

**POLYSULFONE (PSF)/SILICOALUMINOPHOSPHATE (SAPO-34)
MEMBRANE INCORPORATED WITH 1-ETHYL-3
METHYLIMIDAZOLIUMBIS (TRIFLUOROMETHYSULFONYL) IMIDE
[EMIM][TF₂N] FOR CARBON DIOXIDE SEPARATION**

NG WON HUEI

UNIVERSITI SAINS MALAYSIA

2018

**POLYSULFONE (PSF)/SILICOALUMINOPHOSPHATE (SAPO-34)
MEMBRANE INCORPORATED WITH 1-ETHYL-3
METHYLIMIDAZOLIUMBIS (TRIFLUOROMETHYSULFONYL) IMIDE
[EMIM][TF₂N] FOR CARBON DIOXIDE SEPARATION**

by

NG WON HUEI

**Thesis submitted is partial fulfilment of the requirement
for the degree of Bachelor of Chemical Engineering**

June 2018

ACKNOWLEDGEMENT

Foremost, I would like to express my sincere gratitude to my respectful supervisor Assoc Prof. Dr. Leo Choe Peng for the continuous support, patience, motivation, enthusiasm, and immense knowledge throughout the tenure of my project in spite of her hectic schedule who truly remained driving spirit in my project and her experience gave me the light in handling research project.

I would also like to extend further appreciation postgraduate students, Ms Naimah and Ms Aini for their kindness cooperation and helping hands in guiding me carrying out the lab experiment. They are willing to sacrifice their time in guiding and helping me throughout the experiment besides sharing their valuable knowledge. Without their guidance and persistent help, this dissertation would not have been possible.

Besides that, I would like to convey my appreciation to assistant engineers in School of Chemical Engineering that have helped me in completing this research. They have been very helpful in teaching me to use the equipment as well as conduct the sample analysis for me.

Once again, I would like to thank all the people, including my family who keep motivating me and give support in this venture and to those whom I might have missed out and also my friends who have helped me directly or indirectly. Their contributions are very much appreciated. Thank you very much.

NG WON HUEI

June 2018

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF SYMBOL	ix
LIST OF ABBREVIATIONS	x
ABSTRAK	xi
ABSTRACT	xii
CHAPTER ONE	1
1.1 Global Issues and Strategy on CO ₂	1
1.2 Introduction of Carbon Capture Technology	2
1.3 Membrane Gas Separation for CO ₂ Separation	3
1.4 Introduction of Mixed Matrix Membrane (MMM)	5
1.5 Problem Statement	6
1.6 Objectives	8
1.7 Research scope	8
CHAPTER TWO	9
2.1 Removal of CO ₂ Technology	9
2.1.1 Polymeric Membrane	12
2.1.2 Inorganic Membrane	15

2.2	Emergence of Mixed Matrix Membranes (MMMs)	17
	2.2.1 Zeolite for MMMs Gas Separation	19
2.3	Introduction of Ionic Liquids (IL)	24
	2.3.1 CO ₂ solubility in ILs	26
	2.3.2 Ionic Liquid-Based Membrane for CO ₂ capture	28
	CHAPTER THREE	31
3.1	Materials and Chemicals	31
3.2	Equipment	32
3.3	Project management plan	33
3.4	Synthesis of asymmetric PSf / SAPO-34 MMMs	33
3.5	Post-impregnation of PSf/SAPO-34 MMMs	34
3.6	Characterization of membrane	35
3.7	Gas permeation experiments	35
	CHAPTER FOUR	37
4.1	Membrane Characterization	37
	4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)	37
	4.1.2 Membrane hydrophobicity	39
	4.1.3 Membrane morphology	42
4.2	IL for post-impregnation method	46
	4.2.1 Selection of IL on gas separation performance	46
4.3	Gas Performance Analysis	47
	CHAPTER FIVE	55

5.1	Conclusions	55
5.2	Recommendations	56
	REFERENCE	57

LIST OF TABLES

	Page	
Table 2-1	Materials for gas separation membranes	12
Table 2-2	Comparison between organic and inorganic membranes	17
Table 2-3	Gas permeance and ideal selectivities of different combination of MMMs	23
Table 2-4	Comparison of gas separation performance IL based MMMs in literatures	30
Table 3-1	List of chemicals and materials used	31
Table 3-2	List of equipment used in this work	32
Table 4-1	Water contact angle of membrane samples	41
Table 4-2	Comparison of ILs in gas separation performance	47
Table 4-3	Comparison of gas separation performance of pure PSf membrane,	49

LIST OF FIGURES

		Page
Figure 1-1	Trend in CO ₂ emission from fossil fuel combustion	2
Figure 1-2	Schematic diagram of mixed matrix membrane	6
Figure 2-1	The basic concept of membrane gas separation	11
Figure 2-2	Trade-off line curve of oxygen permeability and oxygen/nitrogen.	14
Figure 2-3	The total number of publications on inorganic membranes in the literature according to Scopus database	15
Figure 2-4	The most common anions and cations forming ILs	25
Figure 2-5	Structure of a common IL, 1-ethyl-3-methylimidazolium.	26
Figure 2-6	Effect of fluorination groups on CO ₂ solubility	27
Figure 3-1	Schematic Flow Diagram of Experimental Activities	33
Figure 3-2	Equipment for gas permeation test	36
Figure 4-1	FTIR spectra of (a) PSf, (b) PSf/SAPO-34, (c) PSf/SAPO-34 0.2M [Emim][Tf ₂ N], (d)PSf/SAPO-34 0.4M [Emim][Tf ₂ N], (e) PSf/SAPO-34 0.6M [Emim][Tf ₂ N]	38
Figure 4-2	FTIR spectra of (a) PSf, (b) PSf/SAPO-34, (c) PSf/SAPO-34 0.2M [Emim][Tf ₂ N], (d)PSf/SAPO-34 0.4M [Emim][Tf ₂ N], (e) PSf/SAPO-34 0.6M [Emim][Tf ₂ N]	38
Figure 4-3	Contact angle measurements for (a) PSf, (b) PSf/SAPO-34, (c) PSf/SAPO-34 0.2M [Emim][Tf ₂ N], (d)PSf/SAPO-34 0.4M [Emim][Tf ₂ N], (e) PSf/SAPO-34 0.6M [Emim][Tf ₂ N]	42

- Figure 4-4 SEM image for the surface of (a) PSf, (b) PSf/SAPO-34, (c) 44
PSf/SAPO-34-0.2M [Emim][Tf₂N], (d) PSf/SAPO-34-0.4M
[Emim][Tf₂N] and (e) PSf/SAPO-34-0.6M [Emim][Tf₂N]
- Figure 4-5 Cross section morphology for (a) PSf, (b) PSf/SAPO-34, (c) 46
PSf/SAPO-34 0.2M [Emim][Tf₂N], d) PSf/SAPO-34
0.4M[Emim][Tf₂N] and (e) PSf/SAPO-34-0.6M [Emim][Tf₂N]
- Figure 4-6 CO₂ Permeance of PSf and PSf/SAPO-34 MMM membrane at 50
ambient temperature and 3.5 bar
- Figure 4-7 Ideal selectivities of PSf and PSf/SAPO-34 MMM at ambient 50
temperature and 3.5 bar
- Figure 4-8 CO₂ Permeance of PSf/SAPO-34 membranes with and without IL 52
modification
- Figure 4-9 Ideal selectivity of PSf/SAPO-34 membranes with and without IL 52
modification

LIST OF SYMBOL

	Symbol	Unit
<i>A</i>	Effective membrane area	cm ²
α	Selectivity	-
<i>l</i>	Membrane layer thickness	cm
<i>P</i>	Permeability	GPU
ΔP	Pressure difference	cmHg
<i>Q_{STP}</i>	Volumetric flow rate at standard temperature and pressure	cm ³ /s

LIST OF ABBREVIATIONS

[BMIM][Tf ₂ N]	1- Butyl-3-Methylimidazolium bis(Trifluoromethylsulfonyl)
CH ₄	Methane gas
CO ₂	Carbon Dioxide
DMac	Dimethylacetamide
EDX	Energy Dispersive X-ray Spectroscopy
[EMIM][Tf ₂ N]	1- Ethyl-3-Methylimidazolium bis(Trifluoromethylsulfonyl)
FTIR	Fourier Transform Infrared
IL	Ionic Liquid
MMM	Mixed Matrix Membrane
N ₂	Nitrogen gas
PSf	Polysulfone
SAPO-34	Silicoaluminophosphate
SEM	Scanning electron microscopy
THF	Tetrahydrofuran

**POLYSULFONE (PSF)/SILICOALUMINOFOSFAT (SAPO-34) MEMBRAN
DIGABUNGAN DENGAN 1-ETIL-3 METILIMIDAZOLIUMBIS
TRIFLUOROMETHYSULFONYL) IMIDE EMIM][TF₂N] UNTUK
PEMISAHAN KARBON DIOKSIDA**

ABSTRAK

Karbon dioksida (CO₂) adalah penyumbang utama kepada kesan rumah hijau sejak revolusi perindustrian. Cecair Ionik (ILs) telah diperkenalkan secara meluas dalam era globalisasi ini kerana IL mempunyai kebolehtapan dan kelarutan CO₂ yang tinggi. dan secara tidak langsung dapat meningkatkan prestasi pemisahan CO₂. Dalam kajian ini, imidazolium-cecair ionik telah digunakan untuk meningkatkan and memperbaiki di antara muka polysulfone (PSf) dengan SAPO-34 zeolit dalam asimetri matriks campuran membrane (MMM) yang telah disediakan dengan kaedah penyongsangan fasa bagi mengurangkan rintangan pemindahan jisim. PSf/SAPO-34 MMMs telah diubahsuai dengan merendamkan membrannya dalam IL larutan (1-Etil-3 Metilimidazoliumbis Trifluoromethysulfonyl) Imide). Objectif utama kajian ini adalah untuk mengkaji kesan kepekatan IL pada membran dan prestasi pemisahan CO₂. Morfologi pengubasuain IL dengan menggunakan mikroskop elektron pengimbas (SEM) membuktikan penyebaran telaga daripada SAPO-34 tertakluk kepada meningkatkan polimer / antara muka pengisi. Fourier mengubah spektrum inframerah (FTIR) juga mengesahkan bahawa IL telah berjaya dilarutkan ke dalam MMM dan direkodkan untuk menyemak bon kewujudan dalam sampel membran. Membran dengan pengubasuain IL telah dapat meningkatkan kenalan di antara muka polimer dengan zeolite. Kelarutan CO₂, pemilihan CO₂/N₂ dan CO₂/CH₄ muka kedad yang menggunakan 0.2M MMM IL telah dipertingkatkan, dikenai 319.73%, 601.69% dan 605.84% lebih tinggi daripada MMMs.

**POLYSULFONE (PSF)/SILICOALUMINOPHOSPHATE (SAPO-34)
MEMBRANE INCORPORATED WITH 1-ETHYL-3
METHYLIMIDAZOLIUMBIS (TRIFLUOROMETHYSULFONYL) IMIDE
[EMIM][TF₂N] FOR CARBON DIOXIDE SEPARATION**

ABSTRACT

Carbon dioxide (CO₂) is the main contributor to greenhouse effect since industrial revolution. Ionic liquids (ILs) have been extensively studied in the recent years to improve the performance of CO₂ separation due to the high CO₂ solubility and selectivity. In this study, imidazolium-based ionic liquid was used to improve and functionalise the interface between polysulfone (PSf) and SAPO-34 zeolite in the asymmetric mixed matrix membrane (MMM) which was prepared by phase inversion method for minimum mass transfer resistance. PSf/SAPO-34 MMMs were post-modified by immersing the membranes into IL solution (1-Ethyl-3 Methylimidazoliumbis (Trifluoromethylsulfonyl) Imide). The main objective of this work is to study the effects of IL concentration on the membrane morphology and separation performance in CO₂. The morphology of the IL modification by using scanning electron microscopy (SEM) proved the well dispersion of SAPO-34 subjected to improve polymer/filler interface. The fourier transform infrared spectra (FTIR) were also confirmed that IL was successfully incorporated into MMM and recorded to check the existence bond in the membrane sample. The post-impregnation of the membrane with IL improved the interface contact between the polymer and zeolite. The interface sealing using 0.2M IL enhanced the CO₂ permeance, both of the CO₂/N₂ and CO₂/CH₄ selectivity of IL-modified MMM, about 319.73 %, 601.69 % and 605.84 % higher than the CO₂/N₂ and CO₂/CH₄ selectivity of unmodified MMMs.

CHAPTER ONE

INTRODUCTION

1.1 Global Issues and Strategy on CO₂

The threat of global climate change is considered as one of the most challenging environmental issues in the world (Worrell et al., 2001). Carbon dioxide, CO₂ is one of the major greenhouse gases (GHGs) which is enhancing to the greenhouse effect and eventually lead to global warming effect (Houghton, 2007). In this era globalisation, the control of anthropogenic emission of greenhouse gases such as carbon dioxide is one of the most challenging environmental issues which contributing to the global climate change facing by industrialized countries (Brunetti et al., 2010). It has been reported by the International Energy Agency that the emission of primary greenhouse gas, CO₂, increases by about 0.6% every year, due to the dependence of world economic on fossil fuels as energy source (Dai et al., 2016). CO₂ gases contributes 60 % of the global warming impact due to high amount of CO₂ exit in the atmosphere (Houghton, 2007). Combustion of fossil fuels, deforestation, unsustainable combustion of biomass, and the emission of mineral sources are the anthropogenic source of CO₂ which contributing to the global climate change in the world (Worrell et al., 2001). The CO₂ concentration in the atmosphere had reached 360 ppm in the dawn of industrial age. CO₂ emission from existing fossil plant into atmosphere is more than 2 billion tonnes of CO₂ annually, including for roughly two-third of the total CO₂ emission from the US. Power sector. CO₂ emission increased from zero to 26.6 Gt per year as the growing world energy supply still dependent upon fossil fuel as shown in Figure 1-1 (Quadrelli and Peterson, 2007). The fossil fuels is about 81 % act as the total primary energy source, the world energy supply is continued to rise by 52% between 2004 and 2030, CO₂ emissions are expected to continue to rise and reach 40.4 billion tonnes in 2030 (Quadrelli and Peterson, 2007).

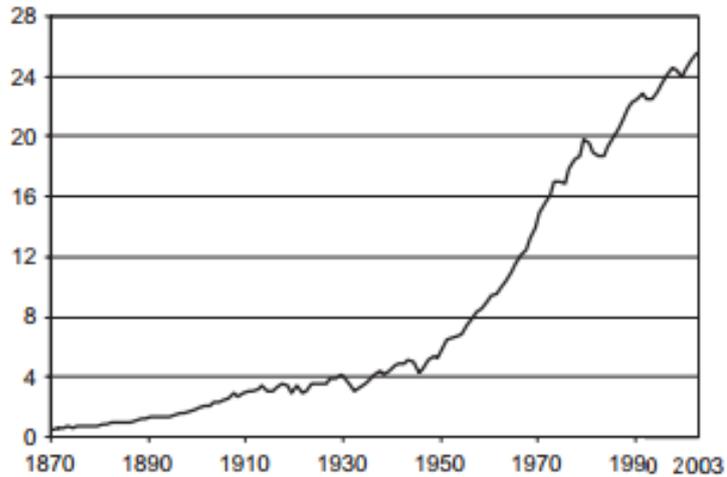


Figure 1-1: Trend in CO₂ emission from fossil fuel combustion

1.2 Introduction of Carbon Capture Technology

All the existing coal-fired power plants present emit about 2 million tons of CO₂ per year (Brunetti et al., 2010). The regulation of the CO₂ indicates that the development of CO₂ capture technologies that can be used to existing power plants with the goal to attain 90% of CO₂ capture limiting the increase in cost of electricity to no more than 35%. Carbon capture and storage (CCS) has been widely acknowledge as an economical technique to regulate the carbon emissions.

Up to date, there are a lot of strategies have been investigated and developed for the CO₂ separation from the gas mixture such as chemical absorption , physical absorption, membrane separation and chemical looping. The high energy demand and high capital cost bring down the development of fully integrated commercial CO₂ separation process. With higher separation efficiency, it helps to decrease the energy demand and the capital cost of the process.

Chemical absorption using aqueous alkanolamine solution is proposed to be the most applicable technology for CO₂ removal before 2030 (Aaron and Tsouris, 2005). This method has been used and applied in the chemical and oil industries for over 60 years.

For instance, amine-based absorption with an aqueous monoethanolamine (MEA) solution is used for post-combustion capture which can capture 90% of CO₂(Salazar et al., 2013). Nevertheless, this process has some disadvantages such as high equipment corrosion rate, high energy consumption in regeneration and a large absorber volume required. The cost of amine-based absorption for CO₂ separation is in the range of \$50 to \$100 per ton of carbon, which is high for the most technologies (House et al., 2011).

Furthermore, the physical absorption using cold methanol, dimethyl ether of polyethylene glycol (solexol) and propylene carbonate are widely used physical solvent for CO₂ separation. In general, they are separated CO₂ from the gas streams with high CO₂ partial pressure, released the pressure during solvent regeneration, thus creating the low energy demand. However, there are few disadvantages for physical solvents, such as low CO₂ selectivity, low CO₂ absorption, high capital and operating cost. Nowadays, ionic liquids (ILs) has been introduced with the applications in these technologies (Hanioka et al., 2008). Among these technologies, membrane separation has the potential to be more environmental friendly and energy saving but yet not so advance and mature compared to the currently technologies which is amine absorption. Thus, by preventing the world's CO₂ gas rising, membrane for CO₂ separation need to be studied and developed from various sources at different separation condition.

1.3 Membrane Gas Separation for CO₂ Separation

In recent years, membrane technology is most often listed as potential candidate and received extensive attention in the field of gas separation. Merkel et al. reported that using amine sorption to capture 90% (volume %) CO₂ from flue gas would consume 30% of the electricity produced by a power plant, which transcribe to a CO₂ capture price range from US \$40 to \$100 per ton. Thus, if a membrane separation system with a CO₂-N₂

selectivity of 50 and CO₂ permeance of 1000 GPU is used, the price could be reduced to \$23 per ton of CO₂ capture and only require 16% of energy from the power plant (Li et al., 2011a). Therefore, membrane technology could be a more efficient method to capture CO₂. Up to now, there are only eight or nine polymer materials have been used to make at least 90% of the total installed gas separation membrane base (Dai et al., 2016). The first large industrial application of gas separation membranes was in 1980 where Permea company had launched its hydrogen-separating prism membrane (Baker, 2002). Cynara, Separex, and GMS were using cellulose acetate membrane to remove CO₂ from natural gas (Spillman, 1989). After that, the sales of membrane gas separation has grown into \$150 million / year business during the past 20 years (Baker, 2002). Baker (2002) also predicted that the market scale of membrane gas separation technology in year 2020 will be 5 times of that of year 2000.

Membrane separation is an energy efficient and economical way in gas separation applications to reduce the environmental issues. Polymeric membrane is currently dominate in global membrane separation processes (Sanders et al., 2013) such as landfill gas recovery, production of oxygen enriched air, air separation from natural gas and flue gas separation (Powell and Qiao, 2006, Takht Ravanchi et al., 2009). Polymeric materials have attracted attention from many researchers due to excellent film forming properties of polymeric materials, mechanical stability and low cost. For example, polysulfone, poly(ethersulphone), polyamide, polyimide.

Although it have a lot of advantages of polymeric materials, but the separation performance of polymeric membrane is limited by trade-off between permeability and selectivity. Plasticization and aging are also major drawbacks of polymeric membrane (Sanders et al., 2013). In addition, the surface-to-ratio volume and brittleness of inorganic membranes are also the challenges to fully optimize their applications for gas separation

industries. Therefore, in order to improve the separation performance of polymeric membrane, different type of modification need to be applied to the polymeric membrane such as polymer blending, combining polymer and inorganic phases in the form of mixed matrix membrane, grafting and coating with protective layer (Adewole et al., 2013). In this project, mixed matrix membrane (MMM) is proposed in the current study.

1.4 Introduction of Mixed Matrix Membrane (MMM)

MMM is a well-known technology to enhance the properties of polymeric membrane. It is based on solid-solid system comprised of inorganic material in the form of microparticle or nanoparticle incorporated into polymer matrix (Bastani et al., 2013, Brunetti et al., 2010). It is recently getting more attention as an attractive candidate for membrane-based separation where it has a bright future as an alternative to conventional polymeric and inorganic membrane. The addition of inorganic particles in polymer matrix such as zeolite, carbon molecular sieve (CMS) and carbon nanotube have the potential to achieve high selectivity and/ or permeability with their inherent superior characteristic relative to exiting polymeric membrane. Due to its high porosity, uniform pore size, excellent thermal and chemical stability, zeolite is the one of the commonly used inorganic filter incorporated into polymer matrix during development of mixed matrix membrane (Kosinov et al., 2016). Silicoaluminophosphate (SAPO) zeolites are highly attractive due to the CO₂ adsorption affinity among the zeolite filter for MMMs fabrication. The schematic of mixed matrix membrane diagram is shown in Figure 1-2.

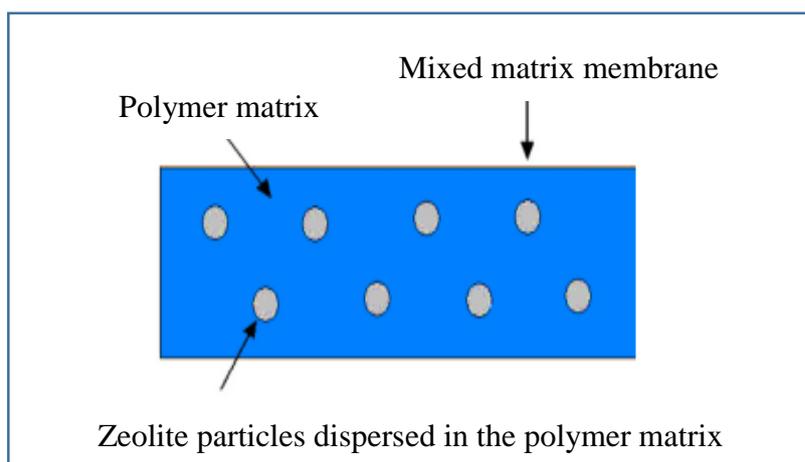


Figure 1-2: Schematic diagram of mixed matrix membrane

1.5 Problem Statement

Carbon dioxide is the largest contributor amongst the greenhouse gases (GHGs). In the foreseeable future, fossil fuels play an important role in the electrical power generation and industrial manufacturing in many countries. Thus, the CO₂ separation is strongly believed to have an enormous market due to strong need to deal with environment issue which is global warming and rapidly-increasing energy consumption in the future. Membrane separation has been one of the most widely studied by the researcher to develop more efficient and robust membranes for CO₂ separation from flue gas. The incorporation of the filters can cause interfacial voids and rigidified polymer layer attributable to stresses which arise during membrane formation when solvent evaporation or removing. Rigidified polymer layer formation near the particle was related to uniform stress around the particles. If the stress directions are not uniform around the inorganic particles, interface voids will be formed in the particle–polymer interface. Most of the researchers found that IL helps to improve and enhance the interfacial voids in the MMMs. Some researchers synthesized CO₂ selective MMMs using porous particles impregnated with IL after particle synthesise, whereas some other researcher confined IL

in the porous particle during synthesis. To date, the post-impregnation of IL on the MMMs has not been widely studied. It is believed that this post-impregnation of IL on MMM (PSf/SAPO-34) is able to attract attention as IL can help to improve and enhance the interfacial voids in MMM. Therefore, in this study, PSf/SAPO-34 (MMM) membranes were post-impregnated with IL drawn a great attention on membrane characteristics.

There are various types of combination for anion and cation of IL that widely used to enhance and functionalize the interface in the asymmetric MMMs such as 1-Ehyl-3-Methylimidazoliumbis (Trifluoromethylsulfonyl) Imide ([emim][Tf₂N]), 1-butyl-3-methylimidazolium acetate ([bmim][Ac]), 1-ethyl-3-methylimidazolium tetracyanoborate ([emim][B(CN)₄]) and the list go on. In this study, the IL used for post treatment method was [emim][Tf₂N]. Varying concentration of IL have the direct correlation to the performance of membrane gas separation. When the IL concentration increased, the performance of membrane gas separation increased. Up to date, there are no reports have addressed the gas separation performance by MMM comprising of PSf polymer matrix and SAPO-34 zeolite and post-impregnation by using various concentration of IL solution which is 1-Ehyl-3-Methylimidazoliumbis (Trifluoromethylsulfonyl) Imide, [emim][Tf₂N]. Thus, it is believed that this MMM treated by different concentration of IL is able to attract attentions by combining the advantage of both MMM (high CO₂ solubility) and IL (enhance the requirement for effective CO₂ separation) for gas separation process. Therefore, it is important to investigate the effect of IL concentration on MMM for the permeability and selectivity of carbon dioxide separation.

1.6 Objectives

The main objectives of this research are:

- i. To synthesis and characterize of mixed matrix membrane modified using IL for carbon dioxide separation.
- ii. To study the effect of different concentration of IL modification on MMMs for the permeability and selectivity of carbon dioxide separation.

1.7 Research scope

Fabrication of mixed matrix membrane has been studied in order to improve the performance of carbon dioxide separation. In this research, SAPO-34 nanoparticles was chosen as inorganic filler to be incorporated with the PSf membrane. SAPO-34 nanocomposite which can produce same sieving ability as that as zeolites offer opportunity to prepare high performance hybrid polymeric materials and can enhance CO₂ separation. The effects of concentration of [emim][Tf₂N] modification (0.2, 0.4, 0.6 M %) is studied and have been characterized using scanning electron microscope, (SEM), Fourier transform infrared, (FTIR) and contact angle while gas transport properties were investigated using pure gas permeation tests of N₂, CH₄ and CO₂.

CHAPTER TWO

LITERATURE REVIEW

2.1 Removal of CO₂ Technology

The existing coal-fired power plant present over the world today emit about 2 billion tons of CO₂ per year (Brunetti et al., 2010). The atmospheric CO₂ concentration has risen to over 370 ppm from 280 ppm in pre-industrial. Burning of coal, oil, natural gas for electric generation, transportation, industrial and domestic uses are the factors of contribution the increase in level CO₂ in the atmosphere (Thomas and Benson, 2015). Besides, based on the report from the International Energy Outlook 2010, the world energy-related CO₂ emission increased from 29.7 billion metric tons in 2007 to the estimated 42.4 billion metric ton in 2035 (Islam and Ahiduzzaman, 2012). With the rapid development of modern civilization today, carbon dioxide is produced in the enormous quantity which will contributes to global warming, urban smog, acid rain and health problems (Li et al., 2013). Thus, CO₂ removal is very important to combat the problems.

In order to improve the sequestration of CO₂, carbon dioxide capture and storage (CCS) technique is considered as the most efficient, economical and applicable technique option to regulate CO₂ from the industries (Dai et al., 2016). There are three main technological pathway for the CO₂ capture from fossil fuel plant which including pre-combustion capture, post-combustion capture and oxy-fuel combustion (Kanniche et al., 2010). Post-combustion capture applies primarily to the majority of exiting coal-fired power plant; pre-combustion capture applies to gasification plants; oxy-combustion capture is applied to retrofitted and new plants (Figueroa et al., 2008). The removal of CO₂ from post-combustion has been the main concern in the carbon capture and storage (CCS) (Dai et al., 2016).

There are many researchers have been making great effort to improve the current method and develop more efficient technology to CO₂ separation. There are various techniques can be applied for separation of the CO₂ such as chemical, physical absorption, membrane separation and cryogenic separation (Olajire, 2010) but the choice of the suitable and preferable method will mainly depend on the characteristics of treated gas and the process condition (He and Hägg, 2011). Up to now, the membrane technology and chemical absorption method are the most practical techniques for CO₂ removal in the industries (Zhao et al., 2008).

Chemical absorption namely amine-based absorption with an aqueous monoethanolamine MEA solution is currently regarded as the most feasible technology for post combustion CO₂ capture and it has been used for more than 60 years (Dutcher et al., 2015) to regulate the CO₂ emission which is primarily applied in the natural gas sweetening and biogas upgrading process. Fluor Daniel Inc., Dow Chemical Co., Kerr-McGee Chemical Corp., and ABB Lummus Crest Inc. were the initial developers of MEA-based technology for CO₂ capture (Rao and Rubin, 2002). This technology is capable to achieve high concentration of CO₂ capture about 90 % from flue gas due to fast kinetic and strong chemical reaction (Brunetti et al., 2010). Nevertheless, the conditions of flue gas and natural gas are substantially different such as the low partial pressure of CO₂ and high temperature of flue gas which can lead to thermal degradation of amines and losses through evaporation. Furthermore, amine solvents are corrosive and require significant amounts of energy for sensible heating, heat of reaction, stripping and in the form of low-pressure steam to regenerate the liquid solvent for reuse (Dutcher et al., 2015, Figueroa et al., 2008).

Membrane technology uses permeable or semi-permeable materials that enable for selective transport and separation of CO₂ from flue gas (Ciferno et al.). It is a pressure-

driven process. The membrane is a selective barrier that has the capability to transport one component more easily via the membrane than others owing to differences in physical and/or chemical properties between the membrane matrix and penetrants as shown in Figure 2-1 (Ismail et al., 2005).

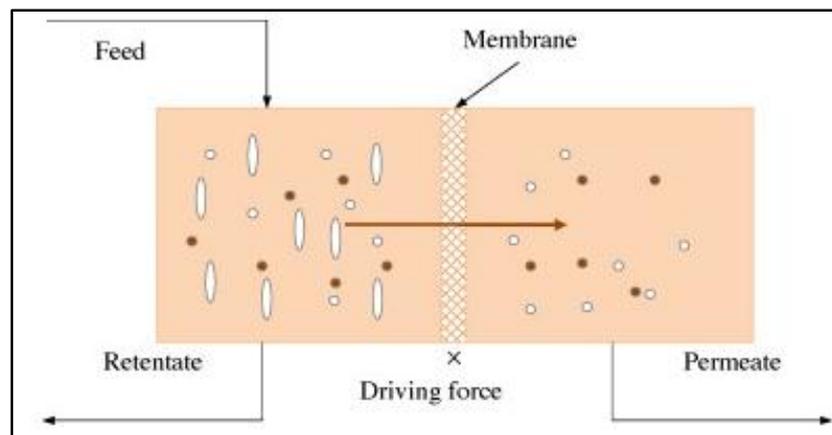


Figure 2-1: The basic concept of membrane gas separation

Membrane separation processes offer a number of advantages over to traditional separation process which are low capital and processing costs smaller unit sizes, simpler operation, better energy efficiency, low environmental effect and low energy intensive (Dai et al., 2016). Nonetheless, there are many issues regarding to the CO₂ capture from flue gas (Brunetti et al., 2010). In petrochemical plants, refineries and natural gas treatment, heavy hydrocarbons in feed gas streams become an issue for membrane gas separation as the membrane cannot withstand high temperatures and vigorous chemical environment (Bernardo et al., 2009). Additionally, membranes can be plasticized when exposed to high partial pressure of CO₂ / hydrocarbons; their separation abilities can be further reduced even in low concentration of CO₂ in flue gas (Bernardo et al., 2009).

In the past few years, membrane technology is extensively developed to produce wide range of materials with different structures and specific functions for separation

goals. There are two common synthetic membrane materials: polymeric (organic) and inorganic membranes which are the focus of attention in membrane technology, as shown in Table 2-1 (Nunes and Peinemann, 2001). In order to overcome the problems, an innovative membranes have been developed such as mixed matrix membrane (MMM) composed of homogenously interpenetrating polymeric and inorganic particle matrices (Chung et al., 2007) to compete with the current industrial amine-based processes.

Table 2-1: Materials for gas separation membranes

Organic Polymers	Inorganic Materials
Polysulfone, polyethersulfone	Zeolites
Cellulose acetate	Nanoporous carbon
Polyimide	Carbon molecular sieves
Polycarbonate	Ultramicroporous amorphous silica
Polyphenyleneoxide	Palladium alloys
Polymethylpentene	Mixed conducting perovskites
Polydimethylsiloxane	
Polyvinyltrimethylsilane	
Metal Organic Framework	

2.1.1 Polymeric Membrane

Polymeric membranes can be categorized into two basic groups which are glassy and rubbery (Bastani et al., 2013). In the glassy state, the polymers are hard and rigid and usually operate below the glass transition temperature, T_g . They have low chain intrasegmental mobility and long relaxation times. Conversely, in the rubbery state, the polymers become soft and flexible and they operate above their glass transition temperature, T_g . Glass transition temperature is defined as the temperature at which

transition from the glassy to rubbery state occurs (Mulder, 2012). Rubbery polymer membranes usually give a higher permeability as contrasted to glassy polymer membranes. This is because the gas molecules permeate through rubbery polymer quickly owing to the binding force between molecular segments of the polymer is not strong and the segments can move easily to open a channel at which the large molecules also can pass through. Additionally, solubility always has direct correlation to the diffusion characteristics for transport in rubbery polymers. Therefore, volatile organic compounds (VOCs) which exhibit high solubility (strong affinity) for polymeric materials, permeate much faster via a rubbery polymeric membrane as compared to smaller oxygen and nitrogen (Jansen et al., 2010). For instance, polydimethylsiloxane (PDMS) is one of the common rubbery polymer membrane for gas separation which can remove VOCs effectively from air (Bastani et al., 2013). The permeability of rubbery membrane is 1000 times higher than the permeability of glassy membrane (Bernardo et al., 2009). Nevertheless, rubbery membrane always show a lower separation efficiency as a consequence of their lower selectivity (Bastani et al., 2013). On the other hand, glassy polymer membranes exhibit low intrasegmental mobility and long relaxation time. They show higher gas selectivity compare to rubbery membrane due to the more restricted segmental motions in glassy membrane and resulted glassy membrane often dominate industrial membrane gas separation (Bastani et al., 2013). Furthermore, polyimide and polyethersulfone are widely studied and investigated by dozen of researchers because they exhibit higher gas selectivity and permeability compared to other glassy polymers. They have good mechanical properties as well as higher chemical and thermal stability in resulting membranes (Zimmerman et al., 1997, Sea et al., 1997).

In 1991, Robeson raised up an interesting topic which was upper bound trade-off curve, representing the inverse relationship between gas permeability and gas pair

selectivity for varied membranes (Robeson, 1991). In other words, there is an increase in the gas pair selectivity along with a decrease in the gas permeability and vice versa. The trend still continues even though the synthesis of polymeric materials has been remarkably developed and advanced. All polymeric materials are lying on or below the straight line of upper bound as shown in Figure 2-2. Thus, it is very important to synthesis the new membrane materials that exhibit both high selectivity and permeability in membrane-based gas separation technology.

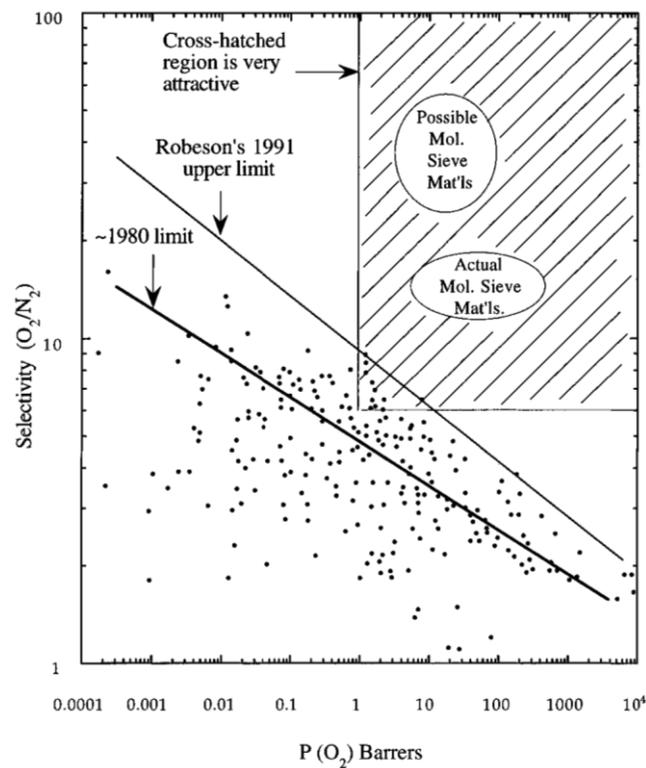


Figure 2-2: Trade-off line curve of oxygen permeability and oxygen/nitrogen. (Robeson, 1991)

2.1.2 Inorganic Membrane

Inorganic membranes technology is rapidly receiving global attention due to the superior separation properties such as high chemical, thermal, and mechanical stabilities, which allowing them can withstand in harsh conditions including corrosive and high temperature environments. The number is annual publications from the Scopus database is continuously increasing from less than 450 publications in 2000 to double up in 2016 when “inorganic membranes” was used as the keyword as shown in Figure 2-3 (Kayvani Fard et al., 2018).

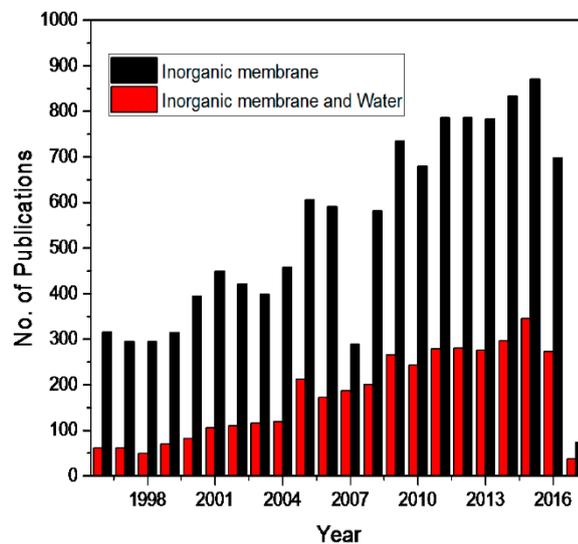


Figure 2-3: The total number of publications on inorganic membranes in the literature according to Scopus database (Kayvani Fard et al., 2018)

Inorganic membranes can be categorized into two parts based on the structure which are porous and dense. In porous inorganic membranes, a porous thin top layer is supported on a porous metal or ceramic support, which imparts mechanical strength but provides minimum mass-transfer resistance. The porous membrane are prepared mainly from ceramics including Al_2O_3 , ZrO_2 , and TiO_2 , glass, carbon, silica and porous stainless steel (PSS) , or a combination of these materials. Additionally, the inorganic porous membranes can be further classified based on the pore size (average diameter) which are

macroporous ($50\text{nm} < d < 2\mu\text{m}$), mesoporous ($2\text{nm} < d < 50\text{nm}$) and microporous ($d < 2\text{nm}$). On the other hand, the dense inorganic membranes comprised of a thin layer of metal such as palladium and its alloys, or solid electrolytes such as zirconia. These membranes are highly selective for hydrogen or oxygen separation but they have low permeability which restrict its intended applications as compared to porous inorganic membranes (Tan and Li, 2015). Molecular sieve membranes is one of the type of inorganic membranes that offer extremely superior performance with a high productivity and selectivity (Morooka and Kusakabe, 1999). In addition to that, they are more chemically resistant to organic solvents, chlorine and other chemicals better than organic membranes. Due to this, it helps significantly in water treatment applications where water is dosed with chlorine or other disinfectants which may deteriorate the organic membranes. Besides, the inorganic membranes are mechanically robust and are invincible to microbial attack. Nevertheless, their high cost and stiffness are their main disadvantages (Tan and Li, 2015). There are a comparison between organic and inorganic membranes in terms of their characteristics, advantages and disadvantages shown in Table 2-2 (Kayvani Fard et al., 2018).

Table 2-2: Comparison between organic and inorganic membranes

Properties	Polymeric membrane	Inorganic Membrane
Material	Rubbery or glassy type membranes based on the operating temperature.	Inorganic materials i.e, glass, ceramic , silica, etc.
Characteristic	Rigid in glassy form and flexible in rubbery state.	Chemically and thermally stable, mechanically robust, operational under harsh feed condition.
Advantages	Cost-effectiveness, good selectivity, easy processability.	Withstand harsh chemical cleaning, ability to be sterilized and autoclaved, high temperature (up to 500 °C) and wear resistance, well-defined and stable pore structure, high chemical stability, long life time.
Disadvantages	Fouling, chemically non-resistant, limited operating temperature and pressure, short life time.	Fragile, rigid.

2.2 Emergence of Mixed Matrix Membranes (MMMs)

Lately, polymeric membrane technology has gained attention due to its robustness and ease of fabrication. Nevertheless, the trade-off between permeability and selectivity is one of the major challenges faced by the polymeric membrane which greatly limit the performance of the membrane in further application (Jusoh et al., 2016, Bastani et al.,

2013). On the same time, inorganic membrane able to demonstrate significant and excellent performance but unfortunately, it is difficult to process and fabrication is costly (Jusoh et al., 2016). Thus, mixed matrix membrane started to emerge as an interesting approach in membrane technology to overcome the limitations (Aroon et al., 2010).

There were several significant review papers on the prospects of MMM about its capability as alternative membrane materials for gas separation process have been well published since the Zimmerman et al., (1997) published a pioneering literature suggesting that the benefit of MMM for gas separation such as provided economical and high separation performance compared to inorganic and polymeric membrane (Zimmerman et al., 1997).

In 1970s, the investigation of MMMs for gas separation was first studied with the addition of 5A zeolite into rubbery polymer polydimethyl siloxane (PDMS) and resulted large increases in the diffusion lag for CO₂ and CH₄ (Paul and Kemp, 1973). Furthermore, the researchers who were the first to report that MMM might yield excellent separation performance compare to polymeric membrane and they observed that the selectivity increased from 3.0 to 4.3 for O₂/N₂ when silicate content is added into the polymer cellulose acetate (CA) membrane (Kulprathipanja et al., 1988). The concept of MMM using CA/silicate for CO₂/H₂ separation demonstrated by Kulprathipanja and he found that CA/silicate (MMM) gave a high CO₂/H₂ selectivity of 5.12 ± 2.2 compared to CA membrane with a selectivity of 0.77 ± 0.06 (Kulprathipanja, 2002).

Additionally, in 2008, Jha and Way (2008). showed that the incorporation of SAPO-34 molecular sieve in rubbery substituted polyphosphazene membrane (PPZ) for formulation of MMMs increased the separation factor from 8.5 for the pure PPZ to 53 at 22°C for CO₂/H₂. Besides, Ismail et al. (2011) proved that MMM with 0.5 wt% multi-walled CNTs loadings produce the highest gas selectivity for CO₂/CH₄ and O₂/N₂ which

were 250.13 and 10.65 respectively (Ismail et al., 2011). These indicate that MMM can provide outstanding gas separation performance. MMMs were usually prepared by blending inorganic filler into polymer matrix and selection of inorganic filler and polymer is vital to ensure the improvement of separation performance was achieved without defects on MMMs (Jusoh et al., 2016).

2.2.1 Zeolite for MMMs Gas Separation

MMM materials, comprised of rigid permeable and impermeable particles, for an example, zeolites, carbon molecular sieves, silica and carbon nanotubes, inserted in a continuous polymeric matrix phase have the potential for high performance gas separation compared to traditional dense polymer membranes (Aroon et al., 2010). MMM offer the advantages of both polymer membranes which are low cost and ease of process ability and inorganic membranes which are high selectivity and permeability (Liu et al., 2010). Consequently, MMM had been considered as the significant potential of membrane material for advancing the current technology of CO₂ separation. Membrane researchers has been carried out worldwide academic studies on the MMM subject as it demonstrates the tremendous separation performance (Goh et al., 2011).

Currently, there are numerous types of inorganic filters have been used as filters in the fabrication of MMMs to improve the properties of polymer matrix compare to polymer and inorganic membrane. Zeolite is one of the example of inorganic filter which has been incorporated into polymer matrix for gas separation as many research of on it has been done (Süer et al., 1994a, Tantekin-Ersolmaz et al., 2000, Chung et al., 2007). Over the past decades, zeolite has received great attention due to wide range of structure that have different chemical composition and physiochemical properties (Bastani et al., 2013). The general properties of zeolites are high surface area, high adsorption capacity,

molecular sieving effect, high ion exchange capabilities, tunable hydrophilicity, high thermal stability, acidity basicity, and modulation of electronic properties of the active sites (Corma, 2003).

Jia et al. (1991) were the first to determine zeolite-filled rubbery polymer membrane comprised of PDMS, a rubbery polymer and silicalite-1 (hydrophobic zeolite) and they found that the silicalite-1 (Si) acted as the molecular sieve in the membrane by promoting the permeation of smaller molecules but preventing the permeation of larger molecules. The selectivity for CO₂/N₂ and CO₂/CH₄ with 70 wt % silica were 17.1 and 8.88 respectively at 30 °C and the CO₂ permeability was 3835 Barrer (Jia et al., 1991).

Zeolite 4A is another type of zeolite used in MMM for enhancing the gas separation performance. Sen Deger and co-workers proved that the selectivity of CO₂/CH₄ and CO₂/N₂ increased from 23.5 to 37.6 and 32.6 to 39.1 respectively with 30% of zeolite 4A loading into polycarbonate (PC) polymer matrix. However, the CO₂ permeability was found to slightly decrease from 8.8 to 7.0 Barer compare to neat polycarbonate membrane (Sen et al., 2006). Furthermore, in 2011, Adams et al., (2011) stated that an impressive increment in CO₂/CH₄ selectivity up to 63% was achieved using 50% loaded zeolite 4A incorporated into PVAc MMM under high CO₂ partial pressure. Apart from that, the enhancement of CO₂ permeability was recorded by Murali et al., (2014) from 71.4 to 155.7 Barrer and the CO₂/CH₄ selectivity increased from 26.4 with a neat Pebax 1657 membrane to 41.3 with 30 wt % of zeolite 4A embedded into Pebax 1657 membrane.

Furthermore, Zhang et al. (2008) found that incorporation of ZSM-5 in Matrimid phase enhanced CO₂/CH₄ ideal selectivity to 67.2, associated to pure Matrimid, with CO₂/CH₄ selectivity of only 34.7. In addition, higher CO₂/CH₄ selectivity of 67.4 was obtained for this membrane in binary gas separation (75% CO₂, 25% CH₄). In the recent

years, the incorporation of SAPO-34 zeolite particles into MMMs had been studied by a number of researchers (Junaidi et al., 2014a, Hudiono et al., 2011, Cakal et al., 2012). SAPO-34 zeolite is a silicoaluminophosphate molecular sieve with the chemical composition $\text{Si}_x\text{Al}_y\text{P}_z\text{O}_2$ where $x= 0.01-0.98$, $y=0.01-0.60$ and $z=0.01-0.52$ and its pore size is 0.38nm which has shown to be effective for removal of CO_2 in gas separation even in high feed pressure (Li and Fan, 2010). In addition, Briend et al. (1995) found that SAPO-34 zeolite was highly stable in humid atmospheres at temperatures over 100 °C.

In 2008, Jha and Way (2008) observed that there were increase of CO_2/N_2 and CO_2/CH_4 selectivity from 42 to 53 and from 15.3 to 17.5 when 25% of SAPO-34 was added into polyphosphazane (PPZ) phase. Elif Karatay and co-workers found that CO_2 permeability was significantly increased from 2.88 to 5.12 and its selectivity was 24.9 after incorporating 20 wt% of SAPO-34 into polyethersulfone (PES) (Karatay et al., 2010). Furthermore, Peydayesh et al. (2013) reported that the CO_2 permeability and CO_2/CH_4 selectivity were enhanced from 4.42 to 6.90 and from 34.00 to 66.99 when 20 wt% of SAPO-34 zeolites were incorporated into Matrimid membrane. Moreover, the CO_2 permeability was improved from 111 to 338 barrer and the CO_2/N_2 and CO_2/CH_4 selectivity were 52 and 16 by addition of 50 wt% of SAPO-34 into PEBAS 1657 phase reported by Zhao et al. (2014). Besides, Junaidi et al. (2014b) found that the gas permeance increased from 22.01 to 314.02 when 10 wt% of SAPO-34 zeolites incorporated into polymeric membrane and the selectivity of CO_2/N_2 and CO_2/CH_4 improved from 16.5 to 26.1 and from 17.3 to 28.2 as compared to neat polymeric membrane. Other than that, the Pebax 1074 incorporated with 20 wt% SAPO-34 zeolite contributed the increment of selectivity of CO_2/CH_4 and CO_2/N_2 by 70 % and 15% respectively at 20 wt% of SAPO-34 loading as compared to neat membrane studied by

Rabiee et al. (2015). Separation performance of the fabricated membranes were summarized and tabulated in Table 2-3.

Table 2-3: Gas permeance and ideal selectivities of different combination of MMMs

MMM materials			Selectivity		Permeability (Barrers) P _{CO₂}	Reference
Polymer	Zeolite content (%)	Filter	CO ₂ /CH ₄	CO ₂ /N ₂		
PDMS	Si	70	8.88	17.1	3835	(Jia et al., 1991)
PC	zeolite 4A	30	37.6	39.1	7	(Sen et al., 2006)
PVAc	zeolite 4A	50	40.6	-	4.33	(Adams et al., 2011)
Pebax- 1657	zeolite 4A	30	26.4	-	155.7	(Murali et al., 2014)
PPZ	SAPO -34	25	17.5	53	48	(Jha and Way, 2008)
PES	SAPO- 34	20	24.9	-	5.12	(Karatay et al., 2010)
Matrim id	SAPO- 34	20	66.9	-	6.90	(Peydayesh et al., 2013)
PEBAS 1657	SAPO- 34	50	16	52	338	(Zhao et al., 2014)
PSf	SAPO- 34	10	28.2	26.1	314.02	(Junaidi et al., 2014b)
Pebax 1074	SAPO- 34	20	32	72	170	(Rabiee et al., 2015)

2.3 Introduction of Ionic Liquids (IL)

In the past 15 years, ionic liquids (ILs) has been extensively studied by number of researchers and emerged as promising solvent for CO₂ capture. ILs are molten organic salts under ambient temperature and pressure. ILs usually melt below 100 °C and are often already molten at room temperature called Room temperature Ionic Liquids (RTILs). RTILs appear in liquid formed at ambient temperatures primarily owing to the low intermolecular interaction, poor packing and charge delocalization (Ahmad et al., 2017a). There are some ILs exhibit good absorbent of CO₂ since the electrical charges of these ILs can interact with quadruple moment of CO₂ molecules physically. There are approximately 10¹⁸ different anion-cation combinations are probable for IL synthesis (Gutowski et al., 2005). The most widely studied cation and anions of ILs can be shown in Figure 2-4. The most commonly used cation for IL: aza-heterocyclic cation (e.g imidazolium cation, pyridinium cation and pyrrolidinium cation; ammonium cation and phosphonium cation. Predominant anion species constitute ILs comprised of halides (chloride, bromide, iodide), carboxylate anions (acetate), fluorinated anions (bis(trifluoromethylsulfonyl)imide, trifluoromethylsulfonate and hexafluorophosphate. The functionalization of ILs using various type of anions can improved the chemical capture of CO₂ efficiently and effectively.