EILERS GRADUATE STUDENT FELLOWSHIP
FINAL REPORT

EILERS FELLOW:	Michael P. Dugas
FACULTY ADVISOR:	Dr. William A. Phillip
REPORT PERIOD:	2022
PROJECT TITLE:	Understanding Electrostatic Interactions in Functionalized Copolymer Organic Solvent Nanofiltration Membranes
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	(X) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear ( ) Smart Storage and Distribution ( ) Transformation Solar ( ) Sustainable Bio/Fossil Fuels ( ) Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Assess and characterize the functionalization of the copolymer membrane	Completed Zeta potential, FTIR, and ion rejection experiments as a function of pH to show that chosen functionalities were reacted to the membrane and remained permanently charged.	100%
Understand how the functionalization effects the transport through the membrane	Ion rejection experiments demonstrated that each functionalization electrostatically rejected the ions dissolved in methanol and ethanol. Additionally, the primary amine functionality demonstrated electrostatic rejection, suggesting the amine was still protonated in organic solvent.	90%
Utilize the knowledge and apply to industrially relevant feed solutions	Unfortunately, the project was cut short due to a job opportunity with Los Alamos National Laboratory. This goal was not completed.	0%

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) ACS Applied Polymeric Materials, The Role of Solvent Affinity in Transport Through Crosslinked Copolymer Membranes for Organic Solvent Nanofiltration, M. Dugas, S. Zhong, B. Park, J. Ouimet, J. Xu, J. Schaefer, and W. Phillip, Submission Pending. ACS Applied Materials and Interfaces, Understanding the Electrostatic Interactions of Charged Copolymer Organic Solvent Nanofiltration Membranes, M. Dugas, M. McClure, J. Ouimet, L. Lair, D. Latulippe, and W. Phillip, Submission Pending.
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location) Dissertation Defense, DESIGNING COPOLYMER MEMBRANES FOR ORGANIC SOLVENT NANOFILTRATION AND ADSORPTION MEMBRANE APPLICATIONS, Dec. 5, 2022, Zoom
EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) Dr. David Latulippe, McMaster University, To experimentally understand the charge density of the copolymer membranes using Zeta Potential analysis
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail) From the fellowship funding, I was able to complete and successfully defend my dissertation, titled "DESIGNING COPOLYMER MEMBRANES FOR ORGANIC SOLVENT NANOFILTRATION AND ADSORPTION MEMBRANE APPLICATIONS"

The membranes were reacted to increase the resilience of the membrane as well as incorporate functional groups that alters ion transport. These membranes were reacted first with diaminohexane to incorporate crosslinking as well as amine functionalities that induce a positive charge through protonation. These functionalities can be further reacted to incorporate permanent charges into the membranes. In this study, glycidyl trimethylammonium chloride and 4-sulfophenyl isothiocyanate sodium salt were chosen to incorporate either a permanent positive or negative charge to the membrane, respectively.[1] The trimethyl ammonium functionality was reacted using the same base-catalyzed epoxide ring opening reaction that was used to react the diamine to the membrane.[2] However, triethylamine was added to the reaction solution as a catalyst to ensure that the reaction was successfully completed.[3,4] The sulfonic acid functionality was incorporated into the membrane using an amine-isothiocyanate reaction.[5] These functionalities were reacted in water to preserve membrane integrity. Figure 1 shows the FTIR spectra for membranes reacted with diaminohexane, trimethylammonium, and sulfonic acid reacted films. The peak at 1580 cm^{-1} shows the amine functionalities for both the diaminohexane and the trimethylammonium. In addition, the shoulder peak seen at 1101 cm^{-1} corresponds to the C-N stretch in both the amine and ammonium functionalities.[1,6,7] For the sulfonic acid functionality, the appearance of the peak at 1031 cm^{-1}, from the sulfonic acid vibration, suggests that the sulfonic acid reacted with the amines.[1] The presence of these peaks indicate that the desired functionalities reacted with the membranes to form charged membranes.
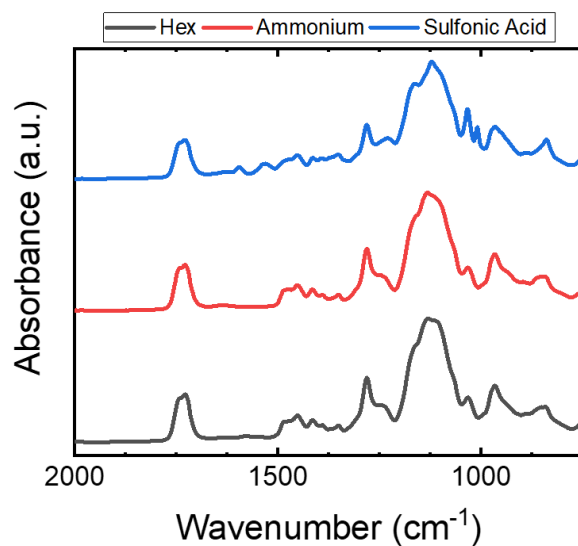

Figure 1: FTIR spectra of reacted films with diaminohexane (Hex), glycidyl trimethylammonium (Ammonium), and sulfonic acid functionalities. The spectra were normalized with 1735 cm^{-1} C=O peak for comparison.

Zeta potential analyses were conducted to understand the surface charge given by the charged functionalities. Figure 2 shows the zeta potential of the PVDF support and the membranes functionalized with diaminohexane, trimethylammonium, and sulfonic acid. These experiments were completed by Matthew McClure at McMaster University using an Anton-Paar SurPASS3 with 1 mM KCl solutions that were titrated to specific pHs. As seen in the figure, each functionality shows a different charge characteristic. The PVDF support was also measured, seen in Figure 2A, to ensure the membrane surface charge was not influenced by the support itself. As seen in the figure, the isoelectric point for PVDF is observed around pH 3. The negative charge has been seen in other studies with PVDF.[8] The diaminohexane-reacted film, seen in Figure 2B, shows a positive charge, indicative of the protonation of the amine functionality. The isoelectric point was observed around pH 8.5, which is close to the pKa of the amine group (~10).[1,9] The loss of charge is consistent with the amine deprotonated and therefore assuming a neutral charge. The ammonium and sulfonic acid functionalities, on the other hand, are permanent charges, and therefore not affected by the pH of the surrounding solution. This charge is observed by the lack of an isoelectric point for both moieties. The ammonium functionality exhibits an average zeta potential of 2.0 ± 1.7 mV. The sulfonic acid membrane shows an average zeta potential of -3.5 ± 0.2 mV. These analyses show that the permanently charged functionalities maintain a charge on the membrane surface regardless of solution condition.
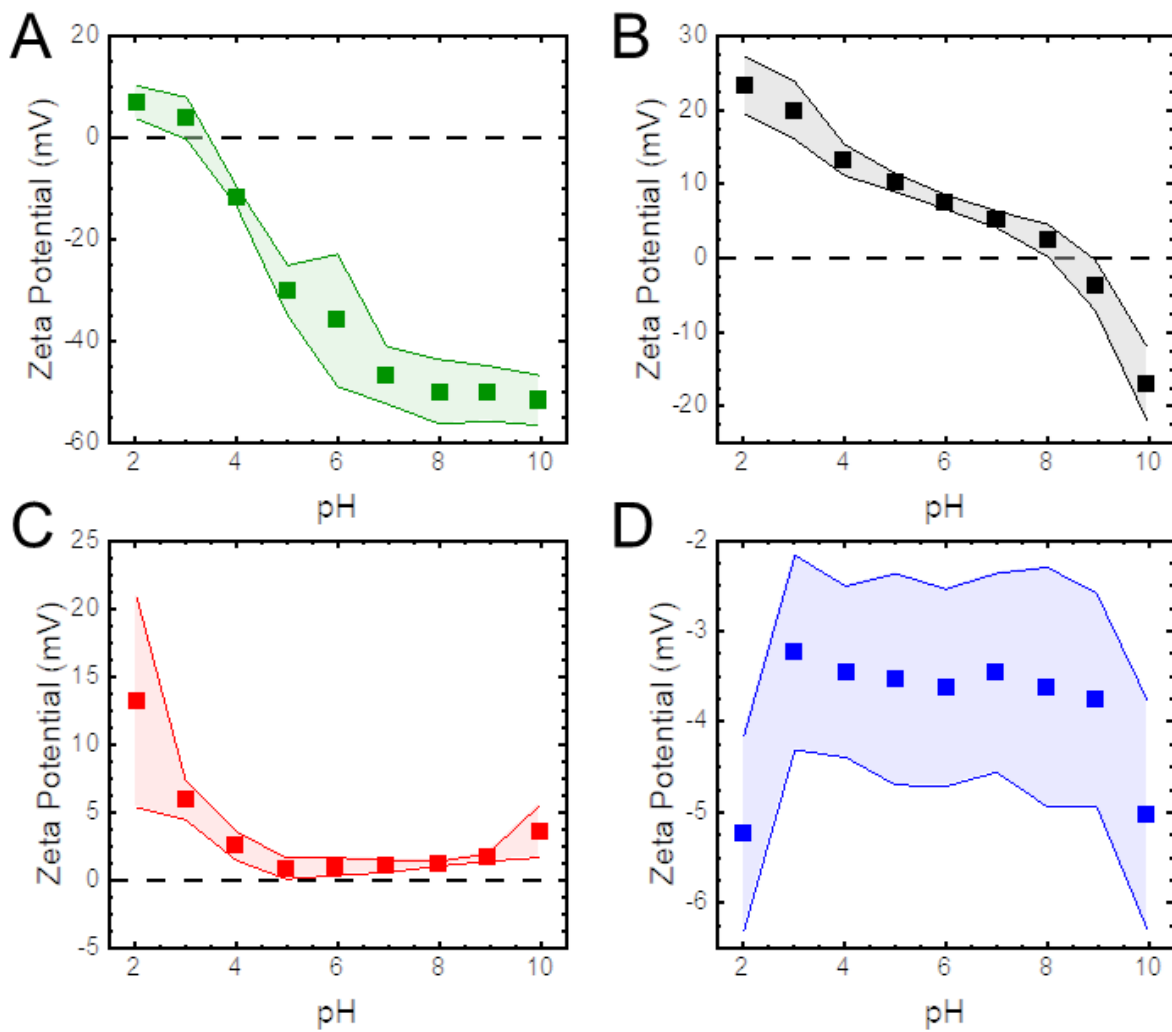
Figure 2: Zeta potential analysis for A) PVDF substrate, B) diaminohexane-reacted copolymer film, C) trimethylammonium-reacted membrane, and D) sulfonic acid- reacted film. The values and shaded regions are based on the average and standard deviation of n=3 membrane samples.

Aqueous ion transport experiments help to further understand the electrostatic interactions between the functionalized membrane and the solution. Figure 3 shows the ion rejection experiments conducted with $CaCl_2$ at unaltered pH (~5.5) and pH 11. This pH was chosen since it is above the pKa of the diamine while limiting the Debye screening effect caused by the increase in feed ion concentration. Seen in the figure, the diaminohexane-reacted film shows a high rejection of calcium ions until the pH is increased. When the amine functionalities are deprotonated, the membrane loses its charge, causing the ion rejection to plummet. The trimethylammonium and the sulfonic acid functionalities are permanent, and therefore not affected by the pH of the solution. This is seen in the ion rejection experiments. There is a small change in the rejection, which can be attributed to the increase in the ion concentration from the calcium hydroxide screening some of the charge. These rejections not only show that the membranes were functionalized with the moieties, but also that these charges are permanently attached to the membrane.
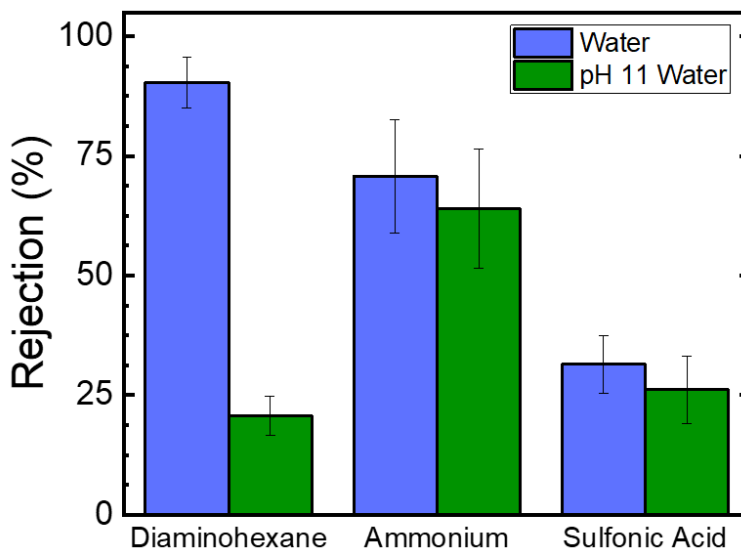
Figure 3: 1mM Ca(NO₃)₂ rejection at unaltered pH (~ pH 6) and at pH 11. The values are an average of n=3 samples with error bars being the standard deviation

Once the membranes were analyzed with water, ion rejection experiments were conducted with different organic solvents. These experiments were to help understand how the charged functionalities affect the ion transport behavior in each organic solvent. Figures 4 and 5 show the results of the ion rejection experiments for 1mM Ca(NO₃)₂ and 1 mM NaNO₃ solutions, respectively, for each solvent, including water. The rejections for isopropanol are called into question due to the decrease in the solvent permeability over time. This decrease eventually lead to the membrane completely degrading and becoming impermeable after approximately 4 hours. This phenomenon suggests that the isopropanol is able to solvate the membrane, thereby causing the nanostructure to degrade, which further supports the hypothesis that was formulated during casting. The rejection results in each organic solvent for the diaminohexane-reacted membrane indicate that the functionality is still protonated, and therefore charged. This charge could orginate from water contamination, since the solvents were not chemically scrubbed for water, that allowed the functionality to protonate and maintain its charge. The lower rejections from trimethylammonium functionalities compared to diaminohexane-reacted films suggest that the charge associated with the ammonium functionalities is not as strong as the diamine. This is also seen in the lower zeta potential for the trimethylammonium versus the diamine. The lower rejection could be attributed to the charge of the ammonium being stabilized by the C-N bonds allowing to distribute the charge.[10] For both the diamine and ammonium-functionalized membranes, the rejections decrease as the solvent identity was changed. This trend is similar to the lower Debye lengths that were calculated as the permittivity was lowered. The sulfonic acid rejections, on the other hand, show an increasing trend as the solvent is changed, which is inconsistent

with the lower Debye length. This result suggests that the sulfonic acid functionality has a more complex interaction than previously thought.
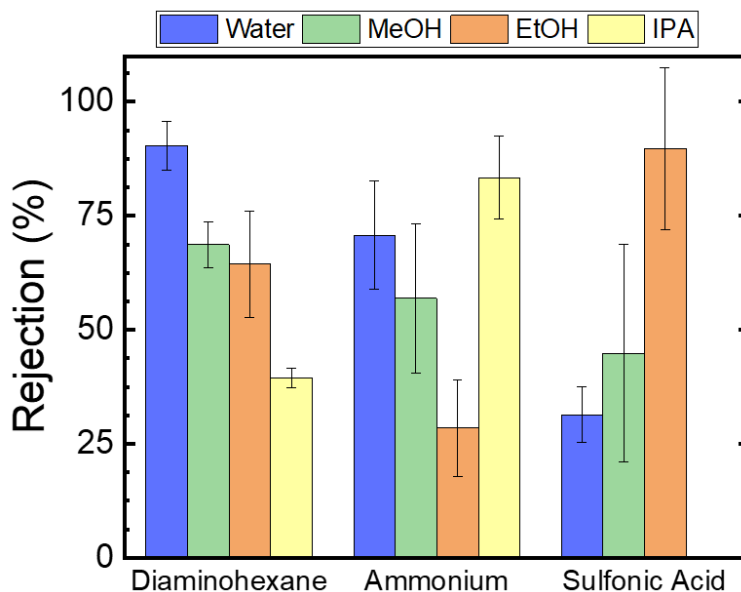

Figure 4: 1mM Ca rejections for each reacted film as a function of solvent and functionality. The values and errors are from the mean and standard deviation, respectively, of n=3 membrane samples. Each membrane was permeated with pure organic solvent prior to ion experiments to prevent any cross contamination from previous experiments.

Figure 5: 1mM Na rejections for each reacted film as a function of solvent and functionality. The values and errors are from the mean and standard deviation, respectively, of n=3 membrane samples. Each membrane was permeated with pure organic solvent prior to ion experiments to prevent any cross contamination from previous experiments.
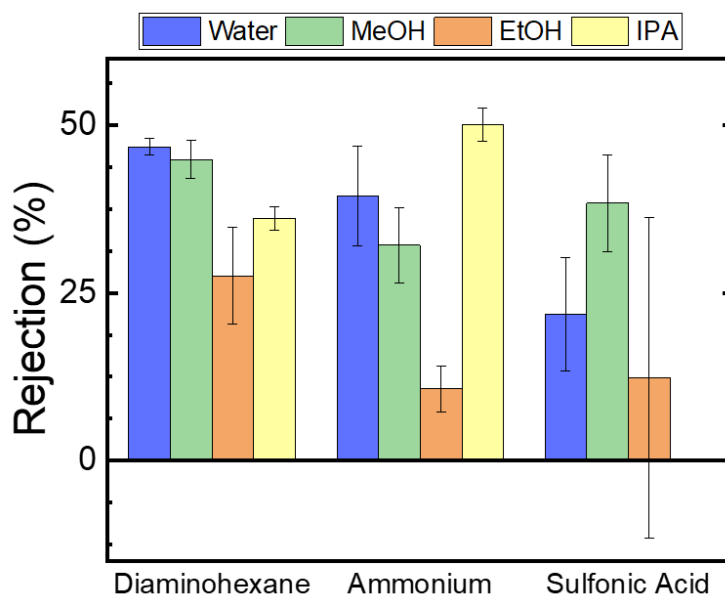
REFERENCES

(1)   Qu, S.; Dilenschneider, T.; Phillip, W. A. Preparation of Chemically-Tailored Copolymer Membranes with Tunable Ion Transport Properties. *ACS Applied Materials and Interfaces* **2015**, *7* (35), 19746–19754. https://doi.org/10.1021/acsami.5b05592.

(2)   Barbey, R.; Laporte, V.; Alnabulsi, S.; Klok, H. A. Postpolymerization Modification of Poly(Glycidyl Methacrylate) Brushes: An XPS Depth-Profiling Study. *Macromolecules* **2013**, *46* (15), 6151–6158. https://doi.org/10.1021/ma400819a.

(3)   Pawar, H. S.; Wagh, A. S.; Lali, A. M. Triethylamine: A Potential N-Base Surrogate for Pyridine in Knoevenagel Condensation of Aromatic Aldehydes and Malonic Acid. *New Journal of Chemistry* **2016**, *40* (6), 4962–4968. https://doi.org/10.1039/C5NJ03125G.

(4)   Chesterman, J. P.; Amsden, B. G. Triethylamine-Based Catalysts for the Melt Polymerization of Carbonate Monomers. *Polymer Chemistry* **2016**, *7* (45), 6946–6953. https://doi.org/10.1039/C6PY01248E.

(5)   Pannone, M. C.; Macosko, C. W. Kinetics of Isocyanate Amine Reactions. *Journal of Applied Polymer Science* **1987**, *34* (7), 2409–2432. https://doi.org/10.1002/app.1987.070340707.

(6)   Rathee, V. S.; Qu, S.; Phillip, W. A.; Whitmer, J. K. A Coarse-Grained Thermodynamic Model for the Predictive Engineering of Valence-Selective Membranes. *Molecular Systems Design and Engineering* **2016**, *1* (3), 301–312. https://doi.org/10.1039/c6me00045b.

(7)   Chi, W.; Qin, C.; Zeng, L.; Li, W.; Wang, W. Microbiocidal Activity of Chitosan-N-2-Hydroxypropyl Trimethyl Ammonium Chloride. *Journal of Applied Polymer Science* **2007**, *103* (6), 3851–3856. https://doi.org/10.1002/app.25476.

(8)   Ma, Z.; Lu, X.; Wu, C.; Gao, Q.; Zhao, L.; Zhang, H.; Liu, Z. Functional Surface Modification of PVDF Membrane for Chemical Pulse Cleaning. *Journal of Membrane Science* **2017**, *524*, 389–399. https://doi.org/10.1016/j.memsci.2016.11.063.

(9)   Vijisha K., R.; K., M. The PKa Values of Amine Based Solvents for CO 2 Capture and Its Temperature Dependence— An Analysis by Density Functional Theory. *International Journal of Greenhouse Gas Control* **2017**, *58*, 62–70. https://doi.org/10.1016/j.ijggc.2017.01.009.

(10)   Rohani, M. M.; Mehta, A.; Zydney, A. L. Development of High Performance Charged Ligands to Control Protein Transport through Charge-Modified Ultrafiltration Membranes. *Journal of Membrane Science* **2010**, *362* (1–2), 434–443. https://doi.org/10.1016/j.memsci.2010.06.069.