



The development of an engineering model for the separation of C_xF_y gases

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ABSTRACT

South Africa is a land blessed with an abundance of mineral deposits. Yet, despite this, very little value adding of minerals exists. Most of the mined minerals are exported, where it is reworked into valued items. The country subsequently imports the valuable items at a much higher cost. In the 2006/7 financial year, the government made the decision to support several projects aimed at adding value to the mined minerals and by so doing, creating job opportunities. One such project was identified for the mineral Fluorite (CaF_2). Fluorite is exposed to a controlled burn in a plasma reactor, producing an array of different fluorocarbon gases used in the electronics industry and for commercial polymers like Teflon®. Currently, fluorocarbon gases are separated using a series of cryogenic distillation columns. Although this technique has proven to be successful, it has several negative aspects such as the high cost involved when operating at cryogenic conditions as well as difficulty handling the gases at these sub-zero temperatures.

It was proposed to study the possibility of using membranes to separate fluorocarbon gases at ambient conditions. Several membranes were screened to determine which one is best suited for this application. Two Teflon® based membranes were selected from this data. One of the membranes had a PAN support, while the other had a PEI support.

Pure gas data for both membranes showed promising results. It yielded the highest flux for C_3F_6 , followed by N_2 and CF_4 . $\text{C-C}_4\text{F}_8$ was not used because it was demonstrated that the gas tends to condensate at low pressures. It is recommended to rather use pressure swing condensation to remove this gas from the mixture before the remainder is purified using membranes. Both membranes behaved similarly, with selectivity between C_3F_6 and CF_4 , and N_2 and CF_4 , all above 10. By including the permeate pressure in the Solution-diffusion model, it was possible to model the pure gas data

Binary feed gas mixture experiments showed a large amount of coupling existing between the feed gas mixtures. The result is a decrease in the selectivity as well as the total flux of the gas mixture. Partial fluxes were modelled by introducing a thermodynamic factor that was shown to follow a power law equation. The PAN-supported membrane outperformed the PEI-supported one; it was decided to use this membrane from this point onwards.

Analysis of the ternary feed mixtures showed a strong selectivity towards the gas abundant in the feed blend. The existence of convective diffusion was proven, and included in the modelling, as well as a breakthrough pressure constant. This is indicative of strong interaction between the different gases and the membrane. Throughout the study it became clear that the difference in surface charge between the gases and the membrane were decisive. Opposite charges between a gas (C_3F_6) and the membrane aided in gas permeation.

Membrane separation of fluorocarbon gases at ambient conditions is possible. Teflon® based membranes are recommended. It will be advantageous to study the effect of elevated temperatures on the separation efficiency of such a system.

Keywords: Membranes, Gas separation, Fluorocarbon gases.

OPSOMMING

Suid-Afrika is 'n land wat geseë is met 'n groot verskeidenheid mineraal nedersettings. Ten spyte hiervan word baie min waardetoevoeging tot die minerale gedoen. Meeste minerale word uitgevoer as rouprodukte, waarna die vervaardigde items weer ten duurste ingevoer word. Tydens die 2006/7 finansiële jaar het die Suid-Afrikaanse regering 'n besluit geneem om verskeie projekte te ondersteun wat waardetoevoeging tot minerale tot gevolg sal hê. Een so 'n projek is geloods vir die mineraal Flouriet (CaF_2). Wanneer Fluoriet in 'n plasma reaktor onder beheerde toestande verbrand word, produseer dit 'n reeks C_xF_y gasse. Hierdie gasse word onder andere gebruik in die elektroniese industrie en vir die vervaardiging van kommersiële polimere soos Teflon®. Tans word die koolstof-fluor gasse geskei deur 'n reeks van kriogene distillasie kolomme. Nie net is hierdie proses baie duur nie, maar dit veroorsaak verskeie hanterings probleme van die gasse by temperature laer as vriespunt.

'n Projek is voorgestel om die moontlikheid van die gebruik van membrane vir die skeiding van koolstof-fluor gasse by kamertemperatuur en lae druk te ondersoek. Verskeie membrane is getoets en dit is bevind dat twee Teflon® gebaseerde membrane die beste moontlikheid toon. Een van die membrane het 'n PAN ondersteuningslaag terwyl die ander 'n PEI ondersteuningslaag het.

Die suiwer gas data vir beide die membrane het baie belowende resultate gelever. Dit het die hoogste vloed vir C_3F_6 gelever, gevolg deur N_2 en CF_4 . $\text{c-C}_4\text{F}_8$ is nie gebruik vir die membraan skeiding nie aangesien dit 'n baie lae dampdruk het wat tot gevolg het dat die gas kondenseer in die pype van die eksperimentele opstelling sodra 'n druk van 200kPa oorskry word. Dit word dus aanbeveel om $\text{c-C}_4\text{F}_8$ deur drukverandering te laat kondenseer en sodoende van die ander gasse te skei. Beide membrane het 'n soortgelyke uitwerking op die ander gasse gehad en toon selektiwiteite van bo 10 vir C_3F_6 teenoor CF_4 asook N_2 teenoor CF_4 . Dit was moontlik om die suiwer gasse te modelleer deur van 'n aangepaste *Solution-diffusion* model gebruik te maak. Die model is aangepas deur 'n ekstra permeaatdruk term in berekening te bring.

Tydens die binêre voermengsel eksperimente is daar bewys dat daar 'n groot mate van koppeling tussen die verskillende gasse is. Dit veroorsaak 'n afname in die selektiwiteit van

die membrane sowel as die totale vloed. 'n Termodinamiese faktor is ingebring by die reeds aangepaste *Solution-diffusion* model. Dit het teweeggebring dat dit moontlik was om die data van die binêre voergasmengsel wiskundig te kon voorstel. Met inaggenome die resultate wat tydens die suiwer komponent voer verkry is, kon dit bewys word dat die PAN-ondersteunende membraan die beste is om te gebruik.

Analise van die ternêre voermengsels bewys dat die membraan toon 'n selektiwiteit ten opsigte van die gas wat in oorfloed is in die mengsel. Verder is daar bewys dat diffusie tussen die gasse bestaan, en is daar 'n diffusievloedterm in die model ingebou, sowel as 'n deurbreekdruk konstante. Hierdie is 'n direkte gevolg van interaksie tussen die gasmolekules in die voermengsel.

Daar is deurlopend in die studie bewys dat die oppervlakladinge van die membraan en die gasmolekules 'n beduidende rol in die skeiding van die gasse speel. Die verskil in lading tussen die membraanoppervlakte en C_3F_6 het daartoe bygedra dat hierdie gas die hoogste vloed het.

Dit is moontlik om koolstof-fluor gasse met behulp van membrane by kamertemperatuur een lae druk te skei. Teflon® gebaseerde membrane werk die beste hiervoor. Dit word aanbeveel dat die invloed van verhoogde temperatuur op die skeiding van die gasse met behulp van membrane ondersoek word alvorens die tegnologie op industriële skaal toegepas word.

Sleutelwoorde: Membrane, Gasskeiding, Koolstof-fluor gasse.

DECLARATION

I, Marco le Roux, hereby declare that the thesis entitled '**The development of an engineering model for the separation of C_xF_y gases**' is my work. No plagiarism has taken place and due acknowledgements and references were given.

Marco le Roux, Pr. Eng

Date

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“For You are the Power and the Glory, forever. Thank you Lord”

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*He who doubts the value of his contributions,
believes himself to be a fool.*

- Marco le Roux -

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NOMENCLATURE

Symbol	Description	Units
A	Area	m^2
C	Concentration	mole.m^{-3}
D_i	Diffusion constant	$\text{m}^2.\text{s}^{-1}$
$\bar{D}_i$	Cross-term diffusion constant	$\text{m}^2.\text{s}^{-1}$
J_i	Flux	$\text{mole.m}^{-2}.\text{s}^{-1}$ or $\text{kg.m}^{-2}.\text{s}^{-1}$
J_c	Convective flux	$\text{mole.m}^{-2}.\text{s}^{-1}$
K_i	Sorption constant	Pa^{-1}
N_i	Batch flux	$\text{mole.m}^{-2}.\text{s}^{-1}$ or $\text{kg.m}^{-2}.\text{s}^{-1}$
$\dot{n}$	Molar flow rate	mole.s^{-1}
NM	Number of experimental points	-
P	Pressure	Pa
p_i	Partial pressure	Pa
PM	Number of regressed parameters	-
ρ_i	Permeability	$\text{mole.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ or Barrer
q	Amount adsorped	$\text{cm}^3 \text{ (STD).cm}^{-3}$
R	Universal gas constant (8.314)	
S	Solubility coefficient	$\text{mol.m}^{-1}.\text{Pa}^{-1}$
SD	Standard deviation	-
T	Temperature	K
t	Time	s
V	Volume	m^3
$\dot{V}$	Volumetric flow rate	$\text{m}^3.\text{s}^{-1}$
x,y	Mole fractions	-
z	Length	M

Greek letters		
α	Selectivity	-
γ	Thermodynamic factor	-
μ	Chemical potential	
Π	Breakthrough pressure constant	Pa
Subscripts		
A,B	Differentiating component	
f	Feed side	
H	Henry's law applicability	
i,j,k	Differentiating component	
max	Maximum	
p	Permeate side	
Superscripts		
s	Saturation	

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CHAPTER 1: INTRODUCTION

*Anything that won't sell, I don't want to invent.
Its sale is proof of utility, and utility is success.
-Thomas A Edison*

1.1 Background

South Africa is blessed with an abundance of mineral wealth. With the exception of a few, almost every economically viable mineral is present at levels suitable for mining, giving South Africa the potential to become one of the world's largest and most stable economies. This is however not the case. Bad decision making has entailed that mining operations have developed into an export orientated industry with more than 71% of the primary mineral sales revenue in 2004 originating from exports (DME, 2005:5). The remainder was sold domestically and processed to add secondary value to the minerals. In 2004, these processed minerals, as a group, for the first time outperformed all the other single primary minerals in sales revenue earned for that year (DME, 2005:6).

Statistics like those mentioned above go a long way to proving the importance of adding secondary value to minerals before exporting them. In addition, in the event of the creation of various job opportunities, it is not difficult to see that localised processing of minerals has become an economic and social imperative. This sentiment is shared by the government of South Africa. In the 2006/7 Annual report by the Department of Minerals and Energy (DME), the current (2008) Minister of Minerals and Energy, Minister BP Sonjica, stated that one of the key priorities of the department is the focus on the beneficiation of primary minerals (DME, 2007:14). In a production and sales report in 2005 (DME, 2005:23), the DME also indicated that it is expecting a growth in sales revenue generated from processed minerals for the period 2005 to 2014.

It can therefore be concluded that the beneficiation of primary minerals is a necessity that needs to be considered in order to contribute to the economic growth of South Africa. By beneficiating primary minerals to secondary products, the value of the product will increase exponentially, which in turn will generate more international revenue from the exports of these products, evident in the various reports (DME, 2007; DME 2005).

1.2 Project Motivation

South Africa currently possesses the world's second largest reserve of Fluorspar, the commercial name for the mineral fluorite (calcium fluoride: CaF_2), in the world, and ranks third in the production of Fluorspar (DME, 2006:133). Table 1-1 indicates the world production and reserves of Fluorspar in 2004. It is notable in Table 1-1 that South Africa is producing below maximum capability, leaving much room for increased production. The significance of this is an opportunity for South Africa to grow into a world leader in the field of Fluorspar exports or fluorine based chemicals.

Table 1-1: 2004 world Fluorspar reserves and production (DME, 2006:134)

Country	Reserve Base			Production		
	Mt	%	Rank	kt	%	Rank
China	110	22.9	1	2,700	53.4	1
Mexico	40	8.3	3	808	16.0	2
South Africa	80	16.7	2	265	5.2	3
Mongolia	16	3.3	5	295	5.8	4
Russia	18	3.8	4	170	3.4	5
Spain	8	1.7	7	140	2.8	6
Kenya	3	0.6	9	108	2.1	7
France	14	2.9	6	90	1.8	8
Namibia	5	1.0	8	105	2.1	9
Morocco	na	-	-	81	1.6	10
Other	186	38.8	-	290	5.8	
Total	480	100.0		5,050	100.0	

Some of the possibilities in terms of upgrading Fluorspar are the manufacturing of hydrofluoric acid (HF) and tetrafluoroethylene (TFE), which is the monomer of polytetrafluoroethylene (PTFE or Teflon®) or advanced electronic gasses such as NF_3 , SF_6 , CF_4 , C_3F_6 and $\text{c-C}_4\text{F}_8$. Economically, this makes good sense. Fluorspar is exported at 0.1

US\$/kg, whereas HF can be sold at 1.0 US\$/kg, PTFE at 20 US\$/kg, while the advanced gasses can fetch prices of up to 4500 US\$/kg (DME, 2006:133; NECSA, 2005:3; Van der Walt, 2005).

Perfluorocarbons are widely used as cleaning/etching gasses in the microelectronic and semiconductor manufacturing processes (Tsai *et al.*, 2002:65). Current production of C_xF_y gasses comprise cost intensive, high labour routines with several intermediate steps (NECSA, 2005:4). One such method is the pyrolysis of environmentally unfriendly Freons such as Freon 22. According to the online Oxford dictionary (2008), a Freon is a proprietary name for any group of partially or completely halogenated simple hydrocarbons. These gasses were commonly used as refrigerants and aerosol propellants. However, the production of chlorofluorocarbons (CFC) were banned by the Montreal Protocol (UNEP, 2000:6) as stipulated in Article 2A of this document, due to the ozone depletion potential of these gasses.

This type of legislation is not limited to the emissions of CFCs, but also to the emissions of perfluorocarbons (PFC). PFCs were listed as one of the six major ozone depletion gasses during the third session of the United Nations Convention on Climate Change held in Kyoto in December 1997 (Tsai *et al.*, 2002:66). In listing PFCs as major ozone depletion gasses, the importance of capturing (recovery/recycle) PFC emissions has increased dramatically.

Apart from the environmental impact of these gasses, and the ban proposed on them, the conventional route is also very expensive. Almost 50% of the annual production costs are spent on the purification of the gasses. Current processes make use of cryogenic distillation in order to obtain the desired end product specification (NECSA, 2005:4).

A novel process has been proposed by a consortium consisting of The Nuclear Corporation of South Africa (NECSA), The North-West University (NWU) and Thermtron. This process does away with the burning of the Fluorspar in a rotary kiln and instead, uses a plasma reactor where the Fluorspar is fed into the reactor together with a source of carbon in the form of graphite electrodes. By manipulating the quenching conditions, the required C_xF_y radicals can be formed. These radicals will in turn be separated by using membranes instead of the conventional cryogenic distillation method.

Membrane science and technology has developed immensely since its origin in the 1960s and now forms an accepted part of available separation technology in industry. Although there are certain processes that successfully operate gas separation membranes, currently it is still outrated by conventional gas separation technologies (Fell, 2003:1). However, membrane gas separation equipment has grown to become a US\$150 million per annum business (Baker, 2002:1393). It was also envisaged that this would double by 2010 and double again by 2020 to become a US\$760 million per annum industry (Baker, 2002:1409). With this predicted growth rate of 7-8% per annum, it is clearly evident that industry has established faith in the use of membranes for the separation of gasses. Figure 1-1 illustrates the development of the membrane gas separation industry during the 20th century.

In 2002, Baker (2002:1393) postulated that only 8 or 9 different polymers were used to manufacture approximately 90% of the then current gas separation units. The applicability of these units included the following:

- Air separations
- Hydrogen separations
- Natural gas separations

Several new polymers have been developed during the past few years, with many of them reporting excellent permeability and selectivity numbers (Baker, 2002:1393). Nevertheless, it must be kept in mind that permeability and selectivity are only two of the criteria to be met in the production of membranes. The others include the ability to produce thin, low-cost membranes that are chemically and physically stable under operating conditions (Damle, 2004:1). One such new polymer is Teflon® AF, commercially available in two grades, namely Teflon® AF 1600 and Teflon® AF 2400 (Zang, 2006:3). This offers the possibility of opening up a new field for the separation of fluorine based chemicals.

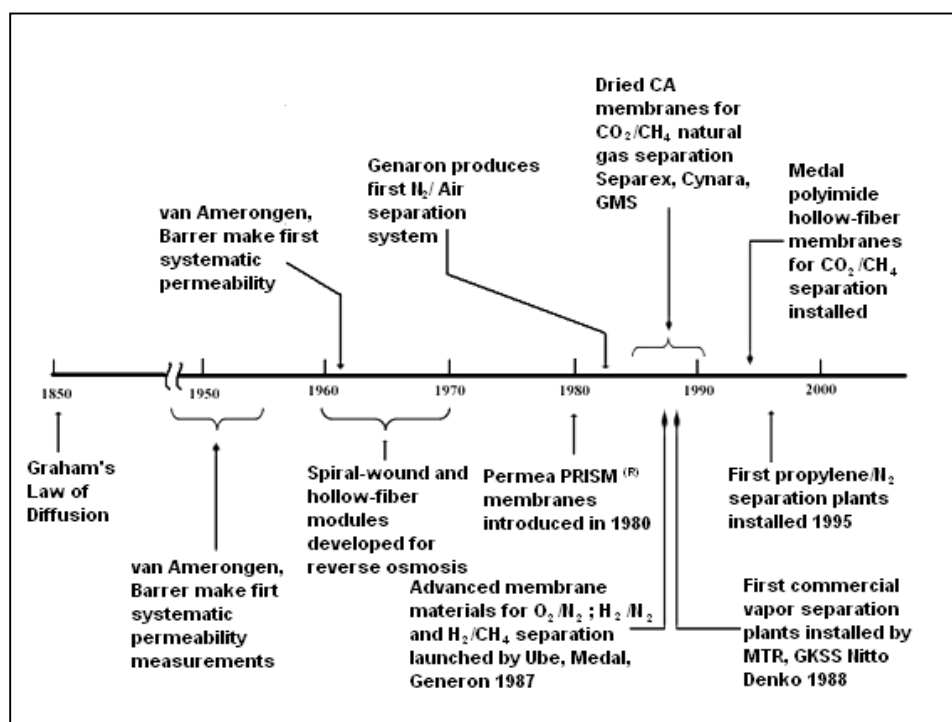


Figure 1-1: Gas membrane development milestones (Taken from Baker, 2002:1394)

Several papers on the permeation of perfluorocarbon gasses through membranes have been published (see Table 1-2 for a summary). Although these publications are useful in establishing a benchmark for comparison, none of them fulfil the needs of delivering sufficient data to consider the use of membranes for industrial scale separation. In most of the papers, only ideal feed (pure gas feed) to the membrane was considered. It was mostly used to characterise the different gas separation membranes. In the odd case where a gas mixture was fed to the membrane, it was limited to a binary mixture which was composed of N_2 and C_2F_6 . The latter will not form part of this study, which again limits the usefulness of the data. None of these papers have reported a ternary mixture as feed gas.

Table 1-2: Published data on perfluorocarbon membrane permeation

gasses	Feed composition	Membrane used	Reference
N ₂ , CF ₄ , SF ₆ and other	Pure gas feed	Silicalite-1	De Luca <i>et al.</i> , 2004
N ₂ , CF ₄ , SF ₆ and other	Pure gas feed	Silica-sodalite	De Luca <i>et al.</i> , 2004
CH ₄ and CF ₄	Pure and binary mixtures	Silicalite	Skoulidas <i>et al.</i> , 2003
N ₂ , O ₂ , CH ₄ and other	Pure gas feed	Teflon® AF1600	Thornton <i>et al.</i> , 2009
N ₂ , O ₂ , CH ₄ and other	Pure gas feed	Teflon® AF2400	Thornton <i>et al.</i> , 2009
N ₂ , CF ₄ , C ₂ F ₆ , C ₃ F ₈ , C ₄ F ₈	Pure gas feed	PF/PEO membrane	Hirayama <i>et al.</i> 1999
N ₂ , CF ₄ , C ₂ F ₆ , C ₃ F ₈ , C ₄ F ₈	Pure gas feed	PEO membrane	Hirayama <i>et al.</i> 1999
N ₂ , CF ₄ , C ₂ F ₆ , C ₃ F ₈ , C ₄ F ₈	Pure gas feed	SR membrane	Hirayama <i>et al.</i> 1999
N ₂ , CF ₄ , C ₂ F ₆ , C ₃ F ₈	Pure gas feed	Teflon® AF2400	Merkel <i>et al.</i> 1999
N ₂ , CF ₄ , C ₂ F ₆ , C ₃ F ₈	Pure gas feed	SR composite membrane	Wijmans <i>et al.</i> 2004
N ₂ , CF ₄ , C ₂ F ₆ , C ₃ F ₈	Pure gas feed	Teflon® AF2400, Hyflon AD60	Wijmans <i>et al.</i> 2004
N ₂ , C ₂ F ₆	Binary gas mixture	Teflon® AF2400, Hyflon AD60	Wijmans <i>et al.</i> 2004

1.3 Objectives of the investigation

An investigation will be carried out to evaluate the effectiveness of separating perfluorocarbons (CF_4 , C_3F_6 and $\text{c-C}_4\text{F}_8$) from a mixture containing nitrogen, by using commercially available membranes. The criteria for the study will include the selectivity of the membrane towards the different gas components as well as the magnitude of the fluxes. The best performing membrane(s) will be further evaluated to establish the optimum operating conditions for use in industrial separation of these gasses. Lastly, a semi-empirical mathematical model that describes the performance of the membrane will be developed.

1.4 Scope of the investigation

This thesis will be written in such a manner that each chapter represents a new objective to be investigated. Repetition of information will be kept to a minimum.

Chapter 1 concludes with the motivation, objectives and scope of this study.

Chapter 2 consists of a literature survey regarding membrane gas separation and the current technologies applicable in industry. The separation of perfluorocarbons is also be discussed.

The experimental process and selection of membranes can be found in Chapter 3. This includes basic screening tests of the selected membranes as well as all the sorption data required for modelling.

Chapter 4 consists of all single gas permeation data, and the determining of the perm-selectivities of the process. Included in this is the modelling of the data to enable a mathematical description of the process.

Chapter 5 is similar to Chapter 4, but instead of focussing on single gas permeations, binary mixtures are discussed.

Chapter 6 consists of the study the behaviour of ternary gas mixtures. Permeation data for different ternary compositions is determined and described mathematically.

The thesis ends with the conclusions and recommendations in Chapter 7.

Additional information can be found in the Appendices as stated throughout this thesis.

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CHAPTER 2: LITERATURE SURVEY

*Nothing in life is to be feared,
It is only to be understood
- Marie Curie*

2.1 Introduction

This chapter consists of all the literature and principles necessary to understand the concept of membrane gas separation as well as the current technologies applicable to industry. Although membrane gas separation is not all that new, very little work has been carried out in the field of fluorocarbon gas separation by means of membranes. Therefore, this chapter will focus on the newest technologies regarding membrane gas separation as well as looking at traditional ways to separate fluorocarbons by means of cryogenic distillation.

2.2 Background

Scientifically, the first observation relating to gas separation was documented by J.K. Mitchell in 1831 (Ismail *et al.*, 2002:1025). It is, however, generally agreed that the first remarkable and influential contribution to the field of membrane gas separation was a systematic study conducted by Thomas Graham in 1860 (Ismail *et al.*, 2002:1025), which led to the formulation of the solution-diffusion model in 1866. Due to economic considerations and poor membrane performance, a long time passed since this study was conducted, until 1979 when membrane gas separation was recognised as an emerging technology with available industrial applications.

Over the past three decades or so, membrane gas separation processes have shown a potential to outperform traditional gas separation processes like cryogenic distillation, absorption and pressure swing adsorption (PSA) in terms of economics and environmental impact. For example, the enrichment of air to 35% O₂ indicates a reduction of 47% in capital and 38% in operating costs when using membranes instead of PSA (Dhingra, 1997:2). Other advantages of using membranes for separation are: they can operate at ambient temperature and low pressures, no additives are needed for separation to take place, and up-scaling and downscaling of these processes as well as their integration into other separation or reaction processes are easy (Ulbricht, 2006:2217). Despite these obvious advantages, polymeric

membrane gas separation units are still very limited because the performance of the polymers is not adequate.

Currently, there is a need for the design of the ‘ultimate’ membrane that would yield a high permeability as well as the desired separation. With such a membrane, the challenge in this industry will shift to the control and optimisation of the process conditions on either side of the membrane in order to minimise concentration polarisation or fouling effects. The choice of trans-membrane pressure then becomes a question of providing sufficient driving force to attain a desirable flux (Fell, 2003:6).

2.3 Characteristics of gas separation using polymeric membranes

2.3.1 Introduction

For a pair of gasses, for example, O_2/N_2 or CO_2/CH_4 , the membrane separation performance can be characterised by the permeability coefficient and the selectivity of the gasses. A trade-off exists between the selectivity and the permeability; a more permeable membrane is less selective, and vice versa. Such a trade-off relationship leads to an upper limit for the performance of the system (Seo *et al.*, 2006:4501). This phenomenon can be viewed in the well known Robeson trade-off graph, depicted in Figure 2-1.

In Figure 2-1, it is clear that the rates of development for membranes lack the requirements for plant performance. Although Baker (2002:1409) predicted that the field of membrane separation would double between 2002 and 2010, and again in 2020, this figure indicates that the development of membranes will be the Achilles heel of this industry. Therefore, the choice of membrane plays a huge role in the success, or lack thereof, of any membrane process. It is estimated that less than ten different polymers make up about 90% of all the membranes used for gas separation (Baker, 2002:1394). This clearly highlights the need to develop polymers that are more permeable, with a high selectivity for specific gasses, are stable, and inexpensive to manufacture.

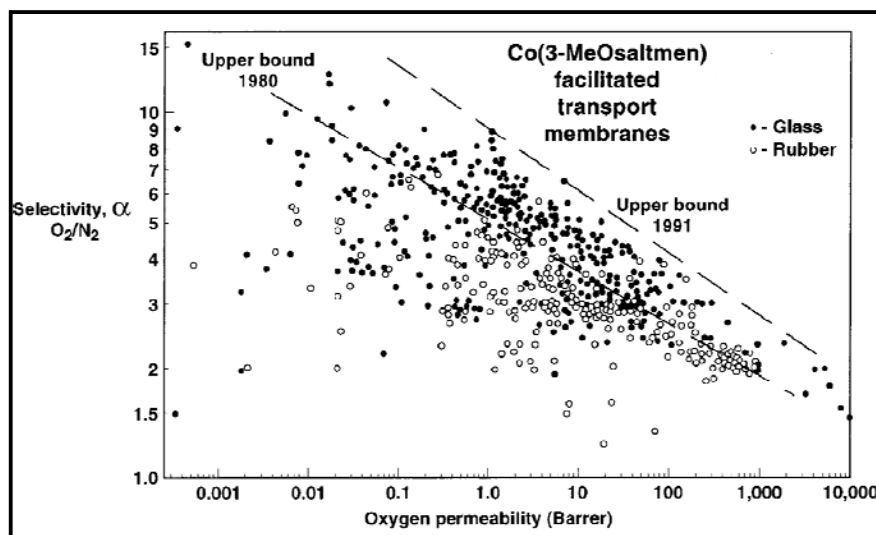


Figure 2-1: O_2/N_2 selectivity as a function of O_2 permeability for all membranes in 1991 (Taken from Robeson, 1991:172)

The upper bound in Figure 2-1 can be determined by the following equation (Robeson, 2008:396)

2.1

New synthetic polymers used as membranes go a long way in helping to overcome this problem. Developing these membranes has attracted much attention from researchers. Major efforts have been devoted to correlating the structure of the polymer with applied permeability and selectivity (Pandey & Chauhan, 2001:853). The development of polymers also depends on the targeted application (Damle, 2004:1).

2.3.2 Membrane characteristics

Simply put, a membrane is either a porous or dense (i.e., non-porous) material used to separate mixtures of gasses and/or fluids (Damle, 2004:1). Mulder (1997:12) defines a membrane as a selective barrier between two components in a mixture. In general, membranes can be classified into two groups, namely symmetrical and asymmetrical membranes, as indicated in Figure 2-2. For gas separation asymmetric membranes are the preferred choice (Ismail *et al.*, 2002:1026). Owing to the need to have high permeability and selectivity, asymmetric composite membranes that consist of a thin, dense skin layer supported by a thick porous support are the most suitable (Wang *et.al*, 1996:88).

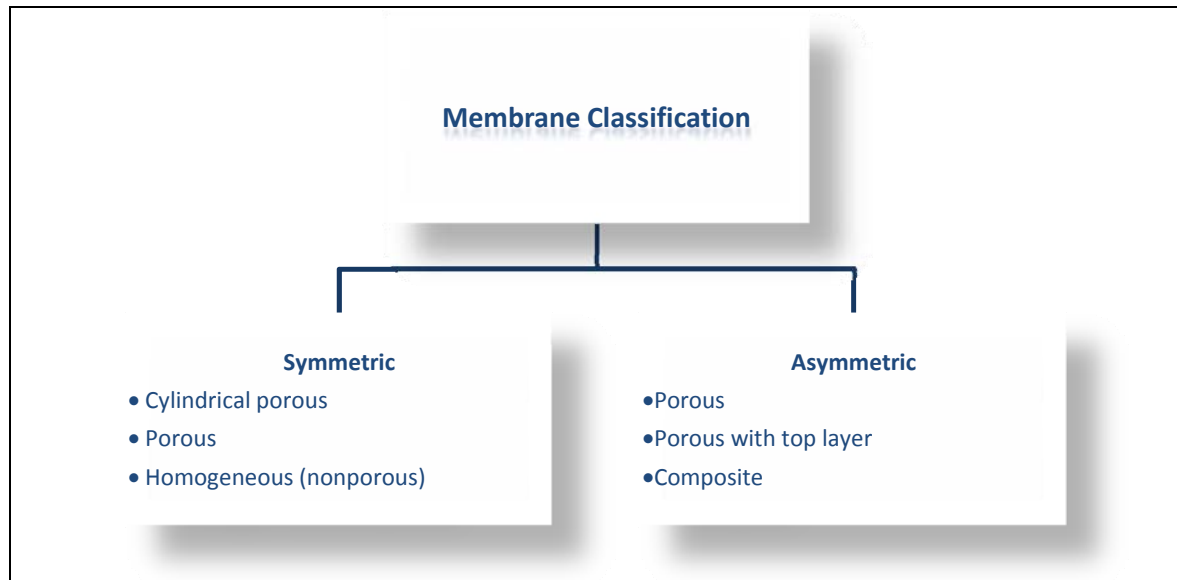


Figure 2-2: Classification of membranes (Taken from Ismail, 2002:1026; Mulder, 1998:13)

The separation of a substance by porous membranes is a function of the permeate character and membrane properties, such as the molecular size of the membrane polymer, pore-size, and pore-size distribution. It can be said that a porous membrane is very similar in its structure and function to the conventional filter. In general, only those molecules that differ considerably in size can be separated effectively by microporous membranes. When using these membranes for gas separation they do exhibit very high levels of flux, but inherently exhibit low selectivity (Basu *et al.*, 2004:1347).

Nonporous or dense membranes are exactly the opposite of porous ones. They possess high selectivity properties, but the rates of the transport of gasses through the medium are usually low. An important property of a nonporous dense membrane is that even permeants of similar sizes may be separated if their solubility in the membrane differs significantly (Basu *et al.*, 2004:1347).

The productivity of a membrane is defined by the permeability flux, which is an indication of the quantity (mass or moles) of a component that permeates a specific area of the membrane for a given unit of time. Mathematically, it is described by Equation 2.2.

$$J = \frac{V}{A\Delta t} \quad 2.2$$

The selectivity of a membrane for the separation of a mixture of components A and B is defined as:

$$\alpha = \left[\frac{y_a/y_b}{x_a/x_b} \right] \quad 2.3$$

where x_i and y_i are the molar fractions of components a and b in the feed and permeate, respectively. The selectivity, α , is chosen in such a manner that the value is greater than unity. If the value of α moves towards unity, no separation will occur. In other words, no separation is possible if $\alpha_{A/B} = \alpha_{B/A} = 1$ (Mulder, 1997:9).

2.3.3 Mechanism of gas permeation through polymer membranes

Various mechanisms for gas separation by means of membranes have been developed, all depending on the properties of the permeating substance and the membrane (Basu *et al.*, 2004:1353). Two of these mechanisms include Knudsen diffusion (the molecular sieve effect) and solution-diffusion. When working with dense membranes, it is common practice to use the solution-diffusion mechanism to describe the system (Basu *et al.*, 2004:1355; Kohl & Nielsen, 1997:1242; Wijmans, 2004:39; Pandey & Chauhan, 2001:859).

The main steps regulating the mechanism are depicted in Figure 2-3 (Kohl & Nielsen, 1997:1242):

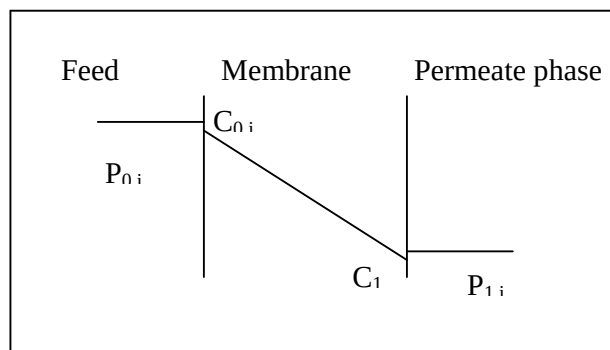


Figure 2-3 Illustration of a nonporous membrane separating two gas phases (Mulder, 2003:309)

Figure 2-3 clearly illustrates that the main steps for permeation to occur are as follows:

- a) Adsorption of the gas to the exposed surface.
- b) Solution of the gas into the membrane.
- c) Diffusion of the gas through the membrane.
- d) The release of the gas from the solution at the other side of the membrane.
- e) Desorption of the gas from the surface.

With regards to the solution-diffusion model, only steps b, c and d are considered in its simplest form. For this to occur the following two assumptions have to be made (Kohl & Nielsen, 1997:1242):

- The concentration of a component in a membrane at its surface is directly proportional to the partial pressure of the component in the gas phase adjacent to the surface.
- The rate at which a component passes through a membrane is proportional to the concentration gradient in the membrane.

The above assumptions represent the laws of Henry and Fick respectively. Fickian diffusion is of importance for all membrane processes, but is of dominant importance in gas permeation (Perry & Green, 1997:22-38). For Fickian transport of a substance, the driving force is indicated by the chemical potential:

$$J_i = -D_i C \frac{d(\mu_i/RT)}{dz} \quad 2.4$$

In most membrane processes, the activity coefficients are close to unity, hence reducing Fick's first law to:

$$J_i = -D_i \frac{dC_i}{dz} \quad 2.5$$

If D_i is assumed to be constant and independent of the concentration, and C_i is in the fluid phase, which in turn is in equilibrium with the membrane, Equation 2.5 may be written as:

$$J_i = D_i \frac{(C_f - C_p)}{z} = D_i \frac{\Delta C}{z} \quad 2.6$$

where z only notates the thickness of the membrane active layer and C_f and C_p are the feed and permeation concentration in the membrane respectively. It is important to keep in mind that the concentration of a substance in the membrane will differ significantly from the concentration of the same substance in any of the fluid phases. The same applies to the diffusivity in the membrane and fluid phases.

If Henry's law applies, the concentrations in the fluid phases and the membrane are related by:

$$C_i = S \cdot p_i \quad 2.7$$

The proportionality factor, S , indicated in Equation 2.7, refers to a specific membrane and a penetrant. If S is only a function of temperature, and the system is operated isothermally, which is generally the case, with the exception of pervaporation, Equation 2.6 can be reduced to:

$$J_i = \left(\frac{S \cdot \bar{D}_i}{z} \right) (p_f - p_p) \quad 2.8$$

where p_f and p_p are the feed and permeate side pressures respectively. The product $S \cdot \bar{D}_i$ is referred to as the permeability of the system, given in $\text{kmol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. In the above equations, the mass of the substance i being transported is indicated by the symbol N_i and has the same units as the flux J_i of a membrane as defined in Equation 2.2. Therefore it is common practice in membrane technology to substitute the transported mass with the flux (Perry & Green, 1997:22-39; Nunes & Peinemann, 2001:41). Chapter 4 will cover the solution-diffusion model in more detail in Section 4.2.

The determination of the different coefficients mentioned above is extremely difficult due to the difference in behaviour of the gas transported through the rubbery or glassy state of the polymer, that is, at temperatures above and below the glass transition temperature (T_g) of the polymer, as well as other influences such as plasticisation and coupling that add to the complexity of the system. The mechanisms for gas transport through polymer membranes are not clearly understood. Consequently, almost all the models proposed in the literature are phenomenological in nature and contain one or more variables that need to be determined experimentally (Pandey & Chaunhan, 2001:860).

To date, it was determined that the major factors influencing the permeability of a gas through a polymer membrane, as well as the perm-selectivity control are (1) the mobility of the polymer chain, in many cases reflected by the glass transition temperature of the polymer, (2) the intersegmental spacing used to measure the mean free volume of the polymer, and (3) the interactions between the polymer and the penetrant, reflected in the solubility of the penetrant gasses in the polymer (Huang *et al.*, 2006:141).

2.3.4 Plasticising effect

Plasticisation of a polymer membrane is the result of the sorption of components into the membrane. Sorbed components in a membrane cause the membrane material to soften and dilate, therefore increasing the rate of diffusion and hence the permeability of the membrane (Damle, 2004:31).

The softening and dilation of the polymer material is caused by an increase in the segmental motion of the polymer chain. This enhanced mobility increases both the frequency and the average size of the transient gaps that enable diffusion, thereby increasing the permeability. Usually this sharp increase in permeability is accompanied by a decrease in the size or diffusion selectivity as the polymer loses the ability to distinguish between the different molecules. Therefore, the flux of the unwanted component might be higher than expected (Damle, 2004:32).

2.3.5 Coupling effect

When investigating possible separation systems (such as membrane systems), the first thing to take into account when defining the efficiency of a system is to look at the difference in value of the transport parameters such as diffusion coefficients and permeabilities for single components. It does, however, often happen that for multiple component systems the value of the transport parameters differs rather drastically from the single component values, hence rendering the system less efficient. One reason for such behaviour is attributed to coupling effects between the components (Simon *et al.*, 1995:231).

Mass transfer of the components is strongly affected by coupling effects, which is an indication of both the interaction of the components with each other as well as their interaction with the separation medium (e.g., the membrane surface).

2.3.5.1 *Solubility coupling*

Henry's law defines the solubility of a penetrant into a polymer at low applied pressures and a large free volume present in the polymer matrix. Positive deviations from pure component sorption can be attributed to the swelling of the polymer matrix in the presence of the penetrants. The swelling causes an increase in the available sorption sites. This is usually observed for the sorption of vapours and water into the polymer.

Negative deviation is caused by a fixed amount of sorption points in the matrix. These points become saturated by the different penetrants and cause a decrease in the solubility. This behaviour is generally observed with gas sorption into glassy polymers (Dhinga & Marand, 1998:47).

2.3.5.2 *Diffusivity coupling*

Very little information is available in the literature dealing with the effect of diffusional coupling during mixed gas transport in a polymer membrane. This is due to limited experimental data and setups used to measure binary gas permeation rates. Several theoretical models to describe diffusivity have been derived. It was found that for an idealised case of equal concentration for two penetrants and for high diffusion coupling, the penetrant flux for each penetrant disobeys the Fickian law, while the binary diffusion coefficient that describes the transport of the components through the membrane becomes a function of the concentration of each component in the membrane. For gas separation using polymers, coupling comes into play for two penetrants whose diffusional rate differs by more than a magnitude. The greatest effect is observed for the gas with the lowest diffusion rate (Dhinga & Marand, 1998:48).

2.3.6 **Concentration polarisation**

Figure 2-4 presents a schematic drawing of the effect of concentration polarisation. It illustrates that during membrane separation, an accumulation of the rejected components may occur on the feed side. This accumulation of the rejected components causes a build up in the boundary layer adjacent to the membrane, thus depleting the concentration of the faster permeating component, effectively hindering its mass transport across the membrane. The result is a decline in the effectiveness and productiveness of the separation process (Bhattachary & Hwang, 1997:73).

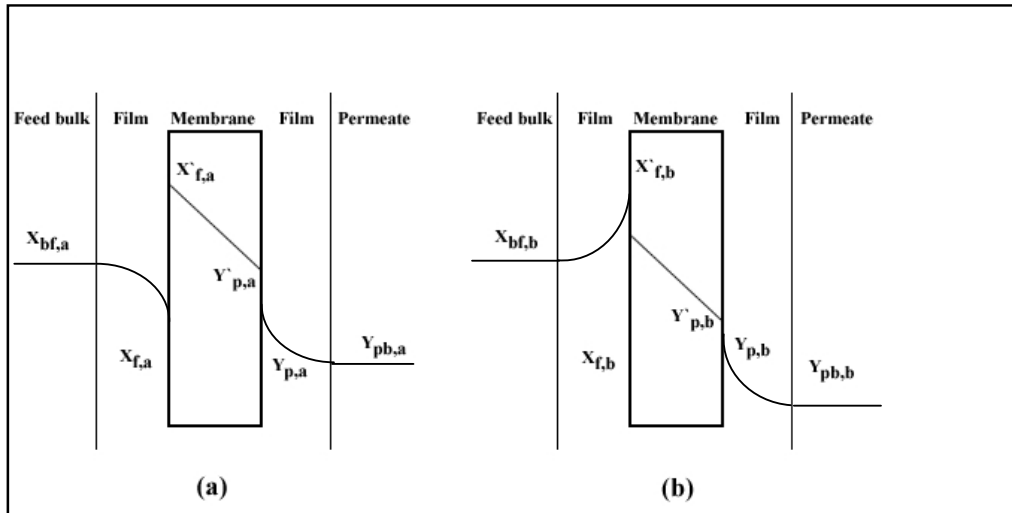


Figure 2-4: Schematic diagram of concentration polarisation for the preferentially permeating component (a) and the slower permeating component (b) (Marx 2002:10)

2.3.7 Binary mixture permeation

Pure gas permeation experiments have often been used to indicate possible performance under ideal conditions. In reality, the transport of a component in gas mixtures is affected by other components either due to the competition among the components or by plasticisation of the polymers. As a consequence, mixed gas separation generally yields lower selectivity for membranes than those of pure gas measurements (Wang *et al.* 2002:967).

Non-ideal gas behaviours also cause deviations from single gas membrane performance. Usually the feed gas is always maintained at a high pressure for practical gas separation applications. At high pressures, the fugacity coefficient of the one component would be lowered by introducing a second component into the mixture, which reduces the driving force compared to single gas permeation. The permeation depression of highly non-ideal gas components is much more severe than that of an ideal gas component and could reduce the selectivity dramatically (Wang *et al.*, 2002:968).

For binary gas mixtures the solution-diffusion model does not include all the effects, namely: solubility coupling and diffusion coupling. The application of Henry's law of solubility and Fick's law of diffusion provides a good approximation for the transport and selective properties of polymers; however, the presence of the coupling effects in binary gas mixtures cannot be overruled. These effects arise from the interactions between mixed gasses, as well

as between gasses and the polymer. These effects can alter the gas permeability and selectivity of the membrane (Dhingra & Marand, 1998:45).

For binary gas mixtures, normally one component (X) possesses a higher permeation rate through the membrane than the other component (Y) under single gas conditions. This means that for binary gas conditions there can be only three results:

- Case 1: Permeability of binary and single gas permeation is the same. This implies an ideal mixed gas system. This means that there are no interactions between the gasses and the gas-polymer surface. gasses also have the same permeability under binary gas and single gas permeation.
- Case 2: Component X shows a higher permeation under binary gas conditions. This means that X dominates the permeation process or that the coupling effect of the components advances the diffusion of X.
- Case 3: Component X shows a lower permeation under binary gas conditions. This means that Y dominates the permeation process or that the coupling effect of Y retards the diffusion of X.

Case 1 is an ideal system and is very unlikely. Case 3 is less common since it is expected that most coupling effects will exert a positive influence on the outcome of a binary system which means that the most likely result will be Case 2 (Dhingra & Marand, 1998:60).

2.3.8 Important current industrial membrane gas separation applications

Industrial membrane gas applications were only introduced in the early 1970s (Lokhandwala *et al.* 1995). Such a late introduction defines membrane gas separation as a developing process. Despite this, several processes are commonly used today. Table 2-1 portrays a summary of current gas separation operations that make use of membranes (Ismael *et al.*, 2002:1026, Basu *et al.*, 2004:1365, Ten Bosch, 2005:1560).

Table 2-1: Current industrial membrane gas separation operations

Gas separation	Application
O ₂ / N ₂	Oxygen enrichment and inert gas production
H ₂ / Hydrocarbons	Hydrogen recovery
H ₂ / N ₂	Ammonia purge gas
H ₂ / CO	Ratio adjustment to Syngas
CO ₂ / Hydrocarbons	Acid gas treatment and landfill gas upgrading
H ₂ O / Hydrocarbons	Dehydration of natural gas
H ₂ S / Hydrocarbons	Treatment of sour gas
He / Hydrocarbons	He separation
He / N ₂	He recovery
Hydrocarbons / Light gasses	Hydrocarbon recovery and pollution control
H ₂ O / Air	Dehumidification of air

Ismael *et al.* (2004:1027) describes the advantages by using membranes for gas separation as follows:

- It offers low capital costs
- It has a low energy consumption
- Operation capabilities are easy
- It is very cost effective per unit volume (even at low volume flow rates)
- It has a relatively small footprint.

It is clearly evident that membrane assisted gas separation is a well established technology that offers an array of advantages over other separation technologies.

2.4 Perfluorocarbons

2.4.1 Introduction

Fluorocarbons are synonymous with refrigeration gasses. They were used extensively in the mid to late twentieth century in appliances such as refrigerators, freezers, air conditioners and even aerosol canisters. As society became aware of the impact of their actions on the

environment, fluorocarbons, especially chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs), were identified as being lethal to the ozone layer (McCulloch, 2003:21). This led to the banning in the use of CFCs and HFCs as refrigerant gasses by the Montreal Protocol (UNEP 2000:6).

These fluorocarbons *per se* do not directly dissolve the ozone layer. They become well mixed in the atmosphere and can travel around the world because they do not decompose. Eventually they are taken up into the stratosphere and once there they are decomposed by UV photolysis or oxidation to release chlorine and bromine (depicted in Figure 2-5). These gasses are then locked into “reservoir” components such as HCl, HBr and ClONO₂.

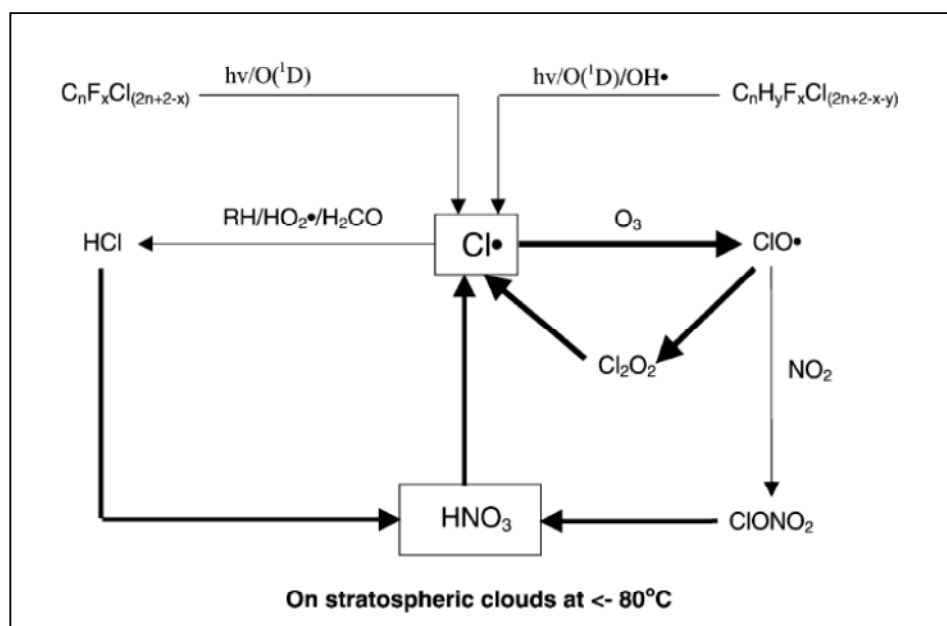


Figure 2-5: Schematic showing of the generation of chlorine radicals and their principal reactions in the non-polar (light arrows) and polar (dark arrows) stratosphere (McCulloch, 2003:22)

Ozone depletion is triggered by reactions on surfaces, particularly the water ice clouds that form in the winter polar stratosphere, which release chlorine from the reservoirs. The released Cl radicals react with the ozone to form ClO which leads to the localised removal of the ozone layer. This effect is particularly visible in the South Polar stratosphere, resulting in the “ozone hole” that has recurred each spring in the arctic since 1980 (McCulloch, 2003:22).

With the phasing out of CFCs and HFCs, it was important to find a substitute for these gasses. Perfluorocarbons (PFCs) were identified as possible alternatives because they do not exhibit any stratospheric ozone depleting potential (Zoellner *et al.*, 2003:193). The influence of replacing CFCs and HFCs with PFCs can be viewed in the graph in Figure 2-6.



Figure 2-6: The size of the annual Antarctic ozone hole (McCulloch, 2003:23)

Figure 2-6 clearly depicts the decrease in the size of the ozone layer after the banning of CFCs and HFCs. It should be further noted that by replacing these gasses with PFCs, the damage to the ozone layer continued to decrease, verifying the statement that PFCs are not hazardous to the environment.

Currently, PFCs are not only used as replacement refrigerating gasses, but have found wide scale application as electronic gasses, inert solvents and blood replacements. In addition to this, well known PFCs like Teflon® are being used as lubricants and non-stick surfaces (Zoellner *et al.*, 2003:193).

2.4.2 Current separation technologies used for Perfluorocarbons

The conventional method of manufacturing HF and C_xF_y compounds follow long, costly and laborious routes, with several intermediate steps. HF is manufactured via the sulphuric acid digestion of fluorspar at 400°C in a rotary kiln. This produces calcium sulphate (gypsum) as a waste product. In 2005, it was demonstrated that a plant with a capacity of 20 000 tpa is required to be profitable. In addition, it will require a 50 000 tpa sulphuric acid plant in close proximity to the HF plant (NECSA, 2005:14).

As mentioned in Section 1.2, the commercial industrial scale method for manufacturing C_xF_y compounds via the pyrolysis of environmentally unfriendly freons, such as Freon 22, possesses a very high ozone depletion potential. This route resulted in the emissions of large volumes of waste, such as HCl, which further aggravated the effect on the environment. This route has proven to be very cost intensive. All the processes require costly gas purification systems such as cryogenic distillation in order to obtain the desired end product specification. The separation cost of C_xF_y products is estimated to be 50% of the annual production cost (NECSA, 2005:14).

The separation of tetrafluoroethylene (TFE) serves as a good example of methods with high separation costs. Several impurities are present in the manufacturing of TFE, and these components, such as hexafluoropropene and chlorotrifluoroethylene, contribute to the formation of azeotropic mixtures. In years gone by, high efficiency columns had to be used for this separation. However, these did not yield extremely high purities for TFE while they also aided in the formation of CFCs (Nikiforov & Barabanov, 1999:10). Modernisation of these plants brought forth the addition of a separating agent which resulted in the use of lower efficient columns with lower reflux ratios, the elimination of CFC formation, a decrease in power consumption and raw material consumption, and the formation and isolation of one more marketable product.

This example serves as proof that there is a need for the modernisation of existing PFC production plants in order to help reduce the costs involved, and to adhere to the ban of environmentally harmful gasses such as CFCs and Freons.

2.5 Concluding remarks

Membrane gas separation as a technology is relatively new in relation to other proven technologies such as distillation. It does however possess the ability to replace distillation in processes which contain an azeotropic mixture, or where all the components have a below zero boiling point. This can also contribute to the elimination of environmentally harmful components which may form during the addition of separating agents, for example.

As explained in Section 2.3.8, several applications for the separation membrane gasses using polymer membranes are already in operation. These processes contribute to proving the validity of the technology as an industrial application. As is the case for most technologies, there are some hurdles to overcome when choosing a membrane best suited for the specific process. One always has to keep aspects like coupling, plasticisation and concentration polarisation in mind when designing the system and testing applicable membranes.

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CHAPTER 3: EXPERIMENTAL SETUP AND PLAN

*You've got to experiment to
figure out what works.
- Andrew Weil*

3.1 Introduction

This chapter will furnish detailed information regarding the experimental setup and equipment design as well as the procedural design used for experimentation. Furthermore, the focus will fall on selected gasses and their properties, the membrane selection criteria, the initial membranes used, and the screening results thereof. Adsorption studies are also included. This chapter will conclude with a final decision on selected membranes to be used further in the study.

3.2 gasses and materials

This study forms part of a larger project (See Chapter 1) that is investigating the effective production of fluorocarbon gasses using thermide plasma technology. The mixtures exiting the thermide plasma reactor consist of an array of fluorocarbon gasses, including CF_4 , C_2F_4 , C_2F_6 , C_3F_6 and $\text{c-C}_4\text{F}_8$, mixed with unreacted N_2 , which will serve as feed to the separation section of the new proposed plant. The laboratory facilities at the North-West University are not accredited to work with C_2F_4 and C_2F_6 and therefore only CF_4 , C_3F_6 and $\text{c-C}_4\text{F}_8$ and N_2 gasses were used in this study. All gasses were supplied by NECSA and were used as received without any further purification or reaction. Refer to Appendix A for material safety data sheets of all gasses used in this study as well as other safety precautions used in the completion of experiments.

3.2.1 gasses

Important characteristics of the gasses used in this study are shown in Table 3-1 (Air Liquide, 2005). Further characteristics and properties of the gasses are listed in the material safety data sheets in Appendix A.

Table 3-1: Gas properties.

gasses	Molecular weight (g/mol)	Melting Point (°C)	Boiling Point (°C)	Critical Temperature (°C)	SG (Air=1)	Vapour Pressure at 20°C
N ₂	28	-210	-196	-147	0.97	n/a
CF ₄	88	-184	-128	-45	3	n/a
C ₃ F ₆	150	-156	-29.6	86.2	5.2	6.4bar
c-C ₄ F ₈	200	-40.2	-6.4	115	6.9	2.7bar

In Table 3-1, one property that is problematic for the objectives of this study stands out. At 20°C the vapour pressure of c-C₄F₈ is only 2.7bar. This entails that if the pressure at that temperature rises above 2.7bar, the gas will start to form a condensate. This will limit the objective of studying gas separation at ambient temperature and low pressures (up to 2barg). The laboratory temperature can be taken as being 25°C in South Africa, but during summer afternoons, this temperature can rise up to between 30 and 35°C, depending on location, etcetera.

This was tested and found to be true. At ambient temperature and pressures just over 2barg, the gas started to condensate in the piping. This result led to the conclusion that membrane gas separation is not the best option for the purification of c-C₄F₈. It is recommended that the gas be condensed by means of pressure swing condensation. The remainder of the gasses can be treated in a membrane process. This study therefore focused only on the three remaining gasses, namely the N₂, CF₄ and C₃F₆.

The molecular diameter, molecular volume and Fukui electron affinity of each gas used in this study was determined through molecular modelling of the molecules using Microsoft® Modelling v.3.2.0.0 Accelrys. The colour scheme used represents a negative charge as red, a positive charge as blue, and green as being almost neutral. The results of the molecular modelling are depicted below in Table 3-2.

Table 3-2: Molecular modelling of gasses used

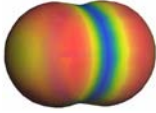
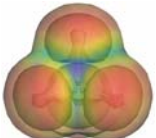
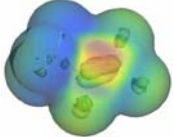
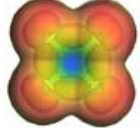
Molecule	Molar volume ($\text{\AA}^3$)	Molar diameter ($\text{\AA}$)	Charge distribution
N_2 	45.17	1.62	Negative surface with positive core
CF_4 	47.60	2.68	Negative surface with positive core
C_3F_6 	85.00	5.52	Positive surface with negative core
$\text{c-C}_4\text{F}_8$ 	108.06	13.34	Negative surface with positive core

Table 3-2 indicates that, apart from $\text{c-C}_4\text{F}_8$, the molecular diameter of the other gasses differs by less than $4\text{\AA}$ which implies that a separation technique that relies on molecular size differences to separate molecules, such as nanofiltration, will not be effective in separating these gasses. Table 3-2 also indicates that, with the exception of Hexafluoropropane (C_3F_6), all the gasses have a predominantly pseudo negative surface charge. This is the first indication that C_3F_6 will behave differently from the other gasses. Depending on the surface charge of the membrane(s) used, the attracting or repelling forces for C_3F_6 will be different from that of the other gasses. Dense membranes with a surface charge could thus be used to separate at least C_3F_6 from the other gasses.

3.2.2 Membranes

There are a vast variety of polymers available for use as membrane materials. Feng and Huang (1997:1055) classified these polymers as being either glassy, rubbery, or ionic. Glassy polymer membranes tend to be more selective towards water while rubbery ones prefer organic compounds. Ionic polymer membranes act on charge differences and are charge selective. Apart from this classification, polymers are also classified as being hydrophobic or hydrophilic. It is well known that hydrophobic polymers are more selective towards organic compounds than towards water.

With all these different classifications of polymers, there is still no clear cut method in selecting a specific polymer for use in specific membrane processes (Marx, 2002:31). This could be mainly attributed to the theoretical fact that polymers can be engineered for a specific purpose. Marx (2002:31) further stated that several attempts have been made to publish guidelines for selecting polymers as membrane materials; none of these have found wide scale application in the field of membrane science. Today, one of the most basic but still very accurate methods is to look at the preferential affinity of the polymer for one or more compounds in a mixture. This approach has been made in the selection of possible membranes to be used in this study.

Teflon® membranes were selected for screening, since it is well known that fluoruous liquids are selective solvents for fluoruous compounds (Zhang, 2006:16). Zhang further stated that there is currently a large drive in the manufacturing of stable Teflon® AF membranes around the world, indicative of the popularity of using Teflon® as membrane material. Two custom made Teflon® AF2400 membranes and one silicon rubber membrane were manufactured by GKSS Forschungszentrum: Institut Fur Polymerforschung in Germany.

The first Teflon® AF2400 membrane consisted of a poly-acrylonitile primary support and a polyester secondary support (referred to in text as PAN-supported membrane). The second Teflon® AF2400 membrane consisted of a poly-ether-imide primary support and a polyester secondary support (referred to in text as the PEI-supported membrane). The silicon membrane had no support structure.

Nafion® membranes are non-reinforced films based on chemically stabilised perfluorosulfonic acid/PTFE copolymers in the acid (H^+) form that was first developed by

DuPont in the early 1960s and has been used for more than 35 years in fuel cells for space travel (Banerjee & Curtin, 2004:1211). Currently, Nafion® membranes play an integral role in the success of recent PEM fuel cell demonstration programmes in portable, stationary and transportation applications. Since it is a fluorinated based membrane, the same principle of affinity will apply for the Nafion® membranes as for the pure Teflon® ones.

Three Nafion® membranes (Nafion®-117, Nafion®-NRE-212 and Nafion®-1135) were purchased from ElectroChem Inc. The Nafion®-117 and 1135 are 7mm and 3.5mm thick non-reinforced extrusion cast films while the Nafion®-NRE-212 membrane is a reinforced 2mm thick solution cast film (Banerjee & Curtin, 2004:1214).

The membranes used were identified by the industrial partners as the preferred membranes to be used in this study. Each of these six membranes were subjected to a series of screening tests in order to identify the best possible membrane(s) for use in the remainder of this study. The results of the screening tests are portrayed in Section 3.3.4 with the subsequent membrane selection and characterisation in Section 3.3.5 of this report.

3.3 Experimental setup and apparatus used

The study of several published articles and theses (Wijmans *et al.*, 2004:206; Wu *et al.*, 2006:52; Bai *et al.*, 1995:80, Zha *et al.*, 2005:301) realised a commonality between the setups for membrane gas separation. Although there are differences in the finer detail, all consists of basically the following units:

- Gas storage cylinders with pressure regulators
- Flow controllers
- A membrane module inserted in a temperature controlled environment such as a water bath or an oven
- Downstream pressure regulators in the form of reservoir tanks or back pressure regulators
- Flow measurement devices such as rotameters or soap flow meters
- Gas analysis devices, usually a gas chromatograph (GC).

The design of the setup used in this investigation was adapted from these generalisations found in literature.

The experimental apparatus design for experimentation using the above list as a guide is depicted in a simplified flow diagram in Figure 3-1 while the actual setup used in the study is illustrated in Figure 3-2. This specific setup was used with success in one previous Masters Degree and one Ph.D. The results obtained in these studies were comparable with published literature, and therefore the setup can be taken as accurate and precise (Zha, 2006, Louw, 2006 and Van Vuuren, 2005). The only adjustments made was to automate the GC sampling procedure. It was believed that this would increase the accuracy even further.

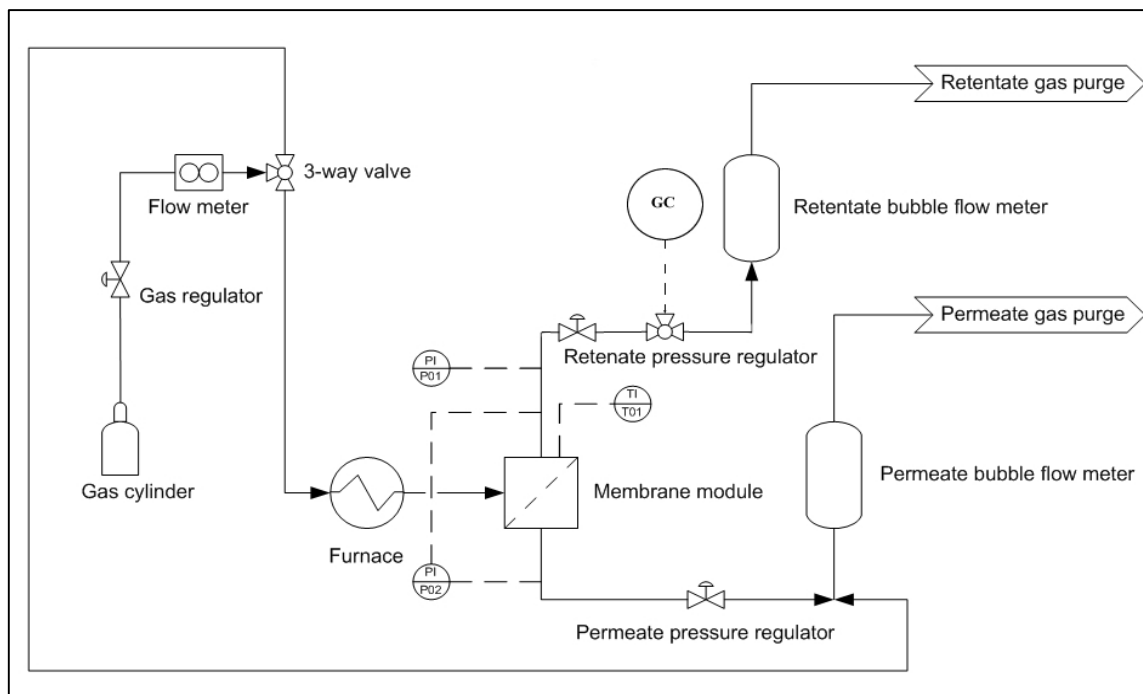


Figure 3-1: Flow diagram of the experimental setup



Figure 3-2: Photo of the experimental setup

The setup is a standard membrane gas separation operation. The process begins with gas cylinders of each gas fitted with pressure regulators (1). From the cylinders, the gas flows to mass flow controllers (2) that are used to make up gas mixtures of the different gasses as required. The gas then flows to a three-way valve which has two valve settings. The first valve setting bypasses the entire setup and feeds the gas directly into soap flow meters (5). The second setting feeds the membrane module situated inside an oven (3). Before entering the module, the gas is allowed to flow through a 50cm long coiled pipe inside the oven. This is to ensure that the gas that enters the membrane module is maintained at a uniform temperature of 25°C (simulated ambient temperature). Inside the membrane module, the gas comes into contact with the membrane and separates into a retentate and permeate stream. Both of these streams exit through separate back pressure regulators (4), either to soap flow meters (5) to measure the flow rate, or to an online gas chromatograph (GC) for component analysis (6). The pressure inside the module, as well as the trans-membrane pressure is controlled by the back pressure regulators. These pressures are shown on a pressure meter and a differential pressure meter respectively (7). The temperature inside the module is measured with a thermocouple. For a complete equipment list, see Table 3-3.

Table 3-3: Complete equipment list

Equipment	Quantity	Supplier	Important specification
Gas cylinder pressure regulators	6	Wika Instruments Ltd.	Max inlet pressure 30 bar
Mass flow controller	4	Brooks Instruments	Max flow rate of 300 ml/min
Furnace	1	Custom Furnaces C.C.	Max temperature of 250 °C
Membrane module	1	In-house design	See Section 3.3.1
Thermocouple	1	Eurotherm	-
Back pressure regulators	2	Swagelok Ltd.	Stainless steel
Non-return valve	4	Swagelok Ltd.	7 kPa feed pressure to open
Pressure meter	1	Wika Instruments Ltd.	-
Differential pressure meter	1	Wika Instruments Ltd.	-
Soap flow meters	2	-	-
Nitrogen gas cylinder	1	Affrox Ltd.	99.999% purity
CF ₄ gas cylinder	1	NECSA	99.99% purity
C ₃ F ₆ gas cylinder	1	NECSA	99.99% purity
He gas cylinder	1	Affrox Ltd.	99.999% purity
Air cylinder	1	Affrox Ltd.	Zero Air
Gas Chromatograph and computer	1	Hewlett Packard	HP6890

The balance of the setup is consists of 1/8" stainless steel and HDPE piping and Swagelock fittings.

3.3.1 Membrane module

A membrane module constructed of 316 stainless steel was used to house the membrane. A 316 perforated stainless steel plate with 1 micron clearance (listed as number 1 in Figure 3-3(b)) was used as a support for the membrane. Standard o-rings (2) with a temperature

resistance of 250°C were used to seal the module. The diameter of the membrane exposed to gas transport was 75mm (3), exposing a membrane area of 4 417.86mm² to the feed gas. A picture of the assembled module as well as the components are depicted in Figure 3-3. Table 3-4 furnishes the specification of each component.



Figure 3-3: Membrane module photo

Table 3-4: Membrane module component specification list

Part Characteristic	Attribute
Inside diameter	95mm
Outside diameter	120mm
Height	50mm
Feed inlet	1/8"
Permeate outlet	1/8"
Retentate outlet	1/8"
Perforated plate diameter	78mm
Perforated plate thickness	3mm
102 mm ID o-rings	x3
83 mm ID o-rings	x1
Membrane diameter	95mm

3.3.2 Flow controller calibration

Brooks 5850S Mass Flow Control valves are controlled by means of a percentage opening of the control valve, accompanied with a non-return valve at the end. Such control will ultimately lead to differences in the flow rate for each gas at the same percentage opening of the control valve. To account for this, the control valve was set at different percentage openings, and in each instance pure gas samples were allowed to flow directly to the soap flow meters to measure the flow rate of the gas. The flow rate as measured by the soap flow meters were plotted against the percentage opening of the valve, as illustrated in Figure 3-4

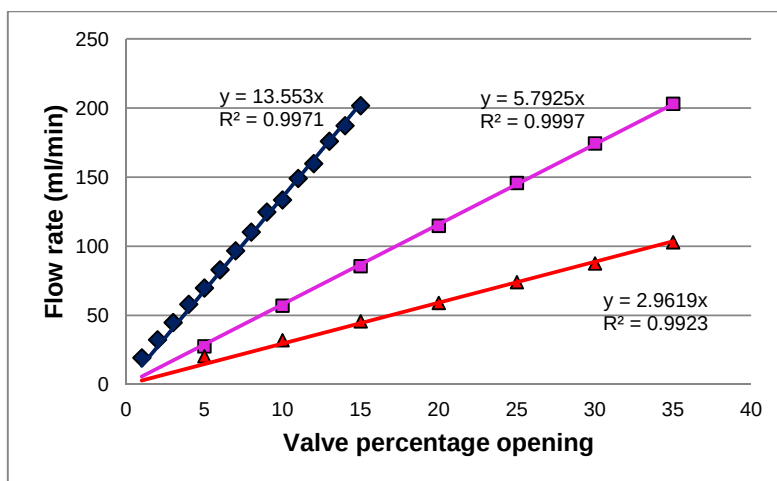


Figure 3-4: Calibration graphs for flow meter 1 (♦ - N₂, ■ - CF₄, ▲ - C₃F₆)

Figure 3-4 is an example of flow meter 1. For information on the other flow meter, refer to Appendix B. The data indicated a linear dependency while a linear equation could be fitted to it. It was subsequently used to determine the percentage opening of a specific valve to yield the required flow rate of a specific gas. This was performed for each valve independently because the flow rates differed from valve to valve.

3.3.3 Analysis

An in-line HP6890 gas chromatograph (GC) system was used for gas analysis. The GC was fitted with two 2m long custom made packed columns fitted in series which were obtained from NECSA and controlled via a computer using Chemstations™ Software. The properties of the column can be found in Table 3-5 and the operational specifics in Table 3-6.

Table 3-5: Single column specifications

Attribute	Specification
Length	2m
Material of construction	Stainless Steel
Support	Hatesep N
Mesh range	100/120
Maximum temperature	165°C

Table 3-6: GC operating conditions

Attribute	Specification
Detector type	TCD
Detector temperature	120°C
Filament temperature	150°C
Initial temperature	50°C
Initial temperature constant time	2min
Ramp rate	10°C.min ⁻¹
Final temperature	160°C
Final temperature constant time	2min

In order to efficiently use the GC, it needed to be calibrated for the different gas combinations. Mixtures of the three gasses, N₂/CF₄, N₂/C₃F₆ and CF₄/C₃F₆ were composed, starting at a 90/10 volume ratio all the way down to a 10/90 volume ratio. Each of these mixtures were sent directly to the GC for analysis. The areas below the peaks were noted and the ratios of these areas were plotted against the feed volume ratio. This yielded a straight line through the origin which was used for calibration. An example of a calibration is shown below in Figure 3-5. Refer to Appendix B for a discussion on the calculations used for the calibration of both the binary and ternary gas mixtures.

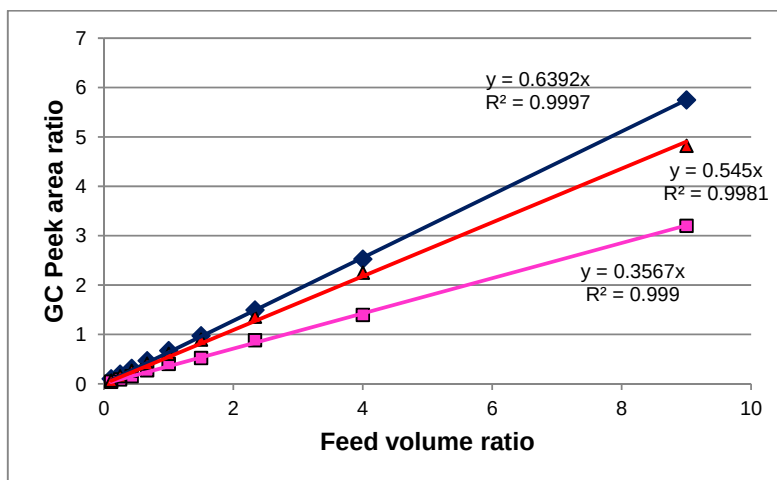


Figure 3-5: GC calibration graphs (♦ - N₂/CF₄, ■ - N₂/C₃F₆, ▲ – CF₄/C₃F₆)

3.3.4 Membrane screening and selection

The six membranes mentioned in Section 3.2.2 were tested for their single component permeation capabilities. 10ml.s⁻¹ of pure N₂, CF₄ and C₃F₆ were fed to the system at pressures of 50-, 100-, 150- and 200kPa respectively. The trans-membrane pressure was held at a maximum for each of the feed pressures. However, while using the PAN- and PEI-supported membranes it was discovered that high trans-membrane pressures at high feed pressures for some of the gasses were impossible to maintain at the selected feed rate. It was therefore decided that the trans-membrane pressure be kept constant at 40kPa. Table 3-7 furnishes a summary of the screening results.

To ensure stable operations, it was necessary to determine the elapsed operating time before steady state was reached. The system was left to run for an undetermined time for each gas and membrane combination. For both the PAN- and PEI-supported membranes, steady state was reached at five minutes operating time.

Table 3-7: Membrane screening result summary

Membrane number	Membrane description	Supplier	Success
PEI-001-NWU	Teflon® AF2400 membrane with PAN primary support	GKSS	✓
PEI-002-NWU	Teflon® AF2400 membrane with PEI primary support	GKSS	✓
PEI-003-NWU	Silicon rubber membrane	GKSS	✗
ELE-001-NWU	EC-NM-117 Nafion 117	ElectroChem Inc	✗
ELE-002-NWU	EC-NM-NRE-212 Nafion-NRE-212	ElectroChem Inc	✗
ELE-003-NWU	EC-NM-1135 Nafion 1135	ElectroChem Inc	✗

In Table 3-7, it is indicated that only the PAN- and PEI-supported membranes demonstrated sufficient gas permeation to be used in this study. None of the Nafion® membranes revealed any permeation for any one of the three gasses, while the permeation of N₂ using the silicone rubber membrane was extremely low. This correlates with results published by Achalpurkar *et al.* (2007:32). For the CF₄ and the C₃F₆ there was no permeation using the silicone rubber membrane.

The screening results for the PAN- and PEI-supported membranes are shown below in Figure 3-6 and Figure 3-7 respectively.

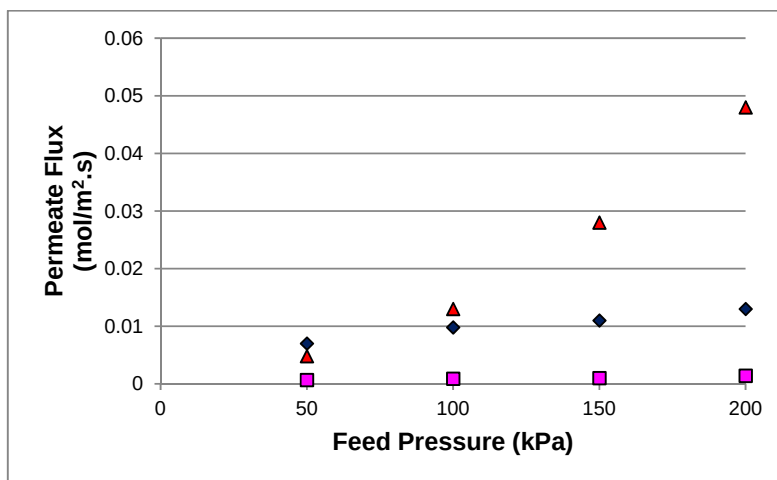


Figure 3-6: Screening results for the PAN-supported membrane at 40kPa trans-membrane pressure (♦ - N₂, ■ - CF₄, ▲ - C₃F₆)

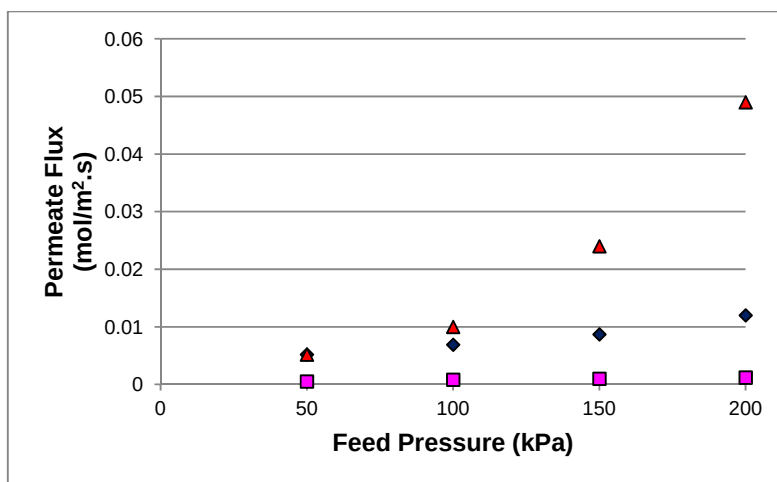


Figure 3-7: Screening results for the PEI-supported membrane at 40kPa trans-membrane pressure (♦ - N₂, ■ - CF₄, ▲ - C₃F₆)

Figure 3-6 and Figure 3-7 exhibit a high degree of similarity between the screening results of the two membranes. This renders it very difficult to select only one of the membranes for detailed testing. In the light of this, it was decided to use both membranes for further study.

3.3.5 Membrane characterisation

As demonstrated above, both the PAN and PEI-supported membranes favour the possibility of separating the gasses. Both these membranes consist of a Teflon® AF2400 layer. Teflon® AF is a glassy copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-

difluoro-1,3 dioxole (PDD) (Zhang, 2006:2). The structure of a Teflon® AF2400 molecule is illustrated below in Figure 3-8, which depicts an outer layer of fluorine atoms which will give the Teflon® layer a predominant negative charge. This is very important considering the difference in the Fukui electron affinity of the gasses tested.

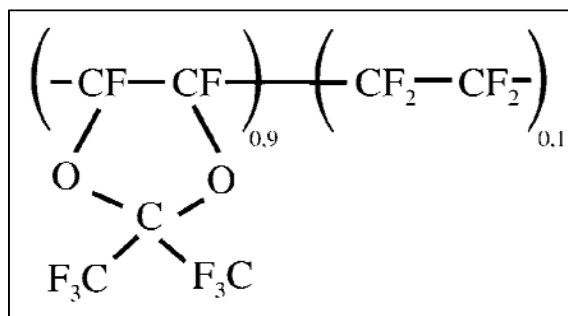


Figure 3-8: Illustration of a repeat unit of Teflon® AF2400 (Pinnau & Toy, 1996:126; Nunes & Peineman, 2006:60)

The Teflon® AF2400 polymer has an exceptionally high free volume (unoccupied space by the macromolecules) of 0.327. In spite of this, it possesses gas transport characteristics of conventional low-free-volume glassy polymers. Teflon® AF is known for its permeability of permanent gasses (oxygen and nitrogen) and is only slightly permeable to organic vapours (Pinnau & Toy, 1996:126). The most important properties of Teflon® AF2400 are summarised in Table 3-8 below.

Table 3-8: Properties of Teflon® AF2400 (Brydson, 1999:378; Zhang, 2006:3)

Property	Value
TFE content	13 mol%
Crystallinity	None
Glass transition temperature	240°C
Density (SG)	1.75
Melt viscosity	1.67Pa.s
Mechanical properties:	
Tensile strength	24.6MPa
Ultimate elongation	6.1GPa
% elongation	7.9%

3.3.5.1 PAN-supported membrane

The PAN-supported membrane consisted of three layers, namely:

- A $7.87\mu\text{m} \pm 13.72\%$ thick Teflon® AF2400 layer. This was a dense membrane layer meaning that no visible holes or flow channels could be observed.
- The second layer was a porous poly-acrillo-nitrile (PAN) layer with a thickness of $35.63\mu\text{m} \pm 8.97\%$, as measured on the Scanning electron microscope (SEM).
- The final layer was a very porous polyester support layer. The thickness of this layer was measured by the SEM to be $157.67\mu\text{m} \pm 2.54\%$.

SEM photos of the membrane side view and the top layer are depicted in Figure 3-9 below. Note that the reported layer thickness is an averaged thickness, which does not necessarily mean a measured thickness that is accurate up to a hundredth of a micron.

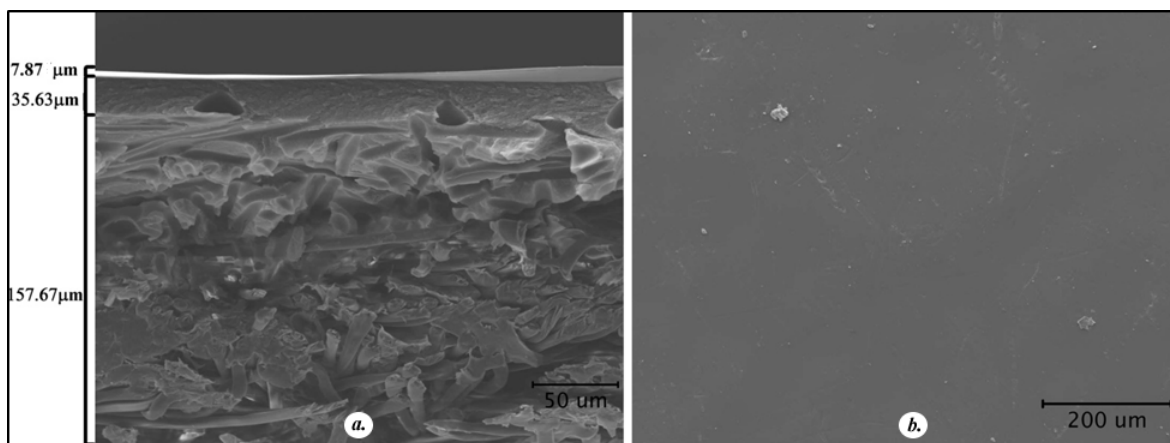


Figure 3-9: SEM photos of the PAN-supported membrane with (a.) The membrane side view and (b.) The dense top layer

Figure 3-9a clearly reveals that the thin Teflon® AF2400 top layer is not uniform in thickness. For this reason the thickness of the layer was measured by the SEM at ten different positions across the membrane and thereafter taken as the average of these measurements. Furthermore, it is clear that the porosity of the membrane increases from the top layer to the bottom one. Figure 3-9b depicts a nearly flawless top layer which is indicative of the dense nature of the membrane. The visible ‘flaws’ observed on the photo can be attributed to dust particles.

3.3.5.2 PEI-supported membrane

The PEI-supported membrane is very similar to the PAN-supported membrane in that only the first support layer, and the thickness of each layer differs. It therefore consists of three layers namely:

- The Teflon® AF2400 top layer. This is again a dense layer, but this time has a thickness of only $1.97\mu\text{m} \pm 20.81\%$.
- The second layer in this case is made of poly-ether-imide (PEI). The PEI layer was measured as being $73.25\mu\text{m} \pm 5.64\%$ thick.
- The membrane is rounded off with a $127.0\mu\text{m} \pm 3.60\%$ thick polyester layer which again lends support to the rest of the structure.

SEM photos of the PEI-supported membrane are shown in Figure 3-10.

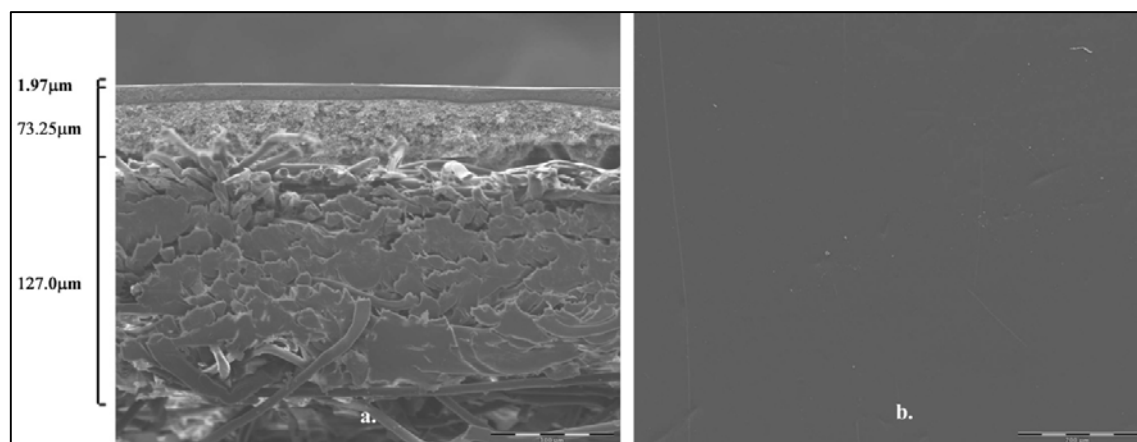


Figure 3-10: SEM photos of the PEI-supported membrane with a. The membrane side view and b. The dense top layer

As in the case with the PAN-supported membrane, the photo in Figure 3-10a again shows an uneven Teflon® layer for the PEI-supported membrane. The indicated thickness of this layer is again an average of 10 measurements. It also shows the dense top layer. As expected by now, the hydro affinity of the membrane is the same as that of the PAN-supported membrane, since the top (or active) layer is manufactured from the same material.

3.3.6 Gas adsorption

Sorption of the gas onto the surface of the membrane forms part of the separation mechanism proposed by the solution-diffusion model (Equation 2.7). It is therefore important to study the adsorption of the gasses on the membrane surface. For this, the membrane was placed in a

low pressure TGA (the maximum pressure is 1bar) to measure any mass gain and/or loss when a specific amount of gas was introduced to the atmosphere surrounding the membrane. This was performed isothermally in order to evaluate the influence of changing pressure on the sorption characteristics of the membrane.

Data obtained from the experiments as described above were then fitted to Langmuir isotherms in order to obtain the adsorption equilibrium constant and the maximum amount of gas adsorbed at each pressure interval. Langmuir isotherms may be used under the assumption that the surface of the pores of the adsorbent is homogeneous and that the forces of interaction between the molecules are negligible (Seader & Henley, 1998:799). The Langmuir isotherm can then be written as:

$$q = \frac{Kq_{max}P}{1+KP} \quad 3.1$$

where K is the adsorption equilibrium constant at a specific temperature and q_{max} is the maximum amount of gas adsorbed. These two constants are treated as being empirical in nature. It can be calculated by fitting a nonlinear equation directly to the data, or by manipulating the data in order to fit it as a straight line (Seader & Henley, 1998:799).

Rearranging Equation 3.1 will yield the following linear equation:

$$\frac{P}{q} = \frac{1}{q_{max}K} + \frac{P}{q_{max}} \quad 3.2$$

Thus, by plotting P/q vs. P will yield a straight line with the slope equal to $1/q_{max}$ and the intercept equal to $1/q_{max}K$.

This process was carried out using helium as a carrier gas and testing the adsorption of N_2 , CF_4 and C_3F_6 on both the surface areas of the PAN and PEI-supported membranes. These results were less than favourable. It showed extremely small amounts of adsorption by the gasses onto the membrane. For N_2 and CF_4 the amounts adsorbed fell within the experimental error range of the TGA and therefore it was not useful. Only C_3F_6 yielded usable results. Bissett (2009) conducted a parallel project using Zeolite based membranes that were coated with Teflon® AF2400 powder. He carried out adsorption tests on pure Teflon® AF2400 powders and achieved similar results for N_2 and CF_4 . The results for C_3F_6 constituted a

significant improvement from the ones obtained by using the membranes. Since the active surface of the membrane consists of Teflon® AF2400 powder, it was decided to use the C_3F_6 results of Bissett (2009) for the sorption modelling thereof.

A literature survey furnished results for N_2 and CF_4 adsorption at high pressures on Teflon AF2400® (Merkel *et al.*, 1999:371; Bondar *et al.*, 1999:6164). In both these cases, the sorption was performed at 35°C and at a pressure range between 0 and 30 atm. The dual mode sorption model (Equation 3.3) was fitted by Bondar *et al.* (1999:6164) using the least squares method, which showed to be a very good fit.

$$q = K_H P + \frac{K q_{max} P}{1 + K P} \quad 3.3$$

It indicated that both Henry and Langmuir sorption took place. An effort to recreate the modelling using the same data and modelling method yielded a zero value for the Henry term, thus leaving only Langmuir sorption as a possibility. This was the case for both N_2 and CF_4 . It was therefore decided to remodel the data presented in both these studies using the Langmuir adsorption equation (equation 3.1). Figure 3-11 displays the original data as reported by Bondar *et al.* (1999) with the Langmuir model fitted to the data.

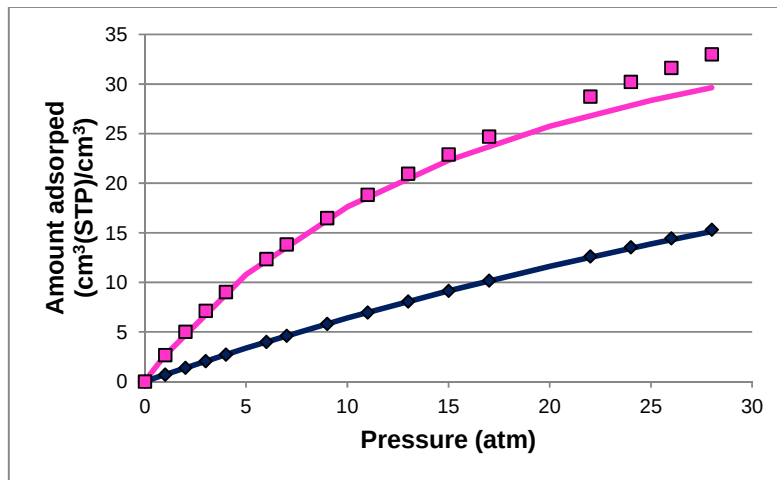


Figure 3-11: N_2 and CF_4 adsorption onto Teflon AF2400® as reported by Bondar *et al.* (1999) and the fitted Langmuir model (♦ - N_2 data, ■ - CF_4 data, — - N_2 model, — - CF_4 model)

The model revealed a good comparison with the data. For the N_2 gas the models fitted across the entire pressure range. This was however not the case for the CF_4 where deviation between

the model and the data is clearly visible at higher pressures only. Since the membrane unit was operated at a maximum pressure of 2bar, these deviations were not deemed to be a problem. Table 3-9 displays the Langmuir parameters for the above models and the standard deviation as calculated by Equation 3.4.

For the C_3F_6 , data was obtained at temperatures starting at 293K up to 333K for 10K increments. At each temperature, the pressures used were 0.05bar, 0.10bar, 0.15bar, 0.17bar, 0.51bar and 0.85bar. Langmuir isotherms were fitted to this data using the least squares method (the parameters resulting from the modelled data are portrayed in Table 3-9). The isotherms were plotted together with the original data that yielded the graph shown in Figure 3-12.

Table 3-9: Fitted Langmuir parameters

Temperature (K)	K	$q_{\max}$ (cm ³ (STD)/cm ³)	Std dev
293	5.432	33.788	0.444
303	5.718	28.557	0.543
313	3.518	23.474	0.163
323	3.098	21.213	0.209
333	3.449	16.523	0.515
N₂ and CF₄ adsorption at 35°C			
Substance	K	$q_{\max}$ (cm ³ (STD)/cm ³)	Std dev
N ₂	0.011	62.635	0.005
CF ₄	0.058	47.732	0.283

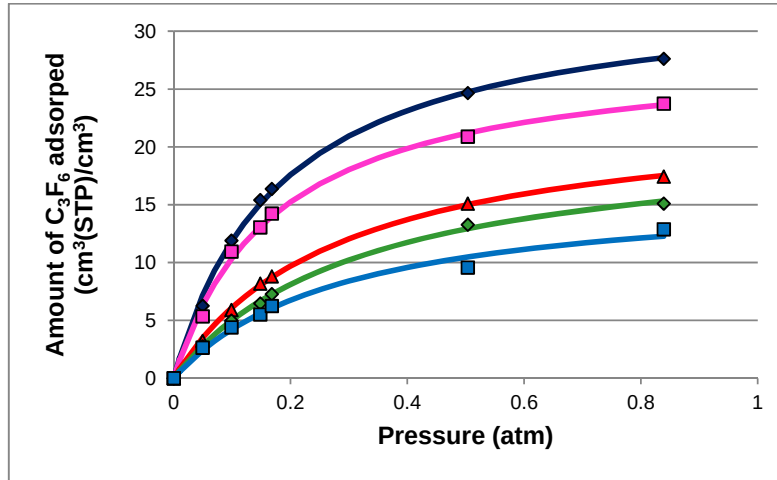


Figure 3-12: Adsorption isotherm of C_3F_6 on Teflon® AF2400 powder (♦ - 293K data, ■ - 303K data, ▲ - 313K data, ◆ - 323K data, ■ - 333K data, — - 293K model, — - 303K model, — - 313K model, — - 323K model, — - 333K model)

Figure 3-12 indicates that an increase in temperature resulted in an overall decrease in the adsorption capability of the powder. In contrast to this, an increase in the pressure resulted in an increase in the adsorption of the gas onto the surface of the powder. This can be explained by looking at the condensability of the gas. Dingemans *et al.* (2008:107) states that the solubility of a gas in a polymer is related to the condensability of the gas, which in turn is a function of the critical temperature of the gas. A high critical temperature means a high condensability which will result in a high solubility of the gas into a polymer. Table 3-1 indicates that the critical temperature of C_3F_6 is by far the highest, which resulted in it having the best sorption characteristics. Thermodynamic equations of state show that an increase in pressure will result in an increase in the adsorbed amount, whereas increases in temperature have an adverse effect.

Also indicated in Figure 3-12 and Table 3-9 is that the model shows a good fit with the experimental data. A specialised standard deviation between the data points and the model was calculated using Equation 3.4 below (Oshoa *et.al.*, 2001:172).

$$SD = \sqrt{\frac{\sum (y_{exp} - y_{calc})^2}{NM - PM}} \quad 3.4$$

where NM is the number of experimental data points and PM is the number of regressed parameters. The values obtained from the calculations are those indicated in Table 3-9 and was found to be very small. This is validated by Figure 3-13. The black line in Figure 3-13 indicates a perfect fit. Almost all data points lie on top of this line, indicative of the correctness of the model.

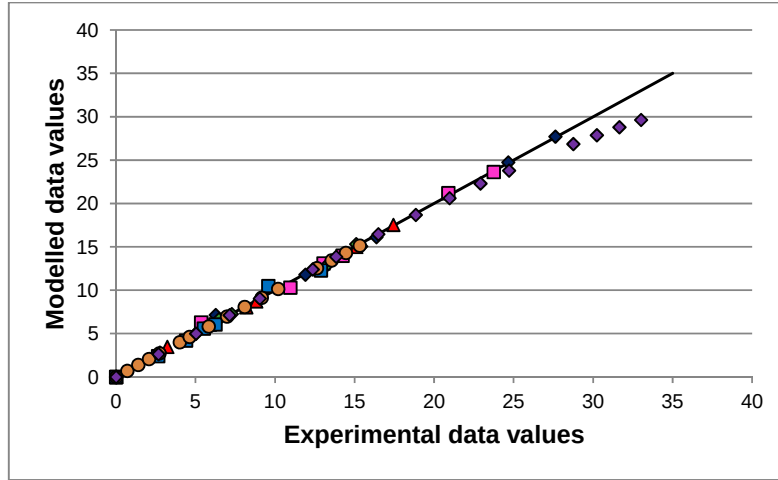


Figure 3-13: A comparison between the adsorption experimental data and modelled data points (♦ - 293K, ■ - 303K, ▲ - 313K, ◆ - 323K, ■ - 333K, ● - N₂, ◆ - CF₄)

Bondar *et al.*(1999:6165) demonstrated the existence of a linear relationship for different gasses when the critical temperature of a specific gas is plotted against its Langmuir affinity parameter (K). To evaluate the validity of the modelled values, it was added to the graph published by Bondar *et al.* (1999:6165) and depicted here in Figure 3-14. The red data points are those obtained in the modelling as discussed above.

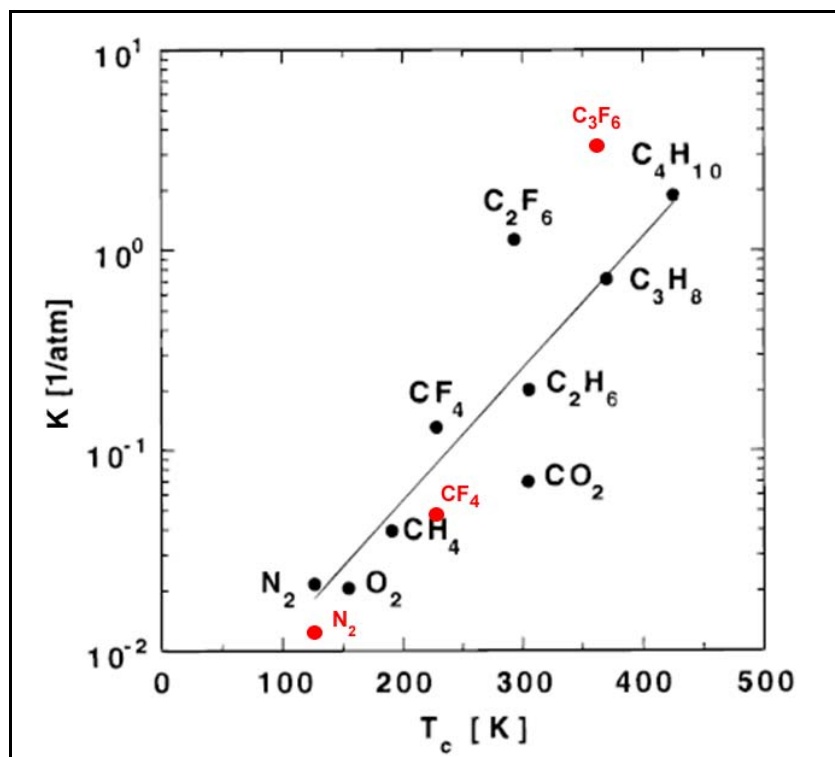


Figure 3-14: The Langmuir affinity parameter (K) as a function of the critical temperature (T_c) of the adsorbed gases in Teflon AF2400® (• - New modelled values) (Bondar *et.al.*,1999:6165)

Figure 3-14 above clearly indicates that there was a significant amount of scatter around the linear line to begin with. The three added values seem to lie within these scattered values which serve as a validation for the modelled parameters. Interesting to note is the decrease in the Langmuir affinity values for N_2 and CF_4 due to the absence of the Henry adsorption regime.

3.4 Experimental design

The experimental design will comprise three sections namely:

- Pure component permeation testing and modelling
- Binary mixture permeation testing and modelling
- Cascade design and testing.

Since the aim of this project was to design a cascading membrane unit process that operates near ambient conditions, it was decided to keep the temperature constant at 25°C throughout this study. This was achieved by placing the membrane unit in a controlled oven at that temperature (see Figure 3-2). The estimated feed rate of gas received from the adjacent plasma reactor would be approximately 100ml.min⁻¹. For this reason it was decided to feed the experimental setup with the same amount of gas. Feed pressures were however varied between 50, 100, 150 and 200kPa, with trans-membrane pressures starting from 10kPa, increasing with increments of 10kPa until the maximum trans-membrane pressure for a particular feed pressure was reached. This was then repeated for each gas individually.

For the binary mixture testing, the operating conditions were the same as described above for the pure gas testing. One difference was that only the best feed pressure that resulted from the pure component testing was used. Gas mixture of N₂/CF₄, N₂/C₃F₆ and CF₄/C₃F₆ were made up in molar ratios of 0.9:0.1, 0.5:0.5 and 0.1:0.9 and fed to the system.

The ternary cascades were carried out very similarly to the binary mixtures. Equimolar mixtures of N₂/CF₄/C₃F₆ were used as feed composition at 200kPa feeding pressure. Apart from that, molar feed ratios were also varied between the following compositions: 80:10:10, 10:80:10 and 10:10:80.

3.5 Summary

A setup that resembles typical membrane testing rigs was designed and commissioned. It was used to screen six different membranes that were obtained for the project. Of the six membranes, only the PAN and PEI-supported Teflon® AF2400 membranes showed promise of separating N₂, CF₄ and C₃F₆. Initially c-C₄F₈ was also earmarked for testing, but examination of the properties of the gasses revealed that the vapour pressure of the gas at room temperature was almost the same as the operating pressure of the setup. This led to the conclusion that it would be easier to separate this gas from the others by means of condensation than to do so with membranes. This gas was therefore eliminated from the rest of the testing.

Sorption of the light gasses onto the membrane surface was difficult to detect with the apparatus used in this study. Similar results were observed when doing the sorption tests with pure Teflon® AF2400 powder. Sufficient C₃F₆ does however adsorb onto the surface of

the Teflon® powder to obtain data that is suitable for fitting Langmuir isotherms and to calculate the adsorption constant and the maximum adsorption.

3.6 References

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CHAPTER 4: SINGLE GAS MEMBRANE PERMEATION

*Isn't it astonishing that all these secrets
have been preserved for so many years
just so that we could discover them!*
- Orville Wright

4.1 Introduction

The obtained results together with the modelling of single gas permeation through both the PAN and PEI-supported Teflon® AF2400 membranes will be discussed in this chapter. These results formed the basis for a provisional patent in 2008 between the North-West University staff members and the Nuclear Corporation of South Africa (NECSA). This patent was filed for completion in 2009.

4.2 Literature survey

Although perfluorocarbon (PFC) separation using membranes are not a novel idea, very little information on PFC diffusion through membranes is available (Merkel *et al.*, 1999:8429). Most studies on the subject focussed on tetrafluoroethelene (TFE, C₂F₄). Pure poly-tetrafluoroethylene (PTFE) shows very low permeability values for both large and small molecule PFCs. Merkel *et al.* (1999:8427) quotes the permeability of N₂ through PTFE to be as low as 1.3 barrer ($4.352 \times 10^{-19} \text{ kmol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$).

Over the years, two models have been proposed for use in permeation processes (Wijmans & Baker, 1995:1). The first of these is the solution-diffusion model. The solution-diffusion model describes the mass transfer process across a membrane surface with the assumption that only the fluid that dissolves into the membrane at the feed side is transported across the membrane by diffusion due to a concentration gradient. Separation of binary mixtures occurs either due to the difference in the amount of fluid for each component adsorbed onto the membrane or by the difference in the rate of diffusion of each fluid through the membrane. The second model proposed is the pore-flow model. In the latter model, separation is achieved by selective flow of fluids through certain pores due to a pressure driven convective flow regime. The introduction of these models in the twentieth century led to a twenty year

debate on the validity and usefulness of each model. In the end, during the 1980s, the solution-diffusion model prevailed and is currently widely recognised as the best model to use for describing permeation processes through solid membranes (Wijmans & Baker, 1995:1).

In Section 2.3.3, the most popular mechanisms by which a gas is believed to permeate through a membrane were discussed in detail. Literature (Yen & Yang, 2003:113; Mauviel *et al.*, 2005:66) demonstrated that the solution-diffusion model, Equation 4.1, offers a good representation of a membrane gas separation system.

$$J_i = \left(\frac{S \cdot \bar{D}_i}{z} \right) (p_f - p_p) \quad 4.1$$

When working at equilibrium, Equation 4.1 reduces to give the steady state permeation flux, J , as (Wu *et al.*, 2006:53):

$$J = \frac{\wp}{z} \Delta P \quad 4.2$$

where $\wp$ is the permeability constant and z is the thickness of the active layer of the membrane. The permeability can then be calculated by:

$$\wp = \frac{J \cdot z}{\Delta P} = S \cdot D \quad 4.3$$

where S is the solubility of the gas in the polymer and D is the diffusivity. The solubility is obtained as follow (Merkel *et al.*, 1999:370; Damle, 2004:26):

$$S = \frac{q}{P} \quad 4.4$$

where q is the sorption amount as defined in Equation 3.1.

Equations 4.1 and 4.2 clearly show a linear dependency of the flux towards the partial pressure difference across the membranes. Mauviel *et al.* (2005:62) stated that this applies only to permanent gasses and that it has been shown that vapour permeabilities depend on operating pressures. When this is the case, variable permeabilities are correlated with partial pressure difference (ΔP) or with partial feed pressure p_f . The question that arose from this is why permeabilities are not also dependent on downstream partial pressure, p_p . This phenomenon is usually neglected in laboratory scale setups. However, it is common practice

to consider the downstream pressure in industrial applications as it has a measureable effect on the flux.

Equation 4.3 shows yet another linear relationship between the permeability (φ) and the solubility coefficient (S) as well as between the permeability (φ) and the diffusion coefficient (D). Mauviel *et al.* (2005:65) showed that if the solubility coefficient forms a linear relationship with the partial pressure of the gas (Henry type), it is expected that the diffusion coefficient be constant across the same partial pressure ranges, or at least also be linear. This can be seen in Figure 4-1 below.

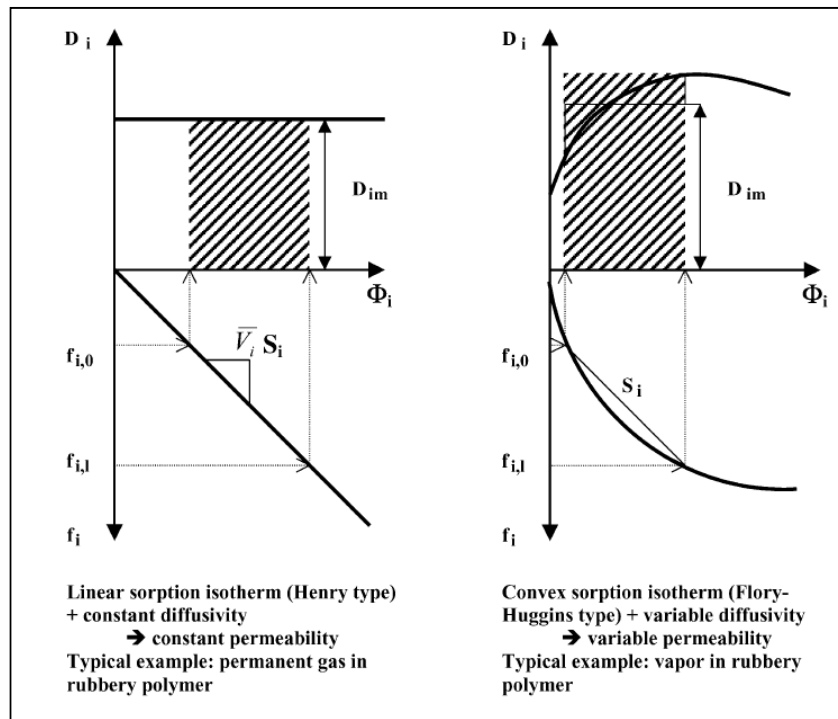


Figure 4-1: Typical sorption isotherms and corresponding diffusivities (taken from Mauviel *et al.*, 2005:65)

However, Figure 4-1 further illustrates that when the solubility coefficient resembles the Flory-Huggins type, which is convex or concave, the resultant diffusion coefficient may increase exponentially or decrease logarithmically.

4.3 Results and discussion for hexafluoropropene (C_3F_6)

Single component gas permeation experiments using hexafluoropropene (C_3H_6), as feed gas to both the PAN-supported and PEI-supported Teflon® AF2400 membranes were conducted

as described in Section 3.3.5.1. The influence of feed side pressure as well as trans-membrane pressure on the flux was investigated. Experimental errors ranged between 0.084% and 0.467%, based on five repetitions. Because of these very small error bands, no error bars are shown in the figures presented below. Details on the calculation of experimental errors can be found in Appendix C. Due to the similarity in the results obtained for the different membranes, descriptive results will be furnished for each membrane in Sections 4.3.1 and 4.3.2 whereafter a discussion will follow in Section 4.3.3.

4.3.1 PAN-supported membrane

The single gas permeation results for C_3F_6 using the PAN-supported membrane is depicted below in Figure 4-2.

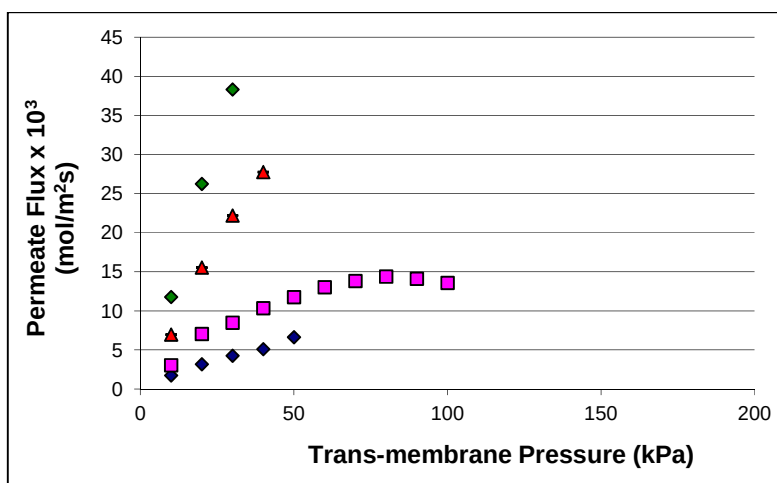


Figure 4-2: Influence of trans-membrane pressure on molar flux through PAN-supported Teflon® AF2400 membrane at different feed side pressures (♦ - 50 kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

In Figure 4-2 it is evident that there was a linear dependency between the flux and the trans-membrane pressure for all but one feed side pressure. At a feed pressure of 100kPa, the flux initially showed a linear relationship with the trans-membrane pressure. However, as the trans-membrane pressure increased, the linearity tapered off to reach a maximum value at 80kPa whereafter there was a decrease in the flux values. This is typical of a system that is dependent on both the upstream and downstream partial pressures. To validate this statement, a graph of the permeate flux versus the product of the trans-membrane pressure and the

permeate side partial pressure would yield a straight line through the origin. This was carried out and is depicted below in Figure 4-3.

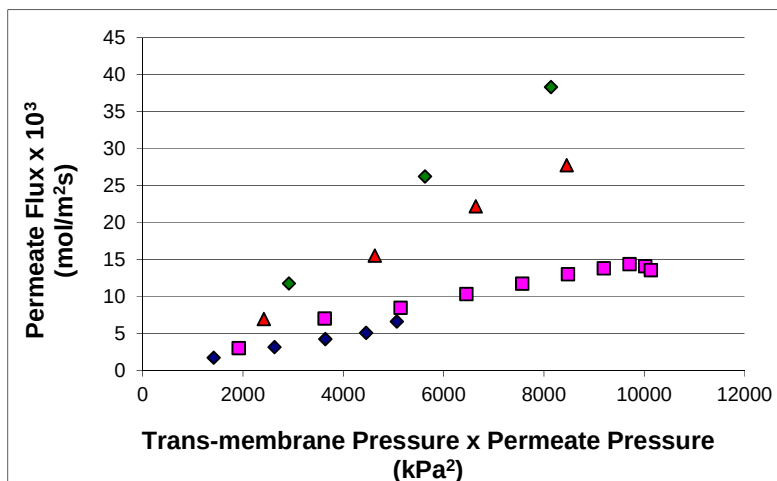


Figure 4-3: Influence of trans-membrane pressure time permeate pressure on molar flux through PAN-supported Teflon® AF2400 membrane at different feed side pressures (♦ - 50 kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

Figure 4-3 clearly illustrates a much-improved linear relationship for all feed pressures. This was found to be true for all gasses using both membranes, and therefore it was decided to present all permeate flux data in this manner. Figure 4-3 further indicates that an increase in the trans-membrane pressure led to an increase in the flux of the gas through the membrane. A maximum flux for C_3F_6 gas of $0.038 \text{ mol.m}^{-2}.\text{s}^{-1}$ was obtained at a feed pressure of 200kPa and a trans-membrane pressure of 40kPa.

The permeability of C_3F_6 through the PAN-supported membrane was obtained by multiplying the thickness of only the active layer of the membrane (see Section 3.3.5.1) with the slope of the curves in Figure 4-3. The influence of feed side pressure on the permeability of C_3F_6 gas through a PAN-supported membrane is presented in Figure 4-4.

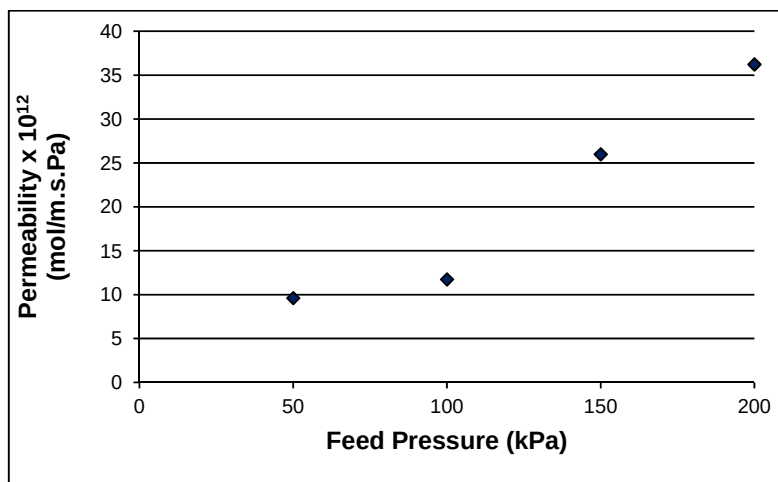


Figure 4-4: Influence of feed side pressure on the permeability of C_3F_6 through the PAN-supported membrane

Figure 4-4 shows a linear relationship between the permeability and the feed pressure from 100kPa onwards. At lower feed pressures this relationship decreased only slightly which indicated a flow resistance for the gas through the membrane. The sorption tests conducted at the same temperature conditions as the permeation tests indicate that the sorption is of the Flory-Huggins type; see Figure 4-5. This implies that there is a non-linear decrease in the sorption coefficient at elevated feed pressures. Since the permeability increases at higher feed pressures, it can be concluded that the main contributor towards permeability is the diffusion coefficient. It will therefore also be the main contributor towards the aforementioned resistance of the gas permeating through the membrane. Merkel *et al.* (2009:8427) found similar trends for different C_xF_y gasses using a 87 mol % 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole [BDD] and 13 mol % tetrafluoroethylene [TFE] membrane (Teflon® AF2400).

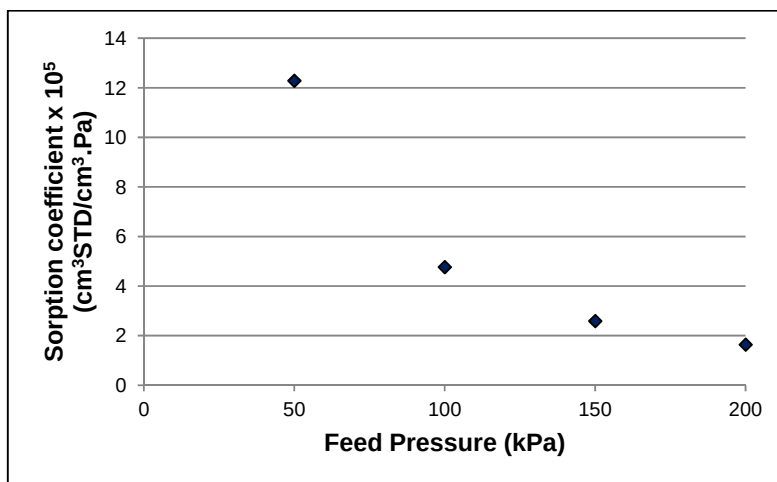


Figure 4-5: Influence of feed side pressure on the sorption coefficient (S)

4.3.2 PEI-supported membrane

For the PEI-supported membrane, similar gas permeation tests were conducted. The results for the pressure influence on the permeating flux are depicted below in Figure 4-6.

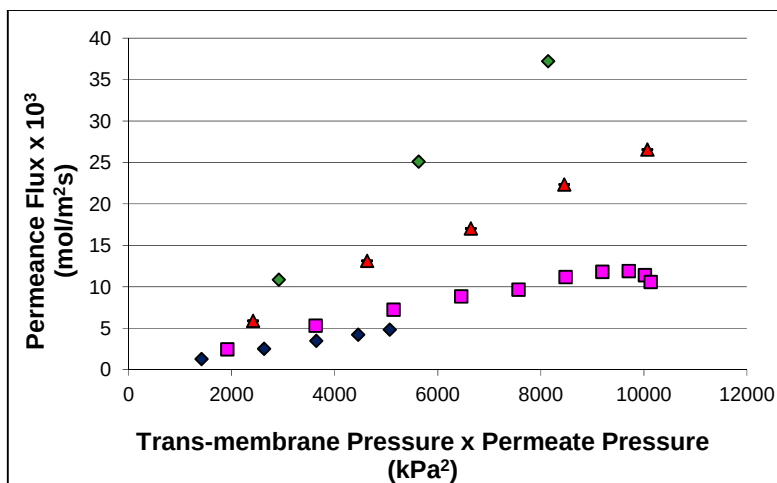


Figure 4-6: Influence of trans-membrane pressure times permeate pressure on molar flux through PEI-supported Teflon® AF2400 membrane at different feed side pressures ($\blacklozenge$ - 50 kPa, $\blacksquare$ - 100kPa, $\blacktriangle$ - 150 kPa, $\blacklozenge$ - 200 kPa)

Figure 4-6 reveals a very similar trend to that in Figure 4-3. It again illustrates the linear dependency between the flux and the product of the pressure differential and permeate

pressure. In addition, Figure 4-6 shows that no permeation was observed for the 150kPa and 200kPa feed pressure tests at high trans-membrane pressures. This is due to the bleeding of the feed pressure because of the rapid permeation rate of the gas at higher trans-membrane pressures. A maximum flux of $0.037 \text{ mol.m}^{-2}.\text{s}^{-1}$ was achieved for a feed pressure of 200kPa at 30kPa trans-membrane pressure.

The permeability graph, depicted in Figure 4-7, illustrates the similarity between the two membranes being investigated. There was only a slight increase in the permeability of the gas at low feed pressures (up to 100kPa). Thereafter a rapid linear increase was observed. As in the case with the PAN-supported membrane, it can be attributed to the existence of a flow resistance that has to be overcome before increases in flow are observed.

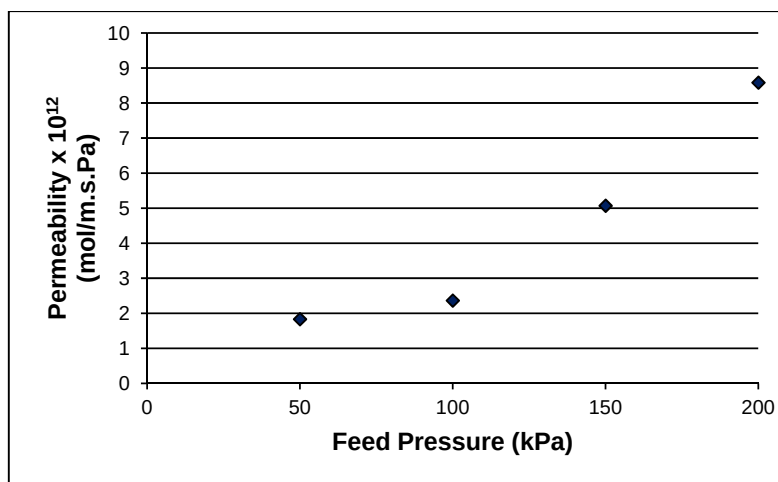


Figure 4-7: Influence of feed side pressure on the permeability of C_3F_6 through the PEI-supported membrane

One noticeable difference between Figure 4-4 and Figure 4-7 is the magnitude of permeability. In Figure 4-4, a permeability value as high as $36 \times 10^{-12} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$ was obtained for the PAN-supported membrane, whereas the corresponding permeability for the PEI-supported membrane was found to be only $8.6 \times 10^{-12} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$. This can be explained by looking at the thickness of the active layers of the membranes. In Section 3.3.5 it was shown that the thickness of the Teflon® AF2400 in the PAN-supported membrane was $7.87 \mu\text{m}$ while it was only $1.97 \mu\text{m}$ thick in the case of the PEI-supported membrane. If the active layer was the only contributor towards the diffusion rate of the gasses,

theoretically, the permeation rate (flux) of the PEI-supported membrane should be significantly higher than for the PAN-supported membrane. Since Figure 4-3 and Figure 4-6 show the permeation flux for the two membranes to be similar, it can be concluded that there is a second layer contributing to the separation. These layers are the PAN and PEI respectively.

Figure 3-9 and Figure 3-10 show that the PAN layer has a thickness of 35.63 μm while the PEI layer's thickness is 73.25 μm . Adding it to the active layer will yield separation zones of 43.50 μm for the PAN-supported membrane and 75.22 μm for the PEI-supported membrane. Due to the Teflon®'s superior separation capabilities the thinner active layer in the PEI-supported membrane will allow gas to pass through it at a quicker rate than for the thicker layer. However, after diffusing through the Teflon® layer, the gas comes into contact with the secondary layer which slows the progression of the gas to such an extent that the resulting permeation rate for the two membranes are similar.

When calculating the permeability, only the thickness of the active layer of the membrane is taken into consideration. Therefore if the permeation fluxes of the two membranes are similar, and the one membrane has a much thinner active layer, the permeability of that membrane will be much lower than for the other one, since the slope of the flux data is multiplied by the membrane thickness. This is precisely what is observed in Figure 4-4 and Figure 4-7.

4.3.3 Discussion

Trans-membrane pressures higher than 50kPa could not be obtained for the C_3F_6 gas in the instances where the feed side pressure was set at 150 or 200kPa. The high rate of permeance resulted in a rapid loss of trans-membrane pressure due to the high rate of permeance of the gas in relation to the feed pressure. High gas permeate rates result in an inability of the feed gas to build up a sufficient pressure at the feed side, resulting in a lower feed pressure and therefore a drop in the trans-membrane pressure of the system occurs. Furthermore, it is observed that, for the 100kPa feed pressure, the graphs in Figure 4-3 and Figure 4-6 show a plateau which is reached from a trans-membrane pressure of 80kPa onwards. This implies a maximum flux for the given operating condition.

As mentioned in Section 3.3.5, Teflon® does have a high percentage free volume. According to Thornton *et al.* (2009:35) it is commonly accepted that, as the percentage free volume in a polymer increases, the pores become more interconnected and provide a flow through path for the permeating gas. This means that the gas diffusion is no longer dependent on polymer chain movements but the gas molecules are now free to move within the maze of connected pores as illustrated by the schematic in Figure 4-8.

This phenomenon implies that gas flowing through the polymer can be described by using the analogy of gas flowing through distorted channels, which is very similar to the dewatering of a filter cake that contains an array of different particle sizes. When working with dewatering, a specific breakthrough pressure (P_b) needs to be overcome before the flow of fluid from the filter cake will commence (Le Roux & Campbell, 2003:1000). This is indicated schematically in Figure 4-9.

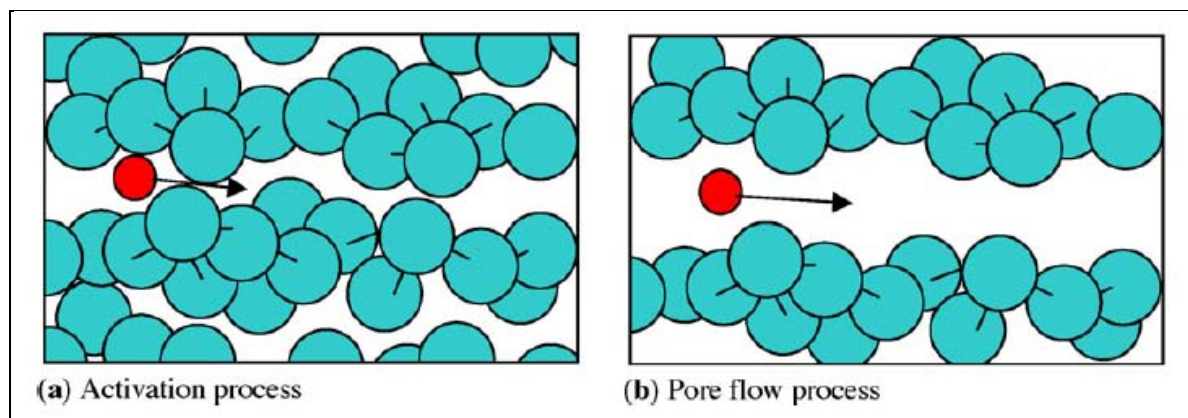


Figure 4-8: Schematic diagram of different diffusion processes within (a) closely packed conventional glassy polymer and (b) high free volume glassy polymer taken from Thornton *et al.* (2009:35)

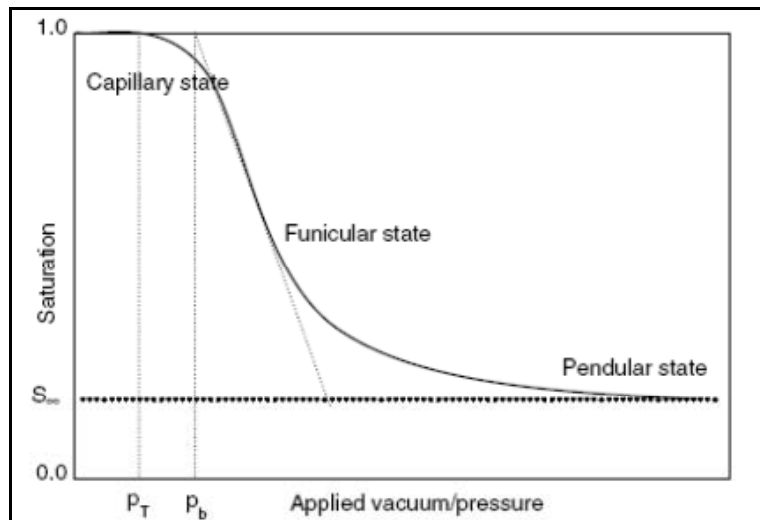


Figure 4-9: Capillary pressure curves for the dewatering of fine particles (Le Roux & Campbell, 2003:1000)

The graph in Figure 4-9 depicts what is called a capillary state where no dewatering occurs. This is due to the existence of capillary forces created by the distorted channels in the filter cake which acts as a resistance to flow. Only when the applied pressure differential across the filter cake becomes greater than the capillary pressure, will the flow start. The capillary pressure generated inside the filter cake is a function of the capillary size; the smaller the capillary size, the larger the capillary pressure and vice versa.

When applying this theory to gasses flowing through a polymer, three distinct differences need to be considered. The first difference has to do with the size and dispersion of the flow channels in the polymer. In the case of dewatering, the size and distribution of the channels will be arbitrary and therefore will differ for each filter cake. For a polymer it can be assumed that these channels will have the same size distribution and dispersion for every sample used. This assumption is valid because of the fact that polymers are synthetically engineered to be as stable and uniform as possible.

The second difference has to do with the size of the application. During dewatering, the size of the molecule of the fluid (mostly water) is negligible in relation to the size of the different particles. This means that the molecule size has almost no effect on the capillary pressure created within the filter cake. This is however not true for the gas flow system. For this system, the size range for both the medium and the fluid is very similar. Therefore the

molecule size of the fluid will have an effect on the capillary pressures experienced within the flow channels. A larger molecule will experience greater capillary pressures in the same sized channels than the smaller molecules would, which will result in higher breakthrough pressures required for larger molecules to flow through the matrix than that for the smaller molecules.

Lastly, because the gas flow system operates at molecular scale, the surface charges of the molecules need to be taken into account. Opposing charges between the molecule and the polymer surface will result in the gas being pulled into the flow channels more easily after which the applied pressure differential is used to only overcome the capillary forces within the structure. The opposite will happen for molecules with similar charges. Added applied pressure is necessary for the gas molecule to enter the flow channels of the polymer before capillary pressure takes over. Therefore it can be stated that a higher applied pressure is needed for the diffusion of molecules with similar charges than for the ones whose charges differ.

When applying this theory to the permeability of C_3F_6 through both membranes, it is clearly evident that feed pressures higher than 100kPa will be needed to overcome the initial flow resistance. Subsequently, the linear increase of the permeability would be an added advantage of the higher feed pressures.

4.4 Results and discussion for tetrafluoromethane (CF_4)

As was described in Section 4.3 above, single gas permeation tests were conducted on both the PAN-supported and PEI-supported Teflon® AF2400 membranes. In this section tetrafluoromethane (CF_4) was used instead of C_3F_6 .

4.4.1 PAN-supported membrane

The results of the single gas permeation tests for CF_4 using the PAN-supported membrane are depicted below in Figure 4-10.

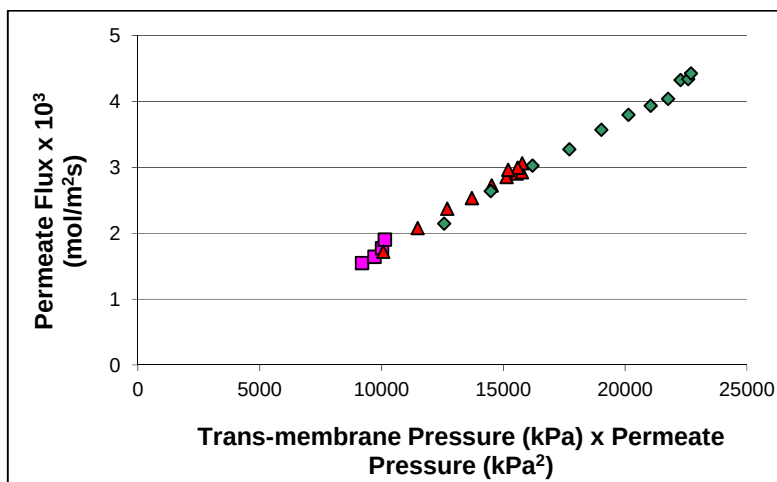


Figure 4-10: Molar flux of CF_4 versus trans-membrane pressure times permeate pressure (■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

The linear trend found in Figure 4-3 is also present in Figure 4-10, indicating that it upheld Equation 2.7. Contrary to the C_3F_6 results, the flux did not show a dependency on the feed pressure when calculating the flux rate. The feed pressure did however influence the total amount of this gas permeating through the membrane. Again, this can be explained by looking at the surface charge distribution of the molecule and the membrane surface. Unlike the positively charged C_3F_6 molecule, CF_4 is highly negative, which is similar to the surface charge of the membrane. This similarity in the charges will cause the membrane to repel the CF_4 away from its surface. By increasing the permeate pressure, and thus decreasing the pressure differential across the membrane, an extra force is added to the system, which will push the CF_4 molecules away from the membrane surface. The function of the feed pressure is thus one of overcoming the resultant force of the charge distribution and the permeate side pressure to allow the gas molecules to interact with the membrane surface. Therefore, at a low feed pressure and a high permeate side pressure, the resultant force will push the molecules away from the surface of the membrane and obstruct the gas from diffusing through the membrane. An increase in the feed pressure will only lead to an increase in the permeate side pressure, which will yield similar results as depicted above in Figure 4-10. At low permeate side pressures, an increase in the feed pressure will only result in an increase in the amount of gas that permeated through the membrane and will not influence the rate of permeation.

A maximum flux of only $4.4 \times 10^{-3} \text{ mol.m}^{-2}.\text{s}^{-1}$ was obtained for a feed pressure of 200kPa at a trans-membrane pressure of 150kPa. At a feed pressure of 50kPa no permeation measurements were observed. The same applied for the other feed pressures at low (less than 50kPa) trans-membrane pressures.

The permeability of CF_4 through the PAN-supported membrane is depicted in Figure 4-11.

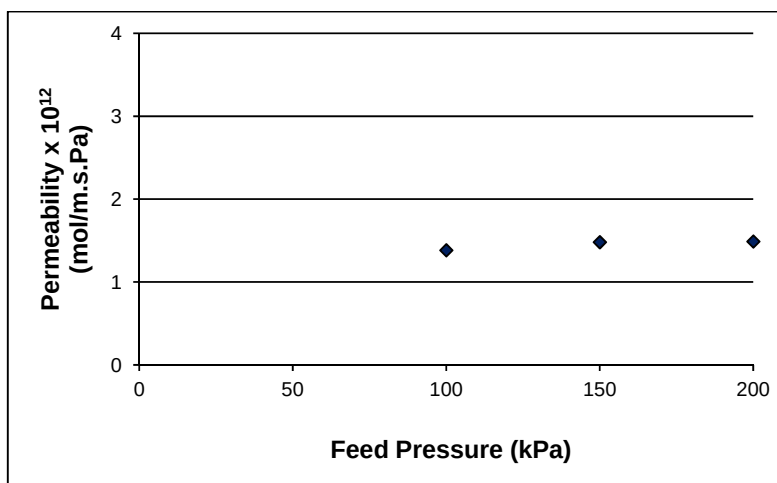


Figure 4-11: Graph of permeability versus feed pressure for CF_4

Figure 4-11 indicates the existence of a constant relationship between the permeability of the gas and the feed pressure. In comparison with the C_3F_6 data, the value of the permeabilities for CF_4 was ten times less. As mentioned above, it can be attributed to the highly negatively charged surface of both the CF_4 molecules and the membrane, which causes the membrane to repel the gas. At higher feed pressures, the resultant force is towards the membrane surface, resulting in more collisions between the gas and the membrane surface. This aids in the sorption of the gas. The higher feed pressures also contribute to a higher driving force, which is needed to overcome any resistance to flow. Even with these aids in gas flux, the difference in the permeability of the gas at high feed pressures versus lower feed pressures is negligible. Note that no value was calculated for a 50kPa feed pressure. This is because of the inability to obtain any flux at the low feed pressure.

It is interesting to note that the sorption coefficient follows the Flory-Huggins type, decreasing slightly, but non-linearly, at elevated pressures, as shown below in Figure 4-12.

Bearing in mind that the permeability remains constant across the different feed pressures, it can be concluded that the solubility and diffusivity contribute towards the permeability in equal amounts.

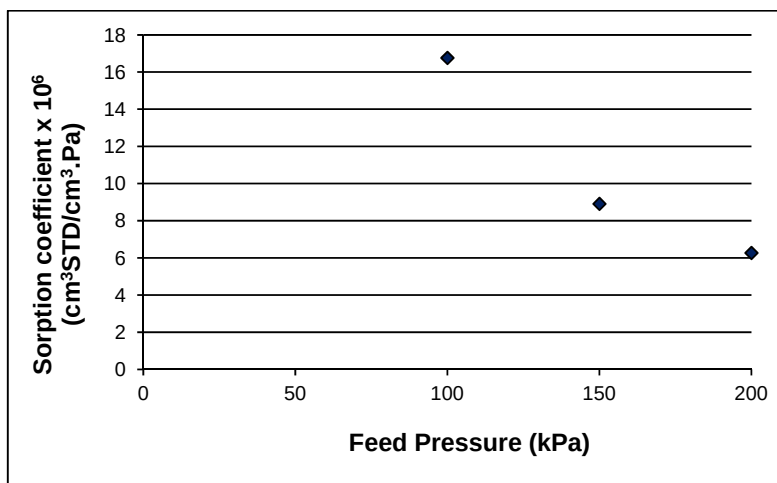


Figure 4-12: Influence of feed side pressure on the sorption coefficient (S)

4.4.2 PEI-supported membrane

The same experiments were repeated using pure CF_4 as feed to the PEI-supported membrane. As expected by now, the results obtained were very similar to those of the PAN-supported membrane. Figure 4-13 portrays the molar flux results for different CF_4 feed pressures using the PEI-supported membrane.

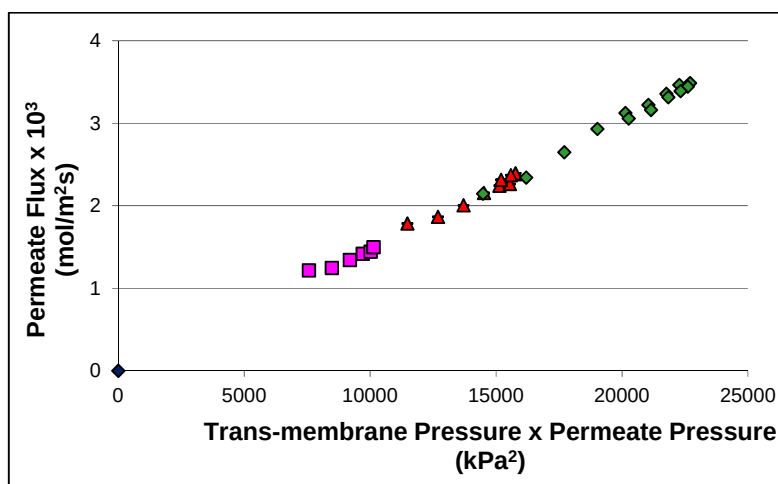


Figure 4-13: Molar flux of CF₄ versus trans-membrane pressure times permeate pressure (■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

Figure 4-13 above reveals a similar trend to that which was observed for Figure 4-10. It is further noteworthy that in this case the flow occurred at pressure differentials below 50kPa, irrespective of the feed pressure. However, from 50kPa onwards, the flux increases linearly until maximum trans-membrane pressures were reached. This trend was not repeated for the 200kPa feed pressure results. For this set of experiments, the flux reached a maximum value at a trans-membrane pressure of 160kPa, whereafter it remained constant. It culminated in a maximum obtainable flux of just over $3.5 \times 10^{-3} \text{ mol.m}^{-2}.\text{s}^{-1}$ for a 200kPa feed pressure at a trans-membrane pressure of 150kPa. From the slopes of the linear part of each line in the graph in Figure 4-13, the permeability was determined, as depicted below in Figure 4-14.

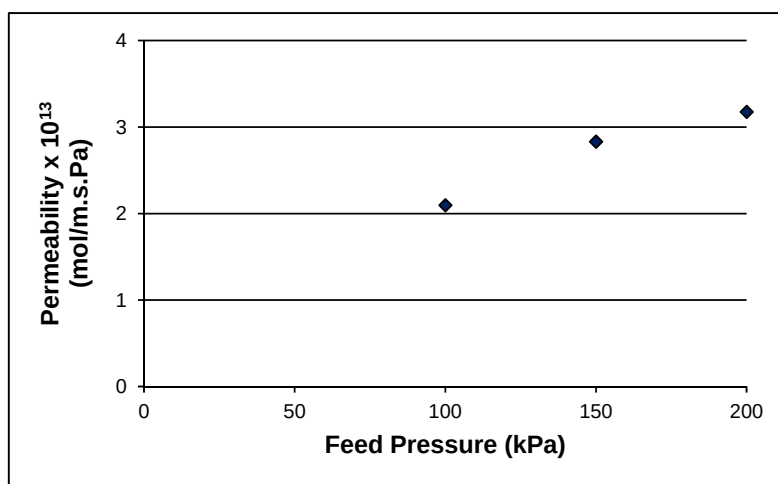


Figure 4-14: Graph of permeability versus feed pressure for CF₄

In Figure 4-14, the constant relationship is again observed for feed pressures higher than 100kPa. In comparison with the PAN-supported membrane, the permeability values obtained was approximately ten times lower. A closer look at Figure 4-10 reveals that the flux obtained for the PAN-supported membrane was slightly higher than for the PEI-supported membrane. Because these higher flux values for the PAN-supported membrane that were used in the calculation of the permeability, together with the fact that it was much thicker than the PEI-supported membrane; a much higher permeability value is expected. This is shown to be true. It is similar to that which was shown for the different membranes using C_3F_6 .

4.4.3 Discussion

The low permeation rate in both membranes is attributed to the surface charge of the molecule in relation to the membrane active layer. The molecular modelling shown in Section **Error! Reference source not found.** indicates that CF_4 has a relatively high negative surface charge. Considering that the active Teflon® layer also has a negative surface charge, it will repel the more negatively charged molecule which will not only lower the sorption characteristics of the molecule, as demonstrated in Section 3.3.6, but will also exert a negative influence on the diffusion rate of the molecule through the membrane. Although the size of the CF_4 molecule is much smaller than that of C_3F_6 , contributing to smaller capillary pressures in the different channels, the contribution of the repelling force clearly outweighs this less significant force (the capillary force).

In the case of the PAN-supported membrane, permeation of CF_4 is non-existing at feed pressures of 50kPa and lower. For the PEI-supported membrane this is true for feed pressures less than 50kPa. At such low pressures, the resistance to flow is much higher than the driving force for gas flow through the membrane; consequently, no flow will take place. Higher feed pressures will overcome this resistance and ensure that flow does occur. At a feed pressure of 100kPa, very low permeation starts to occur at a trans-membrane pressure of 70kPa and 50kPa for the PAN and PEI-support respectively. For both membranes, permeation occurs at feed pressures of 150kPa and 200kPa, and trans-membrane pressures of 50kPa and more. It can be concluded that the force generated by the pressure differences at these conditions is higher than the repelling force between the similarly charged membrane

surface and the molecules as well as the capillary forces generated within the polymer matrix, forcing some molecules through the membrane.

4.5 Results and discussions for nitrogen (N_2)

The results of the permeation tests for pure N_2 feed to the PAN-supported and PEI-supported membranes are reported in the sub-sections below.

4.5.1 PAN-supported membrane

The influence of trans-membrane pressure on the permeation of N_2 is depicted in Figure 4-15 below.

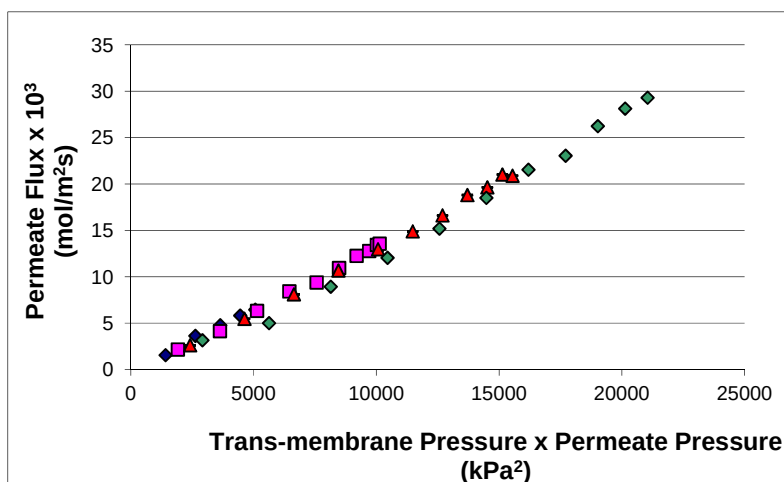


Figure 4-15: Molar flux of N_2 versus trans-membrane pressure times permeate pressure (♦ - 50 kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

Figure 4-15 continues to portray the linear relationship between the molar flux and the trans-membrane pressure times of the permeate pressure for each of the different feed pressures. Figure 4-15 also indicates that flow does occur at low trans-membrane pressures which, according to the reasoning above in Section 4.4.3, are indicative of the charge of N_2 . This is confirmed in Section 3.2.1 where the molecular modelling clearly shows a positively charged band which exists between two negatively charged nitrogen atoms. Therefore, since the charge of the molecule lies in between that of CF_4 and C_3F_6 , it can be expected that the molar flux values will follow suit, which it does. A maximum flux of $2.9 \times 10^{-2} \text{ mol.m}^{-2}.\text{s}^{-1}$ was reached at a feed pressure of 200kPa and a trans-membrane pressure of 110kPa. No gas flow

was measured at trans-membrane pressures higher than 110kPa for both the 150 and 200kPa feed pressures. This was due to the rapid diffusion rate of the gas at those conditions which caused a loss in feed pressure. The permeability results are portrayed below in Figure 4-16.

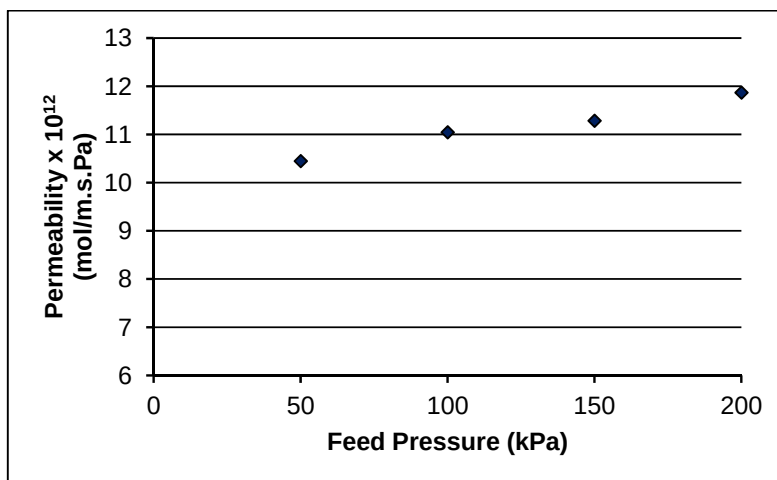


Figure 4-16: Graph of permeability versus feed pressure for N_2

The relationship between the permeability and feed pressure for N_2 using a PAN-supported membrane is shown by Figure 4-16 to scatter a little around a value of 11.5×10^{-12} . The scatter is attributed to small deviations from the linearity of the graph in Figure 4-15. By studying both these graphs, one would expect Figure 4-16 to show a more constant relationship. The relationship between the solubility and the feed pressure is shown below in Figure 4-17.

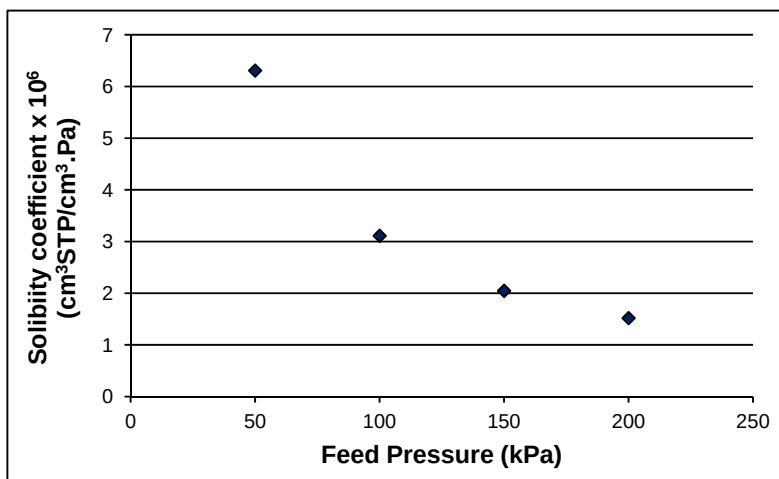


Figure 4-17: Influence of feed side pressure on the sorption coefficient (S) for N_2

Figure 4-17 depicts a non-linear relationship between the solubility coefficient for N_2 and the feed pressure. This will entail that Flory-Huggins type sorption occurs for N_2 and hence may influence the permeability across the different feed pressures. Figure 4-16 indicates an increase in the permeability as the feed pressure increases. When taking into account the significant decrease in the sorption coefficient it can be concluded that there is an almost equal, but opposite increase in the diffusion coefficient of N_2 as the feed pressure increases. This increase can be linked to the size of the N_2 molecule. This molecule is significantly smaller than those of the other two gasses. The diameter of the smaller molecular will cause a decrease in the capillary pressure of the polymer matrix which will ease the flow of the gas molecules that were sorped into the polymer. Therefore, when considering both resistances to flow (sorption and capillary pressures), the rapid decrease in capillary pressure due to the small size of the molecule will cause the flow of gas in the membrane's matrix to increase as the feed pressure increases. This in turn will cause an increase in the permeability, which is observed in Figure 4-16.

4.5.2 PEI-supported membrane

The molar flux curve for the N_2 feed gas using the PEI-supported membrane is shown below in Figure 4-18

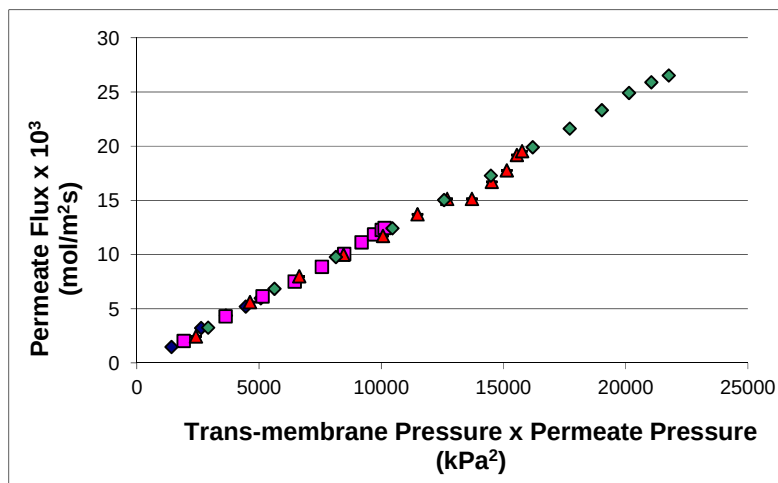


Figure 4-18: Molar flux of N_2 versus trans-membrane pressure times permeate pressure (♦ - 50 kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

Figure 4-18 displays a very similar trend than that found in Figure 4-15. All the feed pressures show a linear flux that starts at the origin. For the PEI-supported membrane a maximum flux was achieved for a feed pressure of 200kPa and a trans-membrane pressure of 120kPa. It was measured to be $2.7 \times 10^{-2} \text{ mol.m}^{-2}.\text{s}^{-1}$. This value is lower than for the PAN-supported membrane and was achieved at a trans-membrane pressure of 10kPa higher for the same feed pressure. The absence of permeation for the gas at high ($>120\text{kPa}$) trans-membrane pressures was observed for both the 150 and 200kPa feed pressures.

The permeability results are shown below in Figure 4-19 and the trend in this graph is similar to the trends observed in the previous permeability graphs, for example, in Figure 4-11. It portrays a constant permeability value, which is expected for this gas, given the linearity of the sorption data shown in Figure 4-17.

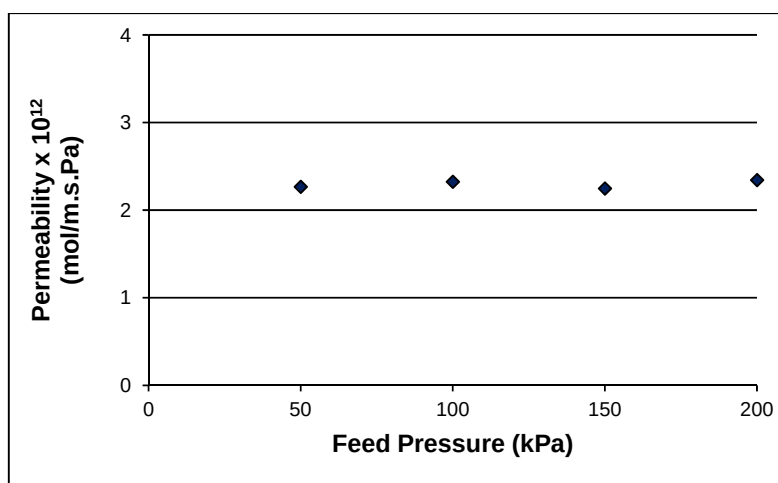


Figure 4-19: Graph of permeability versus feed pressure for N_2

Figure 4-19 completes the phenomenon that indicates that the permeability for the PEI-supported membrane was lower than that for the PAN-supported membrane, even though the active Teflon® AF2400 membrane layer is much thinner. It supports the theory that secondary separation occurs in the primary PAN or PEI support as discussed in Section 4.3.3.

4.5.3 Discussion

The phenomena exhibited by C_3F_6 and CF_4 were repeated for N_2 . This shows a linear trend for the permeating flux against trans-membrane pressure, and an increase in flux as the feed

pressure increases. The flux values for N_2 lie between those of C_3F_6 and CF_4 . Molecular modelling regarding the surface charges of the different molecules indicated a similar trend. N_2 has a less negative surface charge than CF_4 but is much more negative than that of C_3F_6 . A clear progressive flux is observed, starting from the smallest flux for the CF_4 , which has the highest negative surface charge, and increasing to the maximum flux for the almost entirely positively charged C_3F_6 molecule. This comparison of the trends between surface charge and flux for the different gasses serves as validation for the reasons offered for the different flow rates of gasses through the membrane.

The permeability values of N_2 correlate with the values obtained for C_3F_6 at low feed pressures. This means that the combination of low sorption and higher flow due to lower capillary forces results in a similar permeability value for N_2 than for C_3F_6 which is subjected to higher sorption but lower flow at these feed pressures. At higher feed pressures, the capillary forces for C_3F_6 is overcome and exhibit a much higher permeability than for N_2 due to its superiority in sorption.

4.6 Membrane selectivity

As discussed in Section 2.3.2, selectivity is an indication of the ability of one of the components to permeate through the membrane at a different rate than the others. This is calculated using Equation 2.2. This equation, however, is written for binary mixtures. When working with single component systems it can be simplified to yield the ideal selectivity:

$$\alpha_{ij} = \frac{J_i}{J_j} \tag{4.5}$$

Ideal selectivities were calculated for each of the different gas combinations for each of the membranes used. The result of the selectivity data can be used to determine the best ideal operating conditions for the separation of a binary mixture of gasses. Note that the gas with the higher average permeating rate is named first so that the selectivity data can be given as a number greater than one.

4.6.1 Selectivity data for the PAN-supported membrane

The ideal selectivity values of C_3F_6/CF_4 , C_3F_6/N_2 and N_2/CF_4 are shown below in Figure 4-20 to Figure 4-22. Note that the selectivity could be determined only for cases where flow

occurred at the same feed and trans-membrane pressures for two different gasses. There were several instances where there were no comparisons for two gasses under the same conditions, for example, at a feed pressure of 200kPa and low trans-membrane pressures, a very high flow of C_3F_6 occurs, while there was no flow detected for CF_4 . Mathematically, the selectivity at such a point was calculated as infinity. However, despite this, only the measured selectivity values will be reported in the remainder of this thesis.

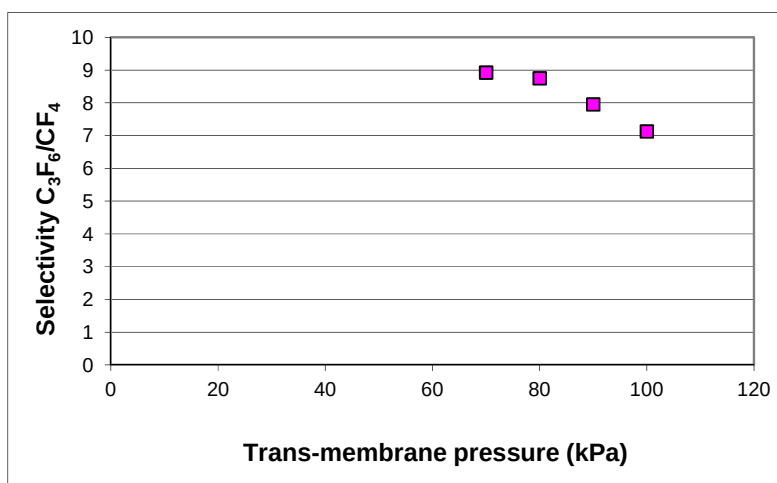


Figure 4-20: Ideal selectivity of C_3F_6/CF_4 for the PAN-supported membrane at different feed pressures (■ - 100kPa)

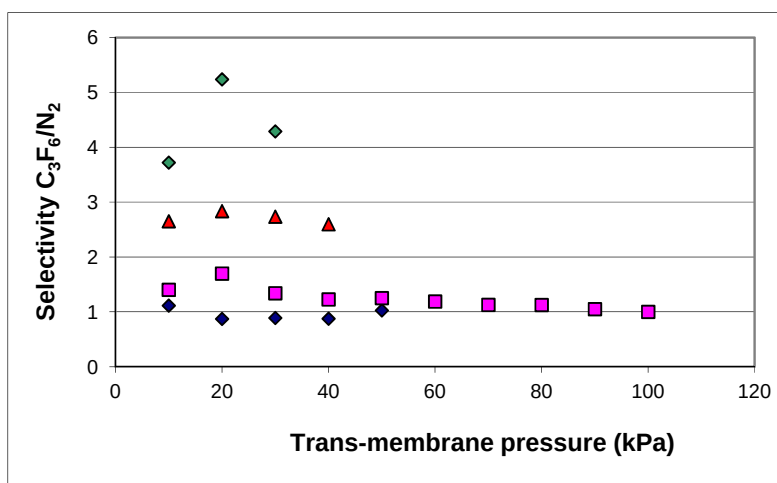


Figure 4-21: Ideal selectivity of C_3F_6/N_2 for the PAN-supported membrane at different feed pressures (◆ - 50kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

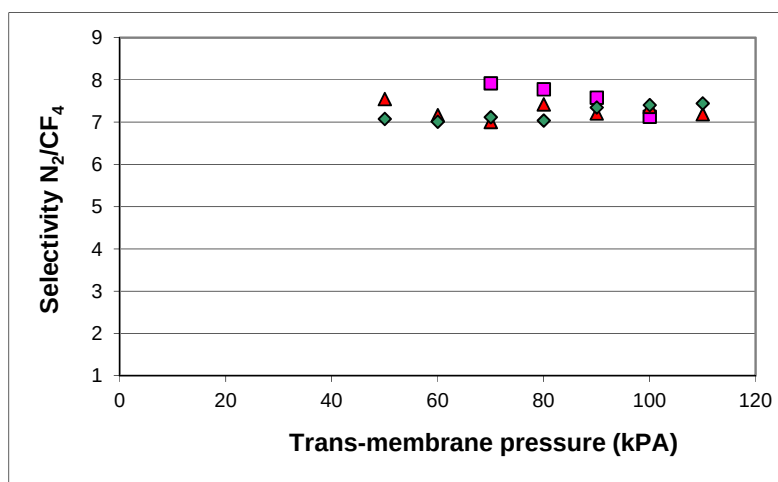


Figure 4-22: Ideal selectivity of N_2/CF_4 for the PAN-supported membrane at different feed pressures (■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

In the preceding figure, Figure 4-20 to Figure 4-22, not much can be said about the selectivity of C_3F_6 versus CF_4 because of the small number of data points that are comparable. The selectivity does however appear to increase at lower trans-membrane pressures. For the other two graphs, Figure 4-21 and Figure 4-22, clear trends are evident. For the C_3F_6/N_2 system (Figure 4-21) it can be concluded that high feed pressures and low trans-membrane pressures favour the permeation of C_3F_6 resulting in the highest selectivity of 5.24. Important to note is that there is very little deviation over the array of trans-membrane pressures for the different feed pressures, except for the 200kPa feed pressure. Here, however, only three data points were comparable, which does not contribute towards identifying a trend.

In Figure 4-22, a constant relationship between the selectivity of N_2/CF_4 and trans-membrane pressure is observed. All the values vary between a selectivity of 7 and 8, with the highest achievable selectivity being 7.92. This indicates that the selectivity of the system is not sensitive towards either the feed pressure or the trans-membrane pressure. Therefore, when deciding on the best operating conditions, it is paramount to consider the highest flux rates.

A summary of the best practice conditions that will yield the highest selectivity values are displayed in Table 4-1. This table also indicates that in all three cases, the ideal selectivity is much higher than the Knudsen selectivity, which implies that separation occurs owing to diffusion.

Table 4-1: Optimum ideal selectivities for the PAN-supported membrane

Gas relation	Ideal Selectivity	Knudsen selectivity	Feed pressure (kPa)	Trans-membrane pressure (kPa)
C_3F_6 / CF_4	8.92	0.77	100	70
C_3F_6 / N_2	5.24	0.43	200	20
N_2 / CF_4	7.92	1.78	100	70

Table 4-1 tends to indicate that the best operating feed pressure is at 100kPa. However, taking into consideration that CF_4 did not record any flow at low trans-membrane pressures, and that the highest flux for N_2 and C_3F_6 occurred at 200kPa feed pressures, it can be mathematically calculated that the selectivity at this point is equal to infinity. Therefore, it can be concluded that the best operating conditions will occur at a feed pressure of 200kPa and low trans-membrane pressures. Separation of C_3F_6 and CF_4 , and N_2 and CF_4 seems much more plausible than for C_3F_6 and N_2 .

4.6.2 Selectivity data for the PEI-supported membrane

Selectivity results for the PEI-supported membrane are shown below (Figure 4-23 to Figure 4-25).

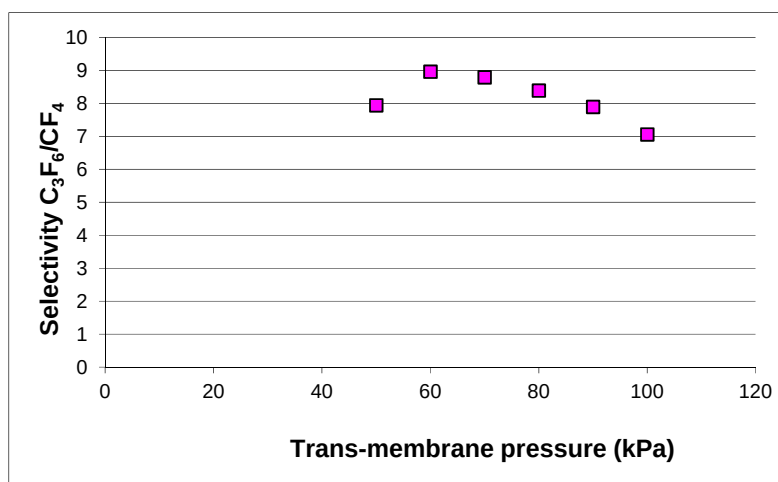


Figure 4-23: Ideal selectivity of C_3F_6/CF_4 for the PEI-supported membrane at different feed pressures (■ - 100kPa)

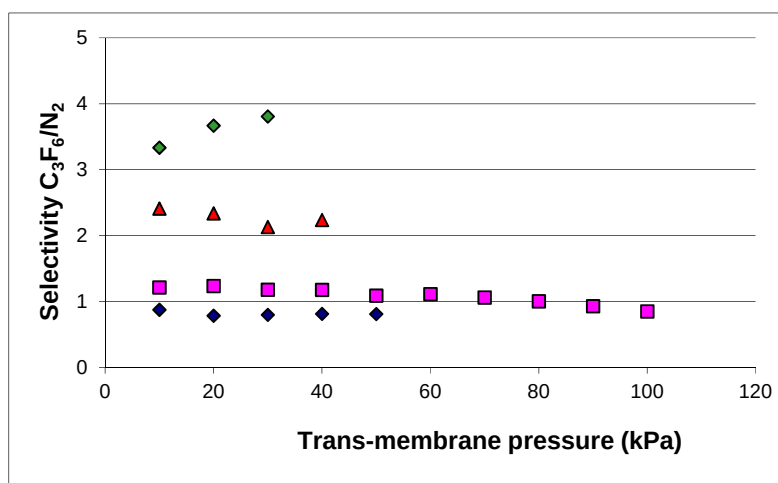


Figure 4-24: Ideal selectivity of C_3F_6/N_2 for the PEI-supported membrane at different feed pressures (◆ - 50kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

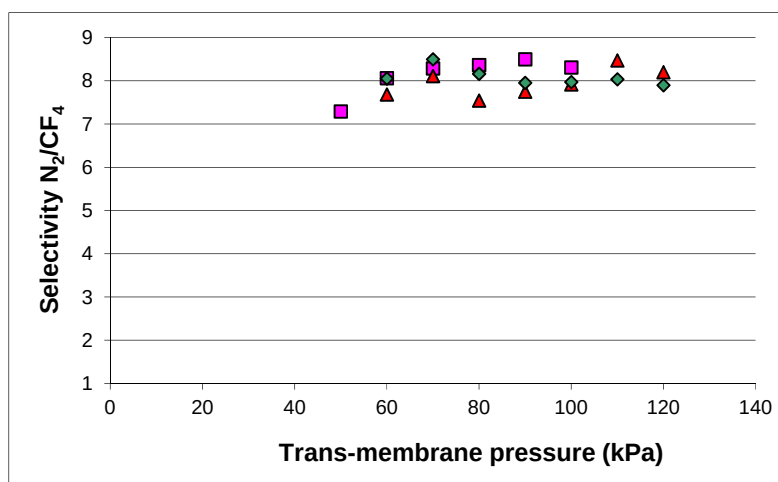


Figure 4-25: Ideal selectivity of N_2/CF_4 for the PEI-supported membrane at different feed pressures (■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa)

Selectivities obtained by using the PEI-supported membrane indicate very similar trends as those for the PAN-supported membrane. Again, it was difficult to calculate the selectivities involving CF_4 at low trans-membrane pressures and hence only the recorded values will be used in the selectivity calculations. Figure 4-24 supports the theory developed for the PAN-supported membrane, that feed pressure plays a role in the selectivity of C_3F_6 and N_2 . This indicates that the higher the feed pressure, the higher the selectivity, due to the adsorption of gas onto the membrane surface.

Figure 4-25 also correlates with the corresponding graph for the PAN-supported membrane. This again shows a consistent oscillation of data points between a selectivity of 8 and 10. This finding supports the conclusion drawn regarding the PAN-supported membrane that neither the feed pressure, nor the trans-membrane pressure plays a role in the selectivity between N_2 and CF_4 .

A summary of the optimum selectivities for the PEI-supported membrane can be found in Table 4-2. The ideal selectivities for the PEI-supported membrane, as for the PAN-supported membrane, are much higher than the calculated Knudsen selectivities.

Table 4-2: Optimum ideal selectivities for the PEI-supported membrane

Gas relation	Ideal Selectivity	Knudsen selectivity	Feed pressure (kPa)	Trans-membrane pressure (kPa)
C ₃ F ₆ / CF ₄	8.97	0.77	100	60
C ₃ F ₆ / N ₂	3.81	0.43	200	30
N ₂ / CF ₄	8.50	1.78	100	90

4.7 Modelling the single gas permeation properties

Linear regression was used to calculate the permeability for each of the gas permeation tests described above. It was performed by calculating the slope of the flux curve and multiplying it by the thickness of the membrane active layer, as described in Section 3.3.5. This is in accordance with Equations 2.7 and 4.3. Permeabilities obtained in kmol/m.s.Pa were subsequently converted to Barrer for comparison with the values found in literature (1Barrer = 3.348×10^{-19} kmol.m⁻¹.s⁻¹.Pa⁻¹) (Perry & Green, 1997:22-61).

The permeability of the CF₄ and N₂ were compared to the values obtained by Merkel *et al.* (1999:8435) who conducted permeation tests for these gasses through Teflon® AF2400 active layer membranes. It should be noted that the active layer of the membranes used by Merkel *et al.* (1999:8429) was 50µm thick, which is significantly thicker (ten times on average) than for either the PAN- or PEI-supported membranes used in this study. They also used several different manufacturing techniques. These differences between the membranes used in this study and the ones reported on give an indication that the permeabilities found in this study should be significantly higher than those found in literature. Merkel *et al.* (1999:8429) reported values for CF₄ to range between 60 and 90barrer while N₂ permeation values varied between 400 to 600barrer.

4.7.1 Modelling results for the PAN-supported membrane.

The modelling of the single gas permeation through the PAN-supported Teflon® AF2400 membrane was carried out. Equation 4.1 was modified to incorporate the permeate pressure and yielded Equation 4.5.

$$J_i = \left(\frac{S_i \cdot D_i}{z} \right) p_p (p_f - p_p) \quad 4.5$$

Equation 4.5 was applied in order to measure the pressure terms as well as the flux, while the solubility was calculated from the sorption data described in Section 3.3.6 by using Equation 4.4. Linear regression was used to calculate the slopes of the different flux curves, and using Equation 4.3, it was possible to calculate the diffusivity (D_i) of the gasses.

The models were able to accurately predict the relationship between the permeate flux and the trans-membrane pressure for each gas and feed pressure used. A comparison between the models and the experimental data can be found in the figures below (Figure 4-26 to Figure 4-28), while the modelled values are portrayed in Table 4-3. The 95% confidence level between the modelled and the experimental values was calculated and found to be 3%, 5% and 1% for the C_3F_6 , N_2 and CF_4 respectively.

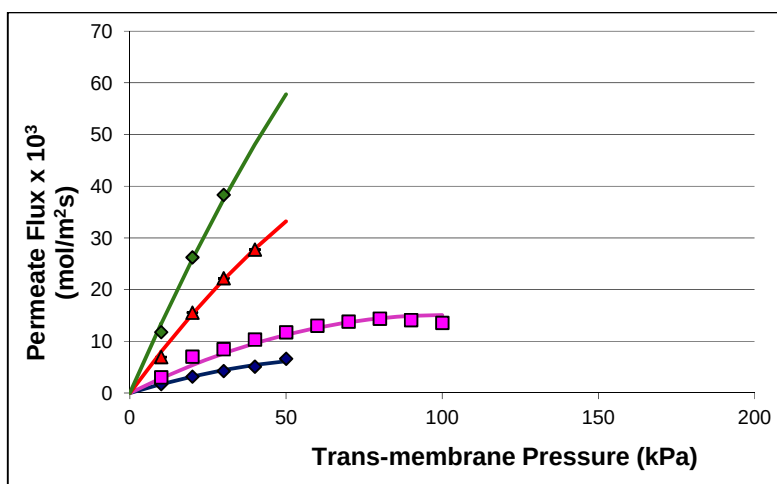


Figure 4-26: Modelling results for C_3F_6 flux through PAN-supported Teflon® AF2400 membrane at different feed side pressures (♦ - 50 kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa). The lines represent the models while the markers represent the actual experimental data

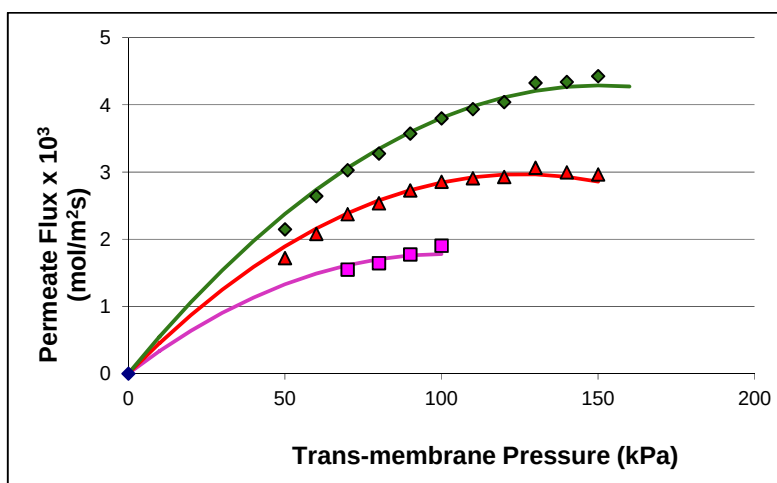


Figure 4-27: Modelling results for CF₄ flux through PAN-supported Teflon® AF2400 membrane at different feed side pressures (■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa). The lines represent the models while the markers represent the actual experimental data

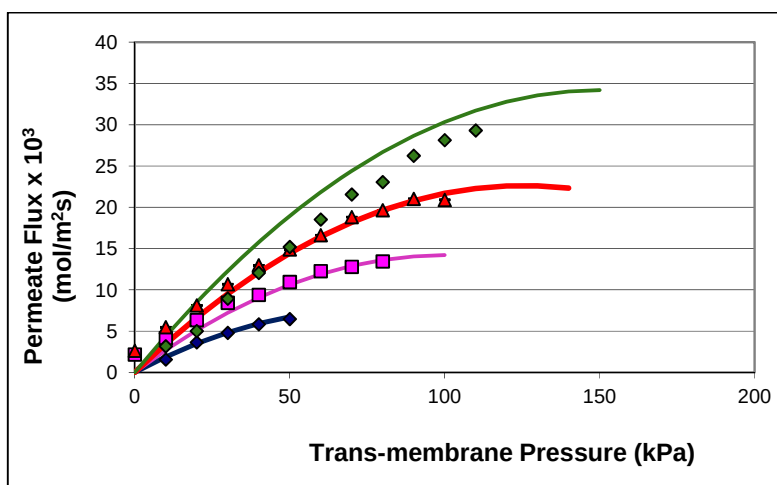


Figure 4-28: Modelling results for N₂ flux through PAN-supported Teflon® AF2400 membrane at different feed side pressures (◆ - 50 kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa). The lines represent the models while the markers represent the actual experimental data

Table 4-3: Modelling results for the PAN-supported membrane

Gas	Feed Pressure (kPa)	P_i (Barrer)	S_i (mol/m ³ .Pa) x 10 ⁵	D_i (m ² /s) x 10 ⁸
C₃F₆	50	28700	12.29	7.82 ± 0.23
	100	35100	4.77	24.62 ± 0.74
	150	77600	2.59	100.34 ± 3.01
	200	108200	1.64	221.05 ± 6.63
CF₄	50			
	100	4100	1.68	8.25 ± 0.08
	150	4400	0.89	16.62 ± 0.17
	200	4400	0.63	23.75 ± 0.24
N₂	50	31200	0.63	165.65 ± 8.28
	100	33000	0.31	355.11 ± 17.76
	150	33800	0.20	551.42 ± 27.57
	200	35500	0.15	781.90 ± 39.10

In Table 4-3 it is evident that the permeability values for CF₄ and N₂ are much higher than the values found by Merkel *et al.* (1999:8435), which was expected. This comparison can be used as another validation for the experimental apparatus and the procedures used in this study. It further implies that the values obtained for C₃F₆ are true and accurate, since no reference to this gas and membrane combination can be found in literature.

After obtaining the permeability values, the solubility coefficient (S_i) was calculated from the data shown in Section 3.3.6 whereafter the diffusivity coefficient (D_i) was calculated using Equation 4.3. Table 4-3 indicates that for CF₄ and N₂ the solubility coefficient remains in a similar size range for each of the different feed pressures. This is also indicated in the graphs in Figure 4-12 and Figure 4-17, which reveals a Flory-Huggins type sorption. Thornton *et al.* (2009:31) states that for light gasses S_i will remain constant over an array of different polymers and operating conditions within each polymer. However, this is not the case for the larger, more complex, C₃F₆ molecule which shows a decrease in the value of S_i as the feed pressure increases.

It is important to note the values of D_i for the different gasses in Table 4-3. CF_4 , shown to be the slowest permeating gas, has very low D_i values that increase slightly as the feed pressure increases. These low diffusivity constant values indicate that the system is diffusion controlled for CF_4 . The opposite is true for N_2 . Although N_2 has only the second highest permeability, it shows the highest diffusivity, which increases linearly as the feed pressure, increases (see Figure 4-29). The solubility coefficients for N_2 remain almost constant and low in relation to the other gasses.

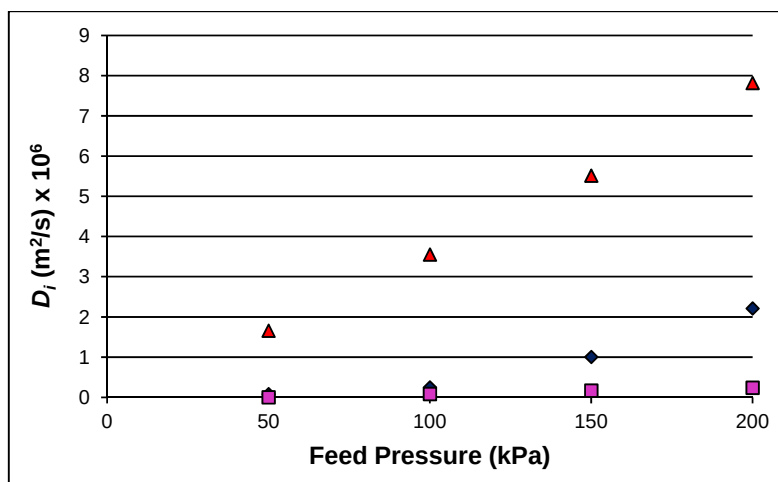


Figure 4-29: Relationship between the diffusivity coefficient and the feed pressure (♦ - C_3F_6 , ■ - CF_4 , ▲ - N_2)

In Figure 4-29, C_3F_6 is shown to behave uniquely. The diffusivity coefficient for this gas increases exponentially, whereas it is linear for the other gasses. Mauviel *et al.* (2005:65) noted that a non-linear increase in the diffusivity coefficient can be expected when the sorption coefficient behaves according to the Flory-Huggins type model. Although it was demonstrated that the sorption coefficient for all three gasses follows this model type, only the diffusion coefficient of C_3F_6 increases non-linearly.

4.7.2 Modelling results for the PEI-supported membrane.

Equation 4.5 was used to model the permeation flux results obtained for the PEI-supported membrane. A similar methodology was used as described in Section 4.7.1 above. For the most part, the model gives an accurate description of the experimental data. The 95%

confidence level for the different gasses was calculated to be as follows: 3% for the C_3F_6 , 5% for CF_4 and 1% for N_2 . The results are depicted below (Figure 4-30 to Figure 4-32).

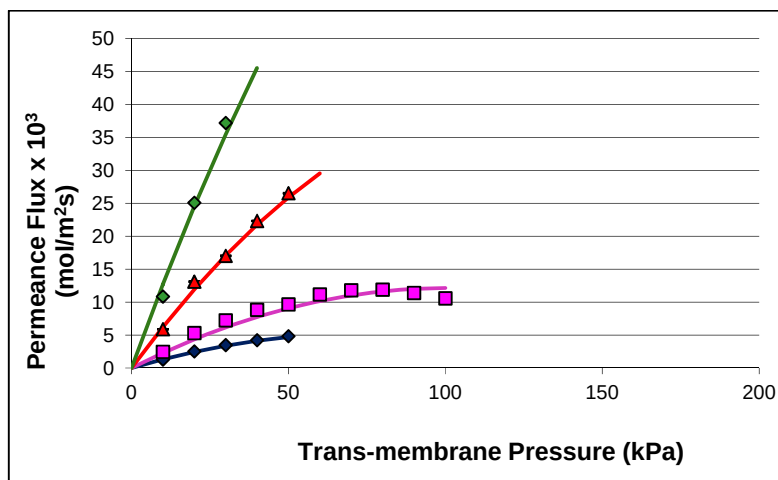


Figure 4-30: Modelling results for C_3F_6 flux through PEI-supported Teflon® AF2400 membrane at different feed side pressures (♦ - 50 kPa, ■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa). The lines represent the models while the markers represent the actual experimental data

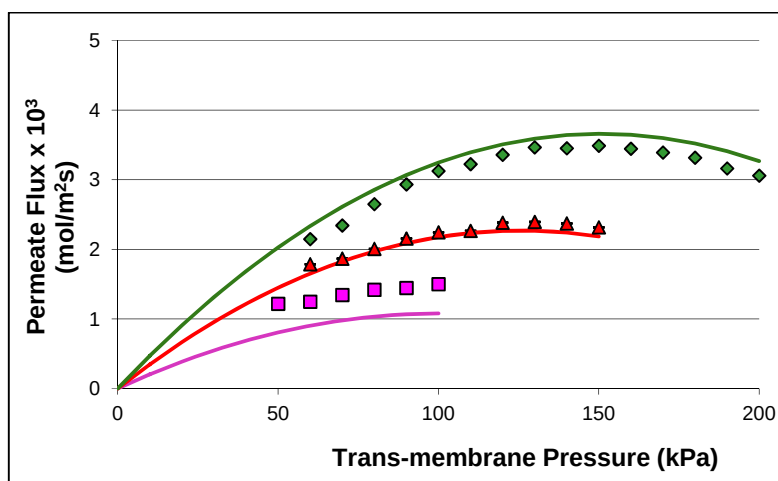


Figure 4-31: Modelling results for CF_4 flux through PEI-supported Teflon® AF2400 membrane at different feed side pressures (■ - 100kPa, ▲ - 150 kPa, ◆ - 200 kPa). The lines represent the models while the markers represent the actual experimental data

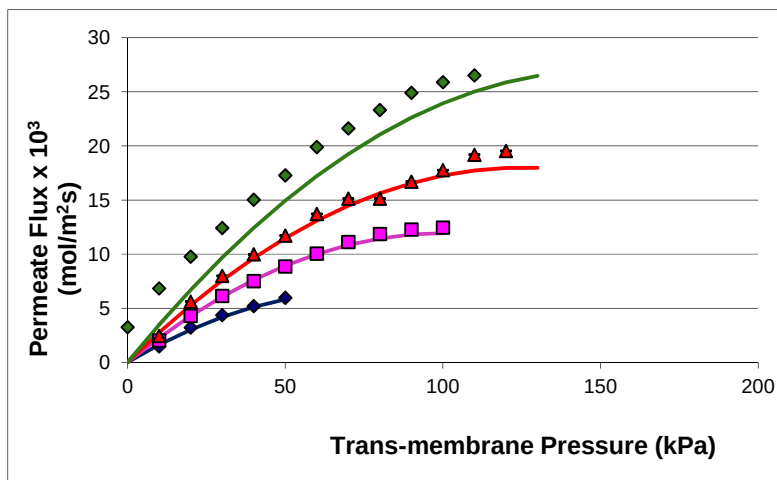


Figure 4-32: Modelling results for N₂ flux through PEI-supported Teflon® AF2400 membrane at different feed side pressures (♦ - 50 kPa, ■ - 100kPa, ▲ – 150 kPa, ◆ - 200 kPa). The lines represent the models while the markers represent the actual experimental data

Figure 4-30 to Figure 4-32 reveal a good relationship between the modelled data and the ones obtained from the experimentation. Similar to the PAN-supported membrane, it indicates that the model of Equation 4.4 accurately describes the diffusion of the gas through the membrane.

A summary of the modelling results obtained for the PEI-supported membrane is shown in Table 4.4 below.

Table 4-4: Modelling results for the PEI-supported membrane

Gas	Feed Pressure (kPa)	P_i (Barrer)	S_i (mol/m ³ .Pa) x 10 ⁵	D_i (m ² /s) x 10 ⁸
C₃F₆	50	5500	12.29	1.49 ± 0.04
	100	7100	4.78	4.95 ± 0.21
	150	15100	2.59	19.57 ± 0.59
	200	25600	1.64	52.36 ± 1.57
CF₄	50			
	100	600	1.46	1.44 ± 0.07
	150	800	0.94	3.02 ± 0.15
	200	900	0.65	4.87 ± 0.24
N₂	50	6800	0.63	35.92 ± 0.36
	100	6900	0.31	74.69 ± 0.75
	150	6700	0.20	109.76 ± 1.10
	200	7000	0.15	154.31 ± 1.54

Table 4-4 indicates that the gasses behave similarly for the PEI-supported membrane as for the PAN-supported membrane. A noticeable difference between the two membranes is the permeability values obtained for the PEI-supported membrane that led to low diffusion coefficients. The role that the primary support layer plays in helping with the separation of the gasses, while also hindering the diffusion thereof, can be used as an explanation for this. A graph of the diffusion coefficients against the feed pressure is depicted in Figure 4-33.

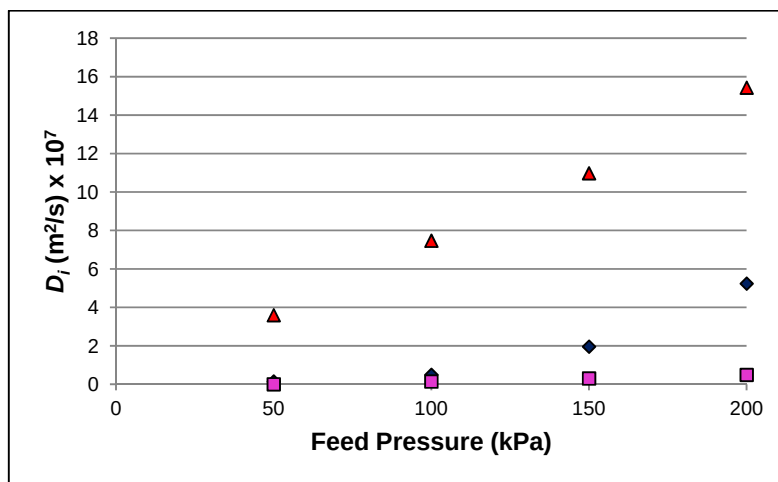


Figure 4-33: Relationship between the diffusivity coefficient and the feed pressure (♦ - C₃F₆, ■ - CF₄, ▲ - N₂)

Figure 4-33 shows that the shape of the different graphs is exactly the same as that found for the PAN-supported membrane (Figure 4-29). The only difference is in the exact values of the diffusion coefficients. This implies that the diffusion coefficients for CF₄ and N₂ increases linearly as the feed pressure increases, whereas the C₃F₆ increases exponentially. This again iterates that which was shown by Mauviel *et al.* (2005:65) in terms of a non-linear relationship for diffusion coefficients when a Flory-Huggins type sorption is present.

4.8 Concluding remarks

Two polymer membranes specifically manufactured for this project were tested for their ability to separate N₂, CF₄ and C₃F₆. For the pure gasses, both membranes showed a high selectivity towards C₃F₆ with a maximum flux of $3.8 \times 10^{-2} \text{ mol/m}^2 \cdot \text{s}$ using the PAN-supported membrane. The selectivity is subsequently followed by N₂, with a maximum flux of $2.9 \times 10^{-2} \text{ mol/m}^2 \cdot \text{s}$, as well as for the PAN-supported membrane, and CF₄ with a maximum flux of $4.4 \times 10^{-3} \text{ mol/m}^2 \cdot \text{s}$, again using the PAN-supported membrane. These fluxes resulted in selectivities of above 8 for C₃F₆ over CF₄ and above 7 for N₂ over CF₄. The selectivity of C₃F₆ over N₂ was a maximum of 5.24.

The ability of the membranes to be used for large scale applications was determined by generating a Robeson plot (Robeson 1991). This is illustrated in Figure 4-34. The dotted line

shows the upper-limit for N_2/CH_4 as given by Robeson (2008:397) and presented in Figure 2-1.

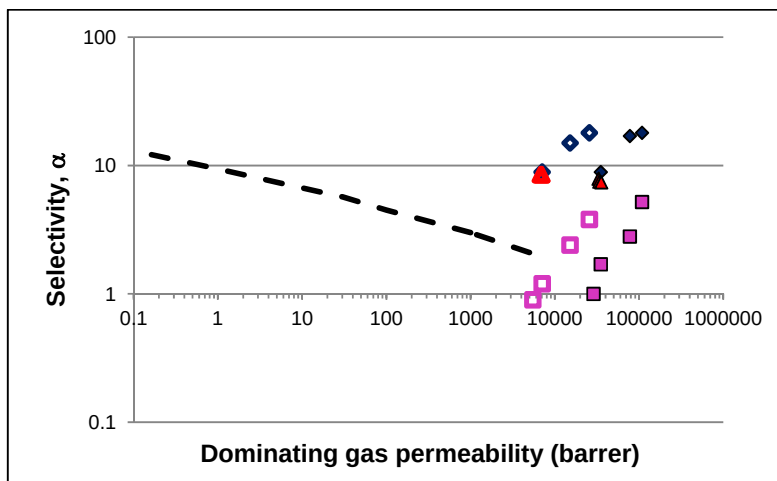


Figure 4-34: Robeson plot for both membranes (♦ - C_3F_6/CF_4 (PAN), ■ - C_3F_6/N_2 (PAN), ▲ - N_2/CF_4 (PAN), ◇ - C_3F_6/CF_4 (PEI), □ - C_3F_6/N_2 (PEI), △ - N_2/CF_4 (PEI))

Figure 4-34 shows that, in general, most points lie above the dotted line, which is a good indication of the ability of the membrane to be used industrially. It indicates good separation for both C_3F_6 and N_2 in relation to CF_4 . The values for C_3F_6/N_2 separation dissect the dotted line for both membranes. For these gasses, the selectivity and permeability need to be studied separately. They demonstrate acceptable permeability values but very low selectivity values which could hinder future operations. In all instances, the best values were obtained at the highest feed pressures, which indicate that the dominating gas permeability is greater than the values given by Robeson.

A comparison of the membranes, both separately and on the Robinson plot, favoured the use of the PAN-supported membrane in terms of the selectivity versus the permeability. This is a bit surprising, keeping in mind that the active layer of the PEI-supported membrane is much thinner than that of the PAN-supported membrane. This was explained by looking at the thickness of the active layer and primary support combined, for which the PEI-supported membrane was much thicker than the PAN-supported membrane. It could therefore be concluded that the secondary layer contributes to the separation of the gasses.

Lastly, it was demonstrated via the modelling that CF_4 is diffusion controlled while N_2 is controlled by the solubility of the gas onto the membrane. C_3F_6 is unique in the fact that these two characteristics complement one another. When the solubility decreases, the diffusivity increases exponentially and vice versa. The result is the highest permeability for C_3F_6 .

4.9 References

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CHAPTER 5: BINARY GAS PERMEATION

*Each problem that I solved became
a rule, which served afterwards
to solve other problems
- Rene Descartes*

5.1 Introduction

The same setup used for the experiments in Chapter 4 and described in Section 3.3 was used for the tests with binary gas mixtures as feed to the membrane. During the binary mixture experiments, the retentate stream tube was removed from the soap flow meter and was coupled to a gas chromatograph in order to analyse the composition of this stream. Subsequently, a mass balance was performed over the entire system in order to obtain the composition of the permeate stream. This was achieved by using both the PAN- and PEI-supported membranes. It was decided to use both membranes for the binary feed tests due to the similarity in selectivity values obtained when using the pure gasses as feed. The rationale behind this decision is to try and isolate the membrane best suited for gas mixture separation.

5.2 Theory

The modelling of binary gas diffusion is well documented in literature. The following papers are examples thereof: Li *et al.* (2007), Raharjo *et al.* (2007), Izak *et al.* (2003), Vignes (1966), Krishna and Van Baten (2006) and Krishna and Wesselingh (1997). One essential aspect highlighted by Wijmans and Baker (1995:2) is the necessity of a driving force for each compound in the feed mixture in terms of its chemical potential gradient. This is required to establish selective mass transfer between the different components in the mixture. This is achieved by applying a partial pressure differential across the membrane. This will yield a system with varying permeation rates of the different components that will adhere to the solution-diffusion model (Vallieres *et al.*, 2003:2767). These pressure differences are achieved by either increasing the feed pressure, used for gas separation, or having a vacuum on the permeate side, as applied in pervaporation.

The ability of a membrane to separate the gas mixture consisting of component i and component j is determined by the selectivity (α_{ij}) of the membrane. It is calculated by determining the molar ratio $y_{k,i}/y_{k,j}$ of the components at the downstream ($k = 2$) point in relation to the upstream ($k = 1$) point (Cecoperi-Gòmez, 2007:54). This is indicated in Equation 5.1 below:

$$\alpha_{ij} = \frac{y_{2,i}}{y_{2,j}} \bigg/ \frac{y_{1,i}}{y_{1,j}} = \frac{\varphi_i}{\varphi_h} \quad (5.1)$$

This approximation of the selectivity by the permeability ratio of component i in relation to component j , can only be performed if it is assumed that the influence of the downstream pressure can be neglected (Cecoperi-Gòmez, 2007:54). This was shown not to be true for the pure gasses in the previous chapter.

Vallieres *et al.* (2003:2770) proposed a simplified calculation for a pervaporation setup where the composition of the permeate side can be calculated using the partial molar flow rates, of the individual components in the feed, through the membrane. The flow rates in turn are calculated by knowing the partial flux of each gas and multiplying that with the membrane area. This system was shown to be valid, providing that perfect mixing occurs on both sides of the membrane, that mass transfer only occurs in the membrane and that component coupling may be neglected. The first two assumptions may be taken as true, but coupling between different components are a real possibility and must always be taken into account when working with real life systems.

Izák *et al.* (2003:294) reported that pervaporation literature uses the term coupling to describe the thermodynamic constraints that govern the flow of the different components in the original mixture, or to describe the mutual drag that exists between the different components. This drag is the result of short-range molecular interaction between the different components, which could lead to a decrease in permeability from pure component data as components may go as far as moving against its own concentration gradient. Simon *et al.* (1996:231) stated that for gaseous or liquid mixtures, the relative permeability of the different components in the mixture usually differs from the single component ones. This should be particularly true

in a system where a difference in the surface charge of the molecules in the mixture will exert Van der Waal's forces on one another, causing an interaction between these molecules.

According to Baikov and Primak (2007:382), the above-mentioned topic of membrane gas separation is currently attracting wide attention as a topic of study. There are multiple factors contributing to the reasons why this topic is still not fully understood. These reasons are, for example, the wide range of gas mixtures that vary in their physical properties, the diverse implementation of the separation modules and membranes that vary in materials, and as a consequence, in their physicochemical properties exerting their influence on permeability and selectivity.

5.3 Results and discussion for C_3F_6 / CF_4 feed

Binary gas mixtures were used as feed to both the PAN- and PEI-supported membranes. Gas mixtures of 90/10, 50/50 and 10/90 mole percentage were composed using mass flow controllers. A feed pressure of 200kPa was used at trans-membrane pressures, which varied from zero to the maximum obtained. The flow rate of the retentate stream was measured using a soap flow meter, while the composition of the permeate stream was analysed with a Gas Chromatograph. From there, mass balance principles were applied to calculate the composition of the retentate stream and hence to calculate the total and individual permeation rates of each of the gasses.

5.3.1 PAN-supported membrane

The results obtained for the C_3F_6 / CF_4 binary feed to the PAN-supported membrane are displayed in Figure 5-1 to Figure 5-3. Figure 5-1 represents the results for a 90mole% CF_4 / 10mole% C_3F_6 mixture (referred to as the 90/10 mixture in this Section), while Figure 5-2 is for a 50mol% CF_4 / 50mol% C_3F_6 mixture (referred to as a 50/50 mixture). Figure 5-3 referred to a 10mol% CF_4 / 90mole% C_3F_6 mixture (referred to as a 10/90 mixture).

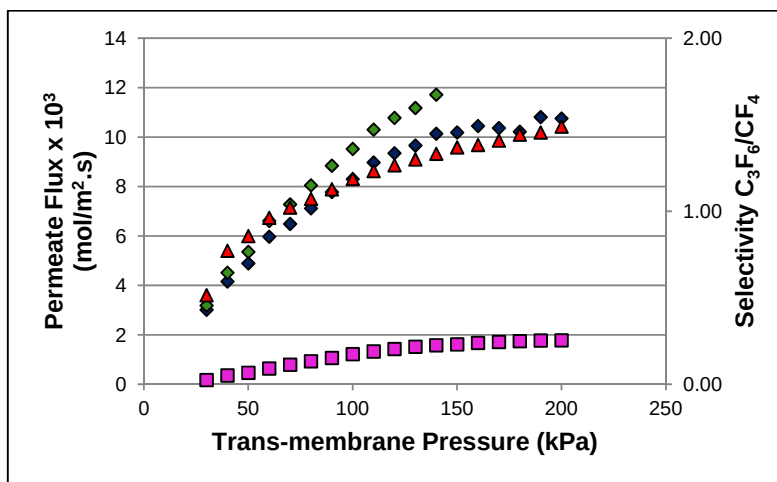


Figure 5-1: Binary gas permeation results for 90 mole% CF_4 / 10 mole% C_3F_6 using the PAN-supported membrane ($\blacklozenge$ - CF_4 flux, $\blacksquare$ - C_3F_6 flux, $\blacklozenge$ - Total flux, $\blacktriangle$ - selectivity)

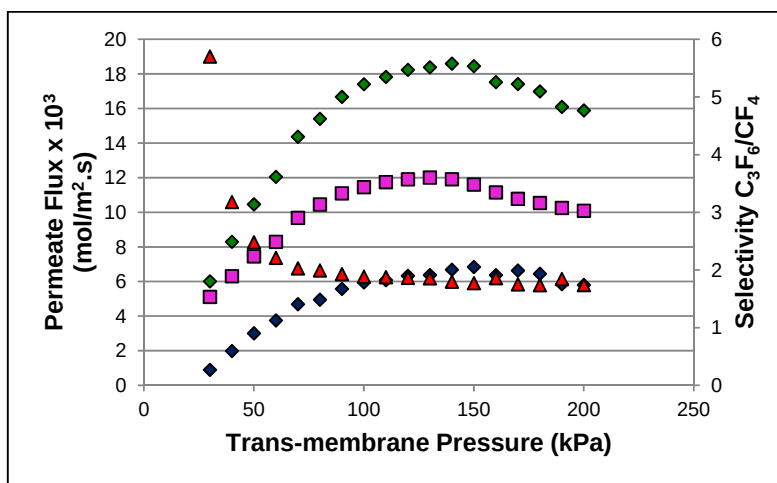


Figure 5-2: Binary gas permeation results for 50 mole% CF_4 / 50 mole% C_3F_6 using the PAN-supported membrane ($\blacklozenge$ - CF_4 flux, $\blacksquare$ - C_3F_6 flux, $\blacklozenge$ - Total flux, $\blacktriangle$ - selectivity)

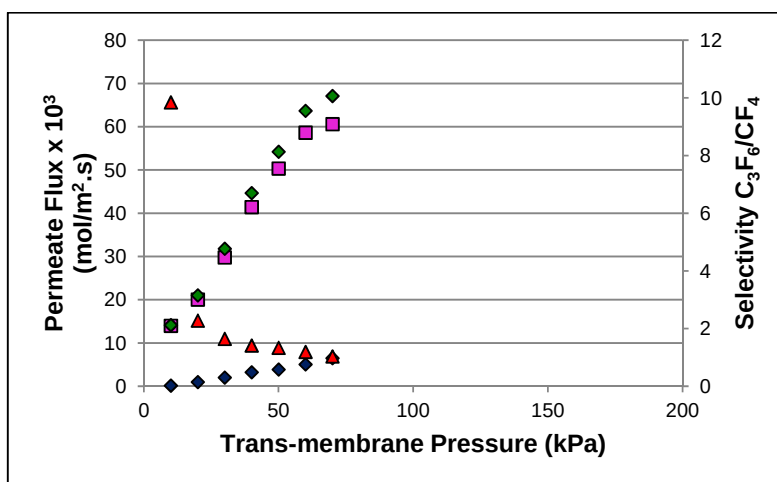


Figure 5-3: Binary gas permeation results for 10 mole% CF_4 / 90 mole% C_3F_6 using the PAN-supported membrane ($\diamond$ - CF_4 flux, $\square$ - C_3F_6 flux, $\diamond$ - Total flux, $\triangle$ – selectivity)

Figure 5-1 to Figure 5-3 adhere to the adjusted Solution-Diffusion model (Equation 4.4) as was used for pure gasses. The graphs indicate that the flux for both the partial gas permeations as well as the total permeation for the mixture started as a straight line from the origin whereafter it flattened as a maximum value was reached.

Figure 5-1 indicates that initially the CF_4 was the main contributor to the total flux at low trans-membrane pressures. At first, no flow was measured up to 30kPa trans-membrane pressure due to the dominance of the CF_4 . This was found to be also true for pure CF_4 permeation (see Figure 4-10). Subsequently, as the trans-membrane pressure increases, C_3F_6 permeation started to dominate. This is confirmed by the selectivity data. The selectivity initially favours the CF_4 up to a trans-membrane pressure of 70kPa. It then switches over to favour the C_3F_6 as the permeation of this gas increases.

The perceived predominance of CF_4 at the lower trans-membrane pressures can be ascribed to the difference in the surface charge of the molecules. The abundance of negatively charged CF_4 molecules will attach to the positively charged C_3F_6 molecules, which will cause the C_3F_6 to be surrounded by negatively charged molecules, hence altering the outer charge to be pseudo negative. The end result is a large molecule that has mainly the same charge as the membrane surface, apart from the oppositely charged core. This is comparable to the charge distribution of pure N_2 , and is found to behave accordingly in relation to the flux value.

In Figure 5-2, it is clearly indicated that there is a distinct difference between the permeation rates of the CF_4 and C_3F_6 , although the feed mixture was equimolar. The faster permeating C_3F_6 is dominant across the total range of trans-membrane pressures. This yields a maximum selectivity of 5.7 at a trans-membrane pressure of 30kPa. At these conditions the rate of permeation is extremely low (only $6 \times 10^{-6} \text{mol.m}^{-2}.\text{s}^{-1}$). For this reason it is more advisable to study maximum conditions where the flux was measured to be $1.86 \times 10^{-5} \text{mol.m}^{-2}.\text{s}^{-1}$, with a corresponding $\text{C}_3\text{F}_6/\text{CF}_4$ selectivity of 1.8. In comparison to the 90/10 mixture, similar values for the flux were obtained. It also showed an absence of permeation at pressure differentials less than 30kPa. The increase in the permeation rate for CF_4 , in comparison to the pure gas flux, is contributed to the existence of positive coupling between the two gasses. In the same manner the decrease of C_3F_6 flux in relation to its pure component flux is ascribed to negative coupling for this molecule.

Figure 5-3 shows that when the faster permeating gas was in abundance, the coupling effects experienced by both gasses, although similar in nature to that experienced by the 50/50 mixture, exerted a lesser influence on the behaviour of the mixture. This was evident by the increase in the flux for CF_4 in relation to the pure gas, while there was only a slight decrease in the flux value for C_3F_6 . A total permeation rate of $6.7 \times 10^{-5} \text{mol.m}^{-2}.\text{s}^{-1}$ was measured at a trans-membrane pressure of 70kPa. Because the behaviour of the 10/90 mixture closely resembles that of the different pure gasses, the high flux rate of C_3F_6 will cause rapid permeation of the gas mixture. This will result in a system that that will lose feed pressure at high trans-membrane pressures. In Figure 5-3, it is evident that the high permeation rate caused a drop in the feed pressure from 80kPa trans-membrane pressure onwards. This reason can be forwarded as an explanation to why this graph in Figure 5-3 differs from the 90/10 and 50/50 mixture results depicted in Figure 5-1 and Figure 5-2 respectively. A similar phenomenon was observed for the pure gas permeation of C_3F_6 . Here the feed pressure was lost after 40kPa pressure differentials. A maximum selectivity of 9.8 was measured in the low flow region. This decreases to just over one for higher flow.

A summary of the maximum measurable selectivities under different conditions for each mixture is displayed in Table 5-1 below.

Table 5-1: Summary of selectivity data for a $\text{CF}_4/\text{C}_3\text{F}_6$ feed mixture using the PAN-supported membrane

Gas mixture	Maximum selectivity	
	Selectivity ($\text{C}_3\text{F}_6/\text{CF}_4$)	Pressure differential
90/10	1.48	200kPa
50/50	5.71	30kPa
10/90	9.85	10kPa

Table 5-1 shows that for mixtures where the composition of the faster permeating gas is equal or higher than for the slower one, the maximum selectivity was found to be at low trans-membrane pressures. At this point, the resistance for the faster permeating gas (C_3F_6) is lower than that for the slower one (CF_4). The CF_4 that permeates the membrane is directly due to the coupling of the molecule to C_3F_6 molecules. Only at a higher trans-membrane pressure does CF_4 overcome the resistance to flow and will therefore cause a drop in the selectivity of C_3F_6 over CF_4 .

For both the 50/50 and 10/90 $\text{CF}_4/\text{C}_3\text{F}_6$ mixtures, the selectivity was above five. This is an indication of good separation between the two gasses. Since the higher pressure differentials are conducive to higher permeation rates, but lower selectivity, it appears that there is a trade off between higher flux and selectivity.

5.3.1.1 Permeability

The permeability of the total gas mixture, as well as each component, respectively, was calculated and presented as a function of the CF_4 composition below in Figure 5-4. The permeability of each gas was calculated by determining the slope of the linear part of the flux of each gas and multiplying it by the thickness of the membrane.

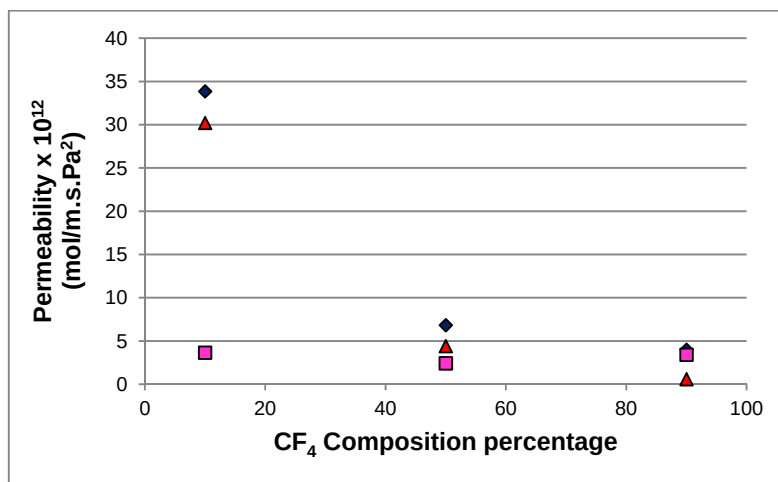


Figure 5-4: Permeability calculations for a CF₄/C₃F₆ feed mixture using the PAN-supported membrane (♦ - Total permeability, ■ - CF₄ permeability, ▲ - C₃F₆ permeability)

In Figure 5-4 it is clearly evident that the total permeability followed the same trend as the C₃F₆ permeability, which is the faster permeating gas. It was clearly the main contributor towards the total gas permeability, except when the feed consisted of 90% CF₄. The permeability of C₃F₆ was lower in the mixture compared to a pure gas feed. At a low molar percentage CF₄, less coupling of this negatively charged molecule to the positively charged C₃F₆ was possible and therefore the detrimental effect on C₃F₆ is limited. At this point there was a close relation between the C₃F₆ permeability value and that of the pure gas. However, at the higher CF₄ compositions a more negative effect was observed. The permeability value for C₃F₆ was in the order of a magnitude of ten to one hundred less than for the ideal case.

On the other hand, the CF₄ benefited from coupling with the C₃F₆ molecule. Under ideal conditions, a permeability value of $1.4 \times 10^{-12} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$ was observed in Figure 4-11, whereas the permeability for CF₄ in the binary mixture varied between 2.4×10^{-12} to $3.7 \times 10^{-12} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$. It had therefore double. Simon *et al.* (1996:231) described these changes in permeability as the coupling between the gasses in the mixture. The effect of the coupling on C₃F₆ is negative whereas for CF₄ it is positive. Therefore, Simon *et al.* (1996) define C₃F₆ as undergoing positive coupling, and CF₄, negative coupling.

5.3.2 PEI-supported membrane

The same set of experiments as described above in Section 5.3.1 were repeated for the PEI-supported membrane. The results obtained from these tests are shown below in Figure 5-5 to Figure 5-7.

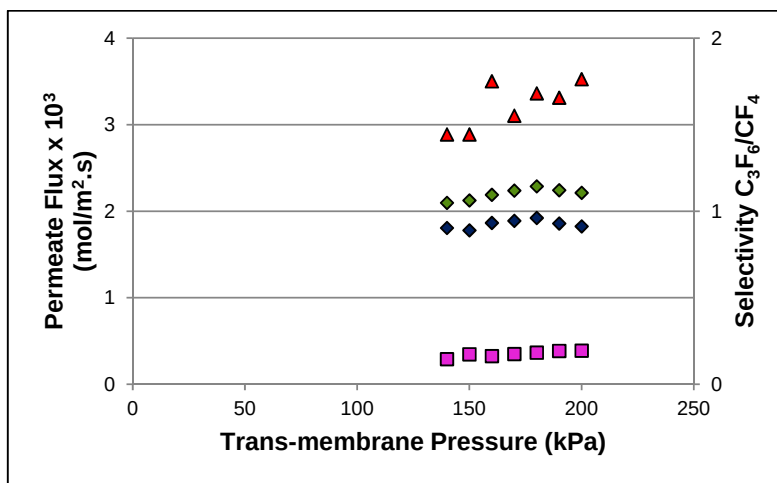


Figure 5-5: Binary gas permeation results for 90 mole% CF₄ / 10 mole% C₃F₆ using the PEI-supported membrane (♦ - CF₄ flux, ■ - C₃F₆ flux, ◆ - Total flux, ▲ – selectivity)

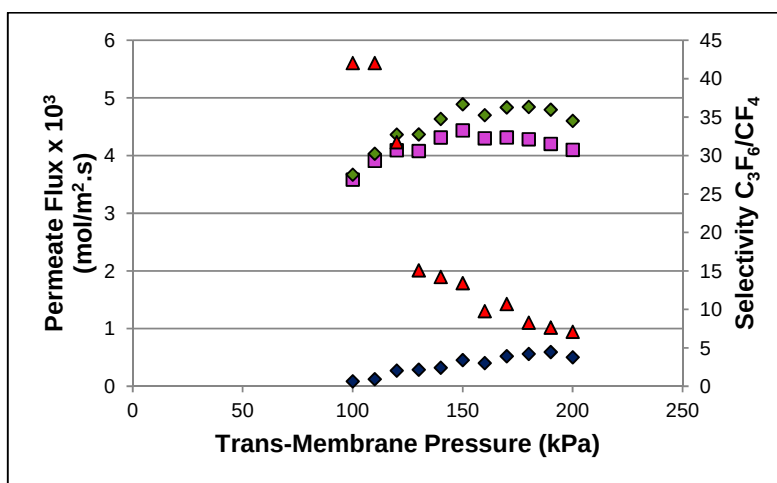


Figure 5-6: Binary gas permeation results for 50 mole% CF₄ / 50 mole% C₃F₆ using the PEI-supported membrane (♦ - CF₄ flux, ■ - C₃F₆ flux, ◆ - Total flux, ▲ – selectivity)

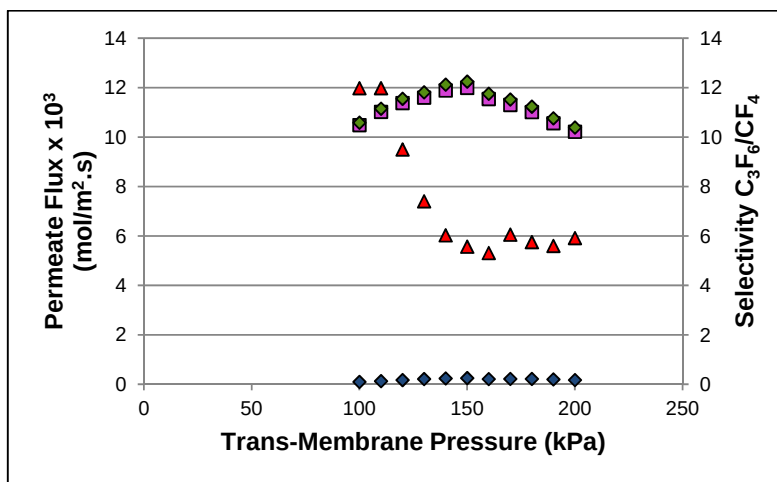


Figure 5-7: Binary gas permeation results for 10 mole% CF_4 / 90 mole% C_3F_6 using the PEI-supported membrane (♦ - CF_4 flux, ■ - C_3F_6 flux, ◆ - Total flux, ▲ – selectivity)

With reference to Figure 5-5 to Figure 5-7, there is a large difference with regards to the permeation flux for the two different membranes. Owing to the higher resistance offered by the PEI-supported membrane (as discussed in Section 4.3.2) no flow was measured at lower trans-membrane pressures.

As shown in Figure 5-1, it appears that CF_4 dominated the permeation rate in Figure 5-5. The same explanation can be given in that the more negatively charged CF_4 molecules attached themselves to the positively charged C_3F_6 . This caused the outer surface of this bigger molecule to become pseudo-negative which was repelled by the membrane surface. Those that do adsorb onto the membrane were exposed to high capillary forces owing to the size of the large conglomerate of molecules, which in turn would cause a significant decrease in their permeation rate. A maximum flux of only 2.2×10^{-3} mol.m⁻².s⁻¹ was found at a pressure differential of 180kPa.

As soon as the membrane is subjected to equimolar feed, the faster permeating C_3F_6 dominates the permeation rate, as illustrated in Figure 5-6. This tendency increases as the C_3F_6 amount increases, evident in Figure 5-7. In both these figures, it is clear that the C_3F_6 is close to being the sole permeant at the lower trans-membrane pressures. This however changes as the pressure differential increases and more CF_4 is carried through the membrane. The shape of the selectivity curve supports this notion. Regarding the 50/50 mixture, a

maximum flux of $4.9 \times 10^{-3} \text{ mol.m}^{-2}.\text{s}^{-1}$ was reached at a 150kPa trans-membrane pressure while the 10% CF_4 / 90% C_3F_6 mixture reached a maximum flux of $1.2 \times 10^{-2} \text{ mol.m}^{-2}.\text{s}^{-1}$ at the same pressure differential. The 10/90 mixture quite easily outperformed the 90/10 and 50/50 feed mixtures, which was expected, owing to the abundance of the faster permeating gas.

A summary of the selectivities obtained appears below in Table 5-2.

Table 5-2: Summary of selectivity data for a $\text{CF}_4/\text{C}_3\text{F}_6$ feed mixture using the PEI-supported membrane

Gas mixture	Maximum selectivity	
	Selectivity ($\text{C}_3\text{F}_6/\text{CF}_4$)	Pressure differential
90/10	1.76	200kPa
50/50	42.03	100kPa
10/90	11.98	100kPa

Table 5-2 indicates very favourable selectivity results for C_3F_6 over CF_4 . The maximum selectivities are very high, particularly for the mixtures containing an equal or higher amount of C_3F_6 . They do however decrease and equalise at high trans-membrane pressures, but they still produce selectivity values above 6 for the 50/50 and 10/90 mixtures of CF_4 and C_3F_6 . For a 90/10 mixture, the selectivity is however much lower, giving a maximum value of only 1.94. This is due to the coupling effects of CF_4 onto C_3F_6 as explained above.

5.3.2.1 Permeability

The permeability for the total gas mixture as well as each individual component was calculated and is shown in Figure 5-8 below.

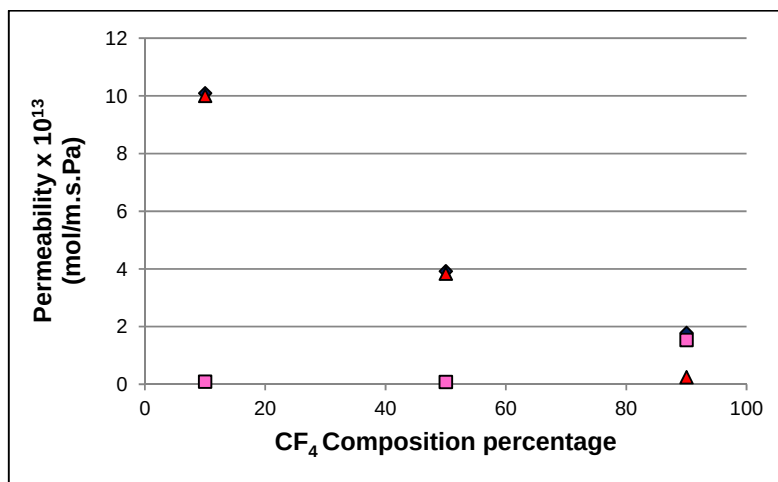


Figure 5-8: Permeability calculations for a CF₄/C₃F₆ feed mixture using the PEI-supported membrane (♦ - Total permeability, ■ - CF₄ permeability, ▲ - C₃F₆ permeability)

Figure 5-8 shows a very similar trend to that of the PAN-supported membrane shown in Figure 5-4. At a low CF₄ percentage composition, the faster permeating C₃F₆ is dominant and contributes the most towards the total permeability. This switches around at the other end of the scale where CF₄ becomes more dominant. In general, the values obtained for the permeability is extremely low in comparison with the PAN-supported membrane's values which is between ten to eighty times higher.

When comparing these values for permeability of both the gasses with the ideal values (yet again a tenfold decrease for the C₃F₆ is recorded), whereas an increase for CF₄ is observed. This confirms the coupling effects present between these two gasses as discussed in Section 5.3.1 above.

5.3.3 Summary for CF₄ / C₃F₆ feed

The behavioural patterns of both membranes were the same. In both cases, an abundance of CF₄ causes coupling with the more positively charged C₃F₆, which results in a negative effect on the permeability and selectivity of the C₃F₆ gas. When there is an abundant supply of C₃F₆, the system behaves in a similar manner as that of pure C₃F₆ in terms of permeability and selectivity. Overall, this binary mixture shows great potential for separation using both membranes. It must, however, be mentioned that the PAN-supported membrane has the far superior permeability, as for the pure gasses, and hence is the best option for industrial use.

5.4 Results and discussion for C_3F_6 / N_2 feed

For the second set of binary gas mixture feed tests, a mixture of the two fastest permeating gasses, namely the C_3F_6 and N_2 were used. Conditions for the tests were kept the same as for Section 5.3, which means that a feed pressure of 200kPa was used for both the PAN- and PEI-supported membranes. The pressure differentials ranged from a minimum to a maximum where the permeate flow was measured.

5.4.1 PAN-supported membrane

The permeate flux results for the PAN-supported membrane for the 90/10, 50/50 and 10/90 mole percentage N_2/C_3F_6 mixtures respectively, are depicted below (Figure 5-9 to Figure 5-11).

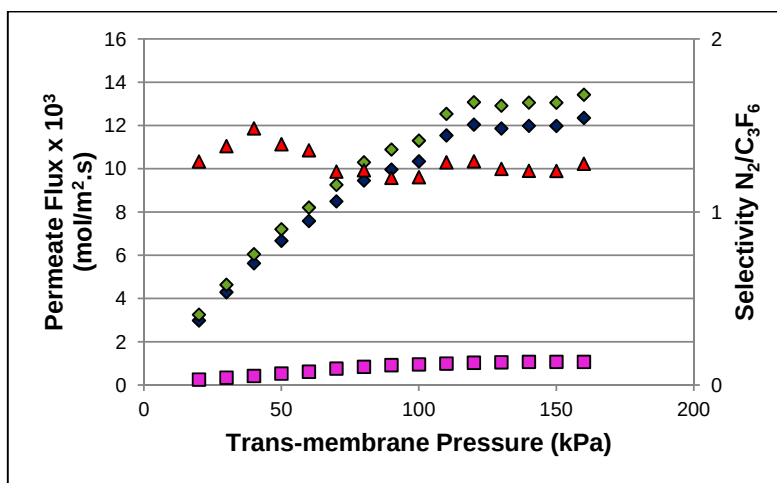


Figure 5-9: Binary gas permeation results for 90 mole% N_2 / 10 mole% C_3F_6 using the PAN-supported membrane (♦ - N_2 flux, ■ - C_3F_6 flux, ◆ - Total flux, ▲ – selectivity)

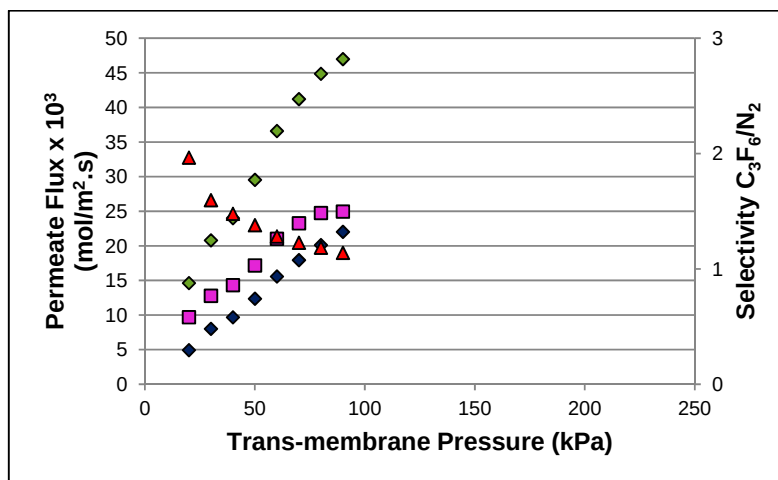


Figure 5-10: Binary gas permeation results for 50 mole% N₂ / 50 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - C₃F₆ flux, ◆ - Total flux, ▲ – selectivity)

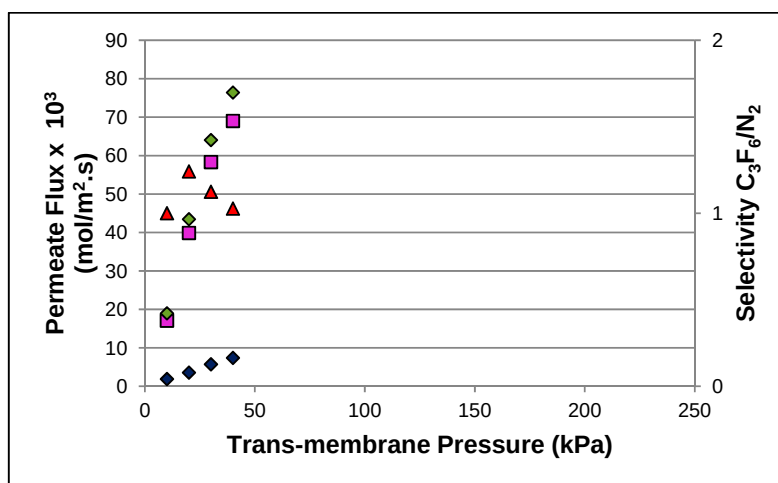


Figure 5-11: Binary gas permeation results for 10 mole% N₂ / 90 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - C₃F₆ flux, ◆ - Total flux, ▲ – selectivity)

By studying Figure 5-9 to Figure 5-11, it is clear that there was a progressive increase in flux rate as the composition of the gas moves from N₂ dominant to C₃F₆ dominant. It culminates in Figure 5-11 where a rapid permeation of flux was observed to the extent that no measurements were possible after a trans-membrane pressure of a mere 40kPa. Trans-membrane pressures higher than this resulted in a loss of feed pressure and hence

destabilisation of the system. These high permeation rates were expected for this gas mixture, since these two gasses revealed the highest pure permeation rates.

Figure 5-9 presents the results for a 90/10 mole percentage N_2/C_3F_6 mixture. In this figure, it is clearly evident that these graphs continue to exhibit the same shape as all the previous flux graphs. The shape begins with linearly until a maximum flux is reached, whereafter it tapers off to form a plateau. Due to the abundance of N_2 in the feed mixture, it contributes the most towards the total gas flux, which was found to be a maximum of only $1.3 \times 10^{-2} \text{ mol.m}^{-2}.\text{s}^{-1}$ at a trans-membrane pressure of 200kPa. It is important to note the selectivity values in Figure 5-9. The values are very close to unity, which is an indication of weak separation. The system also favours N_2 over C_3F_6 . This was unexpected, since the pure component selectivities are the other way around. This is due to the coupling that occurs between the two gasses. Although N_2 possesses a high diffusion coefficient, it has a low solubility, which retards the overall permeation of this gas. However, the surface charge difference between the two gasses allows the N_2 to connect to the C_3F_6 that in turn aids in the sorption of these molecules onto the membrane surface. The faster permeating N_2 will be favoured due to its abundance in the feed mixture. This results in the selectivity towards N_2 .

The 50/50 mixture (Figure 5-10) begins by feeding an equimolar gas mixture to the membrane. Very little separation takes place for this mixture, which is evident in that the composition of the permeate stream is very similar to that of the feed stream. This statement can be verified by looking at the slopes of the two partial flux curves as well as the selectivity values in Figure 5-10. The selectivity, favouring C_3F_6 , starts at a value of 1.97, but quickly drops down to just over 1.1 as the trans-membrane pressure increases. This is indicative of weak separation between these two gasses and was also shown to be true in Figure 5-9. The similarity of the slopes of the partial flux curves depicted in Figure 5-10 entails that the permeation rate of the two gasses was very similar. The same accounts for the contribution to the permeation rate of the total gas mixture, which is very similar for each individual gas. A maximum total permeation of $0.047 \text{ mol.m}^{-2}.\text{s}^{-1}$ was reached at a trans-membrane pressure of 90kPa. Attempts to increase the pressure differential beyond this point led to a decrease in the feed pressure.

Figure 5-11 shows that for the 10/90 mole percentage N_2/C_3F_6 mixture, C_3F_6 dominates the permeation and contributes the most towards the total gas permeation. Even with this

dominance in permeation of the C_3F_6 , coupling causes N_2 to permeate through the membrane in a similar ratio as that which is fed, resulting in a low selectivity. A maximum selectivity value of 1.24 was obtained, as shown in Table 5-3 below. The low selectivity is unfortunate, since a very high flux of $7.6 \times 10^{-2} \text{ mol.m}^{-2}.\text{s}^{-1}$ was reached.

Table 5-3 below indicates that it was not possible to obtain a selectivity higher than 2 under any conditions. The low selectivity values imply that the rate of permeation for the two gasses are very similar when using a binary gas feed as opposed to ideal selectivities as high as 5.3 (see Figure 4-21). The result of these low selectivities is a weak separation between the two gasses when mixed together. For a full scale setup, this would result in several extra membrane units having to be installed in order to give a surface area sufficient for upgrading the concentration of the one gas in relation to the other one.

Table 5-3: Summary of selectivity data for a N_2/C_3F_6 feed mixture using the PAN-supported membrane

Gas mixture	Maximum selectivity	
	Selectivity (C_3F_6/N_2)	Pressure differential
90/10	1.48 (N_2/C_3F_6)	40kPa
50/50	1.97	20kPa
10/90	1.24	20kPa

5.4.1.1 Permeability

The calculated permeability is depicted below in Figure 5-12 as a function of the N_2 composition.

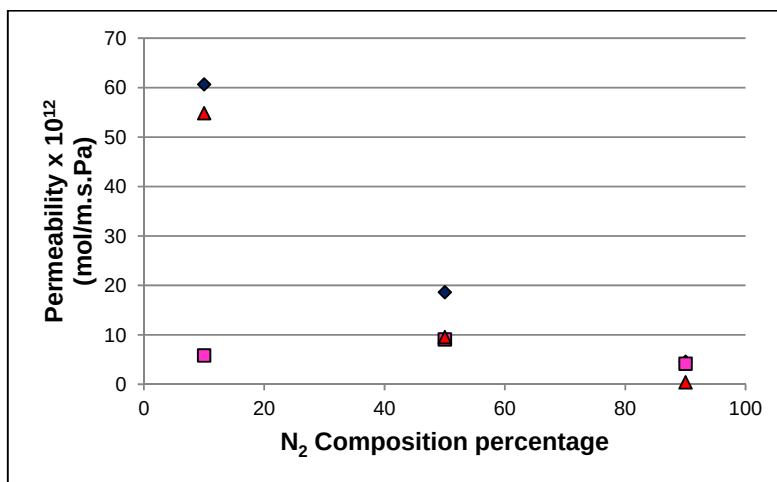


Figure 5-12: Permeability calculations for a N₂/C₃F₆ feed mixture using the PAN-supported membrane (♦ - Total permeability, ■ - N₂ permeability, ▲ - C₃F₆ permeability)

Figure 5-12 continues to exhibit the same trend as that of the permeability of the CF₄/C₃F₆ binary mixture as described in Section 5.3.1.1. The component in the mixture that had the highest permeation rate as a pure gas (the C₃F₆) largely determines the shape of the permeability graph for the total gas mixture. At the lowest N₂ percentage (10 mole percent) the permeability of C₃F₆ dominates that of N₂ and contributes 90% towards the total gas permeability. The permeability for C₃F₆ at this point is $5.48 \times 10^{-11} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$. This is higher than that for the pure component which leads to the conclusion that negative coupling, as defined by Simon *et al.* (1996:231) occurs. In Chapter 4 it was demonstrated that the diffusivity coefficient of N₂ is the highest for all the species. This fact, together with the difference in surface charge of the molecules leads to the N₂ exerting an added repelling force onto the C₃F₆ which resulted in the increase in permeability of this species.

The exact opposite happens to the N₂ where the permeability is lower than for the pure component. The same attraction force credited with the increase in the permeation rate of the C₃F₆, now exerts a negative influence on the fast moving N₂. This force causes the N₂ to slow down, resulting in a decrease in permeability.

At the other two points on the graph (the 50% N₂ and the 90% N₂ composition) the permeability is very low. It does however compare rather well with the permeability of pure N₂. This indicates that when N₂ is in abundance in the feed mixture, the coupling effects

exerted on the C_3F_6 is such that the system as a whole obeys the behavioural patterns of N_2 . Therefore, by looking at Figure 5-12, it will be noted that the permeability of N_2 stays relatively constant throughout the different compositions.

5.4.2 PEI-supported membrane

The same tests, using the same N_2/C_3F_6 binary mixtures were repeated, this time making use of the PEI-supported membrane as a separation medium. The results obtained are shown in Figure 5-13 to Figure 5-15.

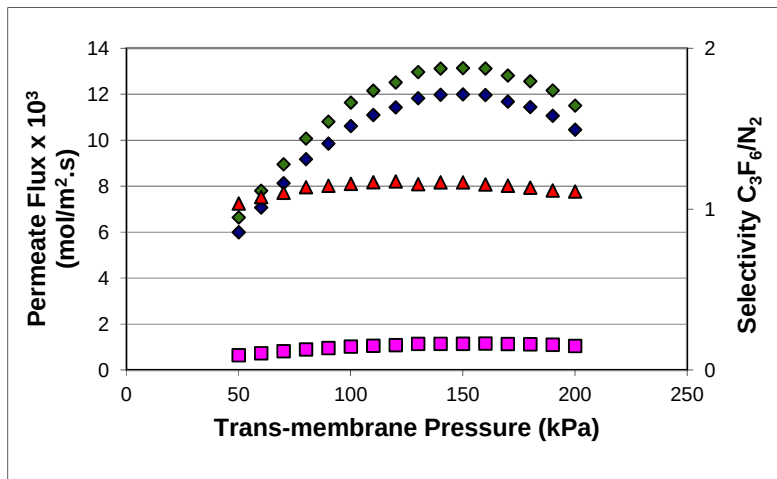


Figure 5-13: Binary gas permeation results for 90 mole% N_2 / 10 mole% C_3F_6 using the PEI-supported membrane (♦ - N_2 flux, ■ - C_3F_6 flux, ◆ - Total flux, ▲ – selectivity)

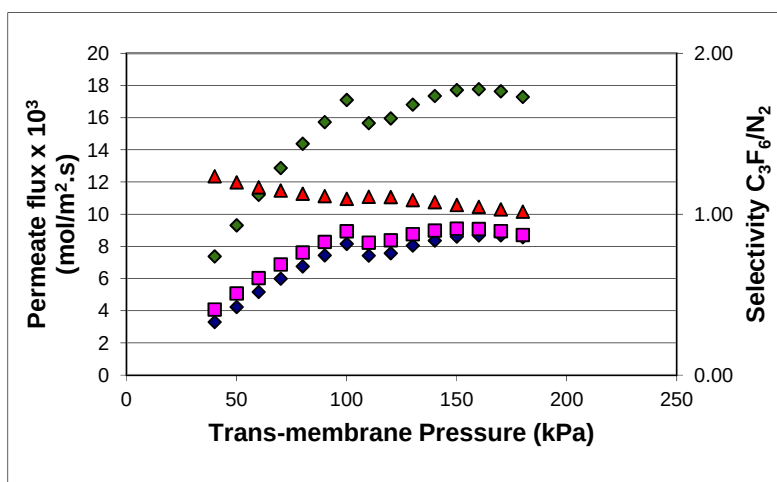


Figure 5-14: Binary gas permeation results for 50 mole% N_2 / 50 mole% C_3F_6 using the PEI-supported membrane ($\blacklozenge$ - N_2 flux, $\blacksquare$ - C_3F_6 flux, $\blacklozenge$ - Total flux, $\blacktriangle$ – selectivity)

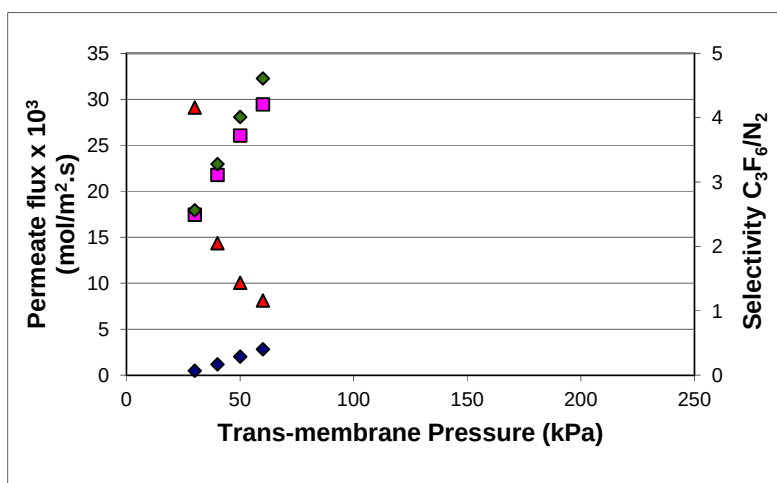


Figure 5-15: Binary gas permeation results for 10 mole% N_2 / 90 mole% C_3F_6 using the PEI-supported membrane ($\blacklozenge$ - N_2 flux, $\blacksquare$ - C_3F_6 flux, $\blacklozenge$ - Total flux, $\blacktriangle$ – selectivity)

With reference to Figure 5-13 to Figure 5-15, the results follow a similar trend than those for the PAN-supported membrane. As expected by now, flow commenced at higher trans-membrane pressures due to the influence of the supportive PEI layer, as discussed previously. For the 90/10 molar percentage N_2/C_3F_6 mixture a maximum flux of $0.013 \text{ mol.m}^{-2}.\text{s}^{-1}$ was reached at a 150kPa pressure differential. The 50/50 mixture resulted in a maximum flux of $0.018 \text{ mol.m}^{-2}.\text{s}^{-1}$ at 160kPa pressure differential, while $0.032 \text{ mol.m}^{-2}.\text{s}^{-1}$ was reached at 60kPa trans-membrane pressure for the 10/90 feed composition.

The selectivities calculated for each test resemble those found for the PAN-supported membrane, and are shown in detail in each of the graphs as well as in Table 5-4 below. However, one clear difference was noted for the 90/10 N_2/C_3F_6 system. When using the PEI-supported membrane, the selectivity favours C_3F_6 , whereas the PAN-supported membrane was selective for N_2 under the same conditions. It should however be noted that in both cases the selectivity was just over one. This implies a very weak favouring of the one gas over the other and is determined by the first support layer. Under the set feed conditions, PAN will slightly favour N_2 over C_3F_6 , whereas for PEI it will be the opposite.

Table 5-4: Summary of selectivity data for a N_2/C_3F_6 feed mixture using the PEI-supported membrane

Gas mixture	Maximum selectivity	
	Selectivity (C_3F_6/N_2)	Pressure differential
90/10	1.17	120kPa
50/50	1.24	40kPa
10/90	4.16	40kPa

In Table 5-4, the maximum selectivity for both the 90/10 and 50/50 percent mixtures are very low. Only a 10/90 mixture shows a relatively high selectivity. This does however occur at the exact point where the first permeate flow was measured (see Figure 5-15) whereafter there is a significant decline in the value of the selectivity to below 2. The graph in Figure 5-15 clearly shows that the selectivity was on a downward trend moving towards unity.

5.4.2.1 Permeability

Permeability calculations were performed and the resultant graph is shown below in Figure 5-16. This graph reveals that the same trends continue for the PEI-supported membrane using a N_2/C_3F_6 binary mixture as for all the previous binary mixture experiments.

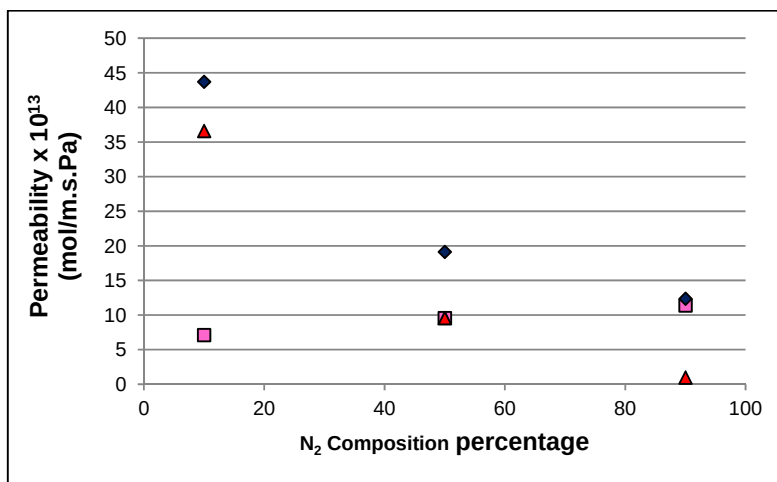


Figure 5-16: Permeability calculations for a N₂/C₃F₆ feed mixture using the PEI-supported membrane (♦ - Total permeability, ■ - N₂ permeability, ▲ - C₃F₆ permeability)

Figure 5-16 shows that for a binary feed mixture where the gas with the highest ideal permeation rate is in excess, it dominates the contribution towards the total gas permeability. At this point a maximum total gas permeability of $4.37 \times 10^{-12} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$ was found. The permeability of the individual gasses is lower than that for the ideal feed in both cases. A combination of gas molecule interactions and difficulty permeating through the PEI-support are to blame for this.

As the N₂ composition increases to 50%, the contribution of the two gasses towards the total gas permeation, take on equal proportions. A further increase towards 90 mole percentage N₂ in the binary gas feed mixture results in the N₂ contributing the most towards the total gas permeation. Also interesting to note is that the permeability of the weaker permeating gas under ideal conditions (the N₂) stays almost constant throughout the different feed compositions. This is the same for all binary permeability graphs to date where the permeability of the weakest permeating gas under ideal conditions stays almost constant regardless of the feed composition. It is attributed to the coupling effect between the two gasses.

5.4.3 Summary for N₂ / C₃F₆ feed

When comparing the two membranes, the high permeability of the PAN-supported membrane in relation to the PEI-supported membrane is first highlighted. When using the PAN-

supported membrane, the permeability of this membrane is approximately ten times more than that for the PEI-supported membrane. It would therefore immediately be labelled as the favourite membrane to use during full-scale operation. However, by adding a comparison of the selectivities to the reasoning, the result may change. All the selectivity values for the different mixtures compare rather well with each other, being between 1 and 2 for both the PAN- and PEI-supported membranes, apart from the last instance (10/90 mixture). Here a selectivity of over 4 was obtained for this mixture using the PEI-supported membrane. It would therefore help with the separation of the two gasses under these circumstances. A horses-for-courses approach is recommended when considering the use of the membrane for separating a N_2/C_3F_6 mixture.

5.5 Results and discussion for N_2/CF_4 feed

The final binary set of experiments carried out was for the mixture of N_2/CF_4 . The same mixture combinations were used in conjunction with the two available membranes. The results for the PAN- and PEI-supported membranes respectively are discussed below. These two sets of experiments differ from the previous four when looking at the expected interaction of the gas molecules. To date, there was always a difference in the surface charge of the two gasses used to compose the binary mixture. This will cause the gasses to attract one another which will lead to coupling effects. When using N_2 and CF_4 as feed gasses, the binary mixture will contain two gasses that have the same surface charge (in this case, both are negative as shown in Table 3-2). This will result in repelling forces between the gasses.

5.5.1 PAN-supported membrane

The first set of results are those obtained for the PAN-supported membrane, and is shown below in Figure 5-17 to Figure 5-19.

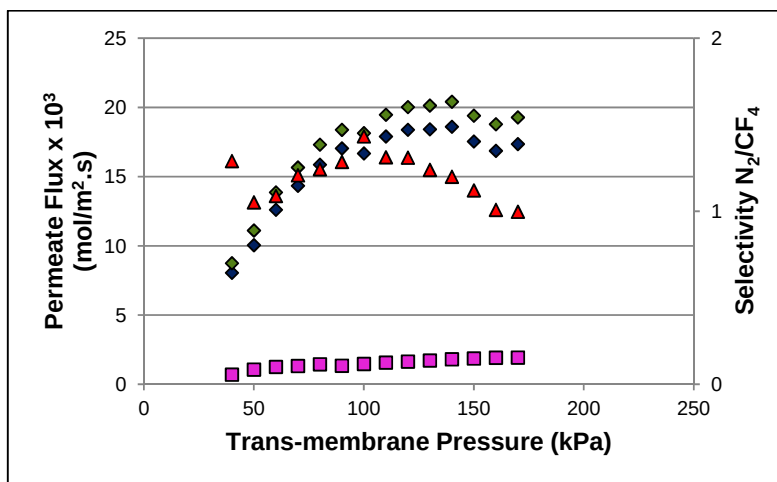


Figure 5-17: Binary gas permeation results for 90 mole% N₂ / 10 mole% CF₄ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ◆ - Total flux, ▲ – selectivity)

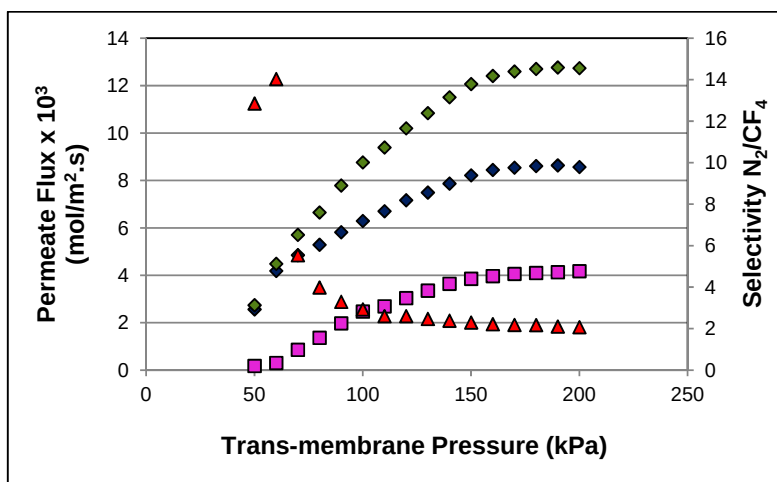


Figure 5-18: Binary gas permeation results for 50 mole% N₂ / 50 mole% CF₄ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ◆ - Total flux, ▲ – selectivity)

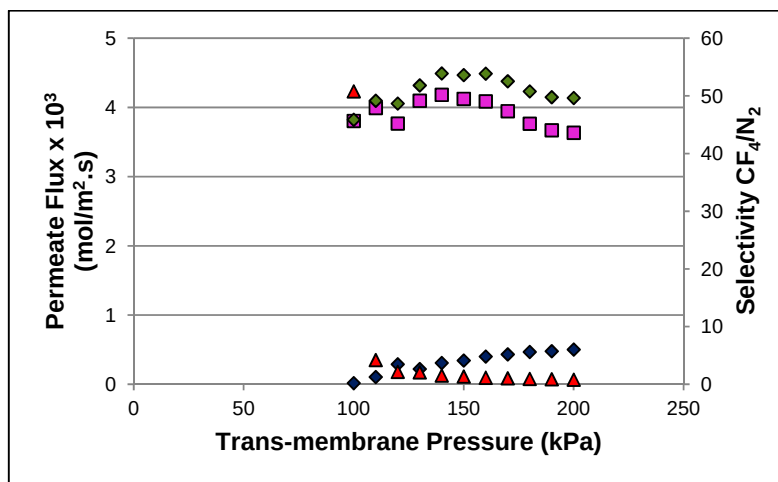


Figure 5-19: Binary gas permeation results for 10 mole% N_2 / 90 mole% CF_4 using the PAN-supported membrane (♦ - N_2 flux, ■ - CF_4 flux, ◆ - Total flux, ▲ – selectivity)

Figure 5-17 depicts the results for a 90/10 N_2/CF_4 feed mixture. The figure indicates that flow was only achieved at pressure differentials of 40kPa and higher. It further reveals that N_2 dominated the permeation and is almost the sole contributor towards the total gas flux, especially at lower trans-membrane pressures. This occurs due to the abundance of N_2 molecules in the feed; regardless of the fact the CF_4 has a higher ideal sorption coefficient. However, as the pressure differential increases above 100kPa, the permeation ratio turns in favour of CF_4 , effectively reducing the selectivity of the system towards N_2 . In the end, the maximum flux obtained by both gasses is smaller than for their respective ideal states.

This trend repeats itself for the equimolar feed in Figure 5-18. The initial flow at a low trans-membrane pressure is dominated by the N_2 flux. At this point, it is safe to assume that both gasses are afforded an equal opportunity to interact with the membrane surface. This will lead to more CF_4 being adsorbed onto the surface. However, because the diffusion coefficient of N_2 is magnitudes higher than that of CF_4 , much more N_2 will permeate through the membrane even though less has been adsorbed. If the pressure differential across the membrane increases, more CF_4 will start to diffuse through the membrane up to a point where maximum sorption and diffusion of the individual gasses are reached. The system will stabilise and the selectivity will remain more or less constant. This is observed in Figure 5-18 from a trans-membrane pressure of 120kPa onwards.

Figure 5-19 is unique for this gas mixture and membrane combination. Keeping in mind the existence of repelling forces between the two negatively charged molecules, it is clear that when the concentration of CF_4 is in abundance in the feed, strong competition exists between the different gasses and the membrane surface. The greater amount of CF_4 will adsorb quicker onto the surface and physically push the N_2 away from it. The result of this action is a system that will be highly dependent on the characteristics of CF_4 permeation and will therefore be selective towards CF_4 . This explanation can be verified by the fact that the maximum flux for pure CF_4 fed to the membrane at 200kPa feed pressure and trans-membrane pressure is the same as that for the 10/90 N_2/CF_4 mole percentage feed mixture.

A summary of the selectivity data is shown below in Table 5-5.

Table 5-5: Summary of selectivity data for a N_2/CF_4 feed mixture using the PAN-supported membrane

Gas mixture	Maximum selectivity	
	Selectivity (N_2/CF_4)	Pressure differential
90/10	1.43	100kPa
50/50	14.03	60kPa
10/90	50.80 (CF_4/N_2)	100kPa

Table 5-5 indicates that the system in general is selective towards N_2 . The exception is for a CF_4 abundant feed mixture where the composition between the two gasses is such that the N_2 is largely prohibited to adsorb onto the surface and ultimately permeate the membrane. This table further indicates that maximum selectivities are achieved at low trans-membrane pressures (usually close to the first measurement of permeability), which means that separation is at its best when there is a low flow rate of gas through the membrane.

5.5.1.1 Permeability

The permeability of the different gasses as well as the total gas was calculated and is shown below in Figure 5-20.

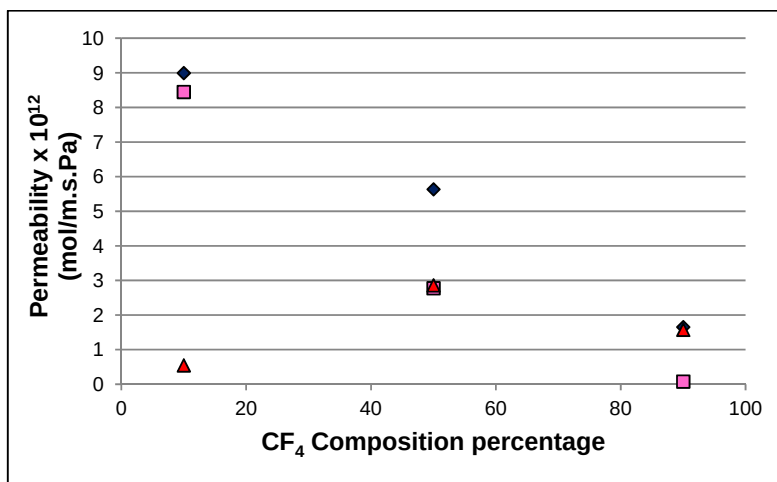


Figure 5-20: Permeability calculations for a N₂/CF₄ feed mixture using the PAN-supported membrane (♦ - Total permeability, ■ - N₂ permeability, ▲ - CF₄ permeability)

Figure 5-20 exhibits the same trend as all the previous permeability graphs for binary feed mixtures. When the faster permeating gas (N₂) is in excess, the total gas permeability is relatively high and consists mainly of N₂. When the feed mixture consists mainly of CF₄, it also makes a dominant contribution towards the total gas permeability; however, the total gas permeability is low. For a 50/50 feed mixture, equal contributions towards a low total gas permeability is observed.

For the two extreme gas mixtures, the permeability of the N₂ are lower than for its ideal state, while the CF₄ is very similar to its ideal state when the mixture contains only 10% CF₄. However, for the 50/50 mixture, only the permeability of N₂ is much lower. The permeability of CF₄ has increased from $1.49 \times 10^{-12} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$ to $2.86 \times 10^{-12} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-1}$. This increase in permeability is very small and does not warrant any investigation.

5.5.2 PEI-supported membrane

The same feed mixture was repeated using the PEI-supported membrane. The results are shown below in Figure 5-21 to Figure 5-23.

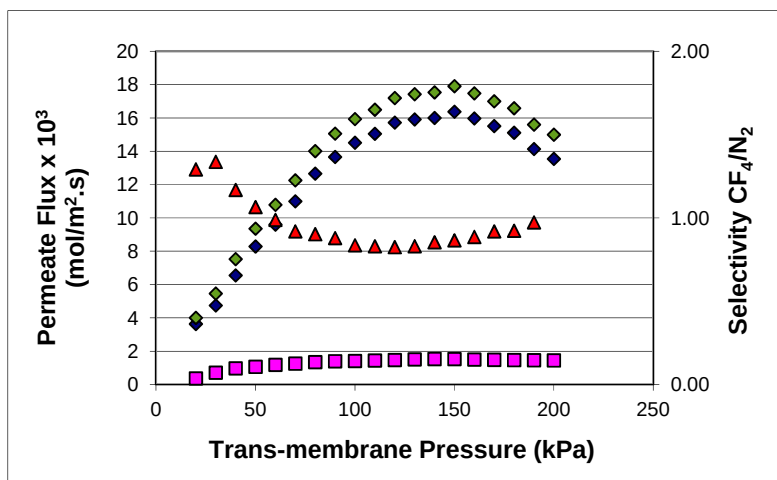


Figure 5-21: Binary gas permeation results for 90 mole% N₂ / 10 mole% CF₄ using the PEI-supported membrane (◆ - N₂ flux, ■ - CF₄ flux, ◇ - Total flux, ▲ - selectivity)

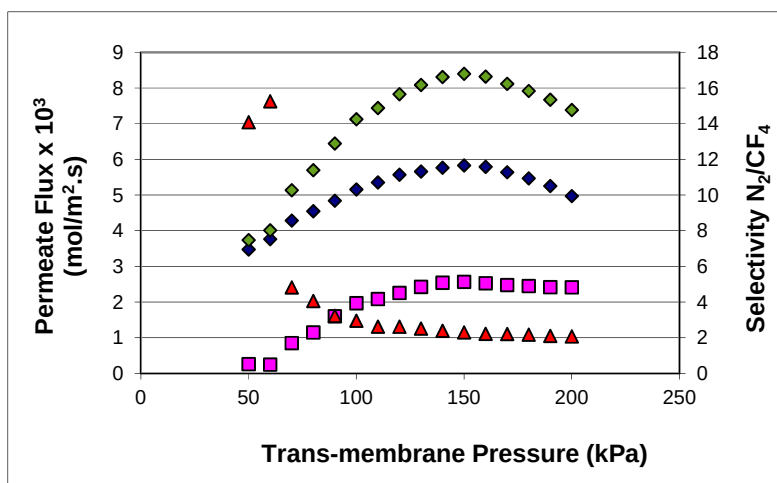


Figure 5-22: Binary gas permeation results for 50 mole% N₂ / 50 mole% CF₄ using the PEI-supported membrane (◆ - N₂ flux, ■ - CF₄ flux, ◇ - Total flux, ▲ - selectivity)

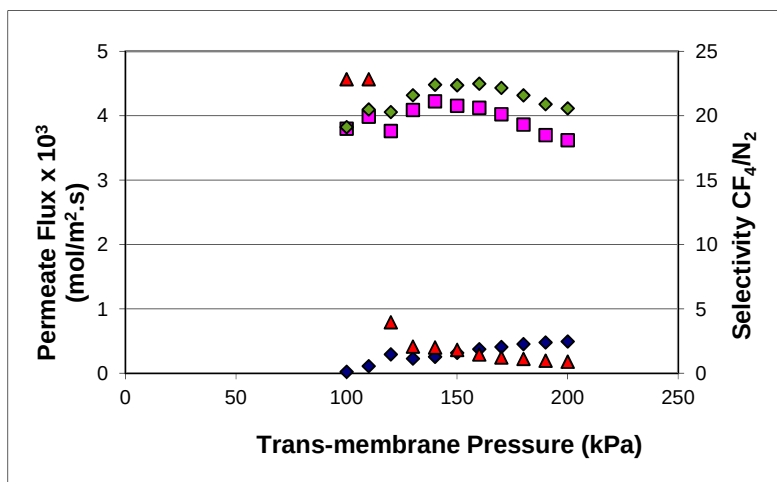


Figure 5-23: Binary gas permeation results for 10 mole% N_2 / 90 mole% CF_4 using the PEI-supported membrane (♦ - N_2 flux, ■ - CF_4 flux, ◆ - Total flux, ▲ – selectivity)

Figure 5-21 to Figure 5-23 show the exact same trend as observed for the PAN-supported membrane using this binary gas mixture as feed. Figure 5-21 reveals that the permeation is dominated by N_2 , which is also in abundance in the feed. This particularly occurs at lower trans-membrane pressures where the N_2 flux contributes almost 100 percent towards the total gas flux. Only from a trans-membrane pressure of 60kPa onwards does the CF_4 's superiority in sorption come into play. From this point onwards the selectivity also favours CF_4 . This situation held true until the 200kPa pressure differential was reached. However, it appears as if the system was moving towards an equilibrium selectivity of one.

This was again observed in Figure 5-22 where N_2 permeation dominates the system at lower pressure differentials. This dominance is attributed to the superiority of the N_2 diffusion in relation to that of CF_4 . As the trans-membrane pressure increases, more CF_4 begins to permeate the membrane. As explained in Section 5.5.1, this is attributed to a state of equilibrium that was reached between the superiority in diffusion by the N_2 and the superiority in sorption by the CF_4 .

The sorption superiority comes into play for Figure 5-23 where CF_4 permeation dominates the total gas permeation when a 10/90 N_2/CF_4 gas mixture is used as feed to the membrane. The abundance of CF_4 molecules occupies most of the available membrane surface, which allows it to repel the similarly charged N_2 molecules. At higher pressure differentials, the

sorbed CF_4 molecules diffuse through the membrane, opening up position on the surface where N_2 can absorb. At this point, the high diffusion of N_2 then causes a shift in dominance in the system and selectivity is switched towards that of N_2 . It began at a trans-membrane pressure of 120kPa.

The summary of selectivity data is exhibited in Table 5-6 below.

Table 5-6: Summary of selectivity data for a N_2/CF_4 feed mixture using the PEI-supported membrane

Gas mixture	Maximum selectivity	
	Selectivity (N_2/CF_4)	Pressure differential
90/10	1.29	20kPa
50/50	15.26	60kPa
10/90	22.83 (CF_4/N_2)	100kPa

Table 5-6 above shows remarkable similarity to the selectivities obtained for the PAN-supported membrane as portrayed in Table 5-5. The highest selectivities usually occur close to the trans-membrane pressure where permeation was measured for the first time. From that point onwards the selectivity value decreases towards much lower values ranging between 1 and 2.07. Such low selectivity values coupled with low flux values are an indication of weak separation by the membrane and therefore it can be concluded that this specific membrane may not be suited to the separation of these gasses.

5.5.2.1 Permeability

The calculated permeability values are shown below in Figure 5-24.

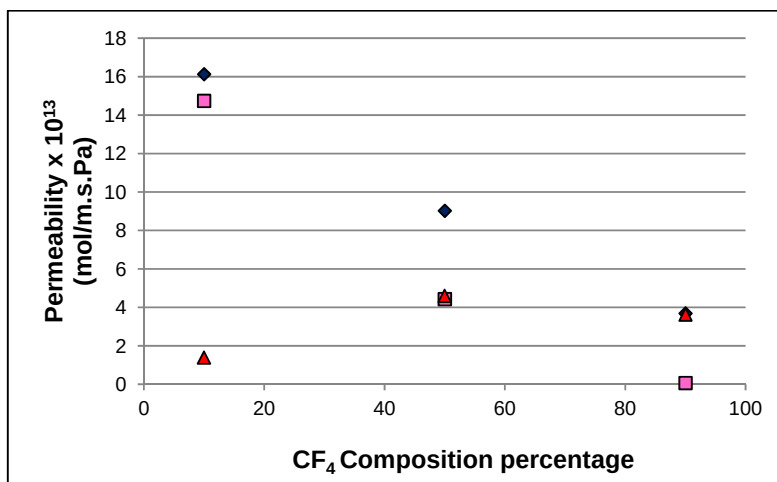


Figure 5-24: Permeability calculations for a N₂/CF₄ feed mixture using the PEI-supported membrane (♦ - Total permeability, ■ - N₂ permeability, ▲ - CF₄ permeability)

The shape of the permeability graph depicted in Figure 5-24 above is exactly the same as for the PAN-supported membrane shown in Figure 5-20. The only difference between the two graphs lies in the actual values obtained for the permeability, which are close to 10 times lower for the PEI-supported membrane than for the PAN-supported membrane.

On an individual basis, the permeability of both gasses is significantly lower for the binary feed than that obtained for the pure gas feeds. The coupling that occurs between the two gasses, together with the PEI support structure, exerts a negative influence on the permeability of both.

5.5.3 Summary for N₂ / CF₄ feed

For this binary gas mixture, the two membranes are comparable with one another in terms of selectivity. Very high selectivities are experienced for mixtures where CF₄ is in abundance. The same can be said for the 50/50 mixture where selectivities of 14 and 15 were measured for the PAN- and PEI-supported membranes respectively. The largest difference between the two membranes is attributed to the permeability of the gas mixture. Similar to the other mixtures, the PAN-supported membrane yields much higher permeabilities, which renders it much more attractive for use in industrial applications.

5.6 Modelling the binary gas permeation

As mentioned above, there are several published works on binary gas separation. The common denominator between all of these papers is the use of the Maxwell-Stefan equations in modelling the flow of a binary gas mixture through a membrane. These equations are capable of describing partial fluxes for the binary components when considering mechanical interactions.

The Maxwell-Stefan theory is derived from the basis that the friction that is experienced by each component balances the driving force for that component. From this basis, the general Maxwell-Stefan theory as applied to surface diffusion is given by (Krishna, 1990):

$$\frac{-\theta_i}{RT} \nabla \mu_i = \sum_{j=1}^n \frac{\theta_j N_j^s}{q_{sat} \rho \mathcal{D}_{ij}^s} + \frac{N_i^s}{q_{sat} \rho \mathcal{D}_i^s} \quad i, j = 1, 2, \dots, n \quad 5.2$$

By making several assumptions, Equation 5.2 can be developed to yield two separate equations, which one can use to calculate the partial fluxes for the fastest diffusing component (Equation 5.3) and the slowest one (Equation 5.4).

$$N_1^s = -q_{sat} \rho \frac{\mathcal{D}_1^s}{(1-\theta_1-\theta_2)} \frac{[(1-\theta_2)+\theta_1] \nabla \theta_1 + [2\theta_1] \nabla \theta_2}{\frac{\theta_2}{\mathcal{D}_{12}^s} + \frac{\theta_1}{\mathcal{D}_1^s} + \frac{1}{\mathcal{D}_1^s}} \quad 5.3$$

$$N_2^s = -q_{sat} \rho \frac{\mathcal{D}_2^s}{(1-\theta_1-\theta_2)} \left[\frac{(1-\theta_1) \nabla \theta_2 + \theta_2 \nabla \theta_1}{\theta_2 \frac{\mathcal{D}_1^s}{\mathcal{D}_{12}^s}} + \nabla \theta_1 + \nabla \theta_2 \right] \quad 5.4$$

These two equations are referred to as the generalised Maxwell-Stefan equations and are based on chemical potential difference as the driving force (Marx, 2002:120). The cross-term diffusivity, $\mathcal{D}_{ij}^s$, is generally calculated from pure component data using the Vignes equation (Vignes, 1966:195). This is indicated below in Equation 5.5.

$$\mathcal{D}_{12}^s = (D_1^s)^{\gamma_1} (D_2^s)^{\gamma_2} \gamma_{12} \quad 5.5$$

By studying Equations 5.3 to 5.5, it is apparent that solving these equations comprises the simultaneous solving of several partial differential equations. Even though modern day computing power makes it possible to solve, it defeats the objective stated in Section 1.3, which stated that a simplified engineering model should be developed for use.

5.6.1 Applicable model

As stated in the paragraph above, the use of the conventional Maxwell-Stefan model to calculate partial fluxes of a binary gas mixture does not comply with the objectives stated for this study. Apart from this, Baikov and Primak (2007:382) averred that there are no reliable models that can predict the process of gas separation at given membrane and gas characteristics. Since a modified version of the solution-diffusion model was used successfully to fit the pure gas permeation data, it was decided to use this model again, and adjust it to comply with binary gas permeation.

The modified solution-diffusion model is given as:

$$J_i = \left(\frac{S_i D_i}{z} \right) p_p (p_f - p_p) \quad 5.6$$

Studying Equation 5.6 clearly indicates that by knowing the process conditions (p_i) and the membrane dimensions (z), the flux for a gas can be calculated at these conditions by knowing both the solubility and diffusion constants. These constants were derived from sorption tests (S_i), Section 3.3.6, and from the pure gas permeation experiments (D_i), Section 4.7. However, as just stated, this was carried out for pure gas permeability, which means that no direct component influence was taken into consideration. Schatzel *et al.* (2001:103) state that coupling influence between gasses is well documented and may be one of the main parameters causing the demise in permeability and selectivity. It is therefore extremely important to consider the influence of gas (1) on gas (2), and the influence exerted on either the sorption or the diffusion of the gasses.

Damle (2004:27) and Marx (2002:119) both describe the coupling influence of the gasses on sorption by a modified Langmuir equation, given below as Equation 5.7.

$$q_i = \frac{q_{max} K_i p_i}{1 + K_i p_i + K_j p_j} \quad 5.7$$

From here, S_{ij} can be calculated by:

$$S_{ij} = \frac{q_i}{p_i} \quad 5.8$$

Therefore, by knowing the pure gas maximum adsorption (q_{max}) and the Langmuir constant (K_i), the sorption coefficient (S_{ij}) can be calculated for each component of the binary mixture.

No literature was found that forwards a way to calculate the diffusivity coefficient for each gas as influenced by the presence of the other, using pure component diffusivities. Vignes (1966) derived an equation that can be used for calculating an overall diffusion coefficient (D_{ij}^s) and which can be used in the Maxwell-Stefan equations (Equation 5.5). This coefficient, also called the cross term-diffusivity, is only applicable in calculating the total flux for the gas. This would, however, require a total gas solubility coefficient. Since no such coefficient is available, and the total flux would not give any information on the partial fluxes of the different components (important for engineering), this diffusion coefficient could not be used.

A modified Vignes equation was used to calculate the partial diffusivity coefficients (D_{ij}) for each component. This equation is given in Equation 5.9 below:

$$D_{ij} = D_i^{y_i \gamma_{ij}} \quad 5.9$$

where γ_{ij} is the thermodynamic factor indicating the influence of component j on component i , and y_i is the molar fraction of component i in the feed to the membrane.

By combining Equation 5.6 to Equation 5.9, a modified solution-diffusion model can be derived that can be used to calculate the partial flux of each component. This is shown in Equation 5.10 below.

$$J_{ij} = \left[\frac{\left(\frac{q_{max} K_i}{1 + K_i p_i + K_j p_j} \right) \cdot (D_i^{y_i \gamma_{ij}})}{z} \right] p_p (p_f - p_p) \quad 5.10$$

Total flux of the system can be calculated as the sum of the partial fluxes. In Equation 5.10, all the pressure terms were measured together with the corresponding flux, while the sorption term was calculated using sorption data found in Section 3.3.6. The diffusion coefficient term, and more specifically the thermodynamic factor (γ_{ij}), was fitted using the least squares method.

5.6.2 PAN-supported membrane

The modified solution-diffusion model derived in Section 5.6.1 (Equation 5.10) was fitted to the binary flux data obtained for the different gas mixtures across the membrane. Partial and total flux data was fitted to the model. Fitted data for the total fluxes are shown in this section while fitted partial flux data are available in Appendix E

5.6.2.1 Modelling of CF_4 / C_3F_6 data

The modelled data for the CF_4/C_3F_6 system is depicted below in Figure 5-25.

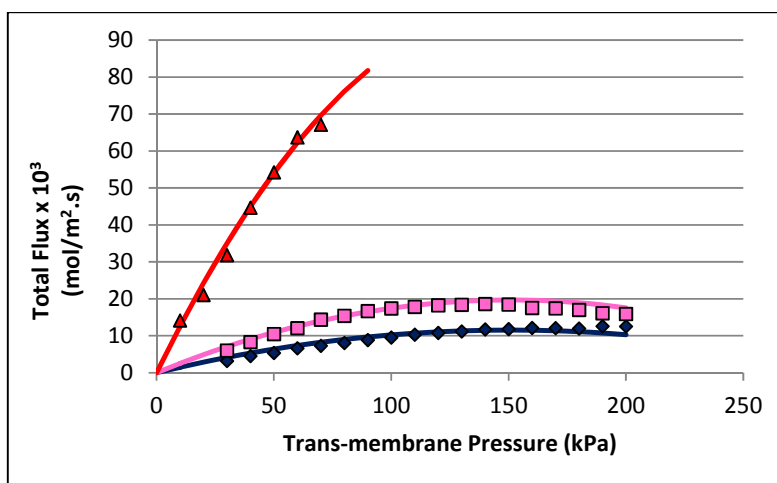


Figure 5-25: Modelling results for CF_4/C_3F_6 flux through the PAN-supported Teflon® AF2400 membrane at different mixtures (♦ - 90/10, ■ - 50/50, ▲ - 10/90). The lines represent the models while the markers represent the actual experimental data

Figure 5-25 is a visual indication that the different derived models are a good fit of the experimental values. The 95% confidence level between the models and the data varies between 2.14% and 2.79%. These low confidence levels are a confirmation of the good fit of the model.

Binary diffusion coefficients for the gasses, calculated by Equation 5.9, are furnished in Figure 5-26.

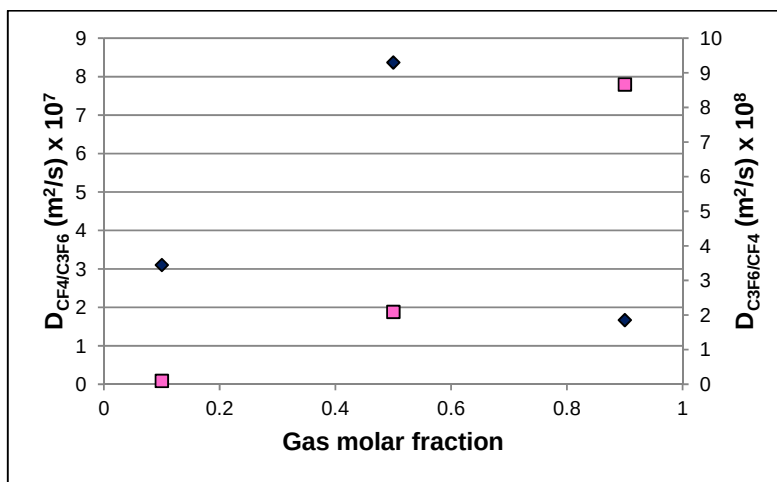


Figure 5-26: Diffusion coefficients for CF_4/C_3F_6 mixture using a PAN-supported membrane (♦ - D_{CF_4/C_3F_6} , ■ - $D_{C_3F_6/CF_4}$)

In Figure 5-26, the negative influence caused by the coupling between CF_4 and C_3F_6 is clearly visible. At low concentrations of C_3F_6 , the diffusion coefficient for C_3F_6 in CF_4 is at its lowest, increasing exponentially as the concentration of C_3F_6 increases and therefore the influence of the CF_4 decreases. Similarly, the positive influence of C_3F_6 on CF_4 is observed. At low concentrations CF_4 , the diffusion graph mimics that of the faster permeating C_3F_6 . This is again attributed to the physical coupling that occurs between the two molecules with opposite surface charges. When CF_4 is abundant, the effect of the positive surface charge of C_3F_6 is negated, which causes the binary diffusion for CF_4 in C_3F_6 in the membrane to be low.

Figure 5-27 below illustrates the relationship between the thermodynamic factor (γ_{ij}) and the fraction of each gas present in the feed mixture.

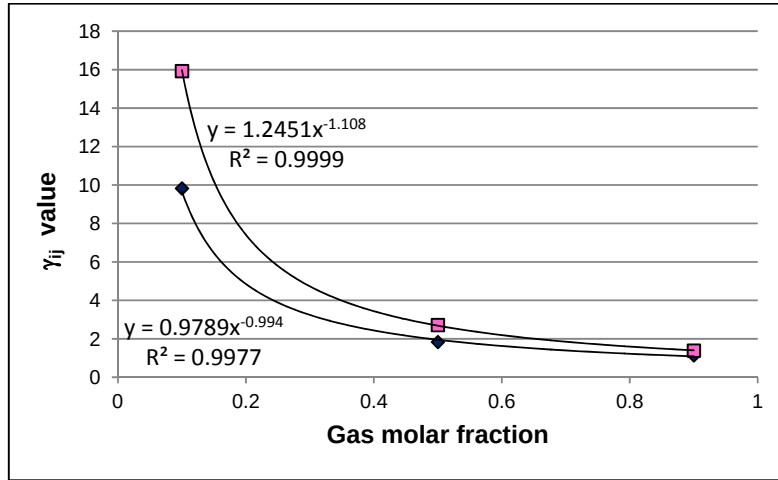


Figure 5-27: Thermodynamic factors (α) for CF_4/C_3F_6 mixture using a PAN-supported membrane (♦ - CF_4 , ■ - C_3F_6)

Figure 5-27 shows that the thermodynamic factor for both gasses follows a power law trend. This was confirmed by fitting an empirical power law curve to the data points which yielded R^2 values of 0.9977 and 0.9999 for CF_4 and C_3F_6 respectively. This process was performed in order to obtain a mathematical relationship between the data points. By amalgamating this fitted curve with Equation 5.9, it is possible to accurately predict the behaviour of any CF_4/C_3F_6 mixture using this membrane. The equations for the different curves are shown on the graph in Figure 5-27. γ_{ij} values with fitted errors are shown in Table 5-7.

Table 5-7: Fitted γ values for a CF_4/C_3F_6 binary mixture ($i = CF_4$; $j = C_3F_6$)

Binary gas mixture (CF_4/C_3F_6)	γ_{ij}	γ_{ji}
90/10	1.14 ± 0.03	15.93 ± 0.44
50/50	1.83 ± 0.04	2.72 ± 0.06
10/90	9.82 ± 0.21	1.39 ± 0.03

5.6.2.2 Modelling of N_2 / C_3F_6 data

Using the same methodology as described above, the results of fitting Equation 5.10 to the total flux data of the N_2/C_3F_6 binary feed mixture are depicted below in Figure 5-28.

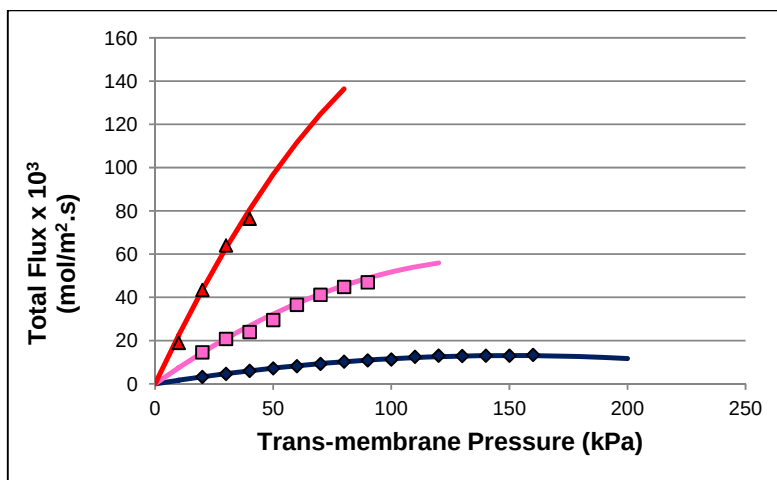


Figure 5-28: Modelling results for N_2/C_3F_6 flux through the PAN-supported Teflon® AF2400 membrane at different mixtures (♦ - 90/10, ■ - 50/50, ▲ - 10/90). The lines represent the models while the markers represent the actual experimental data

Figure 5-28 reveals a good fit of the derived model to the experimental data and demonstrates a steady increase from a low flux, for the case where the slower permeating gas is abundant, to a higher flux when the quicker permeating C_3F_6 is abundant. The 95% confidence levels for the different mixtures were calculated to be 0.54% for a 90/10 N_2/C_3F_6 mixture, 1.78% for a 50/50 mixture and 3.08% for a 10/90 mixture. These low confidence levels are indicative of the good fit achieved as shown in Figure 5-28.

Diffusion coefficients were calculated for each gas in the different mixtures and are furnished in Figure 5-29 below.

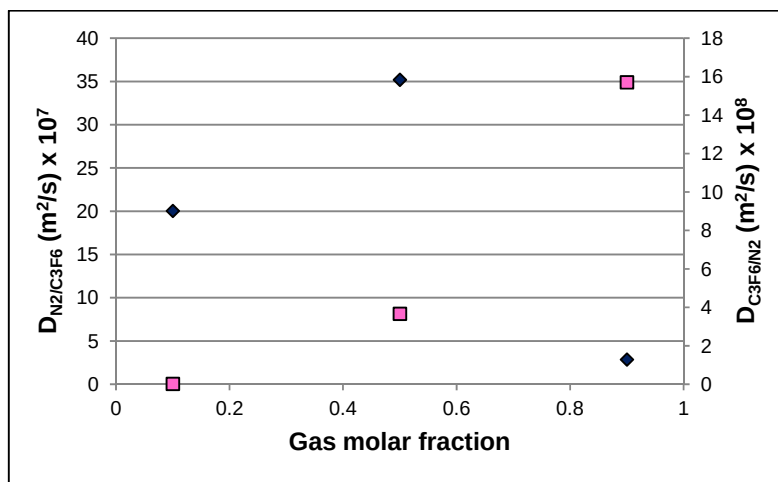


Figure 5-29: Diffusion coefficients for N_2/C_3F_6 mixture using a PAN-supported membrane (♦ - D_{N_2/C_3F_6} , ■ - $D_{C_3F_6/N_2}$)

Figure 5-29 indicates that for the faster permeating gas (C_3F_6), the binary diffusion coefficients increase exponentially as the mole fraction of the gas increases in the feed to the membrane. On the other hand, for the slower permeating gas (N_2), the diffusion coefficient initially increases at the same rate as the faster one whereafter it decreases significantly, as this gas becomes dominant in the feed mixture. This initial increase is ascribed to coupling between the two gasses, which enables the faster permeating gas to drag the other one through the membrane. This coupling effect disappears when the slower gas dominates the mixture composition.

In both instances of extreme mixtures, binary diffusion coefficient of the abundant gas is slightly lower than for the pure gas. The influence of coupling between the gasses that causes a competition for the membrane surface can explain this. The 50/50 mixture, however, exhibits an important anomaly. The binary diffusion coefficient for the slower permeating N_2 is higher at this point than when the feed mixture contained 90% of the gas. Negatively charged N_2 molecules attach to the positively charged C_3F_6 molecules, resulting in an overall charge that is still slightly positive. This positive agglomeration of molecules is subsequently attracted to the negative surface of the membrane, consequently increasing the sorption of the N_2 . At a 90% N_2 mixture, there are insufficient C_3F_6 molecules to make a significant contribution. This small amount of positively charged molecules will attract several negative molecules, which will cover the total surface area of the C_3F_6 , thus rendering the resulting

agglomerate negative. The net result is a larger molecule with weak sorption capability, which will cause a decrease in the permeation rate.

During the modelling process, the thermodynamic factor for each gas at the different compositions was calculated. The relationship between the thermodynamic factor and the molar fraction of the gas present in the feed mixture is shown in Figure 5-30.

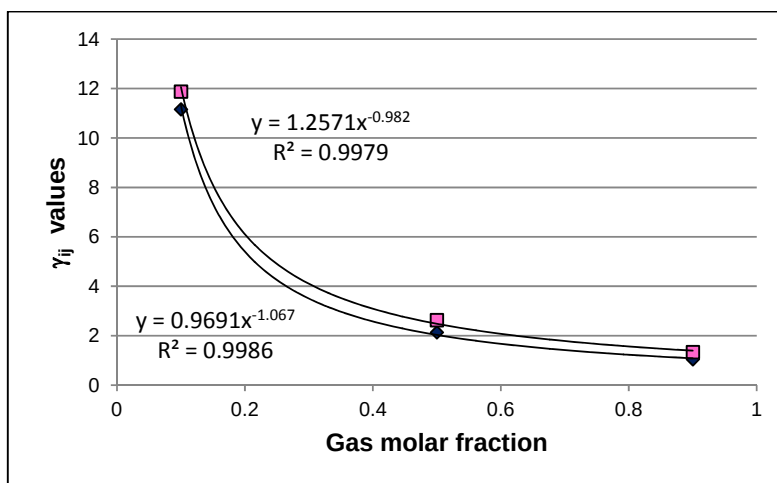


Figure 5-30: Thermodynamic factors (α) for N_2/C_3F_6 mixture using a PAN-supported membrane (♦ - N_2 , ■ - C_3F_6)

Figure 5-30 shows a very similar power law trend to that in Figure 5-27. Empirical power law curves were fitted to the data points, which yielded high R^2 values. The constant values of these curves correlate well with those found in Figure 5-27. The fitted thermodynamic factor (γ) values are portrayed in Table 5-8.

Table 5-8: Fitted γ values for a N_2/C_3F_6 binary mixture ($i = N_2$; $j = C_3F_6$)

Binary gas mixture (N_2/C_3F_6)	γ_{ij}	γ_{ji}
90/10	1.42 ± 0.01	17.10 ± 0.09
50/50	2.14 ± 0.04	2.63 ± 0.05
10/90	11.16 ± 0.34	1.14 ± 0.04

5.6.2.3 Modelling of N_2/CF_4 data

The results of fitting Equation 5.10 to the N_2/CF_4 total flux experimental data are shown in Figure 5-31.

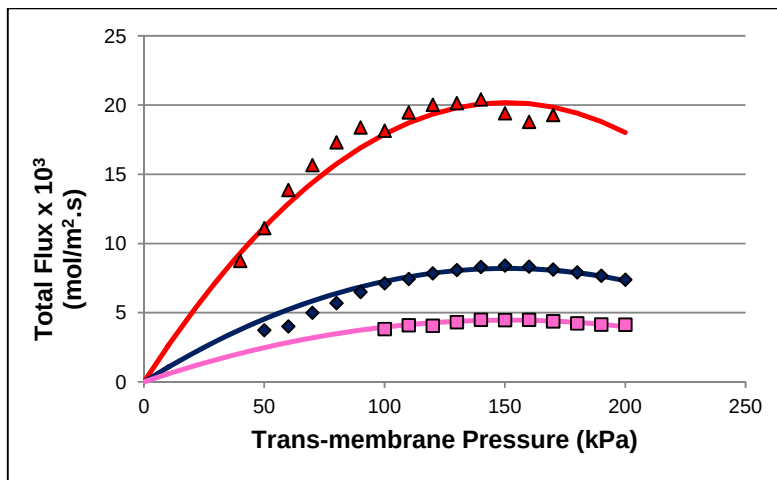


Figure 5-31: Modelling results for N_2/CF_4 flux through the PAN-supported Teflon® AF2400 membrane at different mixtures (♦ - 10/90, ■ - 50/50, ▲ - 90/10). The lines represent the models while the markers represent the actual experimental data

Figure 5-31 illustrates a good fit of the derived model to the experimental data points. The 95% confidence levels calculated for the fitting range between 0.71% and 1.62%, indicate an extremely good fit. Figure 5-31 further shows an increase in the flux of the mixture as the amount of the greater permeating gas increases. This is expected and similar results were found for the other gas mixtures investigated.

The binary diffusion coefficients calculated with Equation 5.9 are shown below in Figure 5-32.

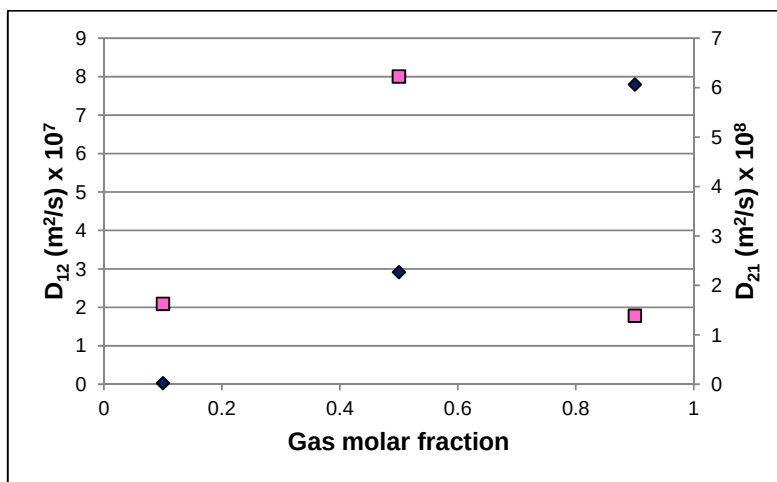


Figure 5-32: Diffusion coefficients for N_2/CF_4 mixture using a PAN-supported membrane (♦ - $D_{\text{N}_2/\text{CF}_4}$, ■ - $D_{\text{CF}_4/\text{N}_2}$)

Figure 5-32 depicts the coupling between N_2 and CF_4 due to the positively charged ring at the centre of the N_2 molecule (see Table 3-2), and the negatively charged CF_4 . The value of the coefficients for N_2 is lower than for a pure gas, or for when coupling occurred with C_3F_6 . This was expected since the influential gas, CF_4 , possesses a highly negative surface charge. Furthermore, it has the lowest permeation rate of all the gasses investigated.

The permeation rate of CF_4 is also lower than for its pure flux as well as in the C_3F_6 mixture. This serves as confirmation of the coupling that occurs due to the difference in the surface charge of the molecules with one another, and the molecules with the membrane.

An empirical relationship between the thermodynamic factor and the fraction of the gas present in the feed mixture to the membrane is given in Figure 5-33, while the fitted values of the thermodynamic factor are also represented.

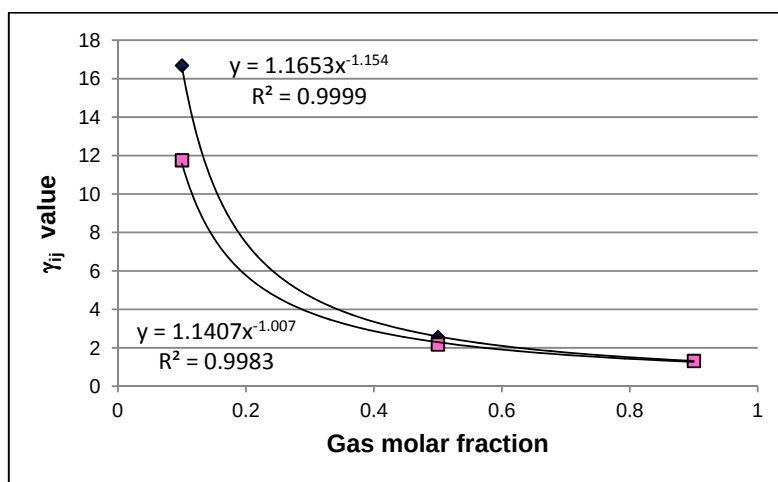


Figure 5-33: Thermodynamic factors (α) for N_2/CF_4 mixture using a PAN-supported membrane (♦ - N_2 , ■ - CF_4)

Figure 5-33 depicts an empirical power law relationship between the thermodynamic factor and the mole fraction of gas in the feed mixture. The constant values also fall within the same range as for Figure 5-27 and Figure 5-30.

Table 5-9: Fitted γ values for a N_2/CF_4 binary mixture ($i = N_2$; $j = CF_4$)

Binary gas mixture (N_2/CF_4)	γ_{ij}	γ_{ji}
90/10	1.33 ± 0.02	11.76 ± 0.19
50/50	2.56 ± 0.04	2.18 ± 0.03
10/90	16.69 ± 0.12	1.32 ± 0.01

5.6.3 PEI-supported membrane

Modelling was performed for all the partial gas fluxes as well as the total gas flux using the PEI-supported membrane. Only the total gas flux for each mixture will be reported in this

section, in like manner as that for the PAN-supported membrane. Details on the partial fluxes can be viewed in Appendix E.

5.6.3.1 Modelling of CF_4 / C_3F_6 data

The first mixture to be modelled for the PEI-supported membrane is the CF_4/C_3F_6 mixture. The results of the modelling are shown in Figure 5-34 below.

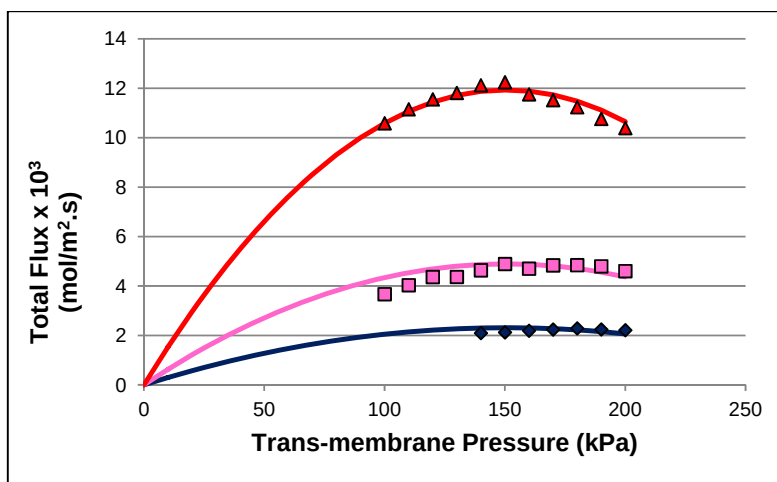


Figure 5-34: Modelling results for CF_4/C_3F_6 flux through the PEI-supported Teflon® AF2400 membrane at different mixtures (♦ - 90/10, ■ - 50/50, ▲ – 10/90). The lines represent the models while the markers represent the actual experimental data

Figure 5-34 shows that the model is a good fit for the different CF_4/C_3F_6 compositions. The 95% confidence intervals were calculated to be 2.85% for the 90/10 mixture, 2.50% for the 50/50 mixture and 0.70% for the 10/90 mixture. These low values fall in the same range as those achieved for the same gas composition, using the PAN-supported membrane.

Partial diffusion coefficients for the different gasses were calculated from Equation 5.9 and are shown below in Figure 5-35.

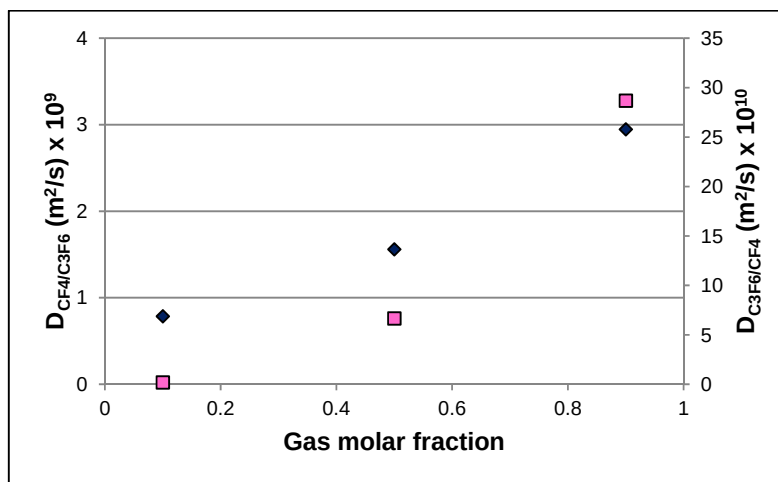


Figure 5-35: Diffusion coefficients for CF_4/C_3F_6 mixture using a PEI-supported membrane (♦ - D_{CF_4/C_3F_6} , ■ - $D_{C_3F_6/CF_4}$)

The first difference between the PAN- and PEI-supported membranes is observed in Figure 5-35. The graph reveals a continued increase in the diffusion coefficient for the slower permeating CF_4 . When looking at all the mixtures using the PAN-supported membrane, there was a constant tendency for the diffusion coefficient of the slowest permeating gas in the feed mixture to drop-off sharply when that gas was in abundance in the feed mixture. However, here, this is not the case. The only possible explanation that can be forwarded at this point is that the PEI layer is CF_4 selective. If this is true, the same trend will be seen later on for the N_2/CF_4 mixture as well.

In general, the diffusion coefficients for both gasses are smaller in the mixture than for the pure components. Both are also smaller for the same gas mixture using a PAN-supported membrane, thus strengthening the case of bias towards using a PAN-supported membrane in full-scale applications.

A graph of the thermodynamic factor versus the molar fraction of the gasses in the feed mixture is depicted below in Figure 5-36.

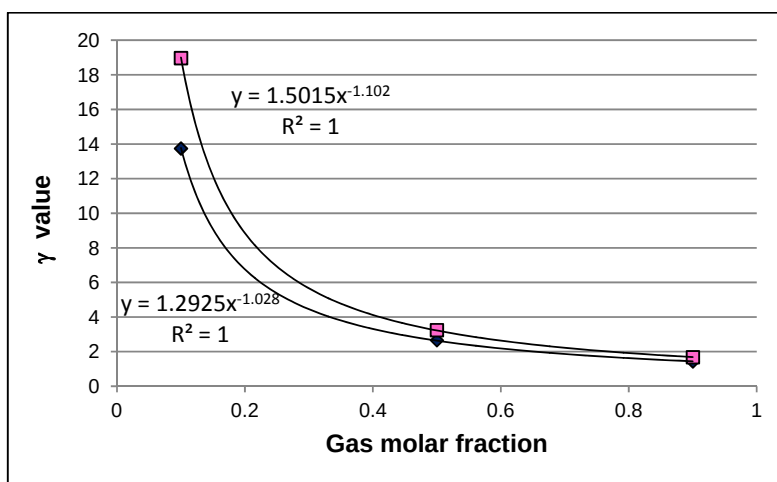


Figure 5-36: Thermodynamic factors (α) for $\text{CF}_4/\text{C}_3\text{F}_6$ mixture using a PEI-supported membrane (♦ - CF_4 , ■ - C_3F_6)

In a continuation from the PAN-supported membrane, Figure 5-36 shows that the thermodynamic factors for the PEI-supported membrane still follow a power law curve, yielding constant values that are comparable to the ones obtained for the PAN-supported membrane. The curves that were fitted to the data points had perfect R^2 values.

Table 5-10: Fitted γ values for a $\text{CF}_4/\text{C}_3\text{F}_6$ binary mixture ($i = \text{CF}_4$; $j = \text{C}_3\text{F}_6$)

Binary gas mixture ($\text{CF}_4/\text{C}_3\text{F}_6$)	γ_{ij}	γ_{ji}
90/10	1.43 ± 0.04	18.97 ± 0.54
50/50	2.65 ± 0.07	3.25 ± 0.08
10/90	13.74 ± 0.10	1.69 ± 0.0

5.6.3.2 Modelling of $\text{N}_2/\text{C}_3\text{F}_6$ data

Modelling of the $\text{N}_2/\text{C}_3\text{F}_6$ feed gas mixture was carried out across the entire composition range. The results of the modelling were very favourable as shown below in Figure 5-37. The calculated deviation between the model and the experimental values yielded 95%

confidence intervals of 0.52% for the 10/90 mixture, 1.28% for the 50/50 mixture and 3.23% for the 10/90 mixture.

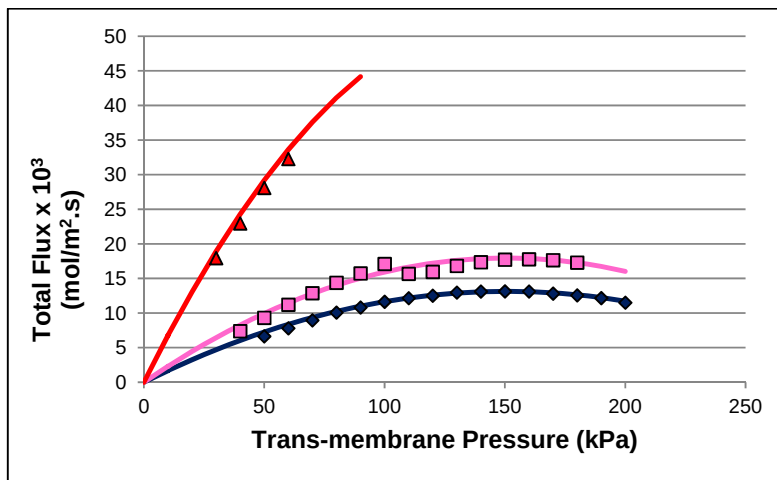


Figure 5-37: Modelling results for N_2/C_3F_6 flux through the PEI-supported Teflon® AF2400 membrane at different mixtures (♦ - 90/10, ■ - 50/50, ▲ - 10/90). The lines represent the models while the markers represent the actual experimental data

The corresponding diffusion coefficients for N_2 and C_3F_6 are given below in Figure 5-38.

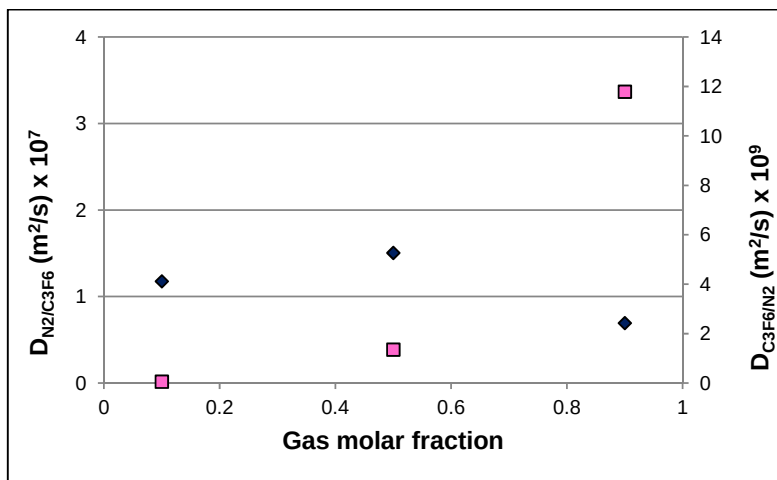


Figure 5-38: Diffusion coefficients for N_2/C_3F_6 mixture using a PAN-supported membrane (♦ - D_{N_2/C_3F_6} , ■ - $D_{C_3F_6/N_2}$)

Figure 5-38 follows the same trend as all the diffusion coefficient graphs for the PAN-supported membrane depicted in Figure 5-29. Since no CF_4 was present in the feed mixture, the PEI layer did not display any bias toward any one of the gasses, allowing normal coupling to exist between the gasses. The values of the diffusion coefficients are smaller than for the pure gas permeations as well as for the same mixtures separated by the PAN-supported membrane. This confirms the slower permeation rates experienced by the PEI-supported membrane, making it possible to, already, discard the use of the PEI-supported membrane during industrial separation.

Figure 5-39 below displays the thermodynamic factor of each composition in the gas mixture.

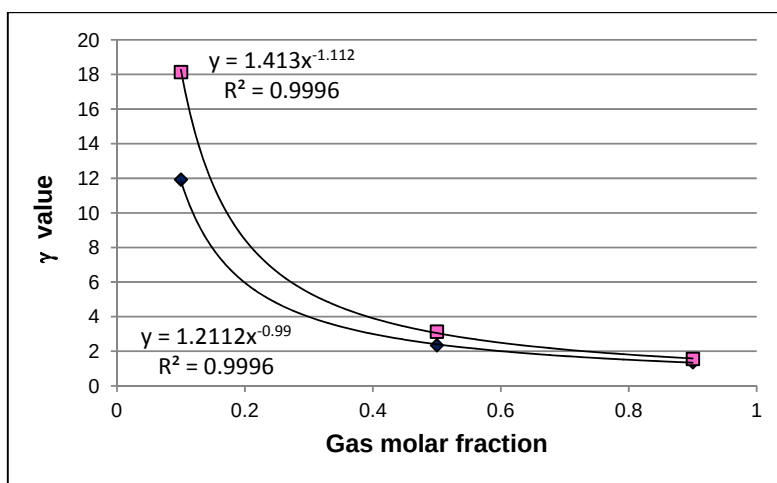


Figure 5-39: Thermodynamic factors (α) for $\text{N}_2/\text{C}_3\text{F}_6$ mixture using a PEI-supported membrane (♦ - N_2 , ■ - C_3F_6)

Figure 5-39 continues to show the existence of an empirical power law relation between the thermodynamic factor (γ) and the molar fraction of the gas in the feed mixture. The constant values for the different equations remain between 1.2 and 1.5, for the pre-variable constant, and between -0.9 and -1.2 for the exponent.

Table 5-11: Fitted γ values for a N_2/C_3F_6 binary mixture ($i = N_2$; $j = C_3F_6$)

Binary gas mixture (N_2/C_3F_6)	γ_{ij}	γ_{ji}
90/10	1.37 ± 0.01	18.14 ± 0.09
50/50	2.35 ± 0.03	3.14 ± 0.04
10/90	11.92 ± 0.38	1.56 ± 0.05

5.6.3.3 Modelling of N_2 / CF_4 data

The last of the feed mixtures, namely a N_2/CF_4 mixture, was modelled using Equation 5.10. These results are shown below in Figure 5-40

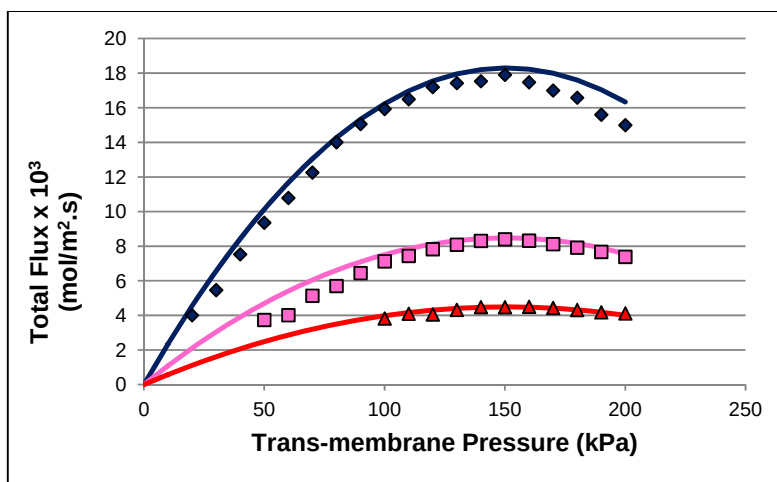


Figure 5-40: Modelling results for N_2/CF_4 flux through the PEI-supported Teflon® AF2400 membrane at different mixtures (♦ - 90/10, ■ - 50/50, ▲ - 10/90). The lines represent the models while the markers represent the actual experimental data

Figure 5-40 is the last flux curve used as an indication of the validity of the model described by Equation 5.10. It reveals a good comparison between the model and the experimental values. This visual comparison is backed up by low 95% confidence intervals calculated between the model and the data. These values are 1.67% for the 90/10 mixture, 2.27% for the 50/50 mixture and a low 0.66% for the 10/90 mixture.

Figure 5-41 portrays the diffusion coefficients as a function of feed gas molar fraction. Since this mixture contains CF_4 , Figure 5-41 can be used to strengthen the hypothesis that the PEI layer is CF_4 selective and contributes towards its diffusion coefficient.

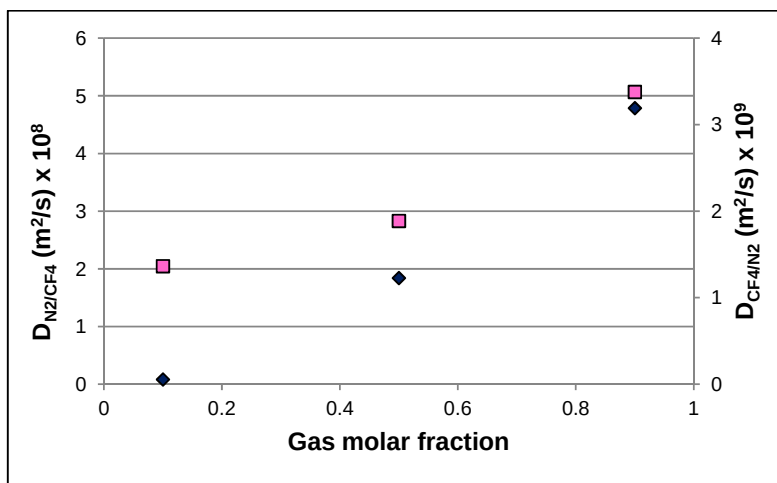


Figure 5-41: Diffusion coefficients for N_2/CF_4 mixture using a PAN-supported membrane (♦ - $D_{\text{N}_2/\text{CF}_4}$, ■ - $D_{\text{CF}_4/\text{N}_2}$)

Figure 5-41 does indeed reveal the same trends as Figure 5-35 did. It differs from all the other binary diffusion coefficient curves in that the coefficients of the slower gas do not drop-off at a high molar fraction of the slower permeating gas, CF_4 . Instead, there is an exponential growth in the coefficient as the molar fraction of this gas increases from low to high values. This phenomenon was observed only for the CF_4 gas, using the PEI-supported membrane. It led to the initial conclusion, which can now be verified, that the PEI layer is selective towards CF_4 . This, together with coupling influences experienced by a faster permeating gas, causes the diffusion coefficient of this gas to increase when this gas is in excess in the feed mixture. The values of the coefficients for both gasses are again smaller than those for the pure components as well as for the mixture using the PAN-supported membrane.

The influence of the molar fraction on the thermodynamic factor was calculated and is shown below in Figure 5-42.

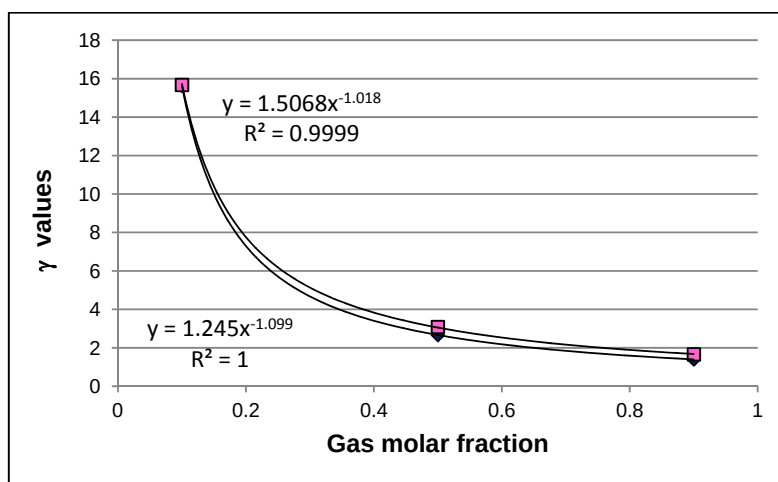


Figure 5-42: Thermodynamic factors (α) for N_2/CF_4 mixture using a PEI-supported membrane (♦ - N_2 , ■ - CF_4)

The above figure continues with the same power law relationship that was shown by the previous five thermodynamic factor graphs. It can therefore be concluded that this is a valid model to use in describing the permeation of the gases through the different membranes when a binary gas mixture is fed to the membrane. The curves fitted to the data points show R^2 values of 1 and 0.9999 respectively, which validates this relationship. The constant values of the curve equations again fall within the same order of magnitude as the previous ones.

Table 5-12: Fitted γ values for a N_2/CF_4 binary mixture ($i = N_2$; $j = CF_4$)

Binary gas mixture (N_2/CF_4)	γ_{ij}	γ_{ji}
90/10	1.40 ± 0.02	15.67 ± 0.26
50/50	2.66 ± 0.06	3.09 ± 0.07
10/90	15.63 ± 0.10	1.66 ± 0.01

5.7 Concluding remarks

Binary mixtures of $\text{CF}_4/\text{C}_3\text{F}_6$, $\text{N}_2/\text{C}_3\text{F}_6$ and N_2/CF_4 were fed to both the PAN- and PEI supported membranes. A great deal of coupling between the gasses was observed, which in general decreased the actual permeation rate of the different gasses. The reason for the coupling was mainly due to the difference in surface charge between the molecules. The more positively charged C_3F_6 molecule experienced the greatest coupling effect when the other two gasses were abundant in the mixture. At these mixtures, the surface of the C_3F_6 molecule was completely altered into a negative charge due to the attachment of the negatively charged N_2 and CF_4 to it. This alteration in the surface charge was detrimental to the sorption of the agglomerate molecule onto the also negatively charged membrane surface. After sorption had occurred, diffusion of the gas decreased as well because of the size of the agglomerate molecules.

During the modelling of the different processes, it was decided to make use of a modified solution-diffusion model due to its simplicity in relation to the more recognised Maxwell-Stefan models. This modified solution-diffusion model can be used to predict the partial flux of the different gasses in the feed mixture whereafter the total flux could be calculated by adding the different partial fluxes. This model consists of an adjusted solubility term that takes the effect of coupling between the two different gasses into account. The partial diffusion coefficients were modelled around the Vignes idea, which entails the use of a thermodynamic factor. This model was shown to be a very good fit to the experimental data with confidence levels ranging between 0.5% and 3.4%. Lastly, it was found that a power law relationship exists between the thermodynamic factor and the molar fraction of a gas in the feed mixture. Curves fitted to this relationship yielded constant values that were comparable across all six data sets.

In conclusion, it was proven that the PAN-supported membrane allowed for much higher permeation rates than the PEI-supported membrane did. Selectivities between the different gasses, apart from one instance, were very similar, irrespective of the different membranes used. This leads to the recommendation to use the PAN-supported membrane for industrial application purposes.

5.8 References

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CHAPTER 6: TERNARY GAS PERMEATION

*A fact is a simple statement that everyone believes.
It is innocent until found guilty.
A hypothesis is a novel suggestion that no one wants to believe.
It is guilty, until found effective.
- Edward Teller*

6.1 Introduction

Both Chapters 4 and 5 showed a preference towards the PAN-supported membrane in terms of flux. The selectivity for both membranes were comparable, which led to the conclusion at the end of Chapter 5 that the PAN-supported membrane is the best suited for large-scale industrial application. Therefore, it was decided to use only the PAN-supported membrane to investigate the flux behaviour of ternary gas mixtures. The same experimental setup was used as for the binary mixtures. The retentate stream was analysed with a gas chromatograph whereafter a simple mass balance was used to calculate the composition of the permeate stream.

6.2 Results and discussion for N_2 / CF_4 / C_3F_6 feed

Four different gas mixtures were made up, using mass flow controllers, and fed to the PAN-supported membrane. The mixtures consisted of 80 mole% N_2 / 10 mole% CF_4 / 10 mole% C_3F_6 , a 10/80/10 mixture of the same order for the gasses, a 10/10/80 mixture and finally an equimolar mixture for the three gasses. The feed pressure of the feed mixtures was held constant at 200kPa, while the trans-membrane pressure was varied between the minimum and maximum obtainable for the system. The sets of results obtained for each mixture will be discussed in the sections below.

6.2.1 80 / 10 / 10 mixture

The partial and total fluxes obtained for the 80/10/10 ternary gas mixture are depicted in Figure 6-1 below.

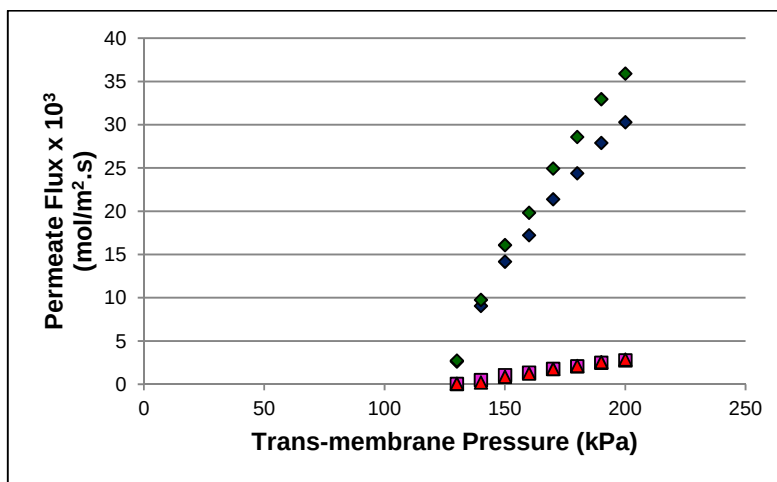


Figure 6-1: Ternary gas permeation results for 80 mole% N₂ / 10 mole% CF₄ / 10 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ▲ - C₃F₆ flux, ◆ - Total flux)

In Figure 6-1, the zero point of the x-axis lies close to 125kPa instead of the origin. In explaining the shift in the zero point, it is important to look at the concept of breakthrough pressure. In a ternary mixture of N₂, CF₄ and C₃F₆, there is much interaction between the gasses owing to the difference of the surface charges of the molecules. A gas mixture containing predominantly N₂ will result in a mixture that has a resultant charge that is slightly negative. The array of N₂ molecules will form an extra resistance layer, which covers the surface of the membrane. The charge of the remainder of the mixture is close to neutral since CF₄ is highly negative and C₃F₆ is highly positive. This will result in an additional pressure needed to force the mixture to the surface of the membrane before sorption and diffusion can take place. This additional pressure is termed a breakthrough pressure.

Figure 6-1 indicates that the total and partial fluxes increase linearly as the trans-membrane pressure is increased beyond 125kPa. When looking at the partial flux values of each gas, it is evident that N₂ (abundant in the feed mixture) dominates the permeation and contributes the most towards the total gas flux. The flux value for N₂ is only slightly lower than its pure component flux. It means that N₂ experienced very little influences from the other gasses. This is expected since the surface charge of the other two molecules is highly negative and positive, respectively. It will cause these molecules to, firstly, interact with one another before interaction with N₂ occurs. The values of CF₄ are also very similar to its pure component flux values. This is due to the coupling interaction of both the C₃F₆ and, to a

lesser extent, the N_2 on this molecule. The same coupling between CF_4 and C_3F_6 can be forwarded as the reason for the drastic reduction in C_3F_6 flux.

6.2.1.1 Selectivity

The selectivity between the different gases are summarised in Figure 6-2 and Table 6-1 below.

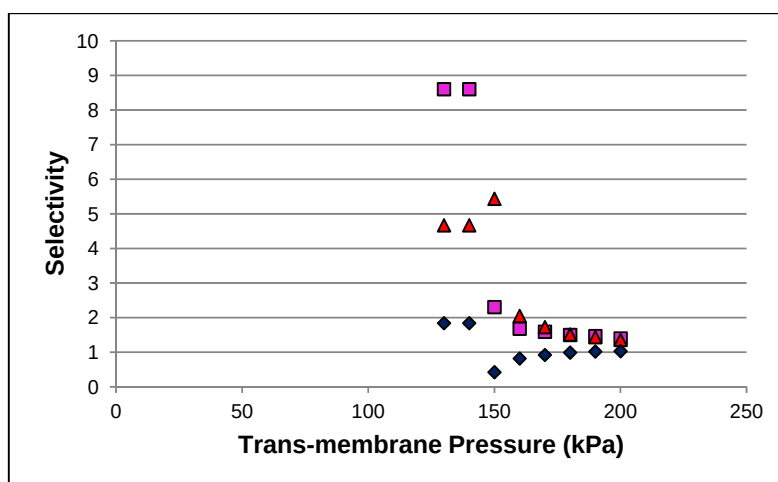


Figure 6-2: Selectivity results for 80 mole% N_2 / 10 mole% CF_4 / 10 mole% C_3F_6 using the PAN-supported membrane (♦ - C_3F_6/CF_4 selectivity, ■ - N_2/CF_4 flux, ▲ - N_2/C_3F_6 flux)

Table 6-1: Maximum selectivity values for an 80/10/10 mixture

Selectivity	Maximum Value	Trans-membrane Pressure (kPa)
N_2/CF_4	8.60	130 / 140
N_2/C_3F_6	5.44	150
C_3F_6/CF_4	1.84	130 / 140

Very good selectivities were obtained for each of the different gas combinations. It is clear that the abundant gas in the mixture (N_2) is favoured above both of the other two gasses. The highest selectivities were obtained at relatively low trans-membrane pressures. At this point, high breakthrough pressures are needed to force the C_3F_6 and CF_4 onto the membrane

surface. When the breakthrough pressures are exceeded, all gas molecules are forced through the membrane at a similar rate and hence little separation takes place from this point on.

6.2.2 10 / 80 / 10 mixture

The partial and total fluxes obtained for the 10/80/10 ternary gas mixture is shown in Figure 6-3 below.

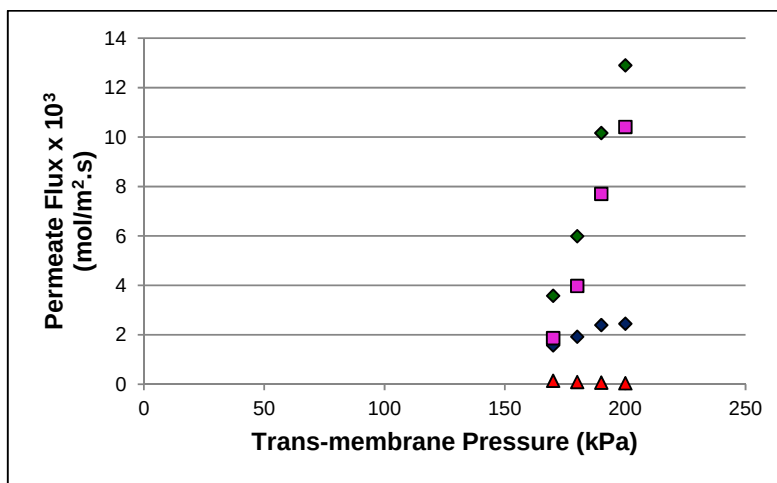


Figure 6-3: Ternary gas permeation results for 10 mole% N₂ / 80 mole% CF₄ / 10 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ▲ - C₃F₆ flux, ◆ - Total flux)

In Figure 6-3 it is evident that the initial breakthrough pressure required before a flux is observed is higher than for the 80/10/10 mixture, that is, 155kPa compared to 125kPa. This higher breakthrough pressure coincides with a feed mixture that is abundant in the highly negative molecule, namely CF₄. The combination of the highly negatively charged mixture and negative surface of the membrane increases the flow resistance defined in Section 6.2.1. A higher flow resistance will lead to an increase in the breakthrough pressure needed to ensure the flow of gas through the membrane.

It is clearly evident in Figure 6-3 that CF₄ contributes the most towards the total gas permeation when comparing the partial fluxes of the gasses. Figure 6-3 further indicates that the degree of coupling experienced by the C₃F₆ molecule is detrimental to its permeation. When a positively charged molecule is surrounded by a sea of negatively charged molecules, these negative molecules will attach to the positive ones, resulting in an agglomerate

molecule that has a net negative charge. A switch in the C_3F_6 surface charge from positive to negative contributes towards the low C_3F_6 partial flux observed in Figure 6-3.

6.2.2.1 Selectivity

The selectivity values calculated for the 10/80/10 mixture are shown below in Figure 6-4 and Table 6-2.

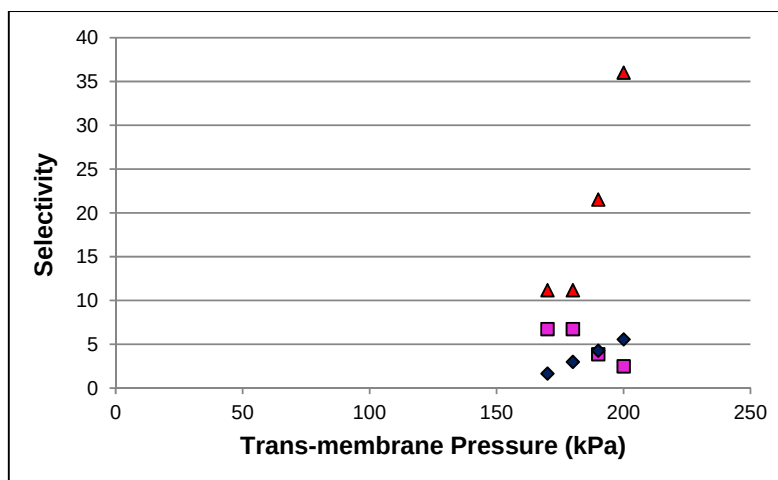


Figure 6-4: Selectivity results for 10 mole% N_2 / 80 mole% CF_4 / 10 mole% C_3F_6 using the PAN-supported membrane (♦ - CF_4/C_3F_6 selectivity, ■ - N_2/CF_4 flux, ▲ - N_2/C_3F_6 flux)

Table 6-2: Maximum selectivity values for a 10/80/10 mixture

Selectivity	Maximum Value	Trans-membrane Pressure (kPa)
N_2/CF_4	6.74	170
N_2/C_3F_6	36.02	200
CF_4/C_3F_6	5.57	200

Figure 6-3 showed that there is a steady increase in the flux of both CF_4 and N_2 , while the C_3F_6 flux showed little increase with an increase in the trans-membrane pressure. Therefore it came as no surprise when both Figure 6-4 and

Table 6-2 indicated that the system was selective towards N_2 , followed by CF_4 and lastly C_3F_6 . For both N_2 and CF_4 , their selectivity towards C_3F_6 was on the increase at a maximum trans-membrane pressure of 200kPa. This resulted in a selectivity of 36.02 for N_2 over C_3F_6 and 5.57 for CF_4 over C_3F_6 . The significance of such high selectivities is an ease in eliminating C_3F_6 from a mixture dominated by CF_4 , hence upgrading the gas mixture towards N_2 and CF_4 .

6.2.3 10 / 10 / 80 mixture

Figure 6-5 below shows the partial and total fluxes obtained for a feed mixture containing 80 mole% C_3F_6 and equimolar amounts of N_2 and CF_4 . Again, linear increase in partial and total fluxes is observed for an increase in trans-membrane pressure. The initial breakthrough pressure required for permeation was 90kPa. C_3F_6 , abundant in this feed mixture, has a highly positive charge and is the quickest permeating gas. The result is that the negatively charged N_2 and CF_4 are attracted by the C_3F_6 , which in turn is attracted to the membrane surface. This mutual attraction on both sides reduces the breakthrough pressure needed for the permeation of the ternary mixture since it is not required to force molecules through a membrane with a similar charge.

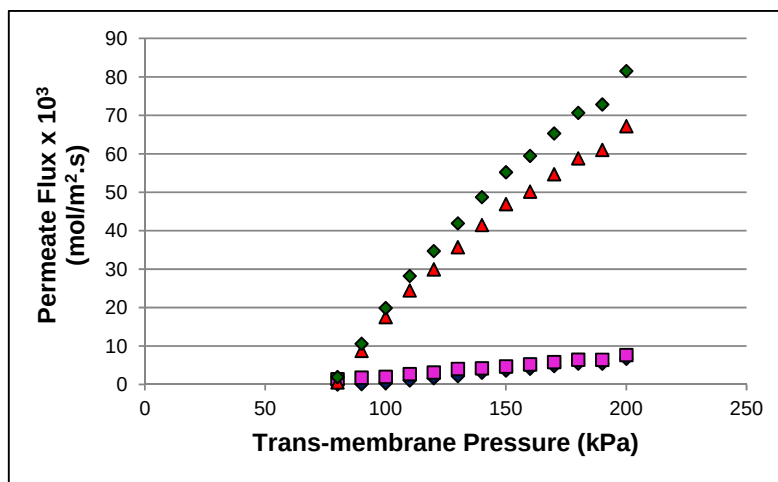


Figure 6-5: Ternary gas permeation results for 10 mole% N_2 / 10 mole% CF_4 / 80 mole% C_3F_6 using the PAN-supported membrane (♦ - N_2 flux, ■ - CF_4 flux, ▲ - C_3F_6 flux, ◆ - Total flux)

Figure 6-5 confirms that the abundant gas in the feed mixture will contribute the most towards the total gas flux. This is especially true at lower trans-membrane pressure for this

system. At higher pressure differentials the contribution of the lesser gasses clearly increases owing to coupling of these gasses to the C_3F_6 . This will influence the selectivity of N_2 and CF_4 towards that of C_3F_6 .

6.2.3.1 Selectivity

The selectivity results for this system are shown in Figure 6-6 and Table 6-3. Extremely high selectivity values are obtained, especially for CF_4 over N_2 . By studying the flux curve in Figure 6-5, the high selectivity between CF_4 and N_2 is not visible due to congestion of the data points and the size of the interval on the y-axis. Closer inspection reveals a clear preference for CF_4 over N_2 at low trans-membrane pressures. This was expected since the highly negatively charged CF_4 will attach itself much more easily to the positively charged C_3F_6 molecule, and hence permeate the membrane at a much higher initial rate than N_2 will. This coupling effect will cause CF_4 to be highly selective over N_2 at lower trans-membrane pressures. This selectivity will typically occur at a lower trans-membrane pressure where the driving forces acting on the molecules are less. At higher trans-membrane pressures, more drop-off will occur due to collisions between the molecules, resulting in less CF_4 permeation at a high rate. In addition to drop-off effects, it can be expected that the different gasses have now overcome the effect of the breakthrough pressure, resulting in similar permeation rates.

The end result will be a stabilised regime in terms of the selectivity of CF_4 and N_2 . This explanation is verified by the low selectivity between CF_4 and C_3F_6 , which entails that C_3F_6 acts as a carrier of CF_4 . It further explains the large selectivity between C_3F_6 and N_2 . As was the case with the previous mixtures, the membrane will be selective towards the gas that is in abundance in the feed mixture.

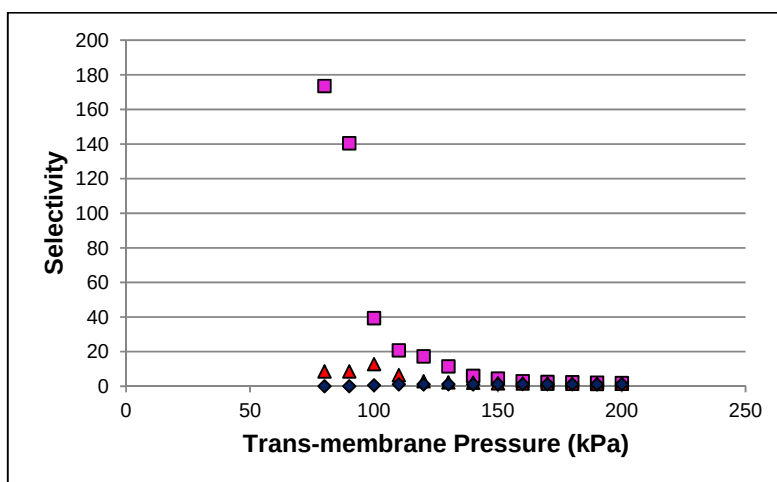


Figure 6-6: Selectivity results for 10 mole% N₂ / 10 mole% CF₄ / 80 mole% C₃F₆ using the PAN-supported membrane (♦ - C₃F₆/CF₄ selectivity, ■ - CF₄/N₂ flux, ▲ - C₃F₆/N₂ flux)

Table 6-3: Maximum selectivity values for a 10/10/80 mixture

Selectivity	Maximum Value	Trans-membrane Pressure (kPa)
CF ₄ /N ₂	173.57	80
C ₃ F ₆ /N ₂	12.83	100
C ₃ F ₆ /CF ₄	1.25	160

6.2.4 Equimolar mixture

The final ternary mixture to be tested was an equimolar mixture of the three gasses. Such a mixture should give some insight into the true preference of the membrane in the presence of several coupling effects experienced by the different gas molecules. The results of the partial and total flux data obtained for an equimolar mixture of N₂, CF₄ and C₃F₆ are depicted in Figure 6-7 below.

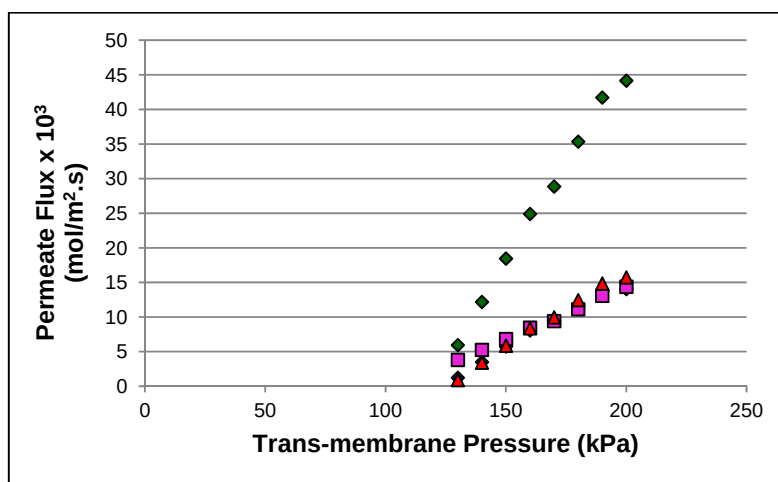


Figure 6-7: Ternary gas permeation results for an equimolar mixture of N₂, CF₄ and C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ▲ - C₃F₆ flux, ◆ - Total flux)

Figure 6-7 shows that an equimolar gas feed mixture resulted in identical partial fluxes for the different gasses. It reveals almost equal contributions towards the total gas flux as well as very similar permeabilities (derived from the slopes of the flux curves).

The initial breakthrough feed pressure required for permeation correlates well with the ternary mixture where N₂ was the abundant gas. In an equimolar mixture, the highly positively charged C₃F₆ and highly negatively charged CF₄ will cancel out in terms of the surface charge. This will leave a feed gas mixture with a similar charge as N₂. It is therefore expected to behave similarly in terms of breakthrough pressure to a ternary mixture containing an abundance of N₂. This was found to be the case when Figure 6-7 is compared with Figure 6-1.

Figure 6-7 reveals that CF₄ benefitted the most from the coupling effects with C₃F₆. On the other hand, the partial flux for N₂ is slightly lower than the pure component values while the C₃F₆ partial flux is significantly lower than the pure component fluxes.

6.2.4.1 Selectivity

The selectivity results are summarised in Figure 6-8 and Table 6-4.

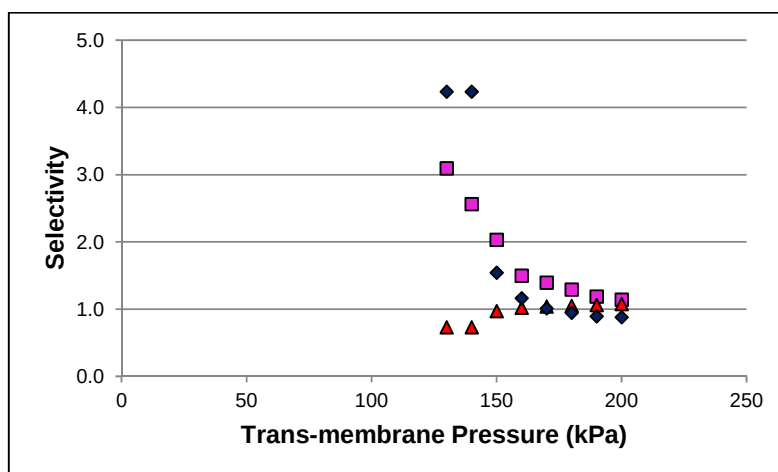


Figure 6-8: Selectivity results for an equimolar mixture of N_2 , CF_4 and C_3F_6 using the PAN-supported membrane (♦ - C_3F_6/CF_4 selectivity, ■ - CF_4/N_2 flux, ▲ - C_3F_6/N_2 flux)

Table 6-4: Maximum selectivity values for an equimolar mixture

Selectivity	Maximum Value	Trans-membrane Pressure (kPa)
CF_4/N_2	3.09	130
C_3F_6/N_2	1.08	200
C_3F_6/CF_4	4.23	130/140

Figure 6-8 is indicative of a system where there is much interaction between the different gasses that make up the feed mixture. The membrane is clearly selective towards C_3F_6 over CF_4 ; likewise for CF_4 over N_2 , where a maximum selectivity of 3.09 was measured. The results indicate a transition from an N_2 selective system at low trans-membrane pressures, to a C_3F_6 selective one at higher pressures. A maximum selectivity of 1.08 was measure for C_3F_6 over N_2 .

6.3 Modelling the ternary gas permeation

The first consideration in modelling the ternary system is the shift in the zero point of the flux curves. The normal solution-diffusion model does not allow for this shift, which, as

explained above, is reminiscent of an osmotic pressure shift during nano-filtration. Incorporating a breakthrough pressure constant (Π) term into the model used for binary modelling will result in Equation 6.1.

$$J_{ijk} = \left[\frac{\left(\frac{q_{max}K_i}{1+K_i p_i + K_j p_j + K_k p_k} \right) \cdot (D_i^{y_i} \gamma_{ijk})}{z} \right] p_p (p_f - p_p + \Pi) \quad 6.1$$

The modelling results using Equation 6.1 while modelling for Π (the breakthrough pressure constant) an γ_{ijk} (the thermodynamic factor) are illustrated below in Figure 6-9.

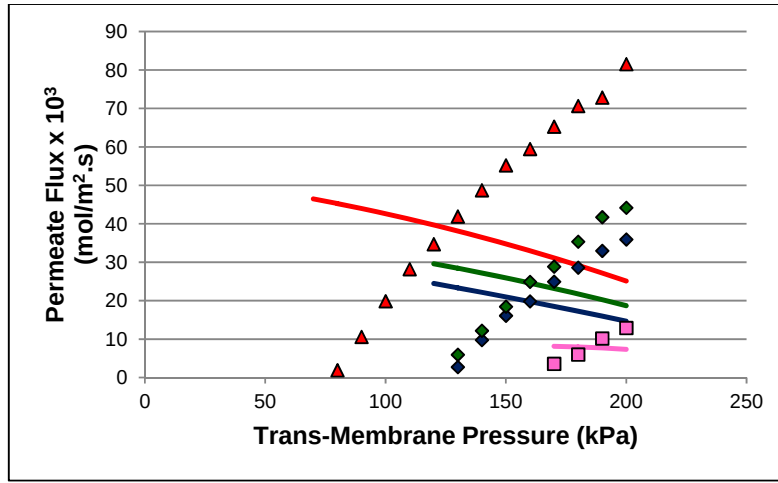


Figure 6-9: Modelling results for a ternary system using the PAN-supported membrane (♦ - 80/10/10 mixture, ■ - 10/80/10 mixture, ▲ - 10/10/80 mixture, ◆ - Equimolar mixture). The data points represent experimental data while the solid lines are the fitted models in Equation 6.1

As evident in Figure 6-9, Equation 6.1 does not show a good fit with the data. Adding a breakthrough pressure constant only caused the model to move down in relation to the y-axis. This brings forth that the flattened part of the curve intersects the data points and hence reveals the poor relationship in Figure 6-9. This is an indication that an interaction, like convective diffusion, exists between the gasses. Adding a convective flux term to the model will modify it to result in Equation 6.2.

$$J_{ijk} = \left[\frac{\left(\frac{q_{max}K_i}{1+K_i p_i + K_j p_j + K_k p_k} \right) \cdot (D_i^{y_i} \gamma_{ijk})}{z} \right] p_p (p_f - p_p + \Pi) + J_c \quad 6.2$$

By using this model, it was possible to accurately describe the partial fluxes obtained for each gas while being part of different feed mixtures. This was achieved by using the preset pressure values, along with the predetermined pure sorption and diffusion coefficients as set values in the model and using the least squares method to determine the breakthrough pressure constant (Π), the thermodynamic factor (γ_{ijk}) and the convective diffusion flux term (J_c). The total flux for each feed mixture was obtained by adding the different partial fluxes. This is shown below in Figure 6-10. Information on the partial fluxes can be found in Appendix E.

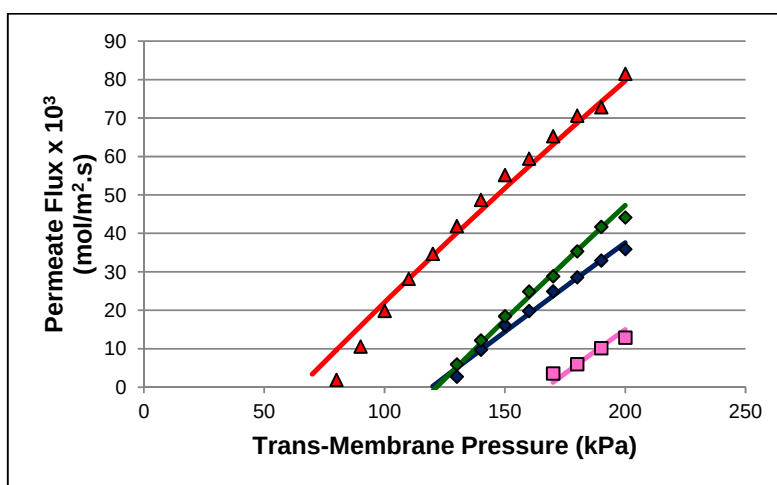


Figure 6-10: Modelling results for a ternary system using the PAN-supported membrane (♦ - 80/10/10 mixture, ■ - 10/80/10 mixture, ▲ - 10/10/80 mixture, ◆ - Equimolar mixture). The data points represent experimental data while the solid lines are the fitted models

Figure 6-10 shows a very good fit of the model with the experimental data for each of gas mixtures investigated. The 95% confidence limit calculated between the modelled values and the experimental ones was 0.00096 across all gas mixtures. The ternary diffusion coefficients for each gas are displayed in Table 6-5 below.

Table 6-5: Modelled diffusion coefficients for a ternary feed mixture ($i = \text{N}_2$; $j = \text{CF}_4$; $k = \text{C}_3\text{F}_6$)

$\text{N}_2/\text{CF}_4/\text{C}_3\text{F}_6$ mixtures	$D_{ijk} \times 10^8 \text{ (m}^2\text{.s}^{-1}\text{)}$	$D_{jik} \times 10^8 \text{ (m}^2\text{.s}^{-1}\text{)}$	$D_{kij} \times 10^8 \text{ (m}^2\text{.s}^{-1}\text{)}$
80/10/10	6.41 ± 0.33	0.02 ± 0.003	0.001 ± 0.0002
10/80/10	5.34 ± 0.91	3.51 ± 0.13	0.002 ± 0.001
10/10/80	0.70 ± 0.08	5.19 ± 0.13	0.56 ± 0.005
Equimolar	6.55 ± 0.79	5.00 ± 0.90	0.40 ± 0.09

Table 6-5 lists the diffusion coefficients for each gas in the different ternary feed mixtures. The first noticeable phenomenon is the extremely low diffusion coefficient values for C_3F_6 . It serves as verification for the low partial flux values observed in each of the flux curves for this gas. As mentioned above, this is due to the coupling effects, where the positive C_3F_6 is constantly pulled towards any one of the two negatively charged gasses (N_2 and CF_4) or the negative membrane surface. This results in a constant interaction between the gasses and the membrane, and hence a decline in the flux of C_3F_6 .

The same coupling effects are credited for the increase in the diffusion coefficient values for N_2 and CF_4 . CF_4 is a highly negative molecule, which attaches itself instantly to the C_3F_6 , which is positive. The CF_4 is subsequently dragged through the membrane by the fast permeating C_3F_6 . The same applies to N_2 , but to a lesser degree because of more closely resembling a neutral molecule.

6.4 Concluding remarks

Ternary gas mixtures were separated by the PAN-supported membrane in order to determine the separation characteristics of this membrane when exposed to a ternary gas mixture. It was demonstrated that the system follows the solution-diffusion mechanism, apart from an additional breakthrough pressure that is required for permeation and convective diffusion within the gas mixture. When including these two terms in the previously derived binary gas

model, it was possible to accurately model the fluxes of the different ternary mixtures. The tabulated ternary diffusion coefficients confirmed a large degree of coupling between the different gasses, especially between the highly negative and positively charged CF_4 and C_3F_6 .

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

*Science without religion is lame,
religion without science is blind.
- Albert Einstein*

7.1 Conclusions

Several conclusions can be drawn from this thesis. To facilitate the understanding of the applicability of the different conclusions, it will be divided according to the chapter from which the conclusions were drawn.

7.1.1 Chapter 3: Experimental setup and plan

- A study of several different membrane gas separation setups led to the conclusion that all of these were basically similar. Each of the setups possessed the following components:
 - o Gas storage cylinders with pressure regulators.
 - o Flow controllers.
 - o A membrane module inserted in a temperature controlled environment like a water bath or an oven.
 - o Downstream pressure regulators in the form of reservoir tanks or back pressure regulators.
 - o Flow measurement devices such as rota meters or soap flow meters.
 - o Gas analysis devices, usually a gas chromatograph (GC).
- The membranes have extremely low sorption capabilities. When the sorption tests were conducted, using the PAN- and PEI-supported membranes, very little to no sorption was measured using a standard TGA and pressures not greater than 2bar. This led to a shift in the approach to use PTFE powder to measure the C₃F₆ sorption, while N₂ and CF₄ sorption data were gathered from published papers at high bars.

- The vapour pressure of $c\text{-C}_4\text{F}_8$ was too low to use in a membrane system that has a feed pressure of 2bar or higher. At these elevated pressures, the gas would condense to form a liquid.

7.1.2 Chapter 4: Single gas permeation tests

- In single gas permeation tests, Teflon® shows a much higher selectivity towards C_3F_6 than in the case of N_2 and CF_4 .
- The preference of the membrane, which has a negatively charged surface, reflects the rule of physics that states that opposite charges will attract one another. It was validated by proving that the flux rate of the different gasses declined in the same order as the degree of positivity of the surface charge of each molecule.
- Secondary separation in the PAN and PEI layer was observed when using these membranes. This led to a situation where the highest flux and best selectivity were achieved in a membrane with the thickest active layer.
- The pressure on the permeate side plays an active role in describing the system. This was proven during the modelling of the gasses using a modified solution-diffusion model, which renders the use of permeate side pressure part of the model.
- According to the Robesson-plot, both membranes exhibit the ability to be used in industrial applications when pure gasses are fed into the system.

7.1.3 Chapter 5: Binary gas permeation

- It was concluded that a great deal of coupling occurs between the gas molecules in a binary feed mixture. The degree of coupling is enhanced when the molecules have strong surface charges that differ among them. The coupling, in general, was detrimental to the permeation of the different gasses and reduced the selectivity between them. Selectivities of just over one were achieved, which placed a serious question on the applicability of the membranes for use in industrial scale separation.
- Binary diffusion coefficients can be calculated with a modified Vignes equation, using a thermodynamic factor. This factor was shown to behave according to a the power law. By adding it to the solution-diffusion equation used in Chapter 4, it is possible to accurately predict the partial fluxes, and hence the total flux of the system.

7.1.4 Chapter 6: Ternary gas permeation

- From the ternary data, it can be concluded that the gas that is abundant in the feed mixture will contribute the most towards the total gas flux. The coupling effects exerted onto the other gasses decreases their permeability and cause the membrane to be selective towards the abundant gas. For an equimolar feed mixture, the coupling between the gasses was such that, partially, each contributed similarly towards the final product.
- During the modelling of the system, it was concluded that the presence of a pressure, similar to osmotic pressure, and the convective diffusion of the gasses between one another, exists. This called for the introduction of an osmotic pressure constant and a convective flux to the already modified solution-diffusion equation used in Chapter 5. This model was able to accurately describe both the partial and total flux of the system.

7.1.5 Evaluation

- When comparing the permeation and selectivity of the different feed compositions, it can be concluded that the interaction between the gasses, and the gas-membrane interface causes a decrease in the permeability of the different gasses, which in turn influence the selectivity of the gasses.

7.2 Recommendations

Stemming from this study, the following recommendations can be made. These are divided into research and industry applicable recommendations.

7.2.1 Research recommendations

- One of the main conclusions of this thesis is that the role of surface charge among the gas molecules and the membrane surface cannot be neglected. As a matter of fact, it was shown to play an extremely important role in determining the preference of the membrane. This theory needs to be tested by creating several membranes with different surface charges, and exposing it to an array of different gasses. These tests indicate that it would be possible to postulate a new theory regarding the influence of charges in membrane separation.

- When working with a binary or ternary gas mixture, the experimental setup should be altered to a point where it is possible for both the permeate and retentate streams to be connected to a bubble flow meter. This would aid in measuring the flow rate at both sides of the membrane. In addition to this, the GC setup should be such that both streams have the ability to bleed off from the feed to be injected into the column of the GC. Such a system would eliminate the use of mass balances to determine the composition and flow rate of any of the exit streams.

7.2.2 Industry applicable recommendations

- When separating c-C₄F₈ from CF₄, C₃F₆ and N₂, it is recommended that temperature or pressure swing condensations be used. The c-C₄F₈ will condense under the correct conditions, which would aid in the separation of this gas from the other.
- It is not recommended to use any of the tested membranes for industrial scale use due to the low selectivity found for the binary mixtures. When purifying the gas, it is inevitable that at some stage, the system must deal with a binary gas mixture. It is at this stage that the two membranes tested will not deliver the performance needed for full-scale application.

7.3 Contributions

This thesis has made the following contributions towards the field of membrane gas separation and carbon fluor gas separation:

- No sorption data for C₃F₆ gas using PTFE powders were available at low pressures. This can be found in Section 3.3.6.
- Single gas permeation data for C₃F₆, CF₄ and N₂, using a Teflon® membrane supported by a PAN- or PEI layer followed by polystyrene, were generated and demonstrated in Sections 4.3, 4.4 and 4.5.
- The influence of permeate side pressure on the description of gas permeation by means of the solution-diffusion model was confirmed during the modelling of the system in Section 4.7.
- Binary gas mixture permeation data for N₂/CF₄, N₂/C₃F₆ and CF₄/C₃F₆ using a Teflon® membrane supported by a PAN- or PEI layer was developed and is shown in Sections 5.3, 5.4 and 5.5.

- A modification was made to the Vignes equation in order to allow for partial gas permeation data to be calculated when included in the solution-diffusion model. The total flux was subsequently determined by adding all the partial fluxes. See Section 5.6.
- Ternary gas permeation data using a Teflon® membrane supported by a PAN layer followed by polystyrene was measured and is shown in Section 6.2.
- Finally, the ternary system was modelled, showing the inclusion of an osmotic pressure constant term and a convective diffusion flux term. The results of the modelling are detailed in Section 6.3.
- It was proven that the difference, or similarity, of surface charge between a molecule and a membrane surface plays a role in the permeation of the gas. These charges also appear to influence coupling that exists between the different gasses.

7.4 Patent

Nuclear Energy Corporation of South Africa & North-West University 2008 Recovery of a gaseous component from a mixture of gaseous components. *WO 2010/001 368 AI*

7.5 Conference presentation

Le Roux, M., Krieg, H.M., Peineman, K-V., Van der Walt, I.J. & Marx, S. *Polymer membrane screening for the separation of C_xF_y gasses.* 14th World Membrane Conference. Hawaii, USA. 2008.

APPENDIX A: MATERIAL SAFETY DATA SHEETS

A.1 C₃F₆



Safety Data Sheet

Product :	Hexafluoropropene (R1216)	Page : 1/5
MSDS Nr : 066_AL	Version : 1.01	Date : 31/07/2002

1 IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY

MSDS Nr	066_AL
Product name	Hexafluoropropene (R1216)
Chemical formula	C ₃ F ₆
Company identification	see heading and/or footer see paragraph 16 "OTHER INFORMATION"
Emergency phone numbers	see heading and/or footer see paragraph 16 "OTHER INFORMATION"

2 COMPOSITION/INFORMATION ON INGREDIENTS

Substance/Preparation	Substance.
Components/Impurities	Contains no other components or impurities which will influence the classification of the product.
CAS Nr	00116-15-4
EEC Nr (from EINECS)	204-127-4

3 HAZARDS IDENTIFICATION

Hazards identification	Liquefied gas Harmful by inhalation Irritating to eyes, respiratory system and skin.
------------------------	--

4 FIRST AID MEASURES

Inhalation	Harmful by inhalation. In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation. In low concentrations may cause narcotic effects. Symptoms may include dizziness, headache, nausea and loss of co-ordination. Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.
Skin/eye contact	Immediately flush eyes thoroughly with water for at least 15 minutes. Obtain medical assistance
Ingestion	Remove contaminated clothing Ingestion is not considered a potential route of exposure.

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Safety Data Sheet

Product :**Hexafluoropropene (R1216)**

Page :2/5

MSDS Nr : 066_AL

Version : 1.01

Date : 31/07/2002

5 FIRE FIGHTING MEASURES

Specific hazards	Non flammable Exposure to fire may cause containers to rupture/explode.
Hazardous combustion products	If involved in a fire the following toxic and/or corrosive fumes may be produced by thermal decomposition: Carbon monoxide Carbonyl fluoride Hydrogen fluoride
Suitable extinguishing media	All known extinguishants can be used.
Specific methods	If possible, stop flow of product. Move away from the container and cool with water from a protected position.
Special protective equipment for fire fighters	Use self-contained breathing apparatus and chemically protective clothing.

6 ACCIDENTAL RELEASE MEASURES

Personal precautions	Ensure adequate air ventilation. Use self-contained breathing apparatus and chemically protective clothing. Evacuate area.
Environmental precautions	Try to stop release. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous.
Clean up methods	Ventilate area.

7 HANDLING AND STORAGE

Handling and storage	Keep container below 50°C in a well ventilated place. Refer to supplier's container handling instructions. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt. Do not allow backfeed into the container. Suck back of water into the container must be prevented.
----------------------	---

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Exposure limit value -TLV(ACGIH)	Not established .
Personal protection	Protect eyes, face and skin from liquid splashes. Keep self contained breathing apparatus readily available for emergency use.

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Safety Data Sheet

Product : Hexafluoropropene (R1216)

Page :3/5

MSDS Nr : 066_AL

Version : 1.01

Date : 31/07/2002

Do not smoke while handling product.
Ensure adequate ventilation.

9 PHYSICAL AND CHEMICAL PROPERTIES

Molecular weight	150
Melting point	-156 °C
Boiling point	-29.6 °C
Critical temperature	86.2 °C
Relative density, gas	5.2 (air=1)
Relative density, liquid	1.3 (water=1)
Vapour Pressure 20°C	6.4 bar
Solubility mg/l water	No reliable data available.
Appearance/Colour	Colourless gas
Odour	Ethereal
Autoignition temperature	Not applicable
Flammability range	Non flammable.
Other data	Gas/vapour heavier than air. May accumulate in confined spaces, particularly at or below ground level.

10 STABILITY AND REACTIVITY

Stability and reactivity	Stable under normal conditions.
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11 TOXICOLOGICAL INFORMATION

General	May have damaging effect on respiratory system, central nervous system and liver.
LC50/1h (ppm)	5600 ppm

12 ECOLOGICAL INFORMATION

General	May cause pH changes in aqueous ecological systems.
---------	---

13 DISPOSAL CONSIDERATIONS

General	Do not discharge into any place where its accumulation could be dangerous. Avoid discharge to atmosphere. Contact supplier if guidance is required.
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Safety Data Sheet

Product :**Hexafluoropropene (R1216)**

Page :4/5

MSDS Nr : 066_AL

Version : 1.01

Date : 31/07/2002

14 TRANSPORT INFORMATION

Proper shipping name	Hexafluoropropylene
UN Nr	1858
Class/Div	2.2
ADR/RID Classification code	2, 2°A
ADR/RID Hazard Nr	20
Labelling ADR	Label 2: non flammable non toxic gas
Other transport information	Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers ensure that they are firmly secured and: - cylinder valve is closed and not leaking - valve outlet cap nut or plug (where provided) is correctly fitted - valve protection device (where provided) is correctly fitted - there is adequate ventilation. - compliance with applicable regulations.

15 REGULATORY INFORMATION

Number in Annex I of Dir 67/548	602-061-00-4.
EC Classification	Xn;R20 Xi;R37
-Symbols	Xn: Harmful
-Risk phrases	R20 Harmful by inhalation. R37 Irritating to respiratory system.
-Safety phrases	S41 In case of fire and/or explosion do not breathe fumes.

16 OTHER INFORMATION

Ensure all national/local regulations are observed.

Users of breathing apparatus must be trained.

Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.

Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.

This Safety Data Sheet has been established in accordance with the applicable European Directives and applies to all countries that have translated the Directives in their national laws.

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Safety Data Sheet

Product :	Hexafluoropropene (R1216)	Page :5/5
MSDS Nr : 066_AL	Version : 1.01	Date : 31/07/2002

This MSDS is for information purposes only and is subject to change without notice. [Prior to purchase of products, please contact your local Air Liquide office for a complete MSDS (with Manufacturer's name and emergency phone number).]

End of document.
Number of pages :5

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A.2 N₂

 AIR LIQUIDE	SAFETY DATA SHEET	Page : 1 / 3
		Revised edition no : 1
		Date : 15/7/2005
		Supersedes : 0/0/0
Nitrogen		AL089A



Label 2.2 : Non flammable, non toxic gas.

1 IDENTIFICATION OF THE SUBSTANCE / PREPARATION AND OF THE COMPANY / UNDERTAKING

Trade name : Nitrogen
 MSDS No : AL089A
 Chemical formula : N₂
 Company identification : AIR LIQUIDE SA
 France
 See paragraph 16 "OTHER INFORMATION"
 Emergency phone nr : See paragraph 16 "OTHER INFORMATION"

2 COMPOSITION / INFORMATION ON INGREDIENTS

Substance / Preparation : Substance.

Substance name	Contents	CAS No	EC No	Index No	Classification
Nitrogen	100 %	7727-37-9	231-783-9	-----	

Contains no other components or impurities which will influence the classification of the product.

3 HAZARDS IDENTIFICATION

Hazards identification : Compressed gas.
 In high concentrations may cause asphyxiation.

4 FIRST AID MEASURES

First aid measures
 - Inhalation : In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation.
 Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.

5 FIRE-FIGHTING MEASURES

Flammable class : Non flammable.
 Specific hazards : Exposure to fire may cause containers to rupture/explode.
 Hazardous combustion products : None.
 Extinguishing media
 - Suitable extinguishing media : All known extinguishants can be used.
 Specific methods : If possible, stop flow of product.
 Move away from the container and cool with water from a protected position.
 Special protective equipment for fire fighters : In confined space use self-contained breathing apparatus.

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	SAFETY DATA SHEET	Page : 2 / 3
		Revised edition no : 1
		Date : 15/7/2005
		Supersedes : 0/0/0
Nitrogen		AL089A

6 ACCIDENTAL RELEASE MEASURES

Personal precautions	: Evacuate area. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. Ensure adequate air ventilation.
Environmental precautions	: Try to stop release.
Clean up methods	: Ventilate area.

7 HANDLING AND STORAGE

Storage	: Keep container below 50°C in a well ventilated place.
Handling	: Suck back of water into the container must be prevented. Do not allow backfeed into the container. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt. Refer to supplier's container handling instructions.

8 EXPOSURE CONTROLS / PERSONAL PROTECTION

Personal protection	: Ensure adequate ventilation.
----------------------------	--------------------------------

9 PHYSICAL AND CHEMICAL PROPERTIES

Physical state at 20 °C	: Compressed gas.
Colour	: Colourless gas.
Odo(u)r	: No odour warning properties.
Molecular weight	: 28
Melting point [°C]	: -210
Boiling point [°C]	: -196
Critical temperature [°C]	: -147
Vapour pressure, 20°C	: Not applicable.
Relative density, gas (air=1)	: 0.97
Relative density, liquid (water=1)	: Not applicable.
Solubility in water [mg/l]	: 20

10 STABILITY AND REACTIVITY

Stability and reactivity	: Stable under normal conditions.
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11 TOXICOLOGICAL INFORMATION

Toxicity information	: No known toxicological effects from this product.
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12 ECOLOGICAL INFORMATION

Ecological effects information	: No known ecological damage caused by this product.
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	SAFETY DATA SHEET	Page : 3 / 3
		Revised edition no : 1
		Date : 15/7/2005
		Supersedes : 0/0/0
Nitrogen		AL089A

13 DISPOSAL CONSIDERATIONS

General : Do not discharge into any place where its accumulation could be dangerous.
To atmosphere in a well ventilated place.
Contact supplier if guidance is required.

14 TRANSPORT INFORMATION

UN No. : 1066
H.I. nr : 20
ADR/RID
- Proper shipping name : NITROGEN, COMPRESSED
- ADR Class : 2
- ADR/RID Classification code : 1 A
- Labelling ADR : Label 2.2 : Non flammable, non toxic gas.
Other transport information : Avoid transport on vehicles where the load space is not separated from the driver's compartment.
Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency.
Before transporting product containers :
- Ensure that containers are firmly secured.
- Ensure cylinder valve is closed and not leaking.
- Ensure valve outlet cap nut or plug (where provided) is correctly fitted.
- Ensure valve protection device (where provided) is correctly fitted.
- Ensure there is adequate ventilation.
- Compliance with applicable regulations.

15 REGULATORY INFORMATION

EC Classification : Not included in Annex I.
Not classified as dangerous preparation/substance.
EC Labelling : No EC labelling required.
- Symbol(s) : None.
- R Phrase(s) : None.
- S Phrase(s) : None.

16 OTHER INFORMATION

Asphyxiant in high concentrations.
Keep container in a well-ventilated place.
Do not breathe the gas.
Ensure all national/local regulations are observed.
The hazard of asphyxiation is often overlooked and must be stressed during operator training.
This Safety Data Sheet has been established in accordance with the applicable European Directives and applies to all countries that have translated the Directives in their national laws.
Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.
Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.
Recommended uses and restrictions : This SDS is for information purposes only and is subject to change without notice. [Prior to purchase of products, please contact your local AIR LIQUIDE office for a complete SDS (with Manufacturer's name and emergency phone number).]

End of document

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A.3 CF₄

Safety Data Sheet

Product :	Tetrafluoromethane (R14)	Page :1/4
MSDS Nr : 116_AL	Version : 1.01	Date : 31/07/2002

1 IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY

MSDS Nr	116_AL
Product name	Tetrafluoromethane (R14)
Chemical formula	CF ₄
Company identification	see heading and/or footer
	see paragraph 16 "OTHER INFORMATION"
Emergency phone numbers	see heading and/or footer
	see paragraph 16 "OTHER INFORMATION"

2 COMPOSITION/INFORMATION ON INGREDIENTS

Substance/Preparation	Substance.
Components/Impurities	Contains no other components or impurities which will influence the classification of the product.
CAS Nr	00075-73-0
EEC Nr (from EINECS)	200-896-5

3 HAZARDS IDENTIFICATION

Hazards identification	Compressed gas
	In high concentrations may cause asphyxiation.

4 FIRST AID MEASURES

Inhalation	In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation.
	In low concentrations may cause narcotic effects. Symptoms may include dizziness, headache, nausea and loss of co-ordination.
	Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.

5 FIRE FIGHTING MEASURES

Specific hazards	Exposure to fire may cause containers to rupture/explode.
	Non flammable
Hazardous combustion products	If involved in a fire the following toxic and/or corrosive fumes may be produced by thermal decomposition:
	Carbonyl fluoride

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Safety Data Sheet

Product :**Tetrafluoromethane (R14)**

Page :2/4

MSDS Nr : 116_AL

Version : 1.01

Date : 31/07/2002

	Carbon monoxide
	Hydrogen fluoride
Suitable extinguishing media	All known extinguishants can be used.
Specific methods	If possible, stop flow of product.
	Move away from the container and cool with water from a protected position.
Special protective equipment for fire fighters	Use self-contained breathing apparatus and chemically protective clothing.

6 ACCIDENTAL RELEASE MEASURES

Personal precautions	Evacuate area. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. Ensure adequate air ventilation.
Environmental precautions	Try to stop release. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous.
Clean up methods	Ventilate area.

7 HANDLING AND STORAGE

Handling and storage	Suck back of water into the container must be prevented. Do not allow backfeed into the container. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt. Refer to supplier's container handling instructions. Keep container below 50°C in a well ventilated place.
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8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal protection	Ensure adequate ventilation. Do not smoke while handling product.
---------------------	--

9 PHYSICAL AND CHEMICAL PROPERTIES

Molecular weight	88
Melting point	-184 °C
Boiling point	-128 °C
Critical temperature	-45 °C
Relative density, gas	3 (air=1)
Relative density, liquid	Not applicable.
Vapour Pressure 20°C	Not applicable.

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Safety Data Sheet

Product :	Tetrafluoromethane (R14)	Page :3/4
MSDS Nr : 116_AL	Version : 1.01	Date : 31/07/2002
Solubility mg/l water	20 mg/l	
Appearance/Colour	Colourless gas	
Odour	No odour warning properties.	
Other data	Gas/vapour heavier than air. May accumulate in confined spaces, particularly at or below ground level.	
10 STABILITY AND REACTIVITY		
Stability and reactivity	Stable under normal conditions. Thermal decomposition yields toxic products which can be corrosive in the presence of moisture.	
11 TOXICOLOGICAL INFORMATION		
General	No known toxicological effects from this product.	
12 ECOLOGICAL INFORMATION		
General	No known ecological damage caused by this product. Not covered by the 'Montreal Protocol'.	
Global warming factor	6500	
13 DISPOSAL CONSIDERATIONS		
General	Do not discharge into any place where its accumulation could be dangerous. Contact supplier if guidance is required.	
14 TRANSPORT INFORMATION		
Proper shipping name	Tetrafluoromethane	
UN Nr	1982	
Class/Div	2.2	
ADR/RID Classification code	2, 1°A	
ADR/RID Hazard Nr	20	
Labelling ADR	Label 2: non flammable non toxic gas	
Other transport information	Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers ensure that they are firmly secured and: - cylinder valve is closed and not leaking	

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Safety Data Sheet

Product :**Tetrafluoromethane (R14)**

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MSDS Nr : 116_AL

Version : 1.01

Date : 31/07/2002

- valve outlet cap nut or plug (where provided) is correctly fitted
 - valve protection device (where provided) is correctly fitted
 - there is adequate ventilation.
 - compliance with applicable regulations.
-

15 REGULATORY INFORMATION

Number in Annex I of Dir 67/548

Not included in Annex I.

EC Classification

Not classified as dangerous preparation.

EC Labelling (Symbols, R&S phrases)

No EC labelling required.

16 OTHER INFORMATION

Asphyxiant in high concentrations.

Keep container in well ventilated place.

Do not breathe the gas.

Ensure all national/local regulations are observed.

The hazard of asphyxiation is often overlooked and must be stressed during operator training.

Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.

Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.

This Safety Data Sheet has been established in accordance with the applicable European Directives and applies to all countries that have translated the Directives in their national laws.

This MSDS is for information purposes only and is subject to change without notice. [Prior to purchase of products, please contact your local Air Liquide office for a complete MSDS (with Manufacturer's name and emergency phone number).]

End of document.**Number of pages :4**

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APPENDIX B: CALIBRATION CURVES

B.1 Mass flow controller calibrations

A mass flow controller for each gas was calibrated by changing the percentage opening of the valve and measuring the gas flow rate by means of a soap flow meter. This information was then used to fit a linear model which could be used to control the opening of the different valves to obtain the required gas flow rate. A graph depicting the calibration results appears below in Figure B-1. Note that Valve 1 was used for C_3F_6 , Valve 2 for CF_4 and Valve 3 for N_2 .

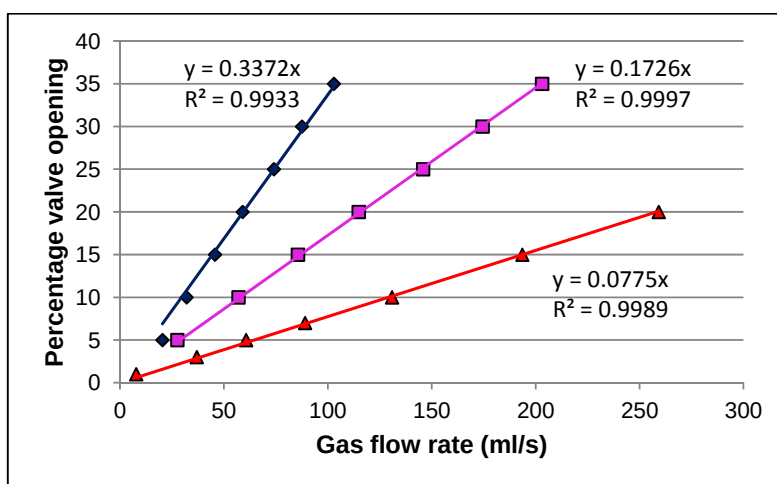


Figure B-1: Mass flow controller calibration curves (♦ - Valve 1, ■ - Valve 2, ▲ - Valve 3)

By using the linear equations obtained by the fitted trendlines in Figure B-1, the valve opening and the specific flow rate required for each gas was calculated.

B.2 GC calibration curves

B.2.1 Binary gas mixtures

In order to properly use the GC, it is necessary to calibrate it before the gas mixtures are to be used. This is done by injecting the GC with a known composition of the two gases. The GC will return an area value for each gas analysed. The value of a specific area for each gas will

differ in relation to the other gas in the feed mixture. Therefore, a graph will be generated showing the area ratio of the two gases versus the molar feed ratio thereof. This will yield a straight line that passes through the origin. From here the slope m_i can be determined by

$\frac{x_2}{x_1} = m \frac{A_2}{A_1}$, where x_i is the molar feed amount and A_i is the area of component i . The slope is

then used to calculate an unknown composition of the gas injected into the GC using the following relation:

$$\begin{aligned} x_1 + x_2 &= 1 \\ 1 + \frac{x_1}{x_2} &= \frac{1}{x_1} \\ x_2 &= \frac{1}{1 + \frac{x_2}{x_1}} \end{aligned}$$

Mixtures of N_2/CF_4 , $\text{N}_2/\text{C}_3\text{F}_6$ and $\text{CF}_4/\text{C}_3\text{F}_6$ using the mass flow control valves were injected into the GC. Feed compositions ranging from 90/10 mole percentage to 10/90 were used to obtain the different area ratio. Graphs as described above were subsequently constructed and used to calculate the value of m_i . This was carried out for all three feed ratios and is shown below in Figure B-2.

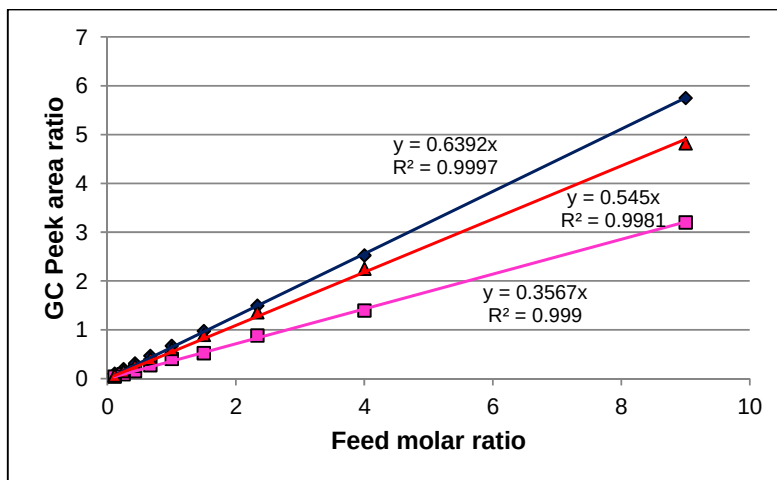


Figure B-2: Binary gas GC calibration curves (♦ - N_2/CF_4 , ■ - $\text{N}_2/\text{C}_3\text{F}_6$, ▲ - $\text{CF}_4/\text{C}_3\text{F}_6$)

B.2.2 Ternary gas mixtures

The same principle as applied to the binary gas mixtures is used for the ternary gas mixtures. However, due to the complexity of a ternary gas mixture, a minimum of four calibration curves are required for use in a single analysis. This derived from the following set of relations. As for the binary gas mixtures, the molar feed ratios are added to give one, and from there manipulated to isolate the required molar feed fraction (Jansen, 1999). This is shown below:

$$\begin{aligned}
 x_1 + x_2 + x_3 &= 1 \\
 \frac{x_1}{x_2} + 1 + \frac{x_3}{x_2} &= \frac{1}{x_2} \\
 x_2 &= \frac{1}{1 + \frac{x_1}{x_2} + \frac{x_3}{x_2}}
 \end{aligned}$$

Similarly it is found that:

$$\begin{aligned}
 x_1 + x_2 + x_3 &= 1 \\
 \frac{x_1}{x_3} + \frac{x_2}{x_3} + 1 &= \frac{1}{x_3} \\
 x_3 &= \frac{1}{1 + \frac{x_1}{x_3} + \frac{x_2}{x_3}}
 \end{aligned}$$

From here it follows that:

$$\begin{aligned}
 x_1 &= 1 - x_2 - x_3 \\
 &= 1 - \frac{1}{1 + \frac{x_1}{x_2} + \frac{x_3}{x_2}} - \frac{1}{1 + \frac{x_1}{x_3} + \frac{x_2}{x_3}} \\
 &= 1 - \frac{1}{1 + m_1 \frac{A_1}{A_2} + m_2 \frac{A_3}{A_2}} - \frac{1}{1 + m_3 \frac{A_1}{A_3} + m_4 \frac{A_2}{A_3}}
 \end{aligned}$$

Due to this complexity, it was decided to obtain a calibration curve for each gas in combination with the other two. This will give enough information to make use of the

relationships above to obtain the composition of any ternary gas mixture injected into the GC (Jansen, 1999). The results are shown in Figure B-3 to Figure B-5 below.

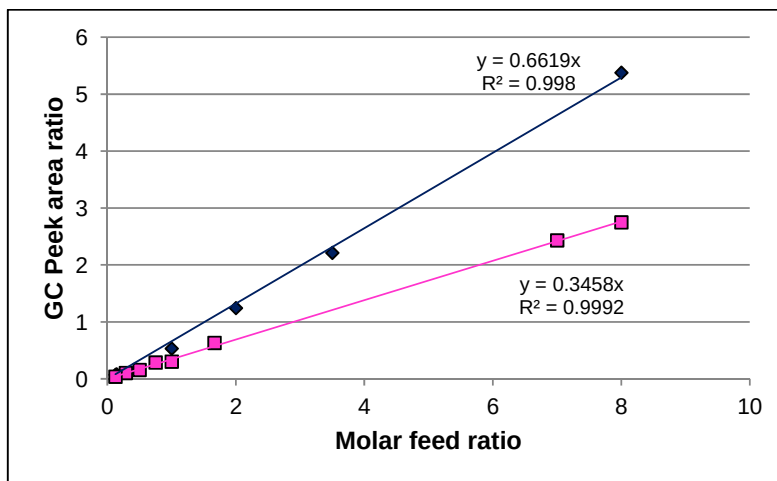


Figure B-3: N₂ ternary calibration curve (♦ - N₂/CF₄, ■ - N₂/C₃F₆)

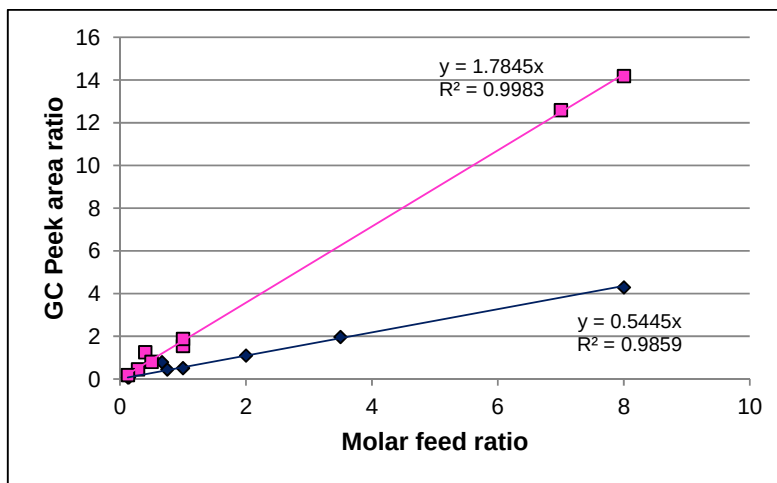


Figure B-4: CF₄ ternary GC calibration curve (♦ - CF₄/N₂, ■ - CF₄/C₃F₆)

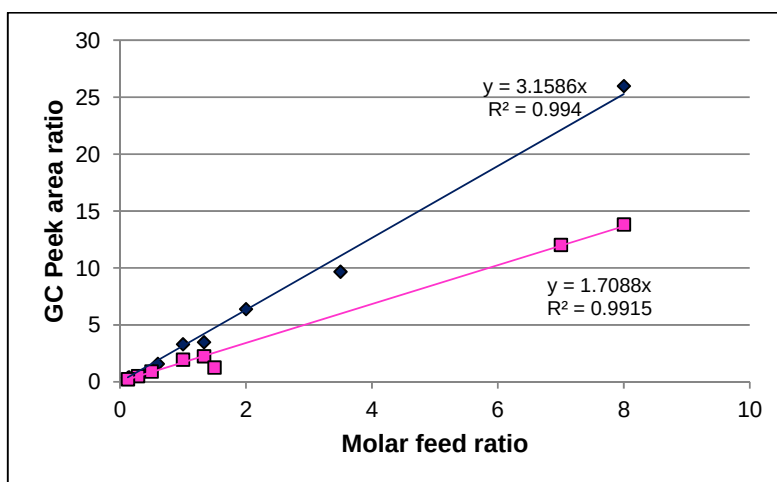


Figure B-5: C₃F₆ ternary calibration curve (♦ - C₃F₆/N₂, ■ - C₃F₆/CF₄)

These curves were used in the calculation of the composition of ternary gas mixtures.

B.3 References

JANSEN, W 1999 Die bepaling van fase-ewewig met betrekking tot die reagense en produkte van die sintese van eters uit iso-amiline. M.Eng. Thesis. PU for CHE. Potchefstroom. South Africa. P262.

APPENDIX C: SAMPLE CALCULATIONS

C.1 Single gas feed experiments

Table C-1 gives an example of the raw data collected for C_3F_6 using the PAN-supported membrane.

Table C-1: Example of raw data collected for C_3F_6 using the PAN-supported membrane

Delta P (kPa)	Permeate Pressure (kPa)	Retentate Time(s/10ml)	Permeate Time(s/10ml)
10	40	6.43	72.13
10	40	6.43	73.53
10	40	6.43	74.97
10	40	6.43	74.52
10	40	6.39	75.51
20	30	7.11	37.62
20	30	7.06	37.6
20	30	7.15	37.65
20	30	7.15	37.48
20	30	7.15	37.62
30	20	7.74	25.92
30	20	7.83	25.74
30	20	7.78	25.78
30	20	7.74	25.74
30	20	7.83	26.19
40	10	8.73	19.8
40	10	8.73	19.89
40	10	8.64	19.84
40	10	8.73	19.89
40	10	8.64	19.67
50	0	10.39	13.95
50	0	10.35	13.99
50	0	10.35	13.86
50	0	10.35	13.86
50	0	10.44	13.86

Flows, both on the permeate and retentate sides, were measured using soap flow meters. The time it took for a soap bubble to travel 10ml was noted. This was repeated five times for the sake of accuracy. This data was used to calculate permeate and retentate flow rates ($\dot{V}_i$) using Equation C.1.

$$\dot{V}_i = \frac{10}{t} \quad (C.1)$$

Ideal gas law behaviour was assumed, which allowed the permeate molar flow rate to be calculated by:

$$\dot{n}_i = \frac{P \cdot \dot{V}_i}{R \cdot T} \text{ where } P \text{ is the absolute permeate side pressure} \quad (C.2)$$

Note that the pressure differential across the active layer of the membrane was assumed to be non-linear which eliminated the use of an arrhythmic average for the pressure differential. With the molar flow rate known, the molar permeate flux was calculated by dividing the flow rate with the membrane area, as shown in Equation C.3

$$J_i = \frac{\dot{n}_i}{A} \quad (C.3)$$

The 95% confidence limit for each pressure differential setting was calculated using equation C.4.

$$95\% \text{ Confidence limit} = 1.96 \frac{(\text{STDEV})}{\sqrt{n}} \quad (C.4)$$

From a graph of the flux (J_i) versus the trans-membrane pressure times the permeate side pressure, the slope of the linear section of the graph was calculated. The slope was then divided by the thickness of the active layer of the membrane to give the permeability.

C.2 Binary gas feed experiments

All calculations for the binary gas permeation tests up to the total retentate and permeate flow rates, remain exactly the same as for the single gas feed experiments as described above in Section C.1. Hereafter it is required to calculate an area ratio from the analysis peaks calculated by the gas chromatograph.

$$A_R = \frac{A_i}{A_j} \text{ where } A_i \text{ and } A_j \text{ represents the areas of the different gases} \quad (\text{C.5})$$

The area ratio is converted to a volume ratio (V_R) by multiplying it with a calibration factor as determined in the calibration curves shown in Section B.2.1. By using this volume ratio, it is possible to calculate the retentate volume flow rate of one of the components as follows:

$$\dot{V}_i = \frac{\dot{V}_R}{(1+V_R)} \quad (\text{C.6})$$

The remainder of the retentate and permeate partial flow rates were calculated by means of a simple mass balance.

By knowing the permeate flow rate for each component, it is possible to calculate the partial gas fluxes by using Equations C.2 and C.3 above. Adding them together yielded the total gas flux. From here, the permeability of the gases, as well as the error bands, were calculated using the same method as described in Section C.1.

C.3 Ternary gas feed experiments

All the calculations for the ternary gas permeation tests were the same as for the binary tests. The only difference was the presence of an extra component.

APPENDIX D: DATA

Due to the magnitude of the data collected in this thesis, it was decided to write all data on an accompanying DVD-ROM. All the first level worked data can be found on this DVD-ROM. Follow the instructions below to gain access to the data.

D.1 Instructions for accessing the DVD-Rom

- Insert DVD into the DVD-Rom
- Auto play will start and navigate to the web browser, displaying the home page.
- In the case where auto play does not work, explore the DVD and open the index page in the root directory.
- Alternatively, click on start, run and type D:/index.htm (where D is the DVD-Rom drive).

APPENDIX E: MODELLING RESULTS

The modelling results for both the binary and ternary partial gas fluxes can be found here.

E.1 Binary gas feed mixtures

E.1.1 PAN-supported membrane

E.1.1.1 CF_4/C_3F_6

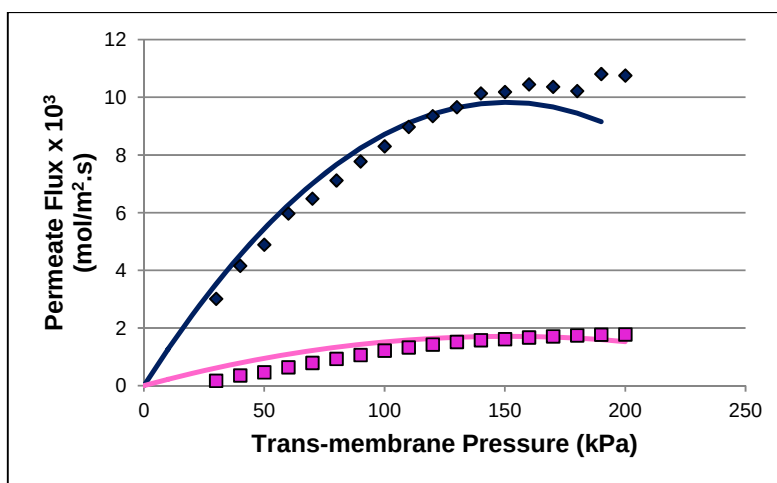


Figure E-1: Binary gas permeation results for 90 mole% CF_4 / 10 mole% C_3F_6 using the PAN-supported membrane ($\blacklozenge$ - CF_4 flux, $\blacksquare$ - C_3F_6 flux). The lines represent the models while the markers represent the actual experimental data

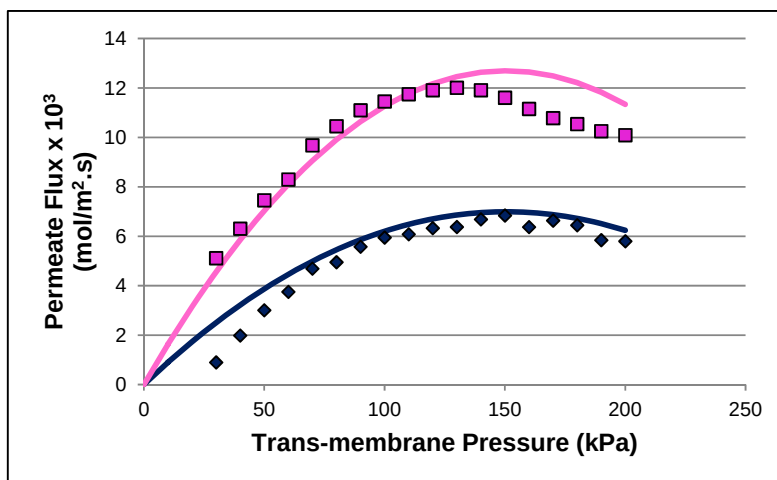


Figure E-2: Binary gas permeation results for 50 mole% CF_4 / 50 mole% C_3F_6 using the PAN-supported membrane ($\blacklozenge$ - CF_4 flux, $\blacksquare$ - C_3F_6 flux). The lines represent the models while the markers represent the actual experimental data

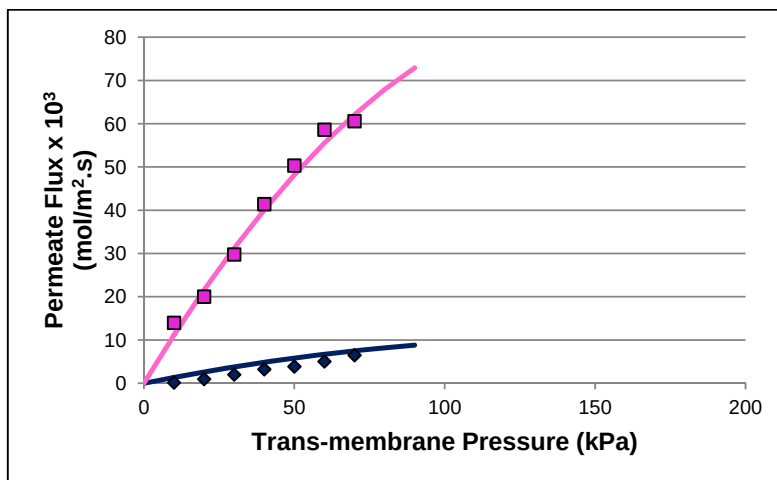


Figure E-3: Binary gas permeation results for 10 mole% CF₄ / 90 mole% C₃F₆ using the PAN-supported membrane (♦ - CF₄ flux, ■ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

E.1.1.2 N₂/C₃F₆

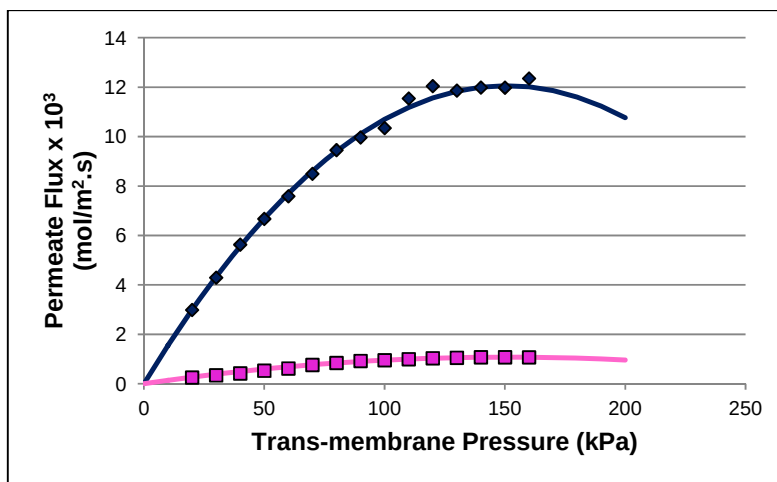


Figure E-4: Binary gas permeation results for 90 mole% N₂ / 10 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

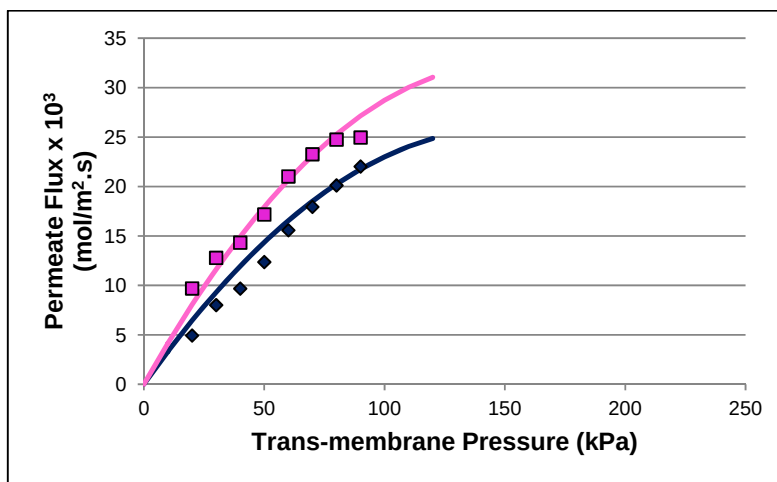


Figure E-5: Binary gas permeation results for 50 mole% N₂ / 50 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

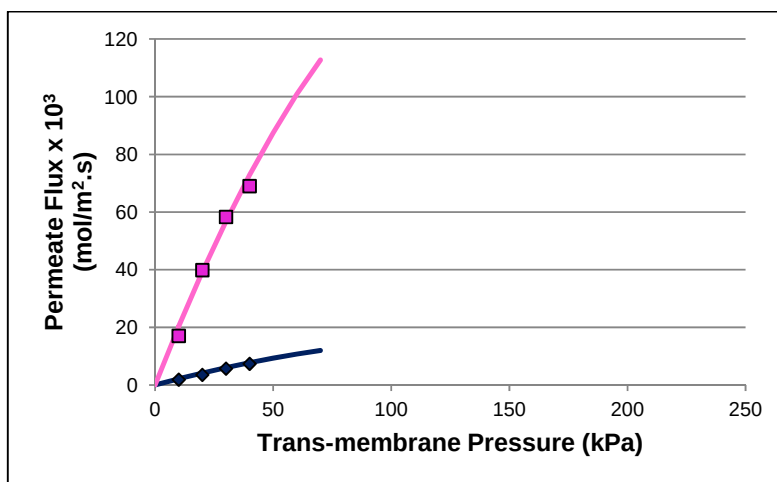


Figure E-6: Binary gas permeation results for 10 mole% N₂ / 90 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

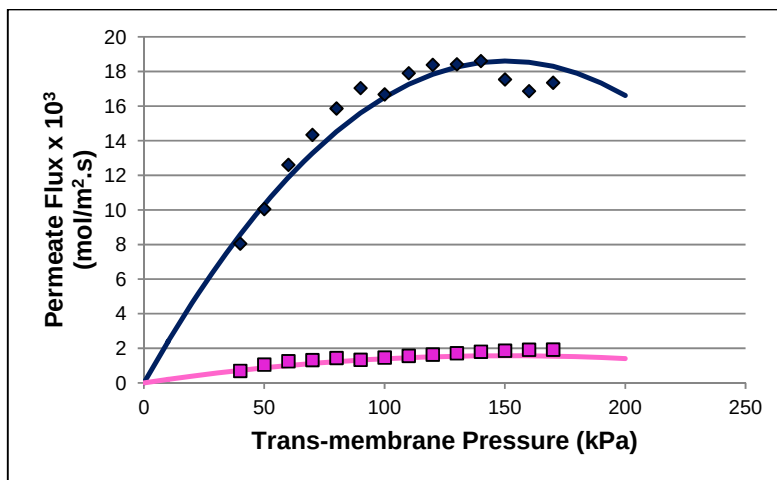
E.1.1.3 N_2/CF_4 

Figure E-7: Binary gas permeation results for 90 mole% N_2 / 10 mole% CF_4 using the PAN-supported membrane ($\blacklozenge$ - N_2 flux, $\blacksquare$ - CF_4 flux). The lines represent the models while the markers represent the actual experimental data

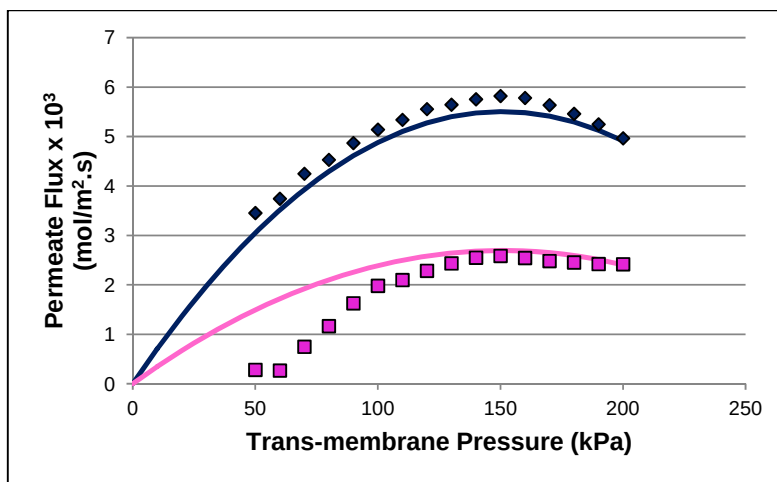


Figure E-8: Binary gas permeation results for 50 mole% N_2 / 50 mole% CF_4 using the PAN-supported membrane ($\blacklozenge$ - N_2 flux, $\blacksquare$ - CF_4 flux). The lines represent the models while the markers represent the actual experimental data

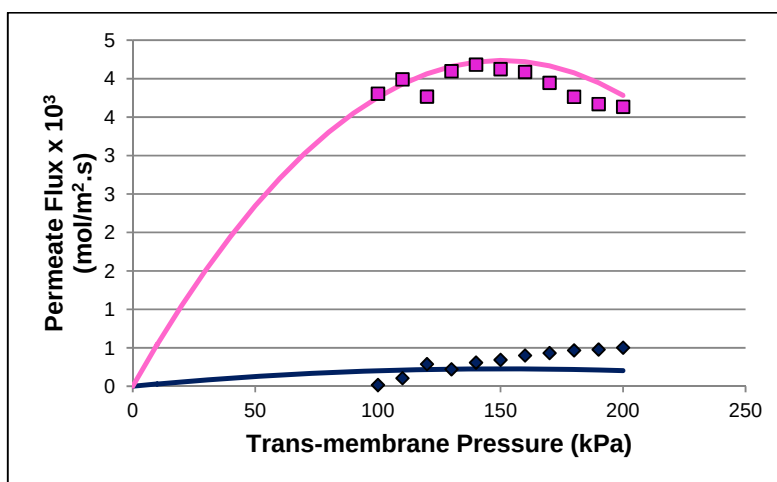


Figure E-9: Binary gas permeation results for 10 mole% N₂ / 90 mole% CF₄ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux). The lines represent the models while the markers represent the actual experimental data

E.1.2 PEI-supported membrane

E.1.2.1 CF₄/C₃F₆

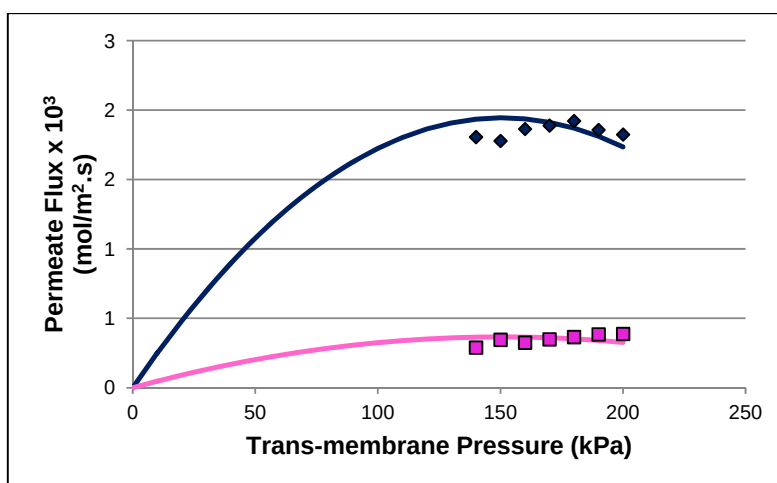


Figure E-10: Binary gas permeation results for 90 mole% CF₄ / 10 mole% C₃F₆ using the PEI-supported membrane (♦ - CF₄ flux, ■ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

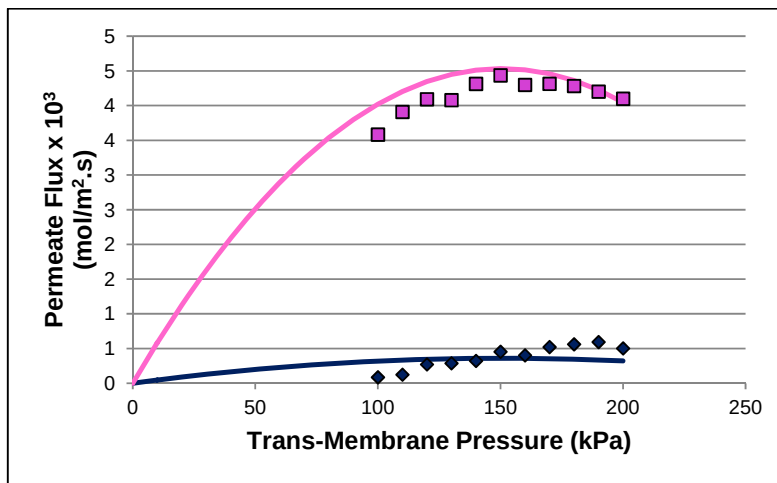


Figure E-11: Binary gas permeation results for 50 mole% CF₄ / 50 mole% C₃F₆ using the PEI-supported membrane (♦ - CF₄ flux, ■ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

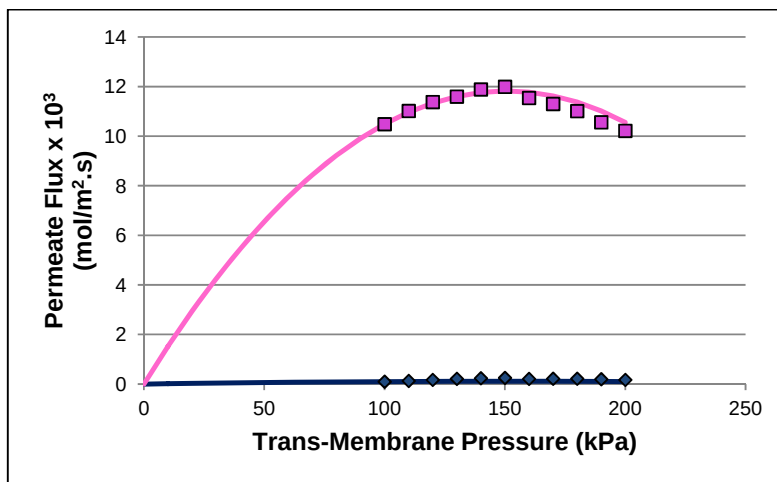


Figure E-12: Binary gas permeation results for 10 mole% CF₄ / 90 mole% C₃F₆ using the PEI-supported membrane (♦ - CF₄ flux, ■ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

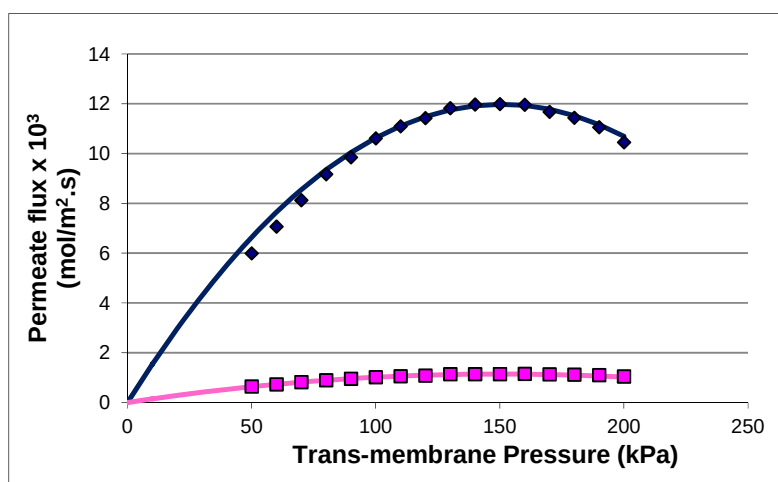
E.1.2.2 N_2/C_3F_6 

Figure E-13: Binary gas permeation results for 90 mole% N_2 / 10 mole% C_3F_6 using the PEI-supported membrane ($\blacklozenge$ - N_2 flux, $\blacksquare$ - C_3F_6 flux). The lines represent the models while the markers represent the actual experimental data

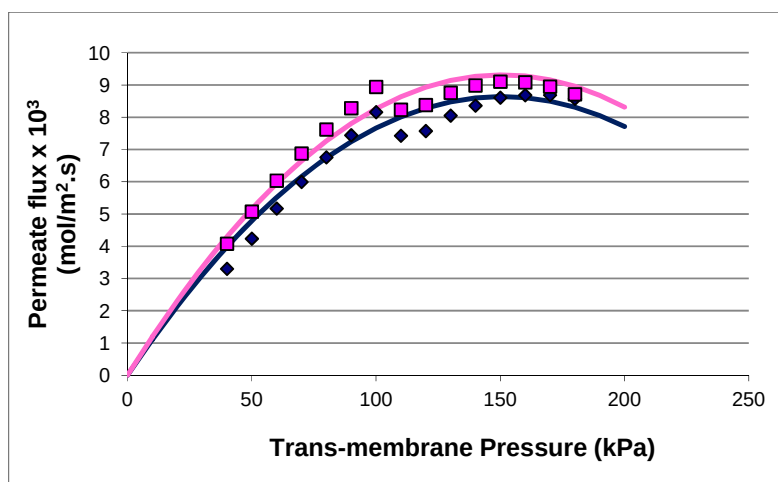


Figure E-14: Binary gas permeation results for 50 mole% N_2 / 50 mole% C_3F_6 using the PEI-supported membrane ($\blacklozenge$ - N_2 flux, $\blacksquare$ - C_3F_6 flux). The lines represent the models while the markers represent the actual experimental data

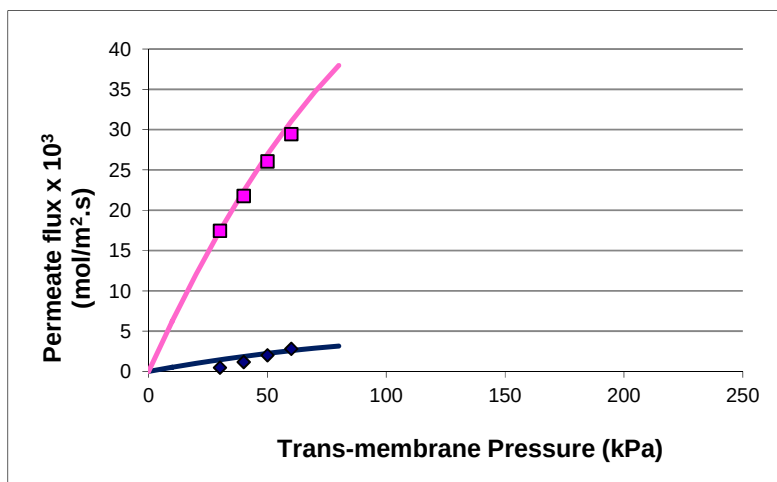


Figure E-15: Binary gas permeation results for 10 mole% N_2 / 90 mole% C_3F_6 using the PEI-supported membrane ($\blacklozenge$ - N_2 flux, $\blacksquare$ - C_3F_6 flux). The lines represent the models while the markers represent the actual experimental data

E.1.2.3 N_2/CF_4

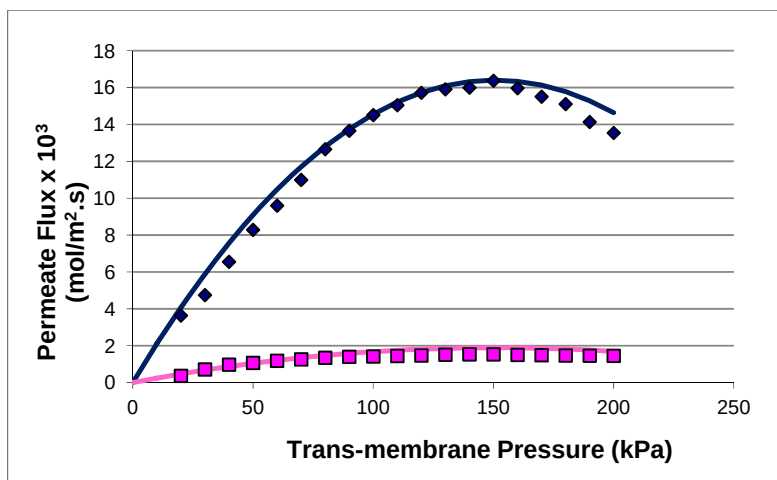


Figure E-16: Binary gas permeation results for 90 mole% N_2 / 10 mole% CF_4 using the PEI-supported membrane ($\blacklozenge$ - N_2 flux, $\blacksquare$ - CF_4 flux). The lines represent the models while the markers represent the actual experimental data

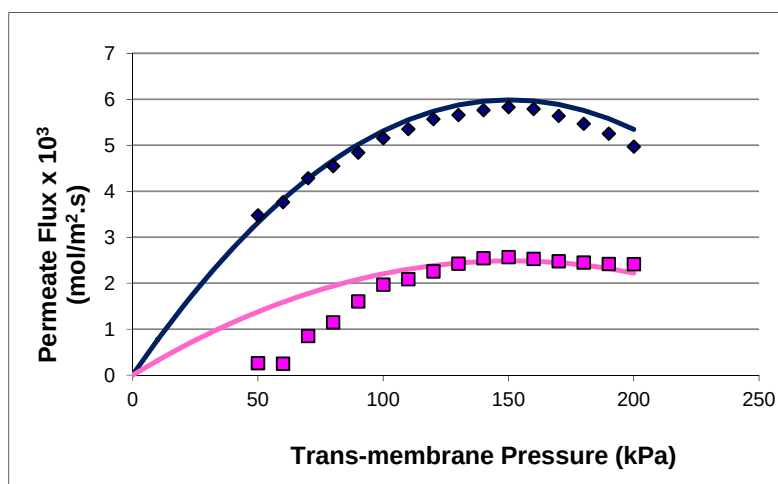


Figure E-17: Binary gas permeation results for 50 mole% N₂ / 50 mole% CF₄ using the PEI-supported membrane (♦ - N₂ flux, ■ - CF₄ flux). The lines represent the models while the markers represent the actual experimental data

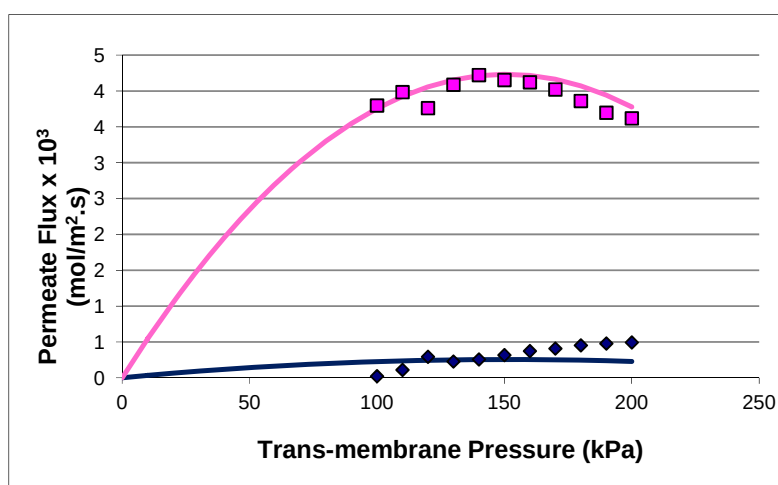


Figure E-18: Binary gas permeation results for 10 mole% N₂ / 90 mole% CF₄ using the PEI-supported membrane (♦ - N₂ flux, ■ - CF₄ flux). The lines represent the models while the markers represent the actual experimental data

E.2 Ternary gas feed mixtures

E.2.1 PAN-supported membrane

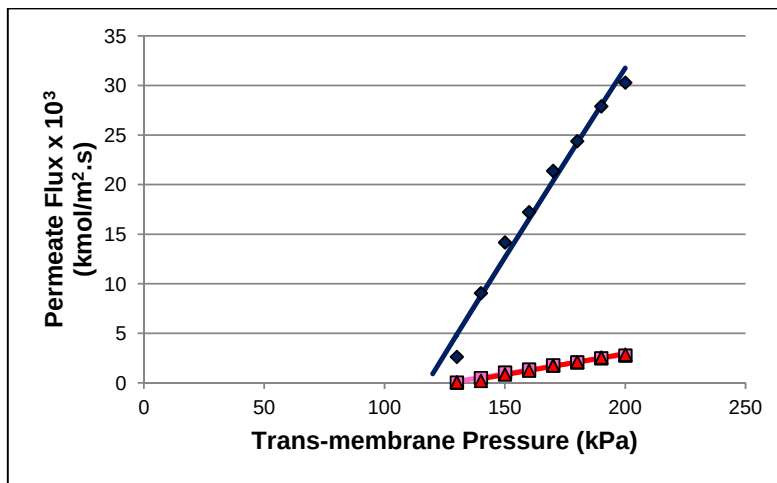


Figure E-19: Ternary gas permeation results for 80 mole% N₂ / 10 mole% CF₄ / 10 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ▲ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

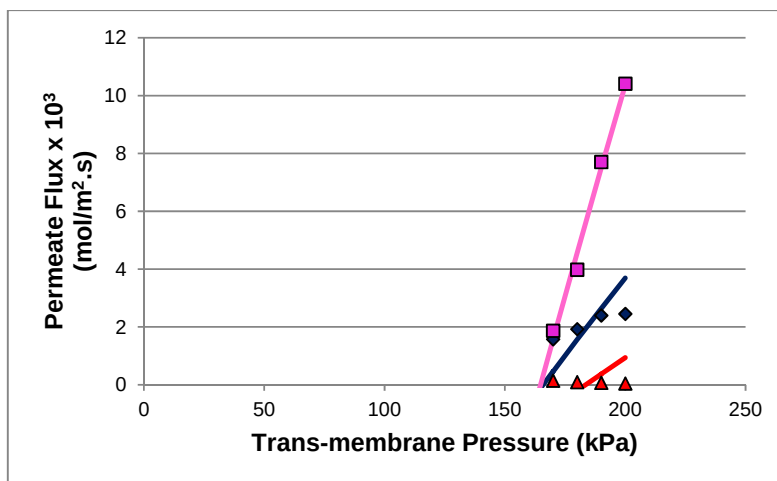


Figure E-20: Ternary gas permeation results for 10 mole% N₂ / 80 mole% CF₄ / 10 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ▲ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

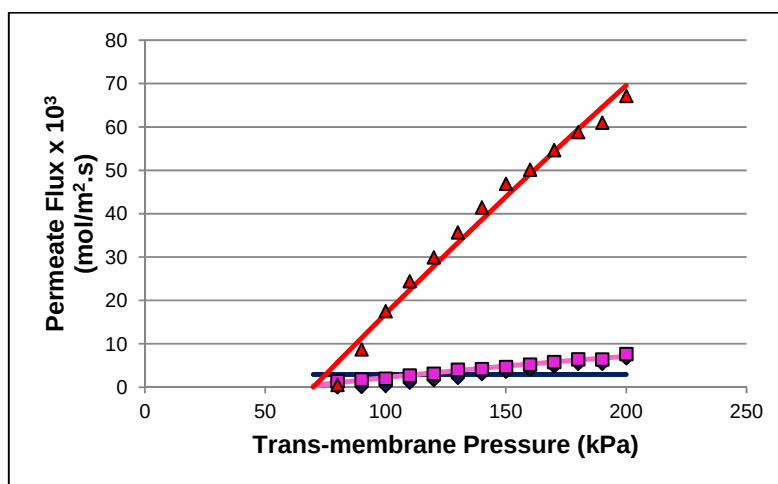


Figure E-21: Ternary gas permeation results for 10 mole% N₂ / 10 mole% CF₄ / 80 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ▲ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data

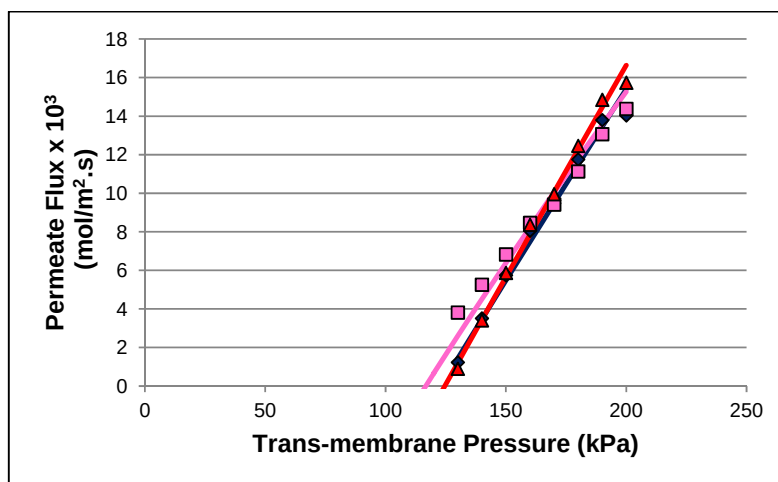


Figure E-22: Ternary gas permeation results for 33.33 mole% N₂ / 33.33 mole% CF₄ / 33.33 mole% C₃F₆ using the PAN-supported membrane (♦ - N₂ flux, ■ - CF₄ flux, ▲ - C₃F₆ flux). The lines represent the models while the markers represent the actual experimental data