

Polymer Electrolyte Membranes for Liquid Olefin-Paraffin Separation

by

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A thesis
presented to the University of Waterloo
in fulfilment of the
thesis requirement for the degree of
Master of Applied Science
in
Chemical Engineering

Waterloo, Ontario, Canada, 2013

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Olefin/Paraffin separation, traditionally carried out by cryogenic distillation, is difficult to achieve due to the similar size and volatility of the components. Recently, many studies have explored membrane separation methods that utilize a metal ion to facilitate preferential olefin transport across the membrane. However, much of this work focuses on smaller molecules, C2-C3, which are gaseous at room temperature, while little work has been done studying separation of larger molecules, C5 and greater, which are generally liquid at room temperature. The processes developed to separate small molecules are not necessarily directly applicable to separate larger molecules.

A polymer electrolyte membrane consisting of an active layer of polyethylene oxide (PEO) and silver tetrafluoroborate (AgBF_4) has shown high selectivity for separating gaseous olefin/paraffin mixtures. The current project investigates the feasibility of applying this membrane to the separation of pentene and pentane (liquid C5 olefin and paraffin). Process variables investigated are the: pure component permeability ratio, equilibrium sorption uptakes, pure component diffusivities, and stable membrane lifetime.

Permeation tests on individual species (n-pentane and 1-pentene) were performed in two operating modes with membranes of varying silver concentrations: direct liquid contact to the membrane, and vapour contact to the membrane. The vapour contact mode showed improved membrane stability in comparison to the liquid contact mode. The olefin/paraffin permeability ratio increases with increasing silver content in the membrane, however, the membrane selectivity is much lower than that achieved with smaller olefin/paraffin pairs.

Selective chemical interactions between pentene and the membrane were observed, as the pentene sorption uptake is higher than that of pentane. In addition, a residual fraction is observed – a fraction of the pentene does not desorb from the membrane at ambient conditions – indicating a permanent or semi-permanent interaction. Desorption of pentane is determined to follow a Fickian diffusion model, while desorption of pentene appears to be governed by pseudo-second order kinetics.

Acknowledgements

Thank you to my supervisor, Professor Xianshe Feng, for his guidance, support, and patience, throughout this work.

Thank you to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Ontario Graduate Scholarship Program (OGS), and the University of Waterloo President's Graduate Scholarship (PGS) for financial support throughout this degree. Research support from NSERC and Imtex Membranes Corp. is gratefully acknowledged.

Thank you to my fellow students in the membrane research group, for their friendship as well as technical assistance, especially Gil Francisco for his valuable help in initiating and executing the permeation testing within this work.

Thank you to my friends and family, for their support during what has been a difficult and, at times, quite overwhelming process.

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List of Abbreviations

CMS = carbon molecular sieve
MMM = mixed matrix membrane
SSE = Sum of Squared Errors
ZIF-8 = Zeolitic imidazolate framework 8

Polymers

6FDA = 2,2-bis(3,4-carboxyphenyl) hexafluoropropane dianhydride
BTDA = 3,3',4,4'-benzophenonetetracarboxylic dianhydride
CA = cellulose acetate
DAM = diaminomesitylene
DAPI = 5(6)-amino-1-(4'-aminophenyl)-1,3-trimethylindane
PA12 = Polyamide 12
PDMS = Polydimethylsiloxane
PEBA = Polyether block amide
PES = Polyethersulfone
PEO = Poly(ethylene oxide)
PMMA = Poly(methyl methacrylate)
POZ = Polyoxazoline
PTMO = Polytetramethylene oxide
PVA = Polyvinyl alcohol
PVDF = Polyvinylidene difluoride
PVP = Polyvinylpyrrolidone
SPEEK = Sulfonated poly(ether ether ketone)

List of Symbols

a	= Elovich pre-exponential factor
α	= Elovich exponential constant
BP	= boiling point ($^{\circ}\text{C}$)
D	= Diffusivity (cm^2/s)
k_1	= 1 st order rate constant
k_2	= 2 nd order rate constant
l	= membrane thickness (cm)
m	= number of oxygen atoms of the polymer coordinated to each silver ion
M_0	= initial mass of membrane sample (g)
M_{eq}	= mass of membrane after equilibrium sorption (g)
M_{FP}	= mass of filter paper (g)
M_t	= mass of penetrant desorbed (g)
M_{∞}	= mass of penetrant desorbed at equilibrium, after desorption complete (g)
MW	= molecular weight (g/mol)
n	= number of olefin molecules coordinated to each silver ion
q	= mass of penetrant desorbed (g)/mass of penetrant desorbed at equilibrium (g) = M_t/M_{∞}
q_e	= q at equilibrium = 1
V_f	= free volume within a polymer matrix

1. Introduction

Olefins are extremely important chemical intermediates, produced through cracking of various hydrocarbon feeds, which are used to produce a wide range of chemical products. These include various polymers, as well as a wide range of smaller chemicals. After cracking, olefin molecules need to be separated from their corresponding paraffin molecules. Olefin/paraffin separation is one of the most difficult separations to achieve because the molecules are similar in size and volatility. Therefore, the traditionally employed method of separating these molecules by physical means (i.e., distillation) is very energy and capital intensive.

One alternative to distillation is using membranes. The simplest membranes for this process are based on size sieving, and because the molecules to be separated are so similar in size, these membranes can hardly achieve a high selectivity. Another class of membranes, known as facilitated transport membranes, utilize metal ions to complex with olefin molecules and facilitate their transfer across the membrane. The most common metal ions used as carriers in facilitated transport membranes are Ag^+ and Cu^+ , due to the reversibility of the complexes formed with olefin molecules. Salts containing silver (I) are generally preferred over copper (I) salts due to their better performance for olefin/paraffin separation.

A wide variety of facilitated transport membrane materials and configurations have been studied for separation of ethylene/ethane and propylene/propane mixtures. Some of these systems, such as immobilized liquid membranes and polymer electrolyte membranes are becoming well

characterized. Silver nitrate (AgNO_3) is commonly used in immobilized liquid membranes because it displays high olefin binding capacity in aqueous environments, whereas silver tetrafluoroborate (AgBF_4) is shown to be very effective in polymer electrolyte membranes due to its high olefin sorption capacity in that environment.

A polymer electrolyte membrane consisting of silver tetrafluoroborate (AgBF_4) dissolved in poly(ethylene oxide) (PEO) has been studied for ethylene/ethane and propylene/propane systems and is shown to result in high olefin fluxes as well as high olefin/paraffin permeability ratios. However, the membrane experiences a permanent decrease in performance after being exposed to the olefin molecules. Also, this membrane system has not been studied using larger olefin/paraffin systems, which are liquid at room temperature.

The objective of this study is to explore the behaviour of a PEO/ AgBF_4 polymer electrolyte membrane in regards to the separation performance of liquid olefin/paraffin systems, specifically n-pentane and 1-pentene. Membranes with different silver contents are tested for pentene and pentane solubility, permeability and diffusivity. The results can then be compared to each other (i.e., solubility ratio, permeability ratio, diffusivity ratio) and to similar results for ethylene/ethane and propylene/propane systems reported in the literature.

Chapter 2 of the thesis is literature review which begins with a discussion of general background information on olefin significance and production. This is followed by an overview of the both the physical approaches to olefin/paraffin separation (i.e., distillation and size sieving) and the chemical methods for olefin/paraffin separation (i.e., utilizing the interaction between olefins and

metal ions). The next section discusses facilitated transport mechanisms in more detail, introducing various membrane formulations and configurations. Section 2.5. elaborates on solid polymer electrolyte membranes, explains what makes an effective polymer matrix and an effective carrier salt, and discusses separation performance with ethylene/ethane and propylene/propane systems. The final section of the literature review discusses studies that specifically target liquid olefin/paraffin separation systems.

Chapter 3 outlines the experimental methods used to prepare the membranes, as well as to determine the permeability, solubility, and diffusivity values.

Chapter 4 presents and discusses the results from each section of the study. The pentene/pentane permeability ratio is determined from the vapour contact pure component permeation testing. This series of experiments also presents a relationship between the silver content of the membrane and the membrane stability. The equilibrium sorption uptakes of pentene and pentane are then determined and compared. This is followed by a discussion of the desorption kinetic data, including the residual fraction, model fitting, and the calculated diffusivities.

Finally, Chapters 5 and 6 present the conclusions and recommendations of the study, respectively.

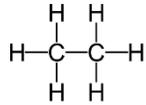
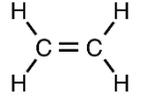
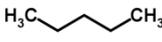
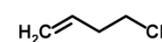
2. Literature Review

2.1. Olefins

Olefins are hydrocarbon compounds with the general chemical formula C_nH_{2n} . They consist of carbon atoms joined together, where at least one pair of carbon atoms shares a double bond. All of the other available bonding sites are filled with hydrogen atoms. Olefins are formed during the processing of oil products (Gray and Handwerk, 2001). Within the overall petrochemical refining process, there are numerous possible processes where olefins are produced (Gray and Handwerk, 2001). Olefins are desirable chemical intermediates. They can be used to make polymers, including plastics and rubbers, as well as a wide range of smaller chemicals, including alcohols, epoxides, amines, and halides (Speight, 1991).

Olefins have different properties and uses depending on their chain length and configuration. Table 1 shows the structures and properties of the straight chain C2 and C5 olefins and paraffins. The only structural difference between each corresponding pair is the presence or absence of the double bond. Olefins can be used to make a wide variety of polymers and chemicals in part due to the varying structures and properties of different sized olefins and their isomers.

Table 1: Structure and Properties of C2 and C5 olefins and paraffins.

	Ethane	Ethylene	n-Pentane	1-Pentene
Structure				
Formula	C ₂ H ₆	C ₂ H ₄	C ₅ H ₁₂	C ₅ H ₁₀
Molecular Weight (g/mol)	30.07	28.05	72.15	70.13
Boiling Point (°C)	-88.6	-103.8	36.06	30.0
Data from: CRC Handbook of Chemistry and Physics (93 rd Ed.)				

2.1.1. Importance/Uses

Beginning in the 1920s, alcohols were produced from ethylene and propylene, which were formed during the cracking of petroleum. With the development of new processes and applications, the utility of olefins expanded, and demand for them increased; so cracking of paraffins and heavy oils began for the specific purpose of olefin production (Speight, 1991). Olefins are now produced in large quantities. For example, global ethylene production was 126.7 million tonnes per year at the start of 2009, and is rapidly expanding (Nakamura, 2009). Five of the ten largest ethylene plants are located in the United States; however most of the growth in olefin production is occurring in the Middle East (mainly Iran and Saudi Arabia) (Nakamura, 2009).

Olefins are the building blocks for a wide range of chemical products and polymers. Alcohols can be produced from olefins and can, in turn, be converted to ketones through catalytic oxidation or dehydrogenation (Speight, 1991). Ethylene glycol, propylene glycol, and glycerin can all be derived from ethylene and propylene feeds. Ethylene glycol is widely used in antifreeze and related applications, while glycerin has many applications including use as a solvent, use in cosmetics, and explosive production (Speight, 1991). Olefins can also be halogenated, and halogenated alkenes can be converted to allyl alcohols, which lead to products such as glycerol (Speight, 1991). Oxidation of ethylene produces ethylene oxide, and analogous products can be made using larger olefins. Esters, mercaptans, sulfides, and amines can all be produced from olefins using one-step reaction pathways (Speight, 1991).

Olefins are used to produce many types and sizes of polymers. Ethylene, propylene, butene, and their mixtures can be polymerized into homopolymers or copolymers with a wide range of properties. Smaller chains, such as dimers, trimers, and tetramers have their own uses, including use in gasolines (Speight, 1991). Generally, for use in these specific reaction and applications, the purity of olefins needs to be very high (<99.9%) (Faiz and Li, 2012a).

2.1.2. Production

Olefins are generally produced by cracking of other hydrocarbons. There are many different types of cracking processes that can be used depending on the feed mixture available and the desired products.

Thermal cracking originated as a process to increase the yield of gasoline from petroleum stocks. Subjecting petroleum hydrocarbons to very high temperatures causes them to thermally decompose into smaller hydrocarbons and produces olefin molecules (Speight, 1991). Various manipulations or changes to the thermal cracking process are used to achieve specific process goals, one of which can be a higher yield of olefin molecules (Speight, 1991). Catalytic cracking, which is similar to thermal cracking, but utilizes a catalyst to facilitate the reaction, has almost fully replaced thermal cracking for gasoline production, as it produces higher quality gasoline as well as a higher fraction of olefins (Gary and Handwerk, 2001).

Steam cracking is a process more specifically geared to producing olefins (as opposed to gasoline). Feedstocks of steam cracking processes for olefin production can be divided into two general categories: those derived from natural gas (e.g., ethane and propane) and those derived from crude oil/petroleum (e.g., naphtha and gas oil) (Ren et al., 2006). Ethane and propane feeds will produce mainly ethylene and propylene, while naphtha and gas oil feeds can produce a wider range of olefins. The steam cracking operation is followed by a series of separation and purification steps in order to collect the olefin products. The first of these is a primary fractionation step to remove all the remaining large hydrocarbon fractions, which can be recycled (Ren et al., 2006).

The final steps in olefin production are product recovery steps. Separation of the products involves distillation, refrigeration, and extraction, and is achieved using chilling trains and fractionation towers. Very low temperatures are normally required (Ren et al., 2006). Low temperature distillation is carried out in large fractionator columns with multiple trays (Eldridge,

1993). The capital and operating costs involved in building and operating these types of columns mean these columns are only economically feasible for separating streams that have a high olefin content (e.g., streams from high capacity ethylene crackers or refinery steam crackers) (Eldridge, 1993). These separation steps will be discussed in more detail later.

More recently, researchers have been investigating methods to increase the yield of olefins produced from cracking units. This work includes modelling steam cracking processes in order to optimize yields (Sadrameli and Green, 2005) and exploring catalysts that will result in higher olefin content in the product streams (Meng et al., 2006; Li et al., 2005). Other research investigates possible less energy-intensive alternatives to steam cracking (Ren et al., 2006).

2.2. Physical Methods for Olefin/Paraffin Separation

Physical separation methods refer to any means of olefin/paraffin separation that employ the physical differences between the species in order to achieve separation. These properties could include size, shape, boiling point, vapour pressure, volatility, etc. The major separation methods utilize either size and shape (size sieving methods) or vapour pressure differences (distillation). Each of these will be discussed in this section.

2.2.1. Distillation

Distillation is used to separate components in a liquid mixture based on the relative volatilities of the components to be separated. When a mixture is heated the more volatile component, or the

component with the lowest boiling point, will preferentially vaporize until an equilibrium state is reached. If the vapour product is then condensed, the resulting liquid will have a higher fraction of the more volatile component than the original mixture. Conversely, the remaining liquid phase will have a lower concentration of the more volatile component than the original blend (Stichlmair and Fair, 1998). This process can be used to separate a wide variety of liquid mixtures.

The power of distillation is amplified by using a distillation column. A distillation column is a staged process and separation, as described above, is achieved at each stage. In a distillation column with trays, the vapour from one tray enters the tray above, while the liquid falls to the tray below. In this fashion, the separation takes place on a continuous basis. Each stage will operate at a slightly different temperature (getting cooler from bottom to top) and will result in different equilibrium compositions in each phase (vapour and liquid). As a result, the fraction of the more volatile species will continue to increase over each stage (Stichlmair and Fair, 1998). The more trays there are in a distillation column, the better the separation of the original feed mixture will be (Speight, 1991).

Distillation columns can be designed to achieve the desired separation performance by manipulating a number of factors. These can include the size of the column, the number of trays/stages, the operating temperature, the feed rate and/or reflux rates, and the design of the trays. Generally, as the desired purity of the final product increases, the number of stages required increases. Therefore the size of the column required will increase. Larger columns are

also required for more difficult separations, such as separating components with very similar volatilities, because a less significant fractionation will be achieved at each stage.

Low Temperature Distillation

Separating olefin-paraffin mixtures resulting from cracking is often done in a series of distillation columns designed for this purpose. A common process scheme is displayed in Figure 2-1. For each olefin-paraffin pair, two columns may be required. The first separates that size of molecule from the rest of the mixture (e.g., separation of ethylene and ethane from the remaining feed) while the second separates the olefin-paraffin pair from each other (e.g., separation of ethylene from ethane). This continues with the larger pairs in order of molecular size (Eldridge, 1993).

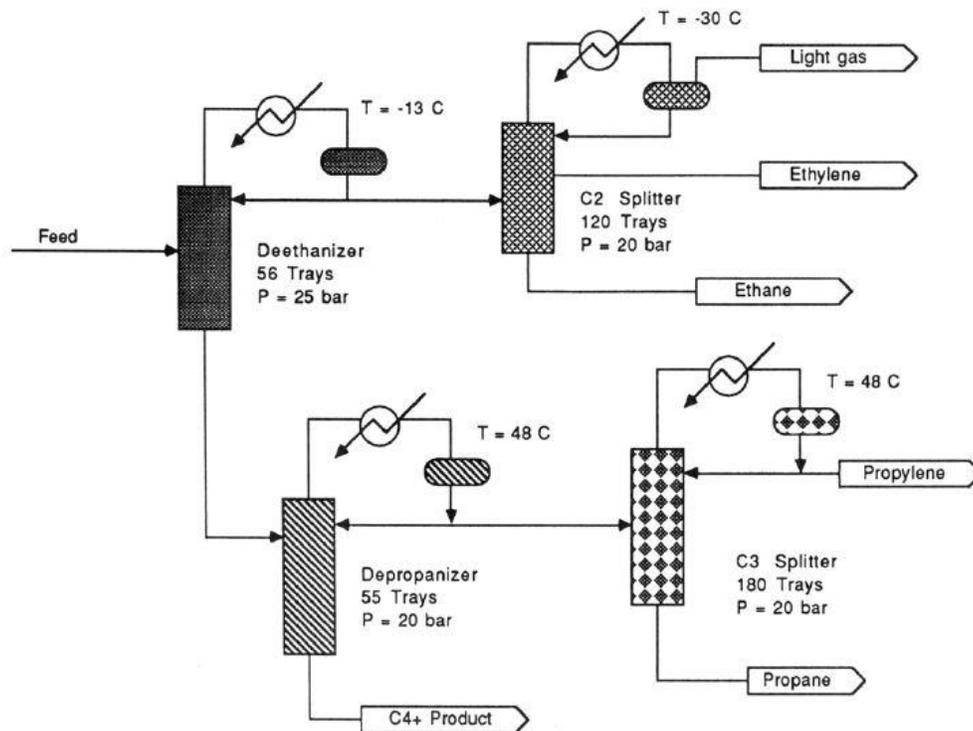


Figure 2-1: Conventional low temperature distillation process for Olefin-Paraffin Separation (Eldridge, 1993).

Distillation columns used for separating small molecules, such as small olefin paraffin mixtures, are generally only a few feet in diameter, but can be up to 200 feet high (Speight, 1991). Another source summarizes that ethylene and propylene recovery columns contain 150-200 trays and operate at a temperature of 183 to 233 K and 16 to 20 bar of pressure (Faiz and Li, 2012a) because of the very similar volatilities of the corresponding olefin-paraffin pairs. Due to the large column size required, the capital costs for building these types of separation trains are very high. In addition, the low temperature requirement resulting from the low boiling points of these molecules places huge energy demands on the process. Cooling very large towers to very low temperatures requires huge amounts of energy.

The results of a case study may be used to give a more specific idea of the temperatures and energy input required for ethylene-ethane and propylene-propane separation. At a feed flow rate to the overall olefin production process of over 2,500 kmol/hr, the temperatures required for each species were: -101 to -30°C for the C2 train, and -30 to 12 °C for the C3 train, and the energy cost of the separation process was determined to be \$17 Million/Year based on optimized operating conditions (Tahouni et al., 2011).

Extractive Distillation

Extractive distillation involves using an additive/solvent to enhance the separation. It is often utilized in distillation where the components to be separated have very similar boiling points and therefore a low relative volatility. The addition of a third component, which may form an azeotropic mixture with one of the initial components, increases the relative volatility of the

mixture and allows for easier distillation (Speight, 1991). It is very important that the additive used in extractive distillation, also known as the entrainer, should be easily separated from each of the products streams so that it can be reused in the process (Stichlmair and Fair, 1998).

Extractive distillation has been studied for use in olefin-paraffin separations. Systems of butane/butene/butadiene can use entrainers of furfural, acetonitrile, dimethylacetamid, n-methylpyrrolidon, or dimethylformamid. Propylene/propane distillation can be aided by the addition of acrylonitrile (Stichlmair and Fair, 1998). Although this technique is promising, the commercial viability of extractive distillation is limited by suitable solvents. It was suggested that extractive distillation offers no economic advantage over regular distillation for olefin/paraffin separations (Eldridge, 1993).

However, more recently, a study investigating the separation of a cyclohexane/cyclohexene system using extractive distillation, showed that certain solvents can be used to increase the relative volatility of the system to the point where extractive distillation may become economically desirable. Diethyl carbonate is identified as the most suitable entrainer for this system (Marrufo et al., 2011).

2.2.2. Membrane Separations

Olefin and paraffin molecules can be separated based on their relative size. Due to the strength of the double bond drawing neighbouring carbon atoms in an olefin molecule closer together,

olefin molecules are generally slightly smaller than their corresponding paraffin molecules. This may be manipulated to separate olefins from paraffins.

The solution-diffusion model of membrane transport discusses diffusion of molecules across a dense membrane (Baker, 2004). In this model, permeants first dissolve in the dense membrane material, and then diffuse across the membrane in the direction of a concentration gradient. A dense membrane indicates that there are no large pores present for fluid to freely flow through. Instead, the free volume within the membrane consists of small gaps between polymer chains that are constantly changing due to the thermal motion of the polymer. The molecules dissolved in the membrane diffuse through these small and dynamic spaces, and as a result will move in the direction of the applicable gradient (usually concentration or pressure).

One of the main assumptions of the solution-diffusion model is that the rates of sorption and desorption of the permeant species into and out of the membrane are significantly faster than the rate of diffusion through the membrane. This is generally satisfied for solution-diffusion membranes that do not involve any chemical interactions between the permeant and the membrane, but may not be satisfied when a chemical reaction or interaction is involved, which is the case for some facilitated transport membranes.

Conventional Polymeric Membranes

The effectiveness of separating olefins and paraffins using conventional (additive-free) polymer membranes is mainly dependant on the properties of the polymer selected, specifically the free

volume available within the polymer matrix. In a review article on this topic, Faiz and Li (2012a) showed that olefin/paraffin pairs generally exhibited the same solubility, and that olefins were slightly more permeable through these types of membranes because of a higher diffusion rate due to their smaller molecular sizes. For a viable separation process, it appears that a moderate V_f (free volume) for the polymeric membrane is required. If the V_f is too small, the permeation rate will be extremely low. As V_f increases, the permeation rates increase. As the V_f increases further all species diffuse across the membrane very quickly, leading to a decrease in the selectivity. The reported olefin/paraffin separation factors for C2 and C3 gaseous systems are generally in the range of 0.9 to 7 (Faiz and Li, 2012a).

Advanced Polymeric Membranes

Faiz and Li (2012a) also discussed advanced polymer membranes that contain additive groups to enhance the separation performance. Adding functional groups or side chains of a specific size can be used to manipulate the V_f of the membrane and therefore its separation properties. Polyimide and co-polyimide membranes follow this approach, and incorporating such additive groups as acid anhydrides and diamines generally results in better olefin/paraffin separation (Faiz and Li, 2012a). For example, using 4,40-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), the ideal selectivity based on pure gas permeation rates is 3-4 for ethylene/ethane and 10-16 for propylene/propane separation (Staudt-Bickel and Koros, 2000). In a patent disclosure, polyimide membranes were claimed to have separation factors in the 10s for 1-butene/n-butane separation, and in the tens of thousands for 1,3-butadiene/n-butane separation (Shimazu et al.

1998). These separation factors display an improvement over the conventional polymers discussed previously.

Carbon Molecular Sieve Membranes

Carbon molecular sieve (CMS) membranes are microporous carbon membranes prepared by pyrolysis of polymers or polymer precursors (Faiz and Li, 2012a). Pyrolysis is carried out in an inert environment at elevated temperatures (usually 500 to 800 °C) and converts organic material to carbon (Baker, 2004). CMS membranes are generally brittle (Baker, 2004) and have poor mechanical strength when used alone (Faiz and Li, 2012a). However, they show promising olefin/paraffin selectivities.

A variety of factors come into play when discussing separation by microporous membranes. Size sieving is the simplest mechanism; smaller molecules will pass through pores more easily than larger molecules. However, there are other dynamics at play as well. When the membrane pores are small enough, molecules will collide with the pore walls more often than with other molecules. This results in a phenomenon known as Knudsen diffusion, in which separation can be achieved between species that move at different average velocities (Baker, 2004). In addition, adsorption occurs on the surface of the membrane and on the pore walls. The components can then diffuse along the pore wall under a concentration gradient according to Fick's law. Therefore, species that more strongly adsorb to the carbon membrane will preferentially pass through the membrane. Through a combination of these factors, some microporous membranes are able to separate pairs of molecules of different sizes (Baker, 2004).

For example, both flat sheet and hollow fibre CMS membranes were prepared using the polymer Matrimid® 5218 (BTDA-DAPI), and an optimum ethylene/ethane selectivity of ~12 was achieved (Xu et al., 2011). CMS membranes were also prepared by pyrolysis of a thin film of phenolic resin coated on the inside of a tube of alumina, and the separation performance was tested using ethane/ethylene and propane/propylene gas mixtures. The resulting ethylene/ethane selectivity ranged from 2 to 11, while the propylene/propane selectivity was in the range of 10-50 over the operating conditions of the study. The membrane performance was found to be stable for at least 220 days (Fuertes and Menendez, 2002).

Mixed Matrix Membranes

Mixed matrix membranes (MMMs) are another type of unconventional membrane. Mixed matrix membranes combine different types of materials in order to take advantage of the desirable properties of each individual material. Mixed matrix membranes are made up of a bulk phase and a dispersed phase. Generally, the dispersed phase is an inorganic solid material that has a very high selectivity towards the desired component. This inorganic material may be, for example, a zeolite, a carbon molecular sieve, or nano-particles, among others. These materials would not make viable membranes on their own due to their brittleness; they are too fragile to be used alone in a membrane process. The bulk phase is generally a polymer, chosen because it is somewhat selective to the desired separation and also inherently flexible. The bulk of the membrane being made of this flexible material is highly beneficial because the membrane will be stronger and more durable (Chung et al., 2007). The resulting MMM has a higher selectivity

than the polymer component would have alone and is more flexible and therefore more viable than the inorganic material alone.

For example, a MMM consisting of a polymer and a zeolite material is shown to have a higher olefin/paraffin selectivity than the polymer alone. Specifically, when combined in a mixed matrix membrane, 6FDA-DAM polyimide and a zeolitic imidazolate framework (ZIF-8) showed increases in propylene permeability and propylene/propane ideal selectivity of 258% and 150%, respectively (Zhang et al., 2012).

2.2.3. Limitations of Physical Separation Methods

Since distillation is based on the relative volatility of the components to be separated, olefin/paraffin separation by distillation is also difficult due to their similar volatilities. As a result, the distillation columns required to separate olefins from their corresponding paraffins need to be extremely large. In addition, smaller olefins and paraffins have very low boiling points. This means that the distillation columns must be operated at very cold temperatures (i.e., cryogenic distillation). Building these large columns is very capital intensive, and operating these large and very cold columns requires large amounts of energy.

The performance of size sieving membranes for olefin/paraffin separation is also limited. In general, a high permeability and selectivity cannot be reached within the same system (Faiz and Li, 2012a). Various innovative membrane variants have been studied in order to improve the overall performance, with varying degrees of success, but the trade-off relationship between

membrane permeance and selectivity still exists. Also, the inclusion of other, more complicated membrane components can lead to further complications such as decreased performance over time. For example, prolonged use of the membrane may lead to plasticization of the membrane and significantly decreased performance (Faiz and Li, 2012a).

Since corresponding olefin/paraffin pairs are so similar in size and shape, they are difficult to separate using physical means. As an alternative, many researchers are investigating separation methods that utilize the chemical difference between the two types of molecules (i.e. the presence or absence of a double bond between carbon atoms) to separate them.

2.3. Chemical Methods for Olefin/Paraffin Separation

In order to utilize the difference in chemical functionality between olefins and paraffins, the chemical method for olefin/paraffin separation must be based upon the double bond. This can be achieved by using a material that will selectively form a specific complex with the double bond in the olefin molecule. Some metal ions are capable of forming this type of complex, and can be applied in different ways to achieve the separation. Specifically, copper (I) and silver (I) ions have been studied and shown to form a reversible complex with olefin molecules. Silver and copper are preferable over other transition metals mainly because of the reversibility of the complexes, their safety and low cost (Azhin et al., 2008). The interaction between the metal ions and the olefin molecules is stronger than simple Van der Waals forces, and specific to the olefin molecules. This allows for a high selectivity and high capacity of olefin sorption and transport (Faiz and Li, 2012a).

There are a variety of methods being investigated to take advantage of these specific complexes. Two categories that have been heavily explored are absorption processes and facilitated transport membranes. Absorption processes involve the transfer of olefin molecules from one phase to another through coordination with the metal ion. Facilitated transport membranes incorporate the metal ion into membranes where the ions act as a carrier or pathway for the olefin molecules across the membrane. These processes can be used alone or in conjunction with other separation technology. For example, a membrane process may be used to reduce the load on a distillation column by feeding the olefin product from the column to a membrane module for further purification. This approach would reduce the required purity of the distillation product, making the overall separation easier and reducing overall energy requirements.

2.3.1. Metal Olefin Complex

Particular transition metals can form a selective complex with olefin molecules. These metals include copper (I), silver (I), palladium (II), mercury (II) and platinum (II). Copper (I) and silver (I) are the most viable for use in olefin separation because the complexes formed are reversible. Conversely, palladium (II), platinum (II) and mercury (II) form relatively stable complexes (Safarik and Eldridge, 1998), which are less promising for use in olefin separation because the complexes are difficult to reverse, which would make the overall separation process more difficult.

The complexes formed between these metals and olefin molecules were first satisfactorily described using the Dewar-Chatt model, and the interaction is termed π -bond complexation (Safarik and Eldridge, 1998). Ionic silver and copper will be discussed further later due to their applicability to olefin separation.

Silver (I) and copper (I) cations each have empty outermost s orbitals due to the electron lost during their oxidation from atom to ion. This empty s orbital acts as an electron acceptor, and interacts with the (full) π bonding orbital of the olefin molecule to form a new orbital sharing the electrons of the olefin π bond. The π^* (antibonding) orbitals of the olefin molecule then accept electrons from the (full) outermost d orbitals of the metal, forming another bond (Eldridge, 1993; Safarik and Eldridge, 1998). These interactions are illustrated in Figure 2-2. Note that the orbital labels indicated represent an Ag^+ ion, however the coordination is the same for a Cu^+ ion.

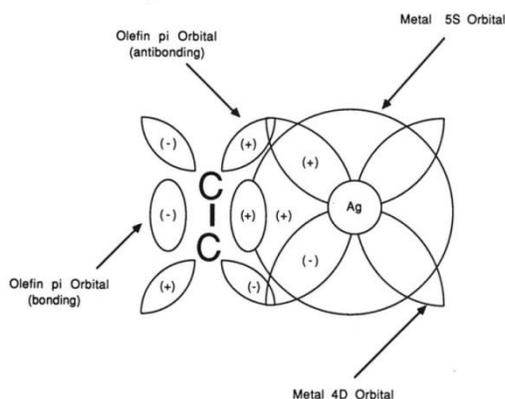


Figure 2-2: Silver-Olefin Complex (Eldridge, 1993).

From an alternate perspective, the olefin-metal complex may be described using resonance structures (Burgess and Steel, 2011). The metal ion can be in one of two states: interacting with

the π bond of the olefin molecule, or ‘breaking’ that bond and interacting with each carbon atom separately. Figure 2-3 shows the general metal-olefin complex with resonance.

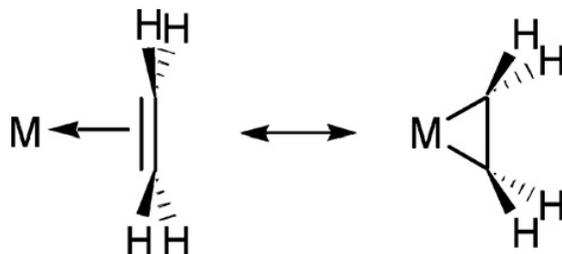


Figure 2-3: Resonance present in the metal-olefin complex (Burgess and Steel, 2011).

To be used in absorption processes or facilitated transport membranes for olefin separation, the metal ion in the system must be available to interact with the olefin. Therefore, the interaction between the metal ion and the other components of the system should be minimized. Accordingly, the metal cation must dissociate from its negative counterion. For this to be thermodynamically favourable, the lattice energy of the salt should be as small as possible. The lattice energy of silver is less than that of copper, and it is thus a better material to use in this type of process (J. H. Kim et al., 2004).

In addition to a weak interaction with the counterion, the metal ion should have relatively weak interaction with the olefin molecule itself. This is because the reversibility of the complex is very important. When the complexes are used for olefin-paraffin separation, it is crucial that the metal ion releases the olefin after interacting with it. Systems involving silver ions are being studied more extensively than others for this reason (Faiz and Li, 2012b).

Silver ions can complex with more than one olefin molecule at a time, and this results in many possible structures for the overall complex. These structures can be extremely large and incorporate a large degree of complexity (Burgess and Steel, 2011). For example, a silver ion can form a larger complex with multiple ethylene molecules at any given time. Measurements of gas phase association energetics between silver ions and ethylene molecules show that it is energetically favourable for a single silver ion to form complexes with up to three ethylene molecules. The first two molecules are shown to complex quite strongly to the Ag^+ ion, while the strength of interaction with the third is smaller but still significant (Jiang and Dai, 2008). More ethylene molecules can interact with the silver ion (up to 6), but beyond the third ethylene molecule, the bond energies become too small to exhibit any stability (Burgess and Steel, 2011).

2.3.2. Reactive Absorption

Reactive absorption, which is based on reversible chemical complexation, utilizes a mass separating agent to separate a desired component from a mixture. The feed mixture is contacted with the mass separating agent that specifically interacts with the target compound. After the system is allowed to reach equilibrium, the phases can be separated using physical means. The phase containing the target compound can then be treated in such a way as to reverse the complex, releasing the target compound and recovering the separating agent. This process can be enhanced by a pressure or temperature change, or the addition of another species (Safarik and Eldridge, 1998).

Absorption processes utilizing copper (I) or silver (I) have potential for use in olefin recovery (Eldridge, 1993). As discussed above, silver salts are generally more favourable. In olefin-paraffin separation processes, the target compound is the olefin molecule and the mass separating agent is the silver ion. The silver ion can be incorporated into a solution as a silver salt, and an olefin-paraffin mixture can be separated through contact with the silver salt solution. The olefin will complex with the silver ion and be transferred into a separate phase, away from the paraffin.

As an alternative to direct contact between the feed stream and the solution containing the mass separating agent, the two phases can be separated by a membrane. This eliminates a step in the overall process, that is, the separation of the two phases after contact is no longer needed. The performance of this type of system will increase further if the membrane used is also selective towards olefins. For example, a SPEEK/polypropylene composite membrane is used to contact an ethylene/ethane feed stream with an aqueous silver nitrate solution, resulting in ethylene/ethane selectivities as high as 2700 (Nymeijer et al., 2004). Modelling of a similar process, utilizing AgBF_4 in place of AgNO_3 , and applied to the separation of propylene/propane mixtures, concluded that the process was physically feasible, and that its economic viability will depend on feed cost (Chilukuri et al., 2007).

2.4. Facilitated Transport Membranes

Incorporating silver ions into membranes in order to achieve selective olefin transport has become a widely researched topic. These membranes come in many forms, but are based on the same basic principle: the silver ion forms a reversible complex with the olefin molecules, and

provides them with a path to move across the membrane. This allows the olefin molecules to cross the membrane in the direction of a pressure or concentration gradient at a drastically faster rate than the corresponding paraffin. The chemistry and coordination theory of the silver-olefin complex is briefly discussed in section 2.3.1.

Facilitated transport membranes for olefin-paraffin separation can be prepared in a variety of ways. They can be homogeneous membranes, composite membranes consisting of more than one layer, or multiphase membranes where one phase is dispersed in the other. Some facilitated transport membranes operate in a hydrated state, some operate dry. Most have a flexible organic polymer as their base component. The silver salt can be included as an aqueous solution, dissolved into the polymer matrix itself, or even as an ionic liquid. These membranes can also be configured in different ways: flat sheets, spiral wound, or hollow fibre membranes. Each variation has advantages and disadvantages, but overall, facilitated transport membranes show better separation performance than size-sieving membranes.

2.4.1. Supported Liquid Membranes

Immobilized liquid membranes for facilitated transport consist of a carrier solution suspended in the pores of a polymer matrix (Faiz and Li, 2012b). For olefin-paraffin separation, the solution contains silver ions that will facilitate preferential olefin transport across the membrane. The carrier solution is held in place by capillary forces within the pores of the membrane (Ravanchi et al., 2010). In this type of membrane, the porous polymer membrane is only a supporting layer

for the liquid containing the active olefin carrier (Azhin et al., 2008). Silver nitrate is a highly studied carrier for use in these types of membranes

Another type of membrane is described in US Patent # 7,361,800 (Herrera et al., 2008). A polysaccharide membrane, specifically chitosan, is chelated with silver (I) or copper (I) and used to separate mixtures of olefins and paraffins. AgNO_3 was used as an appropriate olefin carrier, and the concentration of the solution used ranges from 3-12 M. The membrane operates with water present in the membrane, and in fact requires water to operate effectively. The required pre-treatment steps as specified by the patent are: humidification, demisting, and treatment to remove sulphur compounds (Herrera et al., 2008). The membrane as described shows excellent performance for propane-propylene separation. For example, with an AgNO_3 concentration of 5M, the flux of propylene through the membrane was $16.3 \text{ L}/(\text{m}^2 \cdot \text{hr})$ while the flux of propane was $<0.003 \text{ L}/(\text{m}^2 \cdot \text{hr})$ at room temperature and an operating pressure of ~ 100 psig (Herrera et al., 2008). This type of membrane does not involve free flowing liquid, but the membrane is in a highly hydrated state.

Another example, also using AgNO_3 to separate propane from propylene, employed polyvinylidene difluoride (PVDF) as the polymer support (Ravanchi et al., 2010). These membranes achieved separation factors up to ~ 250 using 50:50 propylene:propane feeds. The concentration of propylene in the permeate stream reached as high as 99.63% (Ravanchi et al., 2010). Based on these two examples, it is evident that supported liquid membranes using silver nitrate as a carrier have potential for use in olefin-paraffin separation applications.

Supported liquid membranes for olefin/paraffin separation often use aqueous solutions of silver. Therefore, they need to operate in a humidified environment to avoid membrane dryout (Azhin et al., 2008). Humidification of the process streams will result in additional operating cost incurred through the humidification and subsequent water removal from the gas streams. In addition, even with humidification of all process streams, the membranes can still experience solvent loss (Faiz and Li, 2012b). Drying of the membrane results in a drastic increase in permeation of both olefin and paraffin, causing a drop in selectivity (Ravanchi et al., 2010). As water leaves the membrane, the silver salts lose their solvent, and the silver ions will no longer be available to facilitate olefin transport. The loss of water also decreases the mobility of the polymer chains, causing the membrane to become rigid, contributing to membrane resistance. Therefore, even with humidification, the system still needs to be periodically shut down and re-hydrated to restore the membrane performance. This is not desirable in an industrial setting.

Another major issue with these types of facilitated transport membranes is the reactivity of the silver ion with various system components or possible contaminants, resulting in inactive carrier or even dangerous by-products. Silver ions can be reduced to silver nanoparticles, which destroys their function as olefin carriers. Silver ions can also react with possible system contaminants such as sulphur compounds. Worst of all is acetylene, which can react with silver ions to form silver acetylide, an explosive compound (Pinnau and Toy, 2001). This imposes a significant safety concern. In order to operate these systems in their current states, all of these harmful contaminants need to be removed.

2.4.2. Flowing Liquid Membranes

An alternative to the supported liquid membranes discussed above is a flowing liquid membrane, in which the carrier solution is flowing in a layer between two hydrophobic microporous membrane sheets (Faiz and Li, 2012b). The membranes are hydrophobic in order to ease hydrocarbon diffusion through the membrane into the carrier solution, which will preferentially transport the olefin molecules. These membranes were also prepared and tested with AgNO_3 as the carrier. The resulting permeability and selectivity were higher than corresponding immobilized liquid membranes (Teramoto et al., 1989). Increasing the silver nitrate concentration in the flowing liquid phase acted to increase the permeation of ethylene through the facilitated transport effect, while simultaneously decreasing the permeation of ethane, through an increase in the solution viscosity and the salting out effect (Teramoto et al., 1989).

Stability of the barrier membranes is a significant issue, as the membrane can be damaged by solvent loss or by impurities in the feed and then needs to be replaced frequently. In particular, silver and silver oxide particles can build up on the membranes, decreasing the permeation rate of olefin through the membrane due to clogging of the membrane and losses of the carrier ions available (Faiz and Li, 2012b).

2.4.3. Ionic Liquid Membranes

In ionic liquid membranes, liquid salts are used between two barrier membranes for olefin transport instead of salt solutions. Ionic liquids have lower vapour pressures than aqueous

solutions, so evaporative loss of liquid is less of an issue. One advantage of ionic liquids is that the silver ion can be incorporated directly into the structure of the membrane itself, as part of the salt, as opposed to being included as a solute (Olivier-Bourbigou et al., 2010). This makes it easier to achieve high levels of silver concentration while still maintaining a mechanically sound membran. It is also possible to incorporate both the silver ion and an olefin ligand into the organic liquid. For examples, incorporating Ag^+ and pentene into an ionic liquid membrane resulted in a pentene/pentane selectivity of ~ 500 (Huang et al., 2008).

Ionic liquids have many advantages, including thermal and chemical stabilities, and the ability to customize an ionic liquid to a wide variety of specific applications (Li et al., 2012). However, ionic liquid membranes are still relatively new, and more studies are needed to have a good understanding about ionic liquids. There is very little data surrounding the long term stability of ionic liquid membranes (Faiz and Li, 2012b). This is something that should be further investigated and considered before ionic liquid membranes can be adapted for use.

The mechanism of transport in ionic liquid membranes containing silver salts and olefin ligands has been investigated. Three possible mechanisms are described: diffusion of the olefin-silver complex with release on the permeate side of the membrane, a hopping mechanism of the olefin molecule from one silver ion to another, or a Grotthus type mechanism similar to the movement of protons through water (Jiang and Dai, 2008). In this type of membrane it is likely that all three of these types of transfer occur at some stage (Jiang and Dai, 2008).

2.4.4. Membrane Electrolytes

Membrane electrolytes, also known as solid polymer electrolyte membranes, are membranes in which a metal salt is dissolved in a polymer matrix (Faiz and Li, 2012b). The polymer chains are sufficiently mobile that all of the components of the membrane can move fairly freely, so no plasticizers or solvents are required (Faiz and Li, 2012b). Solid polymer electrolyte membranes for olefin-paraffin separation make use of a silver salt dissolved in a membrane matrix in order to facilitate olefin transport across the membrane. These membranes will be discussed in detail in the next section.

2.5. Solid Polymer Electrolyte Membranes for Olefin/Paraffin Separation

The performance of a solid polymer electrolyte membrane will depend on interactions between the polymer matrix, the silver cation, the counterion, and the olefin. When choosing the polymer material and the counterion, the relative strength of these interactions needs to be considered. The interaction between the polymer matrix and the silver ion needs to be strong enough to hold the silver in place, but not so strong as to prevent the silver ion from forming a complex with the incoming olefin molecules. In addition, the interaction between the silver ion and the negative counterion should be fairly weak, so that the metal ion is free to interact with the olefin molecules.

2.5.1. Mechanism of Transport in Solid Polymer Electrolyte Membranes

In solid polymer electrolyte membranes, there are two types of transport in effect. Firstly, there is the solution-diffusion movement of uncomplexed olefin and paraffin. The molecules sorb into the membrane matrix and then move by diffusion, or Fickian transport, across the membrane under a concentration gradient. Molecules will travel from a high concentration to a low concentration by diffusion. This diffusion occurs due to segmental motion of the polymer chains (Liu et al., 2004), or the redistribution of free volume (empty space) in the membrane. Both the olefin and the paraffin in the system will cross the membrane by Fickian diffusion at approximately the same rate, as they are very similar in size.

In addition to solution-diffusion of uncomplexed olefin and paraffin molecules, facilitated transport also contributes to olefin transport when a carrier, in this case silver ions, is used to facilitate olefin transport across the membrane. The rate of the facilitated transport of olefin is much faster than the rate of solution-diffusion of uncomplexed molecules across the membrane. This is necessary in order for separation to occur, so that substantially more olefin will pass through the membrane than paraffin. For a highly effective membrane, the non-facilitated transport should be negligible compared to the facilitated transport.

There are different theories as to the mechanism for facilitated olefin transport across these types of membranes. One possibility involves the olefin molecules ‘hopping’ from a silver ion to another silver ion across the membrane in the direction of the concentration gradient, possibly following the polymer chain along the way. Another possibility comprises of an olefin molecule

forming a fairly strong bond with a silver ion, and the pair diffuses across the membrane together (Pinnau and Toy, 2001).

The selectivity achieved depends on the rate of transport of the olefin and the paraffin. Therefore, the effect of the silver salt on the solution and diffusion of the paraffin molecule should also be considered when discussing the separation performance of these membranes. This effect was investigated using PA12-PTMO/AgBF₄ membranes. The polymer PA12-PTMP used was a block copolymer consisting of 20 wt% nylon-12 and 80 wt% tetramethylene oxide (Merkel et al., 2003). The solubility of ethane and ethylene were determined at various AgBF₄ concentrations. Addition of the silver salt greatly increased the sorption of ethylene, as expected, but also significantly decreased the uptake of the ethane (Merkel et al., 2003). A combination of these two effects contributes to the very high selectivity reported with these types of membranes. The diffusivity of both olefins and paraffins initially decreases with the addition of silver salt to a polymer membrane. This is because the addition of silver salt makes the polymer film denser. Once the silver salt concentration reaches a threshold level, the diffusivity of the olefin begins to drastically increase due to the facilitated transport component, but the diffusivity of the paraffin continues to decrease.

A study investigating a poly(N-vinyl pyrrolidone) (PVP)/AgCF₃SO₃ polymer electrolyte membrane for separation of propylene from propane showed an ideal separation factor of almost 1500 (Kim et al., 2002). In order to further clarify the mechanism of olefin transport in these membranes, work was done to characterize the anions in the system using FT-Raman spectra. The CF₃SO₃⁻ anions in the membrane can be in one of three states: free ions, ion pairs with Ag⁺

ions, or ionic aggregates with Ag^+ ions. As the AgCF_3SO_3 concentration in the membrane increases, the ions move from free ions, to ion pairs, and then to ionic aggregates. However, it was determined that when exposed to an olefin environment (in this case exposed to propylene) all of the CF_3SO_3^- anions reverted to free ions, regardless of the AgCF_3SO_3 concentration in the membrane (Kim et al., 2002). This leads to the conclusion that olefin molecules act as a solvent for silver polymer electrolytes, and through their coordination with the silver ions, the olefin molecules break up the ionic interactions of the silver salts. Furthermore, this study characterized PVP/ AgCF_3SO_3 samples with and without propylene using FT-IR, and it was found that the coordination of the silver ion with the carbonyl oxygen atom in the PVP backbone was maintained throughout propylene sorption, though it is weakened (Kim et al., 2002). This information can reveal a partial mechanism for the olefin transport across solid polymer electrolyte membranes with silver ions. Regardless of silver salt concentration and the original state of the ionic interactions, when olefin is introduced to the system, the silver ion will dissociate with the anion to preferentially complex with the olefin molecule, while maintaining the coordinate bond with the polymer backbone.

Although this helps clarify the picture, it still does not determine whether the olefin transport occurs by a “hopping” mechanism or the pair diffusion mechanism. The olefin molecule could interact with a line of silver ions in the manner described above, or could complex with only one silver ion and be transported across the membrane by the movement of the polymer chains.

The observed threshold silver concentration, at which facilitated transport begins to occur, lends support for the “hopping” mechanism. The threshold concentration is defined as the

concentration of silver salt at which facilitated transport is evident and a dramatic increase in olefin/paraffin selectivity begins to occur. At this point the silver ions dispersed in the polymer matrix will be close enough together to allow for “hopping” to occur (Merkel et al., 2003). At silver concentrations below the threshold concentration, both the olefin and paraffin molecules have very low diffusivities, and are slow to move through the membrane, resulting in very little separation despite the drastic difference in their sorption behaviour. However, at a concentration above the threshold, the mobility of the olefin molecules increases dramatically, causing a meaningful separation of the olefin/paraffin pair.

Experiments show that olefins are relatively strongly held by silver ions in polymer membranes, but are rapidly exchanged for other olefins (J. H. Kim et al., 2004). This also lends support to the theory of the “hopping” mechanism.

It is also shown that the total coordination number of the silver ions in a solid polymer electrolyte membrane is fairly constant at ~3. This indicates that the sum of the number of polar oxygen atoms coordinated with a silver ion, and the number of olefin molecules coordinated with a silver ion is a constant (J. H. Kim et al., 2004). This affects the threshold concentration of the membranes because the 3 coordination sites available per silver ion will preferentially fill with oxygen atoms from the polymer. It follows that in order to be an active olefin carrier, the number of silver ions needs to be greater than the number of polymer oxygen atoms divided by three. In other words, the threshold concentration occurs at a [polymer repeating unit]:[Ag⁺] ratio of approximately 3:1 (J. H. Kim et al., 2004). The ratio will vary slightly between polymers due to the strength of the polymer-silver interaction. If the silver-polymer interaction strength is

greater than the silver-olefin interaction, the threshold silver concentration will be larger, and vice versa (J. H. Kim et al., 2004).

In solid polymer electrolytes, both anions and cations have enough mobility to support conductivity and transport through the membrane without any solvent (Pinnau and Toy, 2001).

2.5.2. Selection of Polymer

In choosing a polymer to use with silver ions in a solid polymer electrolyte membrane for olefin separation, there are two main criteria. The first is that the functional group present in the polymer can form coordinate bonds with the silver ion. The second is that the polymer is relatively flexible, which is important because it allows movement and therefore transport through the membrane (Pinnau and Toy, 2001). PEO is a good polymer for these membranes because it has electron-donating ether oxygen atoms that can interact with silver and has low barriers to bond rotation, meaning the polymer chains are flexible (Pinnau and Toy, 2001).

Metal ions can readily coordinate with polar oxygen atoms in all of the following functional groups: ether, amide, ester and ketone (J. H. Kim et al., 2004). Amides form quite strong coordinate bonds with Ag^+ , while the complex between esters and Ag^+ ions are much weaker. Ketone- Ag^+ bonds are of intermediate strength, and similar in strength to the olefin- Ag^+ bond (J. H. Kim et al., 2004). For optimal olefin transport, the bond between the silver ion and the functional group of the polymer should be relatively weak. This will allow the silver ion to interact most freely with the olefin molecule.

The hard-soft acid-base theory can also be used to justify the choice of PEO as a good choice for a solid polymer electrolyte membrane. Hard acids and hard bases (which hold their electrons tightly) will preferentially interact with each other, while soft acids and soft bases (which have a lower electronegativity and hold their electrons more loosely) will preferentially interact with each other as well (Pinnau and Toy, 2001). The Ag^+ ion is a soft acid and the oxygen molecules in PEO are hard bases, so the interaction between them will be relatively weak. This is beneficial because the silver ion is then available to interact with olefin molecules (Pinnau and Toy, 2001).

A negative impact of using PEO as the polymer matrix is that PEO is a polar polymer, and polar polymers can act as reducing agents for silver salts (Kim et al., 2006). This means that Ag^+ ions will be reduced to Ag atoms, and therefore lose their ability to complex with olefin molecules. This will lead to reduction of separation performance over time. This also occurs with PVP and POZ (J. H. Kim et al., 2004). However, research investigating methods to extend the life of these types of membranes is ongoing. One possible solution is to add plasticizers (such as phthalates) to the membrane in order to prevent the reduction of silver ions to silver particles. This is effective because the plasticizers coordinate with the silver ions in such a way as to prevent them from reducing (J. H. Kim et al., 2004).

Another possible solution to this problem is the use of non-polar polymers to disperse the silver salts. This would be beneficial because the non-polar polymers do not act as reducing agents, and therefore would not reduce the silver ions to silver particles, maintaining their ability to complex with the olefin molecules. However, the drawback of this approach is that the non-

polar polymers lack the ability to dissolve the silver salts. They can only physically disperse them. These polymers may still be effective because, as discussed previously, once the membrane is exposed to an olefin environment the olefin molecules can act as a solvent for the silver salts. The olefin molecules would dissolve the silver salts, and the silver cations would then facilitate transport of the olefins across the membrane. This idea was tested using PDMS as a model polymer (Kim et al., 2006). Membranes were prepared using various silver salts at various concentrations. The highest selectivity values were achieved using AgBF_4 ; both the pure gas permeability ratio and the mixed gas selectivity were ~ 200 (Kim et al., 2006). This shows that the olefin can dissolve the silver salt that has been dispersed in PDMS. However, the selectivity values achieved are much lower than those achieved using the PEO/ AgBF_4 system. Studies examining PEO/ AgBF_4 membranes at similar silver concentrations to the PDMS study show olefin-paraffin permeability ratios on the order of 10^3 to 10^4 (Liu et al., 2004), or more specifically 1000-5500 (Pinnau and Toy, 2001). This indicates that the olefin molecules were not able to dissolve all of the silver salt, and that dissolving the salt in the membrane itself is more effective.

The PEO/ AgBF_4 membrane shows a very high selectivity for olefin-paraffin separation. The PEO matrix is rubbery and provides enough chain flexibility to facilitate olefin transport without the use of any solvents or plasticizers. This is not the case for other similar systems. For example, Nafion- AgBF_4 or PVA- AgBF_4 require either the addition of a solvent (such as water) to the system or addition of a plasticizer to the matrix to achieve facilitated olefin transport (Pinnau and Toy, 2001). Neither of these options is desirable. One significant advantage of solid polymer electrolyte membranes is that they can operate in the absence of water.

The mobility of PEO is further increased through the addition of AgBF_4 . Adding silver salts to PEO is shown to disrupt the crystallinity of the polymer, thereby increasing its chain mobility (Sunderrajan et al., 2001). This should in turn be beneficial for Ag^+ -olefin mobility, and therefore for separation performance as well.

2.5.3. Selection of Anion

In solid polymer electrolyte membranes, it is important that the silver ions are free for maximum interaction with the olefin molecules. For this to occur, the silver ion should have minimum interactions with other components of the system. A negative counter-ion is required to balance the charge of the silver ion and stabilize the system, and the properties of this anion have significant impacts on the separation performance of the membranes. An anion that has a weak interaction with the silver ion is desirable. Smaller anions that are strongly electronegative (e.g., F^- , Cl^- and NO_3^-) are less viable candidates for olefin transport because they form stronger complexes with metal ions. Alternatively, larger anions with lower electronegativity values form silver salts with lower lattice energies (i.e., weaker interactions) (Kim et al., 2003). This makes them more suitable for olefin separation applications. Examples of these types of anions include BF_4^- , CF_3SO_3^- and ClO_4^- .

Solid polymer electrolyte membranes consisting of various silver salts dispersed in POZ were studied for propylene sorption with the objective of determining the anion effect. The olefin is most soluble in the POZ/AgBF_4 membranes, and least soluble in the AgNO_3 membranes.

Membranes made with AgCF_3SO_3 showed intermediate sorption capacity (J. H. Kim et al., 2004). This is in agreement with the theory described above; the larger anions result in better olefin interaction capabilities.

Olefin solubility is one measure of the potential effectiveness of olefin separation using a solid polymer electrolyte membrane. Theoretically, a higher olefin solubility in a membrane will result in easier and faster transport of the olefin across the membrane. The solubility of propane and propylene in solid polymer electrolyte membranes consisting of PEO and various silver salts were measured by Sunderrajan et al. (2001). The salts tested included salts recommended above (large with low electronegativity) as well as silver nitrate. It was shown that olefin solubility had a strong dependence on the counteranion present. Olefin solubility in the membrane varied with anion as follows: $\text{AgBF}_4 \gg \text{AgCF}_3\text{SO}_3 > \text{AgCF}_3\text{CO}_2 > \text{AgNO}_3 > \text{PEO alone}$ (Sunderrajan et al., 2001). These results display the importance of the silver salt dissolving in the PEO matrix. A solid polymer electrolyte membrane should be a solid solution, with the silver salt evenly distributed throughout the polymer matrix (Liu et al., 2004). In order for the silver ion to complex with the olefin, it needs to dissolve in the PEO, but in order to do this it needs to dissociate from its counteranion. Silver nitrate shows excellent olefin uptake in aqueous environments, but performs poorly here because it does not absorb well into the PEO (Sunderrajan et al., 2001). Alternatively, silver tetrafluoroborate dissociates fully in PEO, which helps explain the increased olefin solubility of the PEO/ AgBF_4 system.

Wide angle X-ray diffraction data shows that the crystallinity of PEO is disrupted by the addition of silver salts. AgNO_3 and AgBF_4 are both studied, and AgBF_4 is shown to have a greater effect

than AgNO_3 , indicating that AgBF_4 is more readily soluble in PEO than AgNO_3 . In fact, the crystallinity of PEO is completely gone when the concentration of AgBF_4 is $>10\%$ (Sunderrajan et al., 2001). The authors attribute this to the difference in lattice energies of the two salts. Salts with lower lattice energies, or weaker bonds, are more soluble in PEO.

2.5.4. Membrane Performance for Gaseous Olefin/Paraffin Separations

Solid polymer electrolyte membranes, including those made up of poly(ethylene oxide) and silver tetrafluoroborate (PEO and AgBF_4), have been studied for use in separation of gaseous olefin/paraffin mixtures, with promising results. In particular, PEO/ AgBF_4 membranes have been tested for ethylene/ethane and propylene/propane selectivities and displayed very good results.

Sorption refers to the amount of a permeant a membrane can hold at equilibrium. Theoretically, the silver ions in the polymer electrolyte membranes will coordinate with olefin molecules, resulting in higher sorption uptake. For a PEO/ AgBF_4 system with a silver salt content of 81.5g $\text{AgBF}_4/100$ g membrane, the equilibrium propylene uptake was 8.46 g of propylene/100 g film. By contrast, the equilibrium sorption uptake of PEO alone was only 0.30 g propylene/100 g film (Sunderrajan et al., 2001).

Pure gas selectivity, which refers to the permeance of pure olefin divided by the permeance of pure paraffin for a given membrane sample, is shown in Table 2 for a polymer electrolyte membrane consisting of AgBF_4 dissolved in a PEO matrix. Another study reports similar

findings, and an olefin-paraffin permeability ratio on the order of 10^3 to 10^4 was observed (Liu et al., 2004).

Table 2: Pure Gas Selectivity Values for a PEO/AgBF₄ Solid Polymer Electrolyte Membrane (Pinnau and Toy, 2001)

Composition wt % AgBF ₄	Pure Gas Selectivity	
	Ethylene/Ethane	Propylene/Propane
33	1.8	2.0
50	>160	>260
67	>1000	>1000
80	>5500	>4000

However, when tested with mixed gases, the selectivities achieved were significantly lower. The highest selectivity values achieved were ~120 for ethylene/ethane and ~260 for propylene/propane. This is attributed to an increase in the paraffin permeance in a mixed gas setting. The movement of the olefin molecules through the membrane causes more motion in the polymer matrix, allowing easier passage to the paraffin molecules (Pinnau and Toy, 2001).

It is commonly reported that facilitated transport membranes containing silver ions will degrade with time. Exposure to light, water, and polar polymer matrices can all contribute to expediting the reduction of Ag⁺ to Ag (Faiz and Li, 2012b). In the current system, PEO is a polar polymer, which can contribute to the reduction of the silver ions in the membrane (Liu et al., 2004).

In particular, in PEO/AgBF₄ membranes used for olefin paraffin separation, olefin permeance and selectivity tend to decrease with increased pressure. This was attributed to a partial saturation of the membrane (Pinnau and Toy, 2001). Interestingly, cycling feed pressure was

shown to have an irreversible, negative effect on propylene permeability. This may be attributed to silver salt precipitation from the membrane under exposure to the olefin feed (Liu et al., 2004). Another observation indicates that although the selectivity of the membrane remains unchanged for an operating period of 16 hours, the permeance of both the olefin and paraffin decrease by 50%. This can also be attributed to crystallization of the silver salt in the polymer matrix (Pinnau and Toy, 2001).

2.6. Processes for Separating Liquid Olefins and Paraffins

All of the research discussed above focuses on separating gaseous olefin-paraffin mixtures. The referenced studies focused on ethylene-ethane and/or propylene-propane, with a few including butylene-butane. It would be incorrect to assume that these processes can be directly applied to larger olefins, which will be in liquid form at room temperature, and produce the same separation performance. Some properties of liquid hydrocarbon mixtures can be quite different from those of small gaseous hydrocarbons mainly in molecular sizes, hydrophobicity, and vapour pressure. This section will discuss some of the limited work that has been done in this area. Of particular interest are methods for separating pentene-pentane (C₅) and hexane-hexane (C₆) mixtures, and work utilizing facilitated transport membranes with silver ion carriers.

2.6.1. Absorption Processes

Properties of the solvents used in traditional absorption/extraction processes for olefin/paraffin separation contribute to lower than desirable selectivities. Small and volatile organic solvents

can lead to solvent loss or instability of the metal ion carrier, and generally have a small temperature range under which they operate effectively (Li et al., 2012). Ionic liquids offer an alternative. For example, separation of 1-hexene from n-hexane can be achieved through contacting the olefin/paraffin mixture with an ionic liquid separating agent. It has been shown that this the performance of this process improves with the addition of silver ions to the ionic liquid mass separating agent (Li et al., 2012).

2.6.2. Facilitated Transport Membranes

There are a variety of silver containing facilitated transport membranes being investigated for separation of C5 and C6 olefins and paraffins.

Ag⁺-Nafion films of varying thicknesses were investigated for use in separating C6 mixtures (Rabago et al., 1996). These feed mixtures contained n-hexane, 1-hexene, and 1,5-hexadiene dissolved in isooctane saturated water at room temperature – they are not pure olefin/paraffin mixtures. The permeation rates of the paraffin through the membrane were small enough to go undetected, and the study focused on the separation of the mono-olefin from the di-olefin, with selectivities (1,5-hexadiene/1-hexene) ranging from 50-70. In addition, the diffusion coefficients for 1,5-hexadiene and 1-hexene were calculated to be 4.1×10^{-8} and 1.1×10^{-8} cm²·s⁻¹, respectively (Rabago et al., 1996). A benefit of using perfluorosulfonated ionomer membranes like Nafion is that the sulfonate group binds the silver ion in such a way that it prevents the reduction of silver ions to silver particles (Choi et al., 2006).

However, perfluorosulfonated ionomer membranes such as Naifon are both expensive and complex to produce and use (Choi et al., 2006). Sulfonated poly(ether ether)ketone (SPEEK) is a less expensive alternative that can also achieve long term stability. SPEEK-AgNO₃ membranes on polyester supports were used to separate isoprene from n-pentane (Choi et al., 2006). This study was performed at room temperature. The state of the feed stream (vapour or liquid) was not specified, however the use of a gas chromatograph implies that the permeate stream is vapour. Highly sulfonated SPEEK membranes showed the highest di-olefin flux and selectivity, and were stable over at least 100 hours. However, membranes with lower degrees of sulfonation did deteriorate over time (Choi et al., 2006). This implies that silver ion reduction still takes place when not all of the silver ions are bound to sulfonate groups.

Solid polymer electrolyte membrane were also used for the separation of isoprene from pentane. Cellulose Acetate (CA) is used to dissolve either AgClO₄ or AgBF₄ silver salts in order to facilitate transport of the di-olefin (S. H. Kim et al., 2004). The membranes were tested using a mixed gas of 50/50 isoprene and pentane, with a sweep gas of helium on the permeate side of the membrane. The maximum isoprene/pentane selectivity achieved was 53 for the CA-AgClO₄ membranes and 83 for the CA-AgBF₄ membranes (S. H. Kim et al., 2004). These selectivities are very good, however they are smaller than the ethylene/ethane and propylene/propane selectivities achieved using PEO/AgBF₄ membranes discussed earlier.

Heterogeneous hybrid membranes of AgCl dispersed in PMMA have been tested for their sorption properties using liquid cyclohexane and cyclohexene (Shen et al., 2007). These membranes bear resemblance to the mixed matrix membranes described earlier, where an

inorganic but highly selective phase is dispersed within an organic matrix. Recall that these are not polymer electrolyte membranes, as the silver salt is not dissolved in the membrane, rather is it dispersed. The sorption capacity of these membranes for the olefin was quite high, at ~1g olefin sorbed/1 g membrane at ambient conditions. This was much higher than the corresponding paraffin sorption, giving solubility ratios ranging from 50-130 (Shen et al., 2007).

There is a high volume of work available investigating membrane separation processes for C2 and C3 olefin/paraffin mixtures. However, there is much less work discussing the separation of C5 and C6 olefin/paraffin mixtures. In particular, many of the membranes that have been demonstrated to result in excellent olefin/paraffin separation performance for C2 and C3 olefin/paraffin separation have not been tested using larger hydrocarbons. The present study will apply a PEO/AgBF₄ polymer electrolyte membrane that has shown very high olefin/paraffin selectivities for C2 and C3 systems to C5s.

This system will be investigated using pure component permeation, equilibrium sorption uptake, and desorption kinetic studies. The stability of the system will also be evaluated, and the results will be compared to the C2 and C3 data.

3. Experimental

3.1. Membrane Preparation

3.1.1. Membrane Casting

Poly(ethylene oxide) (PEO) (procured from PolySciences Inc, MW = 1,000,000) was dissolved in deionized water at a concentration of 4wt%, and stirred overnight at room temperature until homogeneous. The mass of silver tetrafluoroborate (AgBF_4) (procured from Aldrich Chemicals) required to achieve a desired AgBF_4 :PEO ratio was calculated and then measured. A few drops of deionized water were added to the crystals in an amber bottle until dissolved. This solution was then added to the PEO solution. The two solutions were stirred for ten minutes at room temperature, and there was no observed precipitation. The AgBF_4 , as well as any mixture containing it, were shielded from light at all times, and exposure to air was minimized.

The solution was then cast into a membrane on a plate in one of three different ways. The method used depended on the type of membranes being prepared and the experiment that the membrane was to be used for. The three types of membranes prepared were:

1. A composite membrane consisting of the PEO/AgBF₄ mixture cast onto a polyethersulfone (PES) membrane substrate (procured from Separo); to be used for permeation testing
2. A homogeneous PEO/AgBF₄ solid polymer electrolyte membrane; to be used for sorption/desorption testing
3. A composite membrane consisting of the PEO/AgBF₄ mixture cast onto a piece of filter paper (procured from Whatman International); to be used for sorption/desorption testing of membranes with higher concentrations of AgBF₄ (due to decreased stability in the homogeneous membranes).

The composite membranes were cast onto glass plates, and the homogeneous membranes were prepared on Teflon plates.

3.1.2. Membrane Drying and Storage

Each of the membranes was dried using a multi-step process. First, they were dried in a 40°C, nitrogen (N₂) purged oven for 24 hours. Next, they were dried in a vacuum oven at room temperature for an additional 24 hours. The membranes that were used in vapour permeation testing were dried further inside the permeation cell; they were placed under vacuum for 4-5 hours at room temperature once already in the cell but before permeation testing began.

All of the membrane samples were stored at room temperature in a desiccator and shielded from light at all times. Some membrane samples were also stored in the vacuum oven (under vacuum) for short periods of time (a few days).

3.2. Permeation Testing

To achieve olefin-paraffin separation, the facilitated transport membrane should allow for higher permeation rates of olefin than of paraffin. In this study, n-pentane and 1-pentene were used as the model paraffin and olefin, respectively. In this series of tests, the permeation rates of pentene and pentane through solid polymer electrolyte membranes of various silver salt concentrations were measured separately. A dead end stainless steel permeation cell is used, and vacuum is applied to the permeate side of the membrane. The permeate is collected using a liquid N₂ cold trap and then weighed to determine a permeation rate. The effective area of the membrane for permeation was 14.9 cm². All permeation tests were performed at room temperature (25°C).

3.2.1. Liquid Contact

In the initial experimental set-up, the liquid pentane (procured from VWR) or pentene (procured from Air Liquide) was in direct contact with the solid polymer electrolyte membrane. The apparatus is displayed in Figure 3-1.

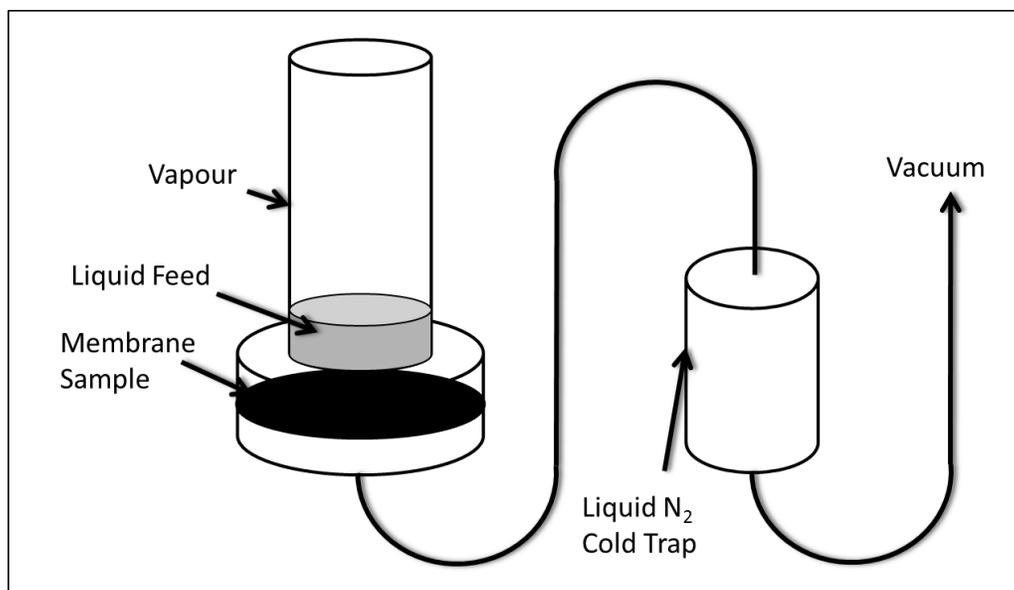


Figure 3-1: Dead End Permeation Cell with Pure Component Liquid Feed – Liquid Contact

However, it was soon determined that the direct liquid contact between the membrane and pentene led to rapid degradation and failure of the membrane. The damage to the membrane occurred so quickly that it was not possible to measure a steady-state permeation rate at any point. Placing a sheet of poly(ether block amide) (PEBA) between the active layer of the membrane and the liquid olefin did little to alleviate the problem. Therefore, the direct liquid contact methodology was set aside.

3.2.2. Vapour Contact

An alternative to placing the liquid olefin in direct contact with the membrane surface is to invert the permeation cell, resulting in the penetrant's vapour contacting the membrane surface instead of the penetrant liquid. A schematic of this is shown in Figure 3-2. The permeation rate of the

olefin and paraffin species can still be measured and compared, and the damage to the membrane is slowed. During the experiments, the vacuum level on the permeate side was maintained at 700 mmHg, while the feed side was at 1 atm.

Each permeation period was timed, and the initial and final mass of the permeate sample collection tube was recorded. From this data, the permeation rate can be calculated by dividing the change in mass by the elapsed time.

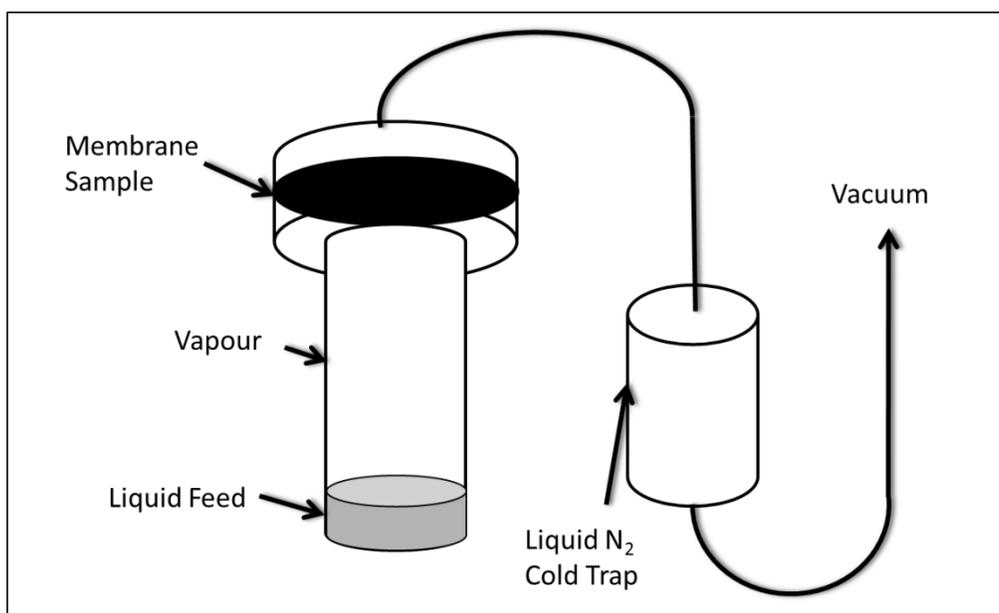


Figure 3-2: Dead End Permeation Cell with Pure Component Liquid Feed – Vapour Contact

The permeation rate can then be normalized by the area of the membrane sample used for permeation in order to calculate the flux. The permeability coefficient is determined from the permeation flux normalized by trans-membrane pressure and membrane thickness. The olefin-paraffin permeability ratio can be calculated by directly dividing the permeation rate of the olefin

by the permeation rate of the paraffin, as the other variables affecting the flux are unchanged (membrane area, membrane thickness, vacuum level on the permeate side).

3.3. Equilibrium Sorption Testing

According to solution-diffusion model, the rate of permeation of a species through a membrane depends on the rates of two separate steps: solution of the penetrant in the membrane matrix, and diffusion of the penetrant through the membrane. The permeability can be roughly approximated by the product of the solubility and the diffusion coefficient. In order to investigate this permeation and separation process further, these variables were studied.

The equilibrium sorption of pentane and pentene in PEO/AgBF₄ solid polymer electrolyte membranes, and the effective diffusion coefficients of pentane and pentene in the membranes, were measured through a series of sorption-desorption tests. Membrane samples of known mass and composition were submerged in pure pentane and pure pentene liquid, separately. They were left overnight to allow the system to reach equilibrium. The membrane samples were then quickly removed to a nitrogen purged balance, where their mass was recorded as a function of time. The highest mass recorded at the beginning of this stage was assumed to be the equilibrium sorption mass.

The equilibrium sorption uptake values of the homogeneous membranes were calculated using:

$$\text{sorption uptake} = \frac{M_{eq} - M_0}{M_0} \quad \text{Eq \#1}$$

The equilibrium sorption uptake values of the membranes cast on filter paper were determined using:

$$\text{sorption uptake} = \frac{M_{eq} - M_0}{M_0 - M_{FP}} \quad \text{Eq \#2}$$

Where:

M_{eq} = mass of the membrane at equilibrium (= M_0 + mass of sorbate)

M_0 = initial mass of the membrane

M_{FP} = mass of the filter paper (for membranes with a filter paper backing)

The pentene/pentane sorption ratio of each membrane sample can be calculated by dividing the sorption uptake of pentene by the sorption uptake of pentane. This will give an idea of the membrane's solubility selectivity and potential for use in liquid olefin-paraffin separation.

3.4. Desorption Kinetics and Modelling

Once placed in the nitrogen purged balance, the penetrant will quickly begin to desorb out of the membrane. This process occurs very quickly due to the high volatility of pentene and pentane. In order to capture accurate kinetic data, the desorption was filmed. A stopwatch as well as the

digital readout of the balance were included within the picture of the video, and these were later tabulated at frequent intervals in order to achieve a full picture of the desorption kinetics.

This desorption kinetic data can be compared to a model in order to estimate the diffusivities of pentene and pentane within the membrane. The membrane can be modelled as a plane of thickness l with diffusivity D . For the situation described above, and assuming a pure diffusion process, the following equation (Crank and Park, 1968) can be used to model the desorption of the penetrant:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \cdot \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-\frac{D(2m+1)^2\pi^2 t}{l^2}\right] \quad \text{Eq \#3}$$

where, M_t is the amount of penetrant desorbed, M_∞ is the total amount of penetrant that will desorb, D is the diffusivity of the penetrant in the membrane, and l is the membrane thickness. This model assumes desorption governed by pure diffusion, from both sides of a membrane film, where the surrounding penetrant concentration has undergone a step change from 100% to zero.

By fitting the desorption data to this model, the diffusivities of the two compounds can be determined and compared, which may give another idea about the diffusivity selectivity of the membrane. Another benefit of the data fitting is to determine whether the desorption process is controlled by simple diffusion, or whether there are some other limiting factors. The interaction

between the silver ions and the olefin molecules may present a complication to this relatively simple model.

4. Results and Discussion

The two main sets of experiments performed in this study were permeation testing of pure pentene and pure pentane through PEO/AgBF₄ solid polymer electrolyte membranes, and sorption/desorption testing of pure pentene and pure pentane in a PEO/AgBF₄ solid polymer electrolyte films. The sorption/desorption testing can give information about the equilibrium sorption characteristics of the membrane, and can be used to determine the effective diffusivity of each penetrant in the membrane.

4.1. Permeation Testing

4.1.1. Permeability Ratio

The pentene/pentane permeability ratio is a measure of the ideal selectivity that can be achieved in a membrane for a given separation. However, the mixed gas selectivity can vary from the pure gas selectivity, possibly due to the olefin ‘opening up’ the membrane and making a pathway for the paraffin. The pentene/pentane permeability ratios for membranes of various silver salt concentrations are displayed in Figure 4-1.

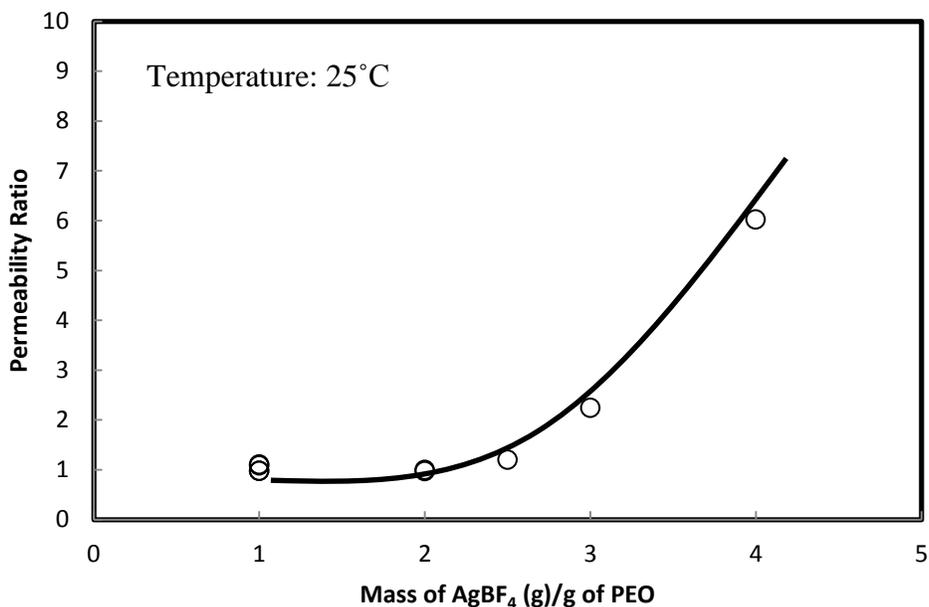


Figure 4-1: Pentene/Pentane Permeability Ratio of PEO-AgBF₄ Membranes with Various Silver Salt Concentrations

The permeability ratio stays at ~1 until an AgBF₄ content of ~2.5g AgBF₄/1g PEO is reached. After this concentration, the permeability ratio begins to increase. This is in agreement with literature data that shows the mixed gas ethylene/ethane selectivity of PEO/AgBF₄ membranes increases with silver concentration in the membrane (Pinnau and Toy, 2001). This result is also congruous with many studies that suggest a threshold concentration, at which the silver ions are close enough together to allow for hopping of the olefin molecules from one silver ion to another (Merkel et al., 2003). Before the threshold concentration, little or no separation occurs, because the silver ions are too far apart to facilitate transport across the membrane. In this case, the threshold concentration appears to be ~2.5 g AgBF₄/g PEO.

4.1.2. Stability

Like the permeability ratio, membrane stability varied with membrane composition. As the silver salt concentration in the membrane increased, the stability of the membrane decreased. A membrane with 1g AgBF₄/1g PEO was tested for durability with pentene permeation. As shown in Figure 4-2, the pentene permeation rate is stable for ~25 hours before beginning to increase quickly. Beyond 38 hours, the permeation rate quickly became too large to measure, indicating complete membrane failure.

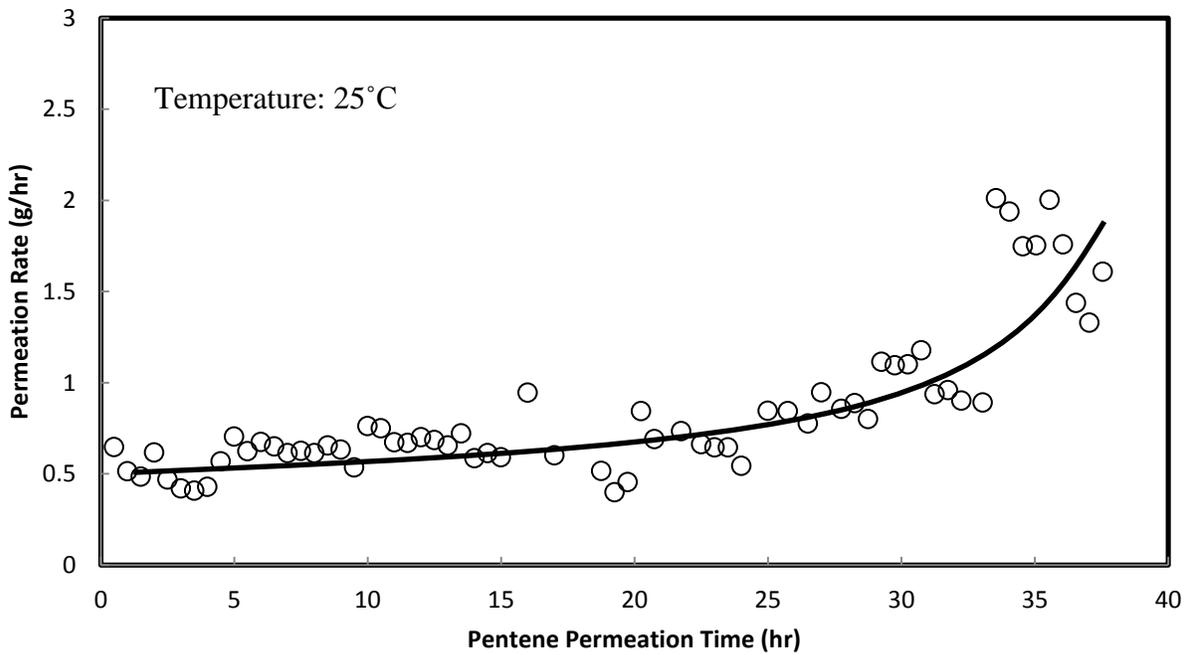


Figure 4-2: Pentene Permeation Rate through a PEO/AgBF₄ membrane with a composition of 1g AgBF₄/1gPEO

This could be a result of two causes: silver ion reduction, leaving behind holes in the membrane matrix, or over-swelling of the membrane, opening pores in the membrane matrix so large they

cause the membrane to fail. This phenomenon occurs more quickly the higher the silver concentration, which also agrees with the results reported in literature. Permeation data for pentene through a membrane with a composition of 3g AgBF₄/1g PEO is shown in Figure 4-3. This membrane operates with fairly stable permeation until ~120 min, or 2 hours. Beyond this time, the permeation rate grew to the point where it was too high to measure, indicating complete membrane failure.

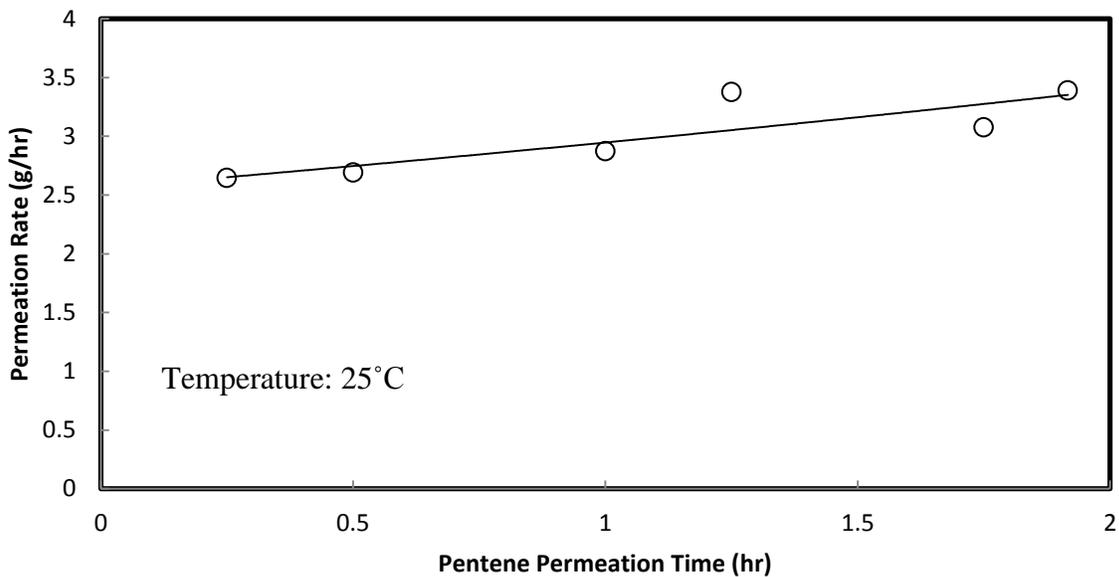


Figure 4-3: Pentene Permeation Rate through a PEO/AgBF₄ membrane with a composition of 3g AgBF₄/1gPEO

Tripling the silver concentration in the membrane from a 1:1 to a 3:1 AgBF₄:PEO ratio (by mass) increases the pentene/pentane permeability ratio from 1 to 2.25, but decreases the stable membrane lifespan from 30 to only 2 hours. This is a drastic change and will need to be addressed before this membrane could be used for pentene/pentane separations.

4.2. Equilibrium Sorption Testing

The equilibrium sorption uptakes of n-pentane and 1-pentene are displayed in Figure 4-4. Due to the volatility of the pentene and pentane, the experimental error in determining the sorption uptake is considerably high (~10%). Nevertheless, at low silver concentrations, the sorption uptakes of the olefin and paraffin are low. However, they both increase up to a silver salt concentration of 2:1 (AgBF₄:PEO by mass), after which they begin to decrease. This could be due to membrane degradation, possibly due to increased membrane swelling, or silver reduction. The membrane sorbs more olefin than paraffin at a given silver concentration in the membrane.

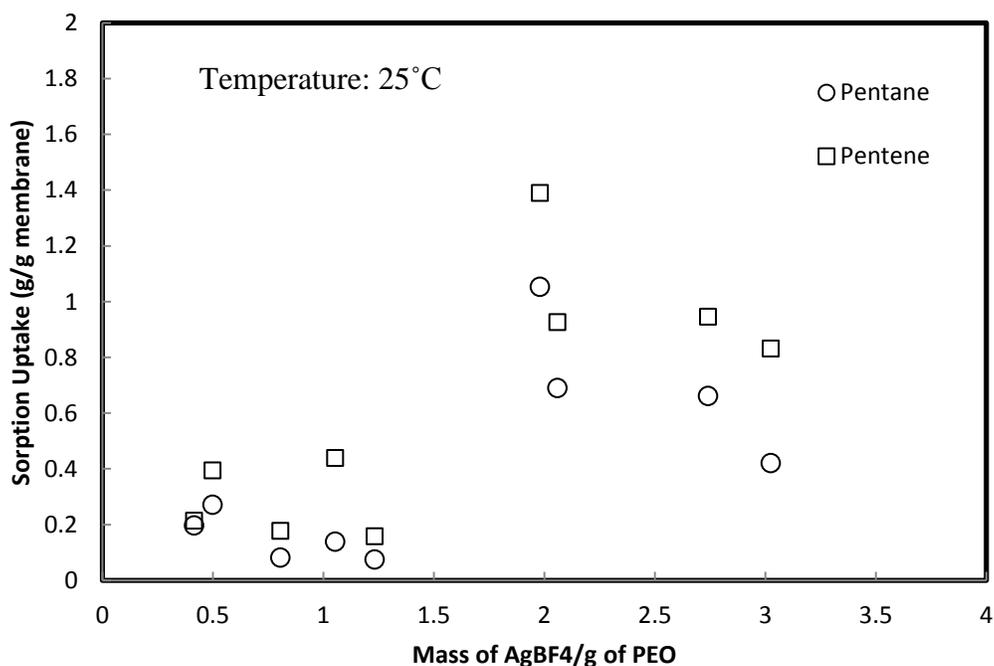


Figure 4-4: Equilibrium Sorption of Pentene and Pentane in PEO/AgBF₄ Membrane with Varying Silver Concentration

The highest sorption uptakes of both pentene and pentane occurs at a membrane concentration of around 1.98 g AgBF₄/g PEO. The increased sorption of pentene occurs due to the interaction of the olefin molecule with the silver ions within the PEO matrix. This can result in swelling of the polymer matrix, which can then allow even more pentene into the matrix. However, when the silver concentration increases beyond this ratio, the sorption uptake of the membrane begins to decrease.

As mentioned above, the sorption uptake of olefin is always higher than the sorption uptake of paraffin. This can be seen more clearly in Figure 4-5, where the sorption ratios for all of the data points are greater than one. This indicates the membrane preferentially sorbs olefins, which is expected. However, the preferential sorption of pentene over pentane is not as significant as the preferential sorption for cyclohexene/cyclohexane reported in the literature where sorption ratios ranging from 50 to 130 were observed (Shen et al, 2007).

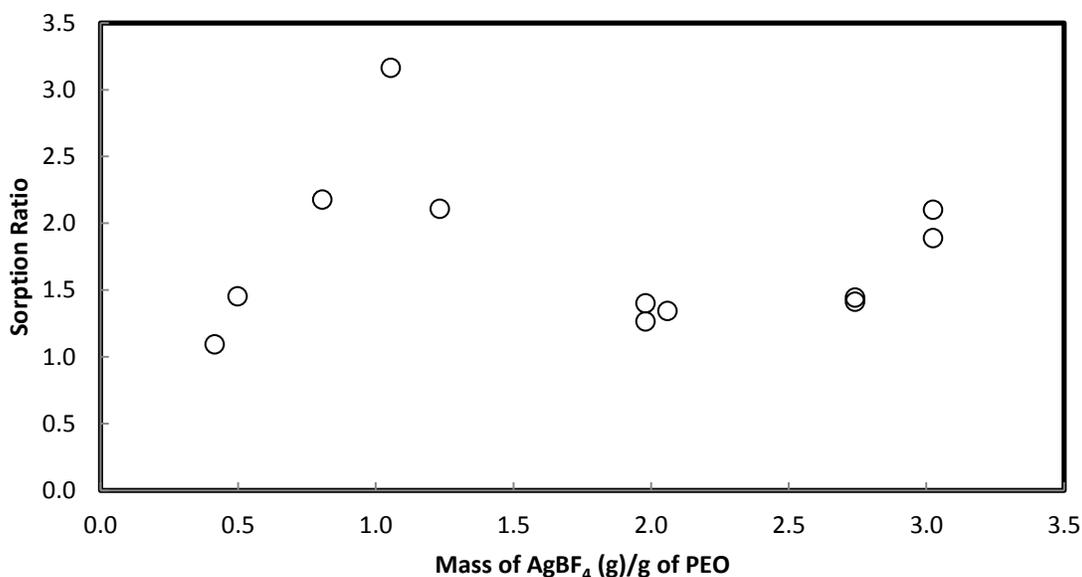


Figure 4-5: Ratio of Pentene Sorption to Pentane Sorption in Membranes with Different Silver Contents

4.3. Desorption Kinetics

The desorption kinetic data collected for n-pentane and 1-pentene leaving PEO/AgBF₄ membranes with various silver concentrations can be used to derive a variety of useful data. Firstly, the amount of penetrant desorbed, when compared to the amount of penetrant sorbed, will give a good indication of the type of interaction occurring between the various components. Secondly, fitting the desorption data to a kinetic model can be used to evaluate the diffusivity of the penetrants in the polymer electrolyte films. Finally, exploring multiple models using the kinetic desorption data and comparing the resulting plots can be used to determine the kinetics of the limiting step in desorption, which may be affecting the overall process.

Figure 4-6 to 4-14, show the desorption kinetics of pentene and pentane from the membranes with different silver contents. They all display similar patterns. The equilibrium sorption uptake of pentene is always greater than that of pentane, as shown in the sorption studies. Pentane desorbs faster in each case and reaches zero fairly quickly. This suggests that there is no chemical interaction or permanent binding between the membrane and the paraffin molecules. However, pentene desorbs more slowly, and there is always a certain amount of pentene remaining in the membrane even after a prolonged period of desorption. This indicates that there are some specific chemical interactions between the olefin and the membrane, and that part of the interactions is permanent or semi-permanent and causes permanent binding of the olefin molecules to the membrane. To the author's knowledge, this phenomenon has not been observed in the work reported in literature.

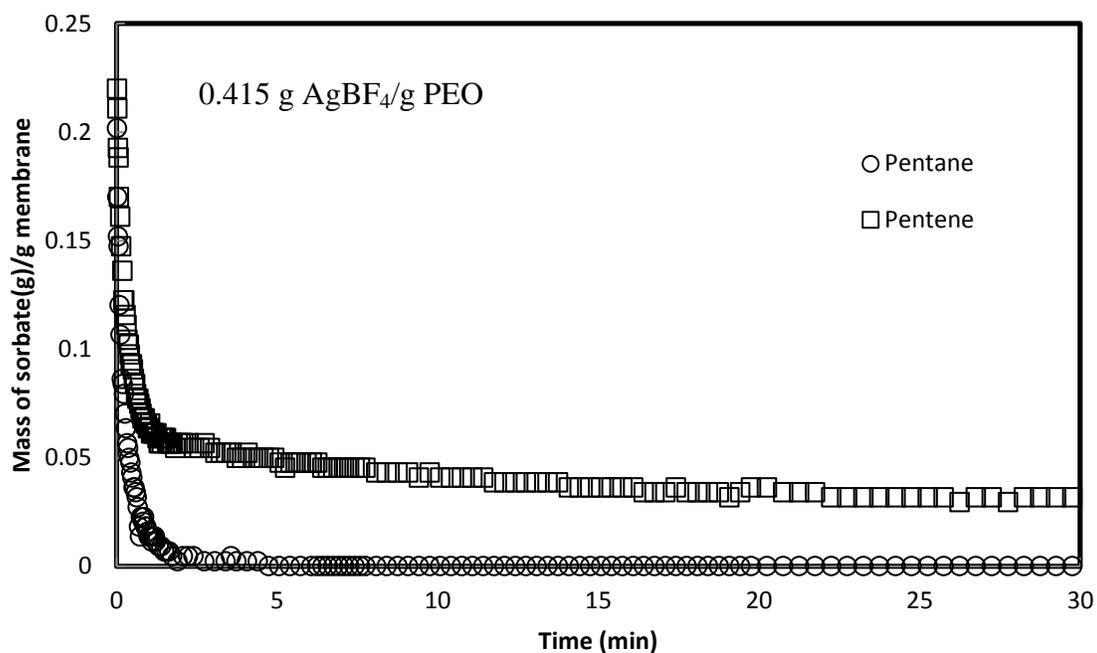


Figure 4-6: Desorption Kinetics of Pentane and Pentene from a Membrane with Silver Content 0.415 g AgBF₄/g PEO

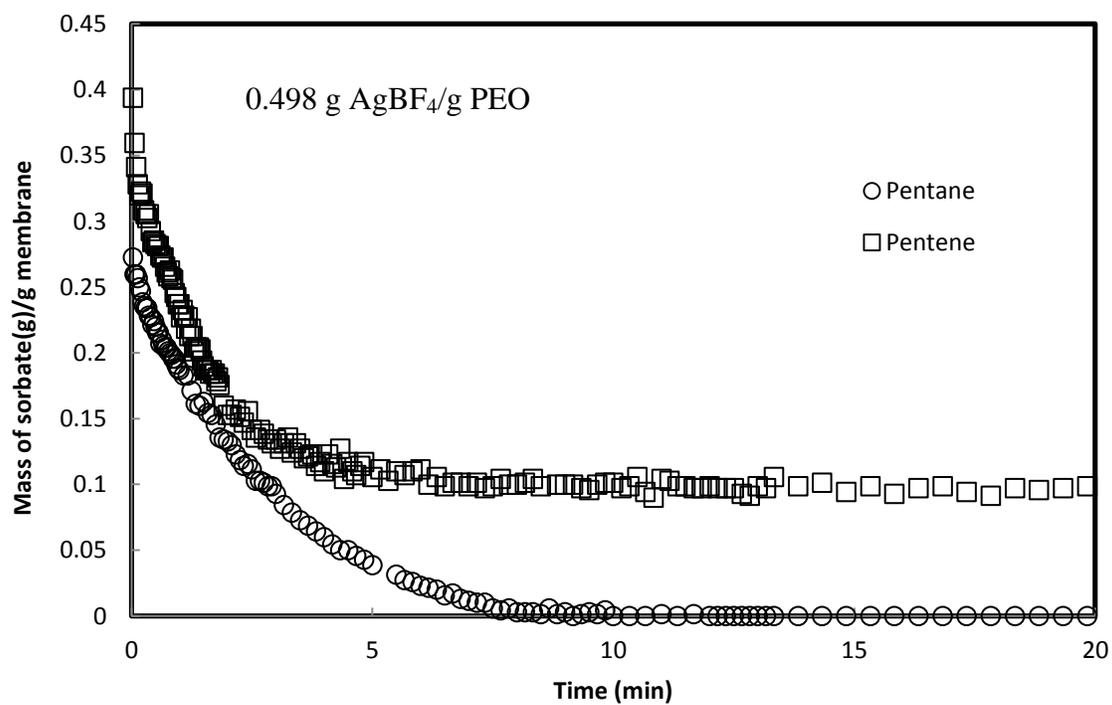


Figure 4-7: Desorption Kinetics of Pentane and Pentene from a Membrane with Silver Content 0.498 g AgBF₄/g PEO

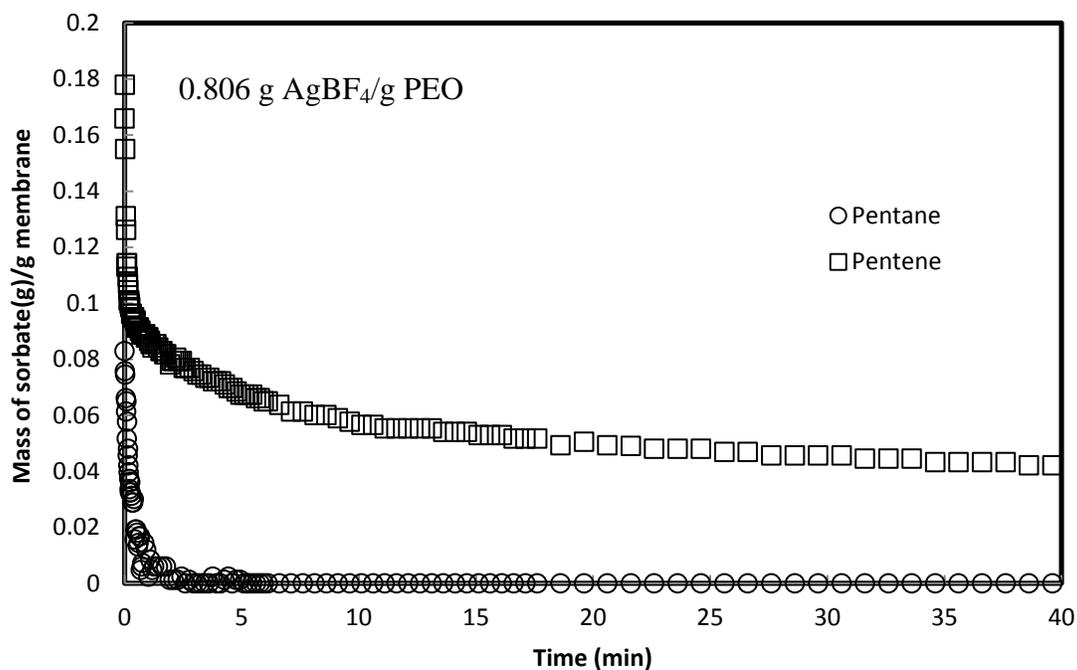


Figure 4-8: Desorption Kinetics of Pentane and Pentene from a Membrane with Silver Content 0.806 g AgBF₄/g PEO

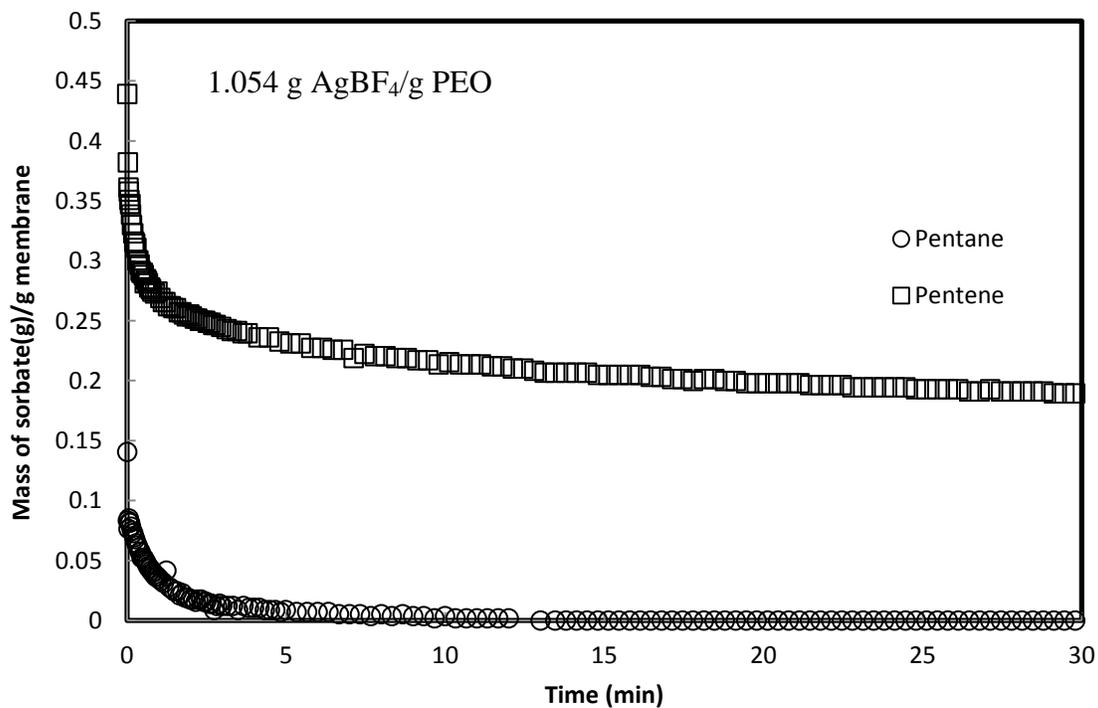


Figure 4-9 Desorption Kinetics of Pentane and Pentene from a Membrane with Silver Content 1.054 g AgBF₄/g PEO

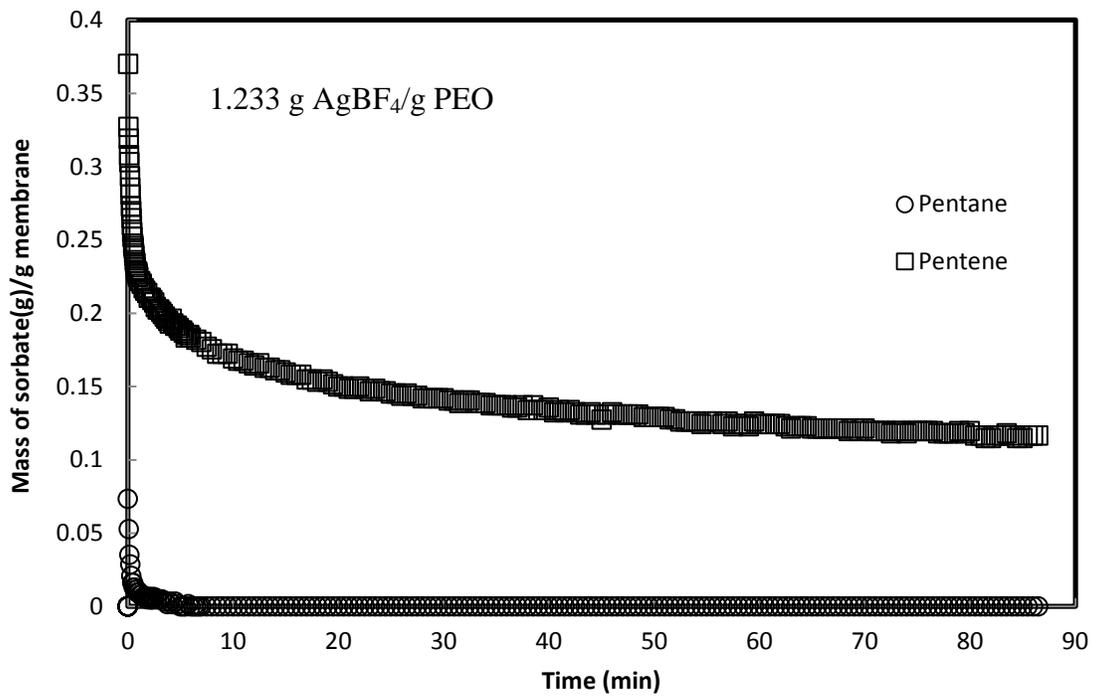


Figure 4-10: Desorption Kinetics of Pentane and Pentene from a Membrane with Silver Content 1.233 g AgBF₄/g PEO

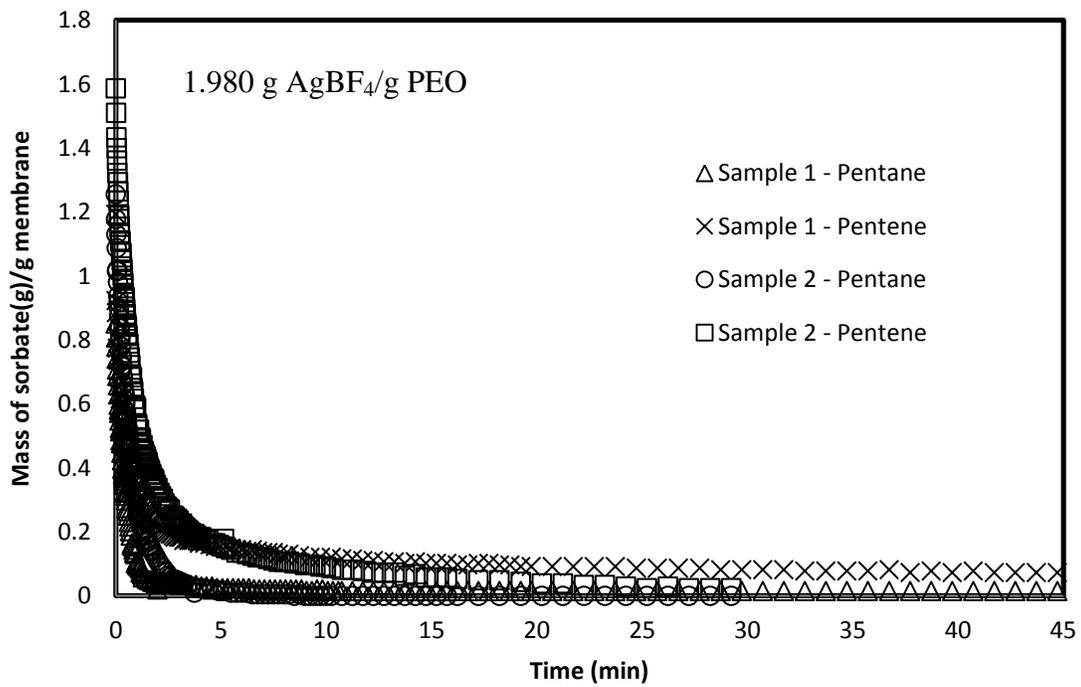


Figure 4-11: Desorption Kinetics of Pentane and Pentene from 2 Membranes with Silver Content 1.980 g AgBF₄/g PEO

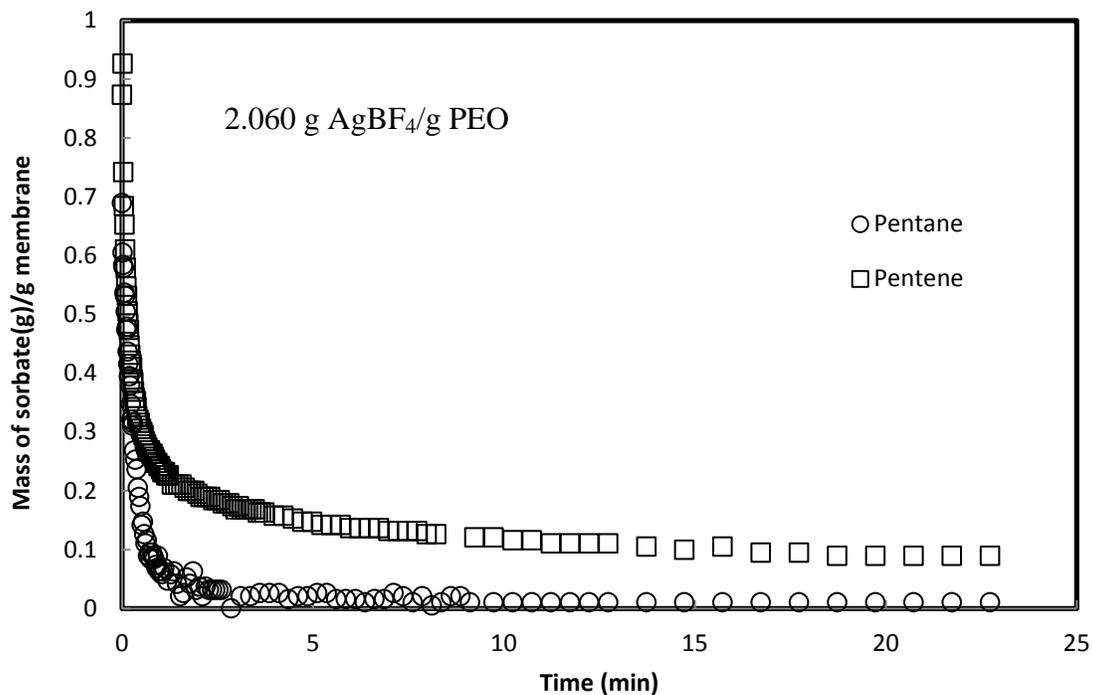


Figure 4-12: Desorption Kinetics of Pentane and Pentene from a Membrane with Silver Content 2.060 g AgBF₄/g PEO

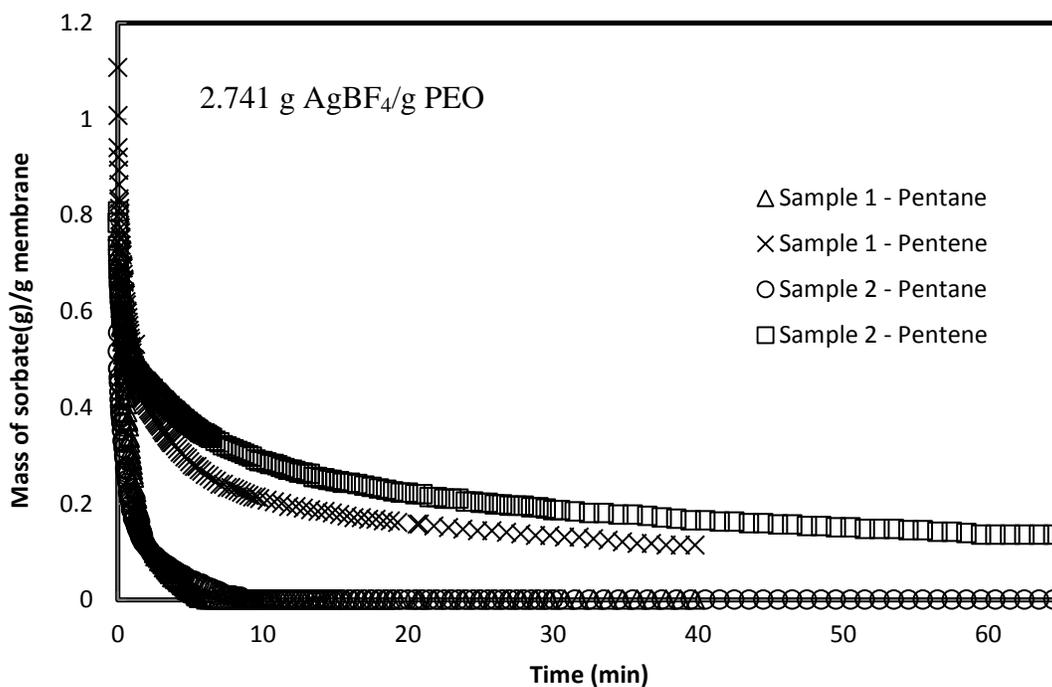


Figure 4-13: Desorption Kinetics of Pentane and Pentene from 2 Membranes with Silver Content 2.741 g AgBF₄/g PEO

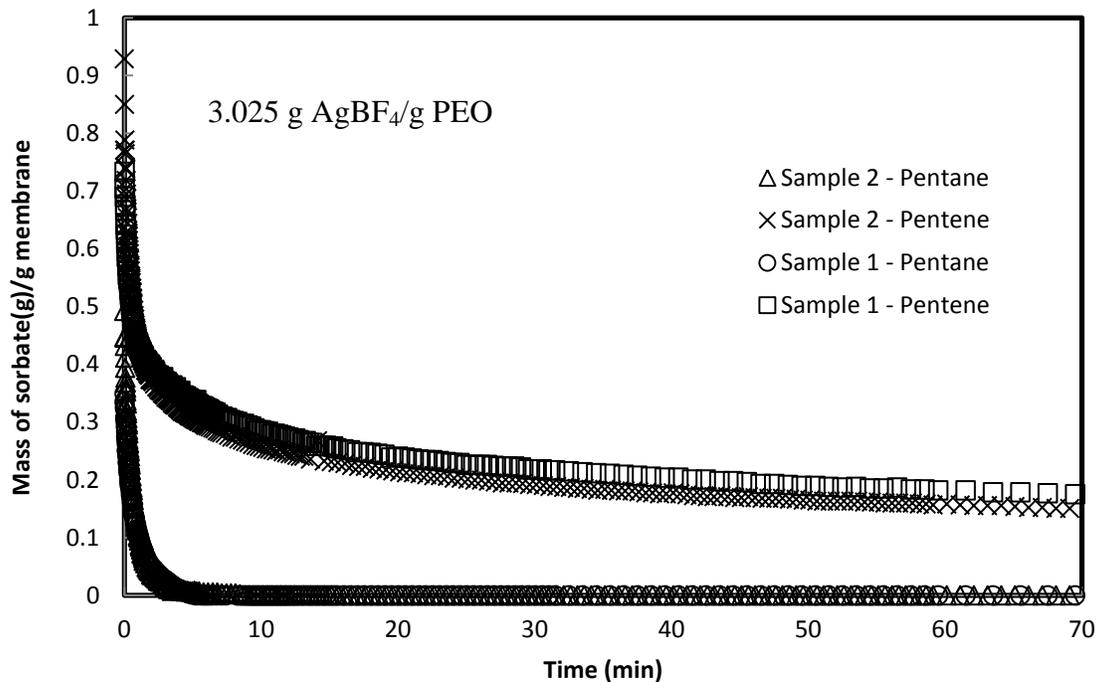


Figure 4-14: Desorption Kinetics of Pentane and Pentene from 2 Membranes with Silver Content 3.025 g AgBF₄/g PEO

4.3.1. Residual Fraction of Pentene in the Membrane

From Figure 4-6 to Figure 4-14, it is clear that the amount of pentene remaining sorbed in the membrane after desorption ceases to occur increases with an increase in the silver content in the membrane. This amount will be referred to as the residual fraction: the fraction of the pentene that sorbs into the membrane that does not come out after desorption. Figure 4-15 shows the residual fraction as a function of the membrane composition.

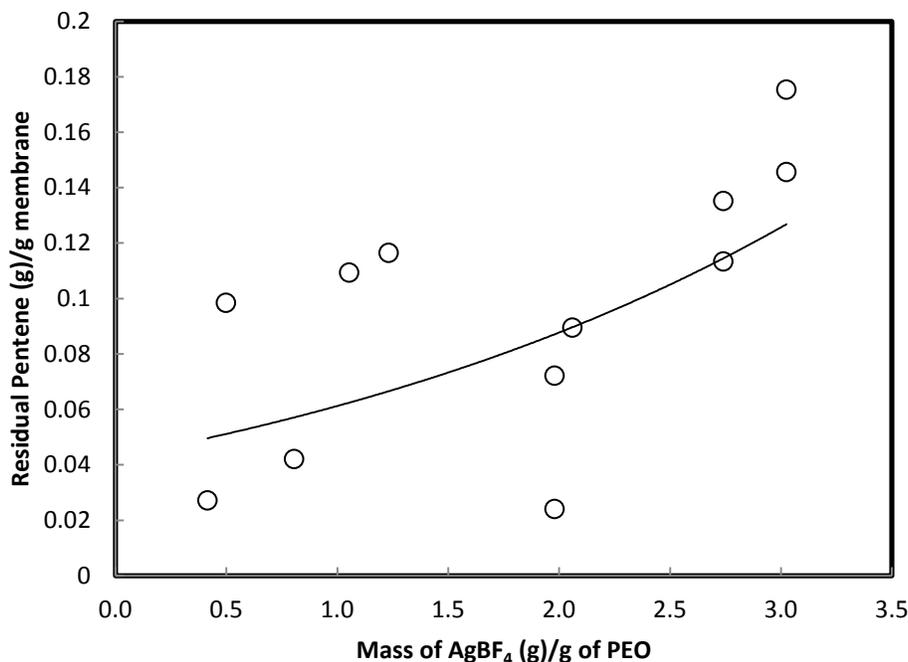


Figure 4-15: Fraction of Residual Pentene in Membrane After Desorption

The residual fraction increases with increasing silver salt concentration in the membrane. This follows logically from the idea that the pentene molecules are strongly sorbed to silver ions in the membrane and some of them will form permanent binding that will not break up when subjected to desorption to release olefin from the membrane. If there are more silver ions present, then more olefin molecules will be held in the membrane.

4.3.2. Calculating Diffusivity from Desorption Kinetic Data

The diffusivity of pentane and pentene in the membrane can be calculated by fitting the desorption kinetic data to a diffusion model (presented in Section 2.4). Figure 4-16 to Figure 4-39 show the fraction of sorbate pentane and pentene desorbed as a function of time. Note that the fractional desorption is defined here as the quantity of the penetrant desorbed divided by the total quantity of sorbate desorbed when desorption ceases to occur.

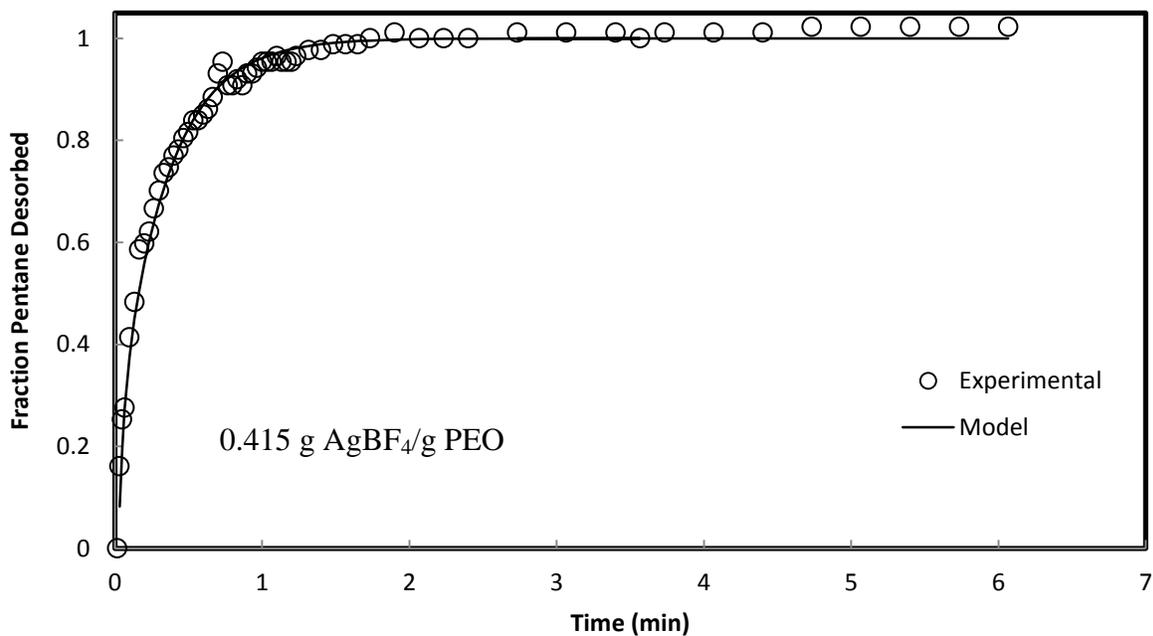


Figure 4-16: Modelling Desorption of Pentane from a Membrane with Silver Content 0.415 g AgBF₄/g PEO

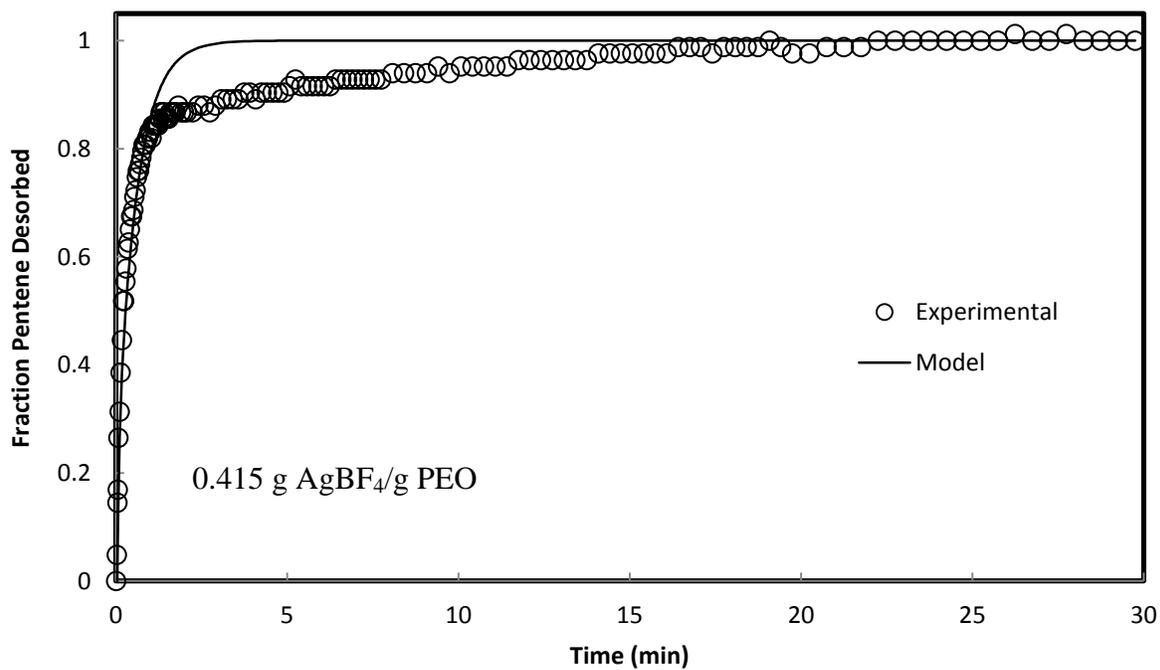


Figure 4-17: Modelling Desorption of Pentene from a Membrane with Silver Content 0.415 g AgBF₄/g PEO

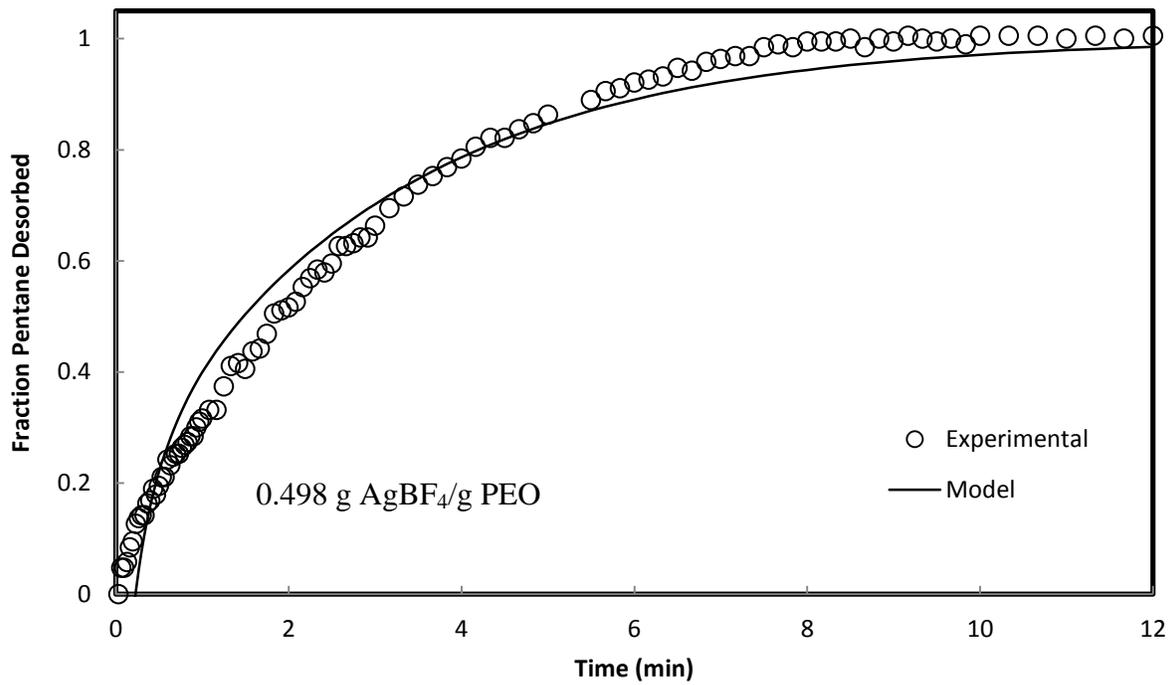


Figure 4-18: Modelling Desorption of Pentane from a Membrane with Silver Content 0.498 g AgBF₄/g PEO

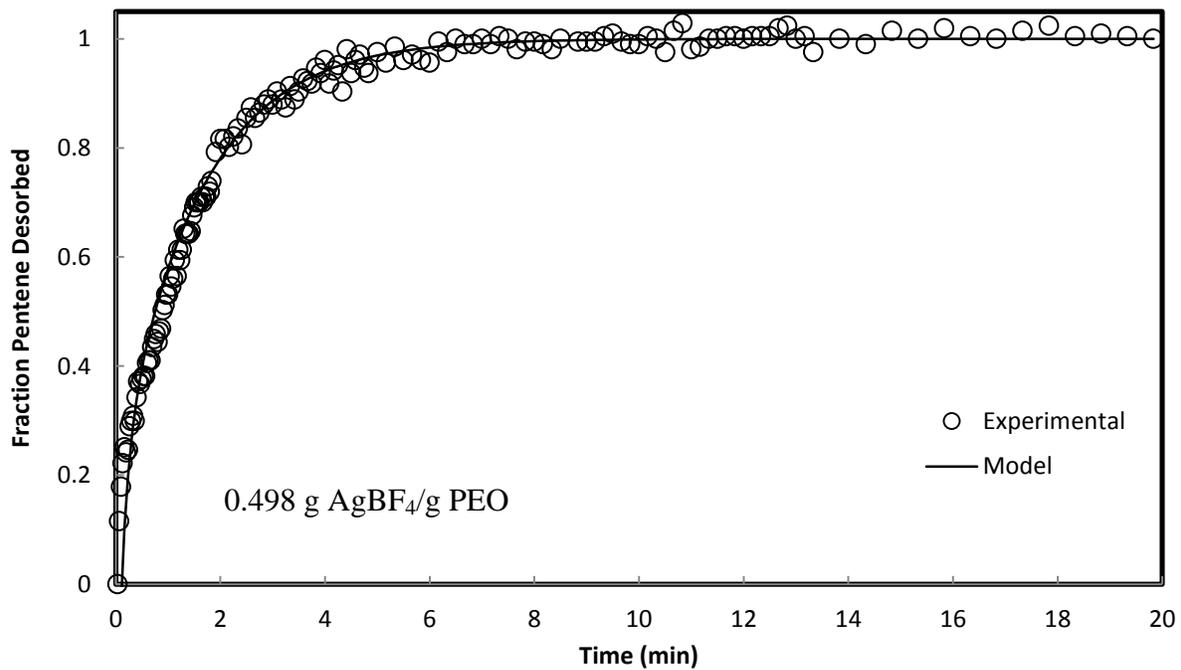


Figure 4-19: Modelling Desorption of Pentene from a Membrane with Silver Content 0.498 g AgBF₄/g PEO

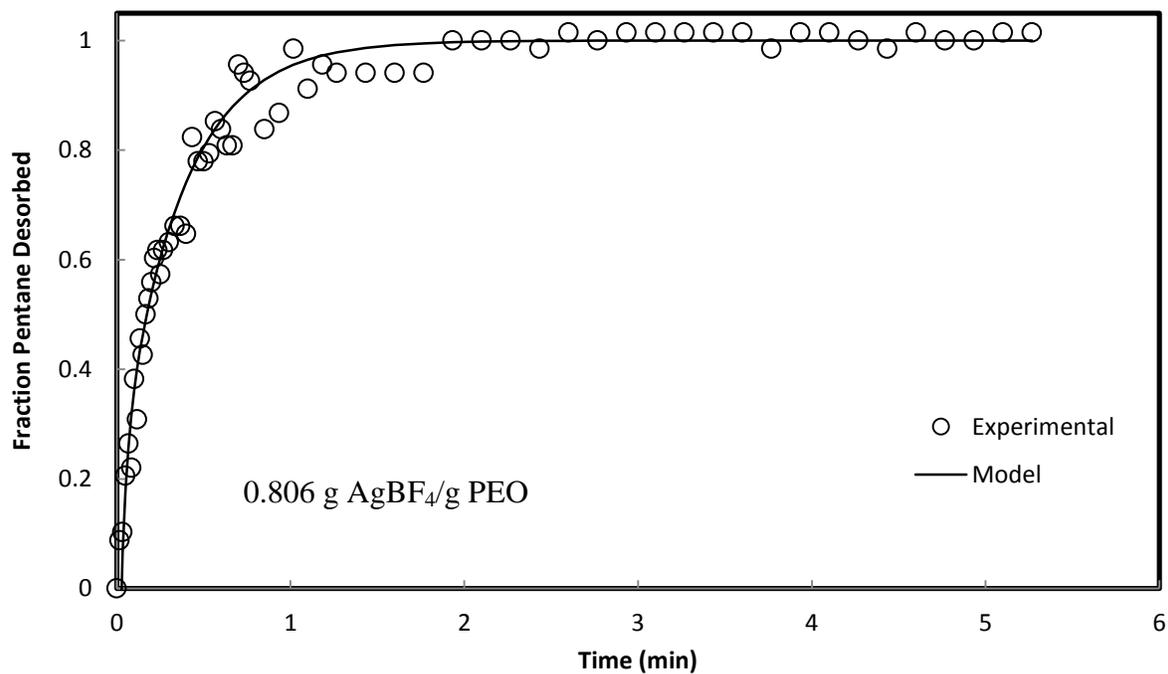


Figure 4-20: Modelling Desorption of Pentane from a Membrane with Silver Content 0.806 g AgBF₄/g PEO

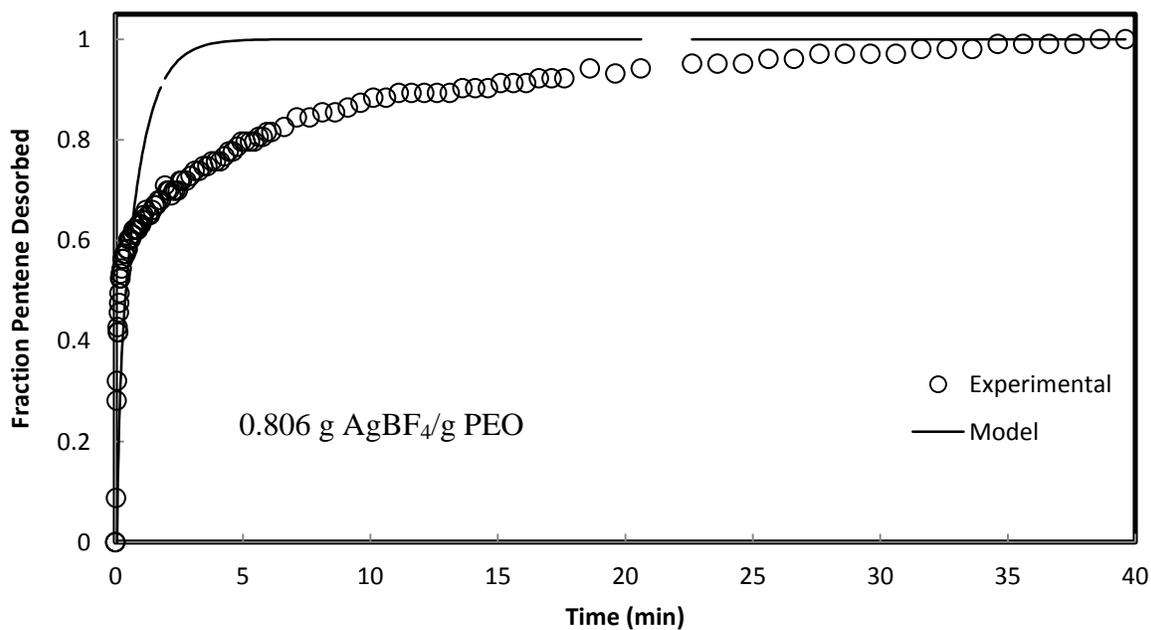


Figure 4-21: Modelling Desorption of Pentane from a Membrane with Silver Content 0.806 g AgBF₄/g PEO

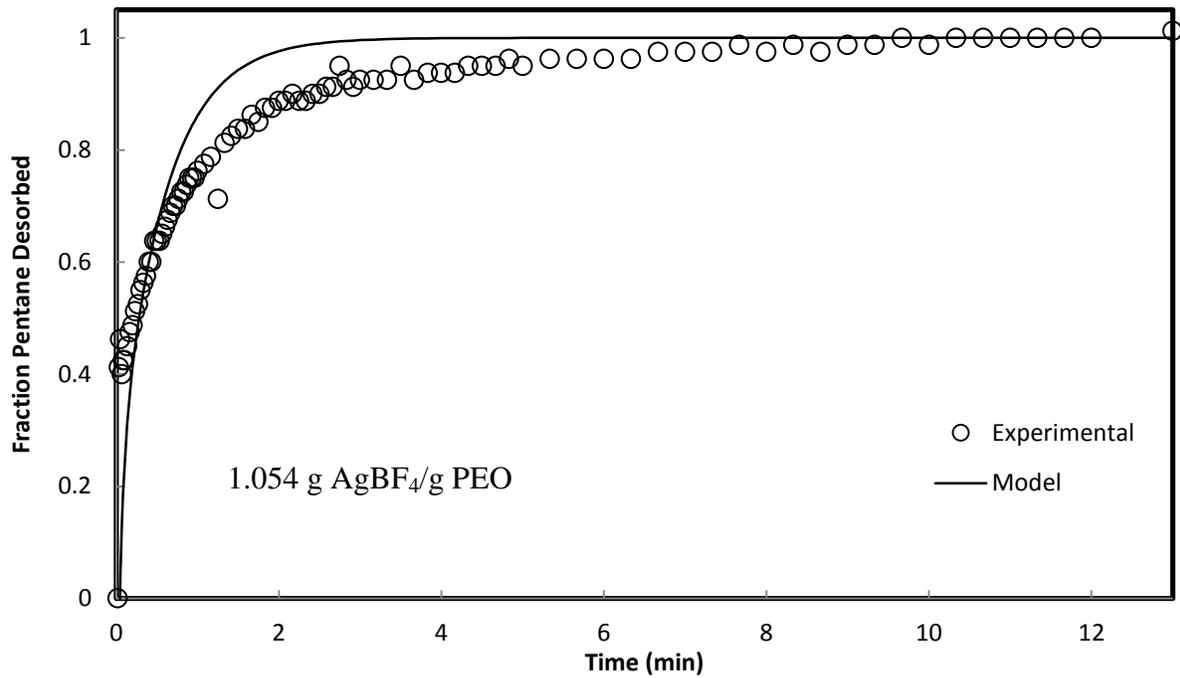


Figure 4-22: Modelling Desorption of Pentane from a Membrane with Silver Content 1.054 g AgBF₄/g PEO

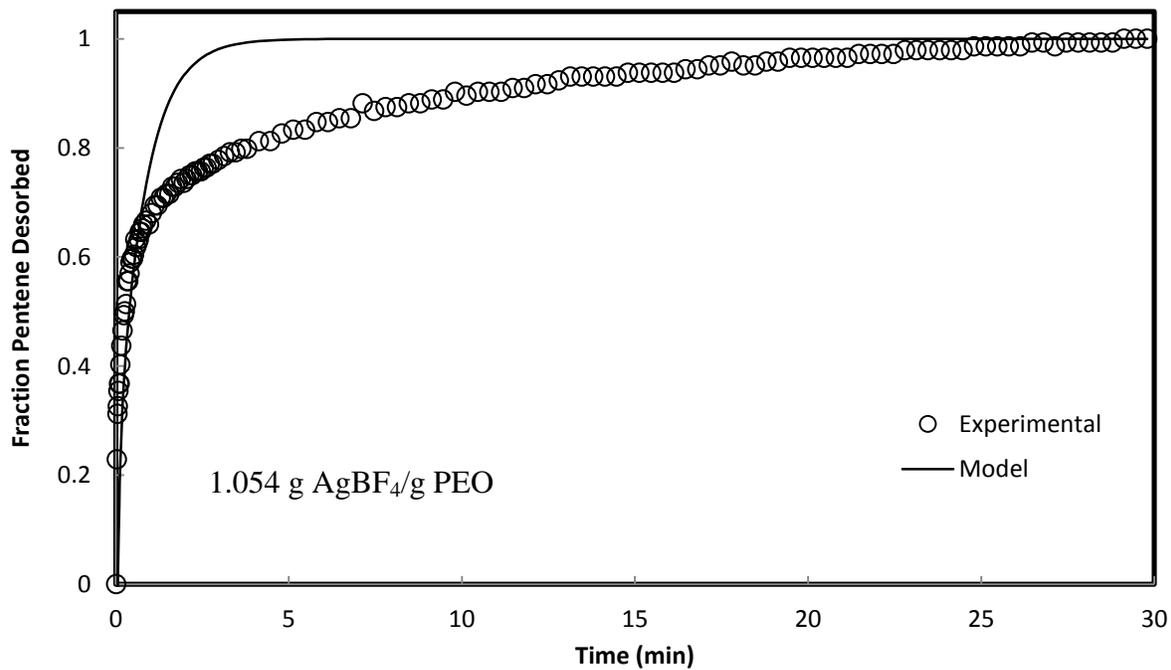


Figure 4-23: Modelling Desorption of Pentene from a Membrane with Silver Content 1.054 g AgBF₄/g PEO

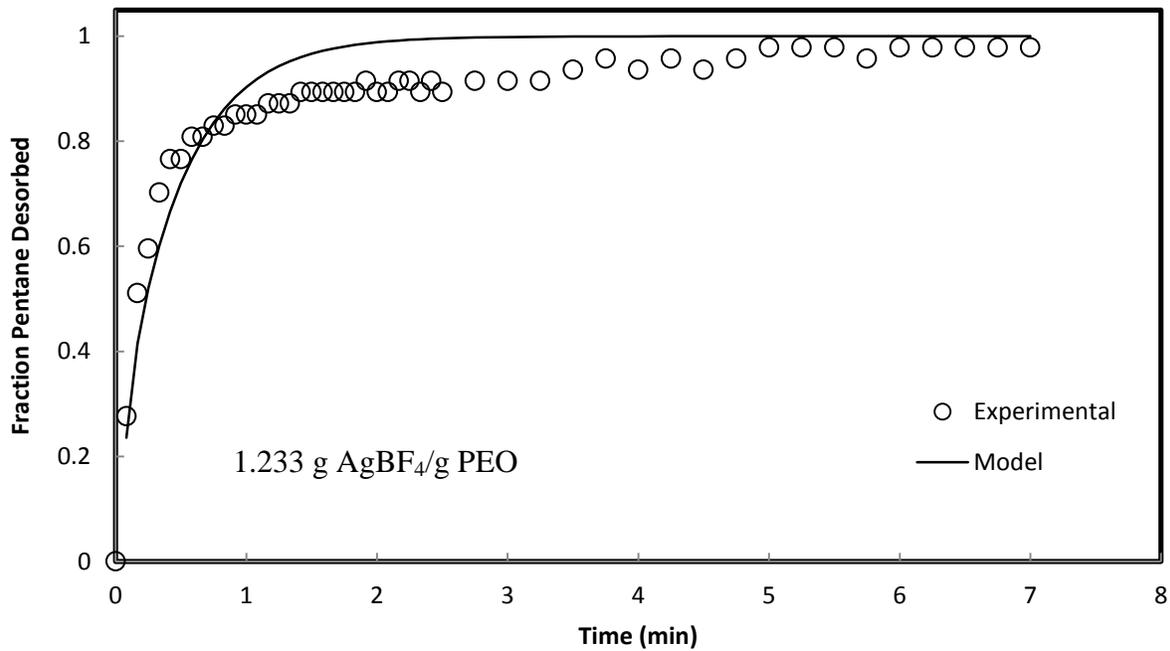


Figure 4-24: Modelling Desorption of Pentane from a Membrane with Silver Content 1.233 g AgBF₄/g PEO

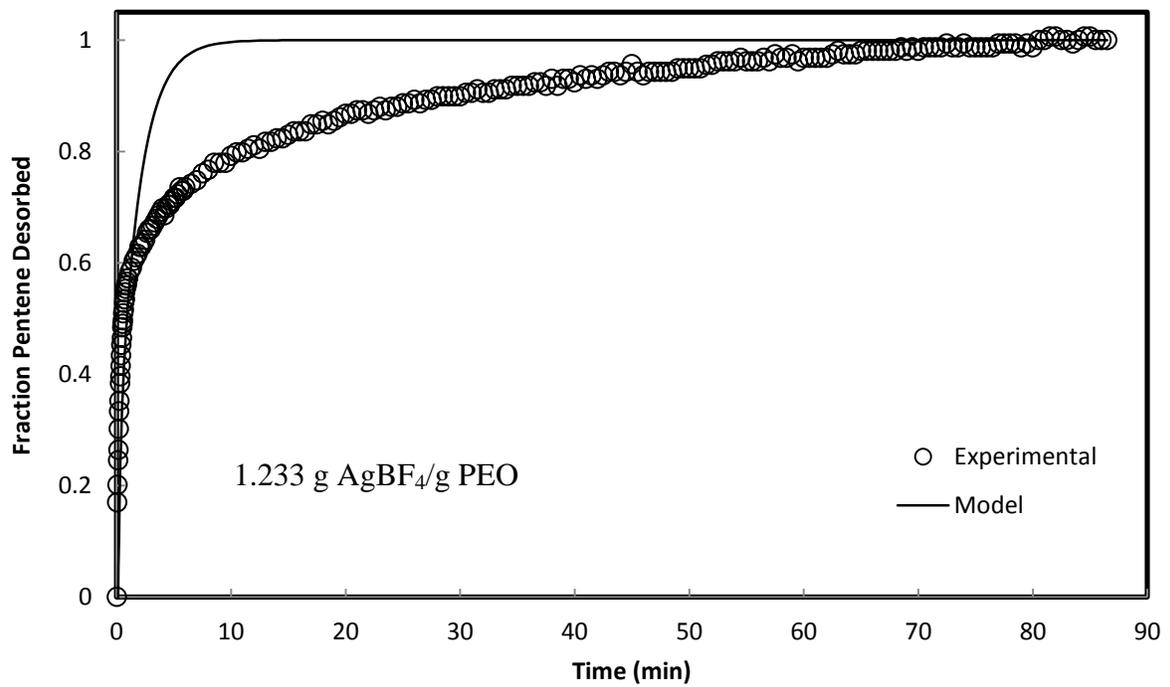


Figure 4-25: Modelling Desorption of Pentene from a Membrane with Silver Content 1.233 g AgBF₄/g PEO

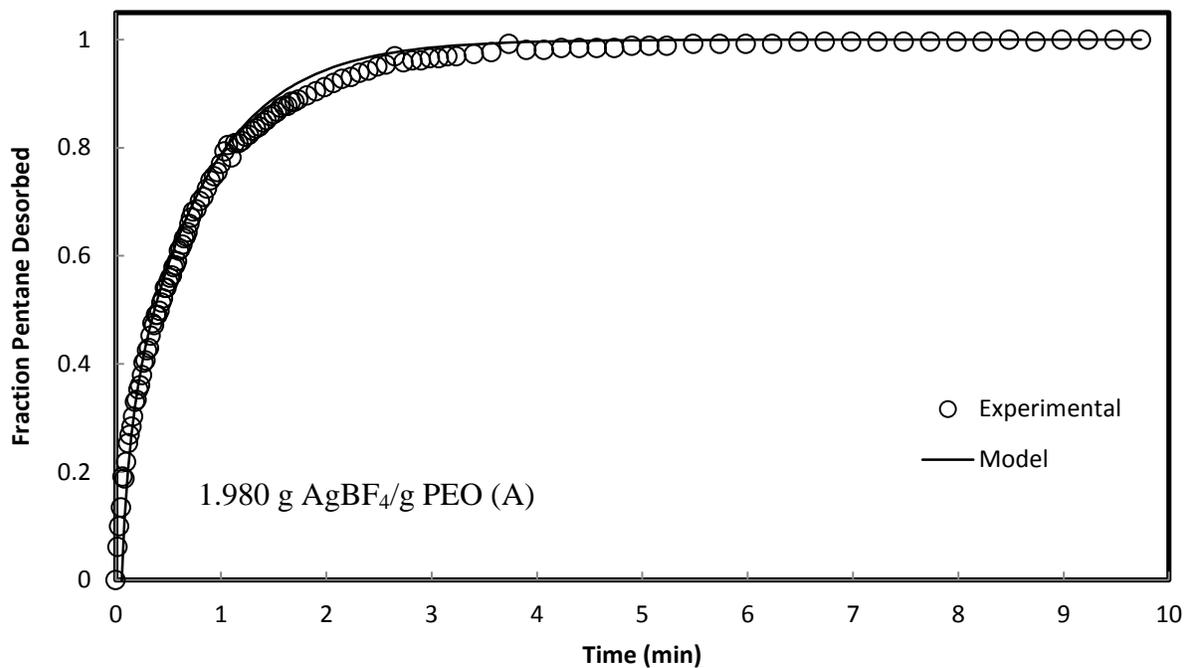


Figure 4-26: Modelling Desorption of Pentane from a Membrane with Silver Content 1.980 g AgBF₄/g PEO (Sample A)

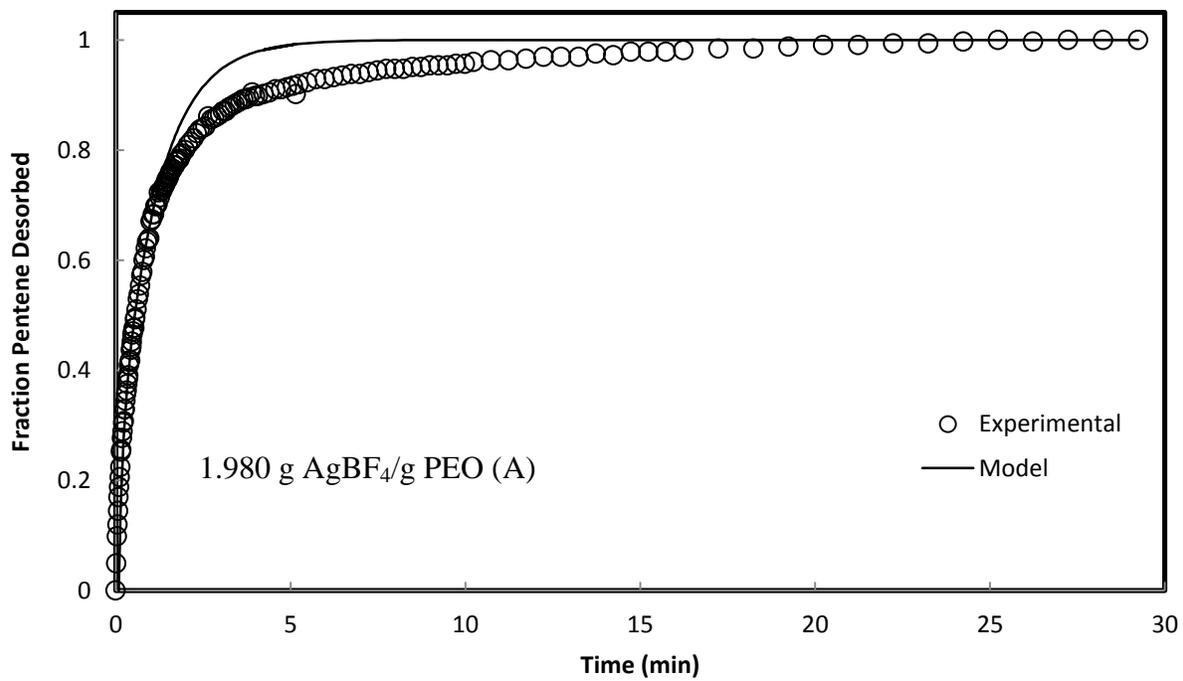


Figure 4-27: Modelling Desorption of Pentene from a Membrane with Silver Content 1.980 g AgBF₄/g PEO (Sample A)

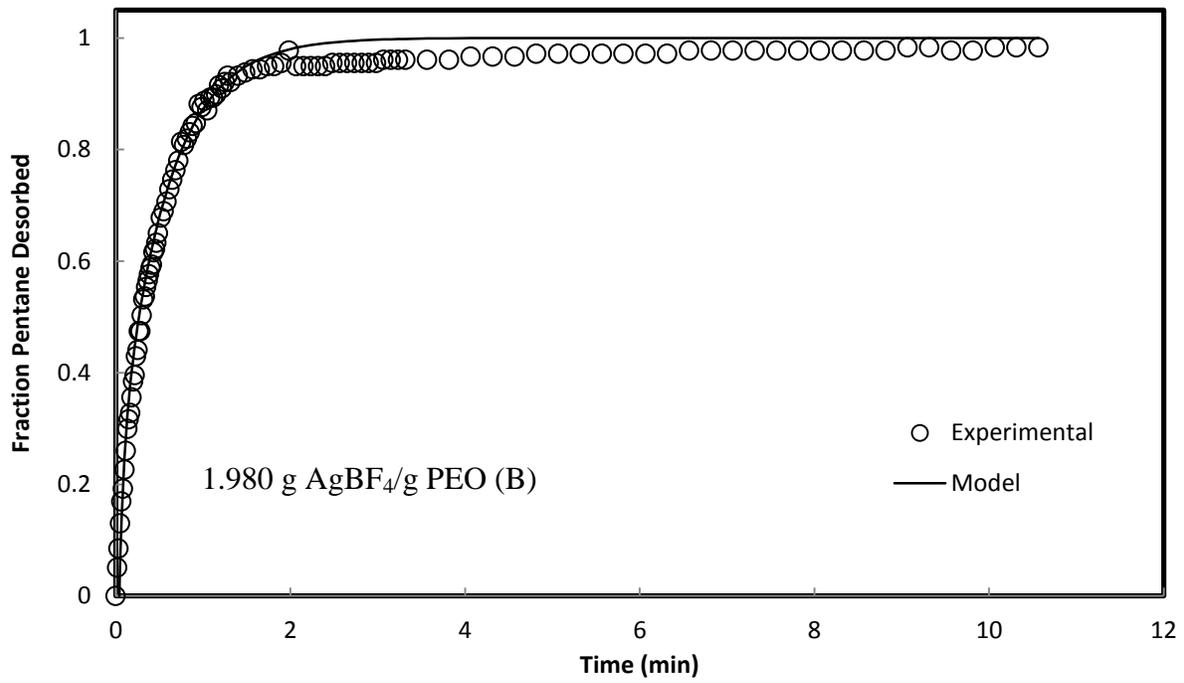


Figure 4-28: Modelling Desorption of Pentane from a Membrane with Silver Content 1.980 g AgBF₄/g PEO (Sample B)

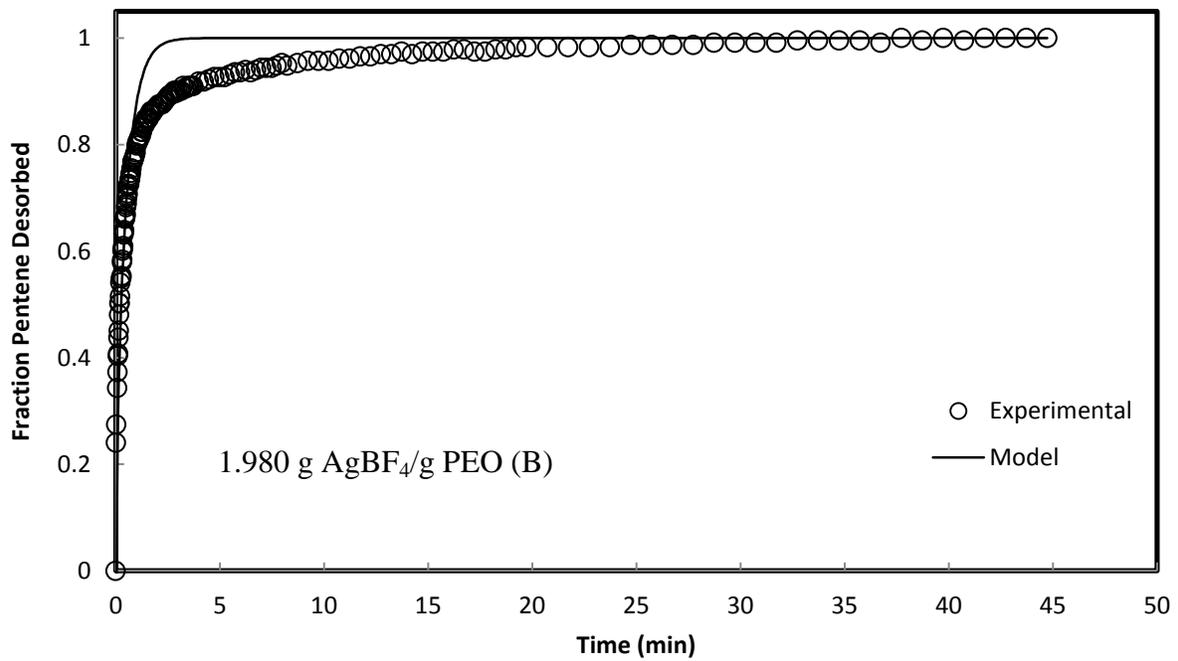


Figure 4-29: Modelling Desorption of Pentene from a Membrane with Silver Content 1.980 g AgBF₄/g PEO (Sample B)

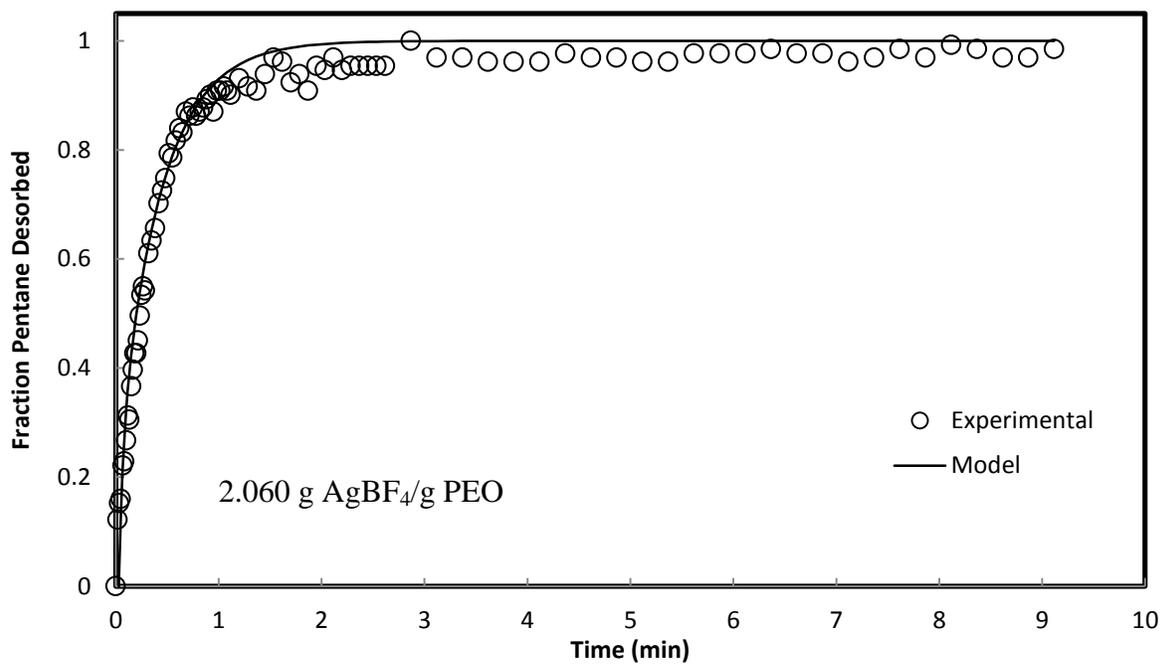


Figure 4-30: Modelling Desorption of Pentane from a Membrane with Silver Content 2.060 g AgBF₄/g PEO

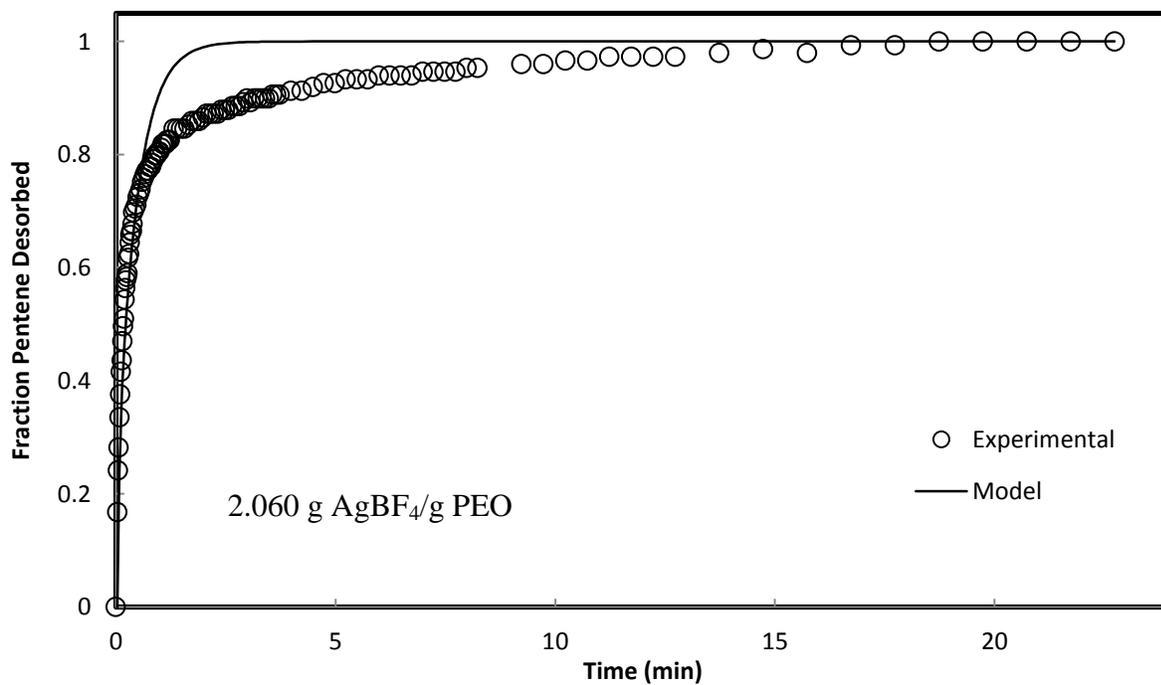


Figure 4-31: Modelling Desorption of Pentene from a Membrane with Silver Content 2.060 g AgBF₄/g PEO

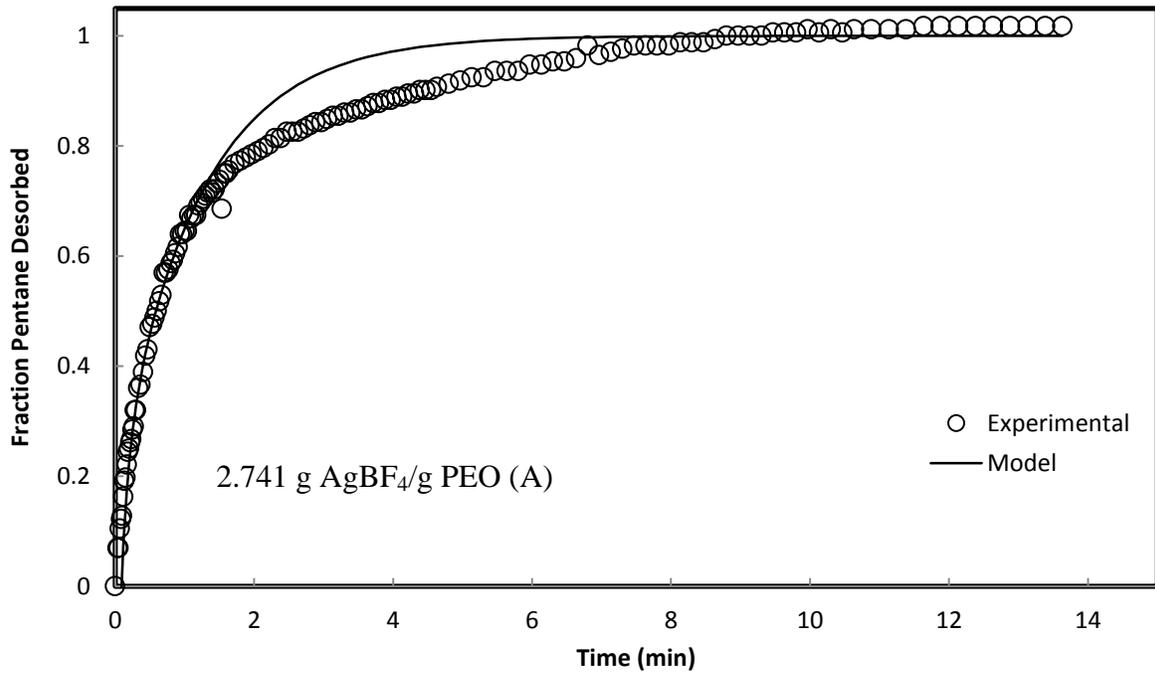


Figure 4-32: Modelling Desorption of Pentane from a Membrane with Silver Content 2.741 g AgBF₄/g PEO (Sample A)

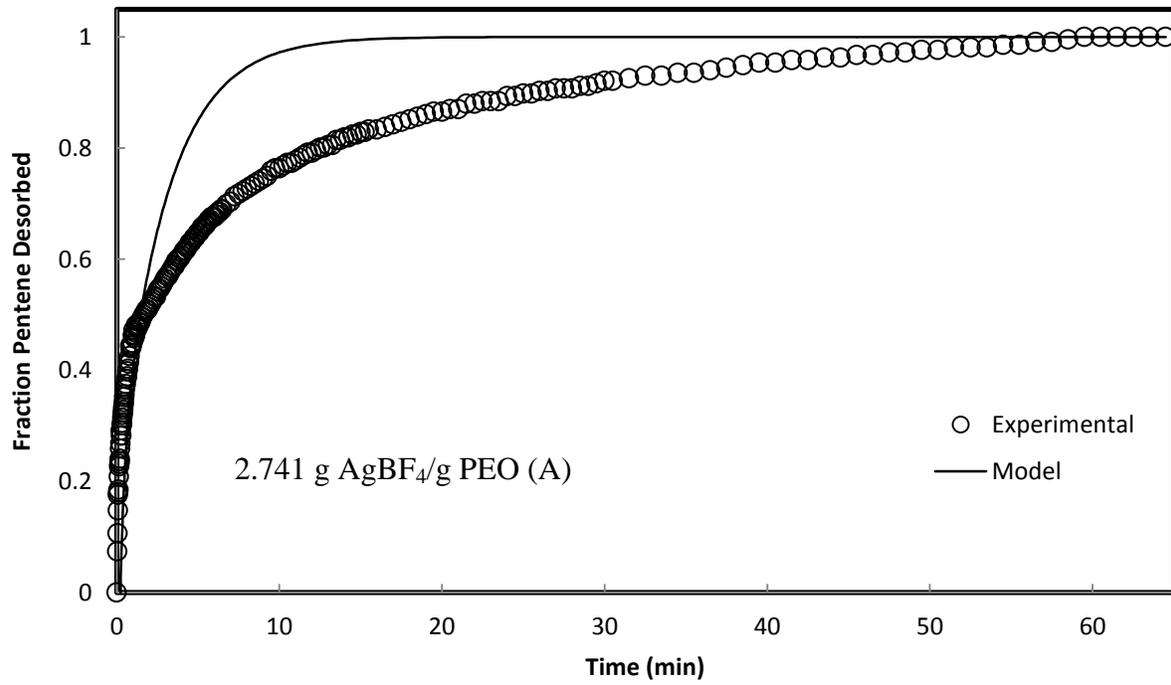


Figure 4-33: Modelling Desorption of Pentene from a Membrane with Silver Content 2.741 g AgBF₄/g PEO (Sample A)

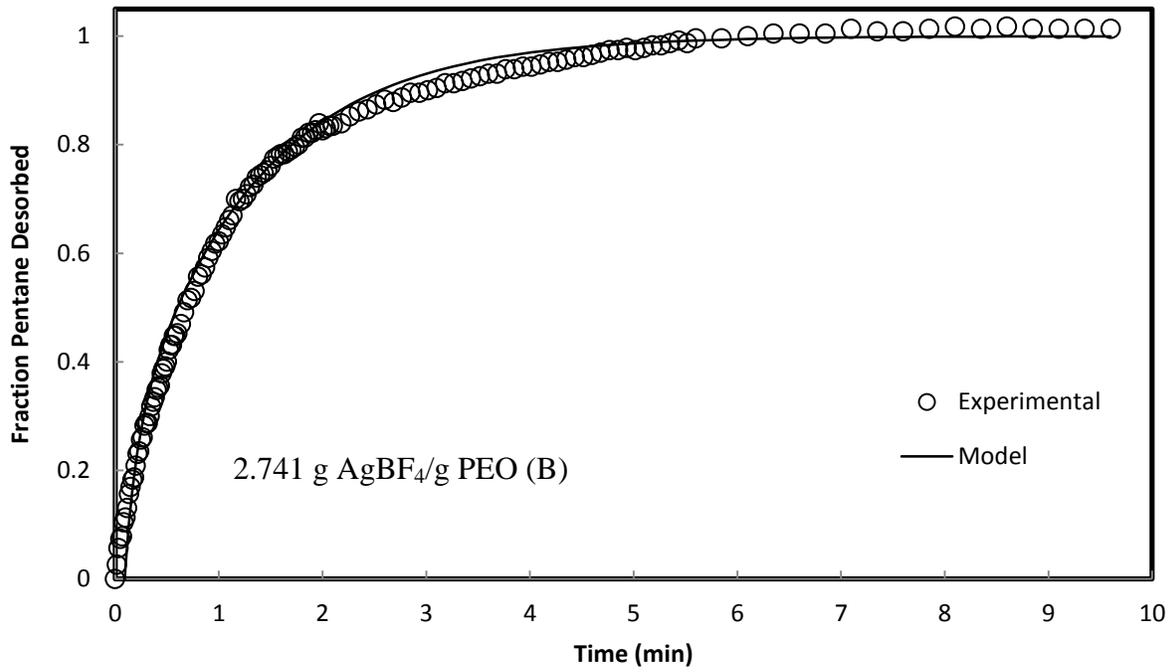


Figure 4-34: Modelling Desorption of Pentane from a Membrane with Silver Content 2.741 g AgBF₄/g PEO (Sample B)

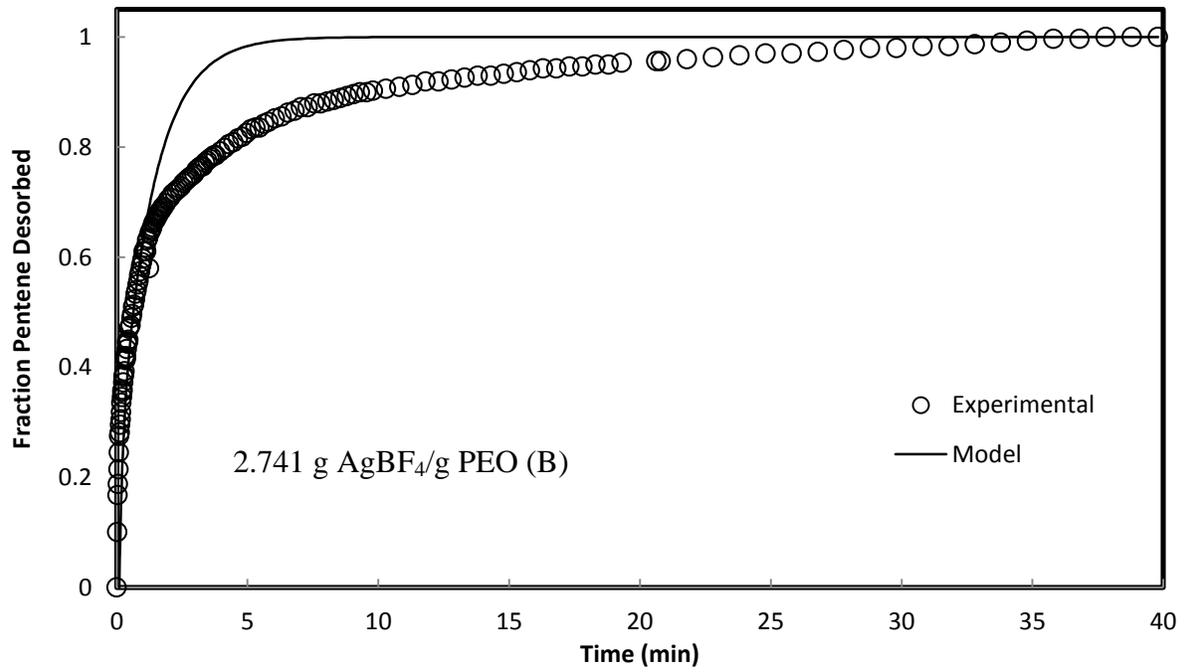


Figure 4-35: Modelling Desorption of Pentene from a Membrane with Silver Content 2.741 g AgBF₄/g PEO (Sample B)

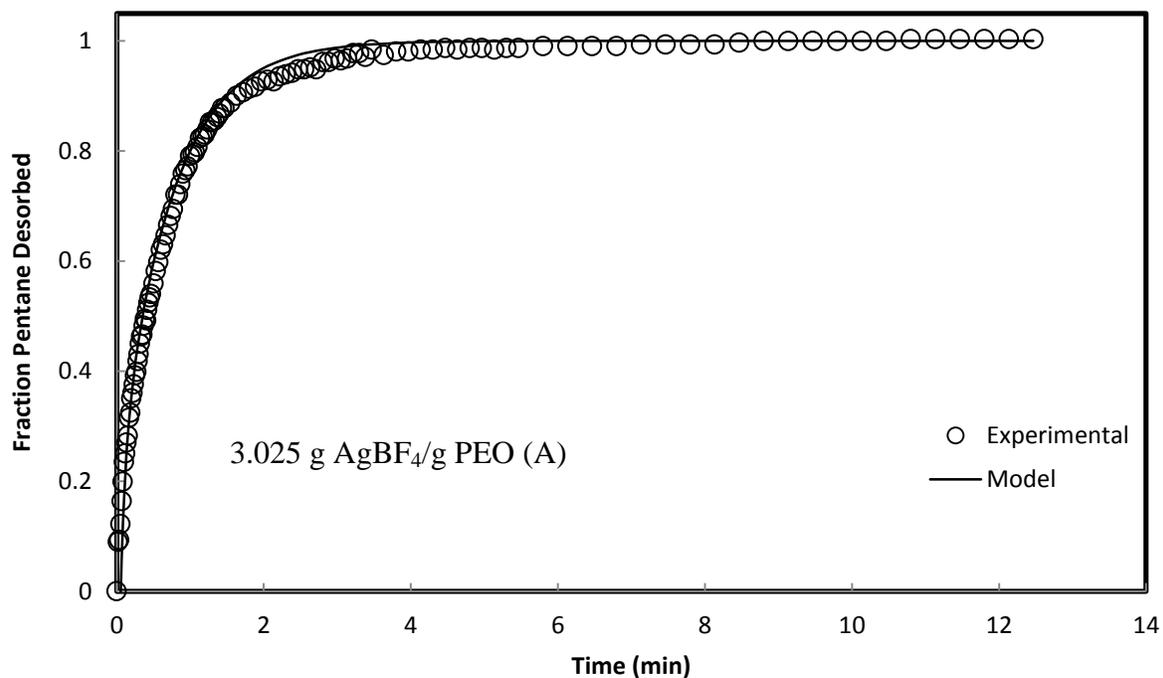


Figure 4-36: Modelling Desorption of Pentane from a Membrane with Silver Content 3.025 g AgBF₄/g PEO (Sample A)

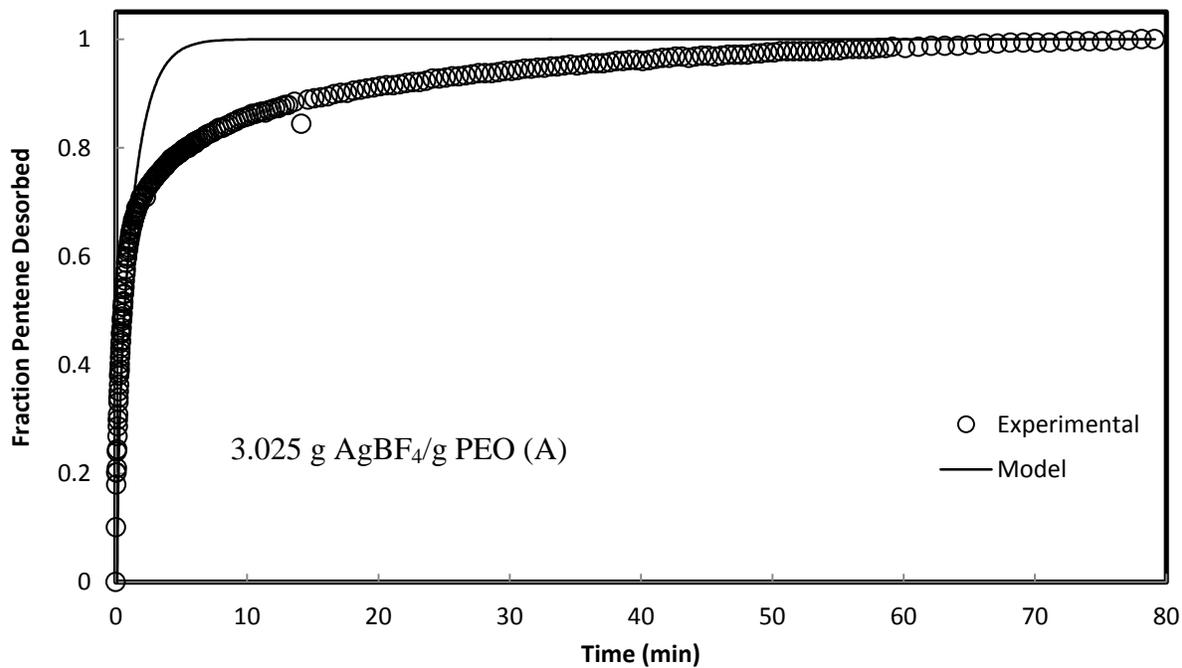


Figure 4-37: Modelling Desorption of Pentane from a Membrane with Silver Content 3.025 g AgBF₄/g PEO (Sample A)

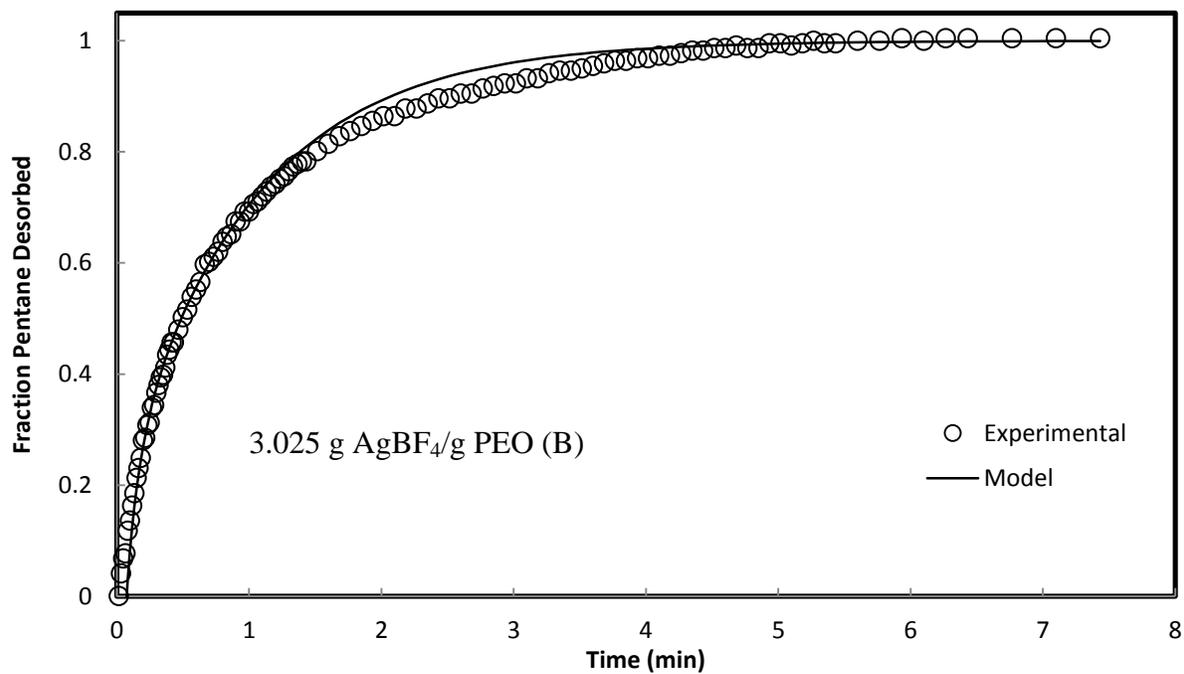


Figure 4-38: Modelling Desorption of Pentane from a Membrane with Silver Content 3.025 g AgBF₄/g PEO (Sample B)

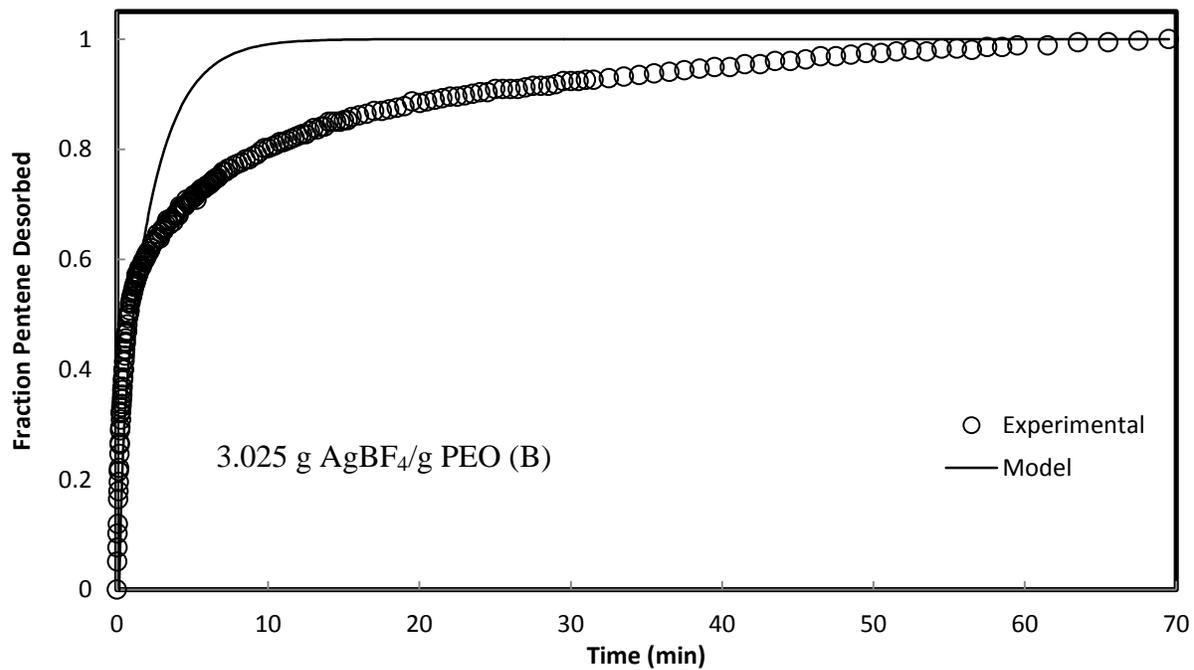


Figure 4-39: Modelling Desorption of Pentene from a Membrane with Silver Content 3.025 g AgBF₄/g PEO (Sample B)

The desorption kinetics data were fit to the diffusion model (Eq #3) and the diffusivities of pentene and pentane were determined. This was done by calculating the sum of squared errors (SSE) between the experimental data the model predictions, which were determined using Eq #3 truncated at $m=10$. The 'solver' function in Excel was used to vary the diffusivity value from an initial guess in order to determine the D value that minimizes the SSE for each case. The model calculations using the diffusivity so determined are also presented in Figure 4-16 to Figure 4-39 for comparisons. It can be seen that the pentane curves fit the model extremely well – in most cases achieving complete overlap with a very low SSE. However, the pentene desorption curves do not fit the model as smoothly. This is because the desorption of pentane in the membrane is purely based on solution-diffusion, with no chemical interaction between pentane and the membrane. Conversely, the deviation of pentene from the model curves suggests that the desorption process may not be diffusion controlled, and that there may be other factors in play, because of their chemical interactions. This is expected, as the silver ions interact with the olefin molecules via complexation. Therefore, not only do the silver ions hold some olefin molecules permanently or semi-permanently as shown by the aforementioned residual fraction, the release of the olefin molecules from the silver containing membranes may not be governed by the Fickian diffusion process alone because the complexation between the pentene molecules and the silver in the membrane needs to be broken in order for the pentene molecules to leave the membrane.

Figure 4-40 displays the observed diffusivity values determined by modelling the desorption kinetics as described above.

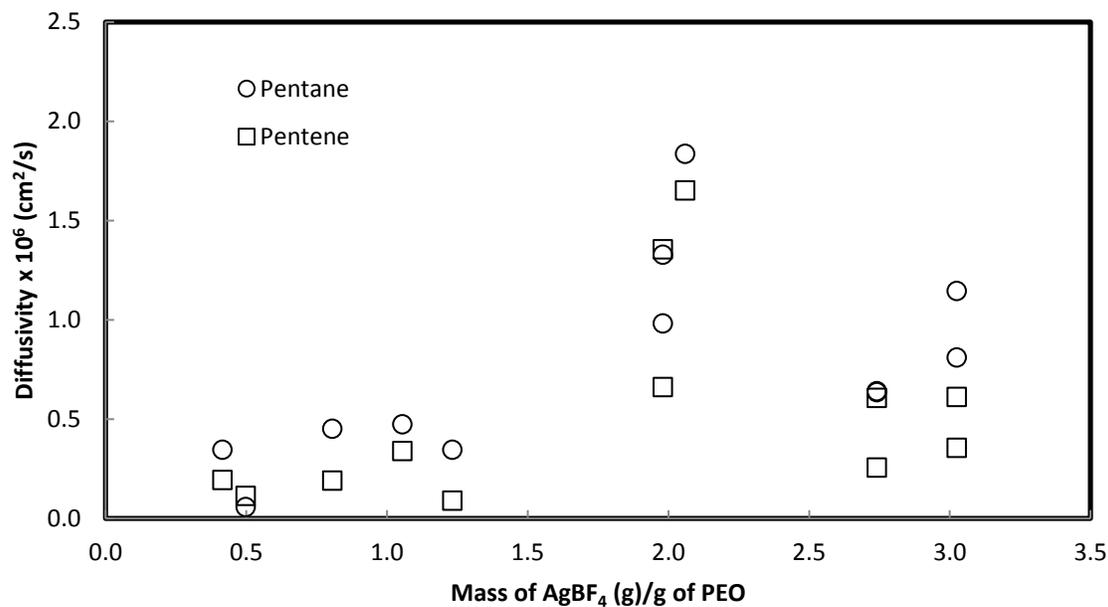


Figure 4-40: Diffusivities of Pentene and Pentane in PEO/AgBF₄ Membranes With Different Silver Contents

Comparing the observed diffusivities, pentane diffusivity is almost always slightly higher than the pentene diffusivity. As mentioned earlier, olefin forms complexes with silver in the membrane, and as a result, the complex needs to be broken in order for pentene to release from the membrane. This results in a slower diffusivity of pentene than pentane. Their diffusivity ratios are calculated and presented in Figure 4-41. Save for one data point, the values for diffusivity ratio are at or below one, indicating that pentane generally diffuses faster through the membrane than pentene. Apparently this suggests that the generally observed faster permeability of olefin molecules than paraffin molecules is primarily due to enhanced solubility of olefin in the membrane by the complexation with silver in the membrane. The silver facilitates olefin transport by enhancing olefin solubility in the membrane.

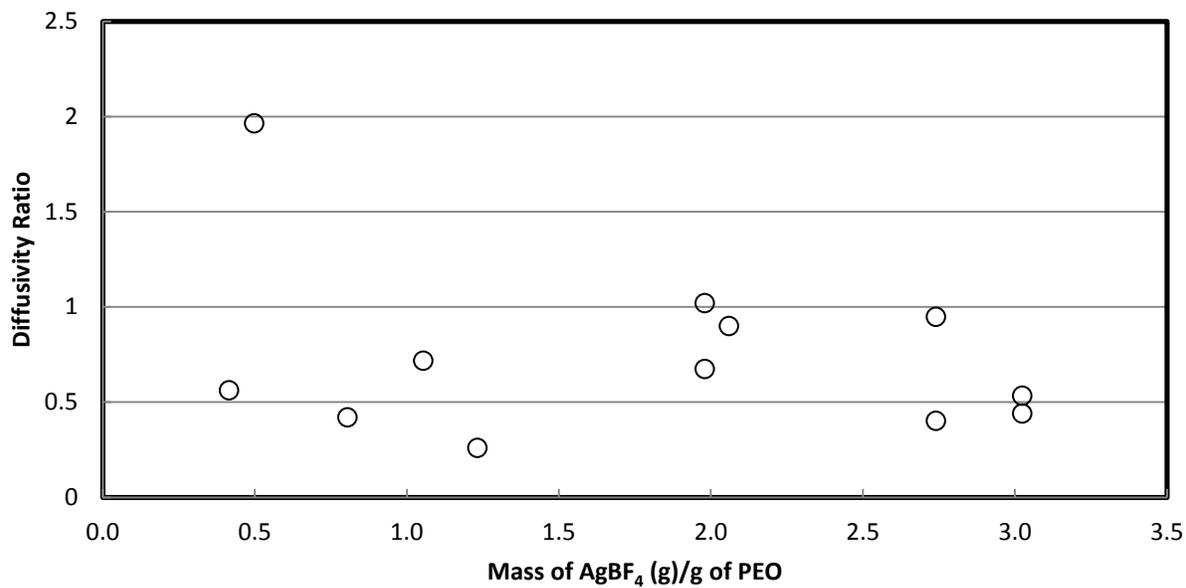


Figure 4-41: Diffusivity Ratio (Diffusivity of Pentene/Diffusivity of Pentane) in PEO/AgBF₄ Membranes With Different Silver Contents

It becomes clear that pentene movement in the membrane is not a simple physical diffusion process of the molecules. This may fit well with previous observations that suggest the silver ions hold onto the olefin molecules and release them more slowly than a pure diffusion process would dictate. This possibility will be explored further next.

4.3.3. Other Models for Pentene Desorption

Pentene desorption from PEO/AgBF₄ solid polymer electrolyte membranes does not fit the diffusion model as well as pentane desorption does. The diffusion model assumes no chemical interactions between the penetrant and the membrane. However, based on the lack of fit of the pentene desorption data with a diffusion model, as well as well as the known interaction between

silver ions and olefin molecules, one can conclude that the process is not governed by the physical diffusion only.

Other possible mechanisms include the pseudo-first order model, pseudo-second order model, or Elovich model. The general equations for each of these models are presented below:

$$\text{Pseudo-first order model: } \left(\frac{dq}{dt}\right) = k_1(q_e - q) \quad \text{Eq \#4}$$

$$\text{Pseudo-second order model: } \left(\frac{dq}{dt}\right) = k_2(q_e - q)^2 \quad \text{Eq \#5}$$

$$\text{Elovich model: } \left(\frac{dq}{dt}\right) = ae^{-\alpha q} \quad \text{Eq \#6}$$

where q represents the amount of pentene desorbed at time t normalized by the total amount of pentene desorbed at equilibrium. In other words q is the fraction of the maximum pentene desorption that has been achieved at time t . k_1 , k_2 , a and α are parameters characterizing the desorption system. Especially, the first and second order equations take into account the chemical interactions between the sorbate and membrane.

The pseudo-first order and pseudo-second order equations can be directly integrated and linearized to give equations #7 and #8. The boundary conditions applied were $q_t = 0$ @ $t = 0$ and $q_t = q_t$ @ $t = t$, where q_e represents the amount of pentene desorbed at equilibrium.

$$\text{Pseudo-first order model: } \ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 t \quad \text{Eq \#7}$$

$$\text{Pseudo-second order model: } \frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad \text{Eq \#8}$$

The Elovich model can be integrated and linearized as well, and by assuming that $akt \gg 1$ and applying the same boundary conditions as above, equation #9 results (Ho and McKay, 2002).

$$\text{Elovich model: } q_t = \alpha \ln(\alpha x) + a \ln(t) \quad \text{Eq \#9}$$

Therefore, by plotting $\ln\left(1 - \frac{q_t}{q_e}\right)$ vs t , t/q vs t , and q vs $\ln(t)$, the data can be compared to the three models (Ho and McKay, 2002). One set of these plots, for a membrane containing 1.233 g AgBF₄/g PEO, is presented in Figure 4-42 to Figure 4-44. Similar results can also be found for other membranes containing different silver contents. For instance, the desorption data for the membrane containing 1.890 g AgBF₄/g PEO as compared to the 3 models are shown in Figure 4-45 to Figure 4-47. For illustration purposes only, membranes with mid-range silver contents (i.e., 1.233 and 1.890 g AgBF₄/g PEO) were chosen as representatives for the evaluation of the pentene desorption mechanism.

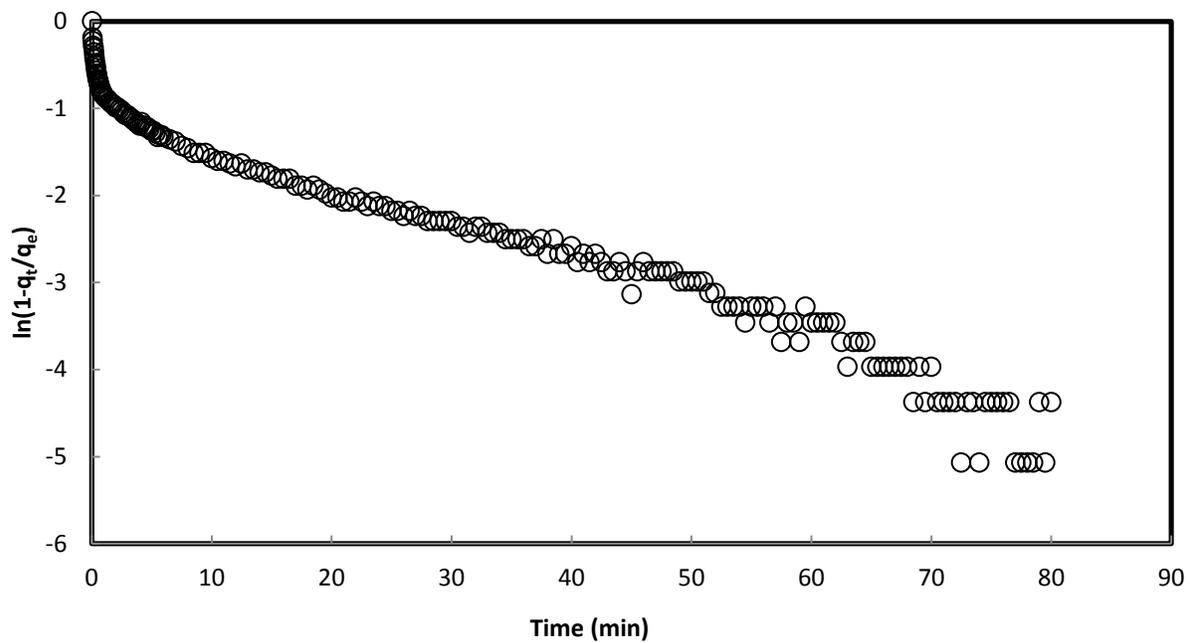


Figure 4-42: Desorption of Pentene from Membrane with Silver Content 1.233 g AgBF₄/g PEO – Testing 1st Order Model

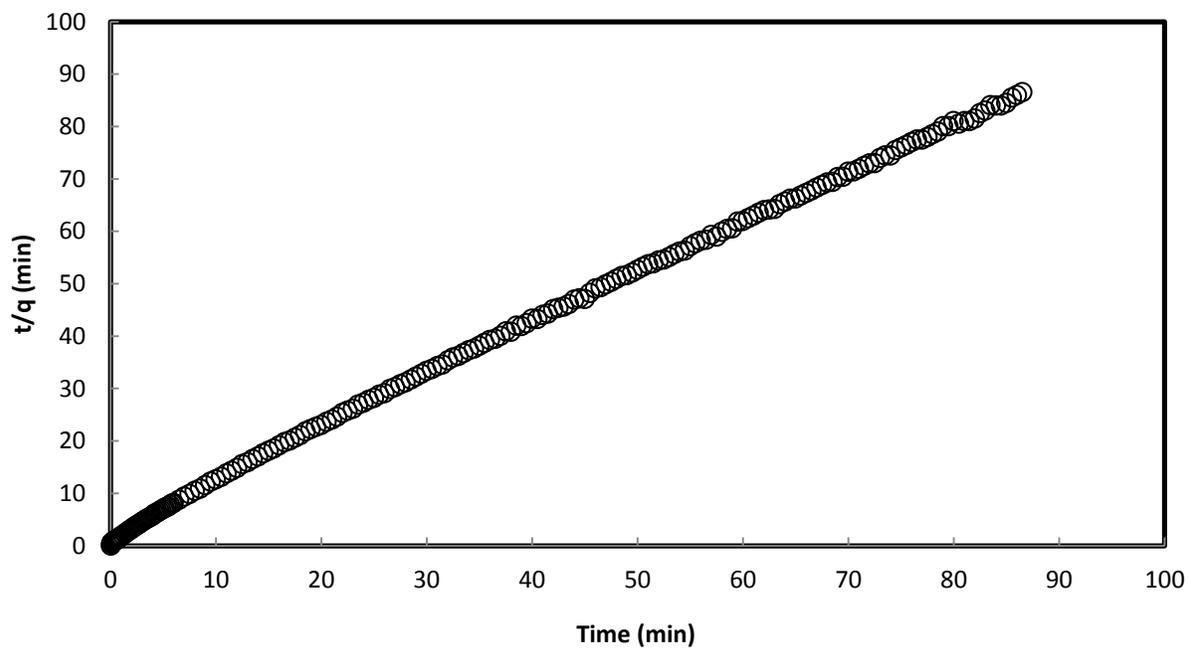


Figure 4-43: Desorption of Pentene from Membrane with Silver Content 1.233 g AgBF₄/g PEO – Testing 2nd Order Model

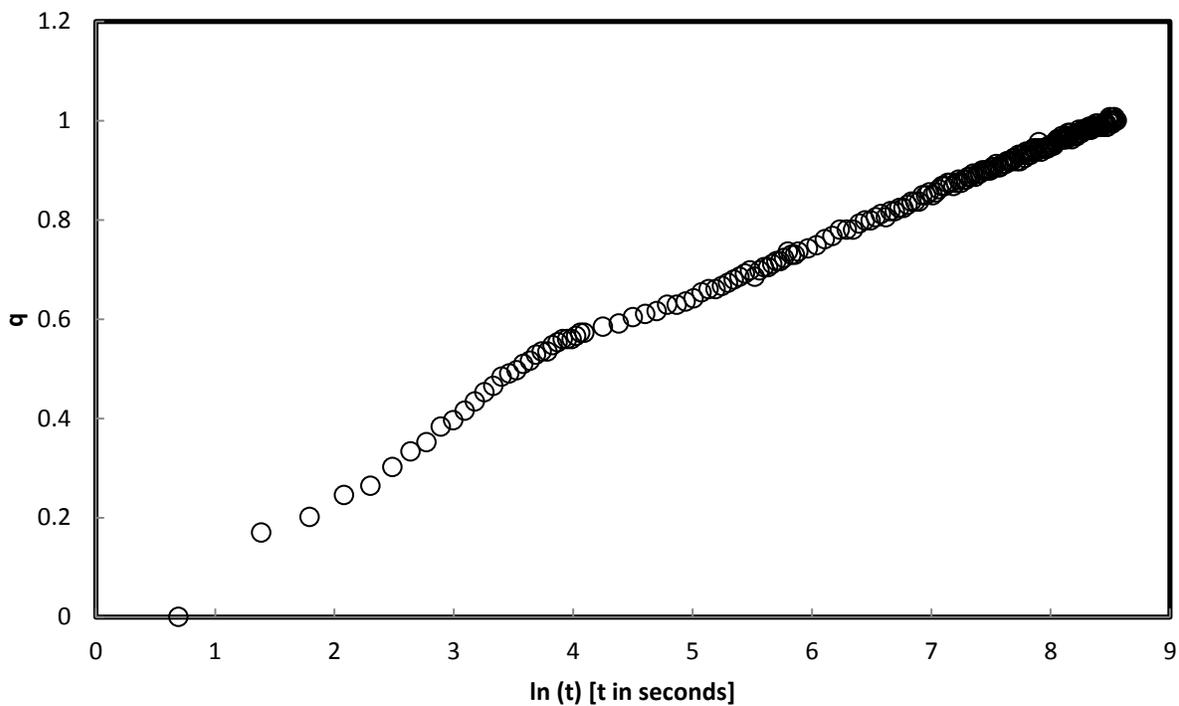


Figure 4-44: Desorption of Pentene from Membrane with Silver Content 1.233 g AgBF₄/g PEO – Testing Elovich Model

The pseudo-second order kinetic model appears to give a good fit, while the first order and Elovich plots are curved. This demonstrates that the interaction between silver ions and olefin molecules in this system most likely follows pseudo-second order kinetics (Eq #5), meaning the rate of olefin desorption is proportional to the square of the amount of pentene remaining in the membrane. It should be mentioned that the fractional desorption amount is based on the total desorbed amount, excluding the portion of pentene permanently trapped in the membrane.

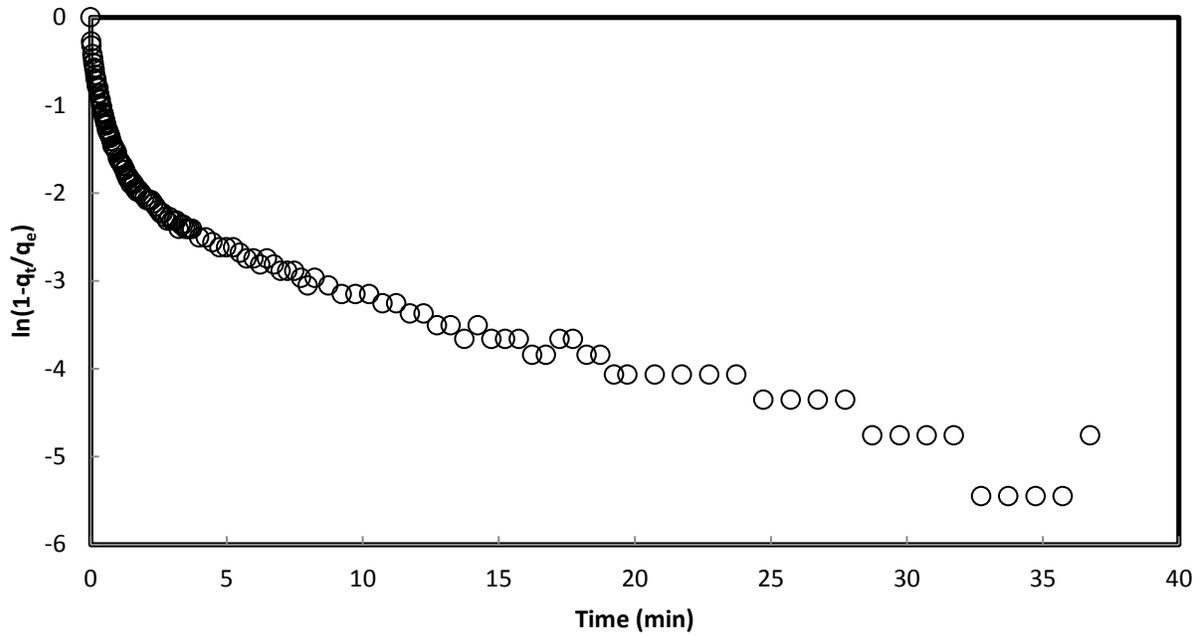


Figure 4-45: Desorption of Pentene from Membrane with Silver Content 1.890 g AgBF_4/g PEO – Testing 1st Order Model

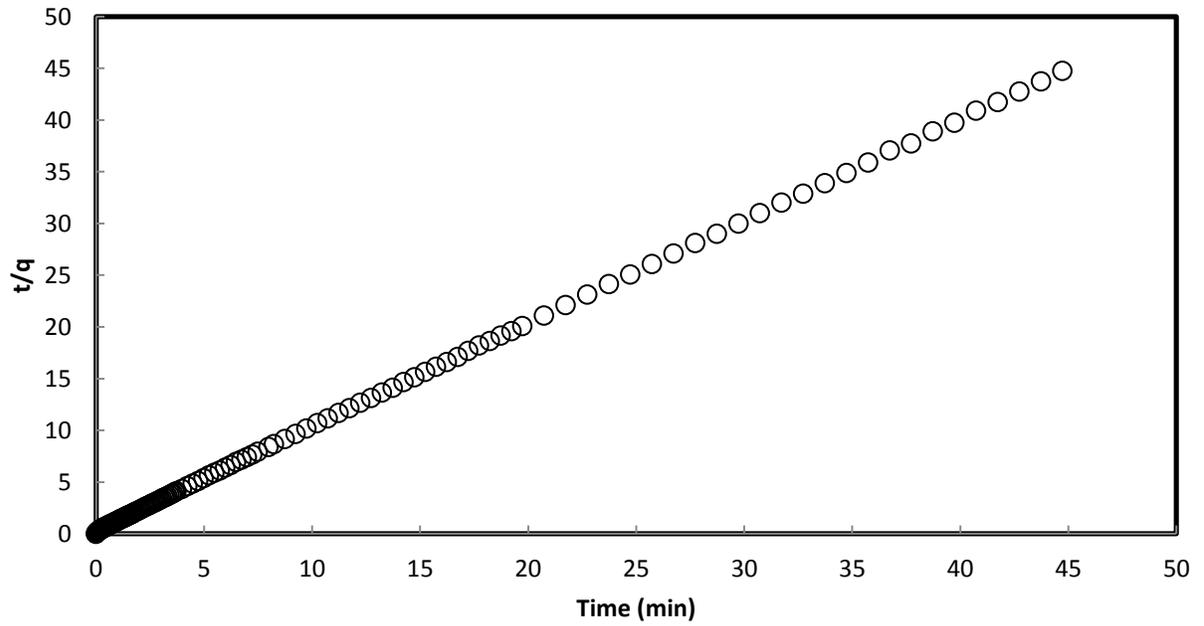


Figure 4-46: Desorption of Pentene from Membrane with Silver Content 1.890 g AgBF_4/g PEO – Testing 2nd Order Model

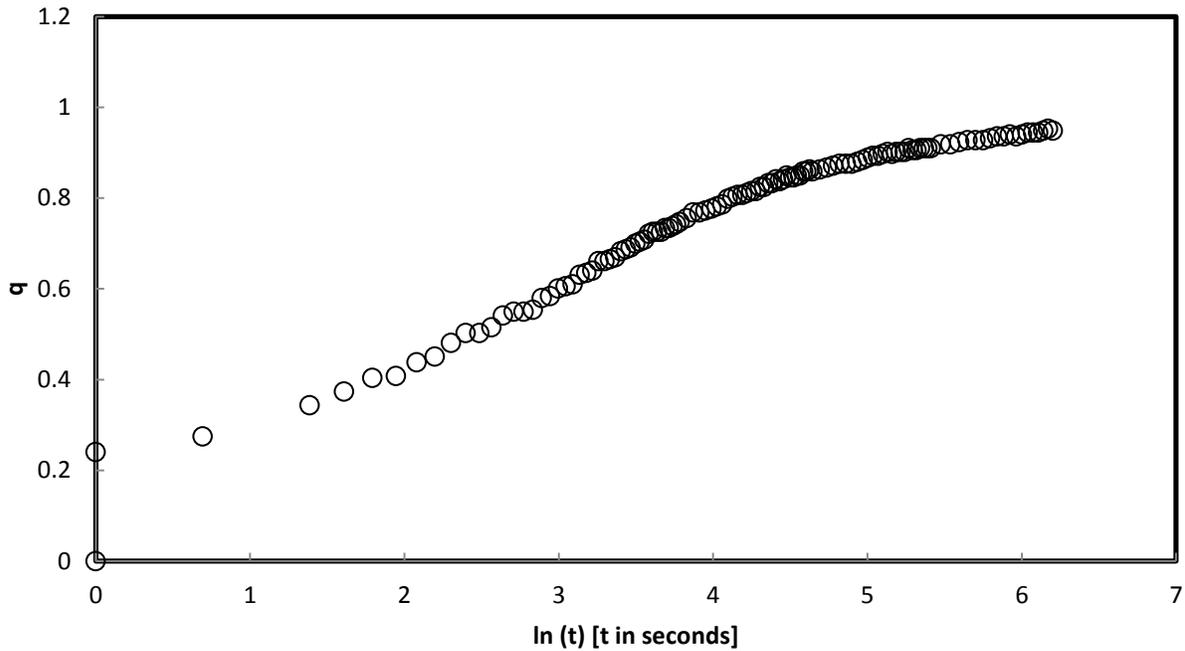


Figure 4-47: Desorption of Pentene from Membrane with Silver Content 1.890 g AgBF₄/g PEO – Testing Elovich Model

This shows that, the process of pentene desorption from the membranes is not diffusion controlled, but limited by a pseudo-second order reaction. The rate of pentene desorption is proportional to the square of the fraction of pentene remaining in the membrane. This behaviour can be observed in the data, as the pentene desorption rate is very fast initially when the fraction of pentene remaining in the membrane is high. However, beyond that range, the rate of pentene desorption slows abruptly. Figures 4-33, 4-35 and 4-37, for example, display this behaviour clearly. The constant in the pseudo-second order model is the proportionality constant between the square of the fraction of pentene remaining in the membrane and the desorption rate (units [=] min⁻¹). This result also implies that the diffusion of pentene away from the membrane

surface is fast. It must be faster than the desorption reaction, because the process is governed by a pseudo-second order reaction mechanism and not by diffusion.

4.4. General Discussion

This study investigates the permeation, sorption, and desorption behaviour of a C5 olefin and paraffin in AgBF₄/PEO polyelectrolyte membranes. The membrane is observed to behave very differently towards pentene and pentane, in both liquid and vapour forms, as to the gaseous C2 and C3 olefins and paraffins.

The equilibrium sorption uptake of pentene is in the range of 0.15 to 1.60 g pentene/g membrane, depending on the silver content in the membrane. This uptake is much higher than propylene uptake (maximum value of 0.084 g propylene/g membrane) reported in literature for a membrane made of the same materials (Sunderrajan et al., 2001).

In terms of membrane stability, olefin molecules tend to have a negative impact on membrane performance. In this study, liquid pentene caused membrane failure. Gaseous olefin molecules have been shown to have irreversible negative effects on the membrane performance, which is noticeable within a short period of time. It appears that the damage to the membrane caused by the liquid olefin is more severe than that caused by the gaseous olefin. This is primarily due to the increased sorption uptake of liquid olefin in the membrane. When the membrane sorbs the liquid olefin molecules, it results in swelling of the membrane, and some of the sorbed olefin molecules form permanent bonds with the silver in the membrane.

5. Conclusions

The threshold silver concentration in the membrane, at which the pentene/pentane permeability ratio begins to increase, appears to be ~ 2.5 g AgBF₄/g PEO. Beyond this concentration, the silver ions in the membrane are close enough together to allow hopping of pentene molecules from site to site across the membrane, thereby transporting pentene molecules across the membrane.

Increasing silver concentration in the membrane significantly decreases the stable operating period of the membrane. For example, increasing the PEO:AgBF₄ ratio from 1:1 to 3:1 decreased the membrane lifetime from 30 to 2 hours. This is found to be correlated to the permanent or semi-permanent bonds between pentene molecules and the silver in the membrane.

The maximum sorption for pentene and pentane was shown to occur at a moderate silver concentration in the membrane. At all silver salt concentrations tested, the pentene sorption was higher than the pentane sorption. This is in agreement with physical reasoning that silver ions in the membrane have a strong affinity to unsaturated olefin molecules.

By fitting the desorption kinetic data of pentene and pentane from the membrane to a diffusion-based model, the effective diffusivity of the penetrant was determined. Pentane was shown to have a generally higher diffusivity than that of pentene. However, the observed pentene

diffusivity is not be the true diffusivity, as the desorption rate is not truly governed by a simple diffusion mechanism.

It was found that a fraction of pentene sorbed in the membrane was held permanently or semi-permanently by the silver ions in the membrane, and this portion of the pentene sorbate could not be released from the membrane when subjected to desorption at ambient conditions. Pseudo-2nd order kinetics was shown to describe the pentene release from the membrane well for the portion that could be desorbed, due to the interaction of the pentene with the silver ions in the membrane.

6. Recommendations

Based on the present study, the following are recommended for further studies:

(1) Investigate possible methods to improve membrane stability. Alternative polymers or polymer blends should be explored in order to minimize membrane swelling and therefore prevent membrane failure. Such polymers should be able to form polymer electrolytes with AgBF_4 , which has been shown to complex olefin molecules and can be used as a facilitating agent for olefin transport across the membrane.

(2) Once the membrane stability is improved, further directions of inquiry should be to:

(A) Test the permeation, sorption, and desorption of a pentene/pentane mixture using the polymer electrolyte membranes. From literature it is evident that the behaviour of olefins and paraffins in polymer electrolyte membranes changes when they are together.

(B) Test the permeation, sorption, and desorption of olefin/paraffin pairs of different chain lengths using the polymer electrolyte membranes. Observing the behaviour of butene/butane and hexene/hexane systems, for example, will give better insight into the effect of chain length of the permeants on their membrane interactions.

References

M. Azhin, T. Kaghazchi and M. Rahmani, "A review on olefin/paraffin separation using reversible chemical complexation technology," *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY*, 14 (2008) 622–638.

Baker, R.W. *Membrane Technology and Applications*. 2nd ed. John Wiley & Sons; 2004.

J. Burgess and P. J. Steel, "Is the silver–alkene interaction a useful new supramolecular synthon," *COORDINATION CHEMISTRY REVIEWS*, 255 (2011) 2094–2103.

P. Chilukuri, K. Rademakers, K. Nymeijer, L. Van der Ham and H. Van den Berg, "Propylene/Propane Separation with a Gas/Liquid Membrane Contactor Using a Silver Salt Solution," *INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH*, 46 (2007) 8701-8709.

H. W. Choi, D. B. Kim, D. K. Choi, B. S. Ahn, H. G. Kim, H. S. Kim, C. H. Lee and J. Y. Sung, "Highly selective facilitated transport membranes for isoprene/n-pentane separation," *JOURNAL OF MEMBRANE SCIENCE*, 279 (2006) 403-409.

T.-S. Chung, L. Y. Jiang, Y. Li and S. Kulprathipanja, "Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation," *PROGRESS IN POLYMER SCIENCE*, 32 (2007) 483–507.

Crank, J. and Park, G.S. *Methods of Measurement*. In: J. Crank and G. S. Park, editors. *Diffusion in Polymers*. Academic Press; 1968.

B. R. Eldridge, "Olefin/paraffin separation technology: A review," *INDUSTRIAL ENGINEERING CHEMISTRY RESEARCH*, 32 (1993) 2208-2212.

R. Faiz and K. Li, "Polymeric membranes for light olefin/paraffin separation," *DESALINATION*, 287 (2012a) 82–97.

R. Faiz and K. Li, "Olefin/paraffin separation using membrane based facilitated transport/chemical absorption techniques," *CHEMICAL ENGINEERING SCIENCE*, 73 (2012b) 261-284.

A. B. Fuertes and I. Menendez, "Separation of hydrocarbon gas mixtures using phenolic resin-based carbon membranes," *SEPARATION AND PURIFICATION TECHNOLOGY*, 28 (2002) 29–41

Gary, J. H. and Handwerk, G. E. *Petroleum Refining; Technology and Economics*. 4th ed. Marcel Dekker; 2001.

W. M. Haynes, CRC Handbook of Chemistry and Physics (93rd Ed). Section 3.

P. S. Herrera, X. Feng, J. D. Payzant and J.-H. Kim, "Process for the separation of olefins from paraffins using membranes," US PATENT # 7,361,800; 2008.

Y. S. Ho and G. McKay, "Application of kinetic models to the sorption of copper (II) on to peat," *ADSORPTION SCIENCE AND TECHNOLOGY*, 20-8 (2002) 797-815.

Hoffman, E. J. Azeotropic and Extractive Distillation. John Wiley & Sons, 1964.

J.-F. Huang, H. Luo, C. Liang, D. Jiang and S. Dai, "Advanced liquid membranes based on novel ionic liquids for selective separation of olefin/paraffin via olefin-facilitated transport," *INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH*, 47 (2008) 881-888.

D. Jiang and S. Dai, "First principles molecular dynamics simulation of a task-specific ionic liquid based on silver-olefin complex: atomistic insights into a separation process," *JOURNAL OF PHYSICAL CHEMISTRY B*, 112 (2008) 10202-10206.

J. H. Kim, Y. S. Kang and J. Won, "Silver polymer electrolyte membranes for facilitated olefin transport: carrier properties, transport mechanism and separation performance," *MACROMOLECULAR RESEARCH*, 12-2 (2004) 145-155.

J. H. Kim, B. R. Min, J. Won and Y. S. Kang, "Complexation mechanism of olefin with silver ions dissolved in a polymer matrix and its effect on facilitated olefin transport," *CHEMISTRY – A EUROPEAN JOURNAL*, 8-3 (2002) 650-654.

J. H. Kim, B. R. Min, J. Won, S. H. Joo, H. S. Kim and Y. S. Kang, "Role of polymer matrix in polymer/silver complexes for structure, interactions, and facilitated olefin transport," *MACROMOLECULES*, 36 (2003) 6183-6188.

J. H. Kim, B. R. Min, J. Won and Y. S. Kang, "Membranes comprising silver salts physically dispersed in poly(dimethyl siloxane) for the separation of olefin/paraffin," *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY*, 12-4 (2006) 594-600.

S. H. Kim, D. B. Kim, D. K. Choi, H. Lee, H. S. Kim and J. Won, "Isoprene/pentane separation using facilitated transport membranes," *JOURNAL OF MEMBRANE SCIENCE*, 233(2004) 113-117.

L. Li, J. Gao and X. Meng, "The influencing factors of the catalytic pyrolysis processes and their product distribution," *PETROLEUM SCIENCE AND TECHNOLOGY*, 23 (2005) 243-255.

R. Li, H. Xing, Q. Yang, X. Zhao, B. Su, Z. Bao, Y. Yang and Q. Ren, "Selective extraction of 1-hexene against n-hexane in ionic liquids with or without silver salt," *INDUSTRIAL AND ENGINEERING CHEMISTRY RESEARCH*, 51 (2012) 8588-8597.

- L. Liu, X. Feng, and A. Chakma, "Unusual behavior of poly(ethylene oxide)/AgBF₄ polymer electrolyte membranes for olefin-paraffin separation," *SEPARATION AND PURIFICATION TECHNOLOGY*, 38 (2004) 255-263.
- B. Marrufo, S. Loras, and E. Lladosa, "Phase equilibria involved in the extractive distillation of cyclohexane + cyclohexene using diethyl carbonate as an entrainer," *JOURNAL OF CHEMICAL & ENGINEERING DATA*, 56 (2011) 4790-4796.
- X. Meng, C. Xu and J. Gao, "Production of light olefins by catalytic pyrolysis of heavy oil," *PETROLEUM SCIENCE AND TECHNOLOGY*, 24 (2006) 413-422.
- T. C. Merkel, Z. He, A. Morisato and I. Pinnau, "Olefin/Paraffin solubility in a solid polymer electrolyte membrane," *CHEMICAL COMMUNICATIONS*, 13 (2003) 1596-1597.
- D. Nakamura, "Global ethylene production rises 7 million tpy in 2008," *OIL & GAS JOURNAL*, (2009) pp 43-53.
- K. Nymeijer, T. Visser, R. Assen and M. Wessling, "Super selective membranes in gas-liquid membrane contactors for olefin/paraffin separation," *JOURNAL OF MEMBRANE SCIENCE*, 232 (2004) 107-114.
- H. Olivier-Bourbigou, L. Magna and D. Morvan, "Ionic liquids and catalysis: Recent progress from knowledge to applications," *APPLIED CATALYSIS A: GENERAL*, 373 (2010) 1-56.
- I. Pinnau and L. G. Toy, "Solid polymer electrolyte composite membranes for olefin/paraffin separation," *JOURNAL OF MEMBRANE SCIENCE*, 184 (2001) 39-48.
- R. Rabago, D. L. Bryant, C. A. Koval and R. D. Noble, "Evidence for parallel pathways in the facilitated transport of alkenes through Ag⁺-exchanged nafion films," *INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH*, 35 (1996) 1090-1096.
- M. T. Ravanchi, T. Kaghazchi and A. Kargari, "Supported liquid membrane separation of propylene-propane mixtures using a metal ion carrier," *DESALINATION*, 250 (2010) 130-135.
- T. Ren, M. Patel and K. Blok, "Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes," *ENERGY*, 31 (2006) 425-451.
- S. M. Sadrameli and A. E. S. Green, "Systematics and modeling representations of naphtha thermal cracking for olefin production," *JOURNAL OF ANALYTICAL AND APPLIED PYROLYSIS*, 73 (2005) 305-313.
- D. J. Safarik and R. B. Eldridge, "Olefin/Paraffin separations by reactive absorption: A review," *INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH*, 37 (1998) 2571-2581.

J. Shen, X. Zheng, H. Ruan, L. Wu, J. Qui and C. Gao, "Synthesis of AgCl/PMMA hybrid membranes and their sorption performance of cyclohexane/cyclohexene," *JOURNAL OF MEMBRANE SCIENCE*, 304 (2007) 118-124.

A. Shimazu, K. Ikeda and H. Hachisuka, "Method of selectively separating saturated hydrocarbon," US PATENT # 5,749,943; 1998.

Speight, J. G. *The Chemistry and Technology of Petroleum*. 2nd ed. Marcel Dekker; 1991.

C. Staudt-Bickel and W. J. Koros, "Olefin/paraffin gas separations with 6FDA-based polyimide membranes," *JOURNAL OF MEMBRANE SCIENCE*, 170 (2000) 205–214.

Stichlmair, J. G. and Fair, J. R. *Distillation; Principles and Practice*. Wiley-VCH; 1998.

S. Sunderrajan, B. D. Freeman, C. K. Hall and I. Pinnau, "Propane and propylene sorption in solid polymer electrolytes based on poly(ethylene oxide) and silver salts," *JOURNAL OF MEMBRANE SCIENCE*, 182 (2001) 1-12.

N. Tahouni, N. Bagheri, J. Towfighi and M. H. Panjeshahi, "Retrofit of low-temperature gas separation section of an olefin plant," *4th International Conference on Modeling, Simulation and Applied Optimization (ICMSAO)*, (2011) 1-4.

M. Teramoto, H. Matsuyama, T. Yamashiro and S. Okamoto, "Separation of ethylene from ethane by a flowing liquid membrane using silver nitrate as a carrier," *JOURNAL OF MEMBRANE SCIENCE*, 45 (1989) 115-136.

L. Xu, M. Rungta and W. J. Koros, "Matrimid derived carbon molecular sieve hollow fiber membranes for ethylene/ethane separation," *JOURNAL OF MEMBRANE SCIENCE*, 380 (2011) 138– 147.

C. Zhang, Y. Dai, J. R. Johnson, O. Karvan and W. J. Koros, "High performance ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations," *JOURNAL OF MEMBRANE SCIENCE*, 389 (2012) 34– 42.

Appendix A – Sample Calculations

Determining Pentene Flux:

For a membrane content of 3g AgBF₄/g PEO:

$$\text{permeation rate} \left[\frac{g}{hr} \right] = \frac{m_{final} - m_{initial}}{\Delta t}$$

$$\text{permeation rate} \left[\frac{g}{hr} \right] = \frac{99.288 \text{ g} - 98.823 \text{ g}}{10 \text{ min} \times \frac{1 \text{ hr}}{60 \text{ min}}}$$

$$\text{permeation rate} \left[\frac{g}{hr} \right] = 3.390 \frac{g}{hr}$$

$$\text{flux} \left[\frac{\text{mol}}{\text{hr} \cdot \text{cm}^2} \right] = \frac{\text{permeation rate}}{MW \times \text{Area}}$$

$$\text{flux} \left[\frac{\text{mol}}{\text{hr} \cdot \text{cm}^2} \right] = \frac{3.390 \frac{g}{hr}}{70.13 \frac{g}{\text{mol}} \times 14.9 \text{ cm}^2}$$

$$\text{flux} \left[\frac{\text{mol}}{\text{hr} \cdot \text{cm}^2} \right] = 3.24 \times 10^{-3} \frac{\text{mol}}{\text{hr} \cdot \text{cm}^2}$$

Determining Pentane Flux

For a membrane content of 3g AgBF₄/g PEO:

$$\text{permeation rate} \left[\frac{g}{hr} \right] = \frac{m_{final} - m_{initial}}{\Delta t}$$

$$\text{permeation rate} \left[\frac{g}{hr} \right] = \frac{108.379 \text{ g} - 107.624 \text{ g}}{30 \text{ min} \times \frac{1 \text{ hr}}{60 \text{ min}}}$$

$$\text{permeation rate} \left[\frac{g}{hr} \right] = 1.510 \frac{g}{hr}$$

$$\text{flux} \left[\frac{mol}{hr \cdot cm^2} \right] = \frac{\text{permeation rate}}{MW \times Area}$$

$$\text{flux} \left[\frac{mol}{hr \cdot cm^2} \right] = \frac{1.510 \frac{g}{hr}}{72.15 \frac{g}{mol} \times 14.9 cm^2}$$

$$\text{flux} \left[\frac{mol}{hr \cdot cm^2} \right] = 1.40 \times 10^{-3} \frac{mol}{hr \cdot cm^2}$$

Determining Pentene/Pentane Permeability Ratio

For a membrane content of 3g AgBF₄/g PEO:

$$\text{permeability ratio} = \frac{\left(\frac{\text{pentene permeation rate}}{\text{membrane area} \times \text{membrane thickness}} \right)}{\left(\frac{\text{pentane permeation rate}}{\text{membrane area} \times \text{membrane thickness}} \right)}$$

$$\text{permeability ratio} = \frac{\text{pentene permeation rate}}{\text{pentane permeation rate}}$$

$$\text{permeability ratio} = \frac{3.390 \frac{g}{hr}}{1.510 \frac{g}{hr}}$$

$$\text{permeability ratio} = 2.25$$

Determining Sorption Uptake

For a homogeneous membrane with silver content 0.415 g AgBF₄/g PEO:

$$\text{pentane sorption uptake} = \frac{M_{eq} - M_0}{M_0}$$

$$\text{pentane sorption uptake} = \frac{0.530g - 0.443g}{0.443g}$$

$$\text{pentane sorption uptake} = 0.196 \frac{g \text{ pentane}}{g \text{ membrane}}$$

$$\text{pentene sorption uptake} = \frac{M_{eq} - M_0}{M_0}$$

$$\text{pentene sorption uptake} = \frac{0.538g - 0.443g}{0.443g}$$

$$\text{pentene sorption uptake} = 0.214 \frac{g \text{ pentene}}{g \text{ membrane}}$$

For a membrane cast on filter paper with silver content 2.741 g AgBF₄/g PEO:

$$\text{pentane sorption uptake} = \frac{M_{eq} - M_0}{M_0 - M_{FP}}$$

$$\text{pentane sorption uptake} = \frac{0.741g - 0.556g}{0.556g - 0.223g}$$

$$\text{pentane sorption uptake} = \frac{0.185g}{0.333g}$$

$$\text{pentane sorption uptake} = 0.556 \frac{g \text{ pentane}}{g \text{ membrane}}$$

$$\text{pentene sorption uptake} = \frac{M_{eq} - M_0}{M_0 - M_{FP}}$$

$$\text{pentene sorption uptake} = \frac{0.817g - 0.556g}{0.556g - 0.223g}$$

$$\text{pentene sorption uptake} = \frac{0.261g}{0.333g}$$

$$\text{pentene sorption uptake} = 0.784 \frac{g \text{ pentene}}{g \text{ membrane}}$$

Determining Pentene/Pentane Sorption Ratio

For a homogeneous membrane with silver content 0.415 g AgBF₄/g PEO

$$\text{sorption ratio} = \frac{\text{pentene sorption uptake}}{\text{pentane sorption uptake}}$$

$$\text{sorption ratio} = \frac{0.214}{0.196}$$

$$\text{sorption ratio} = 1.09$$

For a membrane cast on filter paper with silver content 2.741 g AgBF₄/g PEO:

$$\text{sorption ratio} = \frac{\text{pentene sorption uptake}}{\text{pentane sorption uptake}}$$

$$\text{sorption ratio} = \frac{0.784}{0.556}$$

$$\text{sorption ratio} = 1.41$$