

Desalination Pervaporation Using Modified Zwitterionic Poly(arylene ether sulfone)

Membranes

by

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ABSTRACT

Freshwater is becoming more and more scarce, and the need to make use of other water resources is critical. Although processes such as Sea Water Reverse Osmosis (SWRO) exist, these processes are not without drawbacks, such as a brine with a high salt concentration being a byproduct of SWRO. Pervaporation is a potential solution to this problem, however the membranes used in these processes are prone to fouling and the high salt conditions are difficult to work around. Incorporating zwitterions into the polymeric backbone of these membranes has proven to be an effective way to increase fouling resistance. In this work, sulfobetaine – based zwitterions were incorporated into the backbone of poly(arylene ether sulfone) to synthesize sulfobetaine – modified poly(arylene ether sulfone) (SB-PAES) membranes, which were then tested in a cross-flow pervaporation apparatus to analyze salt rejection.

SB-PAES membranes were cast with two different methods to create a consistent casting protocol. It was determined that casting solutions with a lower weight percent in petri dishes was optimal, but still needs more exploration. The SB-PAES membranes were tested with feed solutions of pure water and salt solutions with concentrations of 1 g/L, 5 g/L, and 10 g/L. Both 50% and 25% charge SB-PAES membranes were tested. The 50% charge membranes showed good flux and salt rejection over 99.9% for a 10 g/L feed solution, while the 25% charge membranes showed less flux and salt rejection around 85% for a feed solution of 10 g/L.

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CHAPTER 1

INTRODUCTION

The amount of potable water pales in comparison to the amount of water on the earth's surface. Factors such as current water usage as well as changes in the climate are leading to a global increase in water scarcity [1]. This decrease in potable drinking water, goes hand in hand with an increase in polluted water due to human consumption, with threatens both the environment and existing human settlements, and existing fresh water sources. Controlling and removing contaminants from wastewater is becoming a more reasonable pathway to solving this problem [2].

Purifying wastewater is not a novel idea; however, it comes with its own myriad of issues that are still being addressed. For example, most methods of treating water produce toxic waste, which while being removed from the water, still needs to be disposed of safely. In addition, these processes usually use large amounts of energy and chemicals, making these projects quite costly [3].

Membrane-separation processes are known for their effectiveness in filtration applications. They can be used in osmotic setups to control salt concentrations in aqueous solutions, which is helpful with seawater applications. Nanofiltration is commonly used for water softening by separating different cations, ultrafiltration is used to separate macromolecules, and microfiltration is used to separate colloids and other particles several micrometers in size [4]. Not only can membrane-separation processes be used for a wide variety of filtration applications, but the methodology is relatively simple and does not consume or produce toxic byproducts. Membranes used in this study are used for desalination of reverse osmosis brine using pervaporation techniques.

Reverse osmosis is currently considered the most developed membrane-separation technology, and it relies on a pressure gradient in which a mechanically applied hydraulic pressure is greater than the osmotic pressure, which allows the flow of water against the salt concentration gradient. However, while these methods are enticing given their simplicity and waste efficiency, reverse osmosis has its own unique issues [5].

Pervaporation instead uses the chemical potential of the membranes as opposed to a pressure gradient to separate components of aqueous solutions. They have been used effectively in applications pertaining to alcohols, separation of volatile and anhydrous mixtures, and dehydration of organic solvents [6]. Pervaporation uses differences in vapor pressure to drive components of the aqueous mixture through the membrane. This can be explained through use of the solution-diffusion model, in which permeants dissolve in the membrane material and diffuse down a concentration gradient [7]. Because of this distinction from pressure driven separation processes, this makes pervaporation a possible solution to the issues that come from reverse osmosis. While reverse osmosis is used to purify seawater, the efficiencies of these systems leave anywhere between 20-50% of the feed as a highly concentrated brine solution [8]. This solution is unable to be purified using reverse osmosis as this would require higher pressures that the membranes cannot withstand, as well as creating an even more concentrated salt solution byproduct which is challenging to dispose. Using pervaporation, these issues with reverse osmosis can be avoided.

Pervaporation has not yet seen widespread use in desalination, despite its advantages. Pervaporation is not limited by membrane hydrophobicity as seen in membrane distillation, and generally has salt rejection over 99% [9]. Because

pervaporation is also able to separate organic substances from aqueous solutions, this makes pervaporation a promising solution for creating drinking water from contaminated sources.

However, pervaporation membranes are not without issues. Membrane separation processes are prone to fouling, which decreases the permeate flux and therefore requires increased pressures and temperatures to meet the required flux. This not only increases operational costs, but also decreases the life of the membranes [5].

One method to decrease fouling effects is to incorporate zwitterions into the membrane through one of a few methods. Zwitterions contain both positively and negatively charged groups, which therefore form a tight hydration layer to prevent fouling through electrostatic forces, as the membrane becomes more hydrophilic. Through this, particles and bacteria are unable to settle onto the membrane surface [10]. There are multiple methods to incorporate zwitterions onto the surface of polymer membranes, or the polymers can be added to the polymeric backbone [11].

Polysulfone membranes are commonly used in membrane separation procedures due to its high thermal, mechanical, and chemical stability [12]. However, polysulfone is naturally hydrophobic, and therefore requires modifications to both increase flux and decrease fouling [10]. Modifications such as sulfonation and chloromethylation are effective in increasing the hydrophilicity of polysulfone [13, 14].

There are still issues with carrying out membrane modifications. For instance, membranes that have undergone surface grafting or initiated chemical vapor deposition are sensitive to chlorine-driven oxidative degradation and have complicated pre-treatment, therefore making it hard to produce feasible numbers without large costs and

energy usage [15]. To combat this issue, the membranes used in this project did not undergo surface modification, but instead went through modification of the membrane matrix. This not only helps with scalable manufacturing, but also increases chlorine resistance, increases membrane performance, and enhances water permeability through reducing internal concentration polarization [13, 16]. Therefore, sulfobetaine-modified poly(arylene ether sulfone) (SB-PAES) membranes were tested for their pervaporation performance by looking at pure water permeance and salt rejection. On top of this, membrane fabrication is a complex process, and multiple factors during synthesis could lead to changes in the physical chemistry of the polymers. Therefore, it is crucial to also standardize a protocol in casting membranes out of the SB-PAES to produce membranes of consistent thickness and structure.

CHAPTER 2

EXPERIMENTAL METHODS

To create the modified zwitterionic polysulfone membranes, the SB-PAES first had to be synthesized. This was done in three major steps using established protocols.

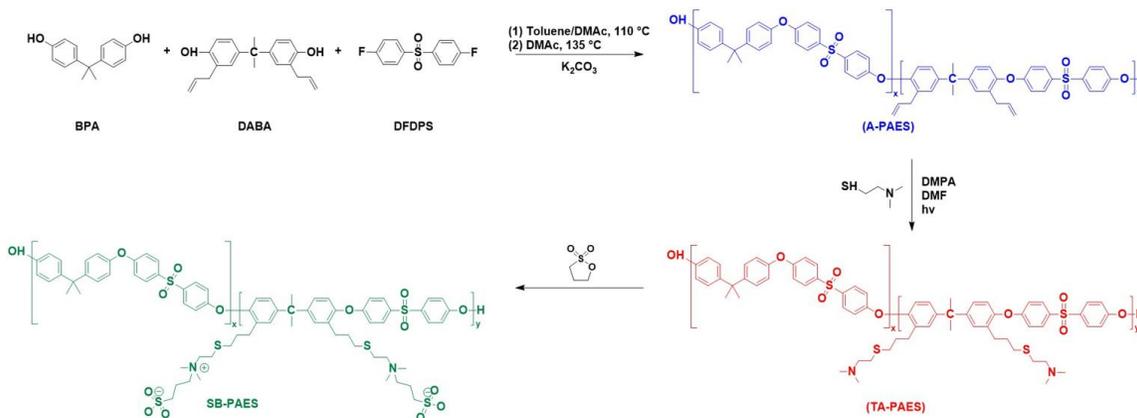


Figure 1: Reaction Scheme for the Synthesis of SB-PAES

Synthesis of allyl-modified poly(arylene ether sulfone)

Step growth polymerization of monomers 2,2' – diallyl bisphenol A (DABA), bisphenol A (BPA), and 4,4' – difluorodiphenyl sulfone (DFDPS) was applied to synthesize poly(arylene ether sulfone) (A-PAES). Charge percent of the polymer was controlled through the ratio of DABA and BPA. For example, a 1:1 mole ratio of DABA to BPA was used for 50% charged polymers. Monomers were added in 1:1 stoichiometric ratio between the aryl halides and phenols (1:1 of DFDPS: BPA+DABA). The monomers were added to a round-bottom reaction flask. K₂CO₃ was also added in 1.2 molar excess of the monomers, as well as dimethylacetamide (DMAC) and toluene to account for 25 wt.% solids. The solution was dissolved, the flask was connected to a dean-stark trap and then purged for 15 minutes with nitrogen. The mixture was then heated to 135° C to

remove the toluene-water azeotrope to remove the water generated from the polycondensation reaction. After toluene-water azeotrope removal the reaction was allowed to run for 6 hours at 145° C to achieve the desired molecular weight. Gel Permeation Chromatography (GPC) and Size-Exclusion Chromatography (SEC) were used to confirm the molecular weight of the product.

The formed polymer was then diluted with THF and HCl was added to neutralize the K₂CO₃. The polymer was then precipitated out in a 1:1 mixture of deionized (DI) water and methanol, and then filtered and dried in a vacuum at 80°C for 24 hours.

Synthesis of tertiary amine-modified poly(arylene ether sulfone)

A thiol-ene click reaction was used to add a tertiary amine to the backbone of the polymer. The synthesized A-PAES was set under a 365 nm UV light along with 2-(Dimethylamino)ethanethiol (5 molar excess) and 2,2-Dimethoxy-2-phenylacetophenone (DMPA) (0.3 equivalent) was used as the photo initiator. N,N-dimethylformamide (DMF) was used as the solvent (20 % solids) and the reaction was run between 3-8 hours at room temperature. Completion of the reaction was confirmed using ¹H NMR Spectroscopy. The mixture was then concentrated using a rotovap and the polymer was precipitated and dried in the same manner used in the synthesis of the A-PAES.

Synthesis of sulfobetaine-modified poly(arylene ether sulfone)

The synthesized tertiary amine-modified poly(arylene ether sulfone) (TA-PAES) along with 1,3 – propane sultone (5 molar excess) were dissolved in DMF and the ring opening reaction was run at room temperature for 1 hour and then for an additional 12 hours at 60°C. Completion of the reaction was again confirmed with ¹H NMR

Spectroscopy and the mixture was concentrated in a rotovap. The polymer was then again precipitated and dried in the same manner as the previous steps.

Two methods were used to cast membranes out of the synthesized SB-PAES. The first method was to dissolve the synthesized polymers into a 25% weight solution of n-methyl-2-pyrrolidone (NMP), and then the solution was stirred for an hour and then placed in a sonicator for another hour to remove any gas bubbles. The solution was then poured onto a clean glass plate and a doctor blade was used to cast a uniform thickness of 200 microns. The glass plates were then transferred to a vacuum oven where they were dried for three days at 25°C, 40°C, and 80°C with 24 hours for each temperature. Once dried, the plate and the membrane were dipped in a DI water bath and the membrane was allowed to swell with water before being removed from the plate. The membranes were stored in DI water until used.

The second method used to cast membranes was to dissolve the synthesized polymers into a 7.5% weight solution with NMP. This solution was then stirred and sonicated for an hour each, and then the solution was poured into petri dishes. A solution with 5 g of SB-PAES was used for two petri dishes. These petri dishes were then placed into a vacuum oven where they were dried with the same protocol as the first method, and then they petri dishes were dipped in DI water to remove the membrane from the dish. These membranes were also stored in DI water until use. Qualitative observations were made about the quality of the casted membranes.

Pervaporation Experiments and Analysis

Pervaporation experiments were carried out in a cross-flow setup with a liquid N₂ trap and a peristaltic pump fed the feed solution at a rate of 1 mL/minute, as seen in Figure 2.

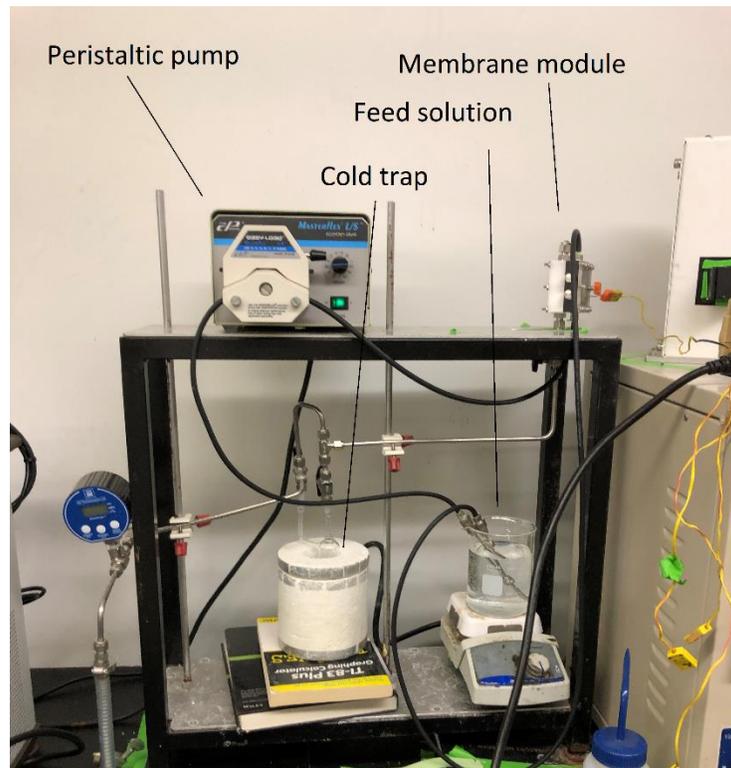


Figure 2: Pervaporation Apparatus

The feed used was either pure water or saline solutions with a salt concentration of either 1 g/L, 5 g/L, or 10 g/L. The SB-PAES membrane was supported in the membrane module with a nonwoven polyester support. Once the membrane was installed in the module, the apparatus was run for 30 minutes to test for any leaks. After the test was done, the cold trap was immersed in liquid N₂ and the test was run with one of the feed solutions for 30 minutes. The collected permeate was then weighed for permeance, and the conductivity

of the permeate was taken to calculate the salt rejection. Each membrane was only run through the pervaporation system once to reduce effects of fouling.

Pervaporation membrane performance was be assessed through the flux, permeance, permeability, and salt rejection of the membranes. These are given in equations 1 through 4, respectively.

$$J = \frac{\text{Permeate}}{At} \quad (1)$$

$$L_p = \frac{J}{\Delta P} \quad (2)$$

$$P = L_p(\text{Membrane Thickness}) \quad (3)$$

$$\text{Salt rejection} = \left(\frac{C_f - C_p}{C_f} \right) \times 100\% \quad (4)$$

J is the flux (L/m² h), A is the membrane active area (m), permeate is the permeate collected (L), t is the time taken to collect the permeate (h), L_p is the permeance (L/m² h bar), ΔP is the transmembrane pressure difference (bar), P is the permeability (L/m h bar), C_f is the salt concentration in the feed, and C_p is the salt concentration in the permeate (g/L).

CHAPTER 3

RESULTS AND DISCUSSION

Membrane Fabrication

The two methods of membrane casting were used to determine optimal strategies for developing membranes for pervaporation tests. For membranes dried on glass plates and cast with a doctor blade, the thickness was relatively consistent, with membranes between 120-150 microns. However, multiple issues would come up during the drying process, which would render the membranes unusable for the pervaporation portion. Most membranes that were cast in this manner would not dry uniformly and would either leave gas bubbles between layers in the membrane itself or would leave large areas with much less thickness in the membrane, even after the solution had been stirred and sonicated for uniformity.

The membranes which were dried in petri dishes would be of uniform thickness and were of much better quality in terms of strength and surface smoothness. Figure 3 shows one of these membranes. However, the membranes dried in the dish would sometimes leave white streaks across the membrane, which could possibly be from NMP not being fully evaporated out of the membrane, as seen in Figure 4. The solution was of a much lower weight percent than the solution used in the glass plate method, to aid with casting, as the glass plate solution was much more viscous which led to issues using the doctor blade. However, with the lower weight percent, the thickness between individual petri dish membranes varied dramatically, and most membranes were too thick to be used in the pervaporation. More experimentation with the petri dish method will need to be done to produce a thickness consistent between membranes.

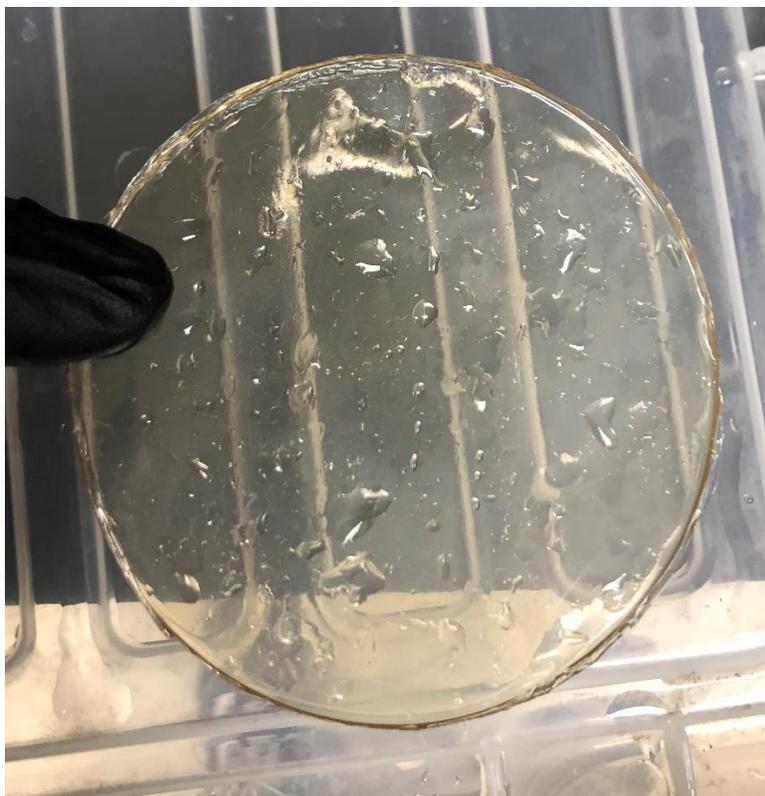


Figure 3: SB-PAES Membrane Cast Using the Petri Dish Method

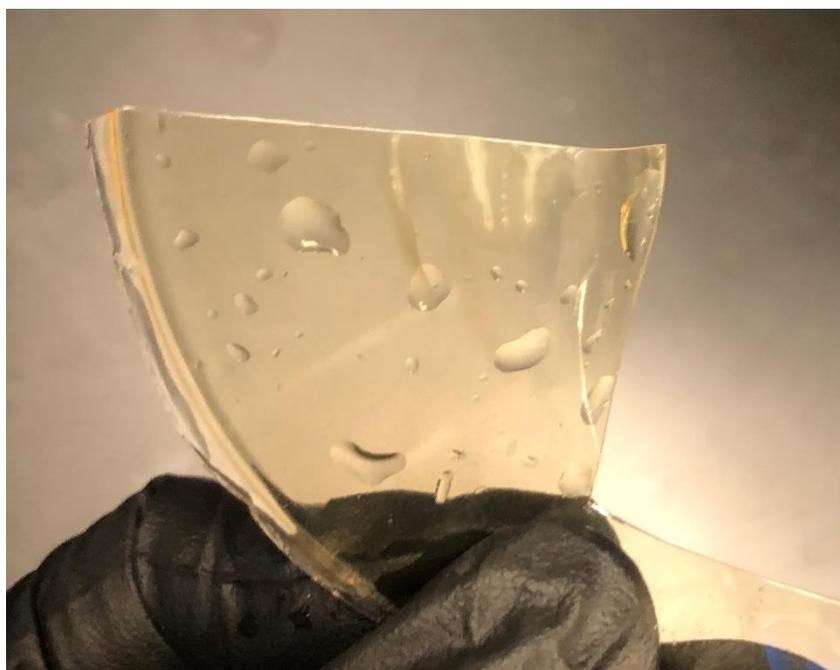


Figure 4: Section of a Petri Dish Membrane Showing NMP Streaks on the Top

Pure Water Permeance, Flux, and Permeability

Pure water permeance, flux, and permeability values for the membranes are given in Table 1. The 50% charge membranes produced from previous tests are included for comparison. Because factors such as membrane thickness and vacuum pressure were different between runs, and these factors can affect the permeability and flux, these values are included in the table. The membrane thickness was measured at 8 different spots and averaged.

Table 1

Pure Water Permeance Data for the SB-PAES Membranes

Membrane Charge %	Membrane Thickness (μm)	Vacuum pressure (bar)	Flux ($\text{L}/\text{m}^2\cdot\text{h}$)	Permeance ($\text{L}/\text{m}^2\cdot\text{h}\cdot\text{bar}$)	Permeability ($\text{L}/\text{m}\cdot\text{h}\cdot\text{bar}$)
50%	140	0.032	3.2852	3.4044	$5.7874\cdot 10^{-4}$
50%	170	0.042	1.5172	1.5674	$2.3511\cdot 10^{-4}$
25%	120	0.286	0.5156	0.7222	$8.6663\cdot 10^{-5}$
25%	120	0.300	1.2010	1.7157	$2.0589\cdot 10^{-4}$
25%	160	0.120	0.3361	0.3819	$6.1100\cdot 10^{-5}$

The variation in flux between the runs can be attributed to the variations in both membrane thickness and vacuum pressure used. It is possible that the charge percent of the membranes could also be a factor, as the 25% charge membranes show much more variability in flux and permeance data, but more data will need to be collected to confirm if these factors are significant. Factors such as membrane thickness and the applied vacuum could also have an effect as they are variable throughout the runs.

Salt Rejection

Salt rejection data for the membranes is shown in Table 2.

Table 2

Salt Rejection Data for the SB-PAES Membranes

Membrane Charge %	Feed Concentration (g/L)	Salt Rejection %	Flux (L/m ² ·h)	Permeance (L/m ² ·h·bar)
50%	1	98.15	1.2689	1.3108
50%	1	99.14	1.5172	1.5804
50%	5	99.43	2.6439	2.6439
50%	5	99.82	2.222	2.3204
50%	10	99.91	1.867	1.927
50%	10	99.91	3.247	3.247
25%	5	83.04	0.5156	0.7222
25%	5	82.50	1.2010	1.7157
25%	10	85.60	0.3361	0.3819

The 50% charge membranes show excellent salt rejection, all above 99%. The 25% charge membranes show a salt rejection between 82%-86%, however more tests will need to be conducted to determine if the charge percent is a factor or if there is another reason for the difference in salt rejection. Notably, the salt rejection stays constant between membranes of the same charge percent but of differing feed concentrations.

The performance of both the 25% and 50% charge SB-PAES membranes are compared to membranes found in literature in Table 3.

Table 3*Comparison of SB-PAES Membrane Performance with Literature*

Membrane	Feed Concentration (g/L)	Membrane Thickness (μm)	Salt Rejection %	Permeance ($\text{L}/\text{m}^2\cdot\text{h}\cdot\text{bar}$)
Graphene oxide/polyacrylonitrile [17]	35	0.1	99.8	345
Sulfonated pentablock copolymer [18]	32	52	99.5	135
Natural clinoptilolite [19]	34	2500	99.7	1.2
Templated molecular sieve silica [20]	35	0.5	98.5	4.353
Poly(vinyl alcohol)/maleic acid/silica [21]	2	5	>99.5	6.896
50% charge SB-PAES	10	170	99.91	2.6439
25% charge SB-PAES	10	160	85.60	1.7157

From comparison to literature, it is shown that while the 50% charge membranes show similar values to other studies, the 25% charge membranes do not show the same degree of salt rejection or permeance as the other membrane types. It is possible that the thickness of the SB-PAES membranes limited the permeance, as the membranes used in this study are much thicker than those of other studies. With the direct comparison between the two charge percents, the 50% charge membranes are much more suitable for brine water desalination.

CHAPTER 4

CONCLUSION AND FUTURE WORK

Sulfobetaine-modified poly(arylene ether sulfone) membranes were tested for their performance in the pervaporation of salt solutions of varying concentrations – 1 g/L, 5 g/L, and 10 g/L. The membranes were also cast in various ways to determine a protocol for casting membranes with consistent thickness and structural integrity. The membranes cast in a 7.5 weight % solution in NMP showed good uniformity and structural integrity, but the thickness between membranes was variable. Membranes cast on a glass plate were too inconsistent to be used in testing. The SB-PAES membranes with a 50% charge showed excellent water flux, permeance, and salt rejection, with a salt rejection over 99.9% for 10 g/L feeds, while the 25% charge membranes showed a salt rejection of just over 85% for 10 g/L feeds, with much less flux and permeance. The 50% charge membranes could potentially be used in brine water desalination.

Further research can be done in creating a membrane casting protocol. Experimenting with different weight percent solutions could help create a consistent thickness across different membranes. It is also possible that the membranes can be dissolved in a solvent other than NMP to aid in the drying process, such as DMF. Membranes with a charge content of 75% have yet to be tested, and 25% charge membranes will need more testing to confirm the trends noticed in this study. Different parameters such as feed concentrations and membrane thickness could also be tested to optimize the potential of these SB-PAES membranes for use in brine water desalination.

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