. This technique for calculating the salt permeability coefficient has been reported by

Figure 5-12. Sodium chloride rejection at (a) at pH 7 (b) at pH 10
previous researchers [5.6, 5.30] for a pressure driven process similar to the one used in this study.

\[ R = \left( 1 + \frac{B}{A(\Delta P - \Delta \Pi)} \right)^{-1} \] (5.1)

Where \( R \) = salt rejection, \( A \) = water permeability (L m\(^{-2}\) hr\(^{-1}\) bar\(^{-1}\)), \( \Delta P \) = pressure difference (bar), and \( \Delta \Pi \) = osmotic pressure difference (bar). The salt permeability coefficients (B) are plotted against absolute value zeta potentials for the three final membrane modifications in Figure 5-13. The PWP significantly decreases as the membrane modification process takes place. The average permeability decreased by approximately 33\% for the activated membranes, and for each of the final membrane modifications the permeability measurements dropped approximately 70\% relative to the virgin PBI membranes. Since all three final surface modifications showed increases in hydrophilicity over the virgin membranes, this PWP decrease is believed to be largely attributed to the change in membrane pore sizes resultant of the larger repeat unit of the PBI backbone for the modified surfaces. Due to the predicted change in pore size, and the significant reductions in PWP readings, comparisons can only be made between the final modifications. The PWP values for all three final modifications were very close to one another so it is believed that the membranes should be similar enough to warrant comparison by way of this technique. The data for each individual membrane can also be compared over different pH values to see the effects of zeta potential on the salt permeability coefficient. As expected, salt permeability coefficients decreased with modifications and with increasing pH.
Figure 5-13. ζ potential readings vs. salt permeability coefficients for the three final membrane surface modifications.

From the plot of salt permeability coefficient vs. zeta potential it seems that the rejection of NaCl is related more by the decrease in pore size than from the differences in zeta potential. It is important to note however, that for all three surface modifications the values of B decrease as the absolute values of the zeta potentials increase. When the membranes are compared to one other the zeta potential readings don’t seem to be the sole contributor to the increase in salt rejection. The decrease in the salt permeability coefficients from the reduced poor size can be attributed to the size of the aromatic ring in the p-phenylene diamine and the sulfonate group in the taurine molecules versus the much smaller ethylene diamine molecule.
5.4 Conclusions

Flat sheet polybenzimidazole membranes were successfully cast, CMBA activated, and modified. ESEM images verified that the membranes were in fact asymmetric with an acceptable thickness proportional to the doctor’s blade setting. From the FTIR spectra, there was clear evidence that surface activation and modification took place, which verified that the modification method proposed by this study is effective. An increase in hydrophilicity showed successful completion of one of the research objectives and was a further means of verification of modification. ζ potential analysis showed an overall increase in surface charge. This also verified chemical modification, and the successful achievement of the other research objective, to increase surface charge. Pure water permeability results showed a significant decrease with the CMBA activation and the final modifications. Sodium chloride rejection decreased exponentially as the feed concentration increased for all modifications, as well as the virgin membrane. Modified membranes always showed higher rejections than virgin membranes. This trend was seen at both feeds of pH 7 and pH 10.

The study presented here shows preliminary characterization data on the effectiveness of surface modifications to PBI membranes in rejecting salts. Future research will involve testing the virgin and modified PBI membranes in forward osmosis mode. The rejection of the NaCl at higher ionic strengths by the modified membranes was still low, which would not be effective for FO systems at this time. The study presented here was a proof-of-concept of the ability for functionalization to increase salt rejection. Ongoing and
future studies will focus on optimizing the membranes (for instance by increasing dope concentrations to make tighter membranes) and draw solutions for the FO process.

5.5 Acknowledgements

The authors would like to acknowledge grant NSF OISE 0832894 that supported the development of the collaboration on PBI FO research between The National University of Singapore and The University of Toledo. PBI Performance Products, Inc. (Charlotte, NC) is thanked for supplying PBI dope for the study. Professor Volodymyr Tarabara (Michigan State University) is also thanked.
Chapter 6

Novel Charged and Hydrophilized Polybenzimidazole (PBI) Membranes for Forward Osmosis

Abstract

Polybenzimidazole (PBI) is a material with excellent chemical resistance, and thermal and mechanical stability. However, significant drawbacks of PBI that prevent its use as a membrane for water purification applications include hydrophobicity and neutral surface charge at neutral pH values. Surface functionalization was investigated as a means to circumvent these drawbacks by modifying PBI membranes to increase hydrophilicity and surface charge. The modifying agents used for functionalization included: p-phenylene diamine, ethylene diamine, taurine, and poly(acrylamide-co-acrylic acid). Functionalized asymmetric flat sheet PBI membranes were investigated in forward osmosis (FO) applications. The FO process involved semi-permeable flat sheet membranes with an ammonium bicarbonate draw solution and a sodium chloride feed solution. The functionalized membrane surfaces exhibit increased hydrophilicity, surface charge, and reduced pore sizes. Additionally, all membrane modifications show increased water permeability and a reduction in sodium chloride transport.
6.1 Introduction

Forward osmosis (FO) is a technology that shows great potential as an alternative to current desalination techniques. The most attractive features of a FO membrane system include lower operational cost and less energy requirement. Unlike reverse osmosis (RO), that uses hydraulic pressure to create the driving force of water permeation, FO processes use an osmotic pressure gradient between the feed and draw solutions to create the driving force across a semi-permeable membrane. Water flows through the membrane, concentrating a saline feed solution, and diluting a draw solution of much higher osmotic pressure.

While emphasis has been placed on developing FO processes recently [6.1], two main drawbacks still exist. Most commercially available membranes were designed for RO processes and have proven to be less than ideal for FO systems. RO membranes are built on thick fabric support layers that suffer high levels of internal concentration polarization, significantly reducing membrane flux [6.2]. The second drawback involves finding an economically viable and easily separable draw solute. Many draw solutes have been examined as possible candidates for FO processes including: ammonium bicarbonate, calcium chloride, potassium bicarbonate, magnesium chloride, magnesium sulfate, and sodium bicarbonate [6.1, 6.3-6.4]. Ammonium bicarbonate was chosen as the draw solution solute for this study due to its ease of separation to allow for feed solute rejection studies [6.5-6.6].

To address the issue of finding a suitable membrane material for FO processes, researchers in Singapore recently developed a PBI nanofiltration (NF) hollow fiber
membrane [6.7-6.8]. PBI is a polymer that exhibits high mechanical strength, thermal stability, and chemical resistance [6.9-6.10]. Through use of the phase inversion technique, asymmetric PBI membranes were formed yielding high water fluxes but low monovalent salt rejection [6.7-6.8].

PBI nanofiltration membranes from these studies showed amphoteric behavior with desirable water flux and high rejection of divalent ions. Rejection of ionic species was found to be highly dependent on the solution pH. pH values determine the phases and sizes of the ionic species, in addition to the surface charge characteristics of the PBI membrane [6.7-6.8]. It was also shown through surface modification of the PBI membranes that the rejection of aqueous solutes is highly dependent on both the membrane pore size and electrostatic interaction between the solute and membrane. Analysis of virgin and modified PBI membranes in pressure driven systems with single electrolyte solutions at various pH values showed a decrease in solute permeability with modification at neutral pH values, with increasingly higher rejection as the pH increased and the membranes took on higher surface charges [6.11-6.13].

In an attempt to enhance the properties of the PBI membranes, the authors have recently demonstrated that asymmetric flat sheet PBI membranes could successfully be cast, and functionalized, using several different modifying agents [6.12-6.13]. The previous study used 4-(chloromethyl) benzoic acid (CMBA) for an activation step and p-phenylene diamine (PD), ethylene diamine (ED), and taurine to functionalize the membrane surface. All three modifications resulted in increases in hydrophilicity and membrane surface charge. Additionally, it was hypothesized that the modifications led to decreases in the
mean pore size over that of the virgin sample. Previous research with PBI membranes chemically modified with p-xylylene has shown that modification could successfully decrease membrane pore size in the selective layer to a molecular level \[6.11\]. Modification with p-xylylene \[6.11\] involves a similar reaction to the activation step with CMBA \[6.12-6.13\] described previously by the authors, but has two reactive chloride groups that result in cross-linking of the PBI chains.

Recent studies have indicated that improvements in the wetting of a membrane surface can be critical in improving the membranes water permeability \[6.14\]. Lack of sufficient wetting exacerbates internal concentration polarization and disrupts continuity of water throughout the membrane structure. Decreased water continuity within the internal membrane pathways reduces the effective porosity, thus reducing water transport. This study \[6.14\] showed that by RO pretreating membranes used in FO application, or through addition of surfactants to the solutions used in the FO process, water permeability could be increased due to the enhanced wetting effect, and subsequent removal of air and vapor trapped in the porous selective layer of the membrane. Each of these techniques affected the various layers of the membrane differently depending on the structure and hydrophobicity of the layer. If the membrane surface is modified to be more hydrophilic, then the wetting effect of the membrane surface can be enhanced.

The focus of this study was to investigate the performance of the functionalized flat sheet PBI membranes in a forward osmosis application. The functionalization of membranes studied included the three modifying agents used previously, and an additional fourth modifying agent, poly(acrylamide-co-acrylic acid). Poly(acrylamide-co-acrylic acid)
(PAcA) was selected for this study due to its ability to crosslink with the activated PBI membrane and because of its natural properties in aqueous environments. PAcA has both amino (-NH$_2$) and carboxyl (-COOH) functional groups (1-2% acrylic acid groups) that can either protonate or deprotonate based on the solution pH, and it is incredibly hydrophilic in nature [6.15-6.17]. A summary schematic of the two-step chemical modification procedure is shown in Figure 6-1. This figure, divided by the two arrows, shows the structures of the virgin PBI repeat unit, the repeat unit of the CMBA activated PBI, and the repeat unit after the final modification step. For simplicity, the modification of the PBI repeat unit is only shown at one of the secondary amines for one of the imidazole rings. This reaction could take place at both imidazole rings for the repeat units on the membranes surface.

Figure 6-1. Chemistry for two-step modification procedure.
6.2 Materials and Methods

6.2.1. Chemicals

All chemistry required for PBI membrane casting, preparation, and surface modification used in this study has been described previously [6.12-6.13]. PBI dope was supplied by PBI Performance Products, Inc. (Charlotte, NC) as a 26 wt% solution. Ammonium bicarbonate, poly(acrylamide-co-acrylic acid), all poly(ethylene glycol) solutes, and sodium chloride were purchased from Sigma-Aldrich (USA). Glycerol, glucose, sucrose, and raffinose were purchased from Fisher Scientific (USA). DI water was supplied by a continuous distillation apparatus.

6.2.2. Feed and draw solutions

For all experiments the draw solution used was a 2M ammonium bicarbonate (NH₄HCO₃) solution made by dissolving reagent grade ammonium bicarbonate in DI water. The feed solutions for all experiments consisted of a 0.1M sodium chloride (NaCl) solution. The osmotic pressure gradient across the membrane was approximately 65 bar [6.1, 6.3].

6.2.3. Polybenzimidazole forward osmosis membranes

All PBI membranes were cast and modified in house. The casting and two-step modification procedure has been previously described [6.12-6.13]. In summary, the PBI flat sheet membranes were cast at 150 µm with a doctor’s blade and formed by way of the phase inversion technique. The selective layer thickness was found to be
approximately 8 µm. After formation, the surface was activated by way of reaction between the highly reactive chloride of the CMBA molecule and the secondary amine in the imidazole ring of the repeat unit in the PBI backbone. The second step involved subsequent modifications performed in a 2-(N-morpholino) ethanesulfonic acid (MES) buffer at pH 6 using N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCH) and N-hydroxysuccinimide (NHS) chemistry. Figure 6-2 shows a cross-sectional view of the asymmetric virgin PBI flat sheet membrane taken by environmental scanning electron microscopy (ESEM). An FEI Quanta 3D FEG Dual Beam Electron Microscope (FEI, U.S.A.) was used to image the sample.

Figure 6-2. SEM image of the asymmetric PBI flat sheet membrane cross-section.
6.2.4. Membrane characterization

6.2.4.1. FTIR, contact angle, and zeta potential

The PBI membranes used in this study have previously been characterized by Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR), contact angle, and zeta potential measurements [6.12-6.13]. FTIR analysis was obtained on a Varian Excalibur Series Fourier Transform Infrared instrument, the FTS-4000 Spectrometer and the UMA-600 Microscope (Randolph, MA). Contact angle was determined using a Tantec Model CAM-MICRO Contact Angle Meter (Tantac, Inc., U.S.A.). Surface charge values were compared from zeta potential readings taken from previous studies [6.13] for the membranes modified with the chemistries presented here. Samples were measured using an electrokinetic analyzer (BI-EKA, Brookhaven Instrument Corp., Holtsville, NY), located at Michigan State University. These techniques have shown the effects of PBI surface functionalization on membrane chemistry, hydrophilicity and surface charge [6.12-6.13].

6.2.4.2. Pore size determination

Total organic carbon (TOC) analysis was used to determine the pore sizes of the membranes developed. Concentrations of the solute solutions used for pore size determination were measured with a Tekmar-Dohrmann, Phoenix 8000 UV-persulfate TOC Analyzer (Tekmar Company, OH). The approach involved introducing feed solutions containing uncharged solutes (Table 6.1) of various Stokes-Einstein radii to the selective layer of the PBI membranes in an Amicon 8010 dead-end filtration cell
(Millipore, USA). All experiments were performed as single solute permeation runs.
The diluted permeate and original feed solutions were sampled in the TOC to determine solute rejection. The apparent solute rejection $R$ (%) was calculated by Equation 6.1:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\%$$  \hspace{1cm} (6.1)

where $C_p$ and $C_f$ are the solute concentrations in the permeate and feed solutions, respectively. The uncharged solute samples are shown in Table 6.1 along with their Stokes-Einstein radii [6.7, 6.15]. Nonionic molecules have been used to determine membrane pore sizes by previous researchers [6.7, 6.11, 6.18-6.20] and a similar procedure was followed for this study.

Table 6.1. Molecular weights and Stokes-Einstein radii of neutral solutes for pore size determinations.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Mw</th>
<th>Stokes radii</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g mol$^{-1}$)</td>
<td>(nm)</td>
</tr>
<tr>
<td>Glycerol</td>
<td>92</td>
<td>0.26</td>
</tr>
<tr>
<td>Glucose</td>
<td>180</td>
<td>0.37</td>
</tr>
<tr>
<td>Sucrose</td>
<td>342</td>
<td>0.47</td>
</tr>
<tr>
<td>Raffinose</td>
<td>504</td>
<td>0.58</td>
</tr>
<tr>
<td>PEG</td>
<td>600</td>
<td>0.61</td>
</tr>
<tr>
<td>PEG</td>
<td>1000</td>
<td>0.80</td>
</tr>
<tr>
<td>PEG</td>
<td>2000</td>
<td>1.41</td>
</tr>
<tr>
<td>PEG</td>
<td>4600</td>
<td>1.75</td>
</tr>
<tr>
<td>PEG</td>
<td>8000</td>
<td>2.31</td>
</tr>
</tbody>
</table>
200 ppm solutions were made of each individual solute in DI water. Each separation experiment involved permeation of a single solute in a pressure driven dead-end flow cell at 4.82 bar. Every membrane-solute combination was repeated three times so the average value could be calculated. The rejection values for all solutes were used to determine the mean effective pore size and the molecular weight cut-off (MWCO) for each membrane modification. The MWCO of a membrane is the molecular weight of the solute that is 90% retained by the membrane [6.18].

6.2.5. Forward osmosis operational set-up

The FO process used in this study is shown in Figure 6-3. The membrane filtration cell was a Sterlitech CF042 acrylic filtration cell (Sterlitech Corporation, Kent, WA) modified for forward osmosis to allow for water to flow through rectangular channels on both sides of the membrane. The channel dimensions of 8.25 cm length and 5.1 cm height provided a total membrane area of 42 cm². The 0.1M sodium chloride feed solution flowed across the selective (dense layer) side of the membrane and the 2M ammonium bicarbonate draw solution across the permeate side of the membrane. Polypropylene mesh feed spacers were used in the channels to provide membrane support and to enhance turbulence and mass transport. Variable speed peristaltic pumps (Fischer Scientific) were used to pump the liquids in co-current flow and at equal flow rates. Due to the endothermic disassociation of ammonium bicarbonate, the draw solution was allowed to equilibrate to room temperature before the FO experiments were begun. The
solution was continuously mixed during the equilibration period. Both the feed and draw solutions were run at room temperature for all experiments.

Figure 6-3. Schematic of co-current flow forward osmosis system.

This experimental set-up allowed for minimization of strain to the membrane as a result of unequal pressure across the length of the membrane; and to reduce the effect that additional parameters (temperature gradient, different fluid velocities, counter-current flow, etc.), other than concentration gradient, would have on the transport of feed solution across the membrane.
The initial experimental approach involved testing a 2M ammonium bicarbonate solution against feed solutions of 0.1M sodium chloride solutions, at both pH 7 and pH 10. The pH adjustments were made with concentrated sodium hydroxide solution. The flow rates of both the feed and draw solution were approximately 65 mL/min. The osmotic pressure gradient between the bulk feed and draw solutions was approximately 65 bar [6.1, 6.3].

6.2.6. Transport properties

Mass transport across the membrane was determined by measuring the weight change of the draw solution in one hour intervals over a five hour period. The weight of the draw solution increases as water permeates across the membrane from the feed solution by way of osmosis. The volumetric increase divided by the membrane area and the selected time period gives the water flux.

Sodium chloride transport was determined by taking a sample of draw solution, after a complete FO run, and boiling the solution until the solvent had completely evaporated. The boiling process resulted in the decomposition of ammonium bicarbonate into ammonia and carbon dioxide gases [6.5-6.6] leaving only sodium chloride and sodium hydroxide crystals remaining. The weight of the remaining crystals was measured after boiling, and the crystals were then diluted with a known volume of DI water after which the pH and conductivity were measured. The concentrations of sodium chloride solutions were measured with a conductivity meter. All solution pH values were measured with a Corning 430 glass pH-electrode and a pH meter (Corning, NY). Pure water permeability from a pressure driven process at 4.82 bar was reported previously by the authors [6.12-6.13] and were used for comparison.
In order to determine the true rejection of the chloride ion by the selective layer of the PBI membranes tested, a chloride selective electrode would be needed. However, since this was not available, a second approach involving calculating the sodium hydroxide concentration from the pH measurements of the diluted salt solutions was used. The weight of the sodium hydroxide present was determined and subtracted from the total weight of the dried salt permeate weighed before dilution. The weight of the sodium chloride sample could then be divided by the weight of the water permeate and presented as the weight fraction to be compared against the other membranes.

6.3 Results and Discussion

6.3.1. Membrane characterization

6.3.1.1. FTIR

The FTIR-ATR spectrum for PBI and the functionalized membranes (Figure 6-4 and Table 6.2) is described in detail in Hausman et al [6.13] and in Chapter 5 for the modifications using ED, PD, and taurine. PAcA modification is confirmed by the C=O band around 1620cm⁻¹, the band around 1645cm⁻¹ associated with the N-H and NH₂ bonds, and the alkane stretch around 2900cm⁻¹. The use of this technique verified the successful modification for the CMBA surface activation and for each of the final membrane modifications.
Figure 6-4. FTIR results for all membrane samples.
Table 6.2. FTIR functional group location.

<table>
<thead>
<tr>
<th>Number</th>
<th>Functional group</th>
<th>Wave number (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C–O</td>
<td>1057</td>
</tr>
<tr>
<td>2</td>
<td>C=O</td>
<td>1620–1640</td>
</tr>
<tr>
<td>3</td>
<td>OH</td>
<td>(\sim 2670)</td>
</tr>
<tr>
<td>4</td>
<td>Secondary amine N–H</td>
<td>1645</td>
</tr>
<tr>
<td>5</td>
<td>Primary amine NH(_2)</td>
<td>1645</td>
</tr>
<tr>
<td>6</td>
<td>S=O</td>
<td>1215</td>
</tr>
<tr>
<td>7a</td>
<td>SO(_2) (symmetrical)</td>
<td>1168</td>
</tr>
<tr>
<td>7b</td>
<td>SO(_2) (anti-symmetrical)</td>
<td>1285</td>
</tr>
<tr>
<td>8</td>
<td>Alkane stretch C-H</td>
<td>2850-3000</td>
</tr>
</tbody>
</table>

6.3.1.2. Zeta potential

In previous studies [6.12-6.13] using the modification technique discussed here the final surface modifications for p-phenylene diamine, ethylene diamine, and taurine showed more charged surfaces than the virgin PBI membranes. The addition of poly(acrylamide-co-acrylic acid) for use in this study is expected to yield an even higher surface charge than the other modifications. PAcA has both amino (-NH\(_2\)) and carboxyl (-COOH) functional groups that can either protonate or deprotonate based on the solution pH. In this study the pH of the feed and draw solutions for all runs equilibrated to approximately 8.3. At this pH value it is expected the carboxyl groups on the PAcA membranes would be deprotonated to a significant degree (isoelectric point around 4.75) [6.15-6.16]. A
membrane with a negative surface charge is expected to have a high rejection of anionic species in the feed solution.

6.3.1.3. Contact angle

Contact angle measurements for the virgin, CMBA activated, and all final modifications are shown in Figure 6-5. The hydrophilicity increased for all membrane modifications.

Figure 6-5. Contact angle measurements for all membrane samples.
Table 6.3 shows the mean pore radius, the molecular weight cut-off, and the pore radius where the molecular weight cut off is reached. All the data shown in this table is discussed in more detail in Appendix A. The effective mean pore sizes of all virgin and modified membranes fall in the nanofiltration range (0.5-2 nm in diameter) [6.7]. The effective mean pore radius of the unmodified membrane was 0.61 nm.

**Table 6.3. Pore size data**

<table>
<thead>
<tr>
<th></th>
<th>Virgin</th>
<th>CMBA</th>
<th>ED</th>
<th>PAcA</th>
<th>Taurine</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean radii (nm)</td>
<td>0.61</td>
<td>0.45</td>
<td>0.38</td>
<td>0.41</td>
<td>0.37</td>
<td>0.33</td>
</tr>
<tr>
<td>MWCO (Da)</td>
<td>7977</td>
<td>4161</td>
<td>1994</td>
<td>1399</td>
<td>1287</td>
<td>886</td>
</tr>
<tr>
<td>MWCO radii (nm)</td>
<td>2.31</td>
<td>1.66</td>
<td>1.14</td>
<td>0.95</td>
<td>0.91</td>
<td>0.75</td>
</tr>
</tbody>
</table>

From Table 6.2 it is observed that every membrane modification showed a reduced pore size over that of the virgin. Additionally, all the final modifications showed reduced pore sizes over the CMBA activated. The ED membrane had a smaller mean pore size than the PAcA but a larger MWCO. This is believed to be attributed to the large size (M\(_w\) = 5,000,000) and cross-linking ability of the PAcA. If the large PAcA molecules are bonding to multiple sites across the membrane surface in random order, the effects of steric exclusion are expected to be more pronounced on larger solutes [6.18-6.20]. As expected the taurine and PD molecules resulted in smaller pore sizes than the ED. They also showed smaller pore sizes than the PAcA. The smaller pore sizes of the PD and taurine modifications over the PAcA are believed to due to the smaller size of these modifying agents. The PD and taurine are small enough to permeate the pores of the activated membrane and react to a greater degree than the PAcA. The large size of the
PACa molecules restricts them from penetrating into the membranes pores. The effective mean pore size and MWCO for each membrane sample was calculated from a polynomial equation of the third degree (an example discussing this approach is shown in Appendix A). The typical rejection curves for uncharged solutes (Table 6.1) followed s-shaped rejection curves [6.18] that were analyzed with polynomial trendlines.

6.3.2. Forward osmosis flux results

While water permeability through all the modified membranes was lower than that of the virgin membranes in pressure-driven mode (Figure 6-6), water permeability through all modified membranes was greater than permeability through the virgin membranes in FO mode (Figure 6-7). Figure 6-7 shows the results of the FO flux data measured for all the membranes where the starting pH of the feed was 7. Each membrane modification was run three separate times to determine average membrane flux values. Relating this to the pure water flux data obtained for the process driven by hydraulic pressure, (pressure-driven nanofiltration process, Figure 6-6), it was observed that the behavior of the membranes was reversed. In the pressure-driven process [6.12-6.13], the driving force for water permeation was the hydraulic pressure (4.82 bar) applied to the membrane. In the pressure driven process, the primary resistance to water flux stemmed from the membrane morphology: mean pore size, pore size distribution, tortuosity, membrane thickness, etc. The CMBA pure water flux was found to be approximately 30% lower than the virgin membrane flux and the modified samples were all found to be 50-60% lower than the CMBA, or 65-75% lower than the virgin.
Figure 6-6. Flux data for all membranes in pressure driven system.

Figure 6-7. Flux data for all membranes in FO system
The results of the FO experiments were the reverse of those in the pressure driven experiments. The two membranes with the lowest flux in the dead-end cell were the PD and PAcA membranes. In the FO process these were the two membranes with the highest flux results. The virgin flux results were 63% and 64% lower than the PD and PAcA, respectively. The virgin was 17% lower than the CMBA and the CMBA was 55% and 56% lower than the PD and PAcA, respectively. The ED and CMBA flux values were very close to one another and not much higher than the virgin. The taurine modified membranes showed an early flux close to the PD and PAcA but began to drop lower as the run time progressed.

The performance of the membranes in FO, as opposed to the pressure driven experiments, was primarily believed to be attributed to the increased hydrophilicity of the modified membranes. In pressure driven experiments, water is forced through the membrane by hydraulic pressure, whereas in the FO system the water solution flows freely past the membrane surface. The increase in hydrophilicity of the modified membranes caused the system to favor water transport. Contact angle measurements for each of the membranes, shown in Figure 6-5, displayed an increased hydrophilicity after functionalization.

The contact angle for the ED membrane was the highest of the modified samples, and ED had the lowest water flux of the final modifications. Additionally, ED was the smallest of the modifying agents, but still caused a 38% decrease in the membrane pore size. The CMBA activation caused a 25% decrease. Since the hydrophilicity was slightly higher with a smaller pore size, this could explain the similar water flux between the ED and
CMBA membranes. Additionally, the mean ED contact angle value was lower than the CMBA but the standard deviation was the largest and actually overlapped the lower end of the virgin standard deviation.

Despite the similar water fluxes, the weight fraction of sodium chloride in the permeate was significantly lower for the ED membranes. Previous work has shown zeta potential results for the ED modified membrane with a higher surface charge than the CMBA [6.12-6.13]. The higher surface charge and reduced pore size seems to explain the lower weight fraction of sodium chloride in the permeate while the water flux remains roughly the same as the CMBA membrane.

It is interesting to note that water transport was far lower in the FO system than the pressure-driven cell. The osmotic pressure gradient between the two bulk solutions was roughly 65 bar [6.1, 6.3], whereas the hydraulic pressure in the pressure-driven cell was only 4.82 bar. This behavior was expected and has been reported previously. Low flux results in FO systems were the result of internal concentration polarization [6.1-6.4]. Concentration polarization reduces the osmotic pressure gradient across the membrane to the point where it is significantly lower than that of the bulk. This affects the performance of the trans-membrane water transport, resulting in much lower water flux across the membrane than would be expected from the bulk osmotic pressure gradient.
6.3.3. Salt transport

6.3.3.1. Salt permeability

Due to the buffering effect of ammonium bicarbonate and sodium bicarbonate, the pH of the draw and feed solutions for the FO experiments equilibrated to a slightly basic value (approximately 8.3) where all the membranes were expected to have some degree of surface charge [6.12-6.13]. From the previous zeta potential studies involving virgin, CMBA activated, taurine, ED and PD modified at pHs 7 and 10, the readings were approximately 1.7, 4.2, -0.4, -4.5, and -7.2 mV, respectively for pH 7 and 0.1, 4.2, -3.7, -7.3, and -11.5 mV, respectively for pH 10. The rejection of 0.1M sodium chloride solutions for all modified membranes in the FO system was significantly higher than the virgin.

In a typical membrane filtration system, the percent rejection is quantified by determining the concentration of salt in the feed solution, and the concentration of the salt that permeates the membrane. Since the relationship between concentration and conductivity of sodium chloride is linear, concentration can be determined by taking conductivity measurements of the feed initially and of the draw solution after the ammonium bicarbonate has been removed. Use of this technique would not be ideal for the process used for this discussion because the rejection values would be for a bench scale system where both the feed and draw solutions were recycled past the membrane many times over. For the 65 mL/min flow rate selected for both streams, the 1000 mL draw solution was recycled past the membrane roughly 19.5 times over a five-hour period. With 19.5 turnovers per experiment, the percent rejection values were deemed subjective. The most
relevant technique for relating salt permeate data in this system is with the salt weight fractions measured for each membrane. This way, the performances of the membrane modifications can be related to one another and the virgin.

Figure 6-8 shows the transport ratios for the weight fraction of the sodium chloride and sodium hydroxide per water permeating the membranes, and the weight fraction of sodium chloride that permeated through the membranes. The thin bar in the back is the weight fraction of the total salt content remaining after the solvent boil off and the thicker bar in the front is the weight fraction for just the sodium chloride. From Figure 6-8, it is clear that every modified surface yielded higher rejection of sodium chloride over that of the virgin. The surface charges of the modified membranes were greater than the virgin at these slightly basic pH values. Additionally, the pore sizes of the modified membranes were smaller and resulted in better rejection. Due to the hygroscopic nature of sodium hydroxide and sodium chloride, the weight readings of the dried salt samples were not entirely accurate. As the heated beaker and remaining salt sample were left to cool some water moisture was trapped and added to the final weight. While the inaccuracy of the salt measurements may negate this as quantitative data, the weight measurements do provide excellent qualitative data to compare the modified samples to one another and to the unmodified.
Figure 6-8. Total salt (back, thin bar) and sodium chloride (front, thick bar) weight fractions for each membrane.

### 6.3.3.2. pH effects

It was clear after only a few experimental runs that testing a feed solution at pH 10 was an impractical endeavor since the buffering strength of the much more concentrated ammonium bicarbonate draw solution equilibrated the pH of both feed and draw solution streams. This effect was observed because both the feed and draw solutions were recycled past the membrane surface, resulting in several turnovers of the process volumes. In addition, one experiment was attempted to bring the draw solution pH up to 10, using ACS grade ammonium hydroxide, but resulted in such a large dilution that the approach was discredited. To bring the pH of 1L of draw solution to 9.98 required 400mL of ACS grade ammonium hydroxide (28-30%), diluting the solution to only
1.43M ammonium bicarbonate, and lowering the osmotic pressure gradient to approximately 47 bar. In a true desalination process, the feed solution would not be recycled past the membrane, and the pH equilibration would not be as prevalent. Even after this experiment however, when the solutions were boiled down and rehydrated to determine sodium chloride rejection, the pH of the final salt solutions of both the feed and draw followed the same trend as seen with all the other samples.

It was observed for all membrane-pH samples that after the five hour run time, the pH of both feed and draw solutions were equilibrated. Previous studies have shown high rates of reverse salt diffusion for ammonium bicarbonate draw solutions [6.3-6.4]. For the samples where there was no pH adjustment for either the feed or draw solutions, and also for the samples where the feed was adjusted to pH 10, the final pH of the feed and draw solutions was always between 8.2-8.4 (this pH range is resultant of the presence of sodium bicarbonate and sodium carbonate which buffer in this pH range). For the experiment with both feed and draw pH values initially around 10, both streams remained around 10.

At the end of a full FO run, a known volume of draw solution was boiled down until all the water evaporated. During this boiling process, all the dissolved ammonium salts decompose into ammonia and carbon dioxide. The remaining solid was then diluted with DI water to the original volume, so information about the salt rejection and membrane performance could be obtained. All the membrane experiments, including the experiment where the initial pH values were both at 10, followed the same behavior.
After the boil off, and subsequent dilution, the pH of the draw solution was over 10, and the pH of the feed solutions was neutral.

These results indicate membrane selectivity of the sodium ions over the chloride ions in the feed stream. This membrane behavior was expected for the slightly basic environment where the membrane takes on a negative surface charge. In addition to surface charge, the anionic species are larger than the cationic. The larger size of the anions leads to an increased size exclusion effect from the dense membrane structure. Considering the pH equilibration for the readings taken immediately after the five-hour experimentation time, but the large pH discrepancy after the solutions were boiled down and diluted, it seems the membrane allowed passage of sodium and ammonium ions much more freely than their anion counterparts.

The selectivity of the membrane for sodium ions was balanced by the reverse diffusion of the small and positively charged ammonium ions, thus obeying the electroneutrality principle. The excess of sodium ions permeating the PBI membranes yielded the higher pH values in the diluted draw solutions. When the draw solution was boiled down the ammonium and bicarbonate ions degrade into ammonia, carbon dioxide, and water. The remaining solute crystals, after completion of boiling, were a mixture of sodium chloride and sodium hydroxide. In the feed solution however, the thermal decomposition of the ionic species leads to a breakdown of all the ammonium and bicarbonate ions. The excess ammonium and chloride ions decomposed into ammonia and hydrogen chloride. With the continued heating, the hydrogen chloride was also boiled off as vapor, and the
remaining salt was simply sodium chloride. The pH of the diluted salt solution for the feed was thus neutral.

This pH phenomenon is a qualitative confirmation of the membranes selectivity for the cationic species, and higher rejection of the anionic species. The higher rejection was attributed to both steric exclusion and Donnan exclusion. The presence of sodium hydroxide in the diluted solution gave an elevated conductivity reading, and thus shows a lower sodium chloride rejection value when conductivity readings are taken. If conductivity readings were used solely to measure salt rejection then the percent rejection values would appear far lower than the actual values.

### 6.4 Conclusion

The overall lower mass transport across the virgin membrane in FO mode, despite the larger pore sizes, was believed to be due to the membranes higher hydrophobicity. All the modified membranes were more hydrophilic than the unmodified samples. The more hydrophilic surfaces should undergo an increased wetting effect, where the membrane-fluid interactions favored water transport. In addition to the effect of the more hydrophilic surfaces, the charged membrane surfaces showed a higher degree of sodium chloride rejection when examined as weight fractions of the permeate transporting through the membranes.

The results of PBI surface functionalization with the intent to increase hydrophilicity, increase surface charge, and decrease the membrane pore size show enhanced membrane
performance both with respect to water flux and salt rejection. The reduced pore size coupled with the use of a feed stream carrying divalent or larger ions mixed with colloidal particles may have the ability to yield excellent results and high purity water. In addition, if the cations chosen were much larger (e.g. transition metals or contaminants in industrial wastewaters) then the overall salt rejection would be expected to increase.

6.5 Acknowledgements

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Chapter 7

Conclusions and Recommendations

Flat sheet polybenzimidazole membranes were successfully cast, CMBA activated, and functionalized with all modifying agents. ESEM images verified that the membranes were in fact asymmetric with a thickness proportional to the doctor’s blade setting. The selective layer was verified to be dense in morphology and smaller than the more porous support layer, with an overall thickness of approximately 8 µm. From the FTIR spectra, there was clear evidence that surface activation and modification took place, which verified the modification method proposed by this study to be effective. Modified membranes had the following characteristics:

- increased hydrophlicity,
- increased surface charge,
- and reduced pore sizes.

In pressure-driven experiments, pure water permeability results showed a significant decrease after CMBA activation and the final modifications. Furthermore, sodium chloride rejection in decreased exponentially as the feed concentration increased for the
virgin and all modified membranes, with modified membranes always showing higher rejections than virgin membranes. This trend was seen at both feeds of pH 7 and pH 10. The higher rejection was attributed to both steric and Donnan exclusions. For both pH values, the modified membranes showed higher sodium chloride rejection over that of the virgin, with the percent rejection increasing at the higher pH. The modified membranes had reduced pore sizes that allowed for greater steric hindrance, while increased Donnan exclusion occurred when the membranes took on higher surface charges as the pH increased.

In FO experiments, the overall lower mass transport across the virgin membrane, despite the larger pore sizes, was believed to be due to the membranes higher hydrophobicity. All the modified membranes were more hydrophilic than the unmodified samples. The more hydrophilic surfaces were believed to undergo an increased wetting effect, where the membrane-fluid interactions favored water transport. In addition to the effect of the more hydrophilic surfaces, the charged membrane surfaces showed a higher degree of sodium chloride rejection when examined as weight fractions of the permeate transporting through the membranes. Additionally, the membranes showed selectivity for the cationic species in the basic pH environment. The results of PBI surface functionalization with the intent to increase hydrophilicity, increase surface charge, and decrease the membrane pore size showed enhanced membrane performance both with respect to water flux and salt rejection. The study presented here shows the effectiveness of surface modifications to PBI membranes for use in forward osmosis applications. In forward osmosis mode, the modified membranes showed higher permeability and lower salt transport than the
unmodified. Additionally, while rejection was not as high in the pressure-driven system, it was shown that the rejection of NaCl at higher ionic strengths by the modified membranes was higher than that of the virgin.

Ongoing and future studies should focus on optimizing the membranes to enhance their effectiveness in forward osmosis processes. Some suggestions for future work include:

- Determine the degree of PAcA crosslinking by examining the degree of dissolution of the PBI membrane before and after modification in a DMAc solvent.
- Increasing the PBI dope concentration to make tighter membrane pores.
- Testing the membranes effectiveness against industrial wastewaters with either elevated pH values or polyvalent cationic species.
- Test modified PBI with a hollow-fiber membrane configuration.
- Form membranes from heterogeneous dope solutions containing PBI and other hydrophilic polymer materials.
References

Chapter 1


Chapter 2


2.6. R.V. Wahlgren, Atmospheric water vapour processor designs for water production: a review, Wat. Res. 35 (2001) 1


2.8. A.W. Works, Microfiltration and ultrafiltration membranes for drinking water (2005)


2.15. S. Loeb, One hundred and thirty benign and renewable megawatts from Great Salt Lake? The possibilities of hydroelectric power by pressure retarded osmosis, Desalination 141 (201) 85-91
2.19. R.E. Kravath, J.A. Davis, Desalination of seawater by direct osmosis, Desalination 16 (1975) 151-155


2.34. S. Loeb, M.R. Bloch, Countercurrent flow osmotic processes for the production of solutions having a high osmotic pressure, Desalination. 13 (1973) 207-215


**Chapter 4**


Chapter 5


Chapter 6


Appendix A

Pore Size Determination

Below is a sample for how the membrane pore size determinations were made using polynomial equations of the third degree. The mean pore size was the pore size where 50% solute rejection was achieved. The MWCO was the value where 90% solute rejection was achieved. This data is for the PAcA results using TOC analysis.

\[ y = 1.9733x^3 - 5.9001x^2 + 5.8674x - 1.0315 \]

\[ R^2 = 0.9918 \]
From the solute radius where 90% rejection was achieved, based on the polynomial equation shown on the figure. The MWCO could then be obtained from the following equation:

\[
\text{Radius (Å)} = 0.262 \times M_w^{0.5} - 0.3
\]  

(A.1)

which has been reported in the literature (Tam et al., [6.18]) to relate the molecular weight of PEG with its Stokes-Einstein radius. This equation is valid for a PEG molecular weight range of 200 Da to 40,000 Da.

The s-shaped curves and polynomial equations for the other membrane samples are shown in the following figures:
CMBA

\[ y = 1.2358x^3 - 4.3729x^2 + 4.8846x - 0.8724 \]
\[ R^2 = 0.9844 \]

PD

\[ y = 3.909x^3 - 9.7973x^2 + 8.0549x - 1.2825 \]
\[ R^2 = 0.991 \]
Taurine

\[ y = 3.1614x^3 - 8.2566x^2 + 7.1515x - 1.171 \]

\[ R^2 = 0.999 \]

ED

\[ y = 2.5464x^3 - 7.242x^2 + 6.8682x - 1.2954 \]

\[ R^2 = 0.9703 \]