

Alcohol-carboxylate transport in phenyl-based membranes of varying chain length transport

by

Sarah A. Gaston

A dissertation submitted to the Graduate Faculty of
Auburn University
in partial fulfillment of the
requirements for the Degree of
Master Thesis

Auburn, Alabama
August 5, 2023

Keywords: Membrane science, Polymer chemistry, Ion exchange membranes,
Multi-solute transport, Charge screening, Crosslinked membranes

Copyright 2023 by Sarah A. Gaston

Approved by

Bryan S. Beckingham, Chair, Associate Professor of Chemical Engineering, Auburn University
Cassandra Porter, Assistant Professor of Chemical Engineering, Auburn University
Maria Auad, Professor of Chemical Engineering, Auburn University

Abstract

As global climate change is a major concern which is accelerated by CO₂ emissions, we need to reduce CO₂ emissions from the environment. In order to do that, researchers conceptualized CO₂ reduction cells which electrochemically convert CO₂ to other chemicals such as CO or methanol. A major problem faced by such devices is the crossover of the CO₂ reduction products (i.e. methanol (MeOH), formate (OFm⁻), and acetate (OAc⁻)) through ion exchange membranes (IEM) which reduces the efficiency of the cell. Therefore, it is critical to design IEMs that suppress the transport of CO₂ reduction products. Towards this goal, our group has been investigating the transport behavior of these products in crosslinked PEGDA-based IEMs, where we observed the diffusivities of cation exchange membranes to OFm⁻ and OAc⁻ increased in co-diffusion with MeOH, which is a concerning behavior. Here, we prepared analogous films with a series of phenyl-containing comonomers of different chain lengths [i.e. phenyl acrylate (PA, $n = 0$), phenyl ether acrylate (PEA, $n = 1$), and poly(ethylene glycol) phenyl ether acrylate (PEGPEA, $n = 3$)]. We then measured the permeabilities of these films to OFm⁻ and OAc⁻, where we observed the permeabilities of films with the shorter chain length [PEGDA-PA ($n = 0$)] to be lower than films with longer comonomer chain lengths. This work lays the foundation for further understanding of transport in these films, where in the future we will measure permeabilities to MeOH, cotransport MeOH-OFm⁻, and MeOH-OAc⁻ as well as the solubilities of these species within the films.

Acknowledgments

I would like to express my sincere gratitude and appreciation to the following individuals for their valuable contributions and support throughout my master's thesis journey: First and foremost, I would like to thank Dr. Auad and Dr. Porter for graciously accepting to be a part of my thesis defense committee. Your expertise, guidance, and insightful feedback have been instrumental in shaping and improving my research work. I would also like to extend my heartfelt thanks to Dr. Beckingham for welcoming me into his research group. Your mentorship, encouragement, and willingness to share your knowledge and expertise have been invaluable to my development as a researcher. I am deeply grateful to Yihung, Pravin, and Antara for their assistance and collaboration during my research project. Your support, discussions, and contributions have greatly enriched my work, and I am thankful for the opportunity to work alongside such talented individuals. Furthermore, I would like to express my appreciation to Dr. Kim for providing me with valuable guidance and assistance at the outset of my research. Your insights and advice have been invaluable in shaping the direction of my study and setting a solid foundation for my work. I am also thankful to all my friends and family members who have provided me with continuous encouragement, understanding, and support throughout this challenging journey. Lastly, I would like to acknowledge the contributions of all the individuals who have directly or indirectly played a part in the completion of my master's thesis. Your collective support and assistance have been indispensable, and I am grateful for your involvement. Once again, thank you all for being a part of my thesis defense and for your unwavering support. I am truly grateful for the opportunity to have worked with such incredible individuals who have enriched my academic and research experience in countless ways.

Table of Contents

Abstract	2
Acknowledgments	3
List of Figures	6
List of Tables	9
List of Abbreviations	10
Chapter 1: Introduction	
1.1 Motivation	11
1.2 Thesis Organization	14
1.3 References	16
Chapter 2: Background	
2.1 Background	17
2.2 Solution Diffusion Model	17
2.3 Physiochemical Properties:	19
2.3.1: Water uptake and water volume fraction	19
2.3.2 Transport Behavior:	21
Permeability, yasuda model, diffusion cell experiment, FTIR, multi-component transport	
2.4 Contact angle	22
2.4.1: Mechanical testing	23
2.5 References	26
Chapter 3: Experimental Methods	
3.1 Materials	29

3.2 Membranes Synthesis	29
3.3 Membrane Physiochemical Characterization	31
3.3.1 Water uptake, Density, and Water Volume Fraction.....	31
3.3.2 Contact Angle	32
3.3.3 Mechanical Properties via Tensile Testing	33
3.4 Membrane Transport Phenomena	33
3.4.1 Single and Multicomponent Permeability.....	33
3.4.2 Single Component Solubility	34
3.5 References	36

Chapter 4: Results & Discussion

4.1 Physiochemical Characterization: Water uptake, Water Volume Fraction, Contact Angle, and Modulus.....	37
4.2 Transport Properties	48
4.2.1 Permeability	48
4.2.2 Solubility	52
4.2.3 Diffusivity	57
4.3 Multi-component transport	60
4.4 References.....	63

Chapter 5: Conclusion & Future work

5.1 Conclusion	65
5.2. Future work	66

List of Figures

Figure 1.1 Nafion ^{®3} , functional groups contained within Selemion AMV. ⁴	12
Figure 1.2 Chemical structures of common polymer membrane chemistries. ²	12
Figure 1.3 Synthesis of PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membrane.	13
Figure 2.1 Schematic of sorption desorption experiment for solute solubilities	19
Figure 2.2 Schematic of solute diffusion through membranes of free volume.....	21
Figure 2.3 illustration of experimental setup outfitted with an in-situ conductivity probe to determine single component solute permeabilities or ions in IEMs	22
Figure 3.1 Synthesis of PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membrane.	30
Figure 3.2 illustration of experimental setup outfitted with an in-situ conductivity probe to determine single component solute permeabilities or ions in IEMs	33
Figure 3.3 Schematic of sorption desorption experiment	35
Figure 4.1 Synthesis of PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membrane	38
Figure 4.2 Water uptake results for PEGDA, PEGDA-PA, PEGDA-PEA, and PEGDA-PEGPEA membranes	41
Figure 4.3 Contact angle (degrees) of with different compositions of PEGDA weight % (A) PEGDA-PA, (B) PEGDA-PEA, (C)PEGDA- PEGPEA.....	43
Figure 4.4 Contact angle image of concentration of PEGDA membrane with DI water droplet.	45
Figure 4.5 Tensile testing ($\times 10^6$ MPA) data of PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA of all compositions	48
Figure 4.6 Permeability results graphs of different PEGDA compositions comparing KAc(outline of marker) and KFm(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (○,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24,	

(◄,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (◻, blue) (D) PEGDE92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(◊, black).....51

Figure 4.7 Solubility results graphs of different PEGDA compositions comparing KAc(outline of marker) and KFm(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (◊,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (◄,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (◻, blue) (D) PEGDA92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(◊, black).....54

Figure 4.8 solubility of water volume fraction results graphs solubility of water volume fraction results graphs of different PEGDA compositions comparing KAc(outline of marker) and KFm(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (◊,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (◄,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (◻, blue) (D) PEGDA 92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(◊, black).....56

Figure 4.9 Diffusivity results graphs of different PEGDA compositions comparing KAc(outline of marker) and KFm(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (◊,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (◄,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (◻, blue) (D) PEGDA 92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(◊, black).....58

Figure 4.10 Diffusivity of water volume fraction results graphs of different PEGDA compositions comparing KAc(outline of marker) and Kfm(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (○,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (◄,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (◻, blue) (D) PEGDA 92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(◇, black)59

Figure 4.11 multi-component of permeability results graphs different PEGDA compositions in KAc(outline of marker) and MeOH(solid marker) of (A) PEGDA 68- PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32(○,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (◄,orange) (C) PEGDA 92-PA8, PEGDA92-PEA8, PEGDA92-PEGPEA8(◇, black) (D) all PEGDA-PA,PEA,PEGPA compositions in KAc (E) all PEGDA-PA,PEA,PEGPA compositions in MeOH.....62

List of Tables

Table 3.1 Membrane pre-polymerization mixtures	31
Table 3.2 Calibration constant for measuring conductivity of Kac and KFm by conductivity meter	34
Table 4.1 Water uptake, water volume fraction, Young's modulus, and density for the range of PEGDA-(PA, PEA,PEGPEA)	40

List of Abbreviations

CEM	Cation exchange membrane
-COOH	Carboxyl
DI	Deionized
DMA	Dynamic mechanical analysis
H ₂ O	Water
HCPK	1-Hydroxyl-cyclohexyl phenyl ketone
HPLC	High-performance liquid chromatography
IEC	Ion exchange capacity
IEM	Ion exchange membrane
KOAc	Potassium acetate
KOFm	Potassium formate
MeOH	Methanol
OAc-	Acetate
OFm-	Formate
-OH	Hydroxyl
PA	Phenyl acrylate
PEA	Phenoxyethyl acrylate
PEGDA	Poly(ethylene glycol) diacrylate
PEGPEA	Poly(ethylene glycol) phenyl ether acrylate

Chapter 1

Introduction

1.1 Motivation

Polymer membranes are critically important for a range of applications including gas separation, energy storage, microfiltration, and ultrafiltration, and fuel cells. For instance, in fuel cells polymer membranes are used as electrolytes to conduct ions to either generate electricity or chemicals.¹ While there are many different types of polymer membranes, in general polymer membranes are made of a thin layer of polymer that facilitates the desired separation. These thin polymer layers can be self-supported flat sheets, surface coatings on porous supports, or spun into hollow fibers. Polymers are comprised of long, covalently bonded, chains or repeating units. The chemistry of these repeating units, and thereby the polymers themselves have tremendous diversity. Some common examples of the polymer chemistries used in polymer membranes (see **Figure 1.1** for structures) include polyamide, poly(ethylene glycol), Nafion[®], Selemion[™]. Depending on the particular polymer membrane chemistry, fabrication process, and membrane geometry, the resulting polymer membranes have different chemical, physical, and transport properties that aim to make them suitable for different applications. This Master's Thesis is focused on understanding the relationships between the polymer membrane chemistry, physical properties (water uptake, water volume fraction, and density) and transport behavior (methanol and carboxylate salts and mixtures thereof) in the context of solar fuels devices. Solar fuels devices, such as the one shown schematically in **Figure 1.2**,² aim to reduce the dependence on fossil fuels.

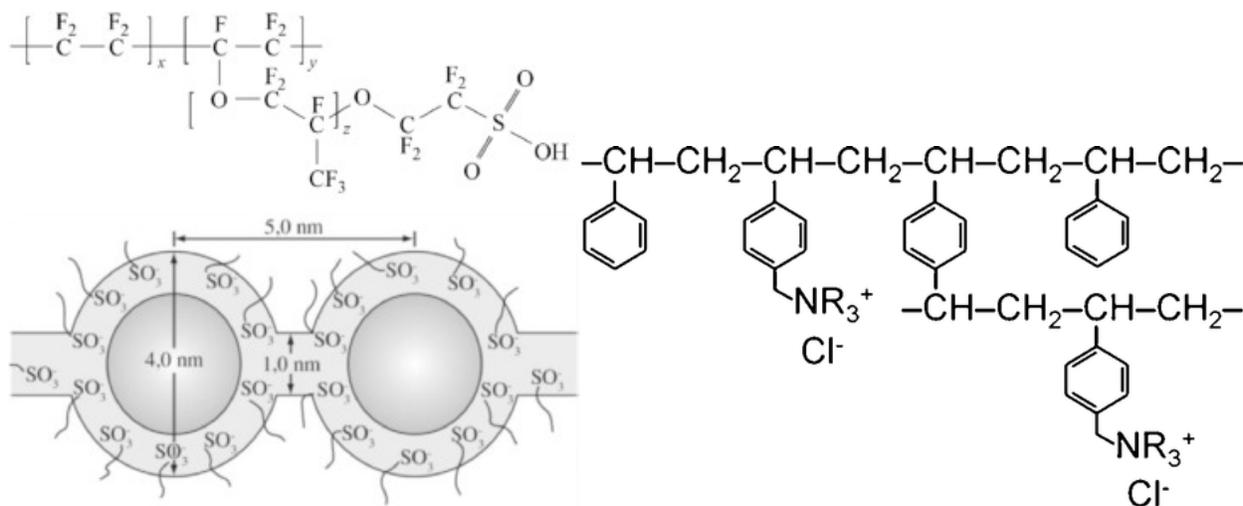


Figure 1.1 Structures of (left) Nafion[®] and (right) Selemion AMV.⁴

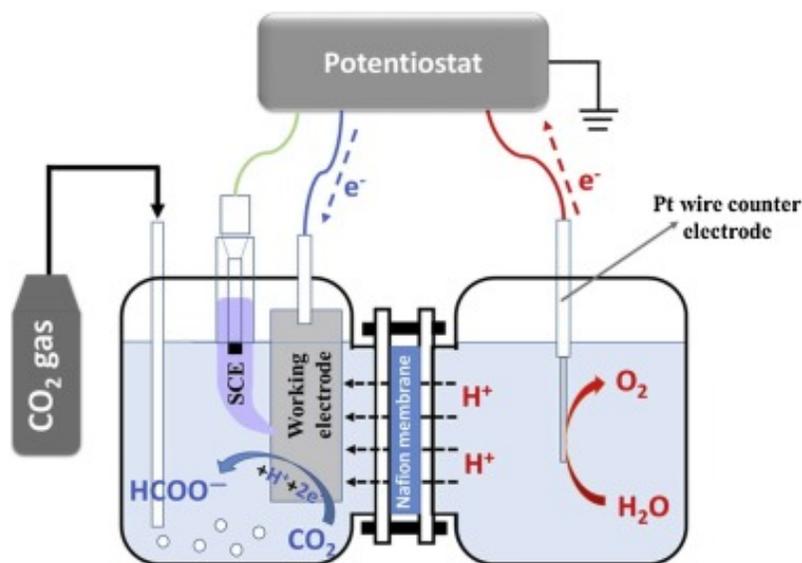


Figure 1.2 Chemical structures of common polymer membrane chemistries.²

One of the issues with current membranes for solar fuels devices is that they allow the permeation of the products (methanol, formate, and acetate) across the membranes, reducing efficiency. This work aims to understand how varying the membrane structure can affect solute transport and physiochemical properties. In particular, a series of crosslinked polymer membranes are prepared

using a UV crosslinker. Poly(ethylene glycol) diacrylate (PEGDA) as the crosslinker, and a series of comonomers are phenyl acrylate (PA), phenoxyethyl acrylate (PEA), poly(ethylene glycol) phenyl ether acrylate (PEGPEA) that each feature a reactive acrylate ethylene glycol side chain and terminal phenyl ring as seen in **Figure 1.3**.

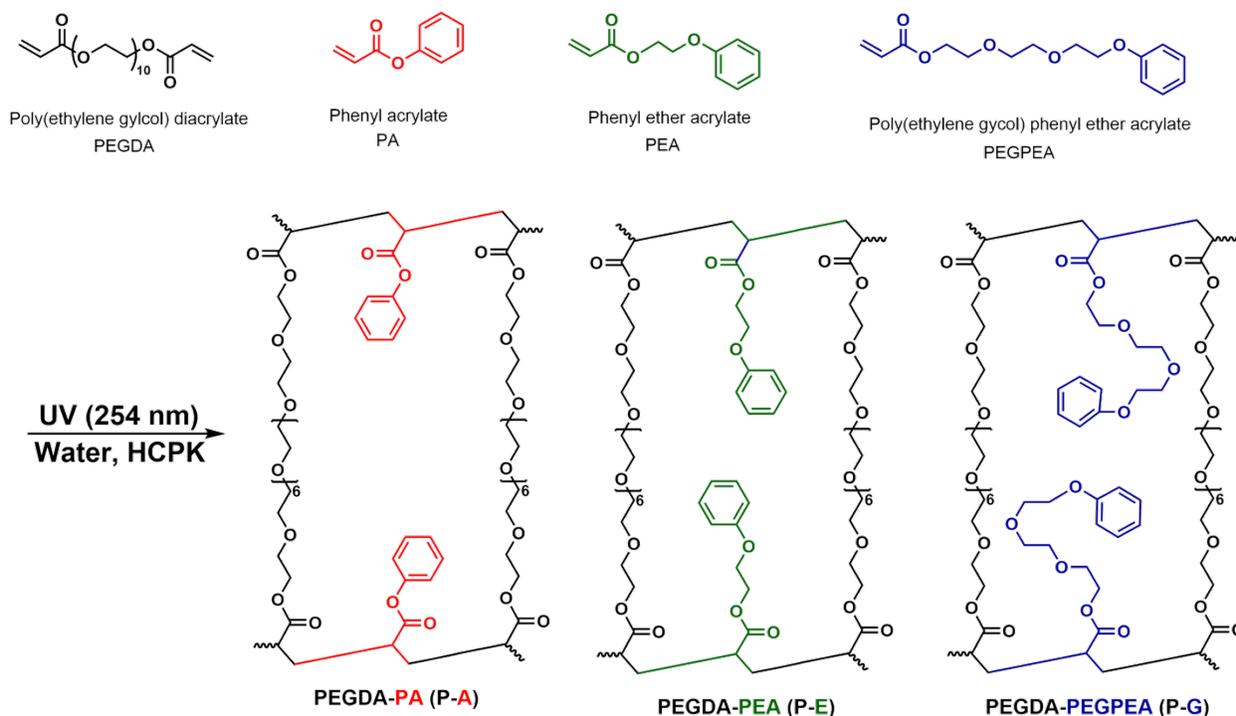


Figure 1.3 Synthesis of PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membrane.

This work is particularly interesting due to the utilization of poly(ethylene glycol) diacrylate (PEGDA) as the crosslinker in the preparation of the polymer membranes. PEGDA is known for its unique properties and wide range of applications in the field of membrane science.⁵ Firstly, PEGDA exhibits excellent hydrophilicity, which can enhance the water uptake properties of the membranes.⁵ By exploring the impact of varying the membrane structure, including the incorporation of different comonomers, this study will provide insights into how PEGDA-based membranes can be tailored to multicompetent transport and cotransport. Secondly, PEGDA possesses a high degree of flexibility and tunability. Its molecular weight and crosslinking density

can be adjusted to modify the mechanical properties of the membranes, making them suitable for different applications that require specific mechanical strength and stability. The influence of different comonomers in **Figure 1.3** also impact, including mechanical properties where we will be investigated towards the membrane structure, in design PEGDA-based membranes with enhanced mechanical properties. Overall, this work tailors membrane structure for understanding how structure impacts properties in which solute transport, water uptake, mechanical strength towards the development of design rules for advanced membranes applications.

1.2. Thesis Organization

The remainder of this Thesis are organized as follows. Chapter 2 provides the background of various transport phenomena that occur within PEGDA membranes, with a focus on the Solution-Diffusion model. A comprehensive background on the examination of the physiochemical properties such as water uptake and water volume fraction, exploration of transport mechanisms including permeability and the Yasuda model, analysis of diffusion cell experiments, utilization of FTIR spectroscopy, investigation of multi-component transport, measurement of contact angle, and evaluation of mechanical testing methods.

Chapter 3 of this thesis will present an in-depth description of the experimental methods employed, including membrane synthesis techniques, physiochemical characterization methods, mechanical property measurement through tensile testing, and investigations into membrane transport phenomena encompassing permeability and solubility analysis for both single and multicomponent systems. This chapter aims to provide a thorough understanding of the experimental procedures undertaken in the study of PEGDA-based membranes, with emphasis on various aspects of investigation.

Chapter 1: Introduction

Chapter 4 will offer a comprehensive analysis of the obtained results, covering the physiochemical characterization and transport properties of the PEGDA membranes. It will encompass parameters such as water uptake, volume fraction, modulus, and contact angle, as well as examine permeability, solubility, diffusivity, and multi-component permeability, providing valuable insights into the membrane's hydration behavior, structure, surface characteristics, and performance in various transport scenarios. Overall, Chapter 4 will present a comprehensive overview of the experimental results related to the physiochemical characterization and transport properties of the PEGDA membranes.

Chapter 5 concludes the study by summarizing the results obtained from investigating the diffusivity and solubility of methanol in single-component testing and the behavior of KAc and KFm with methanol in multi-component testing. It emphasizes the significance of understanding these transport properties for potential applications in separations and purification processes, while also highlighting the need for future research to explore the effects of different membrane compositions and configurations on the transport behavior of these components.

1.3. References

1. Liu, J., & Yan, X. (2020). Polymer electrolyte membranes for fuel cells: A review. *Journal of Energy Chemistry*, 41, 111-132. doi: 10.1016/j.jechem.2019.06.035
2. Shuyu Liang, Naveed Altaf, Liang Huang, Yanshan Gao, Qiang Wang, Electrolytic cell design for electrochemical CO₂ reduction, *Journal of CO₂ Utilization*, Volume 35, 2020, Pages 90-105, ISSN 2212-9820, <https://doi.org/10.1016/j.jcou.2019.09.007>.
3. Lei Hu, Li Gao, Mengting Di, Xiaobin Jiang, Xuemei Wu, Xiaoming Yan, Xianfeng Li, Gaohong He, Ion/Molecule-selective transport nanochannels of membranes for redox flow batteries, *Energy Storage Materials*, Volume 34, 2021, Pages 648-668, ISSN 2405-8297, <https://doi.org/10.1016/j.ensm.2020.10.008>.
4. Guinevere A. Giffin, Sandra Lavina, Giuseppe Pace, and Vito Di Noto *The Journal of Physical Chemistry C* **2012** 116 (45), 23965-23973 DOI: 10.1021/jp3094879
5. Son KH, Lee JW. Synthesis and Characterization of Poly(Ethylene Glycol) Based Thermo-Responsive Hydrogels for Cell Sheet Engineering. *Materials (Basel)*. 2016 Oct 20;9(10):854. doi: 10.3390/ma9100854. PMID: 28773974; PMCID: PMC5456593.

Chapter 2

Background

2.1 Background

The paper will discuss various aspects of PEGDA membranes, including the Solution Diffusion model, physiochemical properties in water uptake and water volume fraction, and transport properties such as permeability and multicomponent transport. The Yasuda model, which is useful in predicting the solubility and diffusivity of gases in polymers, will also be explored. The paper will delve into experimental methods such as diffusion cell experiments and FTIR to measure these properties. In addition, the paper will discuss contact angle measurements and their implications on the transport properties of the membranes. Finally, the mechanical properties of PEGDA membranes will be examined, with a focus on tensile testing. Overall, the paper will provide a comprehensive understanding of the physiochemical and transport properties of PEGDA membranes, as well as their contact angle and mechanical properties.

2.2. Solution diffusion model

The solution-diffusion model is a theoretical model used to describe the transport of molecules across a membrane [1,2]. It is based on the idea that molecules in a liquid or gas phase on one side of the membrane will diffuse through the membrane's pores and into the other side due to a concentration gradient **Figure 2.1**. The properties of the membrane and the permeating molecules, such as the pore size, the diffusivity of the molecules, and the solubility of the molecules in the membrane, determine the rate at which this occurs. The transport of small molecules or ions through hydrated polymeric membranes is commonly explained using the solution-diffusion

model [1,2]. This model characterizes permeation through three sequential steps: absorption into the membrane on one side [1-3], diffusional movements between fractional voids towards the direction of a chemical potential gradient [1-3], and desorption from the membrane on the opposite side of Eq. (1)

$$P_i = D_i K_i \quad (1)$$

The membrane permeability to solute i (P_i) represents the ability of the membrane to allow the transport of the specific solute. It is a measure of how easily the solute can move through the membrane. The membrane diffusivity to solute i (D_i) refers to the rate at which the solute can diffuse through the membrane material. It quantifies the mobility of the solute within the membrane. The membrane solubility to solute i (K_i) represents the ability of the solute to dissolve in the membrane material [2,4]. It indicates the affinity of the solute for the membrane and its tendency to form a solution within the material. The transport behavior of ion exchange membranes for a single solute is commonly investigated using the solution-diffusion model. This model considers the combined effects of membrane permeability, diffusivity, and solubility to describe the overall transport of solutes through the membrane. By understanding and characterizing these parameters, researchers can gain insights into the membrane's performance and its ability to selectively transport specific solutes.

In contrast to the transport behavior of ion exchange membranes for single solutes, the transport behavior of charge-neutral solutes such as methanol is typically dominated by the concentration gradient [2]. This means that the movement of charge-neutral solutes through the membrane is primarily driven by differences in solute concentrations between the two sides of the membrane.

It is important to note that the understanding of multi-component transport through ion exchange membranes is still in its early stages. While the transport of single solutes has been extensively

studied and can be described using models such as the solution-diffusion model, the transport of multiple solutes simultaneously through ion exchange membranes is a relatively new area of research. Therefore, there is ongoing research and development to better understand and characterize the behavior of ion exchange membranes in multi-component transport scenarios.

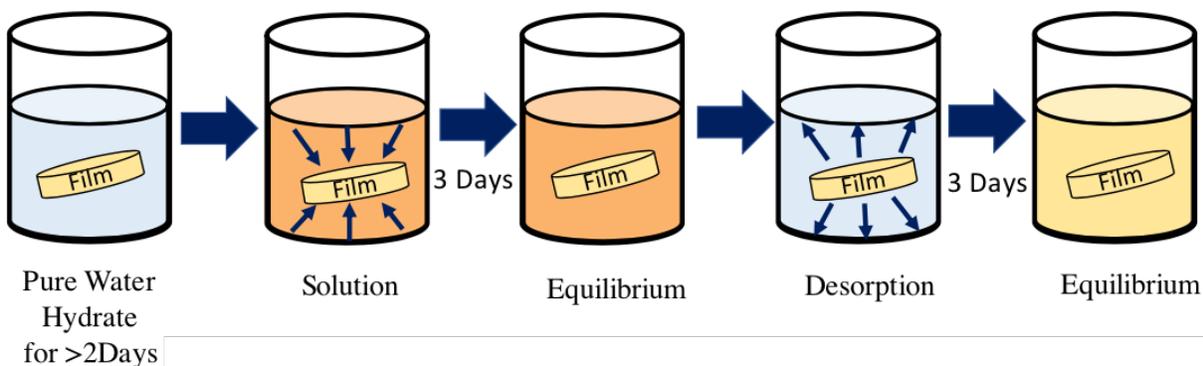


Figure 2.1 Schematic of sorption-desorption experiment for solute solubilities

2.3. Physiochemical Properties:

2.3.1: Water uptake and water volume fraction

Water uptake in membranes refers to the amount of water absorbed by a membrane material. The water uptake of a membrane material is an important characteristic as it affects its mechanical properties, dimensional stability, permeability, and overall performance. The water uptake can be influenced by various factors, such as the chemical composition of the membrane material, the presence of hydrophilic or hydrophobic groups, the degree of cross-linking, and the relative humidity and temperature of the surrounding environment. Water uptake can be either beneficial or detrimental to the performance of the membrane, depending on the application. In some cases, such as in reverse osmosis membranes, high water uptake is desired to increase the permeability of the membrane. Previous studies have demonstrated that an increase in water content [8,9] or the inclusion of higher comonomer content during pre-polymerization leads to an elevation in the

Chapter 2: Background

fractional free volume (FFV) within synthesized membranes [9,10,12]. To evaluate the relative FFV in membranes, researchers typically analyze the equilibrium water uptake and water volume fraction. These parameters serve as estimations of the FFV, as water molecules occupy the available free volume within the dense, hydrated polymeric membranes. The determination of FFV content is crucial for comprehending the transport behavior of the membranes, as it directly affects solute uptake and diffusion through the membrane [9,11,12]. In other cases, such as in fuel cell membranes, high water uptake can be detrimental to the performance of the membrane as it can cause swelling, dimensional changes, and reduced ionic conductivity. There are different methods to measure the water uptake in membranes, such as gravimetric analysis, infrared spectroscopy, and electron microscopy. [13]

The fractional free volume (FFV) is a measure of the amount of empty space in a material that is not occupied by the atoms or molecules of the material. It is typically expressed as a fraction of the total volume of the material. In polymer science, the fractional free volume is an important property that can affect the diffusion and mobility of molecules in the material. The fractional free volume can also be used to understand the properties of polymer membranes. For instance, the FFV of a membrane can be used to predict its permeability molecule providing the transport pathway.

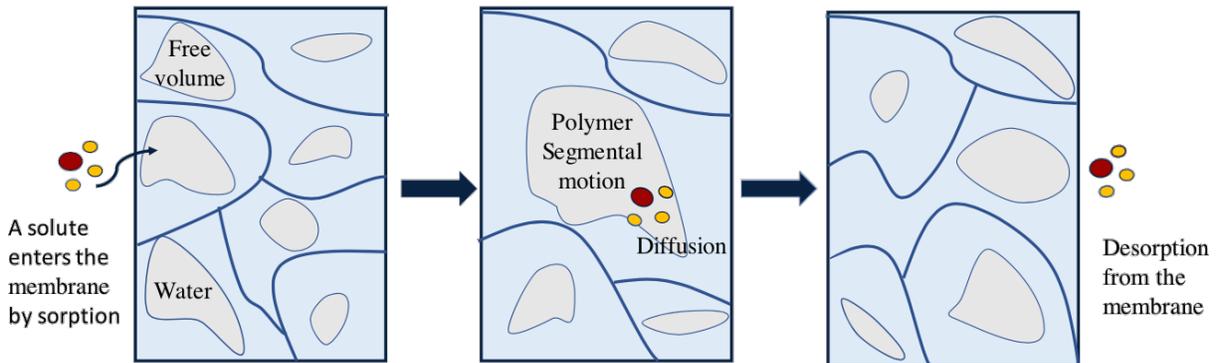


Figure 2.2 Schematic of solute diffusion through membranes of free volume

2.3.2 Transport Behavior: Permeability, yasuda model, diffusion cell

experiment, FTIR, multi-component transport

The Yasuda model is a theoretical model that predicts the permeation rate of gases through polymeric membranes. It is based on the assumption that the permeation rate is proportional to the product of the solubility of the gas in the polymer and the diffusivity of the gas in the polymer. The Yasuda model is an empirical model, which means that it is based on experimental data and can be used to estimate the permeation rate of a gas through a polymer membrane, given the solubility and diffusivity of the gas in the polymer. The Yasuda Model is widely used to predict the permeation rate of gases through polymeric membranes [16,17]. It is often used to compare the permeation rates of different gases through the same polymer membrane, or the permeation rates of the same gas through different polymer membranes. The Yasuda model was first introduced by Yasuda, K. and co-workers in 1968, "Gas permeation through polymeric membrane" *Journal of Applied Polymer Science*, 12(2), 635-655.

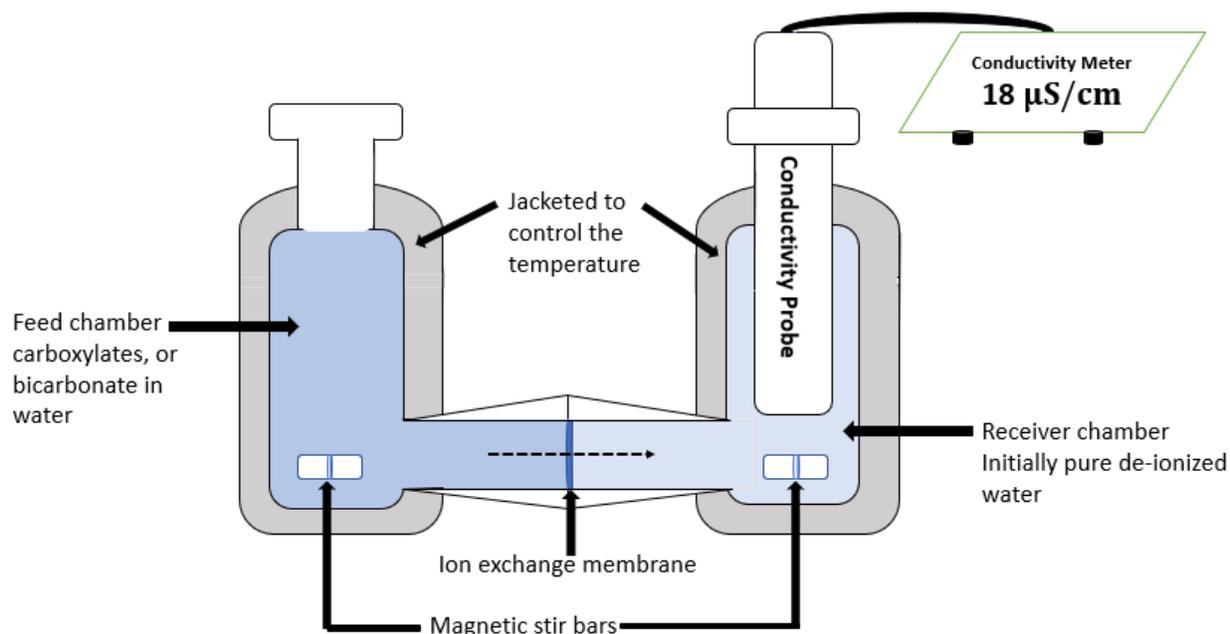


Figure 2.3 illustration of experimental setup outfitted with an in-situ conductivity probe to determine single component solute permeabilities or ions in IEMs¹⁸

A diffusion cell experiment is a commonly used method for measuring the permeation rate of a substance through a membrane or other barrier material. It involves using a diffusion cell to measure the amount of substance that diffuses through the membrane over a period of time. The permeation rate can then be calculated from this data.

2.4 Contact Angle

A surface with a high contact angle is considered hydrophobic, meaning it repels water, while a surface with a low contact angle is considered hydrophilic, meaning it attracts water [6,7].

In the case of membranes, the contact angle is an important parameter because it affects the membrane's permeability and selectivity. A hydrophobic membrane with a high contact angle will repel water and allow only non-polar molecules to pass through, while a hydrophilic membrane with a low contact angle will attract water and allow polar molecules to pass through [7]. The

magnitude of the contact angle depends on the surface chemistry of the membrane, including its surface charge, functional groups, and roughness. For example, a membrane with a smooth, non-polar surface will have a higher contact angle and be more hydrophobic than a membrane with a rough, polar surface. In general, membrane materials used for water treatment and filtration applications are designed to be hydrophilic, with contact angles typically ranging from 10 to 90 degrees [7]. This allows water to wet the surface and pass through the membrane while retaining impurities and contaminants. However, in some applications such as oil-water separation, a hydrophobic membrane with a contact angle greater than 90 degrees may be desirable to repel water and allow only oil to pass through [6,7]

2.4.1: Mechanical testing

Tensile testing is a commonly used mechanical testing method for evaluating the strength and deformation properties of materials, including polymers like PEGDA. This testing technique is particularly valuable for assessing the mechanical properties of PEGDA membranes, such as their tensile strength, Young's modulus, and elongation at break. These properties are important for understanding how the membrane will perform in applications such as filtration, permeation, and separation processes. To conduct a tensile test on a PEGDA membrane, a sample of the membrane is typically cut into a specific shape, such as a rectangular strip, and placed into a testing machine such as a universal testing machine or dynamic mechanical analyzer (DMA). The machine then applies a tensile force to the sample, pulling it in opposite directions until it breaks. During the test, the machine measures the force applied to the sample and the corresponding deformation or elongation of the sample. By analyzing the data obtained from the tensile test, various mechanical properties of the PEGDA membrane can be determined, including its strength, stiffness, and

deformation behavior under stress. This information is valuable for optimizing the design and performance of the membrane for specific applications.

Tensile testing provides insights into the strength and brittleness of the membrane. It helps evaluate the tensile strength, which represents the membrane's ability to resist breaking or deformation under tension. The stress-strain curve obtained from the test can also provide information about the brittleness of the membrane. A brittle membrane would exhibit limited elongation before failure, while a more ductile membrane would demonstrate higher elongation and deformation ability. Another important mechanical property obtained from tensile testing is Young's modulus, also known as the elastic modulus or stiffness. Young's modulus is a measure of the membrane's ability to resist deformation under an applied force [14]. By calculating Young's modulus from the test data, one can gain insights into the membrane's rigidity and its ability to return to its original shape after deformation.

It has been observed that decreasing the PEGDA content in the prepolymerization solution leads to a decrease in both tensile strength (σ_b) and Young's modulus (E') of the prepared membranes. However, there is a slight increase in the breaking elongation (ϵ_b) of the membranes [5].

The composition of PEGDA membranes, including the presence of additives like phenyl acrylates, can influence their mechanical properties. Tensile testing allows for the evaluation of different compositions and thicknesses to assess their effects on properties such as toughness, strength, and elongation. Moreover, the mechanical properties of crosslinked and non-crosslinked PEGDA membranes can also be examined through tensile testing. Crosslinking, which involves chemically bonding the polymer chains, can enhance the mechanical properties of the membrane, including increasing its modulus and strength. Tensile testing enables the quantification of the impact of crosslink density on these mechanical properties.

Chapter 2: Background

The mechanical properties of PEGDA membranes are interconnected with their transport properties, such as permeability and solubility. By understanding the mechanical behavior, researchers can gain insights into how the membrane will perform under stress, resist deformation, and maintain its integrity during filtration, separation, or permeation processes. In summary, tensile testing plays a crucial role in characterizing the mechanical properties of PEGDA membranes. This information is vital for optimizing the membrane's design, improving its performance, and ensuring its suitability for specific applications in aqueous environments.

2.5. References

1. J.G. Wijmans, R.W. Baker, The solution-diffusion model: a review, *Journal of Membrane Science*, Volume 107, Issues 1–2, 1995, Pages 1-21, ISSN 0376-7388, [https://doi.org/10.1016/0376-7388\(95\)00102-I](https://doi.org/10.1016/0376-7388(95)00102-I).
2. Kim J.M., Dobyns B.M., Zhao R., Beckingham B.S., Multicomponent transport of methanol and acetate in a series of crosslinked PEGDA-AMPS cation exchange membranes, (2020) *Journal of Membrane Science*, 614, art. no. 118486, Cited 9 times., DOI: 10.1016/j.memsci.2020.118486
3. Geoffrey M. Geise, Linda P. Falcon, Benny D. Freeman, Donald R. Paul, Sodium chloride sorption in sulfonated polymers for membrane applications, *Journal of Membrane Science*, Volumes 423–424, 2012, Pages 195-208, ISSN 0376-7388, <https://doi.org/10.1016/j.memsci.2012.08.014>.
4. Breanna M. Dobyns, Jung Min Kim, Jing Li, Zhihua Jiang, Bryan S. Beckingham, Multicomponent transport of alcohols in Nafion 117 measured by in situ ATR FTIR spectroscopy, *Polymer*, Volume 209, 2020, 123046, ISSN 0032-3861, <https://doi.org/10.1016/j.polymer.2020.123046>.
5. Guodong Kang, Yiming Cao, Hongyong Zhao, Quan Yuan, Preparation and characterization of crosslinked poly(ethylene glycol) diacrylate membranes with excellent antifouling and solvent-resistant properties, *Journal of Membrane Science*, Volume 318, Issues 1–2, 2008, Pages 227-232, ISSN 0376-7388, <https://doi.org/10.1016/j.memsci.2008.02.045>.
6. *J. Phys. Chem. Lett.* 2014, 5, 4, 686–688 Publication Date: February 20, 2014
<https://doi.org/10.1021/jz402762h>

7. Seyedabbas Rasouli, Nima Rezaei, Hamideh Hamedi, Sohrab Zendehboudi, Xili Duan, Superhydrophobic and superoleophilic membranes for oil-water separation application: A comprehensive review, *Materials & Design*, Volume 204, 2021, 109599, ISSN 0264-1275, <https://doi.org/10.1016/j.matdes.2021.109599>.
(<https://www.sciencedirect.com/science/article/pii/S0264127521001520>)
8. Dobyns, B.M.; Kim, J.M.; Beckingham, B.S. Multicomponent Transport of Methanol and Sodium Acetate in Poly (Ethylene Glycol) Diacrylate Membranes of Varied Fractional Free Volume. *Eur. Polym. J.* 2020, 134, 109809. [Google Scholar] [CrossRef]
9. Mazumder, A.; Kim, J.M.; Hunter, B.; Beckingham, B.S. Controlling Fractional Free Volume, Transport, and Co-Transport of Alcohols and Carboxylate Salts in PEGDA Membranes. *Membranes* 2023, 13, 17. <https://doi.org/10.3390/membranes13010017>
10. Kim, J.M.; Beckingham, B.S. Comonomer Effects on Co-Permeation of Methanol and Acetate in Cation Exchange Membranes. *Eur. Polym. J.* 2021, 147, 110307
11. Yan, N.; Sujanani, R.; Kamcev, J.; Jang, E.-S.; Kobayashi, K.; Paul, D.R.; Freeman, B.D. Salt and Ion Transport in a Series of Crosslinked AMPS/PEGDA Hydrogel Membranes. *J. Membr. Sci.* 2022, 653, 120549.
12. Ju, H.; Sagle, A.C.; Freeman, B.D.; Mardel, J.I.; Hill, A.J. Characterization of Sodium Chloride and Water Transport in Crosslinked Poly (Ethylene Oxide) Hydrogels. *J. Membr. Sci.* 2010, 358, 131–141.
13. Qiongjuan Duan, Shanhai Ge, Chao-Yang Wang, Water uptake, ionic conductivity and swelling properties of anion-exchange membrane, *Journal of Power Sources*, Volume 243, 2013, Pages 773-778, ISSN 0378-7753, <https://doi.org/10.1016/j.jpowsour.2013.06.095>.

Chapter 2: Background

14. Yasuhisa Kodaira, Tatsuma Miura, Yoshinori Takano, Akio Yonezu, Development of biaxial tensile testing for porous polymer membranes, *Polymer Testing*, Volume 106, 2022, 107440, ISSN 0142-9418,
15. *Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications*, pp. 563-574, CRC Press, 2012.
16. Hiroyuki Kanesugi, Keiko Ohyama, Hirotada Fujiwara, Shin Nishimura, High-pressure hydrogen permeability model for crystalline polymers, *International Journal of Hydrogen Energy*, Volume 48, Issue 2, 2023, Pages 723-739, ISSN 0360-3199, <https://doi.org/10.1016/j.ijhydene.2022.09.205>
17. Yasuda, H., Peterlin, A., Colton, C. K., Smith, K. A. & Merrill, E. W. Permeability of solutes through hydrated polymer membranes. Part III. Theoretical background for the selectivity of dialysis membranes. *Die Makromolekulare Chemie* **126**, 177–186 (1969)
18. Aravindhan.P.P. Investigating Structure-Property Relationships in Crosslinked Polymer Membranes. A preliminary dissertation, page 7, 2022

Chapter 3

Experimental Methods

3.1. Materials

Poly(ethylene glycol) diacrylate (PEGDA, $n=10$, $M_n=500$), phenoxyethyl acrylate (PEA) and poly(ethylene glycol) phenyl ether acrylate (PEGPEA), were purchased from Sigma-Aldrich Chemicals (St. Louis, MS). Phenyl acrylate (PA) was purchased from AmBeed. 1-Hydroxycyclohexyl phenyl ketone (HCPK, photoinitiator) was purchased from Tokyo Chemical Industry (Japan). Potassium acetate, potassium formate, and methanol (99.8%) were purchased from British Drug House (BDH®) Chemicals (Poole, UK). Type-1 deionized water produced by a Waterpro BT Purification System from Labconco® (18.2 114mΩ cm at 25 °C, 1.2 ppb TOC) (Kansas City, MO) has been used in this work.

3.2 Membrane Synthesis

UV-photopolymerization of PEGDA-PA, PEGDA-PEA, and PEGDA-PEGPEA membranes in the presence of photoinitiator HCPK (1-hydroxycyclohexyl phenyl ketone) was performed as shown schematically in **Figure 3.1**. Four series of membranes at different compositions were fabricated. Membranes were prepared using the following molar compositions of PEGDA/comonomer (68/32, 76/24, 84/16, and 92/8) for PA, PEA, and PEGPEA as comonomers. All membranes were prepared with constant pre-polymerization water content as solvent (Type-1 deionized water, 1.0 g) and constant photoinitiator content (HCPK, 0.01g). The pre-polymerization mixture was then sonicated for at least 30 minutes to produce a transparent mixture. Once sonicated, the solution is

then pipetted onto a 5 x 5 in quartz plate. Two steel spacers (305 μm) are used and quartz plate placed on top and secured using four jumbo binder clips. It was then crosslinked using a Spectrolinker XL-1500 from Spectroline, under 254 nm for 3 min at 3.0 mW/cm². After crosslinking, films were removed from the plates and immersed in Type-1 deionized water for 48 hours to fully hydrate.

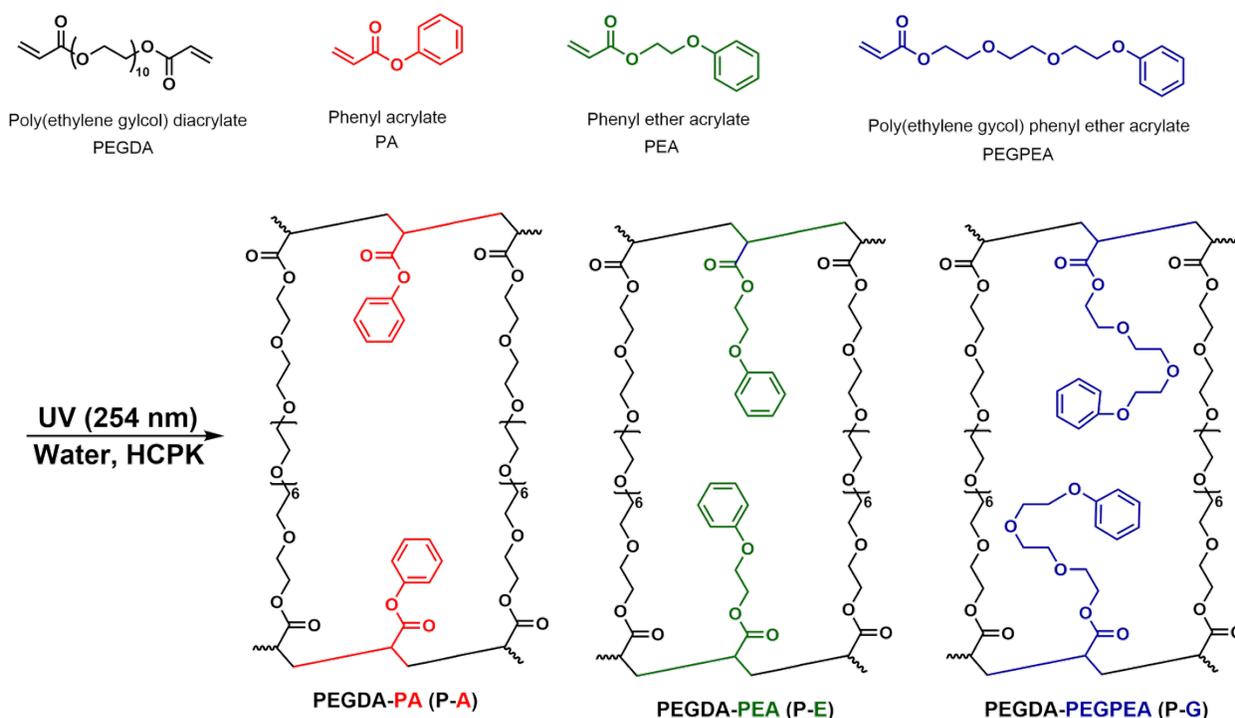


Figure 3.1 Synthesis of PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membrane.

Table 3.1. Membrane pre-polymerization mixtures

	PEGDA (g)	PA (g)	PEA (g)	PEGPEA (g)	HCPK (g)	Water (g)
PEGDA 575-100	4.000	-	-	-	0.04	1.0
PEGDA 68-PA32	3.567	0.433	-	-	0.04	1.0
PEGDA 68- PEA32	3.456	-	0.544	-	0.04	1.0
PEGDA 68- PEGPEA32	3.162	-	-	0.838	0.04	1.0
PEGDA 76-PA24	3.699	0.301	-	-	0.04	1.0
PEGDA 76- PEA24	3.618	-	0.382	-	0.04	1.0
PEGDA 76- PEGPEA24	3.396	-	-	0.604	0.04	1.0
PEGDA 84-PA16	3.813	0.187	-	-	0.04	1.0
PEGDA 84- PEA16	3.761	-	0.239	-	0.04	1.0
PEGDA 84-PEGPEA16	3.612	-	-	0.388	0.04	1.0
PEGDA 92- PEA8	3.928	0.072	-	-	0.04	1.0
PEGDA 92- PEA8	3.907	-	0.93	-	0.04	1.0
PEGDA 92-PEGPEA 8	3.845	-	-	0.155	0.04	1.0

3.3 Membrane Physiochemical Characterization

3.3.1 Water uptake, Density, and Water Volume Fraction

Water uptake was measured using the gravimetric method. A 0.75-inch diameter hole punch was used to cut three hydrated films each of synthesized PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membranes. Once the kim-wipes were used to swiftly blot the surface water, the mass of all the hydrated membranes, W_s , were measured. The dried membrane, W_d mass was then measured succeeding 1 day in a vacuum oven set at 50°C. The water uptake, ω_w , for all films were calculated using Eq. (2)

$$\omega_w = \frac{W_s - W_d}{W_d} \quad (2)$$

Calculated water volume fraction was obtained through the measured density of the dried membrane from the buoyancy method with the density kit (ML-DNY-43, Mettler Toledo) in conjunction with a scale (ML204T, Mettler Toledo). Density, ρ_p , was calculated as Eq. (3)

$$\rho_p = (\rho_L - \rho_0) \left(\frac{W_0}{W_0 - W_L} \right) + \rho_0 \quad (3)$$

in which ρ_L corresponds to the density of water (997.8 kg/m³ at 22 °C), ρ_0 corresponds to the density of air (1.225 kg/m³), W_0 corresponds to the weight of the dried film in air, and W_L corresponds to the weight of the film in water. Eq. (3) was then utilized to calculate water volume fraction, ϕ_w ,

$$\phi_w = \frac{(W_s - W_d) / \rho_w}{(W_s - W_d) / \rho_w + W_d / \rho_p} \quad (3)$$

in which, ρ_w correlates to water density and ρ_p correlates to the polymer density. After 3 days of immersing PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membranes in 1 M potassium acetate, 1M of potassium formate, the thickness of swollen PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membranes were measured to verify the dimensional swelling. Each solution contained 3 hydrated films of each membrane cut from a hole punch prior to immersing and was replaced daily. The thickness, t , of all films were then measured at 5 different points utilizing a digital caliper ($\pm 1 \mu\text{m}$). thickness, t , of all films were then measured at 5 different points utilizing a digital caliper ($\pm 1 \mu\text{m}$).

3.3.2 Contact Angle

Contact angle was done using a Biolin Scientific Attension Theta Lite where the membrane contact angle measured using software by One Attension. The contact angles (in degrees) of samples for each composition of PEGDA-PA, PEGDA-PEA, and PEGDA-PEGPEA were determined using a glass slide with double-sided tape to hold the membrane in place. Droplets of deionized water (DI) were dispensed onto the membrane using an automatic disposable tip dispenser, ensuring accuracy and repeatability.

3.3.3 Mechanical Properties via Tensile Testing

Tensile testing of PEGDA with comonomers of PA, PEA, and PEGPEA can provide valuable information on the mechanical properties of the resulting hydrated membranes. Tensile testing is a method to determine how a material behaves under tension and can provide information on important mechanical properties such as tensile strength, elongation, and modulus. The hydrated membranes were cut into 4 inches x 2 inches dimensions for tensile testing using a TA Instruments RSA2 DMA. Each sample specimen was prepared to have consistent thickness (measured with constant force), width, and length. To obtain the stress vs strain curve, four samples were tested per concentration to obtain an average value.

3.4 Membrane Transport Phenomena

3.4.1 Single and Multicomponent Permeability

For measuring diffusive permeabilities of neutral solutes such as potassium acetate and potassium formate in a single solution and while co-permeating with charged solutes, a custom-built diffusion cell was used seen in **Figure 3.2**.

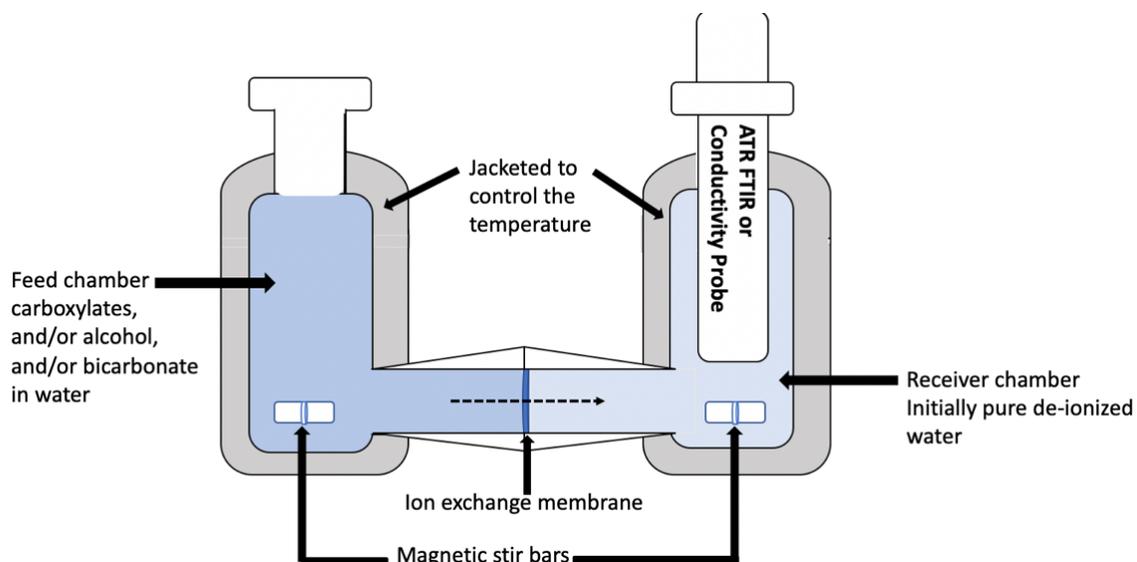


Figure 3.2 Illustration of experimental setup outfitted with an in-situ conductivity probe to determine single component solute permeabilities or ions in IEMs.

As seen one half is the donor cell and the other half is the receiver cell where type 1 water is added. Each half cell has a 1.1423 cm² orifice with a vertical ground glass face. The cells are clamped together whereas the membranes are sandwiched in between, and the solution can pass through the membrane from the donor cell to the receiver cell. Temperature is an important factor to keep in mind and this was controlled constant by glycol chiller, this was used to maintain the diffusion cell temperature at 25 °C. The donor cell was filled with 1 M potassium acetate, or potassium formate. In situ ATR-FTIR spectroscopy (Mettler-Toledo ReactIR™ 15 with shallow tip 9.5 mm DSub AgX DiComp probe) was used to measure the concentration of methanol, and potassium acetate. There are a series of protocols that are taken place to calibrate the conductivity meter for both in-situ and ATR FTIR properly. Both the in-situ ATR FTIR spectroscopy and in situ conductivity probes were calibrated using a series of aqueous solutions of known concentrations (0.01M-0.1M) of methanol, potassium acetate, potassium formate.

3.4.2 Single Component Solubility

Samples containing 0.01 M to 0.1 M potassium formate or potassium acetate were prepared, and the conductivity of each solution was recorded using conductivity probe (PC820 Precision Benchtop Apera Instruments, Schaumburg, IL). Once the conductivity was acquired the slopes of the of the conductivity vs concentration data, effective molar absorptivity, was calculated for both.

Table 3.2. Calibration constant for measuring conductivity of KAc and KFm solutions

Target concentration	KFm gram in 25mL	KAc gram in 25 mL
0.01	0.0211	0.0245
0.02	0.0421	0.0491
0.05	0.1052	0.1227
0.1	0.2103	0.2454

This allows for determining the solubility conductivity probes were calibrated using a series of aqueous solutions of known concentration using a sorption-desorption experiment; Figure 3.3. The membranes were prepared and immersed in a solution of a solute of interest for 24 hours. This process of immersion and equilibration was repeated two times. After the membranes were fully saturated with the solute solution, they were transferred along with the vial containing the solution to pure type 1 water for an additional 24-hour equilibration period. Finally, the solubility reading was obtained by using the probe to measure the solute concentration in the equilibrated solution.

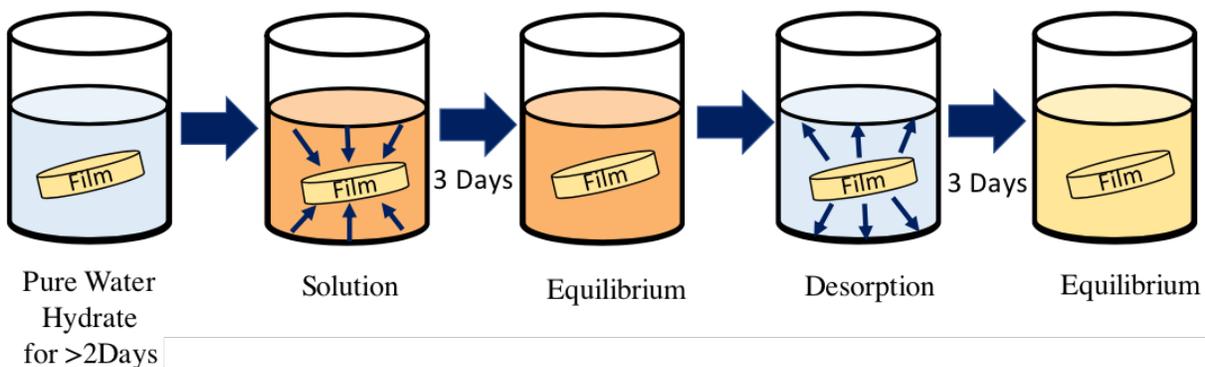


Figure 3.3 Schematic of sorption desorption experiment

3.5 References

[1] N. Yan, R. Sujanani, J. Kamcev, E.-S. Jang, K. Kobayashi, D.R. Paul, B.D. Freeman, Salt and ion transport in a series of crosslinked AMPS/PEGDA hydrogel membranes, *J Membrane Sci.* 653 (2022) 120549. <https://doi.org/10.1016/j.memsci.2022.120549>.

[2] Yasuda, H., Lamaze, C. E. & Ikenberry, L. D. Permeability of solutes through hydrated polymer membranes. Part I. Diffusion of sodium chloride. *Die Makromolekulare Chemie* 118, 19–35 (1968).

Chapter 4

Alcohol-carboxylate transport in crosslinked phenyl-based membranes of varying side-chain length

This chapter will discuss how varied ether side-chain length affects water volume fraction, and salt permeability, solubility, and diffusivity towards different solutes of potassium acetate, potassium formate, and methanol.

4.1 Physiochemical Characterization: Water uptake, Water Volume Fraction, Contact Angle, and Modulus

A series of PEGDA-based membranes were synthesized for investigation; see Figure 4.1. The comonomers used in the PEGDA membranes network can have a significant impact on the properties of the resulting membrane. In this case, the comonomers used were phenyl acrylate (PA), Phenoxyethyl acrylate (PEA), and Poly(ethylene glycol) phenyl ether acrylate (PEGPEA). These comonomers are represented in **Figure 4.1** with varying chain lengths that will be referenced in the graphs shown as 0 for PA, 1 for PEA, and 3 PEGPEA.

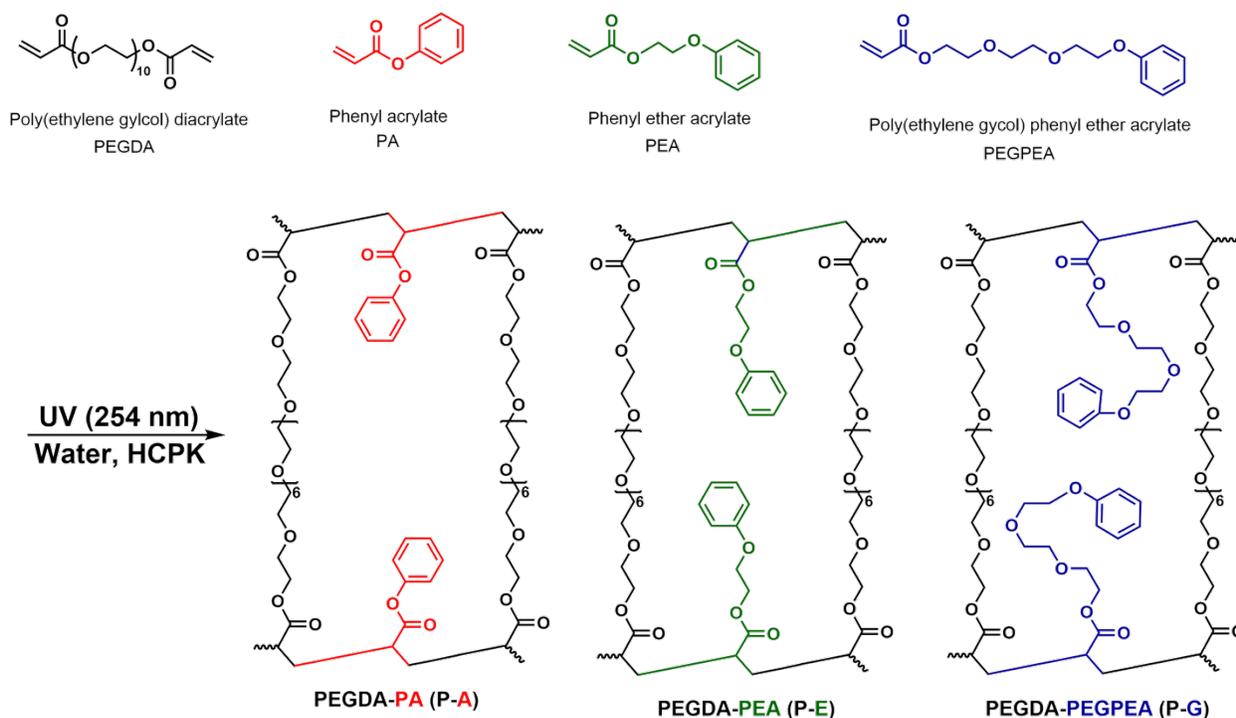


Figure 4.1 Synthesis of PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA membrane

In a hydrated polymer membrane, the water molecules occupy the available fractional free volume. To assess relative fractional free volume, the equilibrium water uptake and water volume fraction are determined, see **Table 4.1** for values, using the methods described in Chapter 3. Water uptake and water volume fraction are commonly utilized as estimates for relative FFV in dense membranes such as those investigated here. As transport is directly correlated with the available FFV in the membrane, characterizing the water uptake and water volume fraction facilitates understanding of the observed transport behavior (1,2). Closely-linked to the water uptake is the hydrophobicity of the membranes. Here, we assess this characteristic through contact angle measurements as described below.

Generally, we hypothesize that water up-take should increase with increasing PEGDA content for the membranes herein as poly(ethylene glycol) diacrylate (PEGDA) is hydrophilic that

Chapter 4: Results and Discussion

is known to have high water absorption and swelling properties. When PEGDA is crosslinked with a comonomer such as PA, PEA, or PEGPEA, it forms a hydrogel network that is capable of absorbing large amounts of water. As the PEGDA content in the membrane increases, there are more hydrophilic groups available for water molecules to interact with. This results in an increase in the hydrophilicity of the membrane, which in turn leads to an increase in water uptake. Additionally, as the PEGDA content increases, the crosslinking density of the membrane increase, which can decrease the water uptake as well. This is because a higher crosslinking density allows for more free volume and space within the membrane network for water molecules to diffuse and interact with the polymer chains. Therefore, based on these factors, it is reasonable to hypothesize that water uptake would increase with increasing PEGDA content in the membranes. However, the exact relationship between PEGDA content and water uptake may depend on other factors such as the specific comonomer. This hypothesis is generally confirmed by the determined water uptake and water fractional free volume, how the addition of this side chain comonomers impacted the water uptake data. For example, I'm seeing, adding PEA lowers the water volume fraction shown in **Table 4.1** and **Figure 4.2**.

Table 4.1 Water uptake, water volume fraction, Young's modulus, and density for the range of PEGDA-(PA, PEA, PEGPEA)

	Water Uptake (g/g dry membrane)	Water Volume Fraction	Young's Modulus (MPa)	Dry Membrane Density (kg/m ³)	Contact angle (degree)
PEGDA 100	53±2	0.37±0.02	0.20±0.03	1115±87	34±3.6
PEGDA68-PA32	46±6	0.36±0.00	0.20±0.01	1208±11	62±3.6
PEGDA 68-PEA32	41±5	0.33±0.00	0.22±0.04	1216±6	51±7.5
PEGDA68-PEGPEA32	45±1	0.35±0.00	0.20±0.01	1201±5	48±0.5
PEGDA 76-PA24	46±7	0.36±0.00	0.13±0.00	1209±11	56±3.7
PEGDA 76-PEA24	43±2	0.34±0.00	0.14±0.06	1208±6	53±3.4
PEGDA 76-PEGPEA24	44±7	0.35±0.00	0.13±0.01	1200±3	51±1.1
PEGDA 84-PA16	48±1	0.36±0.01	0.09±0.06	1180±27	43±0.7
PEGDA 84-PEA16	45±5	0.35±0.00	0.20±0.15	1209±4	50±5.2
PEGDA 84-PEGPEA16	47±6	0.36±0.00	0.17±0.01	1195±8	51±5.5
PEGDA92-PA8	69±2	0.43±0.09	0.15±0.02	1185±18	41±0.8
PEGDA 92-PEA8	49±1	0.36±0.00	0.16±0.01	1182±10	50±3.6
PEGDA 92-PEGPEA8	50±2	0.36±0.00	0.13±0.00	1163±30	46±0.3

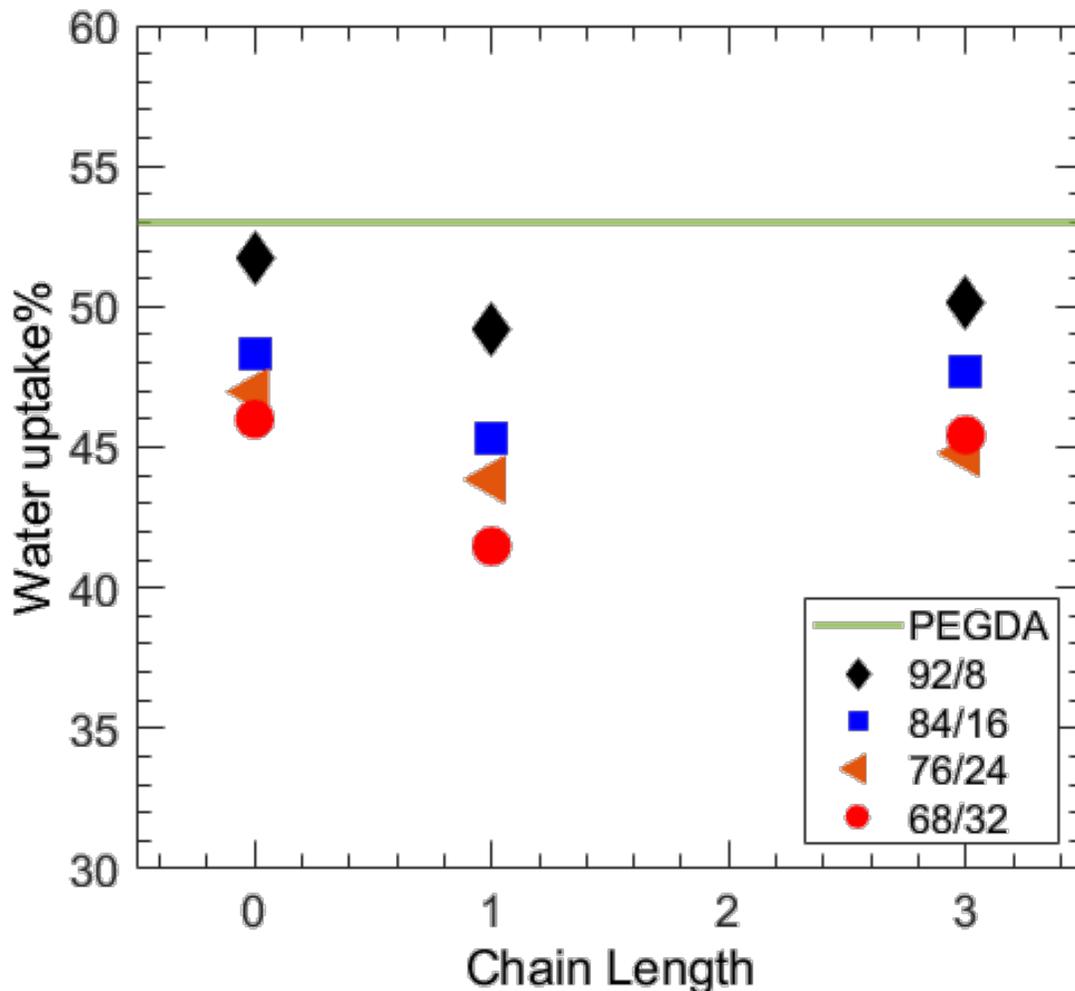


Figure 4.2 Water uptake results for PEGDA, PEGDA-PA, PEGDA-PEA, and PEGDA-PEGPEA membranes (the data shown on the graph is the average of triplicates, with minimal error bar)

As noted above, the relative hydrophobicity is an important factor related to the water uptake behavior. Here, this is assessed through relative contact angle. For these measurements, a droplet of liquid (water) is placed on the surface of the membrane, and the angle between the droplet and the surface is measured using a goniometer. A contact angle of less than 90 degrees indicates a hydrophilic surface, while a contact angle greater than 90 degrees indicates a hydrophobic

surface which is seen the graph. From this we are able to infer the relative hydrophilicity of the membranes, which can be referenced from Chapter 2.4. Contact angle was measured for the membranes investigated, see **Table 4.1** and **Figure 4.3A-C**.

The data, shown in **Figure A.**, suggested that as the ratio of PEGDA to PA monomers decreases (from PEGDA 68/32 PA to PEGDA 92/8 PA), the contact angle decreases. This indicates a shift towards a more hydrophilic surface. The decreasing contact angles imply that the membranes become more prone to wetting by the liquid, which suggests an increased affinity for water-based solvents. Based on the data shown in **Figure B.**, the contact angles for the PEGDA-PEA membranes fall within a relatively narrow range. The average contact angles for all compositions are around 50-54 degrees, suggesting a moderate hydrophobicity of the surfaces. However, there are slight variations in the contact angles among the different compositions.

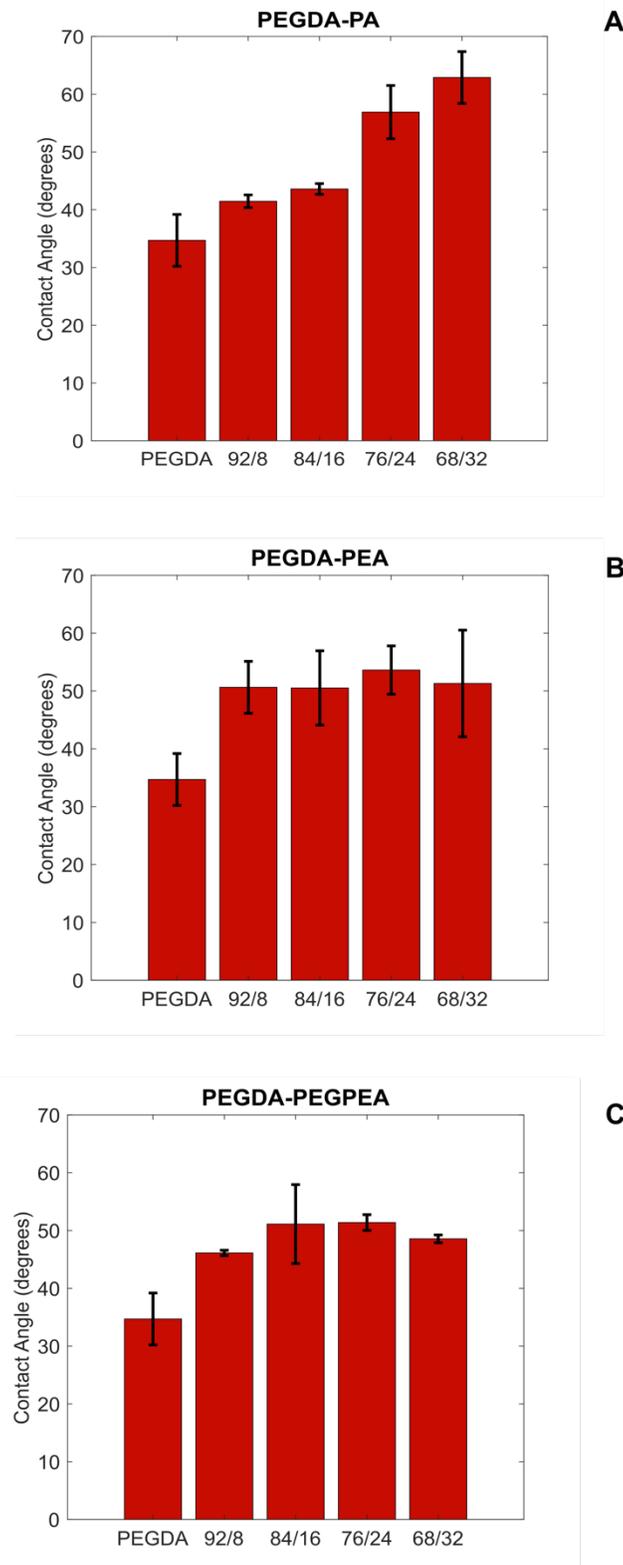


Figure 4.3 Contact angle (degrees) of with different compositions of PEGDA weight % (A) PEGDA-PA, (B) PEGDA-PEA, (C) PEGDA- PEGPEA.

Chapter 4: Results and Discussion

Based on the given data, the contact angles for the PEGDA-PEGPEA membranes vary across the different compositions. The average contact angles range from approximately 46 to 51 degrees, indicating a moderate to slightly hydrophobic surface.

The standard deviation measures the variability or spread of the contact angle values within each composition. A lower standard deviation indicates that the contact angle measurements are relatively close together, implying a higher level of consistency and reliability in the data in **Figure 4.3** in all tables.

The data indicates that the PEGDA-PA, PEGDA-PEA, and PEGDA-PEGPEA membranes exhibit moderate to slightly hydrophobic surface properties, with variations in contact angles among different compositions. The average contact angle of PEGDA is 34.704 degrees with a standard deviation of 3.66258224 degrees. Comparing this with the contact angles of the other compositions, it suggests that the PEGDA membrane has a relatively more hydrophilic surface. However, the standard deviation for the PEGDA membrane is within a similar range as the other compositions, indicating a comparable level of variability in the contact angle measurements. Overall, the provided data suggests that the PEGDA membrane has a relatively lower average contact angle, indicating a more hydrophilic surface, with similar variability in contact angles as the other compositions.

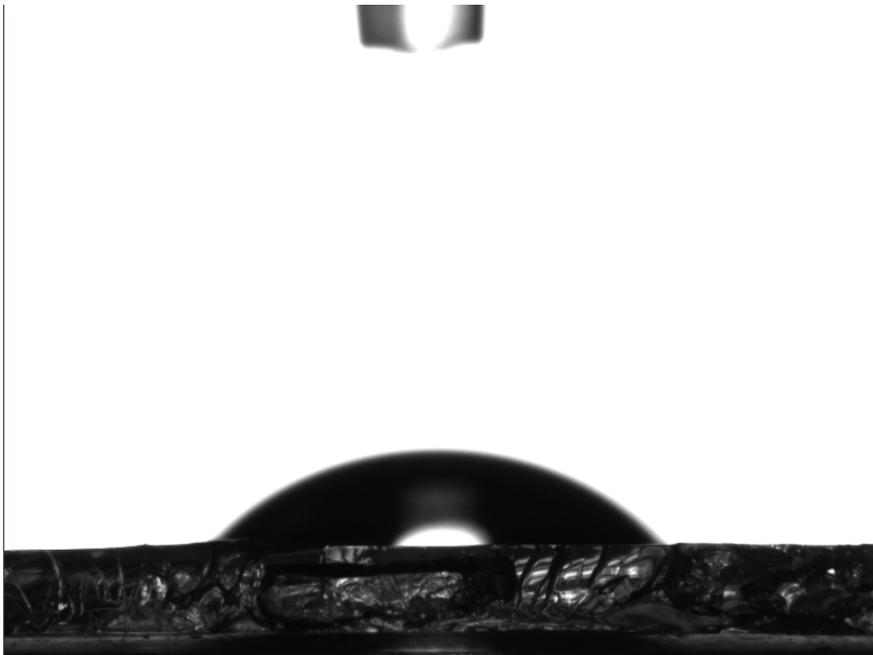


Figure 4.4 Contact angle image of concentration of PEGDA membrane with DI water droplet.

When assessing the impact of the comonomers on hydrophilicity, one looks at their chemical structures. PEA is a hydrophobic comonomer that contains a long alkyl chain. The presence of the alkyl chain reduces the overall hydrophilicity of the membrane network, and as a result, the water uptake of the PEA-containing membrane is typically lower than that of the membranes containing more hydrophilic comonomers such as PA or PEGPEA. This is likely why a decrease is shown in water uptake with increasing PEGDA content in the PEA-containing membranes. On the other hand, PA is a more hydrophilic comonomer than PEA, but it is not as hydrophilic as PEGPEA. This is reflected in the contact angle measurements, where the PEGDA-PA membrane had a higher degree of contact angle than the PEGDA-PEGPEA membranes. The water uptake of the PEGDA-PA membranes is likely to be higher than that of the PEGDA-PEA membrane, but lower than that of the PEGDA-PEGPEA membrane. PEGPEA is the most hydrophilic comonomer used in this study, as it contains both hydrophilic and hydrophobic components. The hydrophilic PEG component makes the PEGDA-PEGPEA membranes more hydrophilic than the PEGDA-PA or PEGDA-PEA membranes, while the hydrophobic alkyl chain provides structural stability to the membrane network. This increased hydrophilicity is reflected in the contact angle measurements, where the PEGDA-PEGPEA membrane had the lowest degree of contact angle. In summary, the differences between the comonomers used in this study can significantly impact the hydrophilicity and water uptake properties of the resulting membrane. PEA, being the most hydrophobic comonomer, resulted in the lowest water uptake, while PEGPEA, being the most hydrophilic, resulted in the highest water uptake. PA, being intermediate in hydrophilicity, resulted in an intermediate water uptake.

Chapter 4: Results and Discussion

In general, we expect that the mechanical properties of the hydrated membranes will be affected by both the PEGDA content and the comonomer type. For example, as the PEGDA content increases, we expect to see an increase in the elongation and a decrease in the tensile strength and modulus of the membranes. This is because PEG segments are hydrophilic and tend to plasticize the material, making it softer and more flexible. Similarly, the choice of comonomer can also affect the mechanical properties of the membranes. For example, as seen in **Figure 4.5** we might expect that the addition of PA, which has a relatively short alkyl chain, could lead to an increase in the tensile strength of the membrane due to increased intermolecular interactions between the polymer chains. On the other hand, the addition of PEA, which has a longer alkyl chain, might result in a softer, more flexible membrane due to increased chain mobility. The addition of PEGPEA, which contains both PEG and alkyl segments, can have a more complex effect on the mechanical properties of the membrane. The PEG segments can plasticize the membrane and reduce its strength and modulus, while the alkyl segments can increase intermolecular interactions and strengthen the material. The net effect on the mechanical properties will depend on the relative amounts of PEG and alkyl segments and their distribution within the polymer chains. In summary, tensile testing of PEGDA with comonomers of PA, PEA, and PEGPEA provides valuable information on the mechanical properties of the resulting hydrated membranes. The mechanical properties will be affected by both the PEGDA content and the comonomer type, with the addition of PEGDA generally resulting in a softer, more flexible membrane, and the choice of comonomer affecting the strength and stiffness of the material. By analyzing the data, it can be observed that the PEGDA component generally has higher average tensile strengths compared to the PA component in each composition. Additionally, the pure PEGDA composition exhibits the highest average tensile strength among all the compositions.

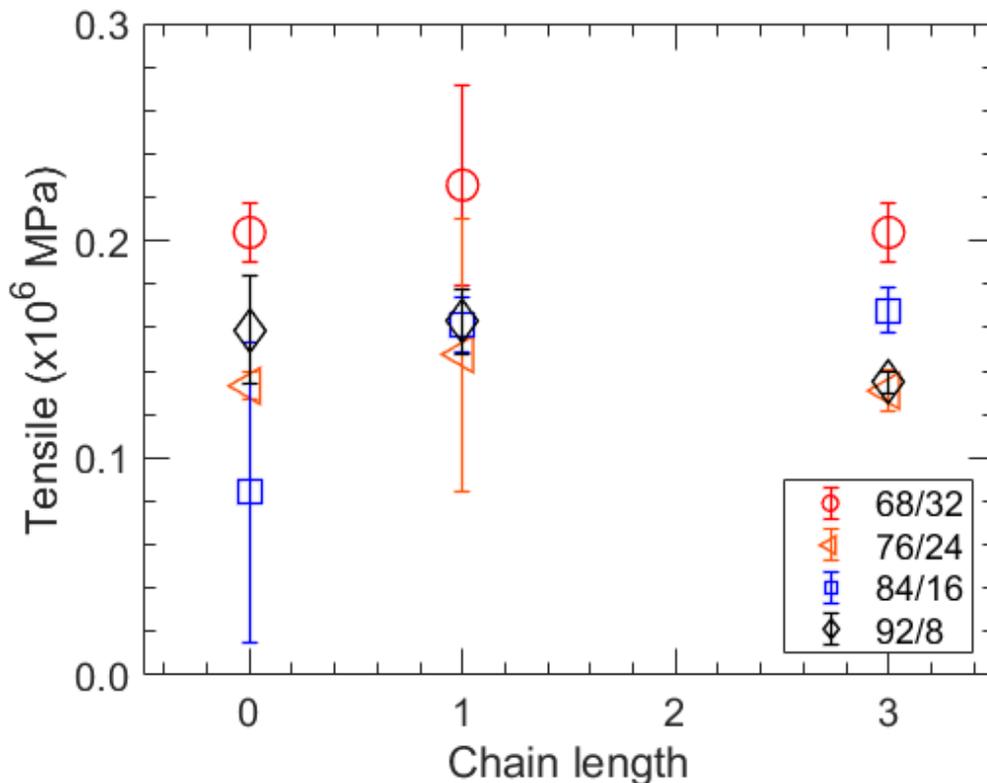


Figure 4.5 Tensile testing ($\times 10^6$ MPa) data of PEGDA-PA, PEGDA-PEA, PEGDA-PEGPEA of all compositions

4.2 Transport Properties

4.2.1 Permeability

Diffusion cell experiments were performed for each of the membranes discussed above to determine their permeability to potassium formate (KFM) and potassium acetate (KAc). As discussed in Chapter 2, these solutes are chosen due to their importance as potential solar fuels products where the minimization of their transport may lead to improvements in device efficiency. The permeability of a membrane can be affected by the PEGDA content, as it can affect the crosslinking density size of the membrane which is seen in **Figure 4.6**. Generally, as the PEGDA content increases which is seen in **Figure 4.6 E and F**, the crosslinking density of the membrane also increases, which can lead to smaller FFV sizes and decreased permeability. However, as

discussed above, PEGDA can also increase the hydrophilicity of the membrane, which can enhance the transport of hydrophilic molecules through the membrane. Therefore, the effect of PEGDA content on the permeability is complex, requiring investigation. The chain length of the comonomer used in the membranes network can affect the hydrophilicity of the membranes. Longer alkyl chains in the comonomer will result in a more hydrophilic membranes, while shorter chains will result in a more hydrophobic membrane. Therefore, membranes containing comonomers with longer alkyl chains will typically have higher water uptake capacities compared to membranes containing comonomers with shorter chains. The comonomer chain length can also affect the permeability of the membrane. Longer alkyl chains in the comonomer can make the membrane more hydrophilic and reduce its permeability to hydrophobic molecules, while shorter chains can decrease the hydrophilicity of the membrane. Therefore, the effect of comonomer chain length on the permeability of the membrane can depend on the specific comonomer used and the types of molecules being transported. Therefore, different types of salts can lead to different swelling behaviors in the membranes. In addition, the salt can also affect the mechanical properties of the membrane network, as some salts can promote or hinder the crosslinking of the polymer chains. Overall, these factors can have complex and interrelated effects on the properties of PEGDA membranes.

From what has been observed, a decrease in PEGDA content as seen in **Figure 4.6 A**, leads to a reduction in the permeation concentration of these compounds, which aligns with expectations of the solution to pass through the membrane. Interpretation, as PEGDA is a crosslinker that is often used in the fabrication of membranes. The concentration of PEGDA can affect the physical and chemical properties of the membrane. Increasing the thickness can impact the permeability of the solution having to travel through the membrane. Generally, a higher concentration of PEGDA

Chapter 4: Results and Discussion

can lead to a more crosslinked and denser membrane and higher permeability. In the case of KFM and KAc, these compounds may be small enough to pass through the membrane, leading to a higher permeabilities. Therefore, reducing the PEGDA content and increasing the comonomer can limit the permeation of these compounds and achieve the desired selectivity. We see the KFM higher due to the hydrated diameter than KAc. We have changed how much PEGDA we have added and changed the chain link for the crosslinker, which changes chemistry, and ion transport we have also changed. Looking at the extra ethylene glycol unit, the Single-component permeability for all solutes increases with increasing water volume fraction.

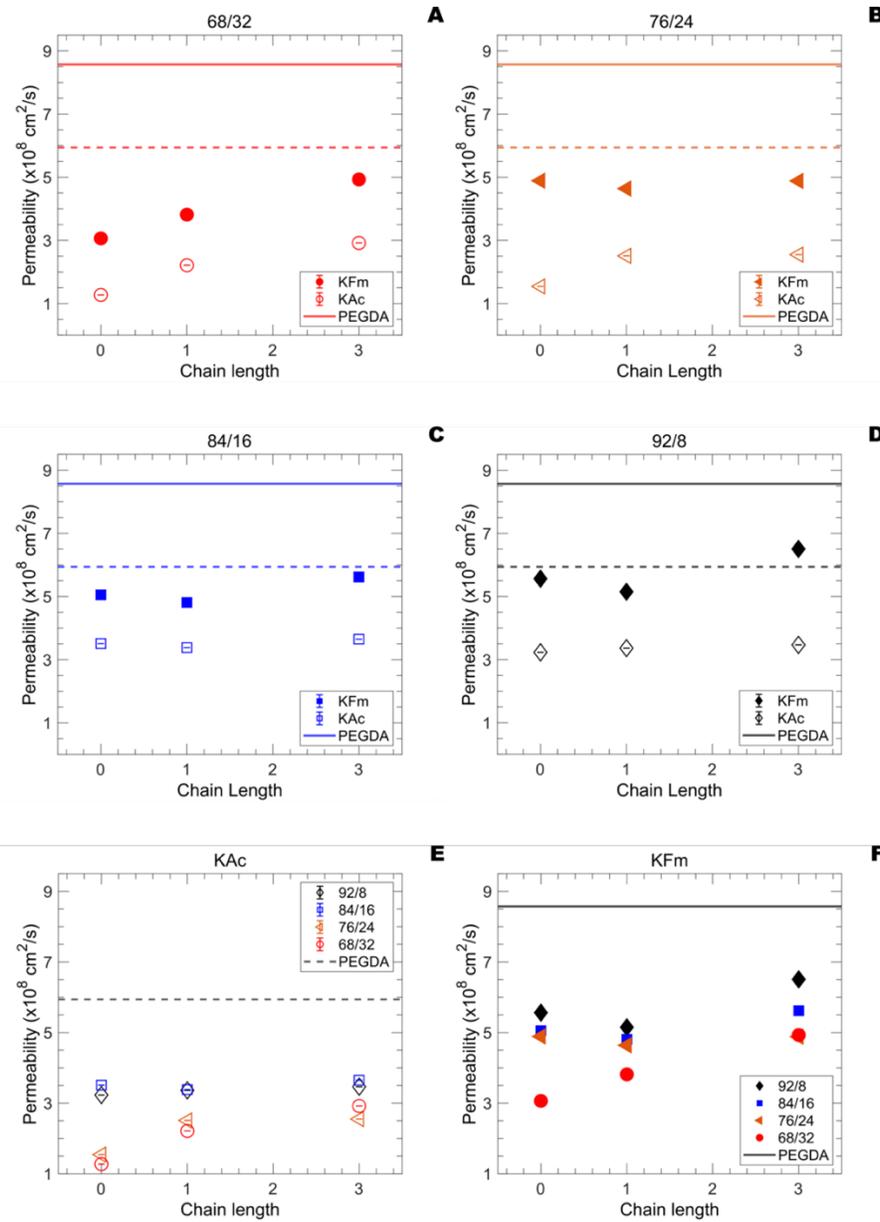


Figure 4.6 Permeability results graphs of different PEGDA compositions comparing KAc(outline of marker) and KFm(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (\circ ,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (\triangleleft ,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (\square , blue) (D) PEGDA 92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(\diamond , black)

4.2.2 Solubility

In the context of PEGDA membranes, solubility testing involves measuring in the membrane concept, it means how much salt dissociates from the membranes based on the external solute concentration. When solubility testing is performed in solutions of KFm (potassium formate in water) and KAc (potassium acetate in water), it is expected that the solubility of PEGDA membranes will differ due to the different nature of the solvents and the interactions between the membrane and the solvents. We know KFm has a higher solubility in water than KAc, which means that a larger amount of KFm can dissolve in water at a given temperature and pressure. When the membrane containing KFm and KAc is placed in type-1 water (i.e., high-purity water), there is an osmotic driving force that tends to pull the water molecules into the membrane, in an attempt to dilute the high salt concentration inside the membrane. As the water molecules move into the membrane, they also carry along some of the dissolved KFm and KAc. However, because KFm has a higher solubility in water than KAc, more KFm is likely to be pulled out of the membrane and into the surrounding water. This results in a lower concentration of KFm inside the membrane, compared to KAc.

The concentration of pure water outside the membrane is affected by the ions that have been pulled out of the solution inside the membrane. As more KFm ions are pulled out of the membrane, the concentration of KFm in the water outside the membrane will increase, and the concentration of KAc in the water outside the membrane will decrease. This can lead to a concentration gradient across the membrane, which can affect the transport of other solutes through the membrane. When a comonomer like PA, PEA, or PEGPEA is added to the membrane, the solubility behavior can be different. The addition of comonomers can alter the solubility of the membrane in different

Chapter 4: Results and Discussion

solvents, depending on the nature and characteristics of the comonomer. Similarly, if PEA is added to the PEGDA membrane, the solubility behavior can be different. PEA has a more hydrophobic nature than PA and may increase the solubility of the membrane in nonpolar solvents like KfM, due to the presence of nonpolar ethyl groups in the comonomer. However, the solubility of the membrane in water-based solvents like KAc may decrease due to the hydrophobic nature of the comonomer. PEGPEA has a longer PEG chain than PEGDA, which can increase the solubility of the membrane in polar solvents like KAc, due to the ability of the PEG chain to form hydrogen bonds with the polar solvent molecules. However, the solubility of the membrane in nonpolar solvents like KfM may decrease due to the presence of the more hydrophobic ethyl groups in the comonomer.

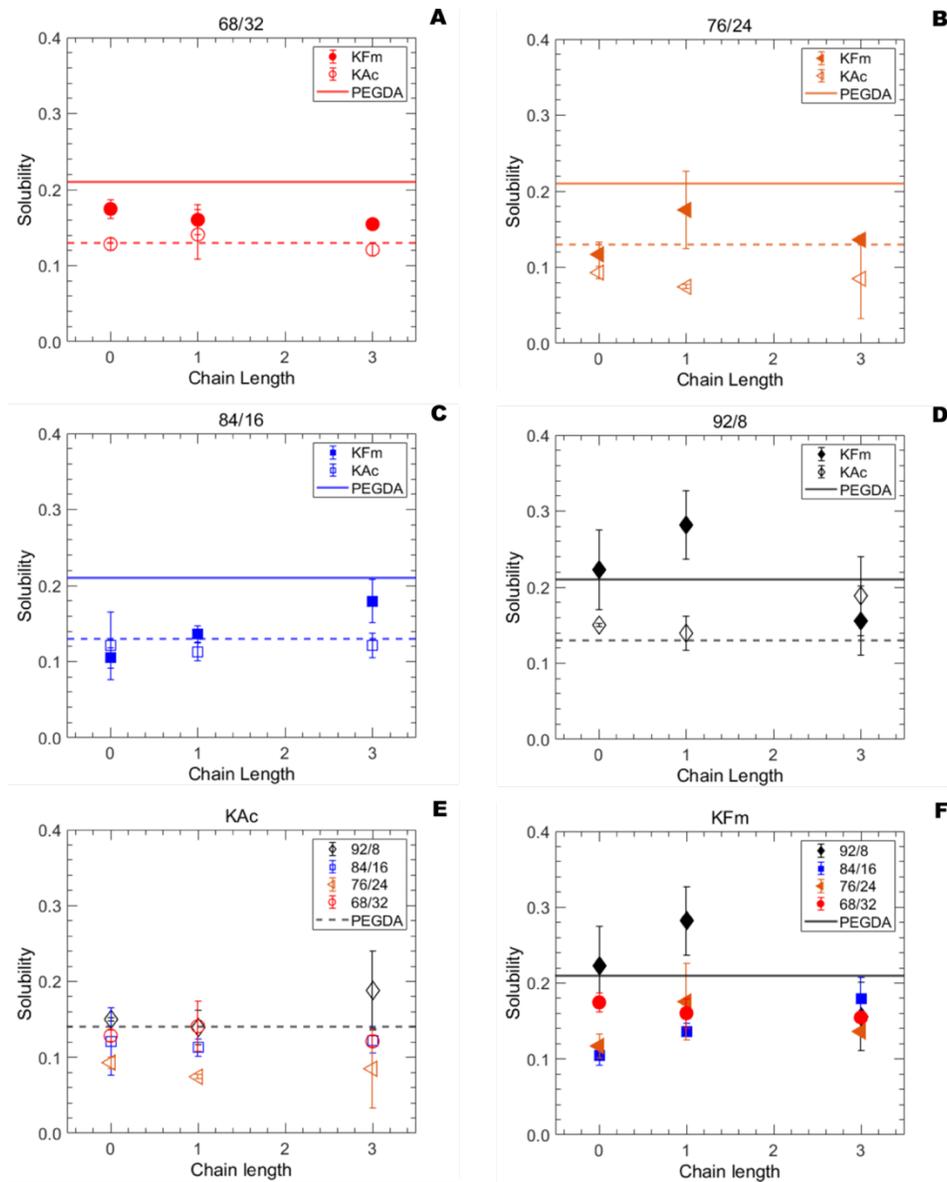


Figure 4.7 Solubility results graphs of different PEGDA compositions comparing KAc(outline of marker) and KFm(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (\circ ,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (\triangleleft ,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (\square , blue) (D) PEGDA 92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(\diamond , black)

Chapter 4: Results and Discussion

Water volume fraction can impact the solubility of solutes such as KFm and KAc. As the water volume fraction increases, the solubility of these solutes in water typically increases. This is because the solute molecules can more easily interact with water molecules when a greater volume of water is available. In addition, water volume fraction can also impact the swelling behavior of polymer membranes containing these solutes. When a polymer membrane is exposed to a solution containing a solute, the solvent (in this case, water) will tend to diffuse into the membrane, causing it to swell. As the water volume fraction increases, the swelling behavior of the membrane can become more pronounced, potentially affecting the permeation properties of the membrane. It is important to note that the effect of water volume fraction on solubility and swelling behavior can depend on various factors. In our case, the chemical properties of the solute and the membrane change the M_w of the crosslinker and commoner.

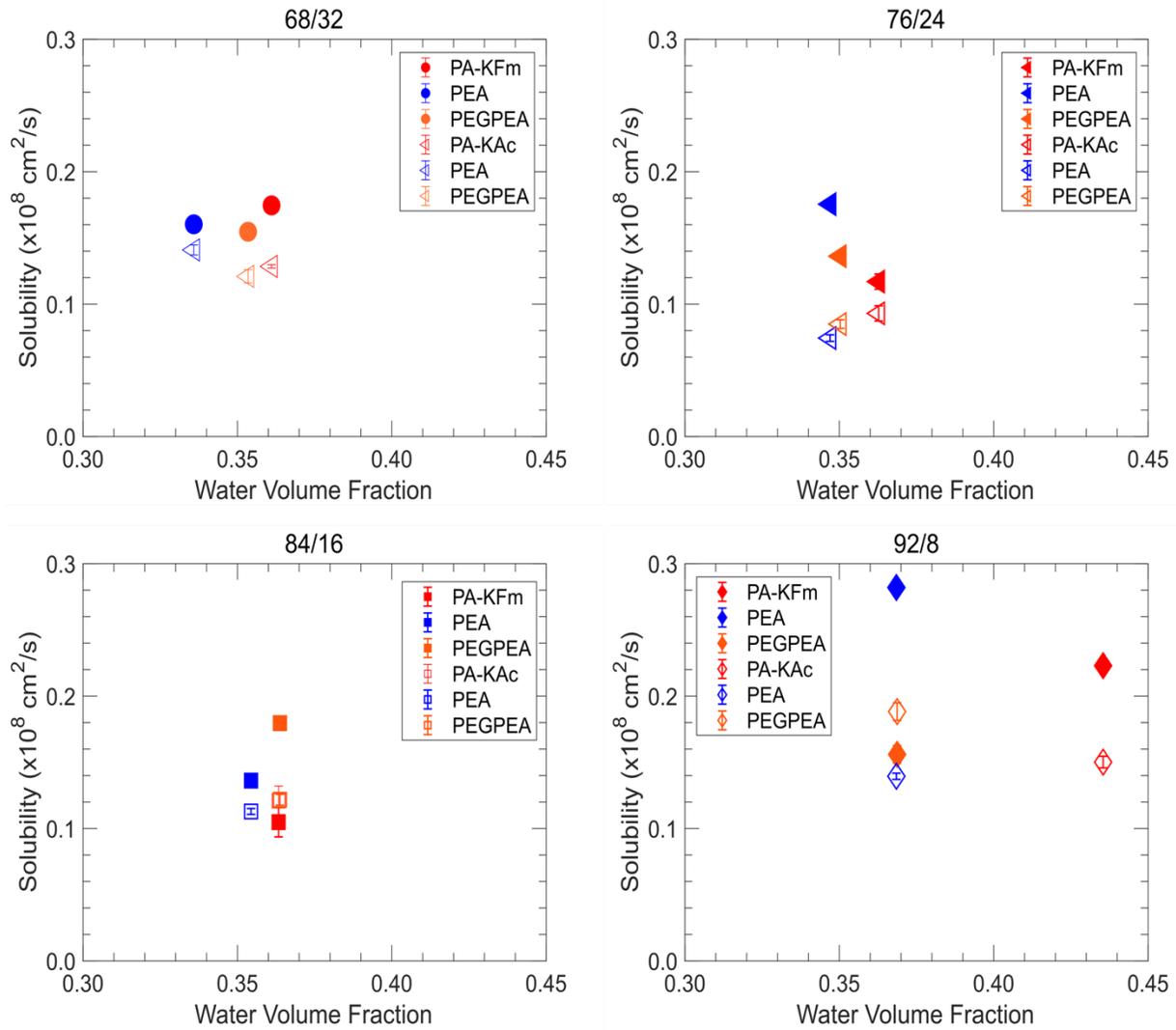


Figure 4.8 solubility of water volume fraction results graphs of different PEGDA compositions comparing KAc(outline of marker) and KfM(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (\circ ,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (\triangle ,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (\square , blue) (D) PEGDA 92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(\diamond , black)

4.2.3 Diffusivity

The mass and velocity of a solute can have an impact on its diffusion behavior. In general, larger molecules with higher molecular weight (M_w) will diffuse more slowly than smaller molecules with lower M_w , because they have lower average velocities due to their larger size and greater inertia. This is because the kinetic energy of a solute is directly proportional to its velocity and inversely proportional to its mass. In the case of potassium acetate (CH_3COOK) and potassium formate (HCOOK), there is a difference in their molecular weights and chemical structures. Potassium acetate has a molecular weight of 98.14 g/mol, while potassium formate has a molecular weight of 84.12 g/mol. Additionally, potassium acetate has an extra CH_3 group, which makes it slightly larger and more complex than potassium formate. Due to these differences in molecular weight and chemical structure, it is possible that potassium acetate may diffuse more slowly than potassium formate. However, it is important to note that diffusion is also influenced by other factors, such as temperature, concentration gradient, and the presence of other solutes or barriers. Therefore, it is possible that these other factors could also impact the diffusion behavior of potassium acetate and potassium formate, and their relative diffusion rates.

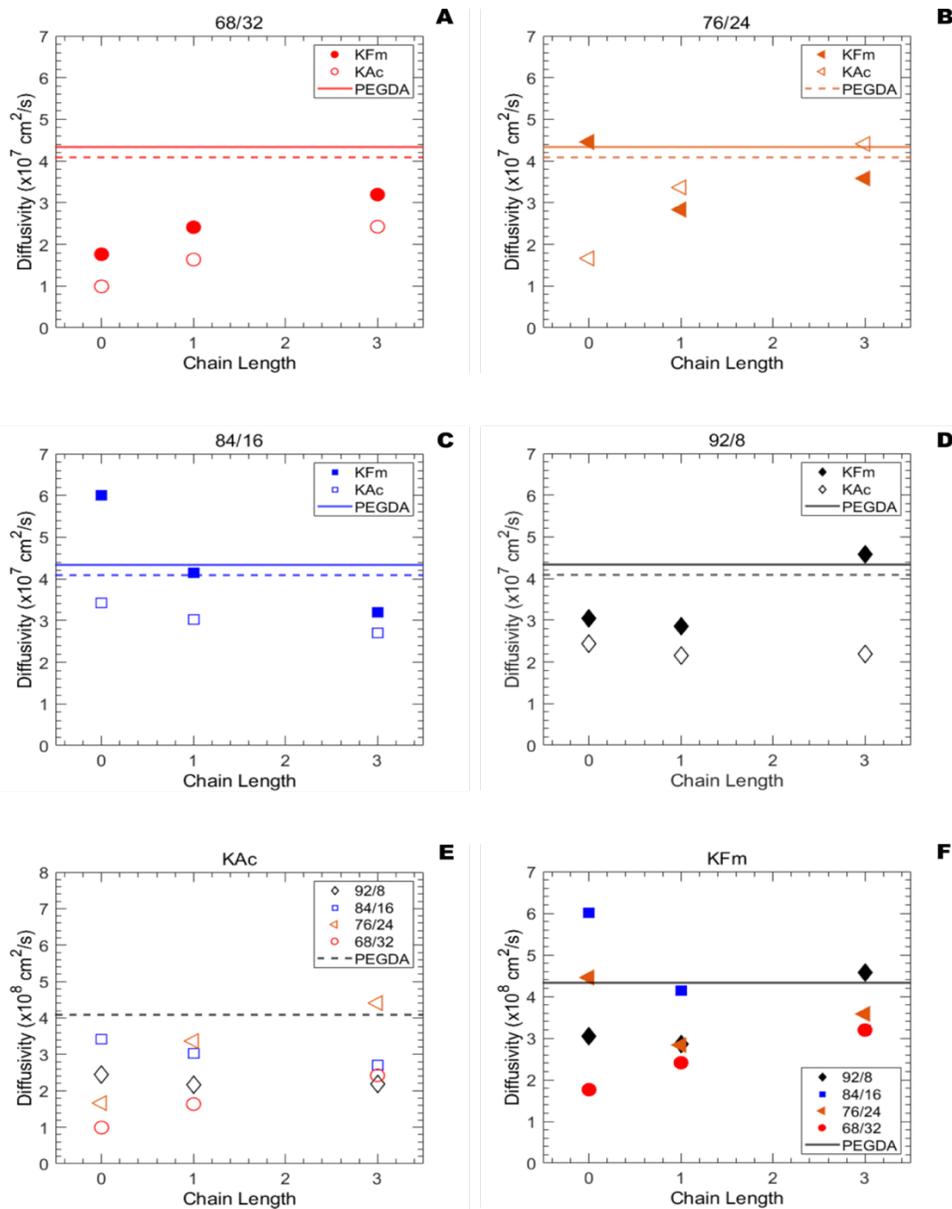


Figure 4.9 Diffusivity results graphs different PEGDA compositions comparing KAc(outline of marker) and KFm (solid marker). ((A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (○,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (◄,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (◻, blue) (D) PEGDA 92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8(◊, black)

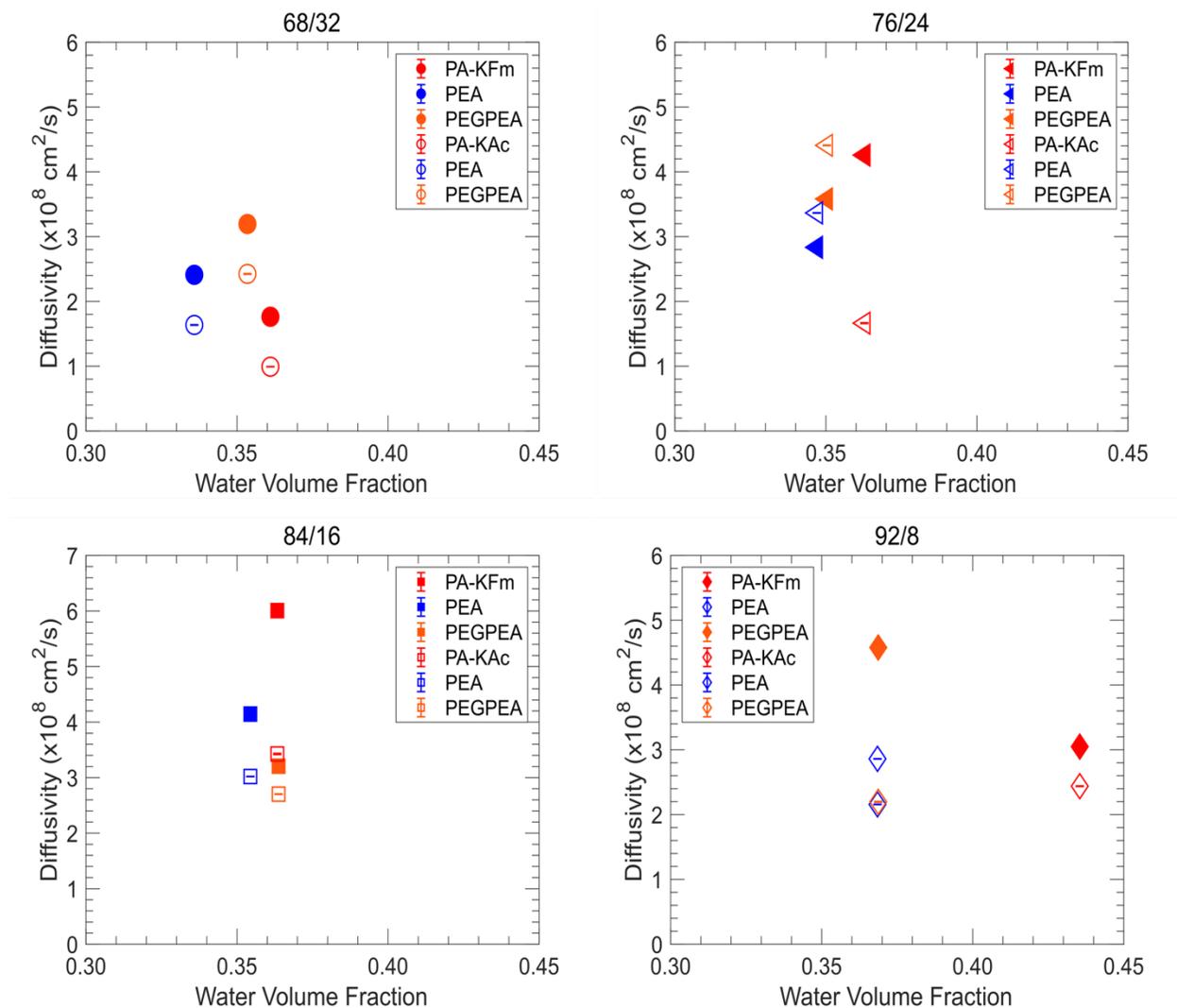


Figure 4.10 Diffusivity of water volume fraction results graphs of different PEGDA compositions comparing KAc(outline of marker) and KfM(solid marker). (A) PEGDA68-PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32 (\circ ,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (\triangle ,orange) (C) PEGDA84-PA16, PEGDA84-PEA16, PEGDA84-PEGPEA16 (\square , blue) (D) PEGDA92- PA8, PEGDA92- PEA8, PEGDA92-PEGPEA8 (\diamond , black)

4.3 Multi-component transport

Methanol is a polar solvent that can interact strongly with polar groups in the membrane, while potassium acetate is a salt that can interact with the charged groups in the membrane. The interactions between the membrane and the solvent or solution can affect the permeation of different solutes through the membrane. The multi-component permeability is also in correlation as when testing the single component permeability that the trend follows increases permeation of 68 to 92. 84/16 was not tested due to having very similar properties when looking at the single component data of permeability. With respect to PEGDA content, we can expect changes in the peak intensity or position of functional groups related to PEG or acrylate, indicating changes in the chemical composition of the membrane. For example, as the PEGDA content increases, we can expect to see an increase in the intensity of the peak corresponding to the C=O bond in the acrylate group, which can indicate an increase in crosslinking density. We may also see changes in the intensity or position of peaks corresponding to the PEG segments, which can provide information on changes in the hydrophilicity of the membrane. Similarly, changes in the comonomer chain length can affect the peak intensity or position of functional groups related to the alkyl chain, indicating changes in the hydrophobicity of the membrane. For example, as the comonomer chain length increases, we can expect to see changes in the intensity or position of peaks corresponding to CH₂ or CH₃ groups, which can indicate changes in the length or branching of the alkyl chain. In terms of solvent or solution type, we can expect to see changes in the intensity or position of functional groups related to the interaction between the membrane and the solvents or solutions. For example, in the presence of a polar solvent like methanol, we can expect to see changes in the intensity or position of peaks corresponding to polar functional groups like OH or COO⁻ groups, which can indicate changes in the interaction between the membrane and the solvent.

Chapter 4: Results and Discussion

Similarly, in the presence of a salt like potassium acetate, we can expect to see changes in the intensity or position of peaks corresponding to charged functional groups like COO⁻ or NH₃⁺ groups, which can indicate changes in the interaction between the membrane and the salt. Overall, ATR-FTIR can provide valuable information on the chemical composition of the membrane and the interactions between the membrane and different solvents or solutions, which can be useful in predicting the multi-component permeability of the membrane.

Chapter 4: Results and Discussion

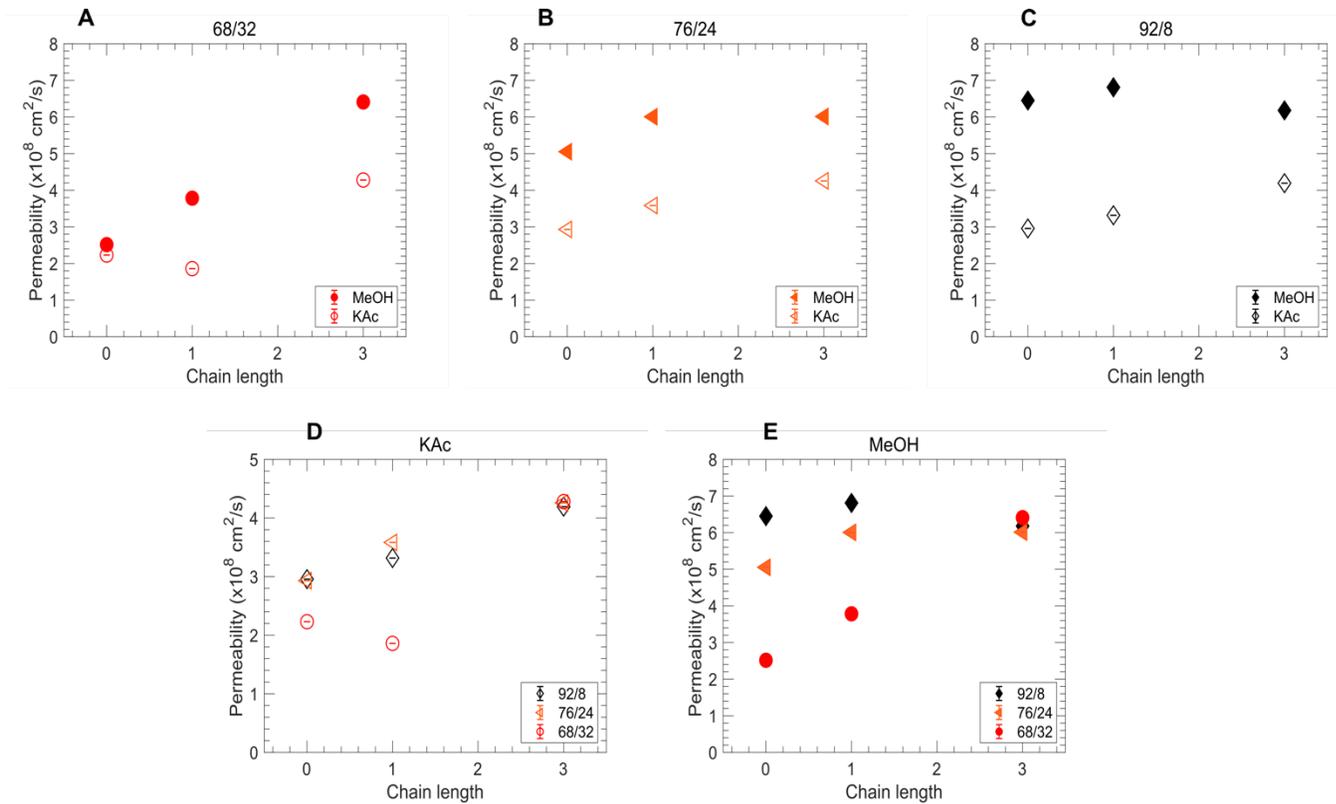


Figure 4.11 multi-component of permeability results graphs different PEGDA compositions in KAc(outline of marker) and MeOH(solid marker) of (A) PEGDA 68- PA32, PEGDA68-PEA32, PEGDA68-PEGPEA32(\circ ,red) (B) PEGDA76-PA24, PEGDA76-PEA24, PEGDA76-PEGPEA24, (\triangleleft ,orange) (C) PEGDA 92-PA8, PEGDA92-PEA8, PEGDA92-PEGPEA8(\diamond , black) (D) all PEGDA-PA,PEA,PEGPA compositions in KAc (E) all PEGDA-PA,PEA,PEGPA compositions in MeOH

4.4 References

[1] N. Yan, R. Sujanani, J. Kamcev, E.-S. Jang, K. Kobayashi, D.R. Paul, B.D. Freeman, Salt and ion transport in a series of crosslinked AMPS/PEGDA hydrogel membranes, *J Membrane Sci.* 653 (2022) 120549. <https://doi.org/10.1016/j.memsci.2022.120549>.

[2] Yasuda, H., Lamaze, C. E. & Ikenberry, L. D. Permeability of solutes through hydrated polymer membranes. Part I. Diffusion of sodium chloride. *Die Makromolekulare Chemie* 118, 19–35 (1968).

Chapter 5

Conclusions & Future Work

5.1 Conclusion

In conclusion, we found that water uptake increases with increasing PEGDA content in the membranes which we hypothesize is due to the hydrophilic nature of PEGDA and its ability to absorb water relative to the comonomers. The presence of comonomers such as phenyl acrylate (PA), PEA, and PEGPEA influence the hydrophilicity of the membranes. PA is less hydrophilic than PEGPEA but more hydrophilic than PEA, while PEGPEA is the most hydrophilic comonomer. Contact angle measurements confirm these differences in hydrophilicity, with PEGDA-PEGPEA membranes exhibiting the lowest contact angle. The mechanical properties of the membranes are expected to be affected by both the PEGDA content and the comonomer type. Increasing PEGDA content generally leads to increased elongation and decreased tensile strength and modulus. Permeability experiments were conducted to determine the membranes' permeability to potassium formate (KFm) and potassium acetate (KAc). The permeability can be influenced by the PEGDA content and the comonomer type. Higher PEGDA content generally leads to a more crosslinked and denser membrane with lower permeability. The comonomer's chain length affects the hydrophilicity and permeability of the membrane. Longer alkyl chains in the comonomer make the membrane more hydrophobic and less permeable to hydrophilic molecules. Shorter chains can increase hydrophilicity and enhance permeability. Solubility testing in KFm and KAc solutions reveals differences in solubility due to the solvents' nature and the interactions with the membrane. KFm has higher solubility in water than KAc, leading to a lower concentration of KFm inside the membrane compared to KAc. The addition of comonomers can indeed affect the solubility

Chapter 5: Conclusion & Future work

behavior of the membrane in different solvents. PEA, being more hydrophobic, is expected to increase solubility in nonpolar solvents like KFm (potassium formate) and decrease solubility in water-based solvents like KAc (potassium acetate). PEGPEA, with a longer PEG chain, can increase solubility in polar solvents like KAc but decrease solubility in nonpolar solvents like KFm. Water volume fraction affects solubility and swelling behavior. Increasing water volume fraction generally increases solute solubility in water and can affect membrane swelling. The Mw and chemical properties of the solute and the membrane also influence solubility and swelling behavior. The diffusion behavior of solutes, such as KFm and KAc, can be influenced by their mass and velocity. Larger molecules with higher Mw tend to diffuse more slowly than smaller molecules due to their larger size and greater inertia. Potassium acetate has a higher Mw and a more complex structure than potassium formate, which can impact their diffusion behavior. Overall, the characterization of PEGDA-based membranes with different comonomers provides insights into their water uptake, hydrophobicity, mechanical properties, and permeability.

5.2. Future work

5.2.1. Solubility study

In terms of future work, there are several important aspects to consider regarding the solubility, permeability, and diffusivity of methanol in single-component testing and the behavior of KAc with methanol and KFm with methanol in multicomponent testing using PEGDA membranes with different comonomers such as PA, PEA, and PEGPEA. Firstly, the solubility of methanol in the PEGDA membranes can be further explored in single-component testing. By investigating the solubility behavior, the study can gain a deeper understanding of how the membrane composition and structure influence the solute-membrane interactions and the ability of the membranes to absorb and retain methanol.

5.2.2 Permeability analysis

The permeability of methanol through the membranes can be studied in both single-component and multicomponent testing. This will provide insights into the transport behavior of methanol across the membranes and how it may be influenced by the presence of other components, such as KAc. It will help understand the selectivity of the membranes towards methanol and other solutes present in multicomponent systems for solar fuels devices.

5.2.3 Diffusivity

Thirdly, the diffusivity of methanol in the PEGDA membranes can be investigated. By measuring the diffusivity, the study can elucidate the rate at which methanol molecules move through the membrane matrix, providing insights into the transport mechanism and kinetics.

5.2.4 Effect of Comonomers

Additionally, the effects of different comonomers, such as PA, PEA, and PEGPEA, on the solubility, permeability, and diffusivity of methanol and KAc can be examined. By incorporating these comonomers into the PEGDA membranes, the study can evaluate how they alter the transport properties and performance of the membranes. This analysis will help determine the optimal composition and structure of the membranes for specific applications. Proposed future work aims to investigate the diffusivity and solubility of methanol in single-component and KAc with methanol in multicomponent testing using PEGDA membranes with a series of comonomers such as (PA, PEA, and PEGPEA). These experiments have the potential to provide valuable insights into the performance of PEGDA membranes and the effects of varying comonomers on their transport properties. The results obtained from this study could have significant implications for the design and optimization of PEGDA membranes for various applications, including separations and purification processes. Therefore, the future work has the potential to contribute significantly

Chapter 5: Conclusion & Future work

to the advancement of membrane technology and its applications in various industries. Through broader polymer membrane structure property transport and relationships.

By addressing these sub-sections, the proposed future work aims to provide valuable insights into the transport properties and performance of PEGDA membranes, considering the influence of different comonomers. This research has the potential to advance membrane technology and contribute to various industries by optimizing the design and application of PEGDA membranes in separations and purification processes