Surface modification of polybenzimidizole membranes for forward osmosis

Brett R. Digman

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A Thesis

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Surface Modification of Polybenzimidizole Membranes for Forward Osmosis

by

Brett R. Digman

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

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The University of Toledo

May 2010
An Abstract of

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Polybenzimidizole (PBI) is a material that is seeing increased use in a number of applications due to high mechanical and thermal stabilities. One such application is membrane filtration. Two drawbacks of PBI membranes for this application are low hydrophilicity and neutral charge at neutral pH values, which leads to low rejections of ions. To address this issue, PBI membranes were cast in the form of flat sheets using the phase-inversion technique. Three monomers (taurine, para-phenyl diamine, and ethylene diamine) were chosen based on their potential to impart charges and hydrophilicity on the PBI membrane. The surface of the PBI membrane was activated using 4-(chloromethyl) benzoic acid (CMBA). Two chemical methods were used to attach the monomers to the surface. Characterization of the membrane was done using fourier transform infrared spectroscopy in attenuated reflectance mode (FTIR-ATR), contact angle measurement, chemical force microscopy (CFM), and environmental scanning electron microscopy (ESEM). The chemical modification, increased hydrophilicity and increased surface charge were verified. Pure water flux was found to decrease by ~33% after surface
activation and by \( \sim 70\% \) after chemical modification as compared to that of the unmodified PBI membrane. Monovalent salt rejection using sodium chloride was done with feed concentrations varying from 3.4 mM to 100 mM and at pH values of 7 and 10. At both pH values salt rejection decreased exponentially with increasing concentration, and modified membranes provided higher rejections than unmodified membranes.
This is for my grandpa who always taught me, “Life is chemistry.” Without your encouragement and wisdom, I don’t know where I would be. Thank you for your continual support and always believing in me.


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Contents

Abstract iii
Acknowledgements vi
Contents viii
List of Tables xiii
List of Figures xiv
List of Abbreviations xvii
List of Symbols xix

1 Introduction 1

1.1 Need For Improved Water Treatment Processes 1

1.2 Proposed Research 4

1.3 Impact of Research 5

2 Literature Survey 7

2.1 Existing Membrane Technology 7

2.1.1 Liquid Process Membrane Technology 7

2.2 Existing Desalination Technology 8

2.2.1 Reverse Osmosis 8

2.2.2 Distillation 10

2.2.3 Membrane Distillation 11
2.2.4 Electrodeionization ................................................................. 12
2.2.5 Capacitive Deionization ......................................................... 14
2.3 Forward Osmosis and Applications ........................................... 15
  2.3.1 Osmosis ............................................................................. 15
  2.3.2 Draw Solutions ................................................................. 17
  2.3.3 Concentration Polarization ................................................ 19
  2.3.4 External Concentration Polarization ................................... 19
  2.3.5 Internal Concentration Polarization .................................... 20
  2.3.6 Current FO Materials ....................................................... 23
2.4 Polybenzimidizole Membranes ................................................. 24
2.5 Surface Modification ............................................................... 26

3 Research Objectives .................................................................. 27

4 Experimental ........................................................................... 29
  4.1 Materials and Methods .......................................................... 29
  4.2 Flat Sheet Preparation ........................................................... 30
  4.3 Membrane Modification ........................................................ 33
    4.3.1 Surface Activation Using 4-(chloromethyl) Benzoic Acid .......... 33
    4.3.2 Method 1: N-ethyl-N(dimethylaminopropyl) Carbodiimide Chemistry ......................................................... 35
    4.3.3 Method 2: N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide Hydrochloride Chemistry ................................. 39
4.4 Analytical Methods.................................................................................. 42

4.4.1 Fourier Transform Infrared Spectroscopy
(FTIR-ATR).................................................................................................. 42

4.4.2 Contact Angle .............................................................................. 42

4.4.3 Chemical Force Microscopy (CFM).............................................. 43

4.4.4 Environmental Scanning Electron Microscopy
(ESEM)........................................................................................................... 44

4.5 Transport Properties ................................................................................. 45

4.5.1 Pure Water Flux ........................................................................... 45

4.5.2 Monovalent Salt Solution For Testing........................................ 46

5 Manuscript ........................................................................................................ 48

Abstract ................................................................................................................ 48

1. Introduction .............................................................................................. 49

2. Experimental ............................................................................................ 53

2.1 Materials ............................................................................................. 53

2.2 Flat Sheet Polybenzimidizole Preparation ...................................... 54

2.3 Membrane Modification .................................................................... 55

2.3.1 Surface Activation using 4-(chloromethyl) Benzoic Acid............. 55

2.3.2 Method 1: N-ethyl-N(3-dimethylaminopropyl) Carbodiimide Chemistry.................................................. 56

2.3.3 Method 2: N-(3-dimethylaminopropyl)-N’-Ethylcarbodiimide Chemistry.............................................. 57
References 81

Appendices

A  Use of the Simpsons Rule to find the area under CFM curves 89
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>A few selected physical properties of monomers chosen for PBI membrane modification</td>
<td>39</td>
</tr>
<tr>
<td>Table 1</td>
<td>Percentage of negative surface charge for all membranes</td>
<td>69</td>
</tr>
</tbody>
</table>
List of Figures

2.1 Comparison of membrane filtration processes ................................................ 8
2.2 Osmotically driven membrane processes ...................................................... 9
2.3 Vacuum distillation schematic for desalination .............................................. 10
2.4 Membrane distillation .............................................................................. 12
2.5 Electrodeionization schematic .................................................................... 13
2.6 Capacitive deionization schematic ............................................................... 15
2.7 Solvent flows in FO, PRO, and RO ............................................................... 16
2.8 Direction and magnitude of water flux as a function of applied pressure in FO, RO, and PRO ............................................................... 17
2.9 Internal concentration polarization profiles ................................................ 22
2.10 Internal concentration polarization in FO membranes .................................. 22
2.11 Chemical structure of polybenzimidizole (PBI) ............................................ 24
2.12 Polybenzimidizole synthesized from different monomers ....................... 25
4.1 Diluted PBI dope placed on a well-cleaned mirror ........................................ 31
4.2 Casting of PBI Dope .................................................................................. 31
4.3 PBI dope upon completion of casting .......................................................... 31
4.4 Partially immersed PBI dope during phase-inversion process ...................... 32
4.5 PBI dope during phase-inversion process .................................................... 32
4.6  PBI membrane at the final stages of the phase-inversion process ................. 32
4.7  Final unmodified PBI membranes ................................................................. 33
4.8  PBI flat sheet membranes during free radical initiation using sodium persulfate ................................................................. 34
4.9  Reaction schematic of PBI surface activation ................................................. 35
4.10 Structure of N-ethyl-N(3-dimethylaminopropyl) carbodiimide ...................... 35
4.11 Unstable EDC Ester Intermediate ................................................................. 37
4.12 Reaction Schematic of EDC Chemistry ....................................................... 38
4.13 EDC chemistry monomers ........................................................................... 38
4.14 Structure of N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride ................................................................. 39
4.15 Formation of NHS Ester Intermediate ......................................................... 40
4.16 Final product formation of EDCH catalyzed chemistry using taurine ............ 41
4.17 Contact angle measurement ........................................................................ 43
4.18 Dead cell flow schematic ............................................................................ 45
  1 Schematic of dead-flow cell .............................................................................. 60
  2 CMBA modified PBI versus unmodified ........................................................ 63
  3 CMBA modified PBI versus Ethylene Diamine modification (method 1 and 2) ........................................................................ 64
  4 CMBA modified PBI versus para-phenyl diamine modification (method 1 and 2) ........................................................................ 65
  5 CMBA modified PBI versus taurine modification (method 1 and 2) .......... 66
  6 Contact angle measurements for all chemistries ........................................... 67
7 Cross-section of asymmetric PBI membrane showing selective and support layers ................................................................. 70

8 Cross-section of unmodified PBI membrane .................................................. 71

9 Cross-section of CMBA modified PBI membrane ........................................ 71

10 Cross-section of para-phenyl diamine modified PBI membrane ............... 71

11 Pure water flux: Method 1 ......................................................................... 73

12 Pure water flux: Method 2 ......................................................................... 73

13 Sodium chloride rejection at pH 7: Method 1 ............................................. 76

14 Sodium chloride rejection at pH 10: Method 1 ........................................... 76

15 Sodium chloride rejection pH 7: Method 2 ................................................ 77

16 Sodium chloride rejection pH 10: Method 2 ............................................... 78
List of Abbreviations

CDI........... Capacitive deionization
CP............. Concentration polarization
CMBA......... 4-(chloromethyl) benzoic acid
CFM........... Chemical force microscopy
COOH.......... Carboxylate group

DI ............ Deionized/distilled water
DMAc .......... Dimethylacetamide
DMap.......... Dimethylaminopyridine

EDC.......... N-ethyl-N(3-dimethylamino) carbodiimide
EDCH......... N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride
EDI........... Electrodeionization (continuous deionization)
ESEM......... Environmental scanning electron microscopy

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

MD............ Membrane distillation
MES........... 2-(N-morpholino)ethanesulfonic acid
MF............ Microfiltration

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

PBI........... Polybenzimidazole
pH............ Potential of hydrogen
PRO.......... Pressure retarded osmosis
PWF.......... Pure water flux

RO............ Reverse osmosis

SAM.......... Self-assembled monolayer
SEM.......... Scanning electron microscopy

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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔP</td>
<td>Applied pressure</td>
</tr>
<tr>
<td>Δμ_w</td>
<td>Effective driving force</td>
</tr>
<tr>
<td>Δπ</td>
<td>Osmotic pressure gradient</td>
</tr>
<tr>
<td>Δπ_{bulk}</td>
<td>Pressure difference between bulk feed and bulk draw solution</td>
</tr>
<tr>
<td>Δπ_{eff}</td>
<td>Effective osmotic pressure driving force</td>
</tr>
<tr>
<td>Δπ_m</td>
<td>Osmotic pressure difference across a membrane</td>
</tr>
<tr>
<td>μ_w</td>
<td>Water chemical potential</td>
</tr>
<tr>
<td>μL</td>
<td>Microliters</td>
</tr>
<tr>
<td>μm</td>
<td>Microns (micrometers)</td>
</tr>
<tr>
<td>π</td>
<td>Osmotic pressure</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
</tr>
<tr>
<td>σ</td>
<td>Reflection coefficient</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees celsius</td>
</tr>
<tr>
<td>$$/m^3$</td>
<td>Cost per volume</td>
</tr>
<tr>
<td>A</td>
<td>Water permeability constant</td>
</tr>
<tr>
<td>atm</td>
<td>Atmospheres</td>
</tr>
<tr>
<td>CH_3</td>
<td>Methyl group</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>g/cm^3</td>
<td>Gram per centimeter cubed</td>
</tr>
<tr>
<td>g/mol</td>
<td>Grams per mole (molecular weight)</td>
</tr>
<tr>
<td>J_w</td>
<td>Water flux</td>
</tr>
<tr>
<td>KJ/Kg</td>
<td>Kilojoules per Kilogram</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>ml</td>
<td>Milliliters</td>
</tr>
<tr>
<td>Mm</td>
<td>Milimolar</td>
</tr>
<tr>
<td>N</td>
<td>Normality</td>
</tr>
<tr>
<td>N/m</td>
<td>Newtons/meter</td>
</tr>
<tr>
<td>pKa/b</td>
<td>Negative logarithm of the acid/base dissociation constant</td>
</tr>
<tr>
<td>psi</td>
<td>Pounds per square inch</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percentage</td>
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Chapter 1

Introduction

1.1 Need For Improved Water Treatment Processes

Fresh potable water is an essential human need and thus looming water shortages threaten the world’s peace and prosperity. Along with the global water scarcity, less and less access to clean water has become a worldwide issue afflicting people, especially in the developing nations (1). Currently, about half of the world’s population suffers from water shortages. Over the next 25 years, the number of people affected by severe water shortages is expected to increase fourfold (2). In the developing countries that are most affected, 80-90% of all diseases and 30% of all deaths result from poor water quality (3). In addition, modern economies cannot develop and thrive without sufficient access to water. Therefore, there is growing recognition by governments and corporations that future peace and prosperity is intimately tied to the availability of clean, fresh water (4).

Wastewater, brackish water, and seawater have great potential to meet future water quantity needs and regulations (5). More and more effort has been put into evaluating the potential techniques to recover fresh water from wastewater and seawater/brine desalination (6). Membrane technology has offered an effective approach to addressing
water scarcity. So far, the most widely used membrane processes for water purification include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). All of these are pressure-driven processes, which require energy to pressurize the system. Of specific interest here is RO. By pressurizing an impure water or saline water feed above its osmotic pressure, RO allows for the recovery of pure water. RO is currently the most effective desalination process. In order to be commercially viable, new desalination techniques must either match or exceed RO in product water cost, water quality, operability and maintenance requirements, water recovery rates, or energy and capital costs.

While pressure-driven membrane processes, such as RO, have dominated for several decades, new desalination processes are now emerging, such as forward osmosis (FO) (7). Like RO, FO uses a semi-permeable membrane to separate water from dissolved solutes. The semi-permeable membrane acts as a barrier that allows water to pass through while blocking salts. Thus, FO may offer the advantage of rejection of a wide range of contaminants. Instead of employing hydraulic pressure as the driving force for the separation, FO uses an osmotic pressure gradient across the membrane to induce a net flow of water through the membrane into a draw solution (generally a high concentration salt solution); thus, efficiently separating the fresh water from its solutes. Because it is driven by an osmotic pressure gradient, FO does not require significant energy input, only stirring or pumping of the solutions. This process has a number of salient advantages; for example, FO consumes only about 20-30% of the energy required by other desalination processes and may use very low quality heat, such as the “waste” heat
from a power plant, as its energy input (8). FO may have higher recovery, resulting in less brine discharge to the environment (9).

However, there are major hurdles to fully explore FO potential as a new water production technology that include a small number of commercially available FO membranes with proper separation performance and lack of user friendly and economic draw solutions (8). FO applications in real-world water purification have long been hindered by three key challenging issues:

- Presently available membranes are mostly made for pressure-driven processes; development of membranes tailor-made and fully effective for osmotically driven FO processes is still in its infancy stage. The selective layer of an FO membrane should be much thinner or have very low transport resistance in order to minimize internal concentration polarization and enhance membrane flux.

- Compared to abundant research in pressure-driven processes, a mechanistic understanding of the unique solute transport phenomena and fouling/cleaning behavior of FO processes is basically lacking. This knowledge gap has severely discouraged systematic development (vs. trial-and-error approaches) of FO membranes.

- Suitable draw solutions that are able to generate high osmotic pressure while containing solutes that can be removed efficiently and completely have not been readily available when FO is used as a stand-alone water purification process.
This thesis focuses on the first issue – FO membrane materials. One approach to overcome current obstacles with respect to low efficiency FO membranes is by surface modification or functionalization of existing membranes to provide targeted properties. For example, by placing a charged monomer on the surface of a membrane, the rejection of monovalent salts (i.e. sodium chloride) increases (11).

Research toward developing FO-competent membranes has been very limited. Recently, membranes that are specifically made for FO purposes have appeared. For example, Hydration Technologies, Inc. (Albany, OR) produced a cellulose acetate FO membrane (9). Although this membrane has relatively high flux, it finds only limited applications due to high material biodegradability, severely shortening the membrane life. Very recently, researchers in Singapore developed a hollow fiber FO membrane made of polybenzimidizole (PBI) (10). The PBI membrane exhibits high flux in FO process and thus is a very promising material for FO membrane development. However the salt rejection of this membrane in the current stage is relatively low. Therefore, there is a pressing need to synthesize high-performance membranes that are fully fit for FO processes.

1.2 Proposed Research

The aim of this research project was to develop novel membranes for potential use in FO with high flux and salt rejection. In order to achieve this goal, PBI flat sheet asymmetric membranes were cast and functionalized through chemical modification. PBI was chosen because of its robust mechanical strength and excellent chemical and thermal stability.
However, in its virgin (unmodified) form, PBI has some major drawbacks for use in salt rejection. It is neutrally charged at normal operating pH (potential of hydrogen) values (around pH 7) and at high ionic strength concentrations (which is normal for FO applications). This leads to decreased electrostatic repulsion between the membrane surface and electrolytes to be rejected, thus a decrease in the rejection of monovalent salts. Additionally, these membranes are hydrophobic and have a tendency for fouling.

For the process of FO, the ideal membrane would be hydrophilic and highly negatively charged at most pH values. To address membrane material design, a PBI membrane was cast as the baseline membrane since PBI membranes have robust mechanical strength, and excellent chemical and thermal stability over a wide range of pH. It is important to design the surface functionality to optimize the balance between maximizing surface charge while minimizing flux decline. Three monomeric groups with varying degrees of hydrophilicity and charge were used to modify the PBI surface. Detailed research objectives are given in chapter 3.

1.3 Impact of Research

Development of a desalination process technology using the FO route has the potential to achieve up to a 75 percent decrease in cost and energy consumption in desalination, in comparison to conventional thermal or reverse osmosis processes (12).

With continued development of more efficient membranes the FO process can be beneficial for seawater desalination, identifying a new resource for fresh water availability, satisfying both economical and environmental concerns (9). Successful
modification of the PBI membrane surface could be a major step towards FO realization as a viable commercial means of desalination.
Chapter 2

Literature Survey

2.1 Existing Membrane Technology

2.1.1 Liquid Process Membrane Technologies

Currently there are several existing liquid process membrane technologies available. These are divided based on pore size and/or the size of the materials they can reject (Figure 2.1). Based on decreasing pore size, membranes are divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO) (not included in figure 2.1). FO membranes are generally found in the NF/RO range.
2.2 Existing Desalination Technology

Below are some examples of the current technologies in water purification/desalination. Though this is not a complete list of what there is to offer, it gives insight as to the amount of work being done in this ever growing and necessary field.

2.2.1 Reverse Osmosis

Currently, RO is the most common pressure-driven water purification technology. RO uses hydraulic pressure to oppose, and exceed, the osmotic pressure of an aqueous feed solution to produce purified water (13) (Figure 2.2). However, RO is not without its faults and suffers from numerous limitations. The pressure needed is directly related to the amount of osmotic pressure necessary to facilitate mass transfer across the membrane. This accounts for most of the energy consumed in RO. Because the concentration of...
dissolved salt is directly related to this pressure requirement, RO is most effective and energetically viable for the treatment of seawater or brackish water.

The osmotic pressure of seawater systems is about 25 bar (14). The operation pressure for brackish water systems ranges from 15-25 bar and for seawater systems from 54-85 bar. The energy requirements reported for RO purification of seawater are typically about 15-30 KJ/Kg of fresh water (15), although values as high as 61 KJ/Kg have been reported (16). Since most of the energy losses for RO result from releasing the pressure of the concentrated brine, large scale RO systems are now equipped with devices to recover the mechanical compression energy from the discharged concentrated brine stream with efficiencies claimed to be up to 95%. In these plants, the energy requirements for seawater desalination has now been reported to be as low as 9 KJ/Kg product (17).

Figure 2.2 – Osmotically driven membrane processes (18)
2.2.2 Distillation

Distillation is another process to convert seawater into potable water. Low amounts of energy, the ability to run off waste energy, and no scaling because of low temperatures have brought attention to this process [19]. The heat energy requirements for desalination using distillation process can be brought down by reducing the boiling temperature. By subjecting seawater to vacuum, the boiling temperature is reduced.

Vacuum distillation is a process by which water is vaporized at lower temperature when subjected to vacuum pressure (Figure 2.3). The boiling temperature of seawater can be lowered to as low as 400°C by the generation of a vacuum [20]. The boiling point of water drops with decreasing absolute pressure. The cost of decreasing pressure is negligible in comparison with the cost of heating to the boiling point [21]. Seawater is vaporized at lower temperatures and is condensed to form potable water.

![Vacuum distillation schematic for desalination](Source: www.pharmaceuticalonline.com)
2.2.3- Membrane Distillation

Membrane distillation (MD) is an emerging technology for desalination. A generalized view of the membrane distillation process is given in Figure 2.4. MD differs from other membrane technologies in that the driving force for desalination is the difference in vapor pressure of water across the membrane, rather than the total pressure. The membranes for MD are hydrophobic, which allows water vapor (but not liquid water) to pass. The vapor pressure gradient is created by heating the source water, thereby elevating its vapor pressure. The major energy requirement is for low-grade thermal energy. It is expected that the total costs for drinking water with MD will be lower than $0.50/m^3, even as low as $0.26/m^3, depending on the source of the thermal energy required for the evaporation of water through the membrane (19). MD is not without its drawbacks. For example, organic solutes present in an aqueous solution reduce the surface tension to the point where spontaneous membrane wetting may occur. At this point, the surface tension is called the critical surface tension at which membrane distillation is no longer possible. High porosities are of special interest in MD since the area available for evaporation is directly related to flux. However, high porosities are usually associated with large pore sizes, which are undesirable as they increase the risk of membrane wetting (18).
2.2.4 – Electrodeionization

Electrodeionization (EDI) (also known as continuous deionization), is a hybrid separation process combining ion-exchange resins with ion-exchange membranes in one unit. In EDI, the dilute compartment is filled with mixed-bed ion-exchange resins which enhance the transport to the membranes under the force of direct current. The ion transport is almost entire through the ion-exchange resins and is not affected through the water (22). Saltwater passes between the membranes. The ions take the place of the ions on the resin and are pulled through the membranes in front of electrically charged plates. Water passes through the resin and is free from the ions producing purified water (23) (Figure 2.5).
The EDI unit is capable of producing water with a resistivity of up to around 16 megaohm×cm, but requires a very high quality feed water. An RO system is therefore almost always used prior to the polishing EDI units. RO/EDI systems have several drawbacks including relatively high capital cost, high EDI stack replacement costs, high energy consumption, and the difficulty in removing weakly ionized contaminants such as silica, carbon dioxide, and organics. The system is susceptible to fouling by colloidal silica or organic material typically found in surface waters, such as humic, fulvic, or tannic acids (24).
2.2.5 Capacitive Deionization

Capacitive deionization (CDI) is an electro-chemically controlled method for removing salt from aqueous solutions. It takes advantage of the excess ions adsorbed in the electrical double layer region at an electrode-solution interface when the electrode is electrically charged by an external power supply (Figure 2.6). When the electrode has a high specific surface area, this excess may become significant in terms of the number of grams of salt adsorbed on a unit weight of electrode material. This factor renders the electrodesorption process qualitative and attractive for water treatment (25). CDI using capacitive adsorption has been suggested to lower water treatment cost and prevent environmental pollution without the disadvantages (i.e. energy consumption) that other processes have (26,27). However, conventional CDI is known to be energy inefficient because of the dissolved salt present in the pore volume of the carbon electrode. When an electric potential is applied, counter ions in the pore adsorb onto the electrode and co-ions are expelled from the electrodes. This means that ion adsorption and desorption occur simultaneously in the pore volume in the electrode, seriously reducing desalination efficiency (28).
2.3 Forward Osmosis and Applications

The section below describes critical aspects of forward osmosis systems and applications (5-10).

2.3.1 Osmosis

The transport of water across a selectively permeable membrane by osmosis takes advantage of differences in chemical potential. Water with high chemical potential flows to water with a lower chemical potential. This chemical potential is directly related to the solute concentration and allows the passage of water through the membrane while rejecting most solute molecules and ions.

Osmotic pressure ($\pi$) is the pressure which, if applied to the more concentrated solution, would prevent transport of water across the membrane. FO uses the osmotic pressure gradient ($\Delta\pi$) as the driving force for water transport through the membrane. The FO process results in concentration of a feed stream and dilution of a highly concentrated
stream, known as a draw solution. RO, uses the difference in hydraulic pressure as the driving force for the transport of water. Pressure-retarded osmosis (PRO) can be viewed as the intermediate process between FO and RO, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient, similar to RO. However, the net water flux is still in the direction of the concentrated draw solution, similar to FO. The general equation to describe water transport in FO, RO, and PRO is (2.1):

\[ J_w = A(\sigma \Delta \pi - \Delta P) \]  \hspace{1cm} (2.1)

Where \( J_w \) is the water flux, \( A \) the water permeability constant of the membrane, \( \sigma \) the reflection coefficient, and \( \Delta P \) is the applied pressure. For FO, \( \Delta P \) is zero; for RO \( \Delta P > \Delta \pi \); and for PRO \( \Delta \pi > \Delta P \). The flux directions of the permeating water for FO, PRO, and RO are illustrated in Figure 2.7. Flux directions and driving forces for the three processes were characterized in the early 1980s by Lee et al. (1981) (29). The FO zone, PRO zone, and RO zone, along with flux reversal point, are illustrated in Figure 2.8 (9).

![Figure 2.7 – Solvent flows in FO, PRO and RO. For FO, \( \Delta P \) is approximately zero and water diffuses to the more saline side of the membrane. For PRO, water diffuses to the more saline liquid that is under positive pressure (\( \Delta \pi > \Delta P \)). For Ro, water diffuses to the less saline side due to hydraulic pressure (\( \Delta P > \Delta \pi \)) (9).](image-url)
Figure 2.8 – Direction and magnitude of water flux as a function of applied pressure in FO, PRO, and RO (9).

2.3.2 Draw Solutions

The concentrated solution on the permeate side of the membrane is the source of the driving force for the FO process. Different terms are used in the literature to name this solution including draw solution, osmotic agent, osmotic media, driving solution, osmotic engine, sample solution, or just brine. For clarity, the term draw solution will be used exclusively in this work. When selecting a draw solution, the main criterion is that it has a higher osmotic pressure than the feed solution. Another important criterion in some applications of FO is the selection of a suitable process for reconcentrating the draw solution after it has been diluted in the FO process. Diffusion of the solute from the draw
solution through the membrane must also be considered. In specific applications where high rejection is desired, multivalent ion solutions may be preferable. In the past, seawater (30), Dead Sea water (31), and Great Salt Lake water (32) have been used or considered as draw solutions for FO or PRO.

Various other chemicals have been suggested and tested as solutes for draw solutions, particularly in seawater desalination applications. Batchelder (1965) (33) suggested using sulfur dioxide solution as the draw solution in desalination of seawater. Glew (1965) (34) 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 was also the first to propose the recycling of the draw solutions in conjunction with FO. Frank (1972) (35) used an aluminum sulfate solution, Kravath and Davis (1975) (36) used a glucose solution in FO desalination of seawater, Kessler and Moody (1976) (37) used a mixed solution of glucose and fructose for seawater desalination, and Stache (1989) (38) used a concentrated fructose solution to create a nutritious drink during FO of seawater. McGinnins (2002) (39) suggested a two-stage FO process that takes advantage of the temperature dependant solubilities of the solutes. 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 (2006) (40-42), 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. In a new
nanotechnological approach, nanomagnetic particles are being tested as potential solute for draw solutions. Nanomagnetic particles can be rapidly separated from aqueous streams using a magnetic field (43).

2.3.3 Concentration Polarization

The water flux in osmotic-driven membrane processes is described in Equation (2.1). In this equation Δπ represents the osmotic pressure difference across the active layer of the membrane. In such processes, the osmotic pressure difference across the active layer is much lower than the bulk osmotic pressure difference, which results in much lower water flux than expected (29,44-47). The lower-than-expected water flux is often attributed to several membrane-associated transport phenomena. Specifically, two types of concentration polarization (CP) phenomena – external CP and internal CP – can take place in osmotic-driven membrane processes as discussed below.

2.3.4 External Concentration Polarization

In pressure-driven membrane processes, convective permeate flow causes a buildup of solute at the membrane active layer surface. Referred to as concentration polarization (CP), this phenomenon reduces permeate water flux due to increased osmotic pressure that must be overcome by hydraulic pressure (48-50). CP due to water permeation is not limited to pressure-driven membrane processes and also occurs during osmotic-driven membrane processes, on both the feed and permeate sides of the membrane. When the feed solution flows on the active layer of the membrane (like in RO), solutes build up at
the active 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 permeating water. This is called dilutive external CP. Both concentrative and dilutive CP phenomena reduce the effective osmotic driving force. 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 (51).

Due to the hydraulic pressure used in FO, membrane fouling induced by external CP has milder effects on water flux compared to the effects in 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 (42).

2.3.5 Internal Concentration Polarization

When an osmotic pressure gradient is established across a completely rejecting dense symmetric membrane (pore size and structure is even throughout the membrane), as depicted in Figure 2.9(a), 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), adding more complexity to the CP phenomena. When a composite or 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 an asymmetric membrane faces the feed solution, as in PRO, a polarized layer is established along the inside of the dense active layer as water and solute propagate the porous layer (Figure 2.9(b)). Referred to as concentrative internal CP (46), 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. In FO application for desalination and water treatment, the active layer of the membrane faces the feed solution and the porous support layer faces the draw solution. As water permeates the active layer, the draw solution within the porous substructure becomes diluted. This is referred to as dilutive internal CP (Figure 2.9(c)) (46). It can be seen in Figure 2.10 that the osmotic pressure difference between the bulk feed and bulk draw solution ($\Delta \pi_{\text{bulk}}$) is higher than the osmotic pressure difference across the membrane ($\Delta \pi_{\text{m}}$) due to external CP. The effective osmotic pressure driving force ($\Delta \pi_{\text{eff}}$) is even lower due to internal CP. Furthermore, similar to the operation of heat exchangers, operation of FO in a counter-current flow configuration (feed and draw solutions flowing tangential to the membrane but in opposite directions) provides constant $\Delta \pi$ along the membrane module and makes the process more effective (52).
Figure 2.9 - Illustration of driving force profiles, expressed as water chemical potential, $\mu_w$, for osmosis through several membrane types and orientations. (a) A symmetric dense membrane. (b) An asymmetric membrane with the porous support layer facing the feed solution; the profile illustrates concentrative internal CP. (c) An asymmetric membrane with the dense active layer facing the feed solution; the profile illustrates dilutive internal CP. The actual (effective) driving force is represented by $\Delta \mu_w$. External CP effect on the driving force were assumed to be negligible in this diagram (42).

Figure 2.10 - (a) Concentrative internal CP and (b) dilutive internal CP across a composite of asymmetric membrane in FO (9).
2.3.6 Current FO Membrane Materials

Some work has been done in developing materials for use in FO. For example, Hydration Technologies, Inc. (Albany, OR) produced a cellulose acetate FO membrane (9). Although this membrane has relatively high flux, it finds limited applications due to high material biodegradability, severely shortening the membrane life. Researches in Singapore developed a hollow fiber FO membrane make of polybenzimidizole (PBI) (10). The PBI membrane can generate high flux in FO process and thus is very promising material or FO membrane development, even though the salt rejection of this membrane in the current stage is relatively low. More recently Yang et al. (2009) (52) have developed a dual-layer polybenzimidizole polyethersulfone/polyvinylpyrrolidone hollow fiber nonofiltration membrane for the enrichment and concentration of pharmaceutical products without denaturing the components of interest (53).
2.4 Polybenzimidizole Membranes

PBI is a class of heterocyclic polymers that were commercially developed by the Celanese Corporation in 1983 (54,55), with the chemical structure as shown in Figure 2.11.

![Chemical structure of polybenzimidizole (PBI)](image)

Figure 2.11 – Chemical structure of polybenzimidizole (PBI)

Brinker and Robinson (56) invented the first aliphatic polybenzimidizoles. Aromatic polybenzimidizoles with impressive thermal properties were then developed by Bogel and Marvel (57,58) at the University of Illinois and later at Du Pont. Since then, high performance polybenzimidizoles have received a great deal of attention by academia, U.S. government, and industry. Hoechst Celanese commercialized polybenzimidizole fiber for thermal protective clothing and fire blocking application in 1983. In the mid 1980’s both Hoechst Celanese and Alpha Performance Company developed the technology to mold polybenzimidizole parts (under the trade name of Celazole®. Alpha took over Celazole® technology completely in 1995 and continued marketing polybenzimidizole molded parts as scalin elements in high-temperature corrosive environments. Poly (2,2’-(m-phenylene)-5,5’ bibenzimidizole) is their product and is
referred to as PBI (59). The synthetic route of PBI is shown in Figure 2.12.

Moreover, PBI membranes have been fabricated for use in reverse osmosis and nanofiltration processes, and as the ion-exchange membrane in fuel cells because of their excellent chemical and thermal stability (60-63). The heterocycle imidazole ring makes it possible for both inter and intra-molecular hydrogen bonding to occur between PBI molecules. As a result, PBI may become self-charged in aqueous environments because the adjacent benzene ring delocalizes the proton of the imidazole group (64). Certain forms of PBI membranes have a much higher rejection to divalent ions but partly permit the monovalent ions to transport and can be employed to fractionate electrolyte mixtures (65).
2.5 Surface Modification

Work has been done on the surface modification of polybenzimidizole for various applications. Wang et al. (2009) cross linked PBI with p-xylylene dichloride for use as high-rejection, high-flux forward osmosis membranes for water reuse and seawater desalination (55). This membrane was also used for the separation of cephalexin, a semi-synthetic cephalosporin with broad antibacterial activities (66). Roziere et al. (2001) grated (4-bromomethyl)benzenesufonate onto PBI as a means of producing a proton exchange polymer with a variable degree of sulfonation (67). Staiti et al. (2001) sulfonated polybenzimidizole by sulfuric acid treatment on pre-formed polybenzimidizole membranes for use in electrodialysis and electrochemical applications (65). This thesis focuses on the surface modification of PBI to increase both surface charge and hydrophilicity.
Chapter 3

Research Objectives

The objectives of this research were to prepare flat sheet PBI membranes in house and chemically modify their surfaces using three separate monomers (taurine, ethylene diamine, and para-phenyl diamine). The monomers were chosen based on their potential to impart negative charges on the surface. From this modification, it was expected that by increasing the overall surface charge, salt rejection would increase. Based on the monomers chosen it was also expected that the overall hydrophilicity would increase.

The surface of the unmodified membranes was activated using 4-(chloromethyl) benzoic acid (CMBA). Two different methods of chemistry were used to attach the monomers to the activated surface. The first method used N-ethyl-N(3-dimethylamino) carbodiimide (EDC) and the second used N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCH) as catalysts for the reactions.
In order to verify successful modification a number of analytical techniques were used. Initially, Fourier Transform Infrared Spectroscopy in Attenuated Total Reflection mode (FTIR-ATR) was used to detect structural changes based on specific functional groups associated with each of the monomers. To determine the changes in hydrophilicity, as well as a secondary means of confirming chemistry, contact angle was measured using a Goniometer. Chemical Force Microscopy (CFM) was used to detect changes in the charge on the membrane surface. Finally, an environmental scanning electron microscope (ESEM) was used to detect any changes in morphology of the membranes during modification.

In order to test the transport characteristics of the unmodified, surface activated, and EDC/EDCH catalyzed modified membranes dead flow permeability cells were used in a pressure driven mode as a proof-of-concept. Pure water flux was determined for all membranes as well as monovalent salt rejection (sodium chloride) in this mode. In order to detect changes in salinity, a conductivity meter was used to test conductance of both the feed and the resulting permeate.
Chapter 4

Experimental

4.1- Materials and Methods

The polybenzimidizole dope was supplied to us by PBI Performance Products, Inc. (Charlotte, NC) at a 26 wt% solution. Taurine, para-phenyl diamine, ethylene diamine, 4-dimethylaminopyridine, dimethylacetamide, 4-(chloromethyl) benzoic acid, N-ethyl N(3-dimethylamino) carbodiimide, N-hydroxysuccinimide, N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride, 2-(N-morpholino)ethanesulfonic acid and sodium persulfate were purchased from Sigma-Aldrich (USA). Acetone, glycerol, and sodium chloride were purchased from Fisher Scientific (USA). 2-mercaptoethanol was purchased from Alfa Aesar. DI water was supplied by a continuous distillation apparatus.
4.2- Flat Sheet Preparation

Flat sheet polybenzimidizole membranes were prepared in house to allow for control of surface modification. Polybenzimidizole dope was supplied by PBI Performance Products Inc. (Charlotte, NC). The procedure used to prepare the sheets was adapted from Wang et al (2006) (62). The initial concentration of the dope was 26 wt% with an overall composition of 26 wt% PBI, 72 wt% dimethylacetamide (DMAc), and 2.0 wt% Lithium Chloride. A desired concentration of 20% was achieved by dilution with DMAc. In order to prevent air bubbles from being trapped in the dope, the beaker was sealed with parafilm and rotated by hand every 10 minutes for approximately 2 hours. The dope was then placed in an even line across a well-cleaned mirror (Figure 4.1). A doctor’s blade set at a thickness of 150 μm was used to push the dope across the mirror forming a flat sheet (Figures 4.2 and 4.3). To insure minimal friction between the blade and the mirror, the rails of the blade were lubricated using motor oil. Once the sheet was cast, the solvent was removed by phase-inversion process (62). A 12-gallon DI water coagulation bath was used to induce phase-inversion and subsequent pore formation (Figures 4.4 and 4.5). Once the phase inversion had taken place, the membrane peeled from the mirror (Figure 4.6). The membrane was thoroughly washed with DI water and ¼ inch circles were punched for use (Figure 4.7). The number of samples obtained from a sheet was dependant on the amount of dope initially used. All membranes were stored in a 50/50 mixture of DI water and glycerol until use. Glycerol was added due to the possibly of water evaporation. It is important to keep the membranes wet. When they are dried they become brittle and are susceptible to breakage.
Figure 4.1 – Diluted PBI dope placed on a well-cleaned mirror

Figure 4.2 – Casting of PBI Dope

Figure 4.3 – PBI dope upon completion of casting
Figure 4.4 – Partially immersed PBI dope during phase-inversion process

Figure 4.5 – PBI dope during phase-inversion process

Figure 4.6 – PBI membrane at the final stages of the phase-inversion process
4.3- Membrane modification

4.3.1 - Surface activation using 4-(chloromethyl) benzoic acid

The initial modification using 4-(chloromethyl) benzoic acid (CMBA) was done as follows: in a 50-ml beaker, a 0.5wt% solution of CMBA was prepared in acetone and was stirred until all the solute was dissolved. In a separate 50-ml beaker, a 1.0wt% solution of sodium persulfate was prepared in DI water and stirred until all the solute was dissolved. Sodium persulfate was used as a free radical initiator for the reaction. The membranes to be modified were then added to the sodium persulfate solution (Figure 4.8).
CMBA was slowly added to the sodium persulfate solution. This was done to prevent the CMBA from coming out of solution as it is insoluble in water. The reaction schematic is given in Figure 4.9. There are two reactive –NH sites on the backbone of the PBI structure. Both sites are susceptible to reaction but for simplicity sake, reaction to one site will be shown throughout the remainder of this paper for all modifications. A 50/50 mixture of both solutions constituted the final volume. The reaction mixture was then placed in an incubator set at 40°C for 48 hours. The temperature was chosen to help keep the reagents in solution and minimize acetone evaporation. No mixing was necessary. Upon completion of the reaction, the membranes were removed and first washed with acetone to remove residual CMBA then they were washed with copious amounts of DI water to remove the remaining sodium persulfate and acetone. Once again the membranes were stored in 50/50 DI water and glycerol.
4.3.2 - Method 1: N-ethyl-N(3-dimethylaminopropyl) carbodiimide chemistry

The subsequent reactions involved N-ethyl-N(3-dimethylaminopropyl) carbodiimide (EDC) chemistry. EDC (structure given in Figure 4.10) facilitates the reaction between –COOH of the carboxylic acid bound to the PBI backbone and the amine group of the functional monomers.
The monomers used for modification (shown in Figure 4.13) were ethylene diamine, para-phenyl diamine, and taurine. Some physical properties of each are given in Table 4.1. Each was chosen due to their potential to impart a negative charge on the surface of the membrane as well as the ability to increase hydrophilicity. EDC reacts with the hydroxyl group contained in the carboxylic acid to form an unstable ester intermediate (Figure 4.11). The amount of reagents used for EDC catalyzed modification was based on the final weight of dried surface activated samples. From the molecular weight of CMBA modified PBI sheets (442 g/mol) a 10 fold molar excess of all reagents were used. Reagents include 4-dimethylaminopyridine (DMP, 122 g/mol), EDC (155 g/mol, $\rho=0.877$ g/cm$^3$) and the above mentioned monomers. DMP was used to help stabilize the intermediate formed. The reaction was done in DI water and run for 48 hours at 55°C. It is important to note that reagent addition times are extremely important. EDC was allowed to mix no longer than five minutes after its addition. The monomer was then immediately added and allowed to mix. If the EDC ester intermediate is allowed to sit in water for too long the unstable ester formed will convert back to its carboxylic acid form. Once the reaction was completed, copious amounts of DI water were used to wash the membranes. They were then stored in 50/50 glycerol and DI water until they were tested. The reaction schematic is shown in Figure 4.12.
Figure 4.11 – Unstable EDC ester intermediate
Figure 4.12 – Reaction Schematic of EDC Catalyzed Chemistry

Where the R groups are:

Phenyl Diamine  
Taurine  
Ethylene Diamine

Figure 4.13 – Reaction Monomers
Table 4.1 – Physical properties of monomers used in modification

<table>
<thead>
<tr>
<th></th>
<th>Taurine</th>
<th>para-Phenyl Diamine</th>
<th>Ethylene Diamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKa/pKb*</td>
<td>9.06</td>
<td>5.30</td>
<td>10.81*</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>125.15</td>
<td>108.10</td>
<td>60.10</td>
</tr>
<tr>
<td>(g/mol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.73</td>
<td>33.72</td>
<td>0.90</td>
</tr>
<tr>
<td>Melting/Boiling</td>
<td>305.11</td>
<td>145.14</td>
<td>116.00*</td>
</tr>
<tr>
<td>Point* (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.3 - Method 2: N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride chemistry

A second reaction method using N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCH) (structure given in Figure 4.14) was investigated based on quicker reaction times, lower cost of reagents and stability of intermediate formed.

![Figure 4.14 – Structure of N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride](image)
The protocol for this chemistry was provided by Thermofisher. Initially a stock solution of 2-(N-morpholino) ethanesulfonic acid (MES) buffer was prepared. In order to do so, a mixture containing 250 ml of 0.1 M MES and 250 ml of 0.5 M sodium chloride was titrated to a pH of 6 using 1 N sodium hydroxide. Relative to the amount of buffer used, EDCCH and N-hydroxysuccinimide (NHS) were added to a concentration of 2 mM and 5 mM respectively. CMBA modified samples were then added having an overall weight between 0.3-0.33g. The reaction mixture was stirred vigorously for ~15 min to form the reaction intermediate (Figure 4.15). It is important to note, similar to the EDC catalyzed reaction, an unstable ester intermediate analogous to that shown in Figure 4.11(a) is formed before the more stable ester intermediate.

![Figure 4.15 –Formation of NHS Ester Intermediate](image-url)
To quench the reaction for monomer addition, 280 μL of 2-mercaptoethanol were added to the reaction mixture and stirred vigorously. In order to optimize the pH for monomer addition (pH 7-7.5), a titration was performed using 0.5 M sodium hydroxide. An equimolar amount of desired monomer (see Figure 4.13) to CMBA modified PBI was then added and stirred vigorously for 2 hours. All reactions were done at room temperature. All samples were washed with copious amounts of DI water and stored in 50/50 DI/glycerol until needed. The final product using taurine is shown in Figure 4.16.

Figure 4.16 – Final product formation of EDCH catalyzed chemistry using taurine
4.4- Analytical Methods

All equipment used was located in the Center for Materials and Sensors Characterization Center at the University of Toledo College of Engineering.

4.4.1- Fourier Transform Infrared Spectroscopy (FTIR-ATR)

Evidence that the chemical bonding occurred was obtained by 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 changes in the vibrational spectra changes in molecular conformation can also be observed. This was done on a Varian Excalibur Series Fourier Transform Infrared instrument, the FTS-4000 Spectrometer and the UMA-600 Microscope (Randolph, MA.)

4.4.2- Contact Angle

A Tantac Model CAM-MICRO Contact Angle Meter (Tantac, Inc., USA) was used to monitor changes to the hydrophilicity and as another means of verifying membrane modification. By placing a small drop of water onto the sample, the angle of the resulting bubble can be determined. In samples that are hydrophobic the angle remains high. In samples that are hydrophilic the angle decreases due to the samples ability to absorb water (Figure 4.17).
4.4.3- Chemical Force Microscopy (CFM)

Membrane surface charge and correlation to its morphology can be assessed using chemical force microscopy. Measurements have been carried out on clean membrane sheets using chemically modified silicon nitride pyramidal tips attached to the end of a V-shaped cantilever with a spring constant of 0.12 N/m. The modified tips have been functionalized with a self-assembled mono-layers (SAM) terminating in methyl (CH₃) end groups (NovaSCAN technologies, Ames, IA). CFM images have been generated by recording traces of cantilever vertical and lateral deflection while the membrane has been scanned back and forth in contact mode. In this manner, the membrane surface topography and membrane surface energy (adhesive or repulsive) have been measured simultaneously. In order to measure CFM of membranes a Veeco Nanoscope IIIa Multimode Scanning Probe Microscope (Veeco, USA) was used.
4.4.4- Environmental Scanning Electron Microscopy (ESEM)

Environmental scanning electron microscopy was used to detect any changes in the porous interior of the membranes during modification steps as well as verify thickness of the cast membrane. An FEI Quanta 3D FEG Dual Beam Electron Microscope (FEI, USA) was used. By freezing small samples of the membranes in liquid nitrogen and cracking them, cross-section areas could be observed. After the samples were frozen and cracked, they were wet using DI water and placed vertically in carbon paste. The advantage of using ESEM over SEM is the (scanning electron microscopy) ability to test wet samples. In aqueous conditions, PBI membranes are very strong and flexible. When allowed to dry they become very brittle and a susceptible to breaking.
4.5 Transport Properties

4.5.1- Pure Water Flux

Pure water flux (PWF) testing was performed using an Amicon 8010 dead flow cell (Millipore, USA) run as a pressure driven process (Figure 4.18).

Testing parameters were as follows: 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 ensure no contaminants were 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 PWF, 1 ml samples were collected over a period of 10 ½ hours. This process was repeated for the unmodified, CMBA activated, and all EDC (method 1) and EDCH (method 2) catalyzed membrane modifications. In order to obtain a standard deviation for the above mentioned membranes, three separate membranes were tested for each surface chemistry.

4.5.2- Monovalent Salt Solutions for Testing

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

Solutions were run through the Amicon 8010 dead flow cell at a constant pressure of 70 psi with the same nylon supports used to determine PWF. Constant stirring was maintained inside the cell in order to prevent salt build up on the surface of the membrane. Initial feed volumes of 10 ml were used for each test. In order to determine the percent salt rejection, the conductivity of each of the feed solutions was tested before sample collection. 2 ml samples were collected and the conductivity of these samples was then measured. The percent rejection was determined using the following equation:

\[
\text{% Rejection} = \left(1 - \frac{\text{Final Conductance}}{\text{Initial Conductance}}\right) \times 100
\]  

(4.1)
As with PWF, standard deviations were determined using three separate membranes for the unmodified, CMBA activated, EDC and EDCH catalyzed membrane modification. For each membrane three 2-ml samples of each concentration and each pH were collected and tested.
Chapter 5

Manuscript

Abstract
Polybenzimidizole (PBI) is seeing increased uses in a number of applications due to high mechanical and thermal stabilities such as membrane filtration. Two drawbacks of PBI membranes are low hydrophilicity and neutral charge at neutral pH values, which leads to low rejections of ions. These drawbacks can hinder the use of PBI membranes in water applications. To investigate methods to increase hydrophilicity and charge them, PBI membranes were cast in the form of flat sheets using the phase-inversion technique. Then, three monomers (taurine, para-phenyl diamine, and ethylene diamine) were chosen based on their potential to impart charges and hydrophilicity on the PBI membrane. The surface of the PBI membrane was activated using 4-(chloromethyl) benzoic acid (CMBA). Two chemical reaction methods were used to attach the monomers to the surface. Characterization of the membrane was done using fourier transform infrared spectroscopy in attenuated reflectance mode (FTIR-ATR), contact angle measurement, chemical force microscopy (CFM), and environmental scanning electron microscopy (ESEM). The chemical modification was varied several methods. Additionally, modification resulted in increased hydrophilicity and increased
Pure water flux was found to decrease by 33% after surface activation by ~70% after chemical modification as compared to that of the unmodified PBI membrane. Monovalent salt rejection was investigated using sodium chloride feed at concentrations from 3.5 mM to 100 mM and at pH values of 7 and 10. At both pH values salt rejection decreased exponentially with increasing concentration, and modified membranes provided higher rejections than unmodified membranes.

1. Introduction

Fresh potable water is an essential human need and thus looming water shortages threaten the world’s peace and prosperity. Along with the global water scarcity, less and less access to clean water has become a worldwide issue afflicting people, especially in the developing nations (1). Currently, about half of the world’s population suffers from water shortages. Over the next 25 years, the number of people affected by severe water shortages is expected to increase fourfold (2). In the developing countries that are most affected, 80-90% of all diseases and 30% of all deaths result from poor water quality (3). In addition, modern economies cannot develop and thrive without sufficient access to water. Therefore, there is growing recognition by governments and corporations that future peace and prosperity is intimately tied to the availability of clean, fresh water (4). Wastewater, brackish water, and seawater have great potential to meet future water quantity needs and regulations (5). More and more effort has been put into evaluating the potential techniques to recover fresh water from wastewater and seawater/brine desalination (6). Membrane technology has offered an effective approach to addressing water scarcity. So far, the most widely used membrane processes for water purification
include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). All of these are pressure-driven processes, which require energy to pressurize the system. Of specific interest here is RO. By pressurizing an impure water or saline water feed above its osmotic pressure, RO allows for the recovery of pure water. RO is currently the most effective desalination process. In order to be commercially viable, new desalination techniques must either match or exceed RO in product water cost, water quality, operability and maintenance requirements, water recovery rates, or energy and capital costs.

While pressure-driven membrane processes, such as RO, have dominated for several decades, new desalination processes are now emerging, such as forward osmosis (FO) (7). Like RO, FO uses a semi-permeable membrane to separate water from dissolved solutes. The semi-permeable membrane acts as a barrier that allows water to pass through while blocking salts. Thus, FO may offer the advantage of rejection of a wide range of contaminants. Instead of employing hydraulic pressure as the driving force for the separation, FO uses the osmotic pressure gradient across the membrane to induce a net flow of water through the membrane into a draw solution (generally a high concentration salt solution); thus, efficiently separating the fresh water from its solutes. Because it is driven by an osmotic pressure gradient, FO does not require significant energy input, only stirring or pumping of the solutions. This process has a number of salient advantages; for example, FO consumes only about 20-30% of the energy required by other desalination processes and may use very low quality heat, such as the “waste” heat from a power plant, as its energy input (8). FO has the potential for high recovery, resulting in less brine discharge to the environment (9).
However, there are major hurdles to fully explore FO as a new water production technology that include a small number of commercially available FO membranes with proper separation performance and lack of user friendly and economic draw solutions (8). FO applications in real-world water purification have long been hindered by three key challenging issues. Firstly, presently available membranes are mostly made for pressure-driven processes; development of membranes tailor-made and fully effective for osmotically driven FO processes is still in its infancy. Ideal FO membranes should have much thinner selective layers or have very low transport resistance in order to minimize internal concentration polarization and enhance membrane flux. Secondly, compared to abundant research in pressure-driven processes, a mechanistic understanding of the unique solute transport phenomena and fouling/cleaning behavior of FO processes is basically lacking. This knowledge gap has severely discouraged systematic development (vs. trial-and-error approaches) of FO membranes. Lastly, suitable draw solutions that are able to create high osmotic pressures while containing solutes that can be removed efficiently and completely have not been readily available.

This study focuses on the first issue – FO membrane materials. One approach to overcome current obstacles with respect to low efficiency FO membranes is through surface modification or functionalization of existing membranes to provide targeted properties. For example, by placing a charged monomer on the surface of a membrane, the rejection of monovalent salts (i.e. sodium chloride and potassium chloride) may be increased.

Research toward developing FO-competent membranes has been very limited. Recently, membranes have appeared specifically made for FO purposes. For example, Hydration
Technologies, Inc. (Albany, OR) produced a cellulose acetate FO membrane (9). Although this membrane has relatively high flux, it finds only limited applications due to high material biodegradability, severely shortening the membrane life. Researchers at the National University of Singapore developed a hollow fiber FO membrane made of polybenzimidizole (PBI) (10). The PBI membrane can generate high flux in FO process and thus is a very promising material for FO membrane development, even though the salt rejection of this membrane is relatively low. Therefore, there is a pressing need to produce high-performance membranes that are fully fit for FO processes.

The objectives of this research were to prepare flat sheet PBI membranes in house and chemically modify their surfaces using three separate monomers (taurine, ethylene diamine, and para-phenyl diamine). The monomers were chosen based on their potential to impart negative charges to the membrane surface. From this modification, it was expected that by increasing the overall surface charge, salt rejection would increase. Based on the monomers chosen it was also expected that the overall hydrophilicity would increase.

PBI membranes were cast via the phase inversion method, and the surfaces of the unmodified PBI membranes were then activated using 4-(chloromethyl) benzoic acid (CMBA). Two different chemistry methods were used to attach the chosen monomers to the activated surface. The first method used N-ethyl-N(3-dimethylamino) carbodiimide (EDC) while the second used N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCH) as platforms for the reactions.

In order to verify surface modification, a number of analytical techniques were used. Initially, Fourier transform infrared spectroscopy in attenuated total reflection mode...
(FTIR-ATR) was used to detect structural changes based on specific functional groups associated with each of the monomers. To determine the changes in hydrophilicity, as well as a secondary means of confirming chemistry, contact angle was measured using a goniometer. Chemical force microscopy (CFM) was used to detect changes to the charge on the membrane surface. Finally, environmental scanning electron microscopy (ESEM) was used to detect any changes in morphology of the membranes during and after modification.

In order to evaluate transport characteristics of unmodified, surface activated and EDC/EDCH modified membranes, dead-end flow permeability cells were used in a pressure-driven mode. Pure water flux was determined for all membranes as well as monovalent salt rejection (sodium chloride) in this mode. In order to detect changes in salinity, a conductivity meter was used to test conductance of both the feed and the resulting permeate.

2. Experimental

2.1 Materials

Polybenzimidizole dope was supplied by PBI Performance Products, Inc. (Charlotte, NC) at a 26 wt% solution. Taurine, para-phenyl diamine, ethylene diamine, 4-dimethylaminopyridine, dimethylacetamide, 4-(chloromethyl) benzoic acid, N-ethyl N(3-dimethylamino) carbodiimide, N-hydroxysuccinimide, N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride, 2-(N-morpholino)ethanesulfonic acid and sodium persulfate were purchased from Sigma-Aldrich (USA). Acetone, glycerol, and sodium
chloride were purchased from Fisher Scientific (USA). 2-mercaptoethanol was purchased from Alfa Aesar. DI water was supplied by a continuous distillation apparatus.

2.2 Flat Sheet Polybenzimidizole Preparation

Flat sheet polybenzimidizole membranes were prepared in house to allow for control of surface modification. Polybenzimidizole dope was supplied by PBI Performance Products Inc. (Charlotte, NC). The procedure used to prepare the sheets was adapted from Wang et al (2006) (62). The initial concentration of the dope was 26 wt% with an overall composition of 26 wt% PBI, 72 wt% dimethylacetamide (DMAc), and 2.0 wt% Lithium Chloride. A desired concentration of 20% was achieved by dilution with DMAc. In order to prevent air bubbles from being trapped in the dope, the beaker was sealed with parafilm and rotated by hand every 10 minutes for approximately 2 hours. The dope was then placed 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 flat sheet. To insure minimal friction between the blade and the mirror, the rails of the blade were lubricated using motor oil. Once the sheet was cast, the solvent was removed by phase-inversion process (62). A 12-gallon DI water coagulation bath was used to induce phase-inversion and subsequent pore formation. Once the phase inversion had taken place, the membrane peeled from the mirror. The membrane was thoroughly washed with DI water and ¼ inch circles were punched for use. The number of samples obtained from a sheet was dependant on the amount of dope initially used. All membranes were stored in a 50/50 mixture of DI water and glycerol until use. Glycerol was added due to the possibly of water evaporation. It is important to keep the membranes wet. When they are dried
they become brittle and are susceptible to breakage.

2.3 Membrane Modification

2.3.1 Surface activation using 4-(chloromethyl) benzoic acid

The initial modification using 4-(chloromethyl) benzoic acid (CMBA) was done as follows: in a 50-ml beaker, a 0.5wt% solution of CMBA was prepared in acetone and was stirred until all the solute was dissolved. In a separate 50-ml beaker, a 1.0wt% solution of sodium persulfate was prepared in DI water and stirred until all the solute was dissolved. Sodium persulfate was used as a free radical initiator for the reaction. The membranes to be modified were then added to the sodium persulfate solution. CMBA was slowly added to the sodium persulfate solution. This was done to prevent the CMBA from coming out of solution as it is insoluble in water. A 50/50 mixture of both solutions constituted the final volume. The reaction mixture was then placed in an incubator set at 40°C for 48 hours. The temperature was chosen to help keep the reagents in solution and minimize acetone evaporation. No mixing was necessary. Upon completion of the reaction, the membranes were removed and first washed with acetone to remove residual CMBA then they were washed with copious amounts of DI water to remove the remaining sodium persulfate and acetone. Once again the membranes were stored in 50/50 DI water and glycerol.
2.3.2 Method 1: N-ethyl-N(3-dimethylaminopropyl) carbodiimide chemistry

The subsequent reactions involved N-ethyl-N(3-dimethylaminopropyl) carbodiimide (EDC) chemistry. EDC facilitates the reaction between –COOH of the carboxylic acid bound to the PBI backbone and the amine group of the functional monomers. The monomers used for functionalization were ethylene diamine, para-phenyl diamine, and taurine. Each was chosen due to their potential to impart a negative charge on the surface of the membrane as well as the ability to increase hydrophilicity. EDC reacts with the hydroxyl group contained in the carboxylic acid to form an unstable ester. The amount of reagents used for EDC catalyzed modification was based on the final weight of dried surface activated samples. From the molecular weight of CMBA modified PBI sheets (442 g/mol) and the final weight of the samples to be modified 10 fold molar excess of all reagents were used. Reagents include 4-dimethylaminopyridine (DMAP, 122 g/mol), EDC (155g/mol, ρ=0.877 g/cm³) and the above-mentioned monomers. DMAP was used to help stabilize the intermediate. The reaction was done in DI water and run for 48 hours at 55°C. It is important to note that reagent addition times are extremely important. EDC was allowed to mix no longer than five minutes after its addition. The monomer was then immediately added and allowed to mix. If EDC ester intermediate is allowed to sit in water for too long the unstable ester formed will convert back to its carboxylic acid form. Once the reaction was completed, copious amounts of DI water were used to wash the membranes. They were then stored in 50/50 glycerol and DI water until they were tested.
2.3.3 Method 2: N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride chemistry

A second reaction method using N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCH) was investigated based on quicker reaction times, lower cost of reagents and stability of intermediate formed. The protocol for this chemistry was provided by Thermofisher. Initially a stock solution of 2-(N-morpholino)ethanesulfonic acid (MES) buffer was prepared. In order to do so, a mixture containing 250 ml of 0.1 M MES and 250 ml of 0.5 M sodium chloride was titrated to a pH of 6 using 1 N sodium hydroxide. Relative to the amount of buffer used, EDCH and N-hydroxysuccinimide (NHS) were added to a concentration of 2 mM and 5 mM respectively. CMBA modified sheets were then added with sheets having an overall weight between 0.3-0.33g. The reaction mixture was stirred vigorously for ~15 min to form the reaction intermediate. It is important to note, similar to the EDC catalyzed reaction, an analogous unstable ester intermediate is formed before the more stable ester intermediate. To quench the reaction for monomer addition, 280 μL of 2-mercaptoethanol were added to the reaction mixture and stirred vigorously. In order to optimize the pH for monomer addition (pH 7-7.5), a titration was performed using 0.5 M sodium hydroxide. An equimolar amount of desired monomer to CMBA modified PBI was then added and stirred vigorously for 2 hours. All reactions were done at room temperature. All membranes were washed with copious amounts of DI water and stored in 50/50 DI/glycerol until needed.
2.4 Membrane Characterization

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR-ATR)

Evidence that the chemical bonding occurred was obtained by 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 changes in the vibrational spectra changes, molecular conformation can also be observed. This was done on a Varian Excalibur Series Fourier Transform Infrared instrument, the FTS-4000 Spectrometer and the UMA-600 Microscope (Randolph, MA.)

2.4.2 Contact Angle

A Tantec Model CAM-MICRO Contact Angle Meter (Tantac, Inc., USA) was used to monitor changes to the hydrophilicity and as another means of verifying membrane modification. By placing a small drop of water onto the sample, the angle of the resulting bubble can be determined. In samples that are hydrophobic the angle remains high. In samples that are hydrophilic the angle decreases due to the samples ability to absorb water.

2.4.3 Chemical Force Microscopy (CFM)

Membrane surface charge and correlation to its morphology can be assessed using chemical force microscopy. Measurements have been carried out on clean membrane sheets using chemically modified silicon nitride pyramidal tips attached to the end of a V-shaped cantilever with a spring constant of 0.12 N/m. The modified tips have been functionalized with a self-assembled mono-layers (SAM) terminating in methyl (CH$_3$)
end groups (NovaSCAN technologies, Ames, IA). CFM images have been generated by recording traces of cantilever vertical and lateral deflection while the membrane has been scanned back and forth in contact mode. In this manner, the membrane surface topography and membrane surface energy (adhesive or repulsive) have been measured simultaneously. In order to measure CFM of membranes a Veeco Nanoscope IIIa Multimode Scanning Probe Microscope (Veeco, USA) was used. In order to determine the charge, the Simpsons (trapezoidal) rule was used to calculate the area under the obtained curves. The general form of the Simpsons rule is given in equation 1 (68).

\[
\text{Area} = \int_{x_o}^{x_n} f(x)dx = \frac{h}{3} \left( f_o + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \cdots + 4f_{n-1} + f_n \right)
\]

where: \( h = \frac{(x_n-x_o)}{n} \)  

(1)

The curves were obtained by checking the frequency at which charges occurred over a range of negative and positive values (i.e. -14 to -12, -12 to -10, 10-12, 12-14 etc.). For each of the membranes tested these ranges were different. Areas for both the positive and negative sides were then obtained. From this, a ratio of negative surface charge to overall surface charge gave the final surface negative charge percentage. An example calculation is given in Appendix A. One sample of each membrane was tested.

2.4.4 Environmental Scanning Electron Microscopy (ESEM)

Environmental scanning electron microscopy was used to detect the impact of surface modification of the membranes as well as verify thickness of the cast membrane. An FEI Quanta 3D FEG Dual Beam Electron Microscope (FEI, USA) was used. By freezing
small samples of the membranes in liquid nitrogen and cracking them, cross-section areas could be observed. After the samples were frozen and cracked, they were wet using DI water and placed vertically in carbon paste. The advantage of using ESEM over SEM is the (scanning electron microscopy) ability to test wet samples. In aqueous conditions, PBI membranes are very strong and flexible. When allowed to dry they become very brittle and a susceptible to breaking.

2.5 Transport Properties

2.5.1 Pure Water Flux

Pure water flux (PWF) testing was performed using an Amicon 8010 dead flow cell (Millipore, USA) run as a pressure driven process Fig. 1.

![Fig. 1 – Dead cell flow schematic](image-url)
Testing parameters were as follows: 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 ensure no contaminants were 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 PWF, 1 ml samples were collected over a period of 10 ½ hours. This process was repeated for the unmodified, CMBA activated, and all EDC (method 1) and EDCH (method 2) catalyzed membrane modifications. In order to obtain a standard deviation for the above mentioned membranes, three separate membranes were tested for each surface chemistry.

2.5.2- Monovalent Salt Solutions for Testing

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

Solutions were run through the Amicon 8010 dead flow cell at a constant pressure of 70 psi with the same nylon supports used to determine PWF. Constant stirring was maintained inside the cell in order to prevent salt build up on the surface of the membrane. Initial feed volumes of 10 ml were used for each test. In order to determine the percent salt rejection, the conductivity of each of the feed solutions was tested before
sample collection. 2 ml samples were collected and the conductivity of these samples was then measured. The percent rejection was determined using the following equation:

\[
\% \text{ Rejection} = (1 - \frac{\text{Final Conductance}}{\text{Initial Conductance}}) \times 100
\]  

As with PWF, standard deviations were determined using three separate membranes for the unmodified, CMBA activated, EDC and EDCH catalyzed membrane modification. For each membrane three 2-ml samples of each concentration and each pH were collected and tested.

3. Results and discussions

3.1 Membrane Characterization

3.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The ATR-FTIR spectra for the unmodified and PBI surface activated using 4-CMBA are shown in Fig. 2. The N-H groups of the imidizole ring are found between 2700 cm\(^{-1}\) and 3600 cm\(^{-1}\) for all spectra. C=N and C=C stretching from the five-member heterocyclic ring was found between 1630 cm\(^{-1}\) and 1680 cm\(^{-1}\) for all spectra. All spectra also had a C-H stretching peak around 800 cm\(^{-1}\). Activation of the PBI was confirmed by the presence of the carboxylic acid associated with 4-CMBA. The large band at 1057 cm\(^{-1}\), the sharp peak at 1643 cm\(^{-1}\), and the broad band around 2670 cm\(^{-1}\) represented the C-O, C=O, and the OH of the carboxylic acid, respectively.
The two functionalization approaches (i.e. EDC vs. EDCH) would result in the same final structure for modified groups. Therefore, the spectra for each monomer will be compared to base CMBA modified PBI membrane. Ethylene diamine modification was confirmed using the spectra given in Fig. 3. The presence of the primary amine was confirmed by the with C-C-N and NH$_2$ bands at 1179 cm$^{-1}$ and 1653 cm$^{-1}$ respectively. Formation of the secondary amide was shown with bands at 1179 cm$^{-1}$ and 1653 cm$^{-1}$ representative of the C-C-N and N-H bonds. The secondary amide carbonyl was found at 1620 cm$^{-1}$. It was initially thought that ethylene diamine may have the ability to crosslink in the backbone due to its amine groups. The NH$_2$ bands showed that it was most likely not being cross-linked and the non-reacted amine was still free.
Fig. 3  PBI functionalized with Ethylene Diamine using the EDC and EDCH method

The spectra for the p-phenyl diamine modification are show in Fig. 4. The formation of the primary amine was confirmed with the C-C-N band at 1179 cm\(^{-1}\) and the NH\(_2\) band at 1645 cm\(^{-1}\). Bands at 1179 cm\(^{-1}\), 1615 cm\(^{-1}\), and 1645 cm\(^{-1}\) represented C-C-N, C=O, and N-H bonds associated with the formation of the secondary amide.
**Fig. 4** PBI functionalized with para-phenyl diamine using the EDC and EDCH method

Confirmation of covalent binding of taurine to CMBA activated PBI is shown in Fig. 5. The C-C-N from the secondary amide of the backbone was found at 1168 cm\(^{-1}\). The secondary amide carbonyl was found at 1647 cm\(^{-1}\) as well as the N-H band overlapped. The symmetrical and anti-symmetrical stretches of SO\(_2\) from the sulfone were found at 1168 cm\(^{-1}\) and 1285 cm\(^{-1}\) respectively. The S=O stretch from the sulfone was found at 1215 cm\(^{-1}\).
From all above spectra, it can be seen that both chemical methods are comparable in terms of final surface modification. The expected peak additions and losses were observed for all three monomers for both methods.

3.1.2 Contact Angle

Fig. 6 shows contact angle measurements for the unmodified PBI and all monomer modifications using both EDC and EDCH methods. One sample of each membrane was tested three times in order to obtain standard deviations. The hydrophylicity of the surface increased after activation and modification for both methods as shown by decreased in contact angle, the taurine functionalized surface PBI were the most

Fig. 5  PBI functionalized with taurine using the EDC and EDCH methods
hydrophilic. This was most likely due to taurine’s greater ability to hydrogen bond. The sulfone 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 resulted in lowest hydrophilicity of the three monomers used in this study. This was expected due to the limited change it brings to the surface of the membrane. Ethylene diamine is an alkane form 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. Based on standard deviations, it can be seen that for each chemistry, the change in hydrophobicity was fairly consistent for each monomer added.

![Fig. 6 Contact angle measurements for all chemistries](image)
3.1.3 Chemical Force Microscopy (CFM)

The change in surface charge coverage was detected using CFM as shown in Table 1. The values presented here represent the percentage of the surface that is negatively charged, and not charge densities. A net negative surface coverage was added to the surface of the membrane. Initially, the negative surface coverage of the unmodified PBI membrane was 41.89%; that is, the membrane surface was mostly comprised of neutral and positive charges. This is consistent with one of the two key drawbacks of PBI membranes for desalination applications— that they are not negatively charged at neutral pH value. When activated using CMBA, the negative surface coverage increased to 52.83%; that is, now the overall surface coverage became more negative than neutral or positive as with the unmodified membrane. This is due to the carboxylic bond added by the CMBA. All monomers used during the final modification step led to an overall increase in the percentage of negative coverage of the modified membrane surfaces, as expected since all monomers were chosen for their ability to impart negative charge to surfaces. Taurine-modified membranes displayed 59.38% and 58.42% negative charge coverage for methods 1 and 2, respectively. Ethylene diamine-modified membrane surfaces had 59.92% and 56.77% negative charge coverage for methods 1 and 2, respectively. Lastly, for method 1 chemistry, para-phenyl diamine-modified membranes displayed 58.75% negative charge coverage, and for method 2, 55.23%. This once again shows that chemical modification was successful with both methods and that modification increased the negative charge to the surface of PBI.

Without further testing, a statistical comparison of both methods cannot be made. However, from the results one can argue with a reasonable degree of certainty that
through surface activation and subsequent modification the overall negativity did increase. Further testing is suggested in this area. Of interest would be repeating Method 2 (due to the cost of the reagents used in method 1). By preparing three separate flat sheets, obtaining samples from each and modifying them, a more solid statistical approach can be taken and the conclusions could be further validated. It is also suggested that the samples be tested at pH 10 to see what effect increasing the basicity has on the overall surface charge of the membrane.

Table 1
Change in net negative surface coverage of membranes due to modification

<table>
<thead>
<tr>
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<th>% Neg</th>
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<tbody>
<tr>
<td>Virgin</td>
<td>42%</td>
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<tr>
<td>CMBA</td>
<td>53%</td>
</tr>
<tr>
<td>ED (1)</td>
<td>60%</td>
</tr>
<tr>
<td>ED (2)</td>
<td>57%</td>
</tr>
<tr>
<td>PD (1)</td>
<td>59%</td>
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<tr>
<td>PD (2)</td>
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<td>Taurine (1)</td>
<td>59%</td>
</tr>
<tr>
<td>Taurine (2)</td>
<td>58%</td>
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</table>
3.1.4 Environmental Scanning Electron Microscopy (ESEM)

As shown in Fig. 7, the overall thickness of the membranes used was actually 170 μm. This was a 20-μm difference from the desired thickness of 150 μm, which was attributed to operator error. The doctor’s blade thickness was set by hand at an approximate value. 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 proof that the phase-inversion process was successful.

Fig. 7 Cross-section of asymmetric PBI membrane showing selective and support layers

Figures 8-10 show some ESEM images of the unmodified, CMBA surface activated, and a para-phenyl diamine modified membrane. The scale of the figures is not the same, so what is seen on the images cannot be compared. Fig. 8 is at a magnification of 50 μm while Figs. 9 and 10 are at 100 μm.
Fig. 8 Cross-section of unmodified PBI membrane

Fig. 9 Cross-section of CMBA modified PBI membrane

Fig. 10 Cross-section of para-phenyl diamine modified PBI membrane
3.2 Transport Properties

3.2.1 Pure Water Flux

As expected, the pure water flux decreased following modification for both functionalization chemistries used for this study. Initially, the unmodified membrane had an average flux of 17.71 L/m²·h with a standard deviation of 0.799. After surface activation with CMBA, the average flux decreased by approximately 33% of that of the unmodified to 12.49 L/m²·h, with a standard deviation of 0.857. This was likely due to pore blockage or the membrane becoming denser after activation and modification, as shown in Figures 8 and 9.

For the first method of modification, the fluxes were all similar to each other, with each of them dropping by ~70% relative to the unmodified PBI membrane flux values. For taurine, the average value was 5.86 L/m²·h with a standard deviation of 0.356. Ethylene diamine had an average flux of 5.78 L/m²·h with a standard deviation of 0.179. Finally, para-phenyl diamine gave an average flux of 5.60 L/m²·h with a standard deviation of 0.282.

Method 2 gave similar results to those of method 1. Once again, all of the average flux values decreased by ~70 relative to the unmodified PBI membrane flux values. Taurine displayed an average flux value of 5.72 L/m²·h with a standard deviation of 0.105. Para-phenyl diamine gave an average value of 5.74 L/m²·h with a standard deviation of 0.160. Finally, ethylene diamine had an average flux value of 5.59 L/m²·h with a standard deviation of 0.094. Average fluxes as a function of time for membranes modified using EDC and EDCH methods are given in Figs. 11 and 12, respectively.
Fig. 11 Pure water flux: Method 1

STD DEV:
Virgin: ±0.799
CMBA: ±0.857
Taurine: ±0.356
Ethylene Diamine: ±0.179
p-Phenyldiamine: ±0.282

Fig. 12 Pure water flux: Method 2
The decrease in flux was most likely due to the modification of the surface, namely pore blockage of the selective layer (and possibly the support layer to some extent) due to that addition of each monomer. It would be difficult to prevent the monomer from entering into the pores and attaching in the same fashion as they do on the surface. The size (i.e. rough estimate of bond molecule bond lengths) of the monomers (CMBA, taurine, para-phenyl diamine, and ethylene diamine) was the probable cause of the almost uniform decrease as modification increases. The most important thing to note is that both chemical method 1 and chemical method 2 showed similar results for the flux in terms of average flux as well as decrease relative to the unmodified membrane.

3.2.2 Monovalent Salt Rejection

The isoelectric point of PBI membranes is approximately 7 (66). That is, a pH values below 7, the membrane would be positively charged, while at pH values above 7, the membrane would be negatively charged. This is consistent with CFM results (Table 1). Operation at pH values below 7 would be important in desalination applications since, to prevent scaling, pH values are kept below 7. On the other hand, for possible FO applications, such as concentrate treatment, operational pH values might be higher than 7 (18).

Fig. 13 shows that with modification, the monovalent salt rejection increased when method 1 was used for monomer addition. Though taurine has a larger negative dipole moment associated with the two pi bonded oxygen groups containing free electrons as well as the hydroxyl group, at pH 7 para-phenyl diamine had the highest salt rejection at lower concentrations. The percent rejections for taurine and para-phenyl diamine
modification when the feed solution contained 3.4 mM sodium chloride were 56.16% and 66.17%, respectively. The standard deviations for the 3.4 mM salt feed solution were 0.59 for taurine and 5.75 for para-phenyl diamine, so the difference in rejection is statistically significant. As the concentration increased the rejection stabilized and there wasn’t a significant difference in the final percent rejected among the modified membranes. However, all modified membranes showed higher rejections than the unmodified membrane for all concentrations tested.

When the feed pH was increased to 10, the outcome was different for method 1 modification (Fig. 14). The taurine-modified membrane showed the highest rejection values at lower concentration. Based on standard deviations at 3.4 mM (taurine: 1.41; para-phenyl diamine: 1.54) there wasn’t a significant statistical difference between the two. The percent rejections for taurine and para-phenyl diamine at 3.4 mM were 75.00% and 71.92%, respectively. Based on standard deviations for para-phenyl diamine at pH 7 and pH 10 there wasn’t much of a change in the rejection (statistically) when the pH was increased. Once again, as the concentration increased, the percent rejection stabilized and there was less of a difference between the modified membranes. It is hypothesized that by increasing the pH, the taurine was able to form its sodium salt, therefore making the monomers charge higher than at pH 7 resulting in higher rejection performance.
Fig. 13 Sodium chloride rejection at pH 7: Method 1

Fig. 14 Sodium chloride rejection at pH 10: Method 1
For method 2, only taurine was investigated for rejection properties (Fig. 15) due to equipment issues. At pH 7 the rejection was 40.63% with a standard deviation of 1.49. At pH 10 the rejection was 76.20% with a standard deviation of 2.66. This is the first place we see an inconsistency between the different chemical methods. At pH 7 the rejection value for method 2 is lower than that of method 1 (40.63% vs. 56.16%). This is a bit of a mystery as the rejection values at pH 10 for both methods are comparable. It is suggested that the chemistry be repeated for this method and membranes tested again at pH 7 and 10 in order to verify these results.

Fig.15 Sodium chloride rejection pH 7: Method 2
4. Conclusions

Flat sheet polybenzimidizole membranes were successfully cast, surface activated and then modified. ESEM images verified that they were in fact asymmetric membranes with an acceptable overall thickness from the desired. From the FTIR spectra, there was clear evidence that surface activation took place followed by modification for both methods of modification. An increase in hydrophilicity also verified that successful attachment of the chosen monomers, and that they achieved one of their purposes – to increase hydrophilicity of the membrane. CFM analysis showed an overall increase in negative surface charge percentage surface activation and modification. This once again verified successful chemical modification and the achievement of the second purpose of the
modification – to increase the negative charge of the surface. Pure water flux testing showed a nearly-linear decrease in flux as the amount of modification went up (i.e. surface activation to final modification). This was attributed to monomer size and subsequent blocking of the pores during modification. Sodium chloride rejection decreased exponentially as the feed concentration increased for all modifications as well as the unmodified membrane, with modified membranes always showing higher rejections than unmodified membranes. This trend was seen for both chemistries and feeds at pH 7 and pH 10. Promising salt rejections were observed upon monomer addition.

From the above work it can be said that both chemical methods had similar performance. Based on this, it would be suggested (aside from a few suggestions made earlier) that method 2 be the chemistry used in the future based off cost, time and safety. It would also be suggested that work be done with more sulfone containing compounds. Many of these are cheaper, in general are safer to use than amine based compounds, and have properties interesting to this study.
Chapter 6

Suggestions for future work

- Chemistry:
  - Continue work doing chemical method 2.
  - Use sulfonated monomers, instead of amine based monomers.

- Characterization
  - Vary the pH of solution used during CFM experiments to see the effect on the overall surface charge.

- Perform fouling experiments to determine effect of hydrophobicity changes.

- Produce modified membranes to be run in FO configuration.

- Use non-ionic monomers for modification, such as ethylene glycol. If all tests are performed in a similar manner, the addition of ethylene glycol would determine if the increase in rejection is due to smaller pores (due to reaction within pores) or due to charge (in this case, the rejection observed by the charged membranes would be higher).

- Use non-ionic polymers, such as poly(ethylene glycol) and dextran, to determine a pore size distribution of the membrane.
References


25. Y. Oren, Capacitive deionization (CDI) for desalination and water treatment-past,present, and future (a review), Desalination. 228 (2008) 10-29.


32. 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.


Appendix A

Use of the Simpsons Rule to find the area under CFM curves

This is a sample calculation showing how the Simpsons Rule was applied to CFM data in order to obtain the area and subsequent percent surface charge. This data is from taurine modification using method 1.
The plot values that were obtained were used to determine the area under each side of the curve. In order to use the Simpsons Rule the increments must be evenly spaced (i.e. 0, 2, 4 etc).

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Using Equation 1 the area under the positive region was found to be 0.987997 and the area under the negative region was 1.4443669. The total area was 2.4323638. By taking the ratio of the negative area to the total, a negative surface charge of 59.38% was obtained. This method was used for all membranes in this research.