QATAR UNIVERSITY

COLLEGE OF ENGINEERING

HIGH PRESSURE CO_2/N_2 AND CO_2/CH_4 SEPARATION USING DENSE

POLYSULFONE SUPPORTED IONIC LIQUID MEMBRANES (DPSILMS)

BY

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Abstract

The separation of carbon dioxide from different sources (e.g. natural gas, flue gas, etc.) has become an important area of research. Some conventional methods of CO_2 separation were used over the years including adsorption (with porous solids), absorption (with amines), cryogenic separation and membranes. Amongst these technologies, Supported Ionic Liquid Membranes (SILMs) technology has been developed in the past few years and became one of the promising techniques in CO_2 separation from gas streams. SILMs technology combines the advantages of both membranes and ionic liquids (ILs) hence it has become an interest of many recent studies. Most of the synthesized SILMs in literature uses porous membranes to support the ionic liquids. Although these SILMs achieve high permeability of CO_2, the separation selectivity to the other gas is very low due to the high permeance of the other gas. Another drawback of porous SILMs is the membrane failure with high pressures due to ionic liquid loss through the pores of the support membrane.

In this work, we look alternative solutions to overcome these disadvantages by synthesizing SILMs using dense (non-porous) polymeric support by which limiting or eliminating ILs loss through the membrane and increase the selectivity of CO_2 separation. Four types of ionic liquids (ILs) were blended with polysulfone (PSF) to produce functional dense polymeric-supported ionic liquid membranes (DPSILMs). These ionic liquids are 1-alkyl-3-methylimidazolium bistriflamide [C_4mim][NTf_2] and Di-iso-propyl 1-alkyl-3-methylimidazolium bistriflamide [DIP-C_4mim][NTf_2], Tributylmethylphosphonium formate [P_{4441}][formate], and Tributylmethylammonium formate [N_{4441}][formate].

The main aim of this study is to investigate the potential use of the synthesized DPSILMs in the industrial gas processing applications for high-pressure CO_2 separation from N_2 and CH_4 streams with less or no loss of ILs. The synthesized DPSILMs were analysed using FTIR and SEM and showed a clear chemical and physical change in the structure PSF and well distribution of ILs in PSF. Binary mixtures of CO_2/N_2 and CO_2/CH_4 (5 mol% CO_2) were used in the study. Selectivity values for the prepared DPSILMs were obtained using a high-pressure membrane unit obtained from Rubotherm Präzisionsmesstechnik GmbH apparatus (System 2). The highest CO_2/N_2 selectivity values were 36 for both PSF-0.5 wt% [DIP-C_4mim][NTf$_2$], PSF-25 wt% [N$_{4441}$][formate], 29 and 21 for PSF-0.5 wt% [C$_4$mim][NTf$_2$] and PSF-50 wt% [P$_{4441}$][formate] respectively. Whereas the highest CO_2/CH_4 selectivity results were 70, 63, 47, and 32 for PSF-2.5 wt% [C$_4$mim][NTf$_2$], PSF-2.5 wt% [DIP-C$_4$mim][NTf$_2$], PSF-0.5 wt% [N$_{4441}$][formate], and PSF-5 wt% [P$_{4441}$][formate] respectively. Another system was used to measure the permeability of each gas (System 1) to be plotted then on Robeson's upper bound (2008) with other PSF blends in the literature for better comparison. The plot showed that the synthesized DPSILMs gave satisfying results and behave as well or better than different types of reported PSF blends. The highest CO_2 permeabilities (with CO_2/N_2 separation measurements) obtained with each IL were 19, 13.6, 10.8, and 8.9 barrer with PSF-25 wt% [N$_{4441}$][formate], PSF-5 wt% [p$_{4441}$][formate], PSF-0.5 wt% [DIP- C$_4$mim][NTf$_2$], and PSF-5 wt% [C$_4$mim][NTf$_2$] respectively. However with CO_2/CH_4 separation measurements, the highest CO_2 permeabilities were 17.3, 13.8, 12.5, and 11.5 barrer with PSF-12.5 wt% [P$_{4441}$][formate], PSF-2.5 wt% [DIP-C$_4$mim][NTf$_2$], PSF-0.5 wt% [N$_{4441}$][formate], and PSF-2.5 wt% [C$_4$mim][NTf$_2$] respectively.

Stability measurements of the synthesized DPSILMs were conducted regarding ILs loss and CO_2/CH_4 separation efficiency. Stability results showed that DPSILMs with 5 wt% [P_{4441}][formate] and [N_{4441}][formate] showed about 30% and 20% ILs loss respectively at 10 bar after 12 hours with small reduction in CO_2/CH_4 selectivity; while no loss of [DIP-C_4mim][NTf_2] and [C_4mim][NTf_2] was observed.

Key words: Ionic liquids, SILM, CO_2 Separation, Dense membrane, polysulfone.

Graphical Abstract
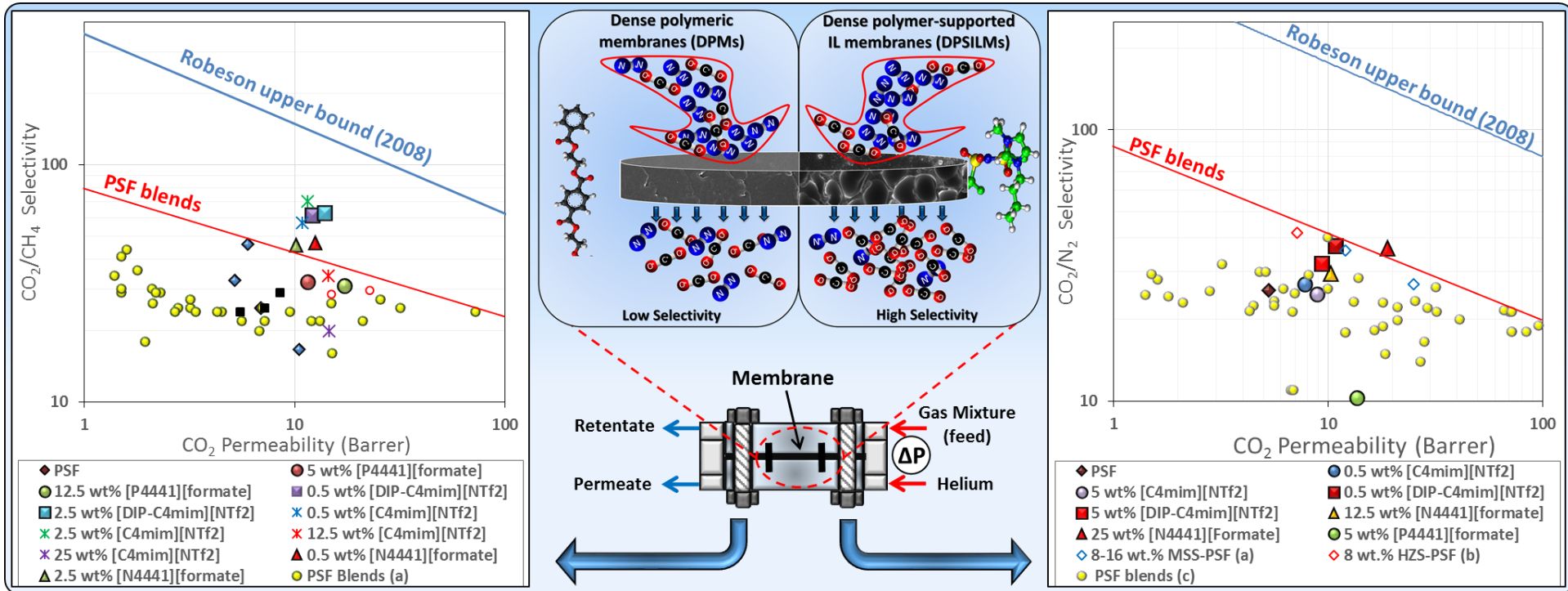
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Dedication

I dedicate this work to my family, advisors, friends, and professors who directly or indirectly helped in this venture. A special feeling of gratitude to my loving parents, brothers and my loving sister who has been a key source of support and encouragement during the challenges of graduate school and life. I also dedicate this thesis to my fiancée who has spiritually supported me throughout writing this thesis.

I am truly thankful for having you all in my life.

Nomenclature

P_F	Feed Pressure (bar).
P_{He}	Helium Pressure (bar).
P_P	Permeate Pressure (containing only CO_2 and N_2 or CH_4) (bar).
P_{total}	$P_p + P_{He}$ (bar).
A	Membrane cross sectional area (cm^2)
l	Membrane thickness
P_i	Permeability of gas i through the membrane (barrer)
J_i	Molar flux of permeate (cm^3 (STP).$cm^{-2}.s^{-1}$)
$\alpha_{A/B}$	Separation selectivity or separation factor
y_A	Molar fraction of the gas A in the permeate
x_A	Mole fraction of gas A in the feed
n_i	Moles number of gas i

Abbreviations

FTIR	Fourier-transform IR spectra
SEM	Scanning electron microscope
DPM	Dense polymeric membrane
DPSILM	Dense polymer-supported IL membrane
SILM	Supported IL membrane.
IL	Ionic liquid
PSF	Polysulfone
PES	Polyethersulfone
PVDF	Polyvinylidene fluoride
MEA	Mono-ethanol amine
MFC	Mass flow controller
PI	Pressure indicator
GC	Gas chromatography

1. Introduction

The separation of carbon dioxide (CO_2) from different emission sources, mainly flue gas from power plants and chemical industries, has become an important area of research as a result of the concern for global warming caused by the effects of greenhouse gases. International Panel on Climate Change (IPCC) expects that, by the year 2100, the CO_2 composition may increase up to 570 ppmv in the atmosphere. This increase may cause a rise of the mean global temperature of about 1.9°C and an increase in sea level of 38 m [1].

Some conventional methods were developed over the years in CO_2 separation fields. These methods include adsorption with porous solids (e.g. activated carbon and zeolites), absorption (with amines), cryogenic separation and membranes [2, 3]. The most common technology is the amines based absorption due to the high capture level of CO_2 (up to 90%) [4]. Adsorption technology is being used also for CO_2 separation using different types of adsorbents. However, its use in the industrial applications is very limited due to the low capacity. Cryogenic CO_2 separation was also being used for CO_2 separation from N_2 streams. In this technology, CO_2 is condensed and collected in multi stages process while N_2 remains in the gas phase and is released through the top of the chamber [3]. Another conventional technology being used in CO_2 separation is membrane separation. The low energy consumption was the main reason beyond the focus of large number of research studies on membranes technology [5]. Conversely, the low selectivity was the main drawback which requires more development on such technology to be used in large scale industrial applications [6].

A huge interest in using ionic liquids (ILs) as an alternative medium for CO_2 capture has become the focus of several studies in the past few years due to their potential advantages compared to other conventional solvents, such as MEA [7]. Their unique properties made these liquids a promising technology that may overcome several problems associated with the conventional technologies of CO_2 separation such as energy consumption [8]. Supported ionic liquid membranes (SILMs) is a novel technology combining ionic liquids and membrane that have been developed as effective method for the selective separation of CO_2 from gas mixtures. SILMs technology have been showing fabulous potential in different applications. However, only few large scale SILMs application were reported in the literature, mainly due to their low stability [9, 10]. A detailed review on these technologies and their application is discussed in section 2. In this study, we try to synthesize functionalized supported ionic liquid membranes using dense polymer support to overcome some drawbacks of the reported SILMs mainly the ILs loss and the low selectivity as discussed in the coming sections.

1.1. Scope of this Thesis

This study aims to develop a world class capability in the field of ionic liquid technology as applied to the oil and gas sector within the College of Engineering at Qatar University (QU). Ionic liquids technology has been chosen as the overall research theme for a number of reasons. Over the last few years there has been a significant increase in research relating to ionic liquids use as possible environmental alternatives for organic solvents in chemical processes. Recently, specialized areas have been studied such as heat transfer fluids, lubricants, and analytical applications. ILs have

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relatively low melting points when compared to inorganic salts hence they are described as organic salts. In this study, we try to overcome the limitations of SILMs technology by synthesis of ionic liquid membranes supported by dense (non-porous) polymeric membranes (DPMs). Blending ILs with dense support is expected to reduce or eliminate the loss of ILs since no pores can allow this. The resulted dense polymeric-supported ionic liquid membranes (DPSILMs) combine both the advantages of ILs and dense polymeric membranes (DPMs). Figure 1.1 shows a scheme of one of dense polymeric membranes (DPMs) development by the incorporation small amounts of ionic liquids.
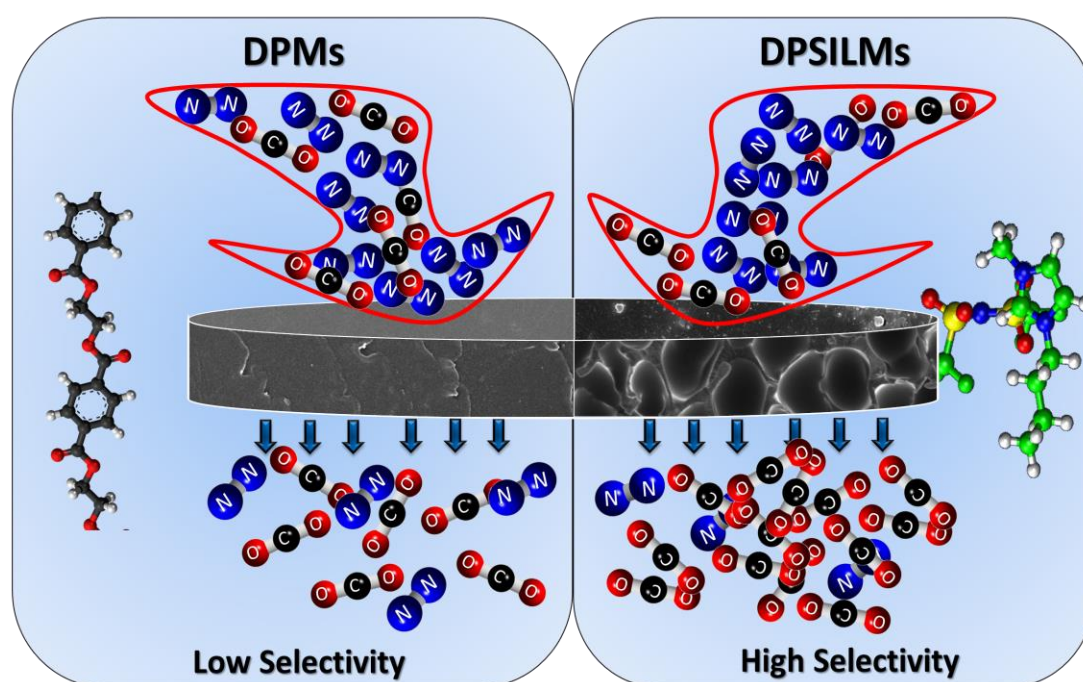
Figure 1.1: Gas separation through dense polymeric membranes (DPMs) and dense polymeric-supported ionic liquid membranes (DPSILMs).

The gas permeation through the synthesized DPSILMs is expected to follow the solution-diffusion mechanism like that in any DPMs. This mechanism govern the gas permeation through DPMs hence separation is not only dependent upon molecular size,

but also relies on the chemical interaction between the gas molecules and the membrane during the diffusion stage (Figure 1.2).
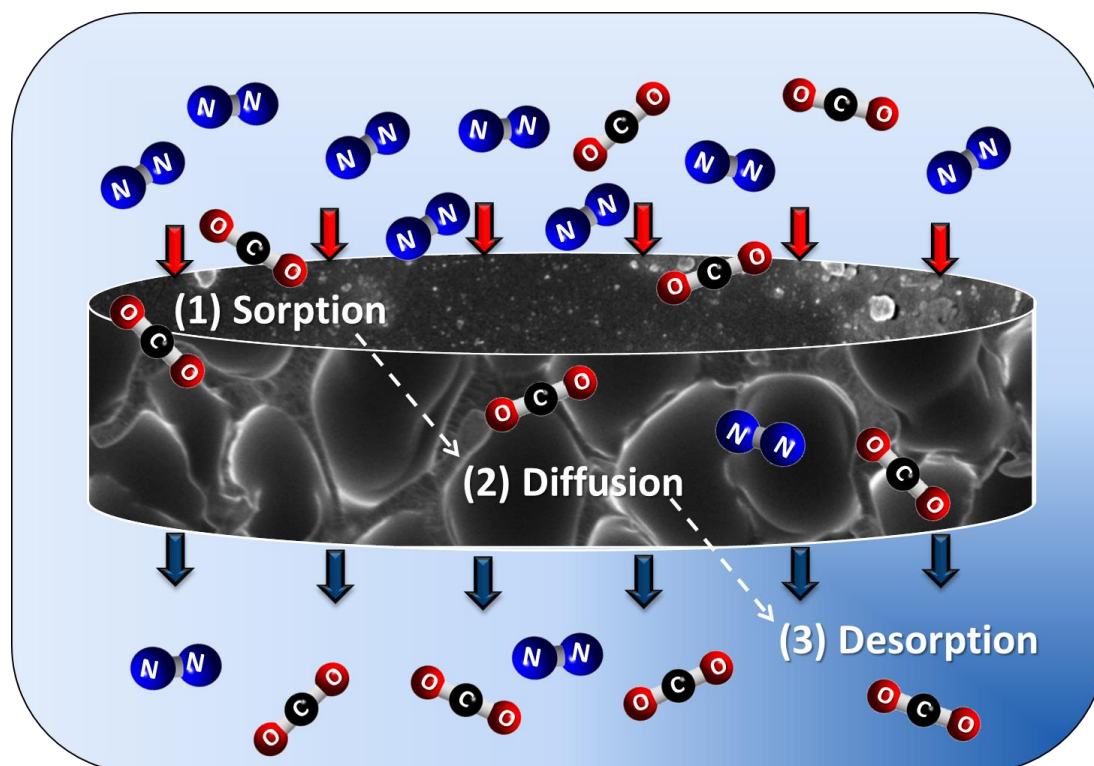
Figure 1.2: Solution-diffusion mechanism through dense membranes.

PSF was selected to be the base polymer due to its low cost, chemical stability and the mechanical strength [11]. In addition, gas permeation measurements will be conducted on mixed gas separation using binary mixtures of CO_2/N_2 and CO_2/CH_4 as mixed gas measurements are more applicable to industrial applications. To author's knowledge, there is no literature know to investigate the application of SILMs in mixed gas CO_2/N_2 or CO_2/CH_4 separation at high pressure using dense support (PSF) as presented in this work.

Generally, the ***objectives*** of this study can be summarized by the following points:

- To develop dense polymer-supported ionic liquid membranes (DPSILMs) using dense polysulfone (PSF) as support to be blended with various ionic liquids.

- To characterise the synthesized DPSILMs to indicate the effect of the added ILs on the chemical and physical structure of the polysulfone (PSF).

- To investigate the effect of the added ILs on high-pressure membrane CO_2/N_2 and CO_2/CH_4 separation compared to the pure polysulfone, other polymeric membranes, and other supported ionic liquid membranes (SILMs) in the literature.

- To test the effect of the high pressure on the ionic liquid loss through the dense supporter and compare it with those having porous supporters.

2. Literature Review

2.1. CO₂ Separation Technologies

Over the years, several technologies have been developed for CO_2 capture and separation from gas streams due to the separation costs which represents the largest financial impediment. These methods include adsorption (with porous solids), absorption (with ammines), cryogenic separation [2] and membranes.

Amine based absorption with aqueous mono-ethanolamine solution (MEA) was developed over 60 years ago in the chemical industries for the removal of CO_2 and hydrogen sulphide (H_2S) from gas streams. It is considered to be the most common technology as it allows achieving high capture level of CO_2 (90% or more) because of fast kinetics and strong chemical reaction [4]. The main drawback of this technology is the significant amount of energy requirements in the regeneration. In fact, MEA-based process could result in a 28% energy loss, and therefore double the cost of electricity usage, due to the heat required to regenerate used aqueous MEA solutions [12].

Solid adsorbents (e.g. activated carbon and zeolites) can be used for CO_2 separation from gas mixtures. Adsorption process involves two main steps: adsorption and desorption. Affinity strength of the adsorbent for capturing CO_2 from a gas mixture is essential for an effective adsorption process. However, the higher the affinity the more difficult to desorb the gas hence the higher energy consumption needed for absorbent regeneration and reuse [3]. The key advantage of adsorption with solids over other CO_2 separation technologies is its simple and energy efficient operation and regeneration. On the other hand, adsorption is not considered effective for large-scale CO_2 removal from gas mixtures due to the low capacity and low CO_2 selectivity of the

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existing adsorbents. Though, it may be effective when combined with another capture technology [13].

Another technology of CO_2 capture is the cryogenic separation of CO_2. This technology is based on that all flue gas components are removed excluding N_2 and CO_2 before cooling. The residual gas is then sent to a cryogenic chamber to manipulate the pressure and temperature causing CO_2 to be liquefied. In the right process conditions, CO_2 will condense and N_2 remains as a gas which escape through the top outlet of the chamber while the high concentrated liquid CO_2 is collected at the end of the chamber. The main advantages of cryogenic CO_2 separation over absorption are that the process can be conducted at atmospheric pressures and that no chemical absorbents are required. However, the main disadvantage of this technology is the numerous costly steps needed for the removal of the water from the feed before cooling units. Another drawback is the drop in process efficiency because of the formation of solid CO_2 onto surfaces of the heat exchanger through the capture cycle.

During the past few years, ionic liquids (ILs) have been changed from poorly understood compounds to the interest of several research activities, both in academic research and industrial applications [14]. Ionic liquids are organic salts which stay as liquids at room temperatures. ILs normally contain an organic cation and a polyatomic inorganic anion or an organic anion. Commonly used organic cations are imidazolium, pyrrolidinium, pyridinium, ammonium, phosphonium; polyatomic inorganic anion such as chloride, hexa-fluorophosphate, tetra-fluoroborate; organic anions like tri-fluoromethylsulfonate and bis[(trifluoromethyl)sulfonyl]imide [15]. A huge interest in using ionic liquids as an alternative medium for CO_2 capture has become apparent because of its potential advantages compared to other conventional solvents (e.g. MEA)

[7]. Ionic liquids are a very versatile group of solvents, due to their unique characteristics, such as the ability to manipulate and tune their physicochemical properties through cation or anion selection [16], non-volatility under ambient conditions, high thermal stability, as well as high CO_2 solubility, may overcome several problems associated with existing CO_2 removal techniques [17]. They give the possibility of decreasing the energy demand for CO_2 stripping during solvent regeneration by as much as 16 % relative to aqueous MEA solutions [8].

Membranes (which generally consist of a semi-permeable, thin, polymeric film) allow selective and specific permeation of some molecules while retaining others [18, 19]. Permeability and selectivity are the two main criteria that must be achieved in producing a useful membrane [5]. A membrane unit is usually small in volume and does not occupy a large area. This technology is less energy intensive, operationally simple and therefore provides low maintenance operation [6, 20]. CO_2 separation can also be performed using a gas absorption membrane. They are microporous solid membranes that act as contacting devices, with a suitable absorption liquid incorporated [21]. The most used absorption liquid for CO_2 separation is an aqueous amine solution [22, 23]. These membranes have the combination of both selectivity and flexibility of absorption [24]. Unlike gas separation membranes, the driving force and selectivity for gas absorption membranes is from the absorption liquid [24, 25]. Therefore, it is important to develop a high efficiency absorption liquid for CO_2 removal. The role of the membranes is just to keep the gas and liquid phases separated [26]. The porous membranes allow gases to diffuse through before the absorbent selectively removes CO_2 from the gas stream [27]. The use of gas absorption membranes is preferable when the partial pressure of CO_2 is low [28].

Supported ionic liquid membranes (SILMs) is one of the promising techniques that combines the advantages of both membranes and ILs hence it have become an interest of many recent studies. In this technology, only a very small amount of ionic liquids needed to be immobilised onto a membrane. Therefore, the operating cost using this technology in large scale CO_2 separation will be greatly reduced. This will all help to counterbalance the apparent economic disadvantage of the ionic liquids, especially in industrial applications [29]. Although SILMs show high affinity in CO_2 capture, they face many difficulties to be applied on large scale. The main difficulty faced in this sector is the limitation of the differential pressure across the membrane to avoid the loss of ionic liquids (ILs) through the pores hence resulting in membrane failure [30].

2.2. Ionic liquids

The field of ionic liquids (ILs) have grown at unpredictable rate during the past few years. Among this rate of development, ionic liquids start leaving academic laboratories and transfer into wide-ranging industrial applications, offering a variety of tunable properties that enhance their performance in many contexts. The key properties that distinguish these compounds is the low volatility and flammability and high chemical and electrochemical stability. Hence, such properties make them possibly perfect as solvents and electrolytes. In addition, their intrinsic ionic conductivity is an essential feature in electrochemical applications [31].

An ionic liquid can be synthesized using organic cations and inorganic or organic anions (Figure 2.1), hence huge number of different ILs can be prepared [32]. Commonly used cations are large and asymmetric such as derivatives of imidazolium, ammonium, sulfonium, phosphonium and pyrrolidinium. Commonly used *inorganic*

anions include halides, tetra-chloroaluminate, hexa-fluorophosphate, tetra-fluoroborate and bis(tri-fluoromethylsulfonyl)imide while typical *organic anions* are tri-fluoroacetate, alkylsulfate, *p*-toluenesulfonate (tosylate) and alkylsulfonate.
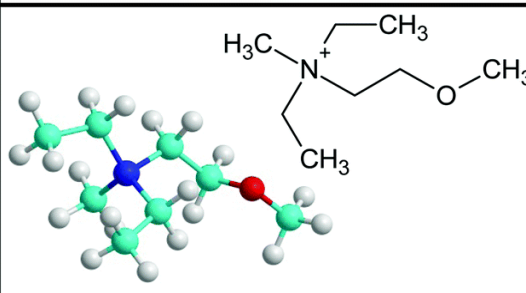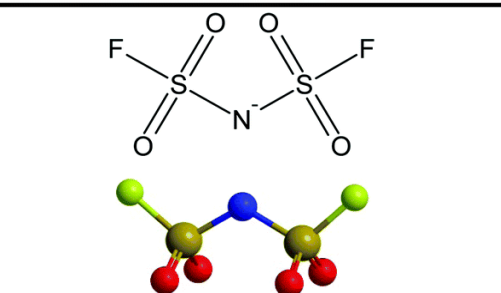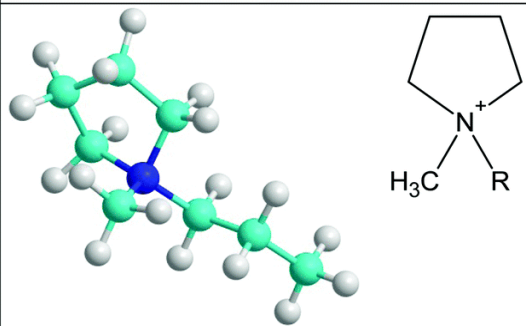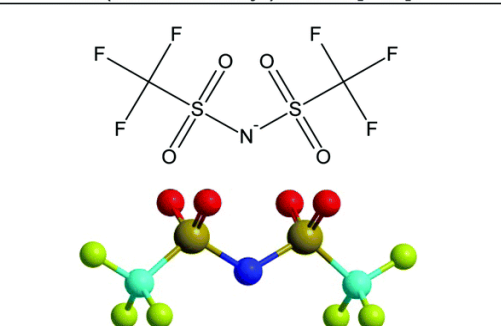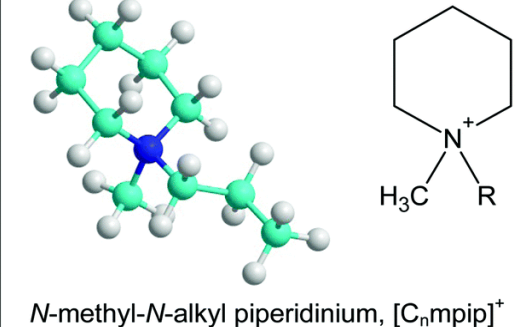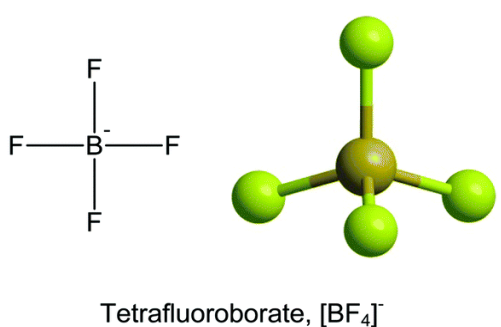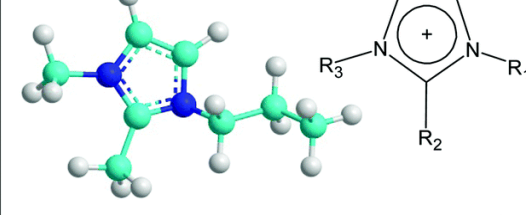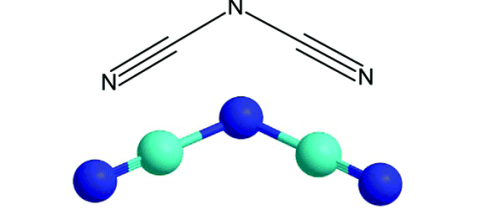
Cations	Anions
N,N-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium, [DEME]$^+$	Bis(fluorosulfonyl)imide, [FSI]$^-$
N-methyl-*N*-alkyl pyrrolidinium, [C$_n$mpyr])	Bis(trifluoromethanesulfonyl)amide,[NTf$_2$]$^-$
N-methyl-*N*-alkyl piperidinium, [C$_n$mpip]$^+$	Tetrafluoroborate, [BF$_4$]$^-$
1,2-dialkyl methylimidazolium, C$_n$C$_n'$mim]$^+$	Dicyanamide, [dca]$^-$

Figure 2.1: Commonly used anions and cations used in ionic liquids synthesis [31].

2.2.1. *Applications of ionic liquids*

Ionic liquids properties can be tuned and adjusted based on their molecular structure. Hence, several studies were conducted to identify and understand these properties in any given application. The major applications of ionic liquids are:

1. *Membrane separation processes*

The usage of ionic liquids in membrane separation technologies became an interest of several activities in both academic and industrial areas. Due to their unique properties, mainly the low melting point, extremely low vapor pressure, and tunable physicochemical properties, ionic liquids were involved widely in membrane development for various separation processes [33]. Several studies investigated the use of ionic liquids for different membrane separation applications. The table below summarizes some examples of these applications:

Table 2.1: Membrane separation applications incorporating ionic liquids.

Application	Ionic liquid	Compounds to separate	Ref.
Membrane absorption	[bmim][BF$_4$]	propylene/propane	[34]
Membrane extraction	[bmim][PF$_6$]	benzene derivatives	[35]
	[dC$_n$im][BF$_4$]	Tetrahydrofuran/ water	[36]
Membrane micro-extraction	[bmim][PF$_6$]	Organochlorine pesticides from soil	[37]
	[hmim][BF$_4$]	pesticides, aromatic amines	[38]
Membrane extractive distillation	[C$_2$OHmim][Cl]	water/tetrahydrofuran	[39]
	[emim][NTf$_2$]	aromatics/alkanes	[40]
Membrane pervaporation	[eeim][PF6] [eeim][Br]	acetone and butan-1-ol/water	[41]
	[N$_{3333}^+$][B(CN)$_4$]	1,3-propanediol	[42]
Membrane gas separation	[emim][NTf$_2$] [emim][dca] [thtdp][Cl]	N$_2$, CO$_2$, CH$_4$	[43]
	[dmim][NTf$_2$] [N$_{(1)888}^+$][NTf$_2$] [C$_8$Py][NTf$_2$]	N$_2$, H$_2$, O$_2$, C$_O$	[44]

2. *Liquid-liquid extraction*

Liquid-liquid extraction is a separation process governed by the chemicals distribution between two different liquid phases. Several advantages distinguish this technique from other separation technologies such as the ability to separate chemicals having high or similar boiling points, with reasonably high capacity and low material and energy consumption [45]. Conversely, the types of extractants that can be used for liquid-liquid extraction processes are relatively few currently. Hence, the separation efficiency is limited for separations of some mixtures, especially those with similar structures. In addition, the volatility of conventional extractants or extraction solvents makes the extractant recovery and subsequent purification of products very difficult especially if the solutes are also volatile as well as contaminating the environment [46].

The use of ionic liquids as extractants could be a potential solution to these problems because of their tuneable properties. ILs could be designed and tuned task-specifically, thus large separation selectivity could be achieved for numerous mixtures [47]. Moreover, ILs have negligible vapor pressures, consequently ILs are considered as environmental extractants and the separation of ionic liquids with volatile components could be simplified [48]. Liquid-liquid extraction using IL as extractant have been investigated in many research studies in the recent years such as:

- Sulfides and nitrides removal from gasoline and diesel [49]
- Aromatics separation from aliphatics [50]
- Pollutants removal from water [51]
- Biological substances separation from aqueous mixtures [52]

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3. *Charge Storage Devices*

The use of ionic liquids in charge storage devises have been the focus of study over the past few years due to their unique properties such as high voltage window and high cations and anions concentration for charge transport processes [53, 54]. Most of these studies have focused on the Purity of ionic liquids [55]. It was found that some impurities such as chloride or water affect the physical properties and the electrochemical performance of charge storage devises as well. Hence, several studies are being conducted about the effect of ILs purity on the electrochemical performance of these devices [55-57].

4. *Preparation of Nanoparticles*

Ionic liquids have been used in the preparation of various types of nanoparticles over the years. Nanoparticles are solid particles having a size of about 10-1000 nm and their structure is mainly dependant on the preparation methods such as nanorods, nanowire, nanoclusters or nanospheres. Nanotechnology is becoming more involved and connected with current sciences (e.g. physics, medicine, chemistry, biology, and electrical engineering) [58].

Several studies investigated the use of ionic liquids in synthesizing different types, such as iridium, palladium and semiconductor nanoparticles (e.g. Ge nanoclusters) [59-62]. All of these studies investigated the potential for electrochemical reactions and the high polarity of ILs in the preparation of nanoparticles [63].

Furthermore, ionic liquids have been used in the advanced battery technologies [64-66], advanced fuel cell technology [67-69], solar cells [70-72] and supercapacitors [73]. Ionic liquids have been also used in thermal storage applications due to their desirable

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features (e.g. adjustable melting point) [74, 75]. Additionally, the use of ionic liquids in CO_2 capture and separation processes have been extensively investigated through many research studies [31, 33]. Section 2.4 gives a detailed review of the reported literature on CO_2 separation using different types of ionic liquids.

2.2.2. *Green aspects of ionic liquids*

Ionic liquids are considered as "green solvents" because they became an excellent alternative of other organic solvents. Ionic liquids are safer solvents compared to conventional organic solvents because of their non-flammability, negligible vapour pressure, and the possibility to be reused [76]. Ionic liquids have been also considered as "designer solvents" [77-79]. In other words, they can adjust their properties to suit the requirements of a specific process. By simple modifications to the structure of the ions, properties like viscosity, density, hydrophobicity and melting point can be adjusted [80].

The key concern about ionic liquids is their unknown toxicity to humans and the environment. During the past few years, a huge interest has been given in studying the toxicity of ionic liquids [81-85]. Different levels of toxicity have been reported in the literature due to the huge variety of ionic liquids. Pretti et al. [83] have studied the acute toxicities of 18 ionic liquids on three water organisms, the cladocerans Daphnia magna, the Selenastrum capricornutum, and the zebrafish. The results showed that long-chain ammonium ILs have higher toxicity to algae, cladocerans, and fish, while ionic liquids based on sulfonium and morpholinium exhibited very low toxicities. It was found also that the replacement of one or two carbon atoms of the long alkyl chain with a higher

electronegative atom (e.g. oxygen or chlorine) reduces the acute toxicity of imidazolium based ionic liquids for algae and cladocerans.

Similar study was conducted by Bernot et al. on the acute effects of ionic liquids based on imidazolium on survival of the crustacean Daphnia magna [81]. It was found that toxicity is associated to the imidazolium cation and not to the anions (e.g. Br-, Cl-, BF4-, and PF6-). Additionally, the toxicity of the studied ionic liquids was found to be comparable to other chemicals that are being used in industrial and disinfection processes (e.g. phenol and ammonia), showing that these ILs can be more harmful to aquatic organisms than existing volatile organic solvents. Hernandez-Fernandez et al. have found that the IL water content affects the toxicity level of PF_6 based ionic liquids due to the degradation of this anion in the presence of water [86].

On the other hand, compared to existing organic solvents, the unmeasurable vapour pressure that is associated with ionic liquids result in less emissions and accordingly in a reduced exposure. Estimations of the risk of ILs on the environment, compared to conventional solvents, should not only consider toxicity but also this probably lowers the exposure to ILs. The limited exposure to ILs is not only because of their low vapour pressure, but also because of the lower bioaccumulation of ILs. Bioaccumulation, as the ability of penetration through the membranes and accumulation in organisms, can be measured by the octanol–water partition coefficient (K_{ow}). K_{ow} is a simple thermodynamic measurement that has been extremely used in estimating the impacts of chemical substance on aquatic environments. The higher octanol–water partition coefficient of a material, the easier to penetrate the membrane of an organic and accumulate in tissues, e.g. brain.

Ropel et al. [87] have measured the octanol-water partition coefficient for twelve imidazolium-based ILs. It has been found that all of K_{ow} values of the tested ILs are less than 15, even for the most hydrophobic ionic liquids, which is significantly less than K_{ow} of other common organic solvents because of the ionic nature of ILs. Hence, these ILs cannot accumulate or concentrate in the environment. The relation between the structure and the toxicity of ionic liquids was also explored by the above studies. For instance, Romero et al. [82] and Pretti et al. [83] found that the toxicity of IL was associated directly with the length of the alkyl chain in the cation while the anion cause slight effect on the toxicity.

Accordingly, the adjustable nature of ILs, and the relationship between the structure and the toxicity of the ionic liquids would allow the design of more environmentally friendly ILs. Nevertheless, more studies and deeper investigations are required to assess the risks assigned with ionic liquids. For that, a wider and more variant set of examination methods should be conducted, including studies concentrating on exposition pathways in addition to bioaccumulation and degradation processes.

2.3. Membranes for CO_2 Separation

Membrane technology is used in several gas separation applications, these applications includes [88]:

- Natural gas treatment (CO_2 separation from natural gas streams)

- Isolation and recovery of hydrogen

- Air separation (such as oxygen enrichment for some medical devices)

- Nitrogen enrichment from air that is used as atmosphere protecting process for oxygen sensitive compounds.

The most common used membrane materials for CO_2 separation are polymeric membranes, which can be processed into high surface area hollow fibres [89]. Inorganic porous membranes are widely used for operation inside combustion chambers due to their ability to withstand high temperatures [90].

The overall use of membranes in CO_2 removal applications is more economical due to small footprint, good mechanical stability and a larger contact area per unit volume [89]. Membrane systems give reductions of over 70 % in size and about 66 % in weight compared to conventional columns [91]. However, high-purity CO_2 separation may require numerous membranes with different characteristics, due to their limited ability to achieve high degrees of gas separation [92]. This then increase complexity, energy consumption and most of all total cost of the operation [18]. Therefore, further improvement is needed before using membranes a large scale for CO_2 capture [93]. Functionalized membranes may contribute to the separation by retaining some components more than others in the diffusion stage.

Gas separation membranes use the differences in partial pressure as their driving force for separation[94]. One component dissolves into the membrane, diffusing through the membrane before passing to the other side in the final stage [21]. The permeability calculation is carried out starting by mole balance around the membrane. Then flux and permeability can be calculated using Eqs. (1) and (2) respectively.

$$J_i = \frac{n_i}{t.A} \qquad (1)$$

$$P_i = \frac{J_i.l}{\Delta P_i} \qquad (2)$$

Where, A is the cross sectional area of the membrane (cm^2), t is the time of the experiment (s), l is the membrane thickness, and ΔP_i is the partial pressure difference of each gas. The permeability P_i and the flux J_i are given in ($\frac{cm^3(STP).cm}{cm^2.s.cmHg}$) and ($\frac{cm^3(STP)}{cm^2.s}$) respectively. The permeability is usually given by the unit (barrer), where (1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}). The selectivity or the separation factor $\alpha_{CO2/N2}$ is calculated using Eq. (3).

$$\alpha_{A/B} = \frac{Y_A/Y_B}{X_A/X_B} \qquad (3)$$

where Y_A and Y_B are the mole fractions of the permeate, whereas X_A and X_B are their corresponding mole fractions in the feed [95].

2.3.1 *Robeson's upper bound*

An essential constraint in the development of a membrane for gas separation processes is the trade-off between selectivity and permeability. This trade-off was established by Robeson's upper bound relationship which was shown to be valid for several gas pairs including H_2/N_2, O_2/N_2, He/N_2, CO_2/CH_4, CO_2/N_2, H_2/CH_4, He/H_2, H_2/CO_2, He/CO_2, and He/CH_4. Robeson's upper bound is expressed by $P_i = k\alpha_{ij}^n$, where P_i is the permeability of the high permeable gas, α is the selectivity or the separation factor, k is called the "front factor", and n is the slope of the log–log limit [96]. The front factor k and the slope values of Robeson's upper bound relationship are tabulated in Table 2.2.

Table 2.2: Values of the front factor k and the slope n of Rubeson's upper bound correlation [96].

Gas Pair	k (barrers)	n
O_2/N_2	1,396,000	−5.666
CO_2/CH_4	5,369,140	−2.636
H_2/N_2	97,650	−1.4841
H_2/CH_4	27,200	−1.107
He/N_2	19,890	−1.017
He/CH_4	19,800	−0.809
He/H_2	59,910	−4.864
CO_2/N_2	30,967,000	−2.888
N_2/CH_4	2,570	−4.507
H_2/CO_2	4,515	−2.302
He/CO_2	3,760	−1.192
He/O_2	NA	NA

Concerning the scope of this study which concentrates on CO_2/N_2 and CO_2/CH_4 separation, Robeson's upper bound curves of these two gases are shown in Figures 2.2 and 2.2.
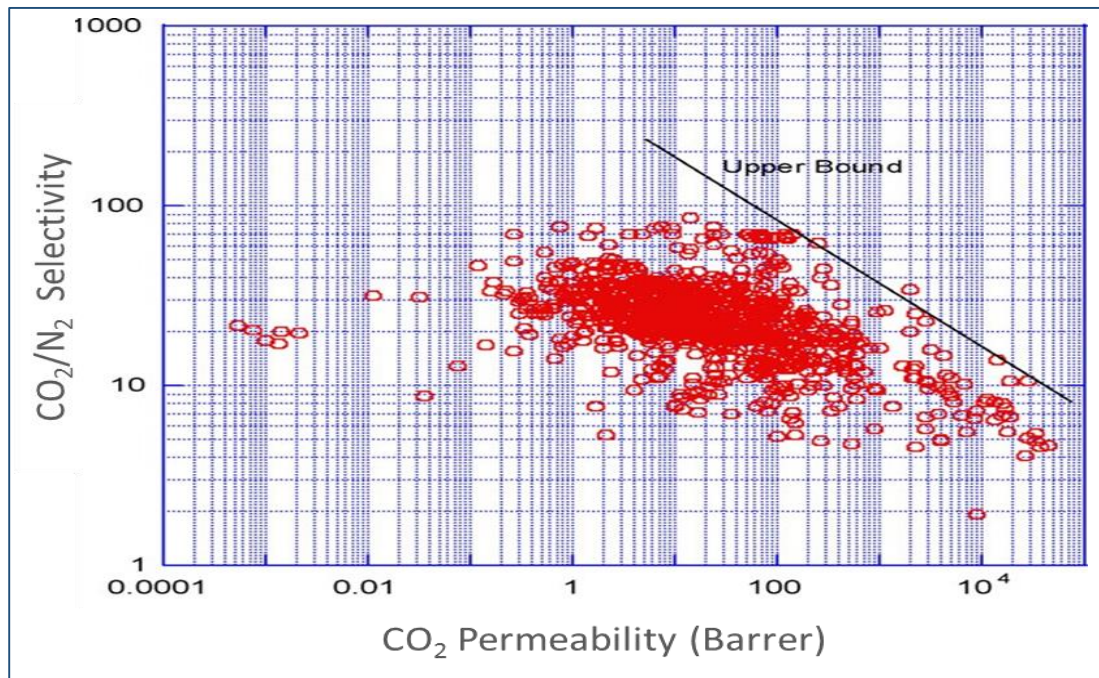
Figure 2.2: Robeson's upper bound correlation for CO_2/N_2 separation [96].
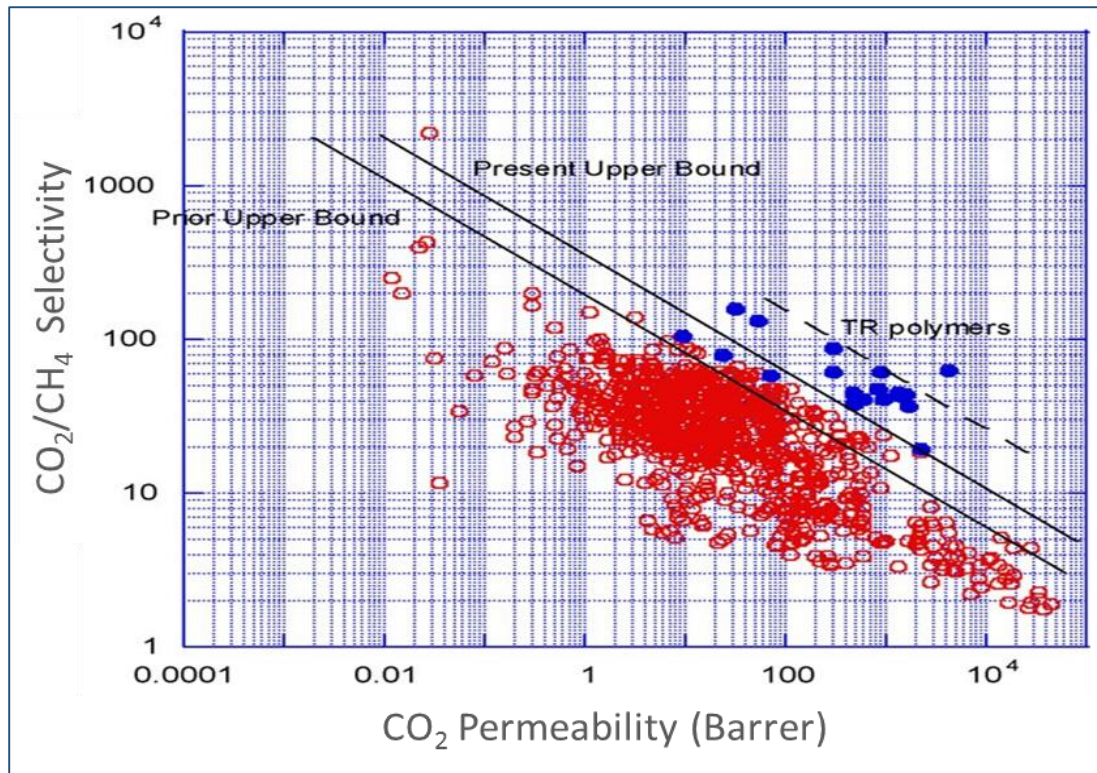
Figure 2.3: Robeson's upper bound correlation for CO_2/CH_4 separation [96].

In figure 2.3, two upper bounds are presented for CO_2/CH_4 separation. "Prior upper pound" is referred to the upper bound that was demonstrated in 1991 by Robeson [97], which was then updated with the latest results in literature to the "present upper bound" in 2008. It shows also a group of polymers (TR (thermally rearranged)) that shows exceptional separation efficiency. However these polymers are unique and considered in the molecular sieving materials class hence they were not included the 2008 upper bound. For CO_2/N_2, only one upper bound was presented in Figure 2.2 since there was no clear correlation before [96]. Robeson's upper bounds are being used in most of membrane research studies to compare the separations efficiency of their work with the reported literature.

2.3.2 *Polysulfones for CO_2 Separation*

Polysulfone (PSF) is considered to be one of the most widely investigated polymeric membrane material for CO_2 separation from several gas streams [98, 99]. Gas permeation properties of PSF blends have been extensively studied because of its low cost, chemical stability and the mechanical strength [11]. These studies include mixed gas and pure gas permeation properties for several gas mixtures including CO_2/N_2 and CO_2/CH_4. Several types of PSF blends were developed over the years for CO_2 separation. However, obtaining high selectivity and maintaining membrane efficiency in the presence of complex feed were the main two challenges of PSF development [88]. Many studies have been conducted to overcome those challenges by developing the synthesis process, formulation, and conducting material modification [98].

Several reviews explored the permeation properties of polymeric membranes incorporating polysulfones for CO_2/N_2 and CO_2/CH_4 separation. Powell and Qiao conducted a review on polymeric CO_2/N_2 separation membranes; the review reported the permeation properties of different polyslufone based membranes (Table A.1) [99]. An extensive review was also conducted on polysulfones membranes for CO_2/CH_4 separation by Julian and Wenten [98] (Table A.2). Both reviews reported results of pure gas measurements at different conditions. Results of mixed gas measurements would differ in values. However, mixed gas data would be more relevant to industrial applications hence this study was conducted on mixed gas measurements.

Plotting he results of both reviews on log-log curve of selectivity versus CO_2 permeability with Robeson's upper bound correlation would give a clear image of the

behaviour of the reported PSF blends compared to other polymers (Figures 2.4 and 2.5).

Figures 2.4 and 2.5 include some reported values of mixed gas measurements.
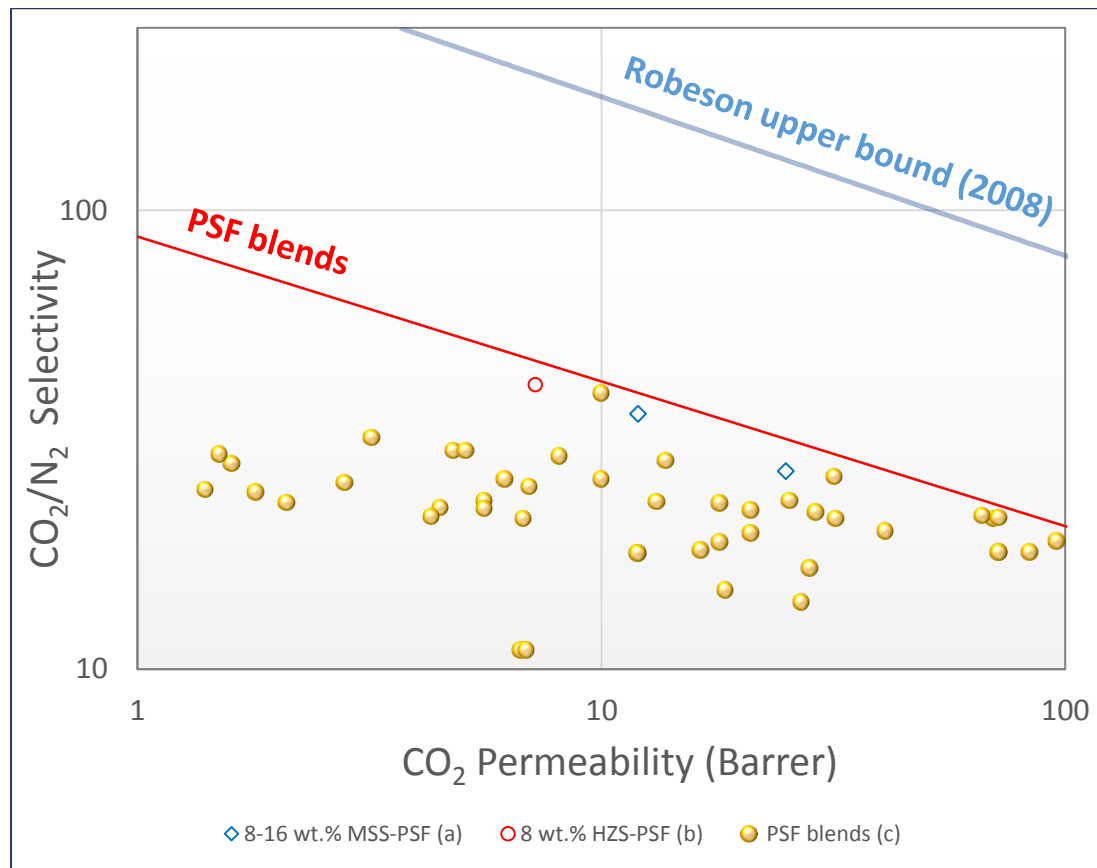
Figure 2.4: Permeability and selectivity values of CO_2/N_2 for (a) Mixed gas (feed: 50/50 mol% CO_2/N_2, 1.75 bars and 35 °C) [100], (b) Mixed gas (feed: 50/50 mol% CO_2/N_2, 2.75 bars and 35 °C) [101], and (c) Dense PSF blends (single gas at different conditions) [99].

Zornoza and co-workers conducted two studies exploring the effect of dispersed mesoporous silica spheres (MSSs) and hollow silicalite-1 spheres (HZSs) on polysulfone efficiency in CO_2/N_2 separation [100, 101]. The two studies were conducted for mixed gas feed with 50/50 mol% CO_2/N_2 at 35 °C and different pressure difference (1.75 and 2.75 bars respectively). Authors found that the optimum MSSs loadings is 8 wt% into PSF which increased the permeability of CO_2 from 5.9 barrer to 12.6 barrer, and the selectivity from 24 to 36. However, loadings of 8 wt% HZSs increased CO_2 permeability to 7.2 barrer and the selectivity to 41.7.
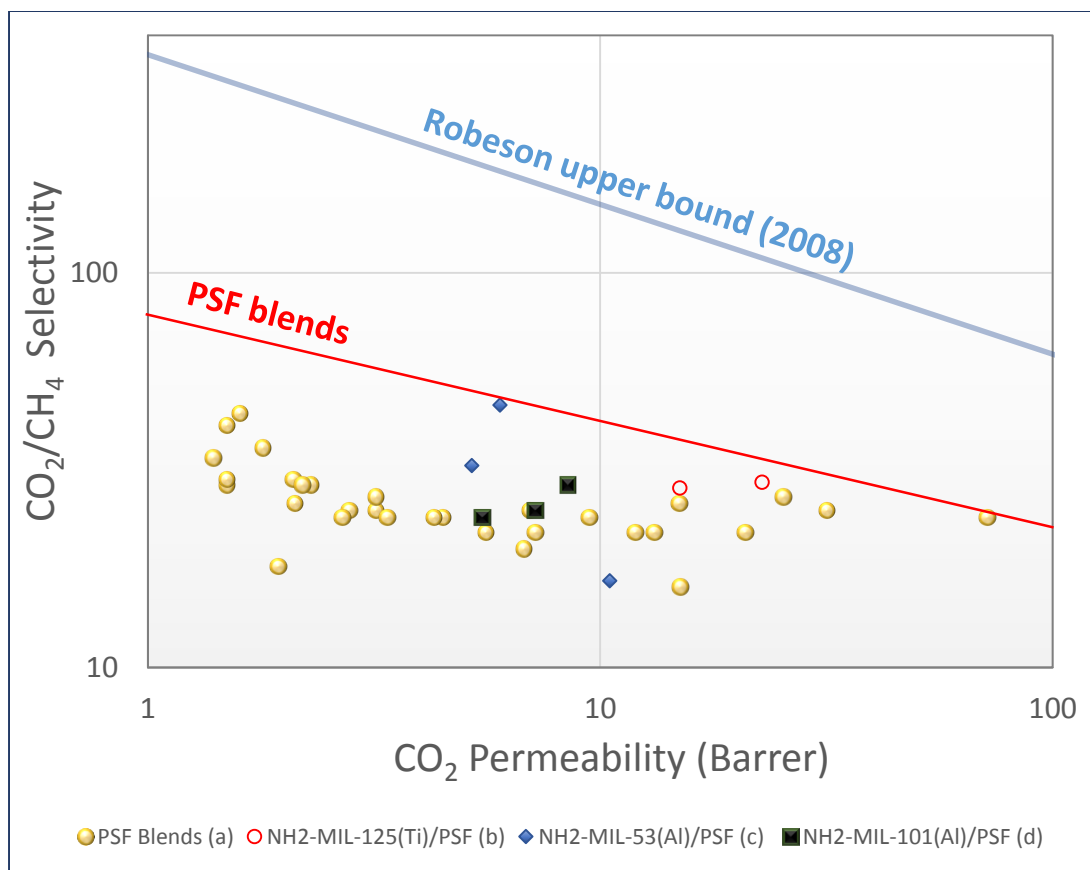
Figure 2.5: Permeability and selectivity values of CO_2/CH_4 for (a) Dense PSF blends (single gas at 10 bars) [98], (b) Mixed gas (feed: 50/50 mol% CO_2/CH_4, 10 bars and 30 °C) [102], (c) Mixed gas (feed: 50/50 mol% CO_2/CH_4, 3 bars and 35 °C) [103], and (d) Mixed gas (feed: 50/50 mol% CO_2/CH_4, 3 bars and 35 °C) [104].

Another study was conducted by Zornoza et al on the effect of the flexible metal organic framework NH_2-MIL-53(Al) on PSF efficiency in CO_2/CH_4 separation [103]. The study used a feed of equimolar CO_2/CH_4 mixture and conducted at 3 bars and 35 °C. The highest performance was achieved with 25 wt% NH_2-MIL-53(Al) which recorded CO_2 permeability of 6 barrer and CO_2/CH_4 selectivity of 46.2. Guo and co-workers prepared polysulfone based mixed matrix membranes (MMMs) incorporated with amine-functionalized titanium-based metal organic framework (MOFs), NH_2-MIL-125(Ti). The prepared membranes were tested on equimolar CO_2/CH_4 mixture separation at 10 bars and 30 °C. At these conditions, PSF loaded with 20 wt% NH_2-MIL-125(Ti) achieved the highest selectivity of 29.5 and CO_2 permeability of 22.8 barrer [102].

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Rodenas and Dalen et al investigated the effect of different loadings of NH_2-MIL-101(Al) on PSF. Mixed separation measurements used an equimolar CO_2/CH_4 mixture at steady operation (3 bars and 35 °C). The highest performance membrane was PSF loaded with 25 wt% of the MOF with CO_2 permeability of 8.5 barrer and CO_2/CH_4 selectivity of 29.

2.4. Supported Ionic Liquid Membranes (SILMs) for CO_2 Separation

One of the most growing processes in the development of membrane science is the supported ionic liquid membranes technology (SILMs). Due to their special properties, e.g. high thermal and chemical stability and low vapour pressure, ILs became an ideal alternative of conventional organic solvents in a wide range of chemical applications at lab scale, such as separation and purification and chemical catalysis [29, 105-109]. The high thermal stability of ionic liquids provides considerable potential to utilise ionic liquids for CO_2 capture applications. Most ionic liquids are stable to over 300 °C and therefore less likely to degrade *via* oxidation, to react with impurities or to be corrosive [110]. In addition, because ILs have negligible vapour pressure, this creates a possibility of ILs regeneration over a wide range of temperatures and pressures. Thus, this offers a new chance for process optimisation that is not achievable using traditional liquid media. Additionally, ionic liquids are considered as green solvents compared to other volatile organic solvents. One of the biggest drawbacks to the large scale use of ILs in CO_2 capture is their higher cost compared to the conventional solvents they are proposed to replace [111]. However, by eliminating or reducing process losses through thermal degradation, chemical or

oxidative destruction and vapour loss, the solvent amount needed for the process may be greatly reduced [14].

Ionic liquids are being investigated for several membrane applications such as membrane absorption, membrane extraction, membrane extractive distillation, membrane pervaporation, membrane vapour separation, and membrane gas separation [33]. Petra and Katalin conducted an extensive review on the current applications of ionic liquids in membrane separation processes [33]. Several gases were examined in these studies including N_2, CO_2, CH_4, H_2, O_2, SO_2, etc. Since the scope of this study is to explore the permeation properties of CO_2, N_2, and CH_4 through the synthesized membranes, section 2.2.1 review the reported literature on SILMs permeation properties of these gases.

2.4.1   *SILMs permeation properties for CO_2/N_2 and CO_2/CH_4 separation*

Advantages of both ionic liquids and membranes can be combined by the synthesis of effective supported ionic liquid membranes (SILMs). Many recent studies have discussed the effect of ILs on CO_2/N_2 and CO_2/CH_4 separation through polymeric membranes. These studies were conducted using different membrane support types, conditions and ILs. Some of these studies were performed on the behaviour of pure gas through the membrane [112, 113], while others concentrated on mixed gas separation [114-116].

Cserjési et al. investigated SILMs using two common and ten novel types of ionic liquids supported by hydrophobic PVDF having porosity of 75% and pore size of 0.22 μm [112]. Only eight of these ILs were used in SILMs preparation because others

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have destroyed the supporting membrane material. Pure gas permeation measurements were conducted at a pressure difference of 2 bars and 30 °C. The obtained CO_2/N_2 selectivities ranges between 10.9 and 52.6 with ECOENGTM 1111P and AMMOENGTM 100 respectively. In contrast, the highest CO_2/CH_4 selectivity was only 13.1 with [emim][CF_3SO_3].

Another study on SILMs for pure gas permeation was conducted by Bara et al. [113]. Three ionic liquids were used in the study supported by polyethersulfone (PES) with porosity of 80% and 0.2 μm pore size. Permeation measueremnts were conducted at 0.85 bar and 23 °C. The obtained CO_2/N_2 selectivities were 27, 21, and 16 with [MpFHim][NTf_2], [MnFHim][NTf_2], and [MtdFHim][NTf_2] respectively. However, CO_2/CH_4 selectivities were 19, 17, and 13 with [MpFHim][NTf_2], [MnFHim][NTf_2], and [MtdFHim][NTf_2] respectively.

Neves and co-workers studied the effect of different ILs on the pure gas permeation properties of Porous polyvinylidene fluoride (PVDF) [114]. PVDF used in the study has 75% porosity and 0.22 μm pore size. The prepared SILMs achieved high CO_2/CH_4 selectivities when compared to literature. CO_2/CH_4 selectivities were 228 ± 1.5, 113 ± 1.6, 187 ± 1.7, and 105 ± 0.5 with [C_4mim][PF_6], [C_4mim][BF_4], [C_4mim][Tf_2N], and [C_8mim][PF_6] respectively. In contrast, the obtained CO_2/N_2 selectivities are lying within the reported results in other literatures and are 23 ± 0.5, 35 ± 0.2, 39 ± 0.1, and 23 ± 0.5 with [C_4mim][PF_6], [C_4mim][BF_4], [C_4mim][Tf_2N], and [C_8mim][PF_6].

Scovazzo et al. studied the pure gas permeation properties of several ionic liquids supported by porous glass fiber support to limit the mass transport to molecular diffusion through ILs only. Pure gas permeability measurements were performed at a

very low pressure (7 Pa) to prevent the ILs from penetrating the support. The highest CO_2/N_2 and CO_2/CH_4 selectivities were 57 ± 4.4 and 23 ± 5.1 respectively and obtained with [emim][dca]; while the lowest selectivities were obtained with [C_6mim][Tf$_2$N] and found to be 15 ± 1.8 and 8.5 ± 0.3 for CO_2/N_2 and CO_2/CH_4 respectively. Table 2.3 summarizes some of the pure gas permeation results reported in the literature.

Table 2.3: Ideal (pure gas) CO₂/N₂ and CO₂/CH₄ selectivity values of commonly used ILs.

Ionic Liquid	$\alpha_{CO2/N2}$	$\alpha_{CO2/CH4}$	Support membrane	Pore size (µm)	Porosity	ΔP (bar)	T (°C)	Ref.
[bmim][BF$_4$]	52.3	8.18	Polyvinylidene fluoride (PVDF)	0.22	75%	2	30	[112]
AMMOENG™ 100	52.6	7.93						
ECOENG™ 1111P	10.9	6.38						
Cyphos 102	41.5	6.87						
Cyphos 103	43.1	5.62						
Cyphos 104	31.6	5.17						
[emim][CF$_3$SO$_3$]	34.0	13.1						
[SEt$_3$][NTf$_2$]	26.2	6.67						
[MpFHim][NTf$_2$]	27	19	Polyethersulfone (PES)	0.2	80 %	0.85	23	[113]
[MnFHim][NTf$_2$]	21	17						
[MtdFHim][NTf$_2$]	16	13						
[C$_4$mim][PF$_6$]	23 ± 0.5	228 ± 1.5	Polyvinylidene fluoride (PVDF)	0.22	75%	0.7	30	[114]
[C$_4$mim][BF$_4$]	35 ± 0.2	113 ± 1.6						
[C$_4$mim][Tf$_2$N]	39 ± 0.1	187 ± 1.7						
[C$_8$mim][PF$_6$]	23 ± 0.5	105 ± 0.5						
[emim][BF$_4$]	44 ± 1.7	22 ± 1.1	Glass fiber support	1	N/A	7×10^{-5}	30	[115]
[emim][CF$_3$SO$_3$]	40.5	18.5						
[emim][Tf$_2$N]	23 ± 1.7	12.2 ± 0.9						
[C$_6$mim][Tf$_2$N]	15 ± 1.8	8.5 ± 0.3						
[bmim][BETI]	16.7	9.9 ± 0.3						
[emim][dca]	57 ± 4.4	23 ± 5.1						

Since supported ionic liquid membranes have potential for large scale use in the industrial applications, several studies investigated SILMs use for mixed gas separation applications (Table 2.3) [114-116]. Neves et al investigated SILMs based on the 1-n-alkyl-3-methylimidazolium cation supported by polymeric membranes for mixed gas separation [114]. CO_2/N_2 and CO_2/CH_4 equimolar binary mixtures were used in the permeation measurements at 30 °C and a pressure up to 0.7 bar. Four ionic liquids were used in mixed gas permeation measurements: [C$_4$mim][PF$_6$], [C$_4$mim][BF$_4$], [C$_4$mim][Tf$_2$N], and [C$_8$mim][PF$_6$] supported by polyvinylidene fluoride (PVDF). The results showed that the synthesized SILMs exhibited CO_2/N_2 selectivity ranging between 20 and 32 which is considered to be normal behaviour compared to the reported literature. However in case of CO_2/CH_4 separation, the prepared SILMs exhibited high selectivity values up to 200 with [C$_4$mim][PF$_6$]. The lowest CO_2/CH_4 selectivity was 98 which was obtained with [C$_8$mim][PF$_6$].

Scovazzo et al. [115]studied separation of the binary gas mixtures CO_2/CH_4 and CO_2/N_2 using continuous feed of the mixed gas. Six ionic liquids were used in this study, [emim][BF$_4$], [emim][CF$_3$SO$_3$], [emim][Tf$_2$N], [C$_6$mim][Tf$_2$N], [bmim][BETI] supported by polyethersulfone (PES) membrane and [emim][dca] supported by polyvinylidene fluoride (PVDF) membrane. The highest CO_2/CH_4 and CO_2/N_2 selectivity results were 27 and 21.2 using [emim][BF$_4$] and [emim][Tf$_2$N] respectively. Both supports, PES and PVDF, used in the study have high porosity of 80%. Permeation measurements were conducted at 30 °C and a pressure difference of 2.07 to 3.07 bars.

Another study on SILMs for mixed gas separation was conducted by Hojniak et al [116]. Authors prepared SILMs using porous γ-alumina discs as membrane support

with different ionic liquids, monocationic and dicationic ionic liquids. The synthesized ionic liquids are shown in Table 2.4.

Table 2.4: List of the synthesized ionic liquids by Hojniak et al. [116]

IL Type	ILs	Ionic liquid Name
Monocationic	**1a**	1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylpyrrolidinium p-toluenesulfonate
	1b	1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylpiperidinium p-toluenesulfonate
	1c	1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylmorpholinium p-toluenesulfonate
	1d	1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylimidazolium p-toluenesulfonate
Dicationic	**2a**	1,8-Bis[1-methylpyrrolidinium)]-3,6-dioxaoctane di(p-toluenesulfonate)
	2b	1,8-Bis[1-methylpiperidinium)]-3,6-dioxaoctane di(p-toluenesulfonate)
	2c	1,8-Bis[1-methylmorpholinium)]-3,6-dioxaoctane di(p-toluenesulfonate)

The obtained results showed that the prepared SILMs exhibited comparable behaviour to the literature as they lie in the same ranges. CO_2/N_2 selectivity results obtained with these SILMs were ranging between 15.2 and 34.7 while CO_2/CH_4 selectivity values were between 12.6 and 31.8. Table 2.5 summarizes some of the mixed gas permeation results reported in the literature.

Table 2.5: Mixed gas CO_2/N_2 and CO_2/CH_4 selectivity values of commonly used ILs.

Ionic Liquid	$\alpha_{CO2/N2}$	$\alpha_{CO2/CH4}$	Support membrane	Pore size (µm)	Porosity	ΔP (bar)	T (°C)	Ref.
[C4mim][PF6]	20 ± 1.6	200 ± 1.5						
[C4mim][BF4]	32 ± 0.1	102 ± 0.6	polyvinylidene fluoride (PVDF)	0.22	75%	0.7	30	[114]
[C4mim][Tf2N]	30 ± 0.5	161 ± 0.5						
[C8mim][PF6]	21 ± 1.6	98 ± 0.5						
[emim][BF4]	N/A	27±0.8						
[emim][CF3SO3]	N/A	22±1.2	hydrophilic polyethersulfone (PES)	0.1	80%	2.07 - 3.07	30	[115]
[emim][Tf2N]	21.2	17±0.9						
[C6mim][Tf2N]	N/A	9.9±0.9						
[bmim][BETI]	12.2	N/A						
[emim][dca]	N/A	24±1.4	hydrophilic polyvinylidene fluoride (PVDF)					
1a[a]	15.2	12.6						
1b[b]	17.2	15.4						
1c[c]	17.6	14.2	Porous γ-alumina discs	0.003-0.005	N/A	N/A	N/A	[116]
1d[d]	16.3	16.1						
2a[e]	27.9	22.4						
2b[f]	24.1	20.2						
2c[g]	34.7	31.8						

The use of single gas permeation measurements to model real mixed gas systems can result in significant error as a result of the competition sorption inside the membrane [117]. Several studies showed that the selectivity decreases with mixed gas systems compared to pure gas systems. Scholes et al. found that the loss percentage in CO_2 permeability is about 3.7% for polysulfone.

Similar results were observed by Neves et al. with respect to CO_2/N_2 and CO_2/CH_4 separation [114]. Separation selectivities with pure gas systems was found to be higher than those with mixed gas measurements. Figures 2.6 and 2.7 compare the CO_2/N_2 and CO_2/CH_4 single gas selectivities (ideal selectivities) with mixed gas selectivities.
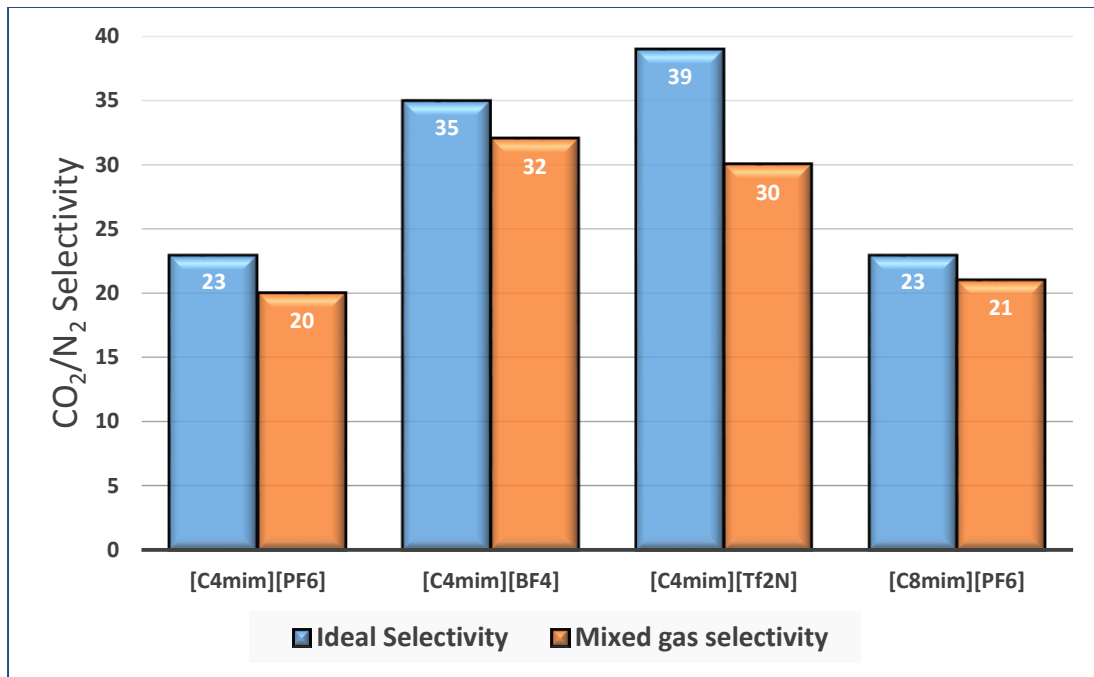
Figure 2.6: Single gas versus mixed gas CO_2/N_2 selectivities for different SILMs reported by Neves et al. [114]
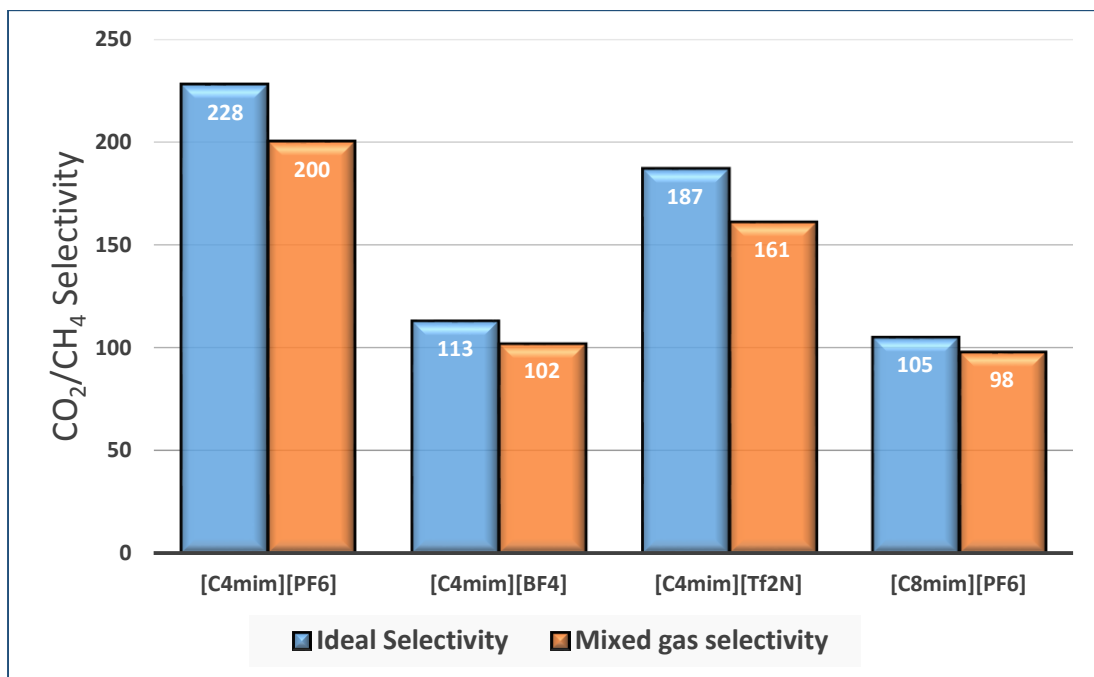
Figure 2.7: Single gas versus mixed gas CO_2/CH_4 selectivities for different SILMs reported by Neves et al. [114]

Figures 2.6 and 2.7 showed that for all tested SILMs, CO_2/N_2 and CO_2/CH_4 mixed gas selectivities are lower than that obtained with single gas system. However, the

difference between the results obtained with the two systems is not significant due to the low pressure applied across the membrane [88, 114].

Scovazzo et al. [115] observed also a slight reduction in the CO_2/N_2 mixed gas selectivities when compared with pure gas selectivities (figure 2.8) using [emim][Tf2N] and [bmim][BETI] supported by polyethersulfone (PES). In contrast, an opposite observation was reported by authors with respect to CO_2/CH_4 measurements. CO_2/CH_4 selectivities obtained with mixed gas system was found to be higher than those obtained with single gas system (Figure 2.9). however, in both CO_2/N_2 and CO_2/CH_4 measurements, the variation between selectivities obtained with pure and mixed gas systems is not significant and this can be due to the low pressure applied across the membrane as discussed above.
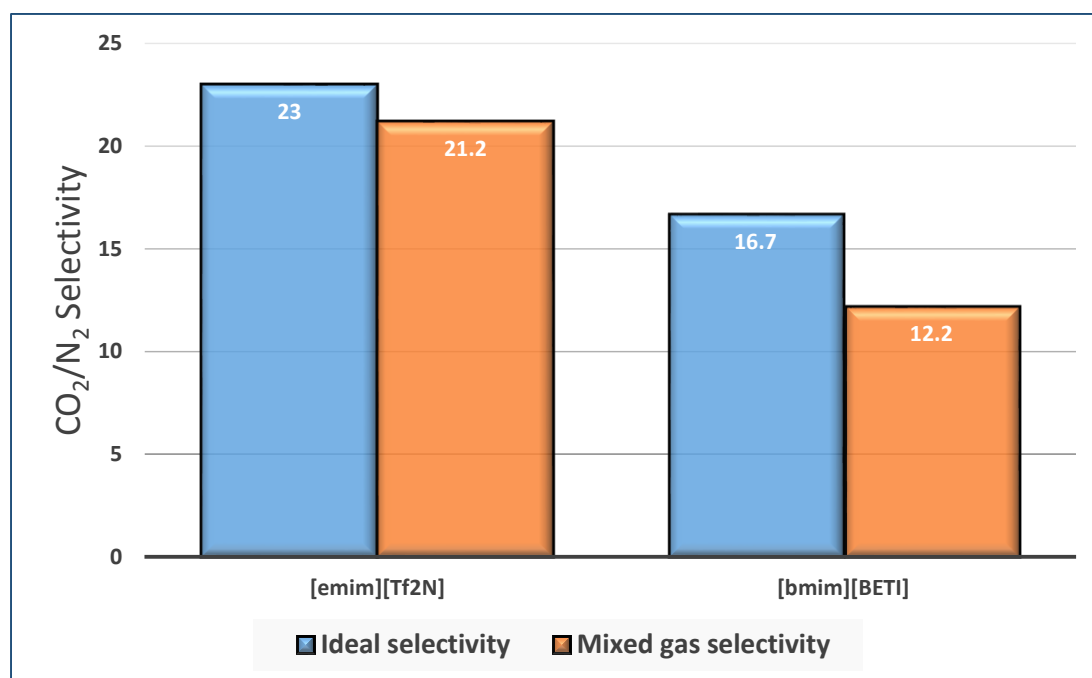
Figure 2.8: Single gas versus mixed gas CO_2/N_2 selectivities for different SILMs reported by Scovazzo et al. [115]
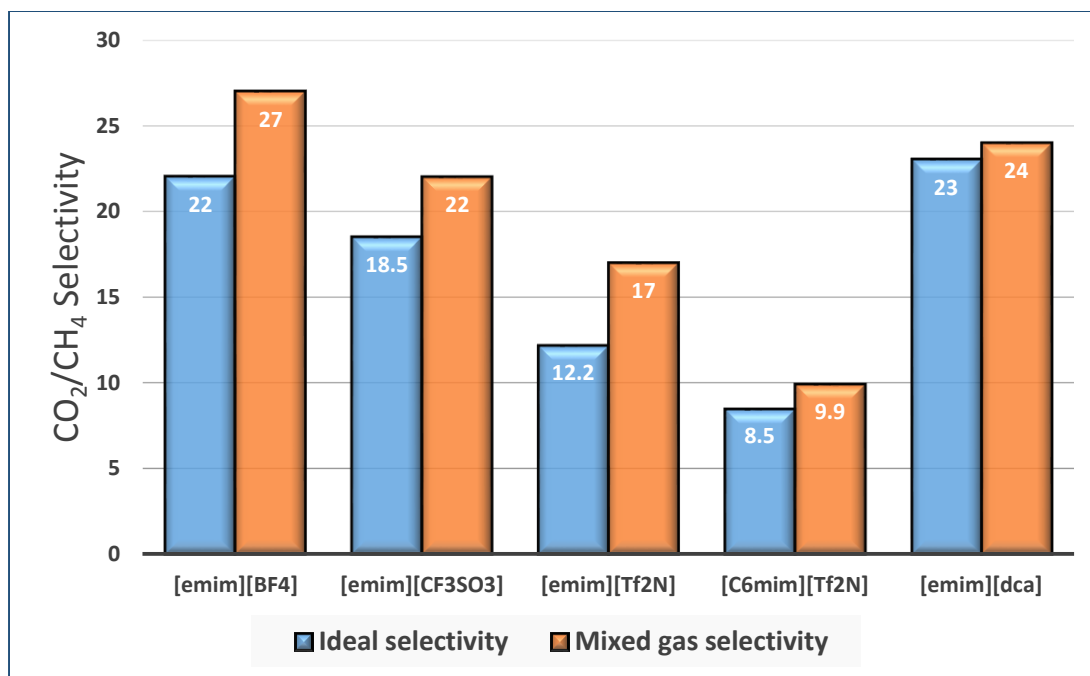
Figure 2.9: Single gas versus mixed gas CO$_2$/CH$_4$ selectivities for different SILMs reported by Scovazzo et al. [115]

2.2.3. SILMs stability in gas separation

One of the most essential parameters of SILMs in gas separation is their stability under different pressures and temperatures. The high porosity of the support membrane, which is common issue in most of the reported studies in the literature, can lead to membrane failure with high pressure due the loss of ILs. Hence, the pressure difference across the membrane is limited to a very low pressure in most of those studies.

Hernández-Fernándeza et al. studied the influence of the immobilization method on SILMs stability with respect to ionic liquids loss [118]. SILMs based on [bmim+][BF$_4$−], [bmim+][PF$_6$−], [bmim+][Cl−] and [bmim+][NTf$_2$−] were synthesized using Hydrophilic Nylon® (polyamide) with 0.45 μm pore size as the support membrane. These SILMs were synthesized by two immobilization methods including pressure or vacuum. In the first method, small amount of the ionic liquids

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was added on the membrane surface and placed in an ultrafiltration unit. Then, N_2 gas was applied with a pressure of 2 bar to force ILs to flow through the membrane pores. The second method involves submerging the support membrane in a small amount of the ionic liquid and a vacuum then was applied to remove the air from the support pores. Stability measurements were conducted using glass diffusion cell for 7 days where TBME and n-Hexane were used as the receiving and feed solutions respectively. Ionic liquid losses were determined by weight difference of the fresh and used membranes. The results of the study are presented in Figure 2.10 and show that SILMs prepared with both methods exhibited large ionic liquid losses.
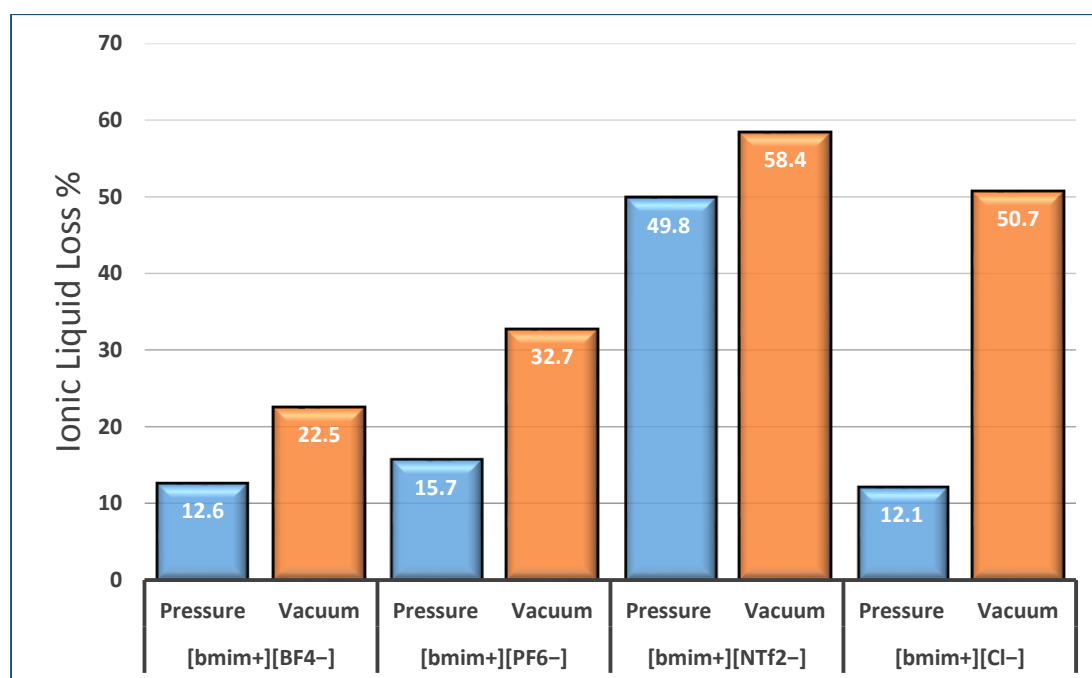
Figure 2.10: Ionic liquid loss of SILMs prepared with pressure and vacuum immobilization reported by Hernández-Fernándeza et al. [118]

Figure 2.10 shows that SILMs prepared with vacuum exhibited a loss of 22.5, 32.7, 58.4, and 50.7 % with SILMs based on [bmim+][BF$_4$−] [bmim+][PF$_6$−], [bmim+][NTf$_2$−], and [bmim+][Cl−] respectively. In contrast, SILMs prepared using immobilization with pressure were more stable and exhibited lower IL losses. The

losses were 12.6, 15.7, 49.8, and 12.1 % with SILMs based on [bmim+][BF4−]
[bmim+][PF6−], [bmim+][NTf2−], and [bmim+][Cl−] respectively.

Neves et al. [114] studied the effect of the applied pressure and the support type on
SILMs stability with respect to ILs Losses. Two distinct polymeric supports were used,
hydrophilic PVDF and hydrophobic PVDF. SILMs weight as function of time is
represented in Figure 2.11 (a) and (b) for SILMs based on hydrophilic and hydrophobic
supports respectively. The results showed that SILMs supported by hydrophilic PVDF
exhibited lower stability since membrane weight declined by 11 to 13% after 10 h with
all SILMs. However, the weight of SILMs supported by hydrophobic PVDF declined
by about 1, 3, and 7% with SILMs based on [C4mim][Tf2N], [C4mim][PF6], and
[C8mim][PF6] respectively after 1 h and then stabilize. Hence, SILMs with
hydrophobic support were considered to be more stable.
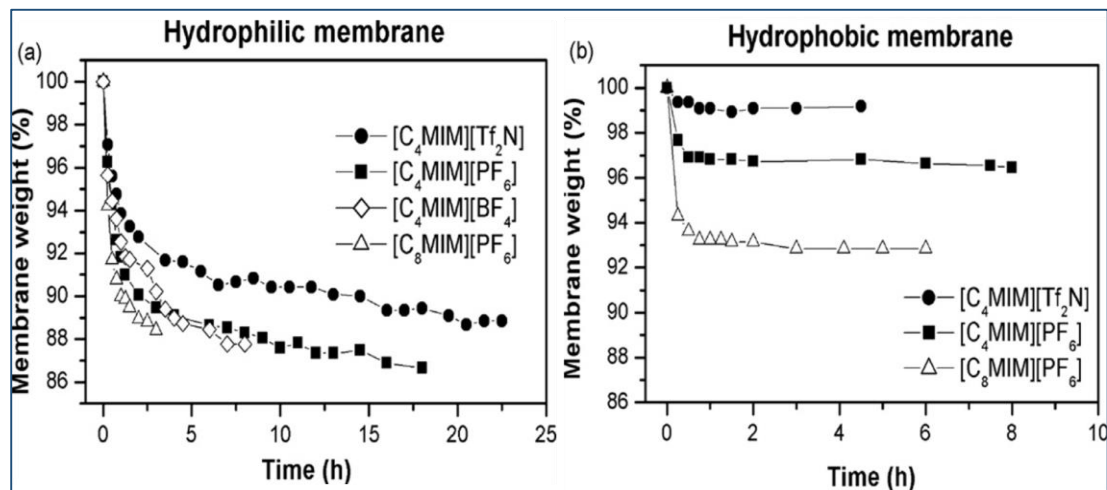
Figure 2.11: Weight of SILMs based on (a) hydrophilic, and (b) hydrophobic membranes immobilised with different ILs as a function of time (pressure difference: 1 bar) [114].

The effect of the applied pressure on the ionic liquid loss was also reported in the study
for hydrophilic and hydrophobic supports respectively. The results showed that
membrane weight of both SILMs have declined at 1 bar and continue decreasing with

higher pressure until the decrease became significant at a pressure of 2 bar, which indicates possibility of membrane failure with the time.

Another study on ionic liquid loss was conducted by Zhao and co-workers [119]. They synthesized SLIMs based on [bmim][BF$_4$] supported by polyethersulfone (PES), nylon 6 (N6), and polyvinylidene fluoride (PVDF). Ionic liquid loss measurements were conducted with respect to gas separation performance and the SILMs weight loss. Ionic liquid losses were determined after a run of 420 min for PES based SILMs. However, losses of SILMs based on N6 and PVDF were tested only at 150 min because of membrane failure after this time. Hence, SILMs prepared with PES showed the highest stability compared to the other two support membranes. Stability results of the study are summarized in Table 2.6.

Table 2.6: Ionic liquid losses as function of pressure and pore size [119]

Membrane	Pore size (µm)	Cross membrane pressure difference (bar)					
		0.8	1	2	2.5	3	3.5
PES	**0.1**	1.8	8.7	45.7	50.3	54.9	68.8
PES	**0.2**	13.6	18.6	53.1	58	62.9	–
PES	**0.45**	14.7	19.7	59.1	–	–	–
N6	**0.2**	15.8	22.6	–	–	–	–
PVDF	**0.22**	25.2	32.8	–	–	–	–

It is shown that all prepared SILMs exhibited a loss of ILs and this loss is proportional to the pressure difference and the pore size as well. Although SILMs with PES support were more stable than other SILMs, the reported results shows about 18.6 and 19.7% loss of ILs with supports having 0.2 µm and 0.45 µm respectively at 1 bar; then ILs loss became more significant (>50%) at higher pressures. On the other hand, SILMs with N6 and PVDF supports exhibited more ILs losses hence caused a membrane failure at low pressure after only 150 min.

3. Methodology & Experimental Work

3.1. *Materials*

Polysulfone with an Average Mw of ~ 22,000 was obtained from Fisher Scientific UK Limited. Chloroform with 99.8% purity (obtained from Sigma Aldrich) was used throughout the experiment as a casting solvent. Ionic liquids were synthesized based on green synthetic routes described by Ferguson *et al* [120] and submitted to first stage purification at The Queen's university Ionic Liquid Laboratories, Belfast (QUILL). These ionic liquids are 1-alkyl-3-methylimidazolium bistriflamide $[C_4mim][NTf_2]$ and Di-iso-propyl 1-alkyl-3-methylimidazolium bistriflamide $[DIP-C_4mim][NTf_2]$, Tributylmethylphosphonium formate $[P_{4441}][formate]$, and Tributylmethylammonium formate $[N_{4441}][formate]$. CO_2/N_2 and CO_2/CH_4 gas mixture, with certified composition of 4.94 mol% CO_2 and 5 mol% and balance N_2 and CH_4 respectively, were obtained from Buzuair Scientific and Technical Gases, Qatar.

3.2. *Synthesis of plain PSF and DPSILMs*

In order to cast ILs within fabricated polymeric membranes, a solvent that can dissolve both the ionic liquid and the polymer simultaneously is essential. A 15 wt.% of PSF in chloroform solution was prepared. Different concentrations of $[P_{4441}][formate]$, $[DIP-C_4mim][NTf_2]$, $[C_4mim][NTf_2]$, and $[N_{4441}][formate]$ were then blended with the polymer solution by direct mixing. The solution was stirred by means of magnetic stirrer for about 24 hr at room temperature (~22 °C). The resulted homogenous solution was then casted uniformly on a flat glass plate with the help of an Elcometer 3700 Doctor Blade (Belgium), maintaining clearance gap of the elcometer at ~80 µm. The

resulting film was then dried for 24 h at room temperature to ensure a complete evaporation of chloroform. The casted membranes were then peeled off the glass plate. Figure 3.1 summarizes the procedure of DPSILMs synthesis. The synthesized DPSILMs were dense, clean, self-supporting, and flexible. Table 3 lists the used ILs in the prepared DPSILMs.
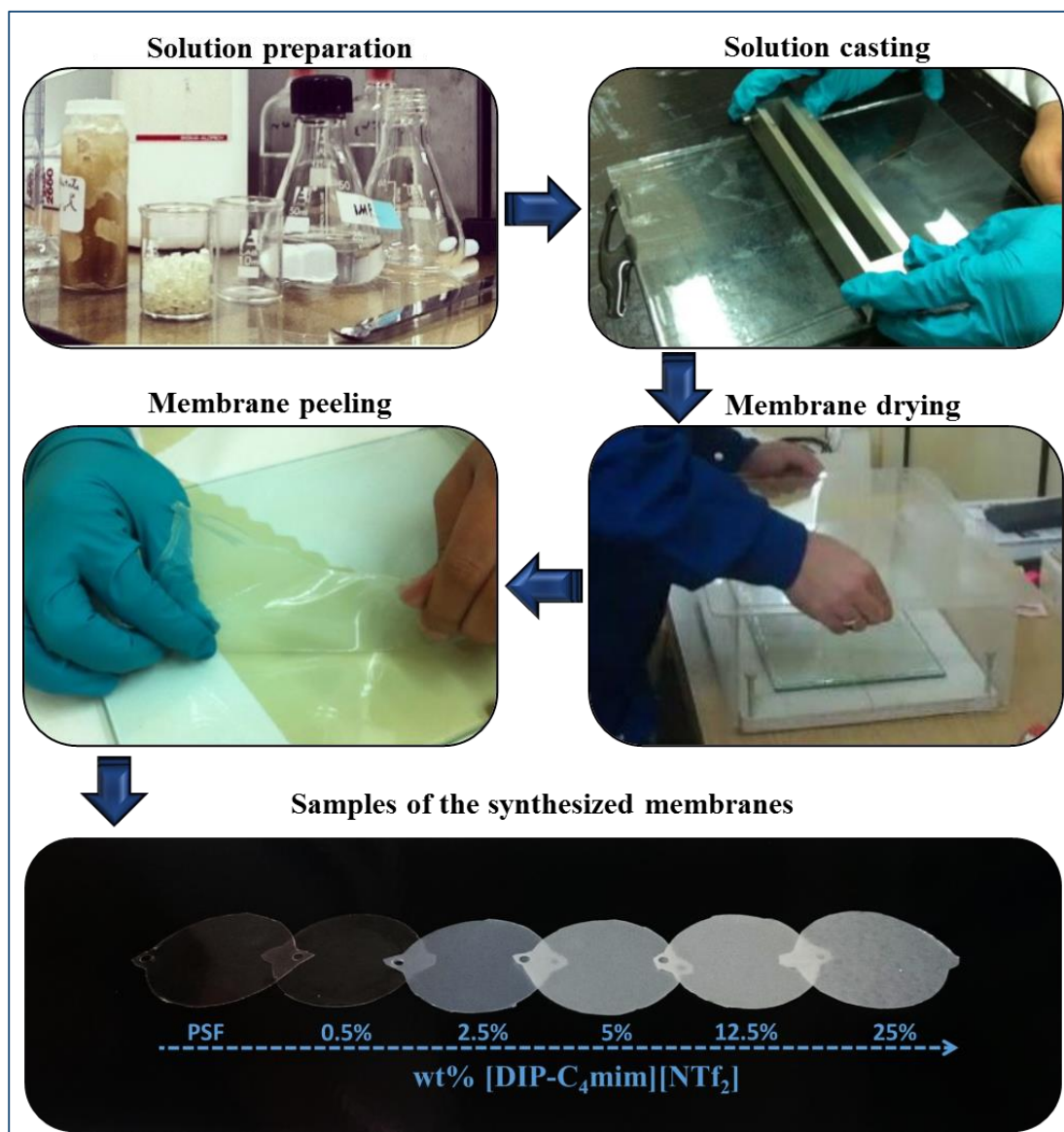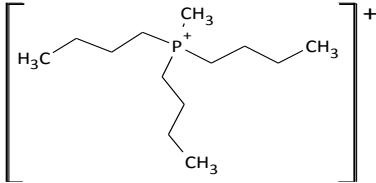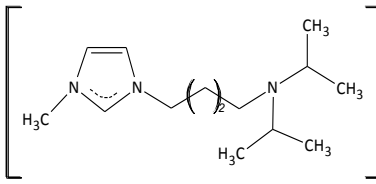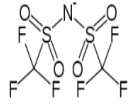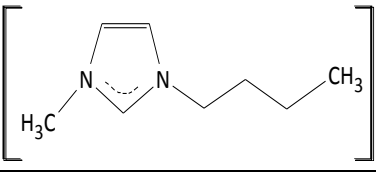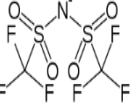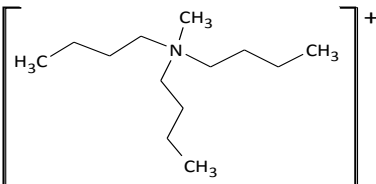
Figure 3.1: DPSILMs synthesis procedure

Table 3.1: List of the synthesized ionic liquid membranes supported with polysulfone.

Name	Abbreviation	Formula	Concentration (wt %)
Tributylmethylphosphonium formate	**[P4441][formate]**	[HCOO]$^-$	**5** **12.5** **25** **37.5** **50**
Di-iso-propyl 1-alkyl-3-methylimidazolium bistriflamide	**[DIP-C4mim][NTf2]**		**0.5** **2.5** **5** **12.5** **25**
1-alkyl-3-methylimidazolium bistriflamide	**[C4mim][NTf2]**		**0.5** **2.5** **5** **12.5** **25**
Tributylmethylammonium formate	**[N4441][formate]**	[HCOO]$^-$	**0.5** **2.5** **5** **12.5** **25**

3.3. Characterization of the Synthesized DPSILMs

The synthesized DPSILMs were characterized by Fourier transform IR spectra (FTIR) to indicate chemical structure because functional groups give rise to characteristic bands, in both intensity and position (frequency). FTIR spectra were recorded on a Jasco FT-IR-281s spectrophotometer for PSF and DPSILMs. The scanning range was 450-4000 cm^{-1} and the resolution was 1 cm^{-1}.

Scanning electron microscopy (SEM) was carried out using a Jeol JSM-840 scanning electron microscope, equipped with energy-dispersive X-ray spectroscopic elemental analysis. Surface and cross-sectioned SEM analysis were conducted on the prepared membranes with magnification ranging between 500 and 20000 magnifications to help investigate basic parameters of the DPSILMs (such as thickness and ionic liquids distribution). For the preparation of a cross-section sample, a freeze-fracturing operation was performed to prevent deformation of the membrane structure by freezing the DPSILMs in liquid nitrogen and fracturing them immediately [121].

3.4. CO_2/N_2 and CO_2/CH_4 separation measurements:

The separation efficiency of the synthesized DPSILMs for CO_2/N_2 and CO_2/CH_4 separation were tested using two flat-sheet membrane systems, the first system (System 1) was designed at Qatar University laboratories as shown in Figure 3.2. The permeation cell of System 1 was manufactured at the Department of Physics, University of Cambridge and is made of stainless steel 316.
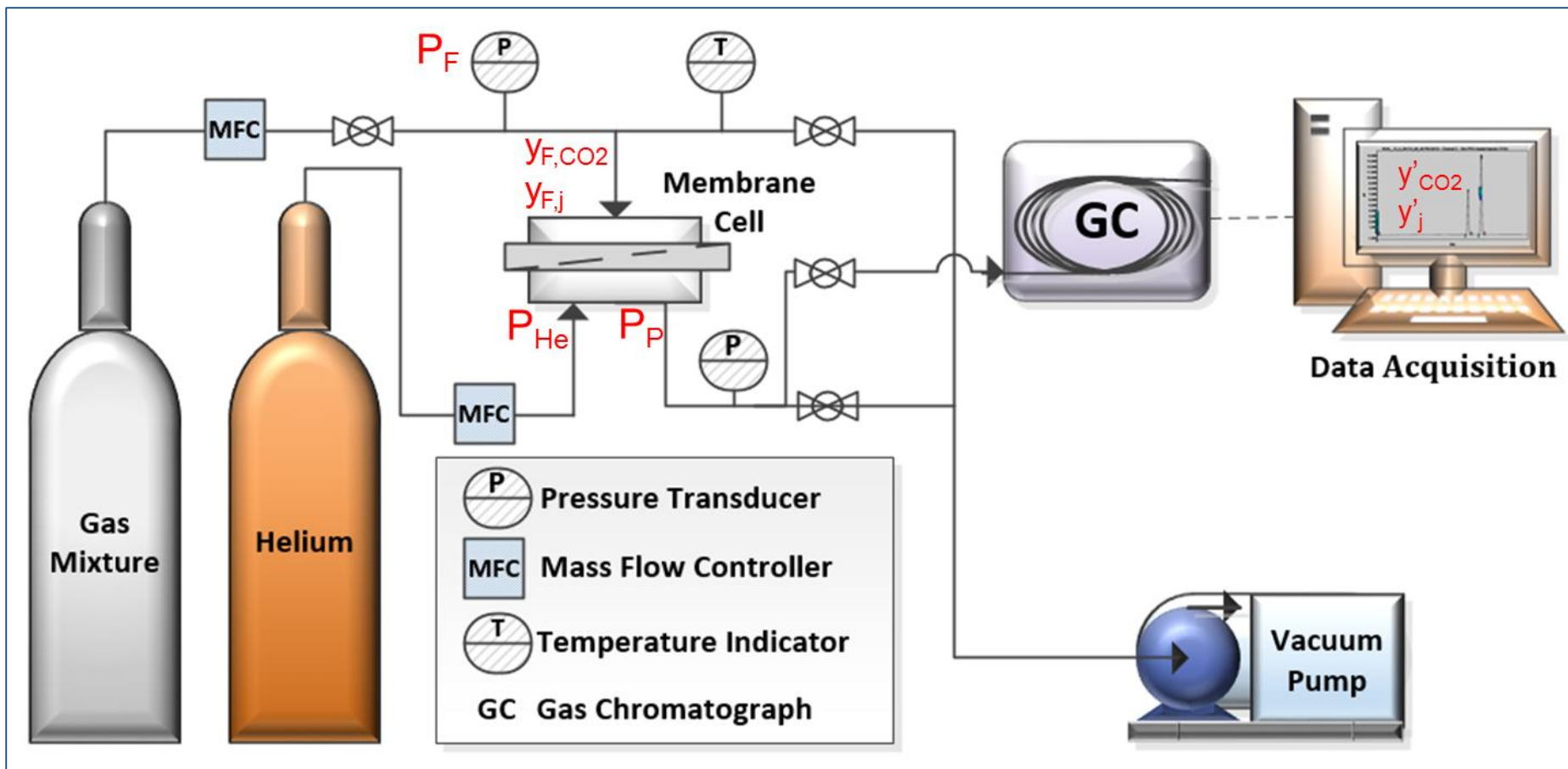
Figure 3.2: Mixed gas permeability system (System 1).

Where:

- P_F: Feed Pressure (bar).

- $y_{F,CO2}$: CO_2 composition in the feed.

- $y_{F,j}$: N_2 or CH_4 composition in the feed.

- P_{He}: Helium Pressure (bar).

- P_P: Permeate Pressure (containing only CO_2/N_2 or CO_2/CH_4) (bar).

- y'_{CO2}: CO_2 composition in the permeate (helium free basis)

- y'_j: N_2 or CH_4 composition in the permeate (helium free basis).

The membrane is installed inside the permeation cell with an effective are of 14.5 cm^2. The cell is evacuated from both sides of the membrane for approximately 20 hours. Then, the feed side of the membrane is pressurized up to 10 bars with the gas mixture (5 mol% CO_2 in N_2 or CH_4) while the permeate side is kept at vacuum. Equilibrium is reached after approximately 3.5 hours, however, the experiments were conducted for 5 hours to ensure reaching the equilibrium. The permeate pressure and temperature are recorded using a pressure-temperature transducer (PA-35X Ei-30 bar) obtained from Keller South-East Asia with accuracy of 0.05 % full scale. The permeate pressure is usually very low, so the permeate side should be pre-charged with helium to around 0.5 bar gauge before the GC analysis. The resulted pressure is also recorded (P_{total}). The permeate is analysed using Varian Micro GC (490-GC Micro-GC) with PPQ Column and heated auto-injector and back-flush option which is applicable for the analysis of CO_2, N_2, CH_4 and C_1 to C_6 components.

The synthesized membranes were also tested using the state-of-the-art high-pressure membrane separation unity by Rubotherm GmbH Permeability Reactor ™

(System 2) shown in Figure 3.3. This equipment is especially designed to measure the separation performance of a membrane with different feed pressures and temperature. The separation process of System 2 is similar to any membrane device. However, the novelty of this equipment is its fully automated design and ability to test gas separation with a pressure difference of up to 50 bar across the membrane. This is considered very high compared to other membrane cells, and is much closer to the industrial applications. The Rubotherm membrane cell is also made of stainless steel 316 allowing an effective membrane area of 3.14 cm^2. Membrane cell is connected to pressure transducer (Paroscientific, US) which was used in a range from vacuum up to 10 bars with an accuracy of 0.01 % in full scale. The temperature was kept constant with an accuracy of $\pm$ 0.5 K for each measurement. Other pictures and illustrations of System 1 and System 2 are shown in Appendix B and C respectively.
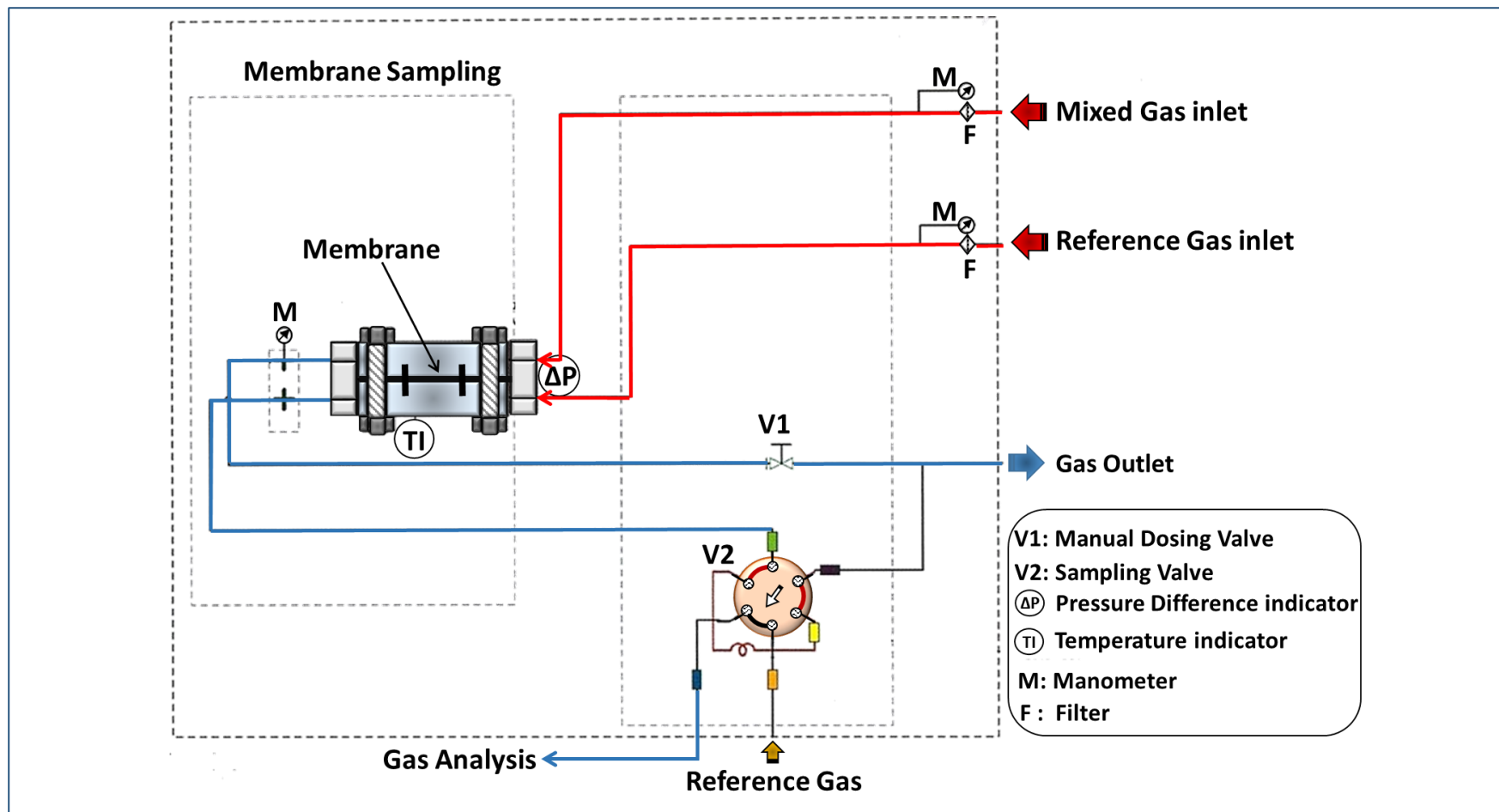
Figure 3.3: Process flow diagram of Rubotherm Präzisionsmesstechnik GmbH apparatus (System 2).

3.5. Permeability and selectivity calculations

The permeability calculation is carried out starting by mole balance around the membrane as follow:

1. Compositions calculations

- $n_{CO2,j} = \frac{P_p V_p}{RT}$ (*moles of CO_2/N_2 or CO_2/CH_4 in the permeate*)

- $n_{Total} = \frac{P_{Total} V_p}{RT}$ (*moles of CO_2/N_2 or CO_2/CH_4, and He*)

- $n_{CO2} = y'_{CO2} \cdot n_{CO2,j}$ (*moles CO_2*) $\;\;\;\rightarrow\;\;\; y_{CO2} = \frac{n_{CO2}}{n_{Total}}$

- $n_j = y'_j \cdot n_{CO2,j}$ (*moles of N_2 or CH_4*) $\;\;\;\rightarrow\;\;\; y_j = \frac{n_j}{n_{Total}}$

2. Partial Pressure Difference Calculations

- $\Delta P_{CO2} = P_{F,CO2} - P_{P,CO2}$ (*cmHg*)

  Where: $\;\;\; P_{F,CO2} = P_F \cdot y_{F,CO2}$ (*cmHg*)

  $\;\;\;\;\;\;\;\;\;\;\;\;\;\; P_{P,CO2} = P_P \cdot y_{CO2}$ (*cmHg*)

- $\Delta P_j = P_{F,j} - P_{P,j}$ (*cmHg*)

  Where: $\;\;\; P_{F,j} = P_F \cdot y_{F,j}$ (*cmHg*)

  $\;\;\;\;\;\;\;\;\;\;\;\;\;\; P_{P,j} = P_P \cdot y_j$ (*cmHg*)

Then flux and permeability were calculated using Eqs. (1) and (2), respectively.

$$J_i = \frac{n_i}{t.A} \qquad\qquad (1)$$

$$P_i = \frac{J_i.l}{\Delta P_i} \qquad\qquad (2)$$

Where, A is the cross surface area of the membrane (cm^2), t is the duration of the experiment (s), l is the membrane's thickness (cm), and ΔP_i is the partial pressure

difference of each gas. The permeability P_i and the flux J_i are given in $(\frac{cm^3(STP).cm}{cm^2.s.cmHg})$ and

$(\frac{cm^3(STP)}{cm^2.s})$ respectively. The permeability is usually given by the unit (barrer), where (1

Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}). The selectivity, or the separation factor,

of CO_2 relative to the other gas is calculated using Eq. (3).

$$\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B} \qquad\qquad (3)$$

where y_A and y_B are the equilibrium mole fractions of the components in the permeate,

while x_A and x_B are their corresponding mole fractions in the feed (retentate) [95].

3.6. Stability of the synthesized DPSILMs

One of the objectives of this study was to reduce or eliminate the ILs loss from the

synthesized DPSILMs as this is the main disadvantage of SILMs. Authors expect that

ILs mixed within the membrane will not be lost since no pores to allow this. However,

small losses of ILs distributed on the surface are possible from the synthesized

DPSILMs due to the high pressure and vacuum appliance. Stability measurements were

carried using System 2 (Rubotherm) by applying a pressure difference of 10 bars across

the membrane. DPSILMs were weighed using Shimadzu AX200 electronic balance

(Japan) with an accuracy of ±0.2 mg at regular time intervals (2 hours) followed by 2

hours of vacuuming to determine the weight decrease which is assumed to be due to

ILs loss. Additionally, CO_2/CH_4 selectivity was measured as described in section 2.4 to

determine their stability with respect to separation efficiency.

4. Results & Discussion

4.1. Characterization of the Synthesized DPSILMs

The FTIR was performed on the plain PSF membrane as the reference line. DPSILMs were then analysed using the same technique to see the changes on the functional groups when the ILs were impregnated into the PSF support, as shown in Figure 4.1 and 4.2 for PSF-12.5 wt% [DIP-C$_4$mim][NTf$_2$] and PSF-12.5 wt% [P$_{4441}$][formate], respectively.
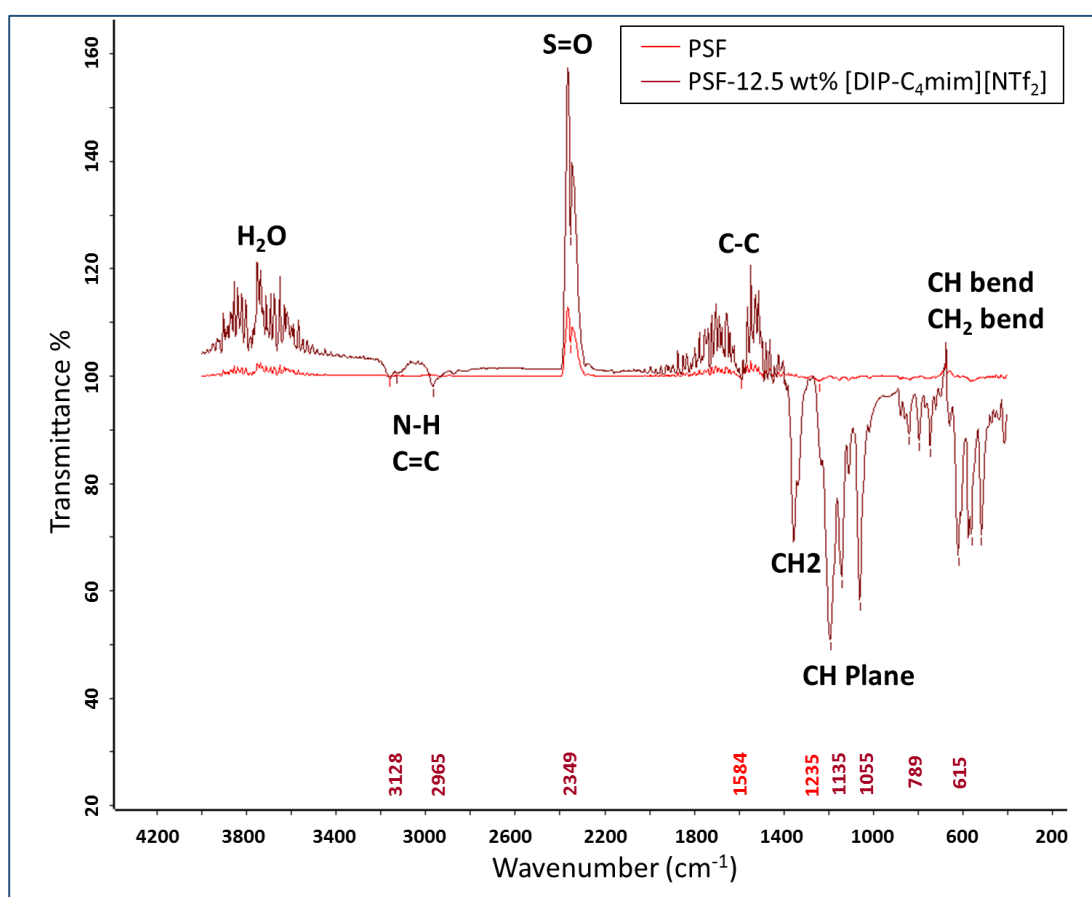
Figure 4.1: Plain PSF overlapped with PSF-12.5 wt% [DIP-C$_4$mim][NTf$_2$].

Both FT-IR spectra showed that the ionic liquids chosen were impregnated successfully within the polysulfone matrix. It can be observed that there is an enhancement on the

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2349 cm^{-1} band, which represents the S = O functional group of PSF on both DPSILM

FT-IR spectra. Both spectra also showed a presence of water (between 3000 – 4000 cm^{-1}), which is expected due to the hygroscopicity of the ionic liquid itself. The main

characteristics observed in the PSF-[DIP-C$_4$mim][NTf$_2$] (Figure 4.1) are at the

frequencies of 3128 cm^{-1} and 2965 cm^{-1}, which represent the N-H and C=C functional

groups, respectively, on the imidazolium ring on the cation. In Figure 4.2, the PSF-

[P$_{4441}$][formate] spectra showed two important bands at 1584 cm^{-1} and 1486 cm^{-1}, that

feature the characteristics of C-C(O)-C and C=O on carboxylic group, which represents

the formate anion.
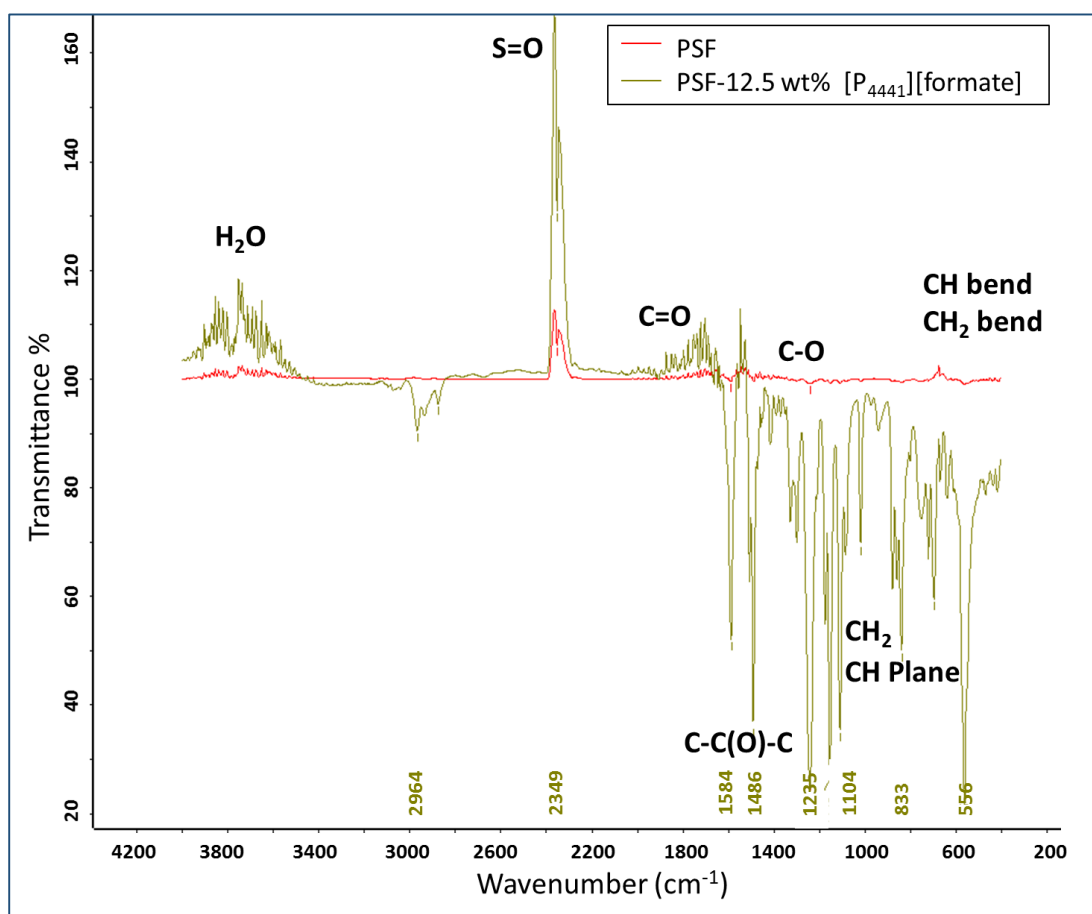
Figure 4.2: Plain PSF overlapped with PSF-12.5 wt% [P$_{4441}$][formate].

In the surface SEM images (Figures 4.3 and 4.4), it can be observed that the ILs distributions on the surface of PSF increased with the increment of the ionic liquid concentration.
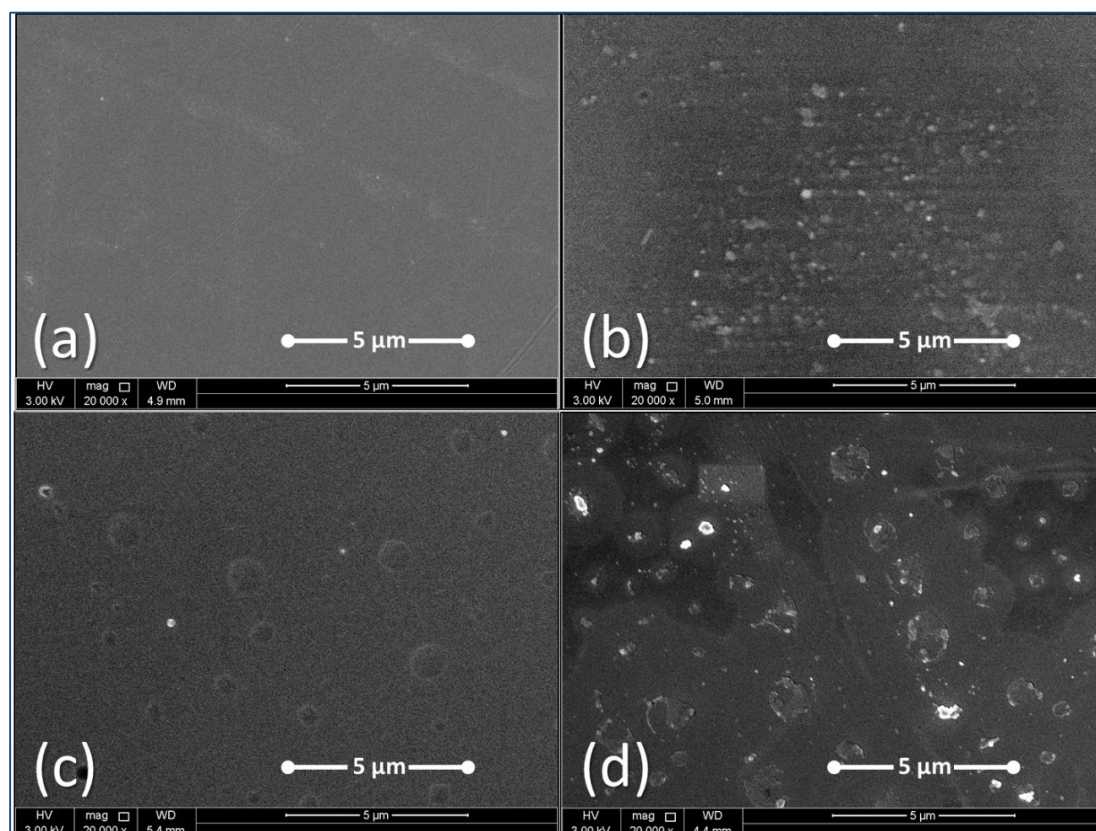
Figure 4.3: Surface-SEM images with 20,000 magnifications of (a) Pure PSF, (b) PSF-0.5 wt% [N$_{4441}$] [formate], (c) PSF-0.5 wt% [C$_4$mim][NTf$_2$], (d) PSF-0.5 wt% [DIP-C$_4$mim][NTf$_2$].

In figure 4.3, the effect of a small amount of ionic liquids (0.5 wt%) is shown. The effect of the these ILs on the PSF surface is not clearly obvious due to the low ILs concentrations. In contrast, the effect of the added ILs in Figure 4.4 on PSF surface is much obvious because of the high concentration of ILs added to the polymer.
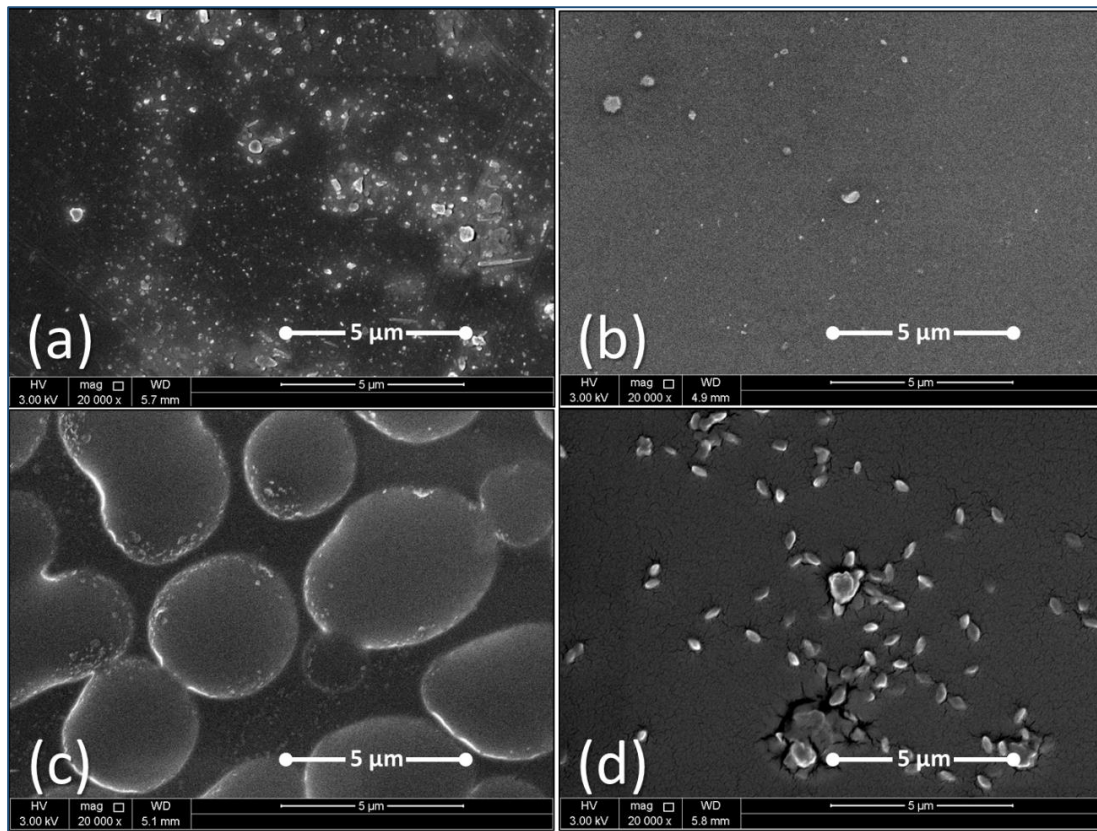
Figure 4.4: Surface-SEM images with 20,000 magnifications of (a) PSF-5 wt% [P₄₄₄₁] [formate], (b) PSF-5 wt% [N₄₄₄₁] [formate], (c) PSF-5 wt% [C₄mim][NTf₂], (d) PSF-5 wt% [DIP-C₄mim][NTf₂].

Figures 4.5 and 4.6 show the effect of $[P_{4441}]$[formate] and [DIP-C$_4$mim][NTf$_2$] concentration on the cross-section structure of PSF. These cross-section SEM images showed ILs have phase separated from PSF and formed separate domains. It is believed that ILs domains may enhance the diffusion of gas molecules through the membrane in the diffusion stage which is the second stage of the solution-diffusion mechanism discussed in section 1; while reducing the possibility of ILs loss since they are well surrounded and attached by PSF matrix.
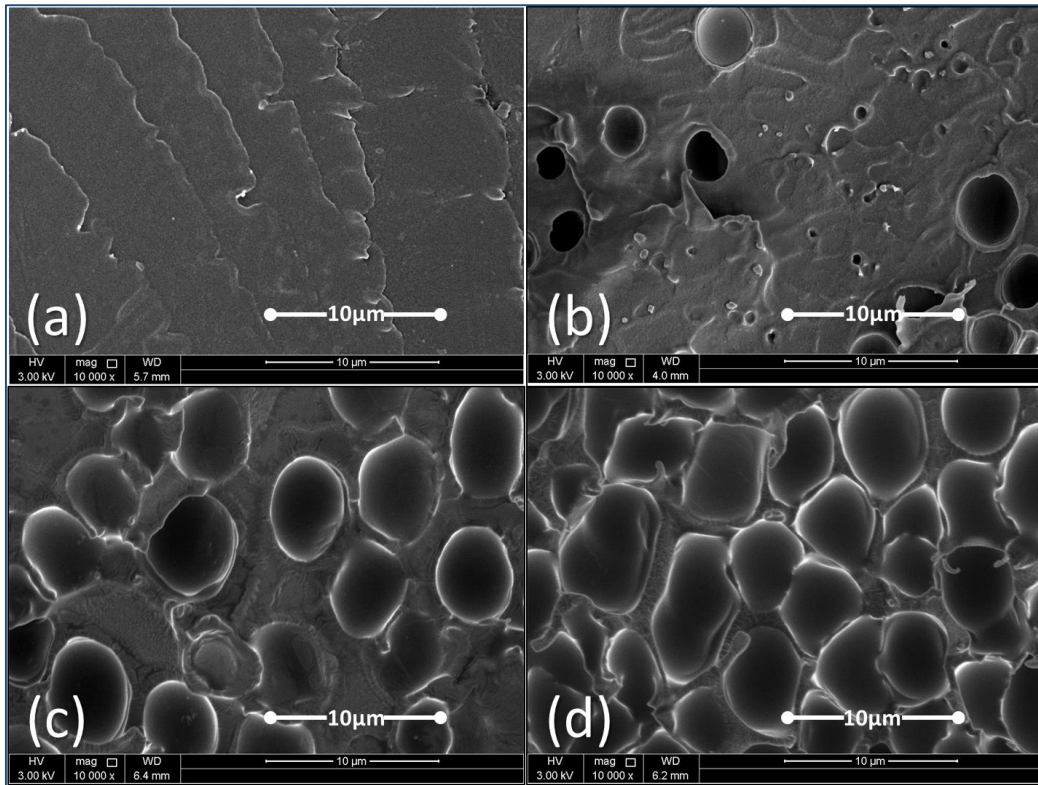
Figure 4.5: Cross-sectioned SEM images with 10,000 magnifications of (a) Pure PSF, and PSF blended with different loadings of [P$_{4441}$] [formate] (b) 5 wt%, (c) 12.5 wt%, and (d) 25 wt%
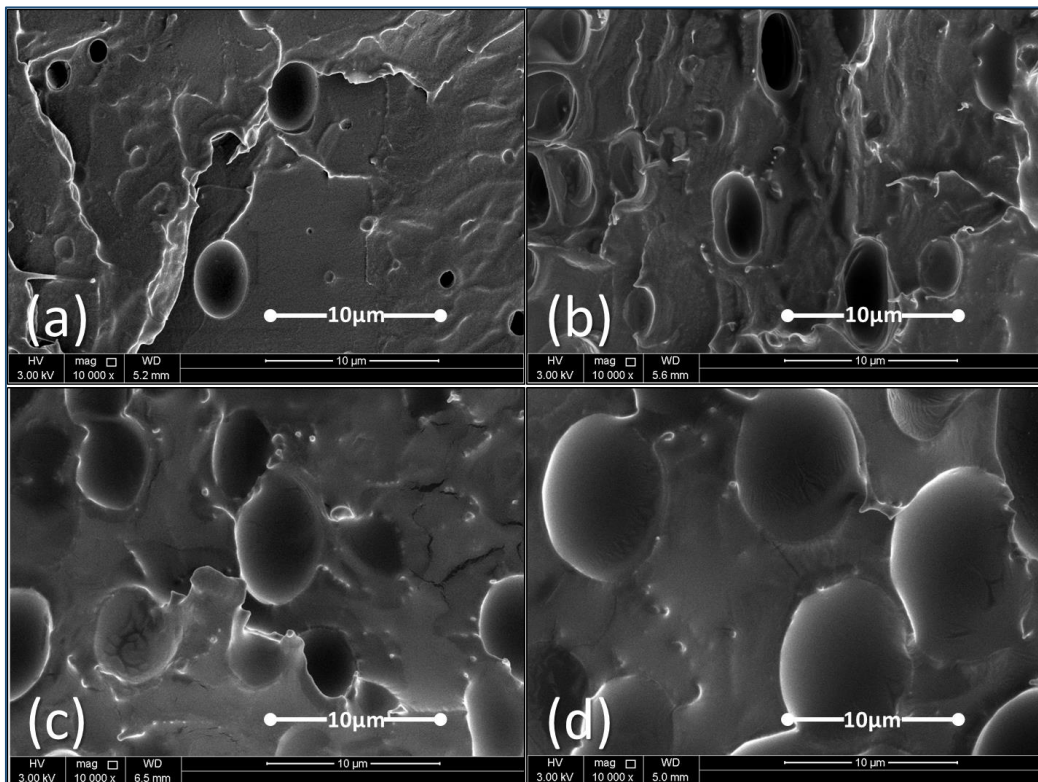
Figure 4.6: Cross-sectioned SEM images with 10,000 magnifications of PSF with different loadings of [DIP-C$_4$mim][NTf$_2$] (a) 2.5 wt%, (b) 5 wt%, (c) 12.5 wt%, (d) 25 wt%.

4.2. CO_2/N_2 and CO_2/CH_4 separation measurements

System 2 was used to screen the synthesized DPSILMs as discussed in section 3.4. The permeate compositions were analysed using the micro GC; and selectivity values were then calculated using Eq. (3). CO_2/N_2 selectivity for pure PSF was found to be 26 which is slightly close to the reported values in literature. Scholes et al tested the mixed gas and pure gas permeability properties of PSF at 6-10 bars and 35 °C. Pure gas selectivity was reported to be 21 while the mixed gas selectivity was not reported [117].

CO_2/N_2 Selectivity results shows that selectivity of the synthesized DPSILMs range from about 12 for PSF-5 wt% $[P_{4441}][formate]$ and PSF-25 wt% $[C_4mim][NTf_2]$ to about 36 for PSF-25 wt% $[N_{4441}][formate]$ and PSF-0.5 wt% $[DIP-C_4mim][NTf_2]$ (Figures 4.7 - 4.9).
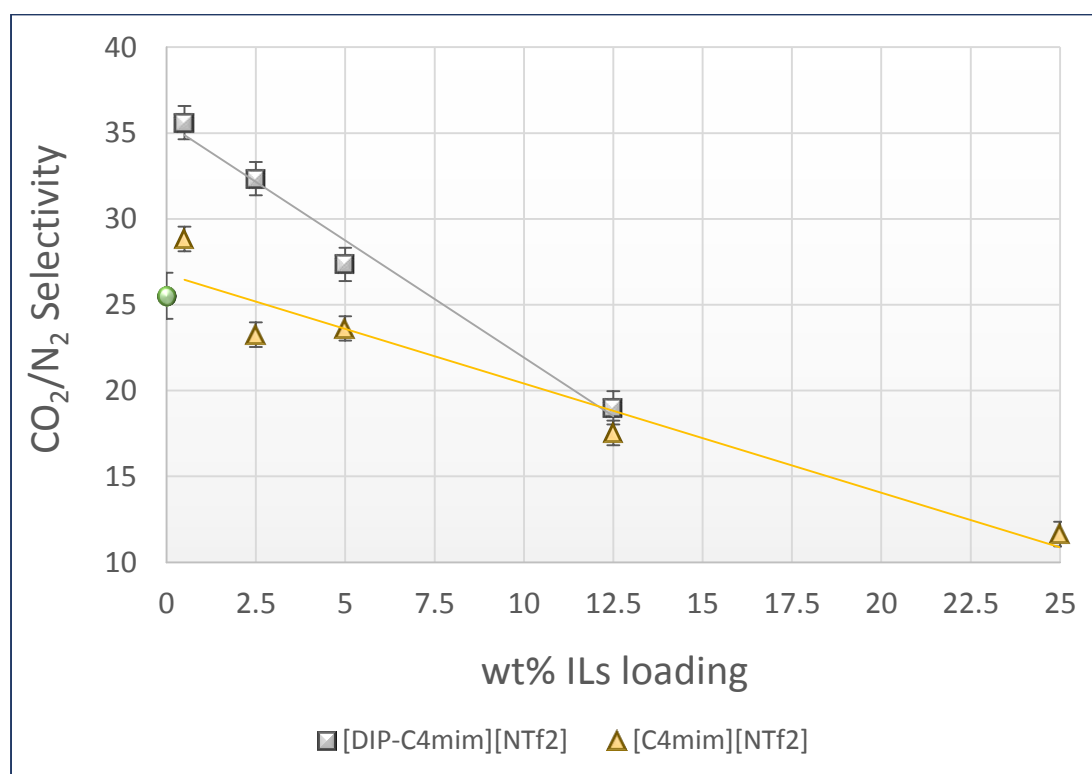
Figure 4.7: CO_2/N_2 Selectivity behavior with different loads of [DIP-C$_4$mim][NTf$_2$] and [C$_4$mim][NTf$_2$] (System 2, 10 bar, 22 °C).

Figure 4.7 shows that CO_2/N_2 selectivity was clearly raised with the addition of low compositions (0.5 wt%) of [C$_4$mim][NTf$_2$] and [DIP-C$_4$mim][NTf$_2$] to 29 and 36 respectively compared to pure PSF that has a selectivity of 26. However, it sharply decreases with more loading of the ILs to about 12 with 25 wt% [C$_4$mim][NTf$_2$] and 19 with 12.5 wt% [DIP-C$_4$mim][NTf$_2$]. Loadings of 25 wt% [DIP-C$_4$mim][NTf$_2$] made the membrane breakable even under vacuum hence no selectivity was recorded.

In contrast, CO_2/N_2 selectivity have shown proportional behavior with respect to loadings of [P$_{4441}$][formate] and [N$_{4441}$][formate] as shown in Figures 4.8 and 4.9. 5 wt% loading of [P$_{4441}$][formate] reduced the selectivity to 12 whereas more loadings increased the selectivity to 21 with 50 wt% which is still lower than value obtained for pure PSF (Figure 4.8). Figure 4.9 indicates that the selectivity was not affected significantly with low loadings of [N$_{4441}$][formate] compared to PSF, however, it increased to around 30 and 36 with 12.5 wt% and 25 wt% [N$_{4441}$][formate] respectively.
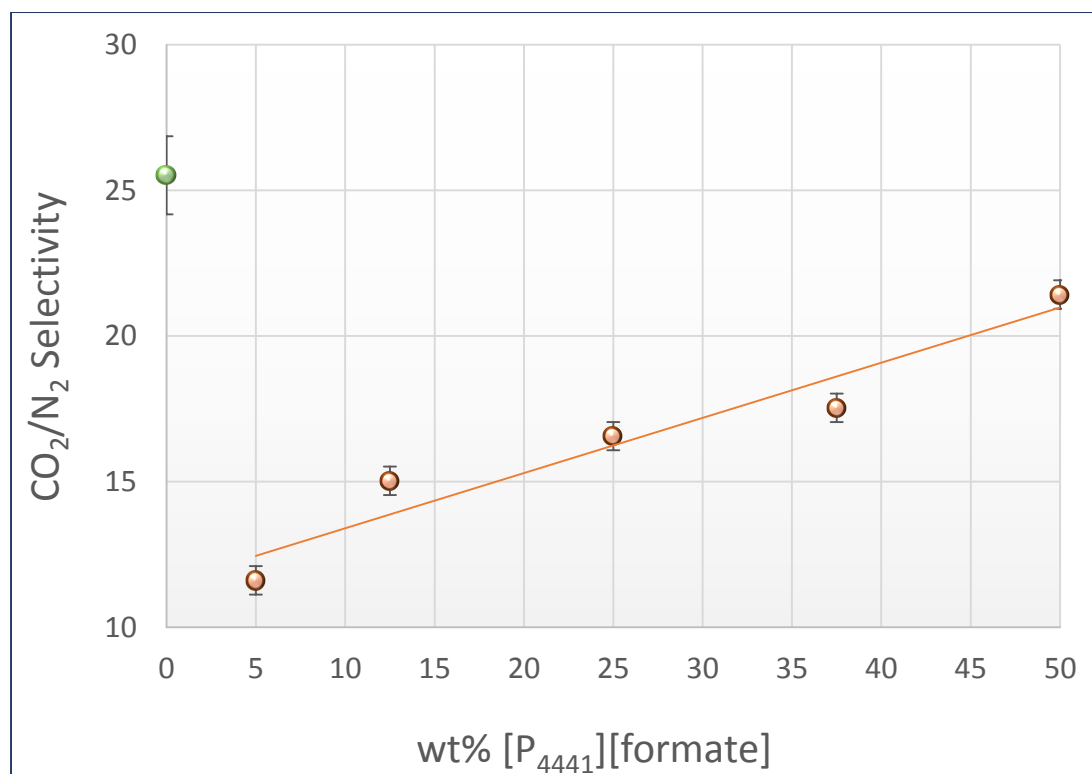
Figure 4.8: CO$_2$/N$_2$ Selectivity behavior with different loads of [P$_{4441}$][formate] (System 2, 10 bar, 22 °C).
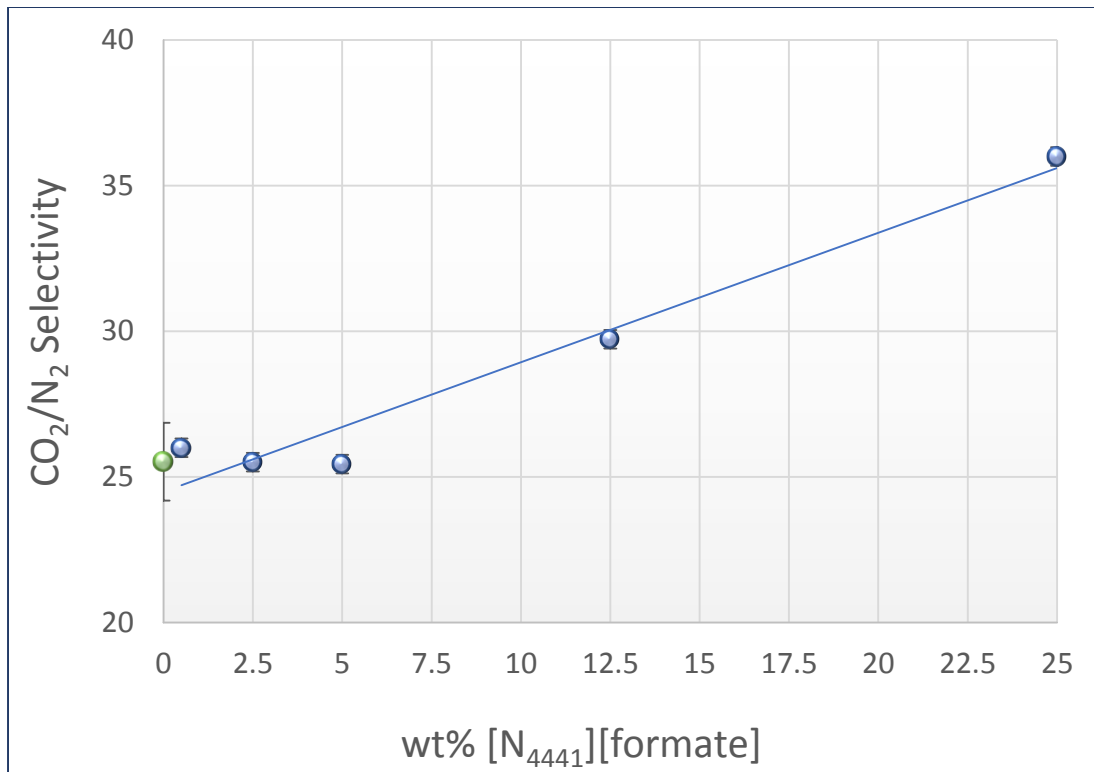
Figure 4.9: CO$_2$/N$_2$ Selectivity behavior with different loads of [N$_{4441}$][formate] (System 2, 10 bar, 22 °C)

CO$_2$/CH$_4$ Selectivity for PSF was measured and found to be 25 which is close to results reported in the literature [102, 122]. Guo et al. studied the mixed gas permeability properties of polysulfone at 10 bars and 30 °C with feed of 50/50 mol% CO$_2$/CH$_4$ and reported the separation selectivity of CO$_2$/CH$_4$ to be 27 [102]. However, the selectivity was found to be 21.9 at the same conditions with pure gas feed by kim and Hong [123]. Almost the same value was obtained by Mchattie et al. with pure gas at 10 bars and 35 °C [122].

The selectivity results shows that selectivity of the synthesized DPSILMs range from 20 for both PSF-50 wt% [P$_{4441}$][formate] and PSF-25 wt% [C$_4$mim][NTf$_2$] to 70 for PSF-2.5 wt% [C$_4$mim][NTf$_2$] (Figures 4.10 – 4.13).
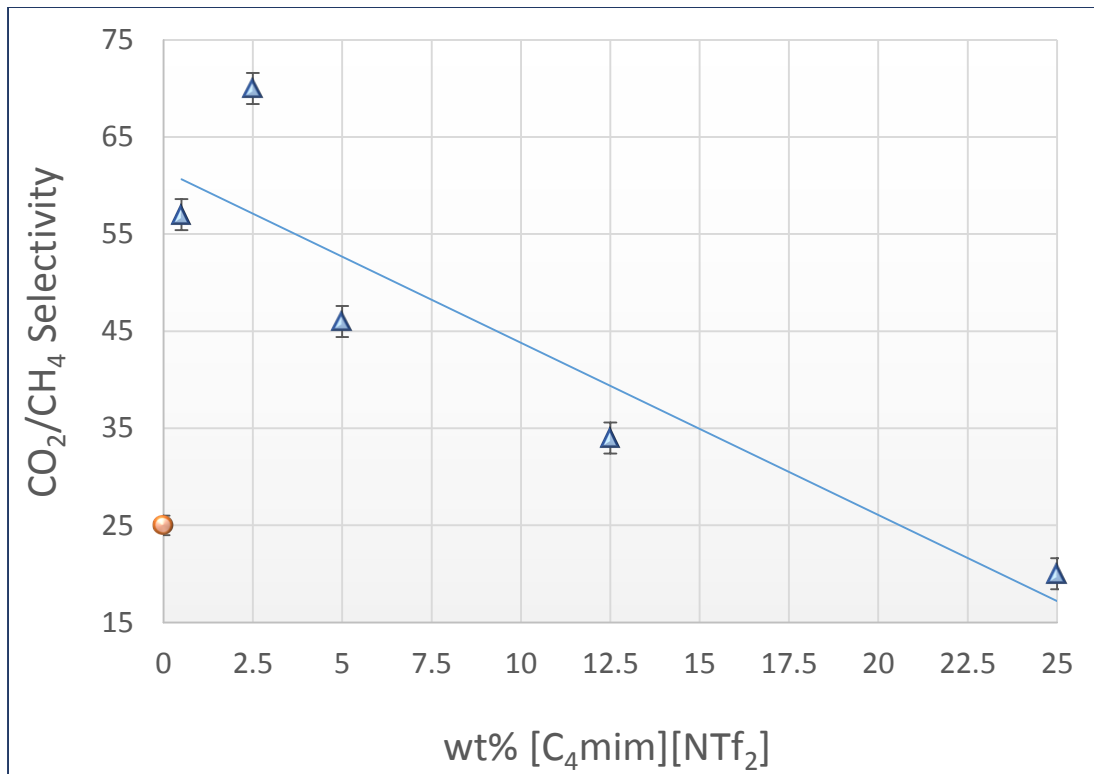
Figure 4.10: CO₂/CH₄ Selectivity behavior with different loads of [C₄mim][NTf₂] (System 2, 10 bar, 22 °C).
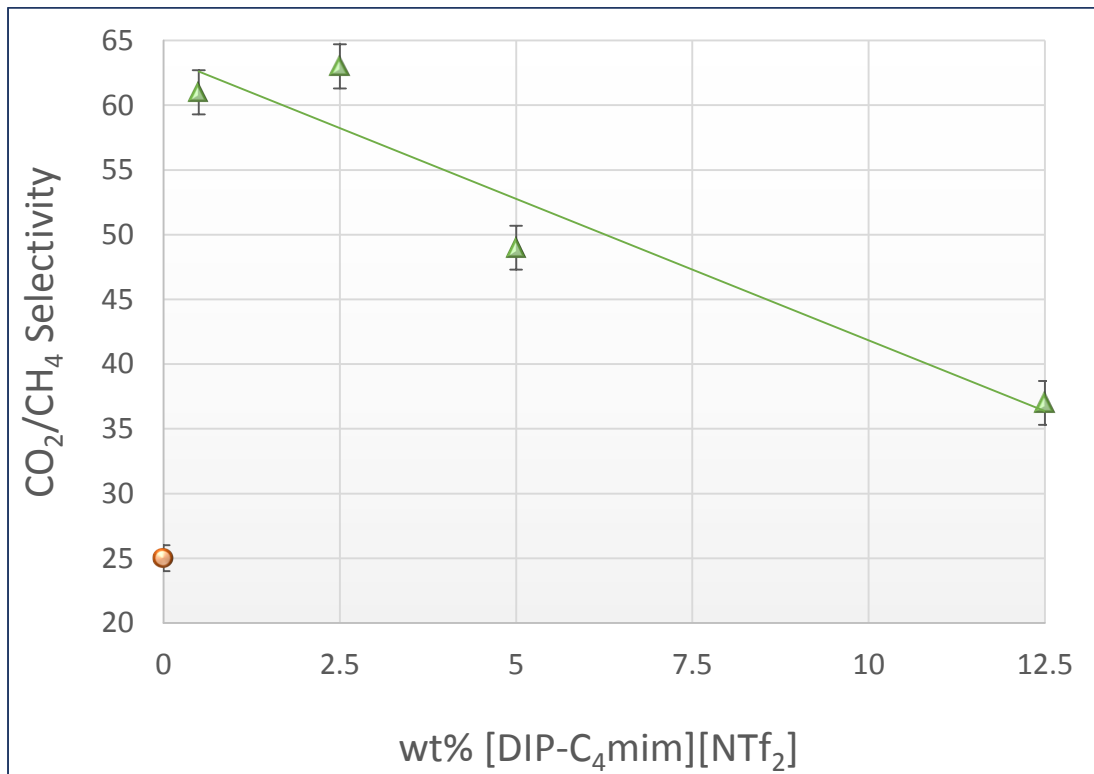
Figure 4.11: CO₂/CH₄ Selectivity behavior with different loads of [DIP-C₄mim][NTf₂] (System 2, 10 bar, 22 °C).

CO$_2$/CH$_4$ selectivity values were increased with addition of small increments of [C$_4$mim][NTf$_2$] (Figure 4.10). Selectivity was raised to 57 and 70 with 0.5 and 2.5 wt% [C$_4$mim][NTf$_2$] respectively. However, more loadings of the IL reduced the selectivity to 46, 34 and 20 with 5, 12.5, and 25 wt% [C$_4$mim][NTf$_2$]. Similar behavior was observed with loadings of [DIP-C$_4$mim][NTf$_2$] (Figure 4.11). The selectivity was increased to 61 and 63 with 0.5 and 2.5 wt% [DIP-C$_4$mim][NTf$_2$] respectively, then decreased to 49 and 37 with 5 and 12.5 wt% [DIP-C$_4$mim][NTf$_2$] respectively.

Figure 4.12 shows that CO$_2$/CH$_4$ selectivity is inversely proportional to [P$_{4441}$][formate] loadings. Selectivity was increased to 32 with 5 wt% loading of [P$_{4441}$][formate] then reduced to 31, and 24 with 12.5 and 25 wt% [P$_{4441}$][formate] respectively and to 20 with both 37.5 and 50 wt% [P$_{4441}$][formate].
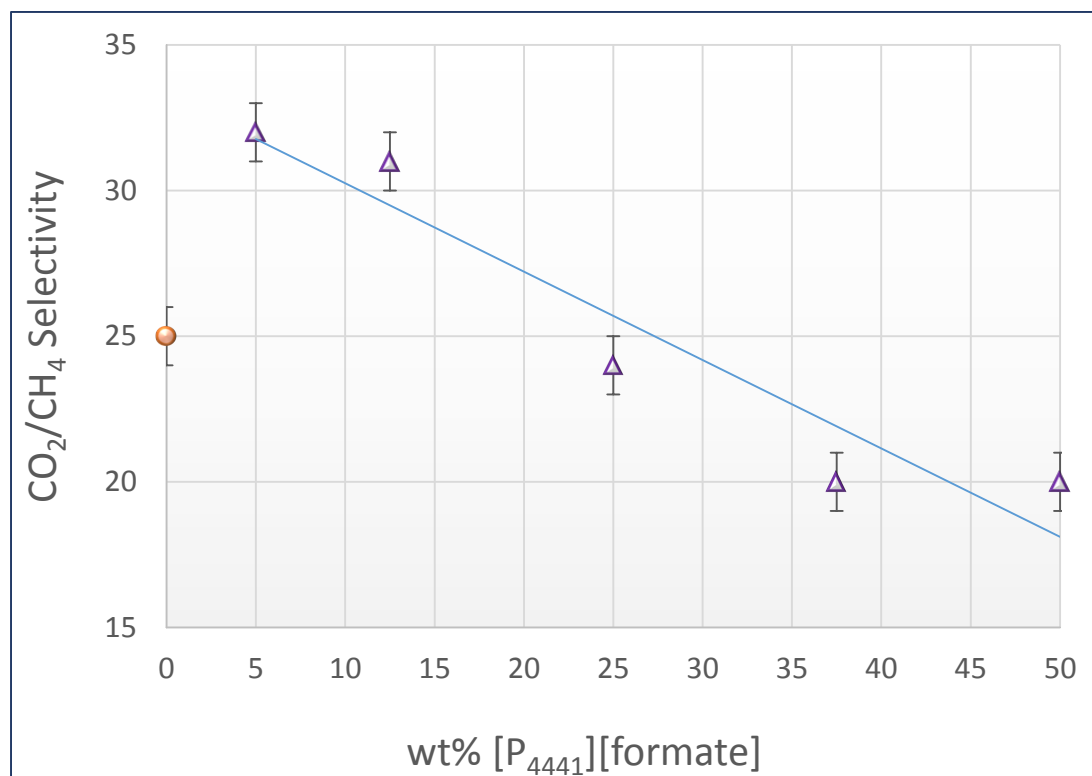
Figure 4.12: CO$_2$/CH$_4$ Selectivity behavior with different loads of [P$_{4441}$][formate] (System 2, 10 bar, 22 °C).

Addition of [N$_{4441}$][formate] increased CO$_2$/CH$_4$ selectivity up to 47 with 0.5 wt% [N$_{4441}$][formate]. The selectivity then decreased slightly with more increments to 46, 43, 42, and 39 with 2.5, 5, 12.5, 25 wt% [N$_{4441}$][formate] (Figure 4.13).
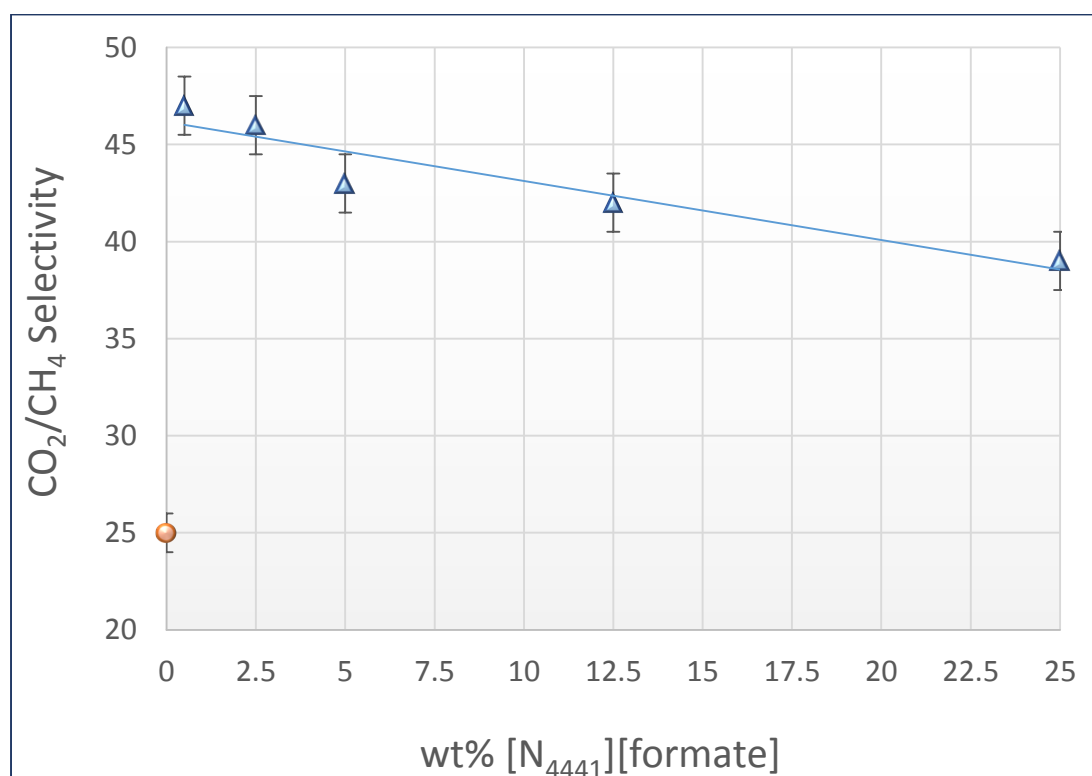
Figure 4.13: CO$_2$/CH$_4$ Selectivity behavior with different loads of [N$_{4441}$][formate] (System 2, 10 bar, 22 °C).

Comparing the separation efficiency of the synthesized DPSILMs with other porous supported SILMs in the literature shows that both of them almost lie in the same range (Table 2.3). Hojniak with other co-workers prepared SILMs using porous γ-alumina discs (3-5 nm pore size) as membrane support with different ionic liquids, monocationic and dicationic ionic liquids [116]. As shown in Figure 4.14, CO$_2$/N$_2$ selectivity results obtained with these SILMs for mixed gas separation range from 15.2 to 34.7 which indicates very comparable behaviour when compared to the results obtained with this work. However, CO$_2$/CH$_4$ selectivities obtained with some DPSILMs in this work (e.g.

[N$_{4441}$][formate], [C$_4$mim][NTf$_2$], and [DIP-C$_4$mim][NTf$_2$]) are higher than those reported by Hojniak that range from 12.6 to 31.8.
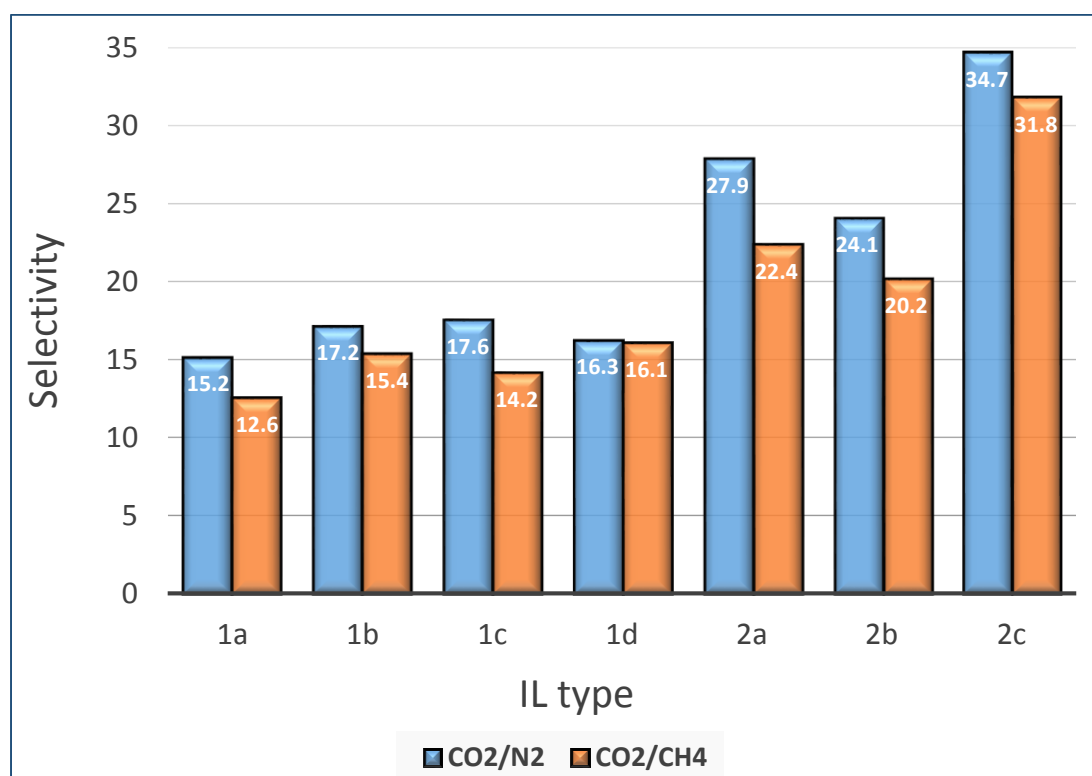
Figure 4.14: Mixed gas selectivities for CO$_2$/N$_2$ and CO$_2$/CH$_4$ separation measurements obtained with SILMs prepared by Hojniak et al. [116].

Scovazzo et al. studied the effect of different types of ILs supported by porous hydrophilic polyehtersulfone (PES) and polyvinylidene fluoride (PVDF) with pore size of 0.1 μm [115]. The obtained selectivity values for CO$_2$/N$_2$ were 12.2 and 21.2 with SILMs based on [bmim][BETI] and [emim][Tf$_2$N] respectively. Mixed gas selectivities with other ILs were not reported. For CO$_2$/CH$_4$ separation measurements, the selectivities were 27, 24, 22, 17, and 9.9 with [emim][BF$_4$], [emim][dca], [emim][CF$_3$SO$_3$], [emim][Tf$_2$N], and [C$_6$mim][Tf$_2$N] based SILMs. All these separation measurements were conducted under feed pressure of 207 kpa. The obtained

selectivities of SILMs prepared by Scovazzo et al. shows almost comparable behaviour to DPSILMs prepared in this work (Figure 4.15).
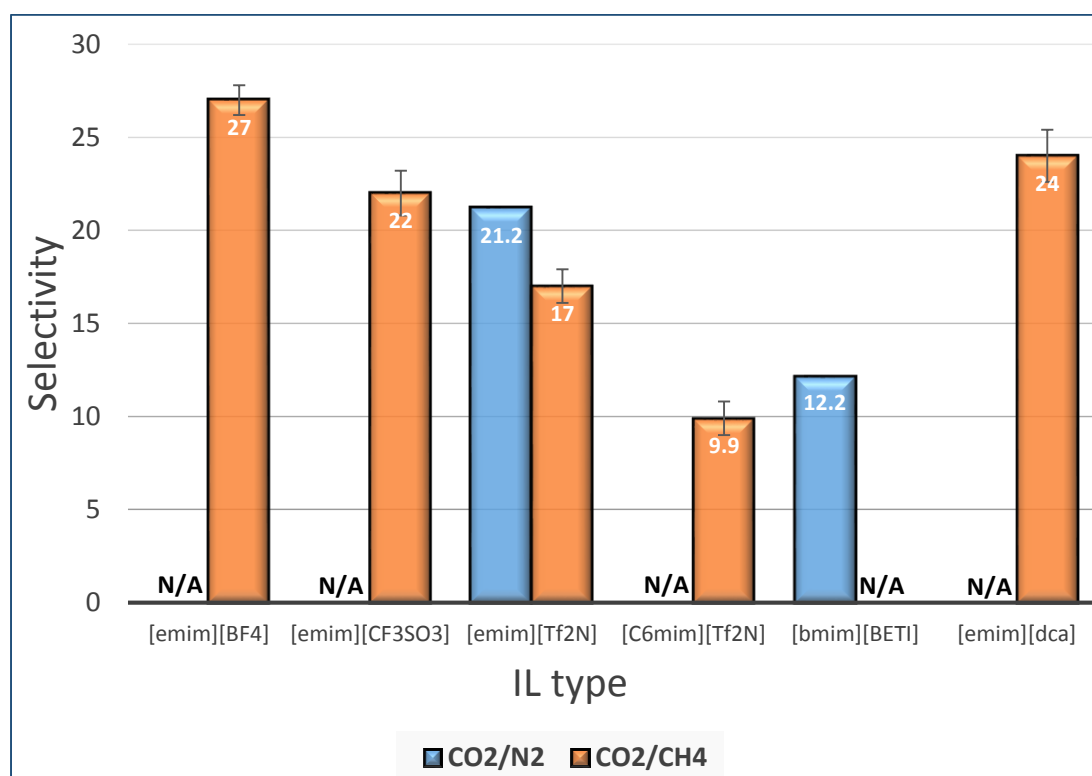
Figure 4.15: Mixed gas selectivities for CO_2/N_2 and CO_2/CH_4 separation measurements obtained with SILMs prepared by Scovazzo et al. [115].

Neves and co-workers used porous polyvinylidene fluoride (PVDF) with pore size of 0.22 μm for mixed gas separation of CO_2/N_2 and CO_2/CH_4 with different imidazolium based ionic liquids [114]. The separation experiments were conducted under 0.7 bar feed pressure and the results are shown in Figure 4.16. The prepared SILMs showed similar behavior with regards to CO_2/N_2 separation where the obtained selectivities were 20, 32, 30, and 21 with SILMs based on $[C_4mim][PF_6]$, $[C_4mim][BF_4]$, $[C_4mim][Tf_2N]$, and $[C_8mim][PF_6]$ respectively. Conversely, SILMs prepared by Neves et al. achieved very high CO_2/CH_4 selectivities compared to DPSILMs prepared in this work and other studies in the literature. The reported CO_2/CH_4 selectivities were

200, 102, 161, and 98 with SILMs based on $[C_4mim][PF_6]$, $[C_4mim][BF_4]$, $[C_4mim][Tf_2N]$, and $[C_8mim][PF_6]$ respectively.
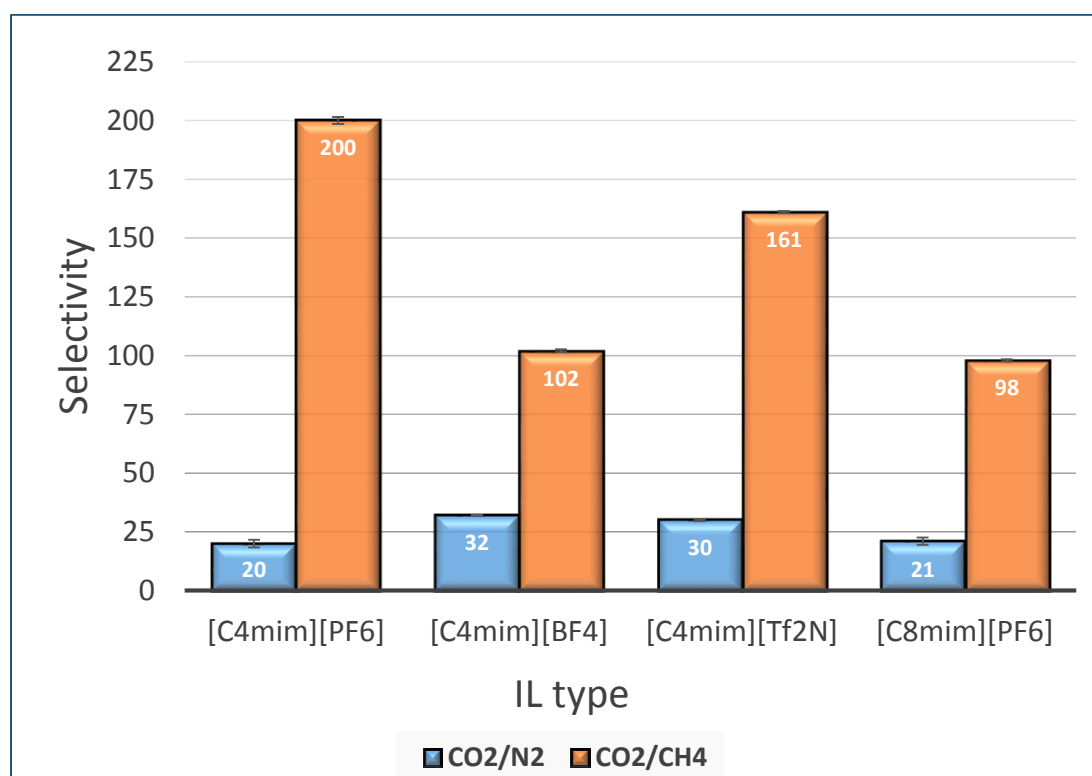
Figure 4.16: Mixed gas selectivities for CO_2/N_2 and CO_2/CH_4 separation measurements obtained with SILMs prepared by Neves et al. [114]

Based on selectivity results obtained from System 2, DPSILMs of each ILs type having high selectivity values were selected to be tested using System 1 to determine the corresponding permeability values for both mixtures CO_2/N_2 and CO_2/CH_4 (Table 4.1 and 4.2). For CO_2/N_2 separation, CO_2 permeability was found to be 5.3 barrer for pure PSF which is close to the value obtained by Scholes et al [117]. However, N_2 permeability was measured to be 0.25 that differs slightly from the reported value of the mixed gas (0.13 barrer) and is much closer to this of pure gas (0.26 barrer). This could be due to the difference in feed compositions used in this study and Scholes et al study (10% CO_2 v/v in N_2).

Table 4.1: permeability and selectivity values of CO2/N2 for the synthesized DPSILMs (System 1, 10 bar, 22 °C) and reported literature.

Membrane	P_{CO_2} (barrer)	P_{N_2} (barrer)	α_{CO_2/N_2}
PSF[a]	5.2	0.13	N/A
PSF[b]	5.4	0.26	21
PSF	5.3	0.25	26
PSF-5 wt% [P4441][formate]	13.6	1.32	10
PSF-0.5 wt% [C4mim][NTf2]	7.8	0.29	27
PSF-5 wt% [C4mim][NTf2]	8.9	0.36	25
PSF-0.5 wt% [DIP- C4mim][NTf2]	10.8	0.29	37
PSF-5 wt% [DIP- C4mim][NTf2]	9.3	0.29	32
PSF-12.5 wt% [N4441][formate]	10.3	0.35	29
PSF-25 wt% [N4441][formate]	19.0	0.52	37

[a] Mixed gas (feed: 10% CO_2 v/v in N_2, 6-10 bars and 35 °C) [117]

[b] Pure gas (6 bars and 35 °C) [117]

Table 4.1 shows that the addition of ionic liquids to the pure PSF caused an increase in permeability of both gases, hence the increase in selectivity was limited. The highest selectivity obtained with System 2 for PSF-[P4441][formate] was 21 with 50 wt% of the IL. However, Table 4.1 shows only PSF with 5 wt% although it has the lowest selectivity. This is because DPSILMs having higher concentration of [P4441][formate] broke during the experiment due to brittleness caused by the high IL concentration. System 1 allows larger surface area of the membrane than system 2 which increase the possibility to be broken. The results obtained from the two systems meet each other and show the increase in concentration of [C4mim][NTf2] and [DIP-C4mim][NTf2], decreases the separation selectivity. Results in Table 4.1 shows that the decrease in selectivity is due to the increase in N_2 permeability with the concentration of [C4mim][NTf2], while it is due to CO_2 permeability reduction with more loadings of

[DIP-C_4mim][NTf_2]. CO_2 and N_2 permeability increased to 10.3 and 0.35 barrer with 12.5 wt% [N_{4441}][formate] and to 19 and 0.52 barrer with 25 wt% [N_{4441}][formate].

Table 4.2: permeability and selectivity values of CO_2/CH_4 for the synthesized DPSILMs (System 1, 10 bar, 22 °C) and reported literature.

Membrane	P_{CO2} (barrer)	P_{CH4} (barrer)	$\alpha_{CO2/CH4}$
PSF[a]	5.6	0.25	22
PSF[b]	4.6	0.21	21.9
PSF[c]	7.3	0.27	27
PSF	6.9	0.28	25
PSF-5 wt% [P_{4441}][formate]	11.5	0.40	32
PSF-12.5 wt% [P_{4441}][formate]	17.3	0.48	31
PSF-0.5 wt% [DIP-C_4mim][NTf_2]	12.2	0.19	61
PSF-2.5 wt% [DIP-C_4mim][NTf_2]	13.8	0.22	63
PSF-0.5 wt% [C_4mim][NTf_2]	10.9	0.19	57
PSF-2.5 wt% [C_4mim][NTf_2]	11.5	0.16	70
PSF-0.5 wt% [N_{4441}][formate]	12.5	0.26	47
PSF-2.5 wt% [N_{4441}][formate]	10.2	0.22	46

[a] Pure gas (10 bars and 35 °C) [122]

[b] Pure gas (10 bars and 30 °C) [123]

[c] Mixed gas (feed: 50/50 mol% CO_2/CH_4,10 bars and 30 °C) [102]

For CO_2/CH_4 separation, CO_2 and CH_4 permeability for pure PSF was found to be 6.9 and 0.28 barrer respectively that are close to the reported values by Guo et al for 50/50 mol% CO_2/CH_4 at the same driving force and 30 °C [102]. Table 4.2 showed that addition of [P_{4441}][formate] caused a clear increase in permeability of both gases hence the selectivity was raised slightly. However, the addition of other ILs, [C_4mim][NTf_2], [DIP-C_4mim][NTf_2] and [N_{4441}][formate], achieved clear increase in CO_2/CH_4 selectivity due to their low CH_4 permeability with high permeance of CO_2. DPSILM

having 12.5 wt% $[P_{4441}]$[formate] has recorded the highest permeability of both CO_2 and CH_4 (17.3 and 0.48 barrer respectively) with CO_2/CH_4 selectivity of 31. The lowest CH_4 permeability was achieved with PSF loaded with 2.5 wt% $[C_4mim][NTf_2]$ (0.16 barrer) and CO_2 permeability of 11.5 hence achieving the highest CO_2/CH_4 selectivity of the synthesized DPSILMs (70).

Figure 4.17 shows that more loadings of $[C_4mim][NTf_2]$ increased the permeability of CO_2 slightly (plotted on the secondary y-axis) with high increase of CH_4 permeability (plotted on the primary y-axis) hence the selectivity dropped to 20 with 25 wt% $[C_4mim][NTf_2]$.
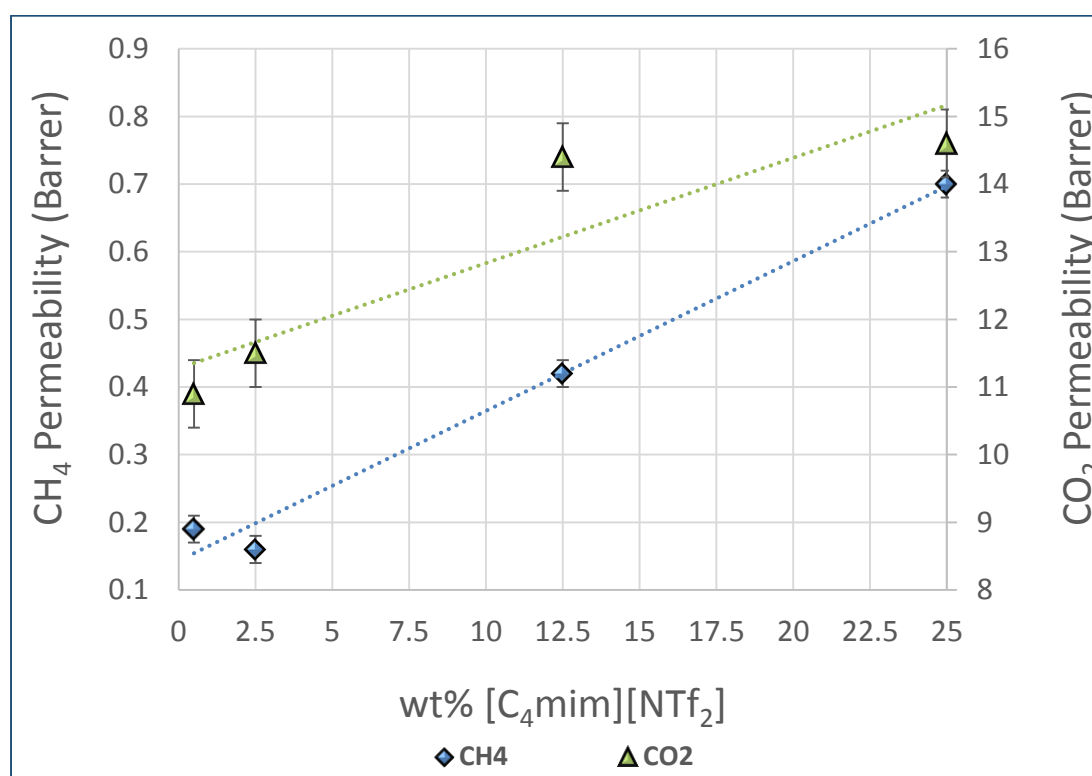
Figure 4.17: CO_2 and CH_4 permeability behaviour with different loads of [C4mim][NTf2] (System 1, 10 bar, 22 °C).

Plotting the Permeability and selectivity values on Robeson's upper bounds (2008) provide better comparison of permeation efficiency of the synthesized DPSILMs and PSF (Figure 4.18 and 4.19). Figures 4.18 and 4.19 also include some

reported values in the literature of PSF blends for different feed compositions and conditions [98-104]. Robeson's upper bounds was plotted using the correlation developed by Robeson [96]. Figure 4.18 and 4.19 shows that the synthesized DPSILMs behave as well or better than different types of PSF blends reported in the literature for both CO_2/N_2 and CO_2/CH_4 separation. However, the permeability and selectivity values are still far below the Robeson's upper bound. Another upper bound was developed in both Figures 4.18 and 4.19 using the highly performance PSF blends in the literature for better comparison with these blends.

Figure 4.18 displays results of CO_2/N_2 separation measurements of the selected DPSILMs, PSF- 25 wt% $[N_{4441}][formate]$ and PSF- 0.5 wt% $[DIP-C_4mim][NTf_2]$ are almost lying on the PSF blends upper bound which indicates almost similar separation efficiency compared to other PSF blends in the literature that lies on the line. Other DPSILMs such as PSF- 12.5 wt% $[N_{4441}][formate]$, PSF- 5 wt% $[DIP-C_4mim][NTf_2]$, PSF- 5 and 0.5 wt% $[C_4mim][NTf_2]$ are nearly approaching the line. Hence, it can be said that they behave as well or better than other PSF blends tested with mixed gas feed such as MSS-PSF and HZS-PSF prepared by Zornoza et al. as well as those tested with pure gas feed that were reported by Clem et al. On the other hand, PSF loaded with 5 wt% of $[P_{4441}][formate]$ is located far away below both PSF blends and Robeson's upper bounds although it achieved higher permeability than some DPSILMs (13.6 barrer). This is due to the very low selectivity compared to these DPSLIMs as a result of the high N_2 permeance as discussed previously.
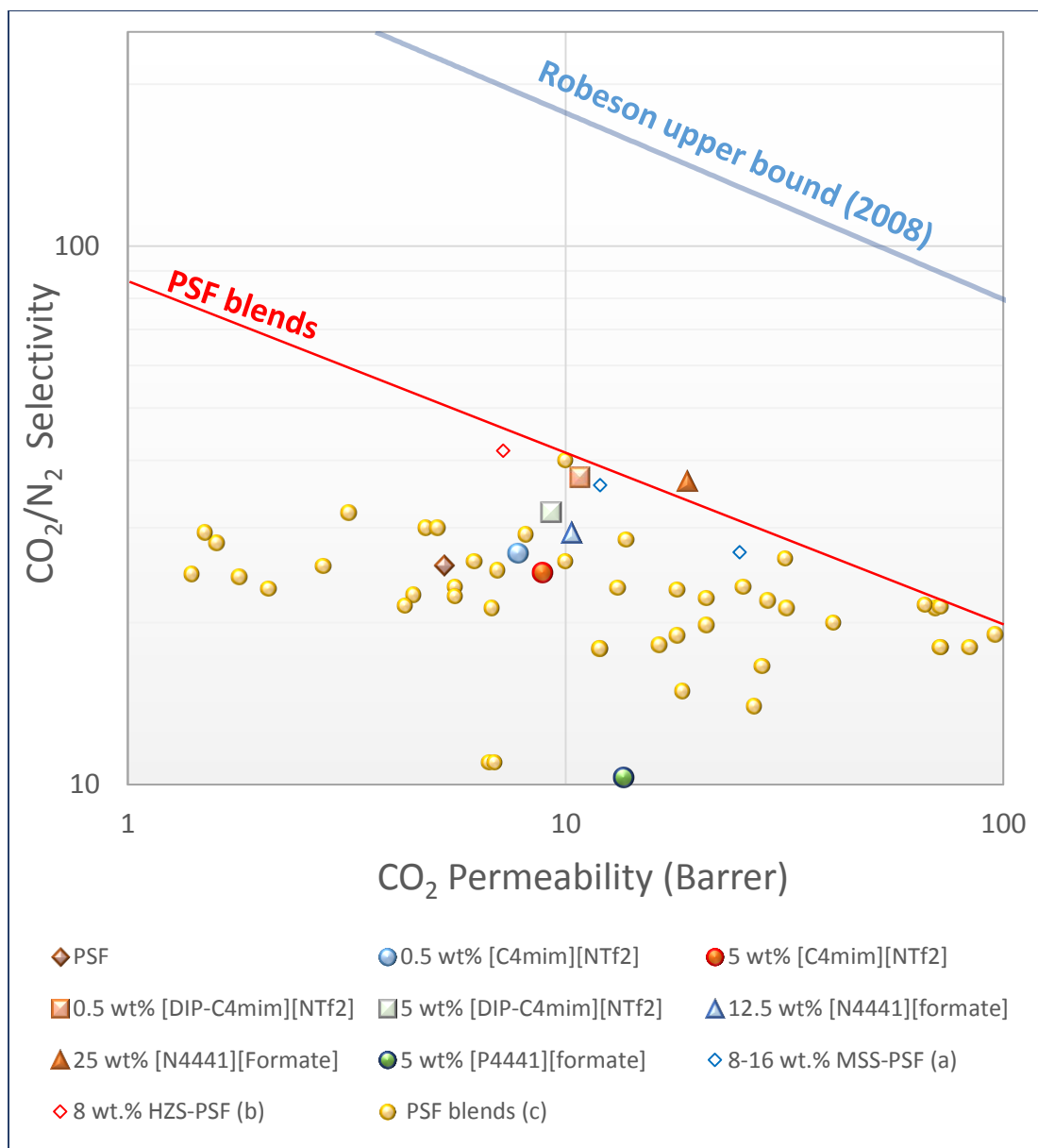
Figure 4.18: Permeability and selectivity values of CO_2/N_2 for the synthesized DPSILMs, PSF (mixed gas, System 1, 10 bars, 22°C), (a) Mixed gas (feed: 50/50 mol% CO_2/N_2, 1.75 bars and 35 °C) [100], (b) Mixed gas (feed: 50/50 mol% CO_2/N_2, 2.75 bars and 35 °C) [101], and (c) Dense PSF blends (single gas at different conditions) [99].

In contrast, the synthesized DPSILMs showed a promising behavior in CO_2/CH_4 separation compared to other PSF blend in the literature. DPSILMs loaded with [N_{4441}][formate], [DIP-C_4mim][NTf_2], and [C_4mim][NTf_2] break the constructed PSF blends upper bound since they recorded higher separation efficiency. In other words, these DPSILMs recorded higher selectivity and permeability than other PSF blends

tested with mixed gas separation measurements such as NH2-MIL-125(Ti)/PSF prepared by Guo et al. [102], NH2-MIL-53(Al)/PSF by Zornoza et al. [103] and NH2-MIL-101(Al)/PSF by Rodenas et al [104] as well as blends tested under pure gas conditions that reported by Julian et al. [98]. However, all prepared DPSILMs are still below the Robeson's upper bound.
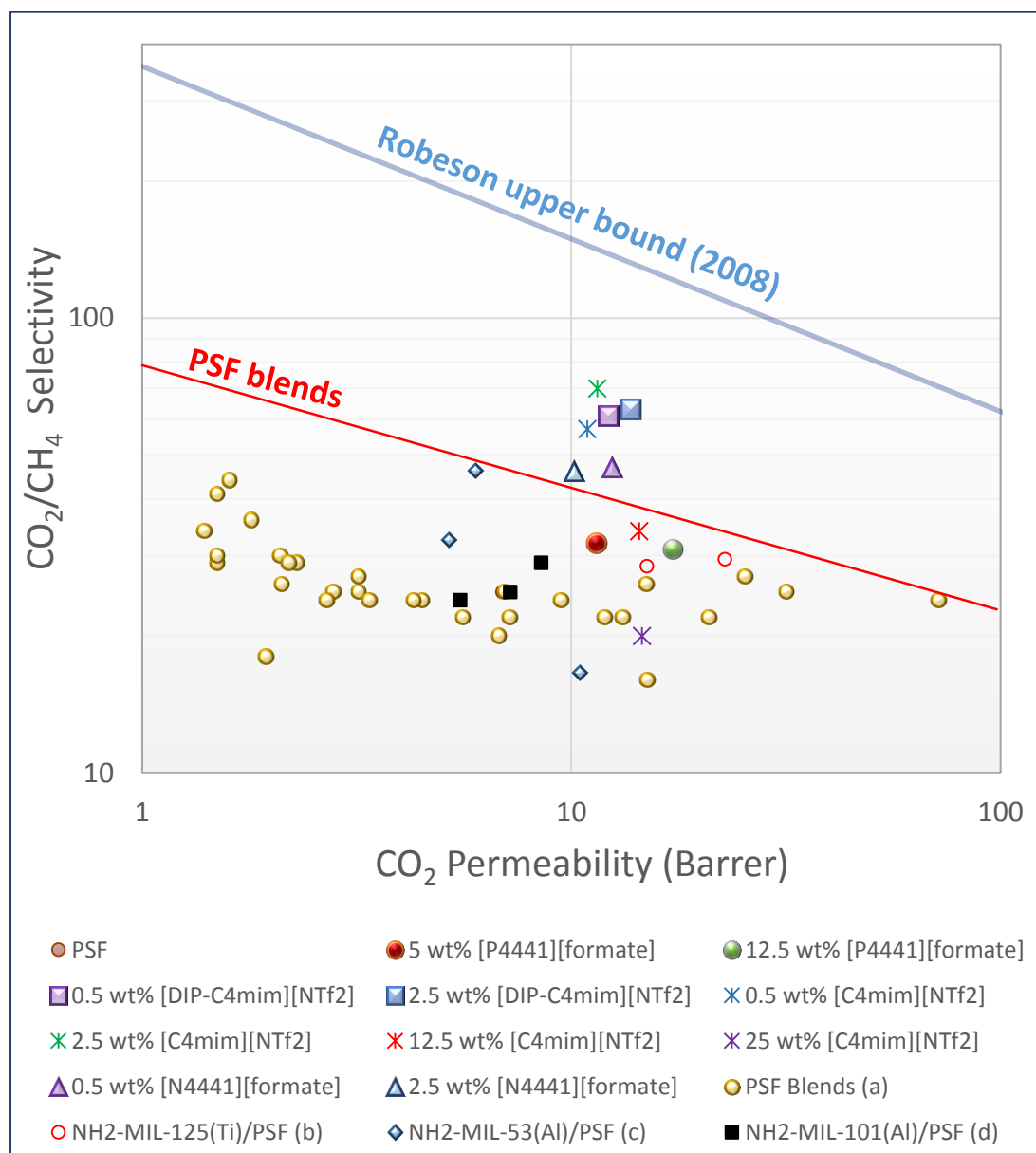
Figure 4.19: Permeability and selectivity values of CO$_2$/CH$_4$ for the synthesized DPSILMs, PSF (mixed gas, System 1, 10 bars, 22°C), (a) Dense PSF blends (single gas at 10 bars) [98], (b) Mixed gas (feed: 50/50 mol% CO$_2$/CH$_4$, 10 bars and 30 °C) [102], (c) Mixed gas (feed: 50/50 mol% CO$_2$/CH$_4$, 3 bars and 35 °C) [103], and (d) Mixed gas (feed: 50/50 mol% CO$_2$/CH$_4$, 3 bars and 35 °C) [104].

4.3. Stability of the synthesized DPSILMs

Stability measurements were conducted for PSF blends having 5 wt% of ILs as described in section 2.5. The results showed no loss of $[C_4mim][NTf_2]$ and $[DIP-C_4mim][NTf_2]$ through the membrane since no weight change was observed. However, in case of $[P_{4441}][formate]$ and $[N_{4441}][formate]$ a small weight loss was observed (Figure 4.20).
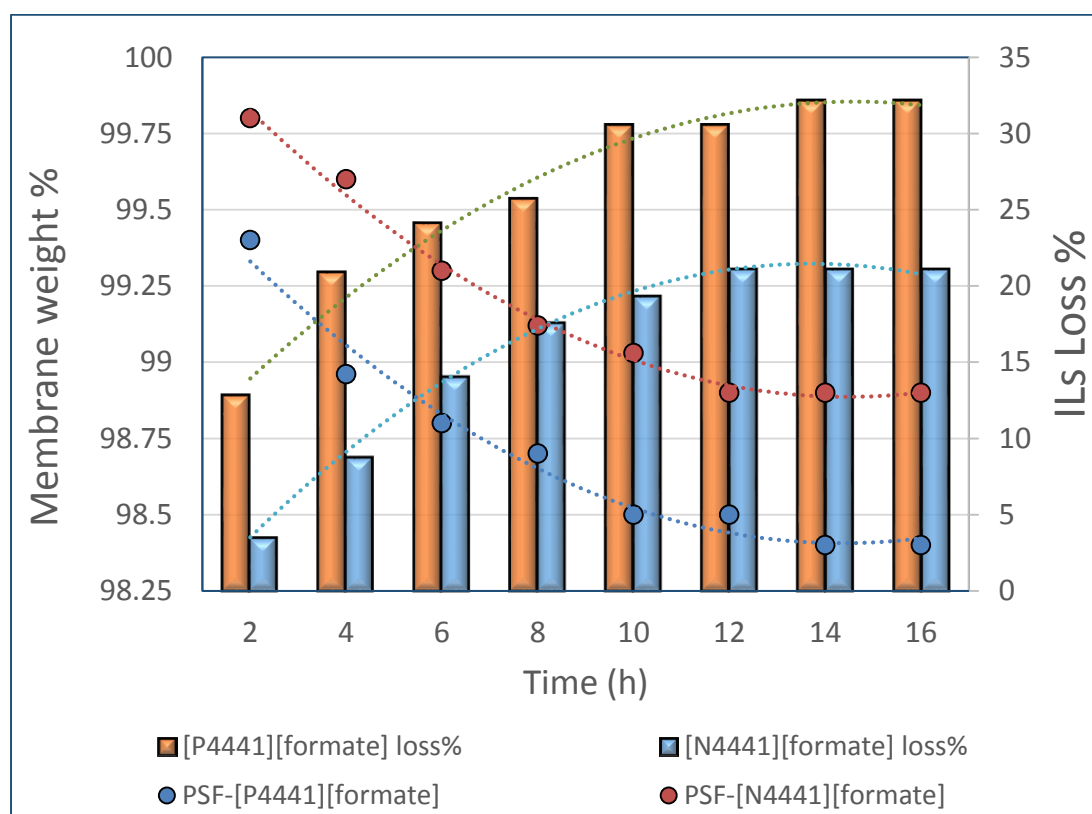
Figure 4.20: membrane weight and ILs loss as function of time (System 2, 10 bars, 22°C)

Figure 4.20 shows the membrane weight change (plotted on the primary y-axis) with the corresponding ILs loss % (plotted on the secondary y-axis) with the time based on the assumption that the loss in membtane weight is only due to ILs loss through the membrane. Almost similar behavior of membrane weight change was observed for both membranes PSF-$[P_{4441}][formate]$ and PSF-$[N_{4441}][formate]$. For PSF-$[N_{4441}][formate]$,

a gradual decrease was observed in the first 8 hours to about 99% of the membrane weight which corresponds to about 17% IL loss followed by slight increase in IL loss to about 21%. However in case of PSF-[P$_{4441}$][formate], membrane weight was decreased to 99% after 4 hours then stabilized at about 98.5% after 10 hours which corresponds to about 32% IL loss.

Zhao et al measured the ILs loss as a function of pressure and pore size using polyethersulfone (PES) support [119]. Figure 4.21 represents the results reported by Zhao et al. The reported results shows about 20% loss of ILs with supports having 0.2 µm and 0.45 µm at 1 bar; then ILs loss became more significant (>50%) at higher pressure. However, ILs loss increased to 50% at 2.5 bars and 70% at 3.5 bars with 0.1 µm support.
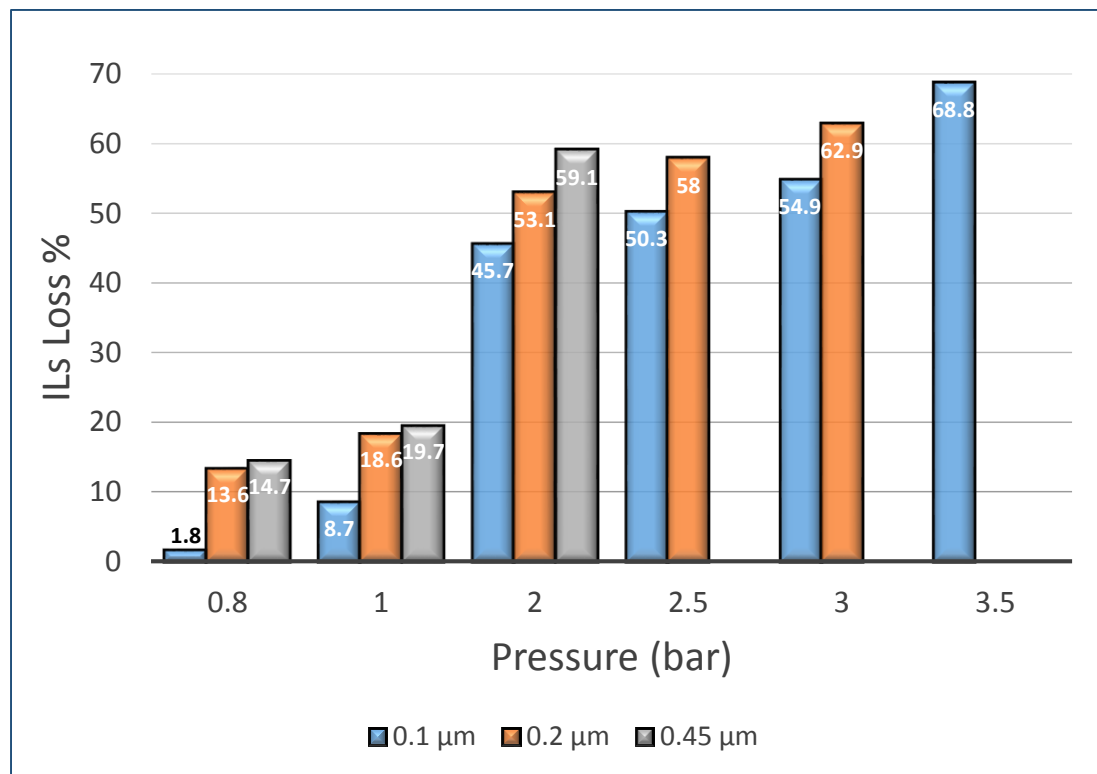
Figure 4.21: ILs loss for SILMs with different pore size as function pressure (Literatrue) [119].

When compared to stability of other SILMs in the reported literature, it can be clearly said that the synthesized DPSILMs are more stable than other SILMs. Neves et al reported SILMs weight loss using hydrophobic and hydrophilic supports with different types of ILs [114]. The reported results shows a reduction to about 88% and 90% of SILMs' weight having $[C_4mim][Pf_6]$ and $[C_4mim][NTf_2]$ respectively with hydrophilic supports after 10 hours at 1 bar. On the other hand, with hydrophobic support the membrane weight stabilized at 93% and 99% after 4 hours. Stability as a function of pressure of SILMs having $[C_4mim][NTf_2]$ supported by hydrophilic membrane and hydrophobic membrane are shown in Figure 4.22 (a) and (b) respectively. With hydrophilic support, a reduction to about 90 % of the membrane weight was occurred after 5 hours to stabilize then at 1 bar. Whereas with hydrophobic support, the reduction was very small (to about 99% of the membrane weight) with 1 and 1.5 bar. However, a significant reduction in membrane weight was observed at 2 bar for both hydrophilic and hydrophobic supports due to ILs loss which resulted in membrane failure.
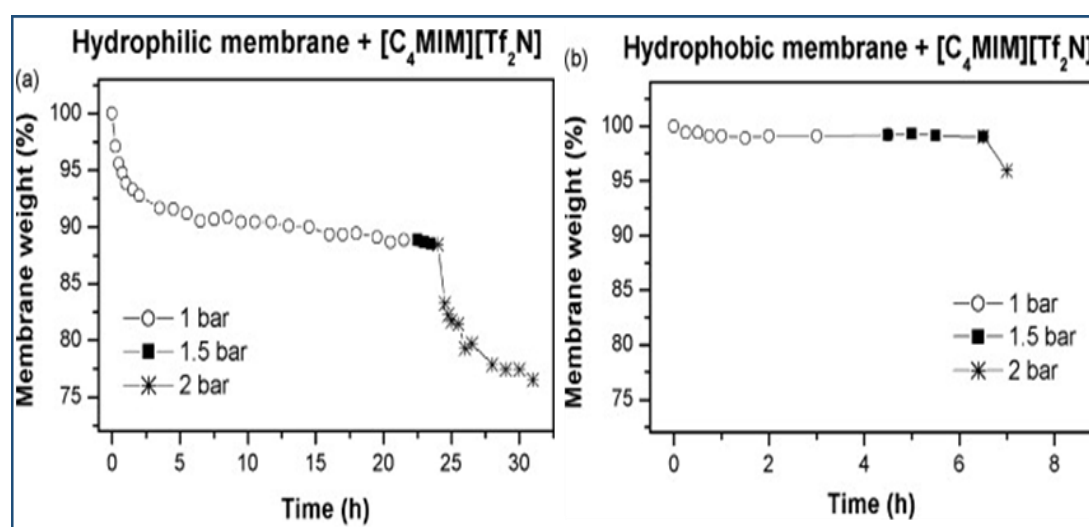
Figure 4.22: Weight of SILMs based on (a) hydrophilic, and (b) hydrophobic membranes immobilised with $[C_4mim][Tf_2N]$ as a function of time, for different applied pressures [114].

CO_2/CH_4 selectivity measurements were conducted for each of the DPSILMs three times in intervals of 5 hours at the conditions described in section 2.4 to indicate the DPSILMs stability regarding the separation efficiency. Stability results based on separation selectivity are shown in Figure 4.23.
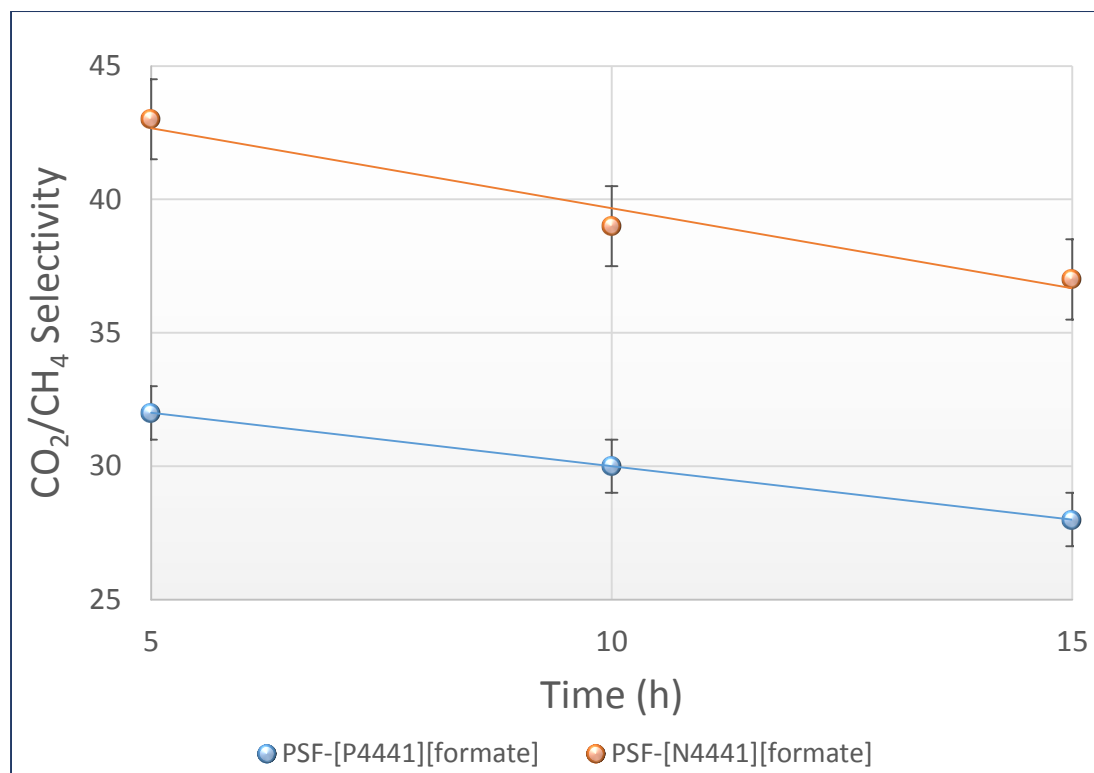
Figure 4.23: CO_2/CH_4 selectivity measurements as function of time (System 2, 10 bars, 22°C)

CO_2/CH_4 selectivity of DPSILMs loaded with $[P_{4441}][formate]$ and $[N_{4441}][formate]$ was reduced slightly as shown in Figure 4.23. The selectivity decreased from 43 to 39 then to 37 after 10 and 15 hours respectively with PSF-$[N_{4441}][formate]$. Similarly with PSF-$[P_{4441}][formate]$, selectivity decreased from 32 to 30 then 28 after 10 and 15 hours respectively.

5. Conclusion & Future Work

The concept of DPSILMs has been demonstrated here using polysulfone as the polymeric matrix. The use of supporting ionic liquids has opened up the possibility to significantly reduce the amount of the "active ingredient" used for CO_2 capture. It was found that DPSILMs prepared in our lab were useful for the selective separation of CO_2 at high pressures and gave promising results for CO_2 separation from N_2 and CH_4 streams. The prepared DPSILMs have been characterized using FT-IR and SEM, and both techniques showed that the selected ILs were successfully impregnated into the PSF and formed effective DPSILMs that can be treated like other dense membranes. Overall, the main work conducted and the main outputs of this thesis be summarized by the following points:

- A study on the separation efficiency of the synthesized DPSILMs was conducted using CO_2/N_2 and CO_2/CH_4 feed mixture containing 5 mol% CO_2.

- The separation selectivity was determined for each membrane using a state-of-the-art high-pressure membrane apparatus (System 2).

- DPSILMs having high selectivity values were tested in another membrane system (System 1) to measure the permeability of each gas through each membrane.

- CO_2/N_2 separation results obtained from both systems showed that the addition of [C_4mim][NTf_2], [DIP-C_4mim][NTf_2], and [N_{4441}][formate] to PSF increased the separation efficiency of CO_2.

- CO_2/N_2 selectivity decreased with the addition of [P_{4441}][formate].

- The effect of IL concentrations on the separation efficiency was investigated.

- CO_2/N_2 selectivity was found to be inversely proportional to the concentrations of [C4mim][NTf$_2$] and [DIP- C4mim][NTf$_2$], whereas it showed a slight increase with the addition of [N$_{4441}$][formate] and [P$_{4441}$][formate] ILs.

- The optimum IL concentrations for CO_2/N_2 separation are 0.5 wt% [C$_4$mim][NTf$_2$] and [DIP- C$_4$mim][NTf$_2$], 50 wt% for [P$_{4441}$][formate], and 25 wt% for [N$_{4441}$][formate].

- All of the used ILs showed increased CO_2/CH_4 selectivity compared to that of pure PSF.

- CO_2/CH_4 selectivity was inversely proportional to the concentration of all the used ILs.

- The highest CO_2/CH_4 selectivities were obtained with DPSILMs having low IL concentrations hence the optimum IL concentrations are 2.5 wt% for [C$_4$mim][NTf$_2$] and [DIP- C$_4$mim][NTf$_2$], 5 wt% for [P$_{4441}$][formate], and 0.5 wt% for [N$_{4441}$][formate].

- Stability measurements on DPSILMs were conducted with regards to IL loss and CO_2/CH_4 selectivty.

- DPSILMs incorporated [N$_{4441}$][formate] and [P$_{4441}$][formate] exhibited small loss of IL compared to that reported in literature and a slight reduction in the CO_2/CH_4 selectivity.

- No loss of [C$_4$mim][NTf$_2$] and [DIP- C$_4$mim][NTf$_2$] was observed. Thus, the synthesized DPSILMs are stable at high pressures for long durations.

Hence, it can be concluded that the synthesized DPSILMs show promising separation efficiency when compared to the reported literature and are expected to have useful applications in the industry and academia.

Numerous lines of research have raised from this thesis which should be pursued in the future:

- The synthesized DPSILMs in this work will be tested for the separation of Olefin/Paraffin mixtures such as ethylene/ethane (C_2H_4/C_2H_6) and propylene/propane (C_3H_6/C_3H_8).

- The effect of the support on the separation efficiency and membrane stability will be conducted by blending the used ILs with different commercial dense polymer-support such as matrimid, polyacetylene, polyimides, etc. and porous supports such as PVDF and PES.

- The effect of moisture content in the feed on the separation efficiency and membrane stability will be also tested.

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Appendix A: Reported Polysulfone permeation properties

Table A.1: CO₂ and N₂ permeation properties for dense membranes incorporating polysulfone (PSF) [99].

Name	Feed Pressure (bar)	P_{CO_2} (barrer)	α_{CO_2/N_2}
PSF	10/5	5.6	22.4
PSF	10/>5	4.9	24.5
TMPSF	10/5	21	19.8
HFPSF	10/5	12	17.9
TMHFPSF	10/5	72	18
PSF-F	10/5	4.5	22.5
PSF-O	10/5	4.3	21.5
PSF-P	10/1	6.8	21.3
TMPSF-F	10/5	5.5	9
TMPSF-P	10/1	13.2	23.2
BIPSF	10/2	5.6	23.3
TMBIPSF	10/2	31.8	26.3
1,5-NPSF	10/2	1.6	28.1
2,6-NPSF	10/2	1.5	29.4
2,7-NPSF	10/2	1.8	24.3
DMPSF	10/5	2.1	23.1
HMBIPSF	10/2	25.5	23.3
DMPSF-Z	10/5	1.4	24.6
PSF-AP	2	8.12	29.2
FBPSF	2	13.8	28.5
PSF-M	1	2.8	25.5
TMPSF-M	10/1	7	25
PSF-BPFL	1	10	40
3,4'-PSF	1	1.5	22.7

Name	Feed Pressure (bar)	P_{CO_2} (barrer)	α_{CO_2/N_2}
1,3-ADM PSF	10/2	7.2	21.8
2,2-ADM PSF	10/2	9.5	20.6
PSF (6% Br, 92% C≡CSiMe3)	1	36.5	17.4
PSF (3% Br, 47% C≡CSiMe$_3$)	1	18.5	14.9
PSF (21% Br, 77% C≡CCMe$_3$)	1	28.2	16.6
PSF (5% Br, 45% C≡CCMe$_3$)	1	16.4	18.2
PSF	1	5.6	22.4
PSF-s-HBTMS	1	21	22.2
PSF-o-HBTMS	1	70	21.3
PSF-CH$_2$-TMS	1	18	18.9
EM3	1	29	22
EM2	1	6.2	26
EM1	1	4.8	30
SM3 (degree of substitution=2.0)	1	18	23
SM3 (degree of substitution=1.0)	1	10	26
SM1	1	5.1	30
PPSF	1	3.2	32
RM3	1	27	14
RM2	1	6.7	11
RM1	1	6.9	11
HFPSF	1	12	17.9
HFPSF-o-HBTMS	1	105	18.6
HFPSF-s-TMS	1	41	20
HFPSF-o-TMS	1	84	18
HFPSF-TMS	1	110	18
TM6FPSF	1	72	18

Name	Feed Pressure (bar)	P_{CO_2} (barrer)	α_{CO_2/N_2}
TM6FPSF-*s*-TMS	1	96	19
TMPSF-TMS	1	32	21.3
TMPSF-*s*-TMS	1	66.3	21.6
TMPSF-HBTMS	1	72	21.4

*Table A.2: CO₂ and CH₄ permeation properties for dense membranes incorporating polysulfone (PSF). Permeability and selectivity measurement were conducted at 10 bars except for * at 4 bars [98].*

Name	P_{CO_2} (barrer)	α_{CO_2/CH_4}
PSF	5.6	22
TMPSF	21	22
DMPSF	2.1	30
DMPSF-Z	1.4	34
HFPSF	12	22
PSF-F	4.5	24
PSF-O	4.3	24
TMPSF-F	15	26
TMHFPSF	72	24
3,4-PSF	1.5	29
PSF-P	6.8	20
PSF-M	2.8	25
TMPSF-P	13.2	22
TMPSF-M	7	25
BIPSF	5.6	22
TMBIPSF	31.8	25
HMBISPSF	25.5	27
1,3-ADM PSF	7.2	22
2,2-ADM PSF	9.5	24
PSF-NH2 (16%)	2.7	24
PSF-NH2 (38%)	3.2	25
PSF-CH2-NH2 (51%)	1.95	18
PSF-CH2-imide (51%)	2.12	26
PSF-NO2(50%)	3.4	24
PSF-NO2 (98%)	2.3	29
PSF-NO2 (192%)	1.5	30
TM-NPSF *	4.85	36.7
HF-NPSF *	4.89	33.5

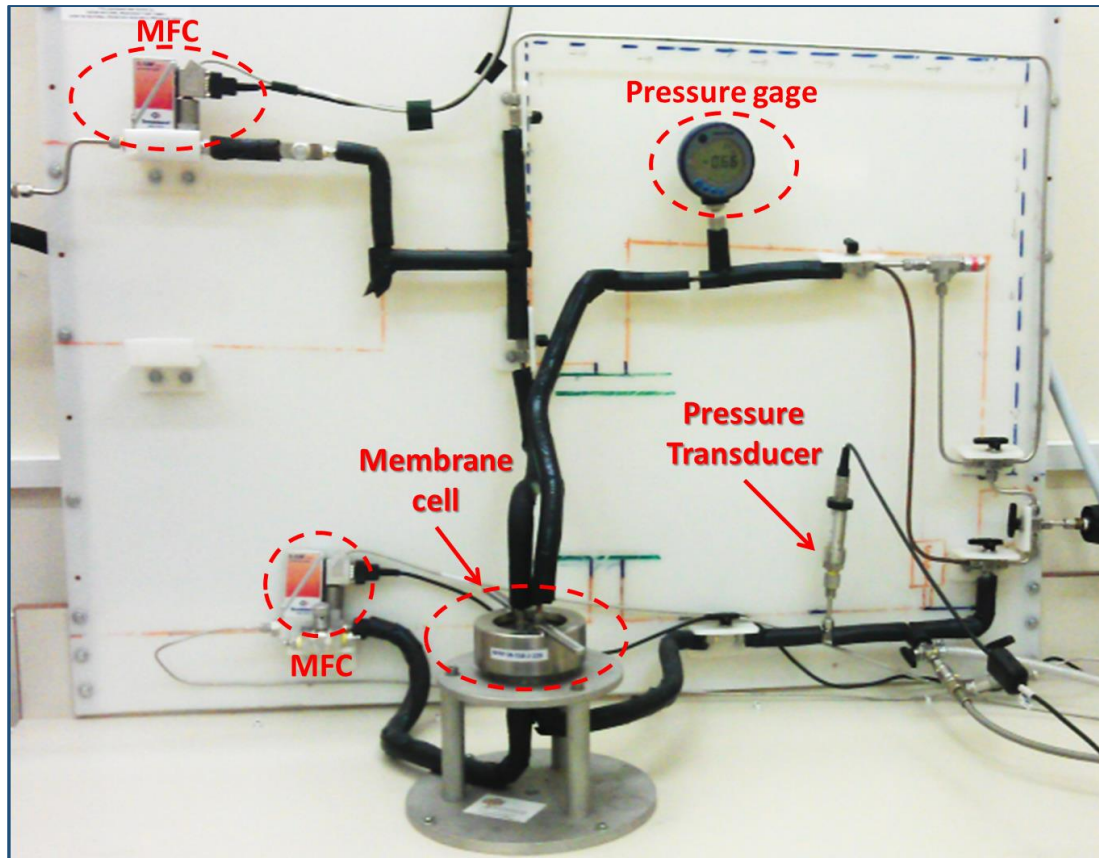| Name	P_{CO_2} (barrer)	α_{CO_2/CH_4}
TMHF-NPSF [*]	6.6	30.4
1,5-NPSF	1.6	44
2,6-NPSF	1.5	41
2,7-NPSF	1.8	36
BPSF	3.2	27
MPSF	2.2	29
TMSPSF	15.1	16

Appendix B: System 1
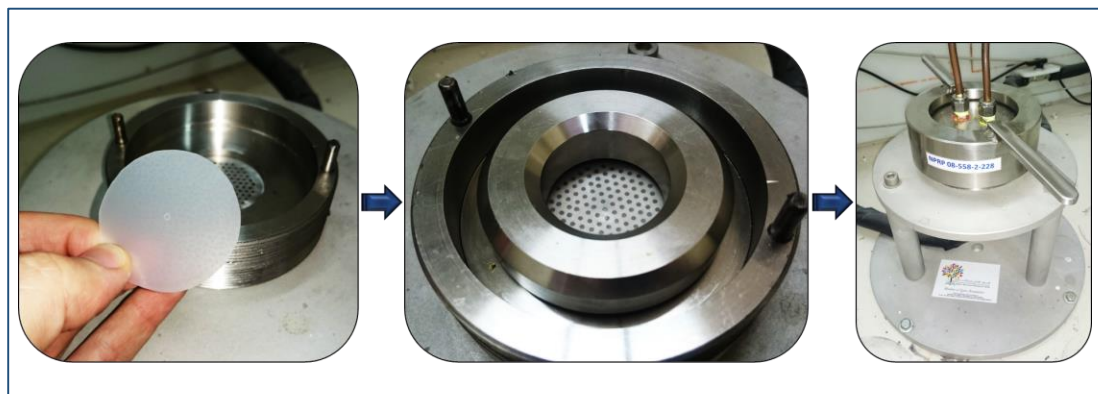

Figure B.1: Actual picture of System 1.

Figure B.2: Membrane cell of System 1

Appendix C: Rubotherm Membrane Reactor TM (System 2)

Figure C.1: Actual picture of the Rubotherm Membrane Reactor ^{TM} (System 2).

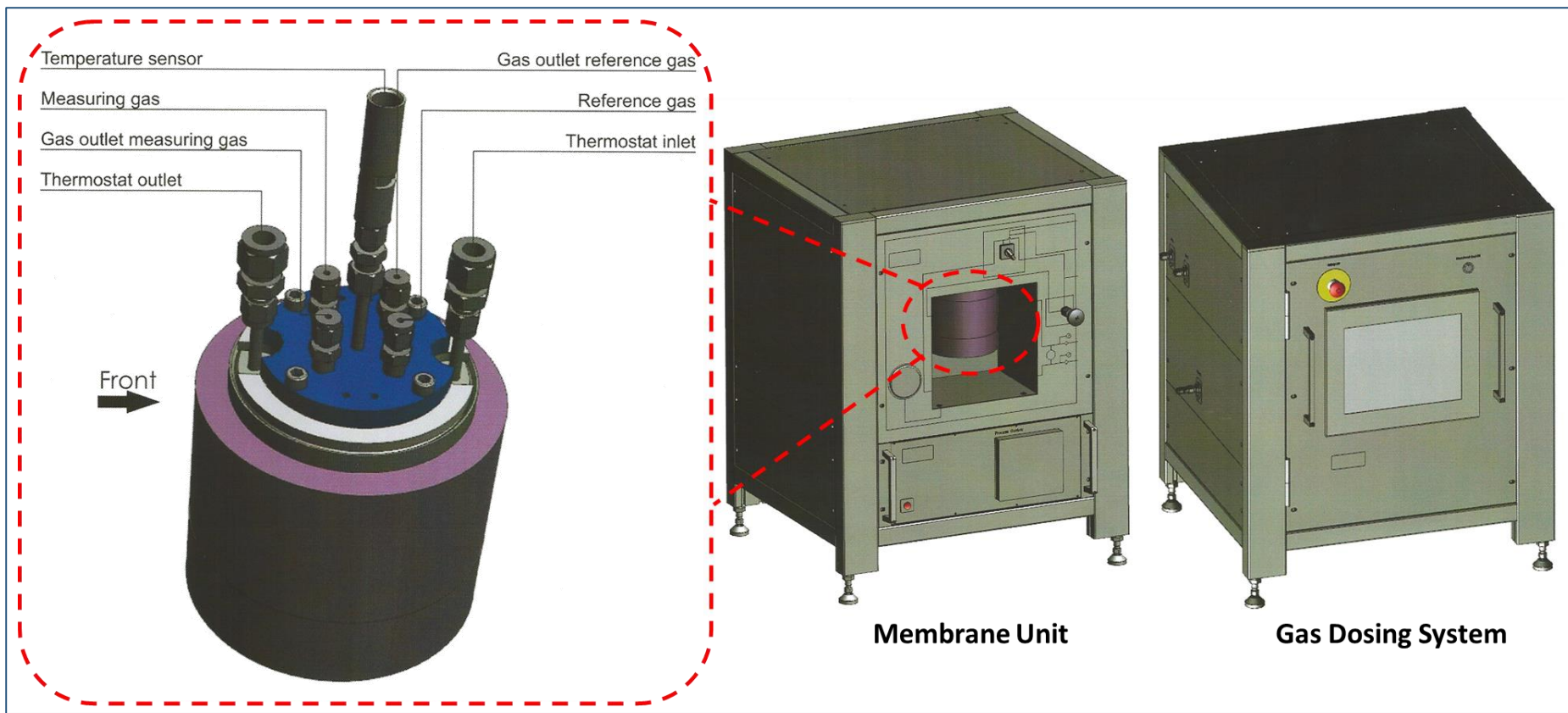*Figure C.2: Membrane holder of Rubotherm Membrane Reactor ^{TM} (System 2).*

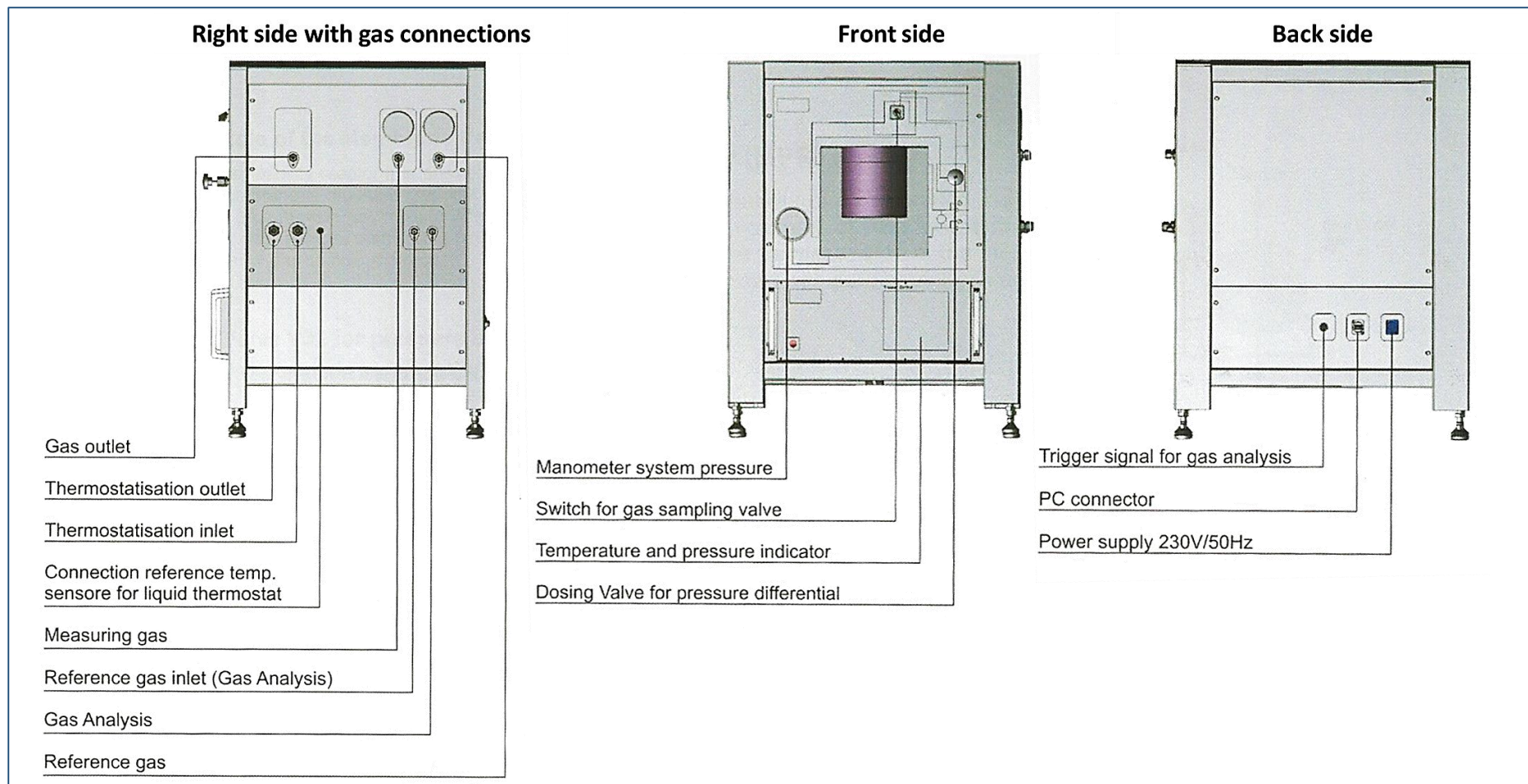Figure C.3: illustrations of the Rubotherm's membrane unit and gas dosing system.

Right side with gas connections

Gas outlet

Thermostatisation outlet

Thermostatisation inlet

Connection reference temp.
sensore for liquid thermostat

Measuring gas

Reference gas inlet (Gas Analysis)

Gas Analysis

Reference gas

Front side

Manometer system pressure

Switch for gas sampling valve

Temperature and pressure indicator

Dosing Valve for pressure differential

Back side

Trigger signal for gas analysis

PC connector

Power supply 230V/50Hz

Figure C.4: illustrations of the right, front and back side of Rubotherm's membrane.

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Disseminations & Publications

The content of this work is under submission process to a peer-reviewed journal titled "High-Pressure CO_2/N_2 and CO_2/CH_4 Separation Using Dense Polysulfone-Supported Ionic Liquid membranes" and the abstract, graphical abstract, and the highlights of the article is below:

Abstract

Four ionic liquids (ILs) were blended with polysulfone (PSF) to produce functional dense polymer-supported IL membranes (DPSILMs). The main aim was to investigate the applicability of the DPSILMs in industrial gas processing applications for high-pressure CO_2 separation from N_2 and CH_4 streams with less or no IL loss. The DPSILMs showed a clear chemical and physical change in the PSF structure and a good IL distribution in PSF. CO_2/N_2 and CO_2/CH_4 binary mixtures (5 mol% CO_2) were used. The highest CO_2/N_2 selectivities were 36 for PSF-0.5 wt% [DIP-C_4mim][NTf_2] and PSF-25 wt% [N_{4441}][formate], and 29 and 21 for PSF-0.5 wt% [C_4mim][NTf_2] and PSF-50 wt% [P_{4441}][formate], respectively. The highest CO_2/CH_4 selectivities were 70, 63, 47, and 32 for PSF-2.5 wt% [C_4mim][NTf_2], PSF-2.5 wt% [DIP-C_4mim][NTf_2], PSF-0.5 wt% [N_{4441}][formate], and PSF-5 wt% [P_{4441}][formate], respectively. Another system was used to measure the permeability of each gas for plotting on the Robeson's upper bound. The DPSILMs afforded satisfying results and behave as well or better than reported PSF blends. DPSILMs with 5 wt% [P_{4441}][formate] and [N_{4441}][formate] showed ~30% and 20% IL loss, respectively, at 10 bar after 12 h with a small reduction in the CO_2/CH_4 selectivity, while no loss was observed for [DIP-C_4mim][NTf_2] and [C_4mim][NTf_2].
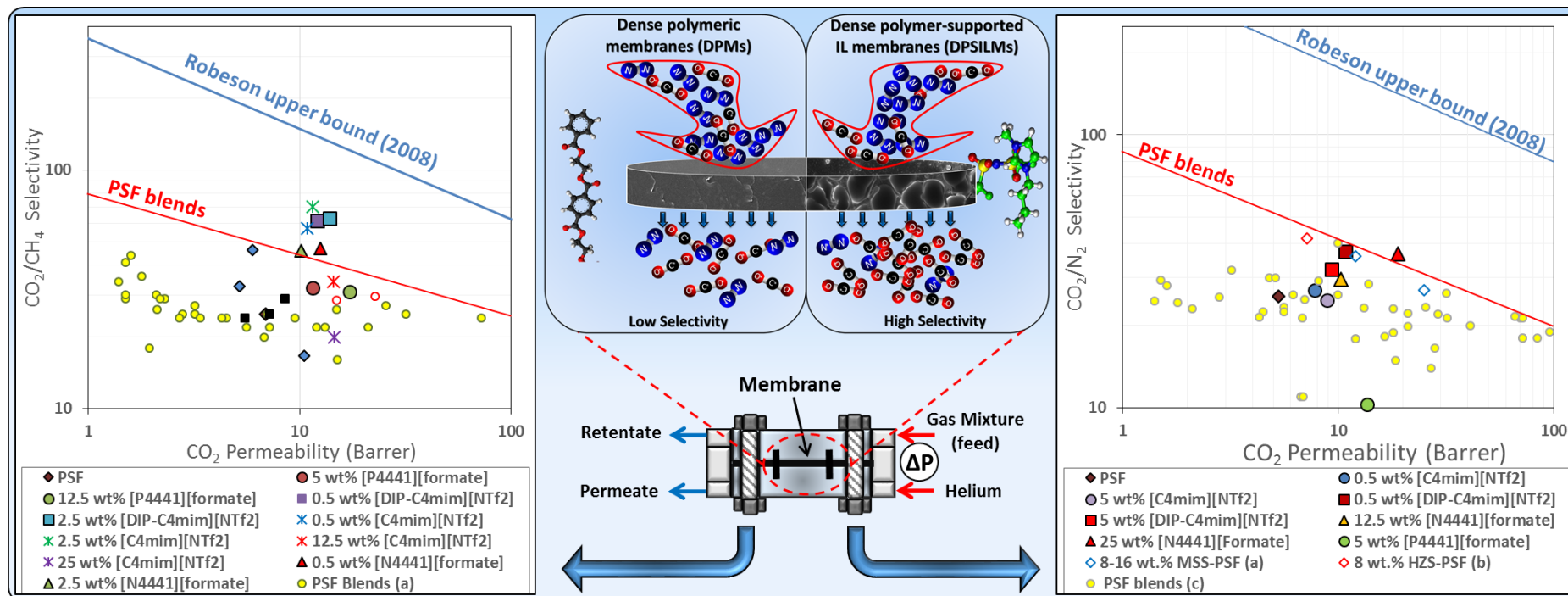
__Highlights__

- Functional dense polymer-supported IL membranes (DPSILMs) were prepared.

- For this, four ionic liquids (ILs) were blended with polysulfone (PSF) matrix.

- FTIR and SEM studies confirm successful impregnation of ILs into PSF matrix.

- DPSILMs were used to separate CO_2/N_2 and CO_2/CH_4 binary mixtures (5 mol% CO_2).

- DPSILMs afforded results as well as or better than reported PSF blends.

Furthermore, this work was accepted by the following conferences, symposiums, and competitions:

- New Trends in Multidisciplinary Research and Practice (NTMRP), Istanbul, 2015.

- My Gateway to Research, Qatar University, Doha, 2015.

- Posters Competition for CENG Research Day, Qatar University, Doha, 23rd May 2013.

- Annual Research Conference (ARC'14), Qatar Foundation, Doha, 2014
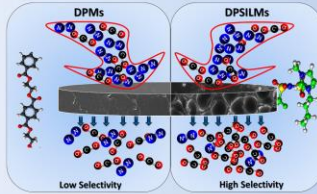
- Research Day, Qatar University, Doha, 2014.

Posters used in these events at different stages of the work are attached in the following pages.

كلية الهندسة
College of Engineering
جامعة قطر QATAR UNIVERSITY

Chemical Engineering Department
Abdulqader Al Khouzaam , Majeda Khraisheh,
Mert Atilhan, Shaheen Al-Muhtasib

High Pressure CO_2/N_2 Separation Using Dense Polysulfone supported Ionic Liquid membranes (DPSILMs)
NPRP 09-739-2-284

ABSTRACT

- Different types of ionic liquids (ILs) were blended with polysulfone (PSF) to produce functional dense polymeric-supported ionic liquid membranes (DPSILMs).
- The synthesized DPSILMs were analysed using FTIR and SEM, and showed a clear chemical and physical change in the structure PSF and well distribution of ILs in PSF.
- Two fully automated apparatuses were used to evaluate the effects of the added ionic liquids to PSF in High Pressure CO_2/N_2 separation.

OBJECTIVES

To investigate the potential use of the synthesized DPSILMs in the industrial gas processing applications for high-pressure CO_2/N_2 separation with less or no loss of ILs.

Background

Many recent studies have discussed the effect of ILs on CO_2/N_2 separation using different membrane support types, conditions and ILs. The high porosity, which is common issue in the reported studies, of the support membrane can lead to membrane failure with high pressure due to the loss of ILs.

In this work, we try to overcome the membrane failure due to ILs loss by blending ILs with dense (non-porous) polysulfone (PSF) hence applying higher pressure difference across the membrane. The resulted membranes are dense hence the permeation will follow Solution-diffusion mechanism.

Solution-diffusion mechanism through dense membranes.

Acknowledgement

METHODOLOGY

Membranes Synthesis
- Different concentrations of $[P_{4441}][formate]$, $[DIP-C_4mim][NTf_2]$, $[C_4mim][NTf_2]$, and $[N_{4441}][formate]$ were blended with PSF solution by direct mixing.
- The solution was stirred for about 24 hr at room temperature (~22 °C).
- The resulted homogenous solution was then casted uniformly on a flat glass plate at ~80 µm.
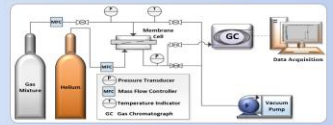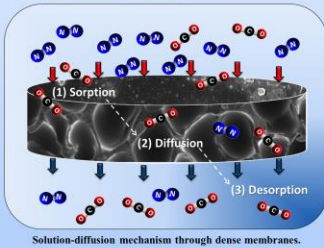- The resulting film was then dried for 24 h at room temperature.

Separation Measurements
The separation efficiency of the synthesized DPSILMs for CO_2/N_2 separation were tested using two flat-sheet membrane systems

System 1
(Rubotherm GmbH Permeability Reactor ™)

System 2
The permeation cell was manufactured at the Department of Physics, University of Cambridge

RESULTS & DISCUSSION

DPSILMs Characterization
The synthesized DPSILMs were analysed using FTIR and SEM, and showed a clear chemical and physical change in the structure PSF and well distribution of ILs in PSF.
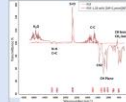
Plain PSF overlapped with PSF-12.5 wt% [DIP-C4mim][NTf2]
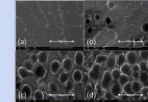
Cross-sectioned SEM images with 10,000 magnifications of (a) Pure PSF, and PSF blended with different loadings of $[P_{4441}]$ [formate] (b) 5 wt%, (c) 12.5 wt%, and (d) 25 wt%

Separation Measurements

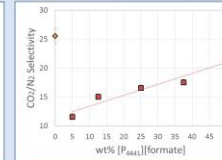**Fig 1: CO_2/N_2 Selectivity behavior with different loads of $[DIP-C_4mim][NTf_2]$ and $[C_4mim][NTf_2]$**

Fig 2: CO_2/N_2 Selectivity behavior with different loads of $[P_{4441}][formate]$
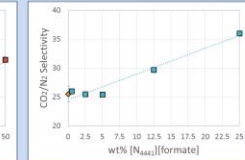
Fig 3: CO_2/N_2 Selectivity behavior with different loads of $[N_{4441}][formate]$

- CO_2/N_2 selectivity was clearly raised with the addition of low compositions (0.5 wt%) of $[C_4mim][NTf_2]$ and $[DIP-C_4mim][NTf_2]$ to 29 and 36 respectively compared to pure PSF that has a selectivity of 26 (Fig. 1).
- 5 wt% loading of $[P_{4441}][formate]$ reduced the selectivity to 12 whereas more loadings increased the selectivity to 21 with 50 wt% which is still lower than value obtained for pure PSF (Fig. 2).
- Figure 3 indicates that the selectivity was not affected significantly with low loadings of $[N_{4441}][formate]$ compared to PSF, however, it increased to 30 and 36 with 12.5 wt% and 25 wt% $[N_{4441}][formate]$ respectively.
- Figure 4 shows that the synthesized DPSILMs behave as well or better than different types of DPMs. However, the permeability and selectivity values are still far below the Robeson's upper bound.
- PSF- 25 wt% $[N_{4441}][formate]$ and PSF- 0.5 wt% $[DIP-C_4mim][NTf_2]$ are almost lying on the PSF blends upper bound which indicates almost better or similar separation efficiency compared to the PSF blends reported in literature.
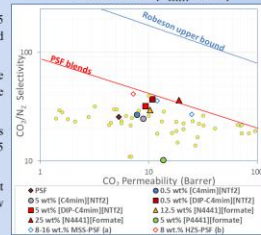

Fig 4: Permeability and selectivity values of CO2/N2 for the synthesized DPSILMs, PSF, Dense PSF blends and other DPMs.

Conclusion

- A study on the separation efficiency of CO_2/N_2 using a feed mixture of 5 mol% CO_2 and the balance N_2 the synthesized DPSILMs was conducted.
- Results showed that the increment of $[C_4mim][NTf_2]$, $[DIP-C_4mim][NTf2]$, and $[N_{4441}][formate]$ to PSF increased the selectivity of CO_2.
- Selectivity was decreased with the addition of $[P_{4441}][formate]$.
- The separation selectivity is inversely proportional to concentration in the case of $[C4mim][NTf2]$, $[DIP-C4mim][NTf_2]$; while it shows a slight increase with the addition of $[N_{4441}][formate]$ and $[P_{4441}][formate]$ ILs.

High Pressure CO_2/N_2 Separation Using Nonporous Polysulfone blended with Molten Salts (Ionic Liquids)

QUILL

**Abdulqader Al Khouzaam , Majeda Khraisheh, Mert Atilhan**

QATAR UNIVERSITY

Different types of ionic liquids were synthesized and blended with polysulfone (PSF) to produce functional dense polymeric ionic liquid membranes (PILMs). The synthesized ionic liquids included phosphonium, imidazolium, and ammonium based ionic liquids. The main aim of this project is to investigate the potential use of the synthesized PILMs in the industrial gas processing applications for high-pressure CO_2/N_2 separation. The synthesized PILMs were analysed using FTIR and showed a clear chemical change in the chemical structure of the pure PSF caused by the doping of the selected ionic liquids. SEM (surface and cross-sectioned) was also conducted on the prepared PILMs and showed the well distribution of ILs crystals in PSF, which enhanced the selective adsorption of CO_2 molecules to the membrane surface.

Two fully automated apparatuses were used in order to evaluate the effects of the added ionic liquids to PSF in CO_2 separation. Binary mixture of CO_2/N_2 (5% CO_2 v/v) was used in the study.
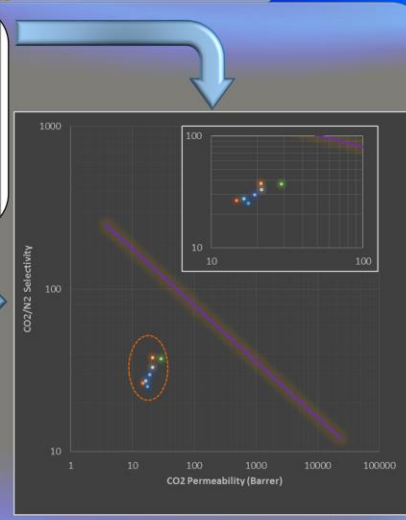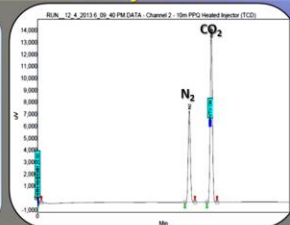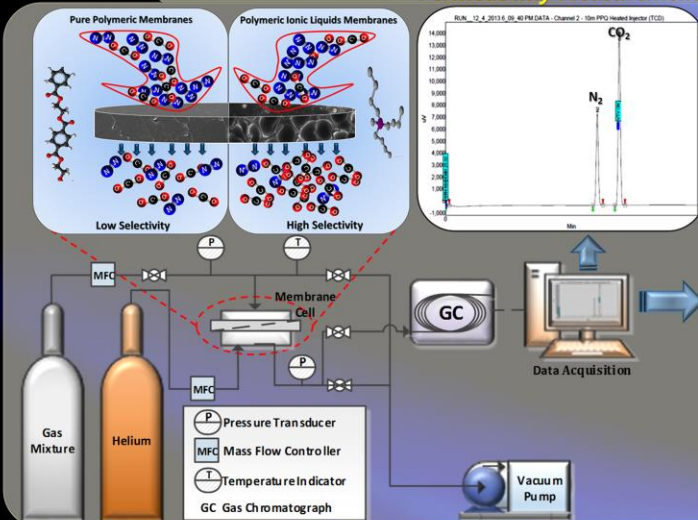
What is an ionic liquid (Molten Salt)?

"Ionic liquids are purely ionic compounds which are liquid below 100 ºC"

polymeric membrane + IL → PILM

Selectivity Measurements Using State-of-the-art Rubotherm® apparatus
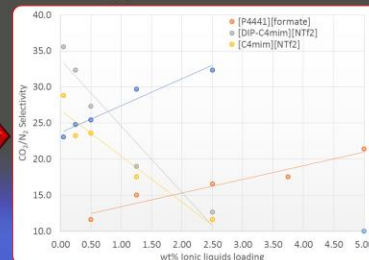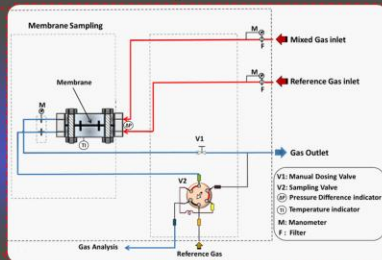
Permeability Measurements

Discussion

CO_2/N_2 selectivity values for the prepared PILMs were obtained using the state-of-the-art high-pressure magnetic suspension balance (MSB) sorption device by Rubotherm Präzisionsmesstechnik GmbH apparatus. The highest selectivity values were 35.6, 32.4, 28.8, and 21.4 obtained with [DIP-C_4mim][NTf$_2$], [N$_{4441}$][formate], [C$_4$mim][NTf$_2$], and [P$_{4441}$][formate] based PILMs respectively. Another system was used to measure the permeability of both gases. Highest CO_2 permeability values were found to be 17.55, 21.35, and 29.01 Barrer with [C$_4$mim][NTf$_2$], [DIP-C$_4$mim][NTf$_2$], and [N$_{4441}$][formate] based PILMs respectively. Permeability and selectivity values were plotted on Robeson's upper bound and showed that tested PILMs behave as well or better than different types of polymeric membranes.

Acknowledgement

Ionic Liquids in Gas Processing: Myth or Reality?

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Over the last decade ionic liquids have grown from relatively poorly understood materials to become integrated into industrial applications. These materials are, quite simply, comprised entirely of ions and are liquid at room temperature. Given their nature they have been described as "designer" solvents, with "tuneable" features that can be adjusted to suit the requirements of a particular process. A huge interest in using ionic liquids as an alternative medium for gas separation has become apparent because of such properties. For example the high thermal stability of ionic liquids provides considerable potential to utilise ionic liquids for CO_2 capture application. This project investigates the potential for ionic liquids in gas processing applications, in particular it presents recent solubility data of relevance to CO_2 separation at well head pressures. Here, we investigate the use of composite polymeric membranes blended with functionalised ionic liquids to produce functional membranes, supported ionic liquid membranes (SILMs) for CO_2/N_2 separations. FT-IR and SEM (surface and cross-sectioned) performed on SILM showed that no chemical or physical change caused by the addition of ionic liquid, however, it affected the permeability and selectivity properties of the tested gases.

What is an ionic liquid?

The empirical definition:

"Ionic liquids are purely ionic compounds which are liquid below 100 ºC"

What makes an ionic liquid a liquid

Ionic solid

Melts at ~ 801 °C

High symmetry ions lead to efficient packing, high lattice energy crystals with <u>HIGH</u> melting points

E.g.: NaCl (table salt)

Ionic liquid

Melts below 100 °C!!!

Large and flexible asymmetric ions result in poorly organised low lattice energy solids with <u>LOW</u> melting points

E.g.: [bmim][NTf$_2$]

State-of-the-art Rubotherm® apparatus

(a) Pure PEO (left) and PEO + ILs membranes (right)

(b) Pure PVdF-HFP (left) and PVdFHFP+ILs membranes (right)

SILM

Composite polymeric membrane + IL → SILM

Process P&ID

Acknowledgements