



## Emerging ionic liquid engineered polymeric membrane for carbon dioxide removal: A review



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### ARTICLE INFO

#### Article history:

Received 26 March 2021

Revised 27 March 2022

Accepted 16 April 2022

Available online 22 April 2022

#### Keywords:

Ionic liquid

Membrane

CO<sub>2</sub> separation

Mixed matrix membrane

Natural gas

### ABSTRACT

Ionic liquid (IL), which possesses excellent properties such as high affinity towards carbon dioxide (CO<sub>2</sub>), negligible vapour pressure and highly viscous is a promising material to be incorporated in membrane gas separation. As conventional membranes carry limitations that hinder the separation performance, the presence of IL has the potential to overcome the problem. However, with the incorporation of IL, membrane stability, high pressure condition application and mechanical strength are among the major drawbacks for IL based membranes. Therefore, this review highlights the progress in IL-enhanced membrane for gas separation application. The progress on IL-enhanced membrane such as supported ionic liquid membrane (SILM), poly(RTIL) membrane, polymer-ionic liquid blend membrane, ionic liquid mixed matrix membrane (IL-MMM) are also critically review in this work. The advantages and challenges associated with the membranes are thoroughly discuss in this review. The performance of IL-based membranes is also plotted against Robeson Upperbound to show the progress of the IL based membrane over the years. Finally, the opportunities for the IL based membranes are deliberate for future development in gas separation.

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## Nomenclature

### Cation

#### Abbreviation Name

|                    |                               |
|--------------------|-------------------------------|
| Emim               | 1-N-Ethyl-3-methylimidazolium |
| Bmim               | 1-Butyl,3-methyl-imidazolium  |
| Omim               | 1-Octyl,3-methyl-imidazolium  |
| Hmim               | 1-Hexyl-3-methylimidazolium   |
| THTDP              | Trihexyltetradecylphosphonium |
| THDP               | trihydrogen diphosphate       |
| C <sub>4</sub> mim | 1-n-butyl-3-methylimidazolium |
| C <sub>6</sub> mim | 1-hexyl-3-methylimidazolium   |
| C <sub>8</sub> mim | 1-octyl-3-methylimidazolium   |

### Anion

|                                      |  |
|--------------------------------------|--|
| FEP                                  | tris(pentafluoroethyl)trifluorophosphate |
| Tf <sub>2</sub> N                    | bis(trifluoromethylsulfonyl)imide        |
| BF <sub>4</sub>                      | tetrafluoroborate                        |
| Cl                                   | Chloride                                 |
| DCA                                  | Dicyanamide                              |
| TFA                                  | Trifluoroacetate                         |
| PF <sub>6</sub>                      | hexafluorophosphate                      |
| TfO/ CF <sub>3</sub> SO <sub>3</sub> | trifluoromethane-sulfonate               |
| Ac                                   | Acetate                                  |

## 1. Introduction

Over the years, natural gas (NG) demand has increased as the alternative source of energy worldwide. It is expected that the total demand would increase by an average of 1.9% per annum from 120 trillion cubic feet (Tcf) in 2012 to 203 Tcf in 2040 [1]. Extracted NG consists of mainly methane (70–90%), other light hydrocarbons (0–20%), and impurities such as carbon dioxide (CO<sub>2</sub>) and other traces compounds (0–10%). The removal of CO<sub>2</sub> is crucial as it can react with water vapour forming acidic condition that could cause corrosion in the pipeline. Therefore, it is important to remove CO<sub>2</sub> from the NG gas stream to prevent problems in the downstream industry as CO<sub>2</sub> could also reduce the calorific value.

Common technologies use for CO<sub>2</sub> separation are adsorption, absorption, cryogenic and membrane separation. However, the aforementioned technologies are also bounded by its energy intensive process. Referring to a case study based in Malaysia for offshore NG field [2], the operational and maintenance cost for membrane separation, chemical absorption (amine-based), physical absorption (UOP Selexol<sup>®</sup>) and cryogenic process is 289.96, 364.51, 271.44 and 356.49 million USD, respectively, targeted for gas production output of 83,512,000 MMBtu per year for 15 years of project lifetime. The techno-economic analysis suggested that Selexol chemical absorption is the most feasible process given the internal rate of return of (IRR) 15% at 7.94 years of payback period. Other challenges associated with the technologies, such as material degradation, safety issue and environment impact, has been highlighted in other review [3].

Meanwhile, membrane for gas separation has been established since 1980 s and the studies has shown remarkable progress ever since [4,5]. The driving force for the separation is through pressure difference between feed and permeate side that allows the gas to transport through the membrane. Smaller kinetic diameter gas molecules and/or higher affinity towards membrane materials are preferable to permeate across membrane compared to larger molecules and/or less affinity. Membrane is particularly easy to operate, having low footprint and low energy requirement [6]. Therefore, membrane separation process is the among promising technology provided that the membrane performance is explored and improved.

Majority of the research works focuses on the developing new polymeric materials, polymer modifications and incorporation of inorganic materials [5,7]. In recent years, a new approach by incorporating ionic liquid (IL) to enhance the separation performance of membrane has been explored. IL is an attractive materials with superior physicochemical properties such as high CO<sub>2</sub> solubility and selectivity, negligible vapour pressure and is able to be tailored according to desired application. A review discusses on IL-based membrane has been reported recently [8]. The review features fabrication method and the membrane stability of various types of IL based membranes. While the gas separation performances of the IL based membranes are discussed, it should be noted that challenges in IL-based membrane, specifically on the effect of IL on membrane gas solubility and diffusivity, mechanical strength, and IL-plasticizer effect, has not been highlighted, presumably due to limited literatures available. This review therefore, aims to highlight the role of IL on CO<sub>2</sub> diffusivity and solubility in various IL-based membrane and challenges associated with the specific IL-based membrane for CO<sub>2</sub> separation. Understanding the IL role in IL-based membrane would provide further insight for researchers to improve the performance and overcome the current challenges in IL based membrane for CO<sub>2</sub> separation.

## 2. Limitation of membranes for CO<sub>2</sub> separation

Membrane for gas separation is becoming an emerging technology for CO<sub>2</sub> separation due to competitive gas separation performance compared to conventional technologies. Despite the advantages it possesses, conventional membranes are often reported to face major challenges including the trade-off limit and plasticization effect [9–14].

As reported by Robeson [9,10], polymeric membranes are bounded by a trade-off between permeability and selectivity (Fig. 1). Flexible polymer chain favours higher permeability, whereas rigid polymer chain favour higher gas selectivity. Hence, attempt to improve permeability would often reduced its selectivity and vice versa. Although inorganic membranes perform well above the upper bound and have shown great potential for gas separation, the complex preparations procedure for continuous, defect-free fabrication and its brittle structure restricts its applica-

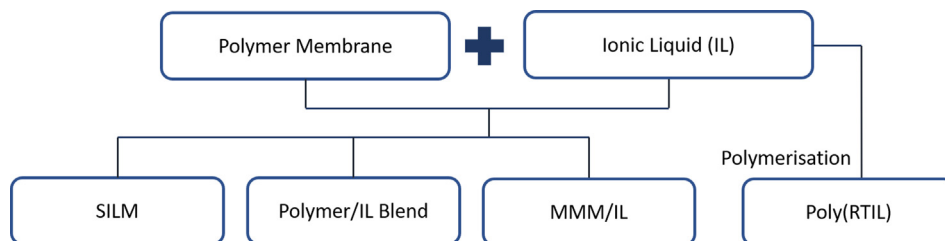


Fig. 1. Overview of IL-based membranes.

tions [15–18]. Hence, the research on inorganic membrane often focuses on the methodology to improve the aforementioned limitations as highlighted by previous reviews [19–21].

One of the strategy to improve the membrane performances is by utilizing both organic and inorganic materials such as carbon nanotubes (CNT) [22], graphene oxide (GO) [23], clay minerals [24], metal–organic framework (MOF) [25], and carbon molecular sieve (CMS) [26], or better known as mixed matrix membranes (MMM) [16,27–29]. While an ideal MMM performs in comparable to its inorganic phase [16,27,28], compatibility between the two phases is often discouraging. Details on the organic–inorganic phase compatibility issue including the rigidified polymer layer along around the fillers, interfacial voids and partial pore blockages in MMM has been thoroughly discussed elsewhere [30–33]. In short, these non-ideal morphologies are resulted from poor interaction between polymer and filler thus deteriorate the gas separation performance [34,35]. Due to this challenges, major breakthrough in MMM is yet to be reported.

Furthermore, another major challenges of glassy polymeric membrane is plasticization phenomena. Plasticization in glassy polymeric membrane occurs due to the dissolution  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  or other polar gases (i.e. water vapour) in the polymer matrix resulted from their highly condensable property. This will then increase the polymer segmental mobility and fractional free volume (FFV), causing loss in mechanical strength, and severe drop in gas selectivity. This effect would further amplify at increasing feed pressure [36,37]. The plasticization behaviour in polymer membrane has been widely studied [11–14].

Overcoming the aforementioned limitations has become a notable challenge to fabricate an ideal membrane for  $\text{CO}_2$  separation. Several strategies have been examined to tackle the problems. Commonly, cross-linking and thermal treatment are applied to minimize the plasticization effect on the membrane [38–40]. To ensure a defect free matrix interphase, polymer/particle grafting and surface modification which improved the poor adhesion between organic/inorganic phase strategy has been widely discussed [41]. Recently, focus has shifted to the incorporation of IL in membrane to enhance the gas separation performance.

### 3. Ionic liquid

Ionic liquid (IL) or Room temperature ionic liquid (RTIL) has emerged as an excellent materials for wide range of applications such as electrolytes [42,43], catalyst [44], metal extractions [45–47], catalyst [44,48–51] and chemical solvents [52] due to its characteristics of having low melting point, negligible vapor pressure and highly viscous [53]. IL is molten salts which possess low melting temperature ( $<100^\circ\text{C}$ ). IL composed of anion, typically from nitrate, acetate and tetrafluoroborate, and cation, most common are from imidazolium, pyridinium and pyrrolidinium.

#### 3.1. Ionic liquid absorbents for $\text{CO}_2$ capture

Over the past years,  $\text{CO}_2$  capture using ILs has been gaining interest mainly due to their specific interaction with  $\text{CO}_2$ , negligible vapour pressure (non-volatile) and tunability to meet feed conditions [53]. Interestingly, as IL is non-volatile,  $\text{CO}_2$  can be easily desorbed from the saturated IL which would reduce the energy for regeneration compared to conventional amine solvent (MDEA) [54,55].

$\text{CO}_2$  solubility in IL is governed by Lewis acid–base interaction between  $\text{CO}_2$  and  $[\text{PF}_6]^-$  anion [56]. Among various anion species, fluorine derivatives has shown to have the highest  $\text{CO}_2$  solubility. Study by Zhang *et al.* [57] found that  $\text{CO}_2$  solubility could be increased up to 70% with the use of  $[\text{FEP}]^-$  anion compared to  $[\text{PF}_6]^-$  due to the presence of six  $\text{CF}_2/\text{CF}_3$  group. As fluorine is the lightest halogen, the ‘ $\text{CO}_2$ -philic’ characteristic of fluoroalkyl group anion ( $[\text{BF}_4]$ ,  $[\text{PF}_6]$ ,  $[\text{TfO}]$ ,  $[\text{Tf}_2\text{N}]$  and  $[\text{methide}]$ ) escalate the  $\text{CO}_2$  solubility in IL compared to non-fluorinated anion ( $[\text{NO}_3]$  and  $[\text{DCA}]$ ). Furthermore, with increasing  $\text{CF}_3$  group in the anion, the  $\text{CO}_2$  solubility has found to be increasing. For example,  $\text{CO}_2$  solubility in  $[\text{methide}]$  is 40% higher than  $[\text{TfO}]$  as  $[\text{methide}]$  anion has thrice the  $\text{CF}_3$  substituents than  $[\text{TfO}]$  anion [58]. Previously, theoretical approach using Statistical Associating Fluid Theory (SAFT) to investigate the  $\text{CO}_2$  solubility in fluorinated ionic liquid (FILs) such as  $[\text{C}_4\text{F}_9\text{SO}_3]$  and  $[\text{C}_4\text{F}_9\text{CO}_2]$  reveal the high potential of these ILs to solubilise  $\text{CO}_2$ . The result confirms the high  $\text{CO}_2$  solubilisation in ILs with fluorinated chains [59,60].

While the solubility of  $\text{CO}_2$  in IL is highly dependent on the anion, cation contributes to the  $\text{CO}_2$  absorption through the diffusivity. The cation is responsible to create free volume in the IL system through large quadrupole moment and Van der Waals forces [61]. For example, in Imidazolium-based IL, as the alkyl chain in cation increases, the density of IL decreases to create greater free volumes. This would improve site accessibility for  $\text{CO}_2$  absorption. A study by Aki *et al.* shown that as the cation alkyl chain increases from butyl ( $[\text{bmim}]$ ) to octyl ( $[\text{omim}]$ ) (using  $[\text{PF}_6]^-$  as anion), the  $\text{CO}_2$  solubility increases from 0.616 to 0.628 mol of  $\text{CO}_2$ . Furthermore, with cation alkyl chain length increase from  $[\text{bmim}]$  to  $[\text{omim}]$  for  $[\text{Tf}_2\text{N}]^-$ , the  $\text{CO}_2$  solubility increases from  $0.69 \pm 0.01$  to  $0.763 \pm 0.007$  mol of  $\text{CO}_2$  [62].

For the importance of design and operation for natural gas processing, the understanding of  $\text{CH}_4$  and other traces gases’ solubility in IL is also crucial. Therefore, numerous studies have been conducted to study  $\text{CH}_4$  solubility by combining various cations and anions for the development of alternative solvents in natural gas processing [63–67]. Based on the solubility model by Camper *et al.* [68], the smaller the IL molar volume (imidazolium based IL), the better the  $\text{CO}_2/\text{N}_2$  selectivity. Study by Anderson *et al.* [67] also demonstrates that the presence of  $\text{CO}_2$  interact strongly with anion, leading to increase in  $\text{CH}_4$  solubility through dispersion forces.  $\text{CH}_4$  then takes up remaining sites in the anion, reducing the  $\text{CO}_2$  solubility relative to pure gas [67,69]. Furthermore, unlike  $\text{CO}_2$

which displays increase in solubility as temperature increase, the effect of temperature on CH<sub>4</sub> solubility is almost negligible. It is suggested that such phenomenon is related to the change of enthalpy of the solution from positive to negative [63]. As for H<sub>2</sub>S, early findings show H<sub>2</sub>S is highly soluble in ILs due to the high interaction of H<sub>2</sub>S and anion [70,71]. It was also found that ammonium-based ILs as well as IL with [C<sub>2</sub>MIM] as cation have high H<sub>2</sub>S affinity [72,73]. Through this finding, by utilizing the tunability properties of IL, various combination of anion and cation can be explored to achieve ideal CO<sub>2</sub> solubility with high selectivity in IL.

Although the applications of ILs in CO<sub>2</sub> capture are promising, IL also possess limitations that could hinder its performance in CO<sub>2</sub> absorption. As ILs possess high viscosity, the solvent might increase the diffusion time and increase the equilibrium time which limit mass transport for absorption [74,75]. As viscosity of ILs are governed by the van der Waals interaction and Hydrogen bond, the alkyl chain lengthening will affect the viscosity. Higher alkyl chain length provide higher van der Waals interaction and causes IL to be more viscous [74]. Furthermore, the highly viscous nature of IL would increase the operating cost (pumping) and could reduce mass-transfer rates and heat transfer. Therefore, less viscous solvent is preferred for optimal absorption. Moreover, the uses of IL in carbon capture industry have been found to impose a high energy penalty with regards to compression process which would then reduce the efficiency of the power plant by 2 folds. Additionally, as IL is highly viscous, the impact can be observed on the capital cost. Heat capacity in particular is proportional with the viscosity of the absorbent. Thus, the uses of IL resulting in high energy requirement (due to the increased size of heat exchanger) and increased capital cost [76].

#### 4. IL based membranes for CO<sub>2</sub> separation

Combination of IL with membrane is an innovative approach in to meet the challenges of both IL and conventional membrane for CO<sub>2</sub> separation. Various types of membranes have been introduced, including supported IL membrane (SILM), polymerized IL membrane (poly(IL) membrane, polymer-IL blend membrane and mixed matrix membrane-IL (MMM-IL) (Fig. 1).

##### 4.1. Supported ionic liquid membrane

To enhance mass transfer area of a liquid absorbent, membrane pores is used to immobilize the absorbent, known as supported liquid membranes (SLM). This approach have been well investigated for various applications including metal ions removal [77], dye removal [78] and gas separation [79,80]. However, loss of solvents by evaporations or dissolution into other phases leading to its short lifetime and operation instability of SLM [77,81,82]. Thus, minimizing the loss of solvent is the most prominent challenge in SLM [83]. IL, having negligible vapour pressure, emerges as an ideal solvent to be used in SLM, better known as supported ionic liquid membrane (SILM) [80,84–86].

Scovazzo et al. [87] investigates the gas transport mechanism of SILM using different IL ([EMIM][Tf<sub>2</sub>N], [EMIM][dca], [BMIM][PF<sub>6</sub>] and [EMIM][CF<sub>3</sub>SO<sub>3</sub>]). It was discovered that that only [EMIM][Tf<sub>2</sub>N] and [BMIM][PF<sub>6</sub>] are govern by facilitated transport based on the Lewis acid/base interaction between CO<sub>2</sub> and the [Tf<sub>2</sub>N]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> anions. However, [EMIM][dca] and [EMIM][CF<sub>3</sub>SO<sub>3</sub>] do not obey facilitated transport as both IL have stronger Lewis base anion. It was postulated that the presence of [F]<sup>-</sup> in hydrated ammonium salts resulted in facilitated transport of CO<sub>2</sub> via catalysed bicarbonate reaction ( $2F^- + H_2O + CO_2 \leftrightarrow HCO_3^- + HF^-$ ) [88] while none in other anion species. Following the report,

researchers have been reporting that the transport mechanism of gas molecules in SILMs is via solution-diffusion mechanism through the IL bulk (Fig. 2). The solubility of CO<sub>2</sub> gas in the IL bulk is the determinant factor for the SILM's gas separation performance [85,89].

ILs can be further tailored to meet a specific condition required for SILMs. For example, the effect of cation structure on membrane mechanical stability has been demonstrated. It was observed that the longer the alkyl chain in cation, the lower the mechanical strength of the resulted membrane. Thus, the longer the alkyl chain, more pores will be filled with IL as the membrane reconstruct its orientation resulting in the expansion of the membrane support. Hence with proper selection of anion and cation for IL, the stability of fabricated SILMs could be maximized [80,85,91]. In term of CO<sub>2</sub> separation performance, SILMs with fluoroalkyl chain shows higher CO<sub>2</sub> permeability (up to 2600 barrer for PTFE- [C<sub>3</sub>NH<sub>2</sub>mim][Tf<sub>2</sub>N] SILM). As fluoroalkyl group is highly reactive with CO<sub>2</sub>, the presence of CF<sub>2</sub>/CF<sub>3</sub> would increase the CO<sub>2</sub> permeability across the SILM [91]. Studies also shows that SILMs with [Tf<sub>2</sub>N]<sup>-</sup> anion are preferable compared to [CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, [dca]<sup>-</sup>, and [Cl]<sup>-</sup> anion owing to the highest interaction with CO<sub>2</sub> that result in high CO<sub>2</sub> permeability [87,91].

Although SILMs have shown to be notable for gas separation in term of stability compared to SLM, the loss of ionic liquid over time is still observed. Rather than loss due to evaporation suffers by typical SLM, the loss of IL in SILM occurs due to migration from pores onto the membrane surface. The severity of IL migration from SILM is influenced by four factors; IL depth in pores, support-IL interaction, membrane pore size and pore structure. When IL occupies the shallow part of the membrane pores, only minimal forces required by the IL to escape from the pores and migrate to the surface. This phenomenon can be represented by Darcy's Law where the higher the pressure difference is, the greater the displacement of IL. It is understandable that the loss of IL will be higher if the IL used was more viscous. The more viscous the IL is, the harder it will be for the IL to be immobilized into the middle part of the pores. Therefore, IL will most likely be immobilized in the most external part of the pores. This will eventually led to the displacement of IL over time during the operation [85].

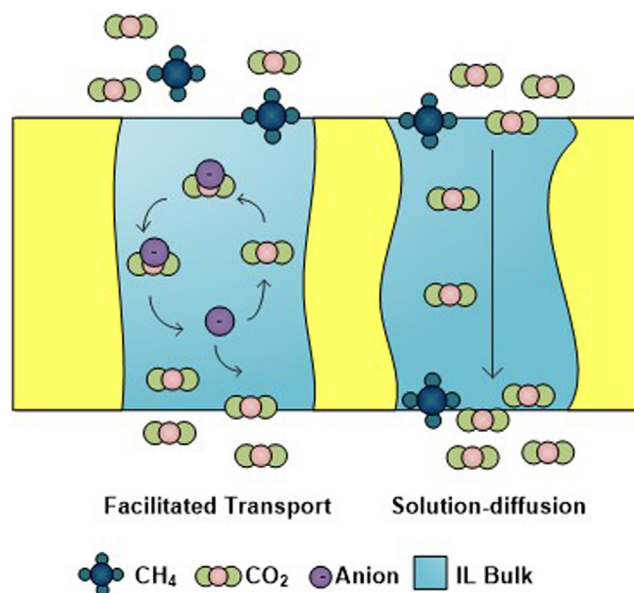
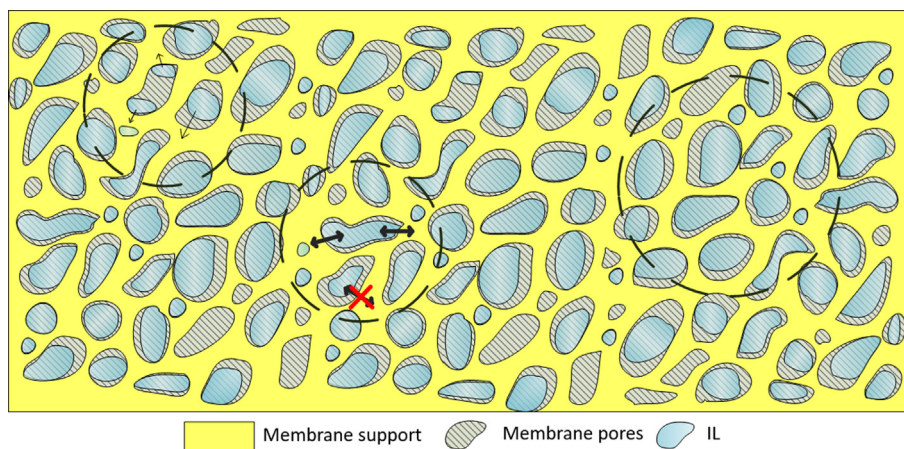


Fig. 2. Gas transport mechanism in SILM via facilitated transport and solution-diffusion mechanism (adopted from literature) [90].

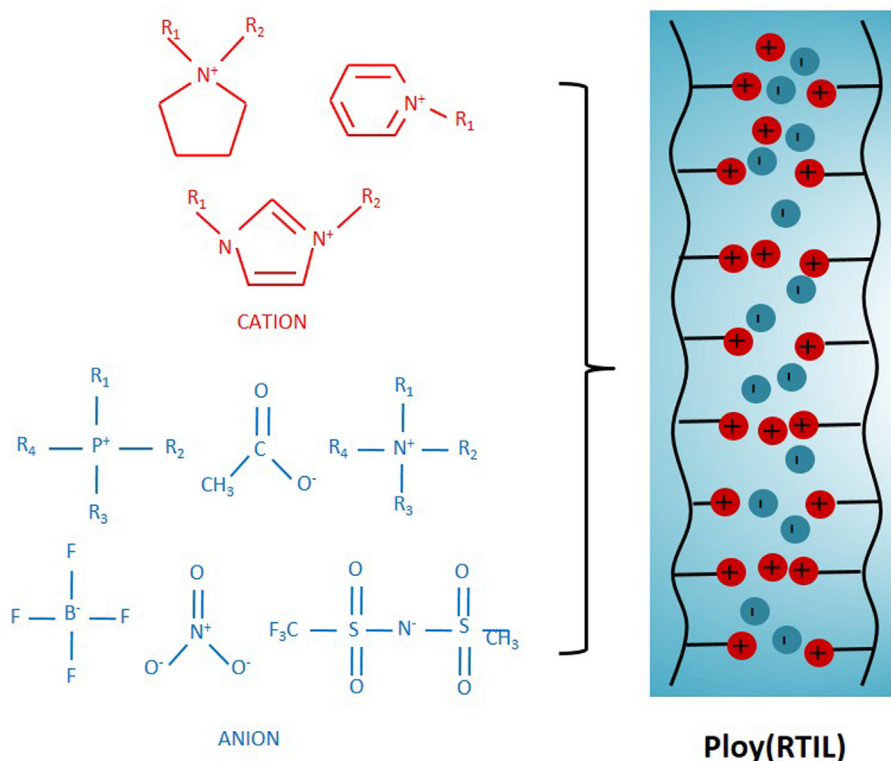


**Fig. 3.** Factors affecting IL migration from SILM (1) IL depth in pores, (2) support-IL interaction, (3), membrane pore size and (4) pore structure [85,92].

Zhao *et al.* [92] reported on the mechanism of IL loss in SILM to have a better understanding on the membrane stability according to the four factors affecting the IL migration. Findings from the study displayed that the higher the interaction between support and IL, the lower the loss of IL. It was also discovered that the loss of IL can be depressed with the use of membrane with the smaller pores and the least interconnected pore network. According to Darcy's Law, as the size of membrane pores reduced, the pressure difference in the membrane pores as well as the IL displacement will be minimal. Furthermore, result shows that the least interconnected membrane shows the lowest interaction energy due to the low interaction between IL and membrane support. Thus, membrane with small pores and less interconnected pore network would create less pressure difference in the membrane and could prevent the displacement of IL in SILM (Fig. 3).

#### 4.2. Poly(RTIL) membrane

The unique properties of IL for CO<sub>2</sub> separation can also be exploited by using IL as monomers to create new class of polymer, namely poly(RTIL). While gas absorption sites accessibility in IL is limited by its viscosity, poly(RTIL) membrane has abundant free volume, creating more accessible sorption sites. Hence, poly(RTIL) membrane has higher gas absorption capacity with enhanced absorption and desorption rate compared to regular polymer membrane [93–99]. Poly(RTIL) membranes are largely consisted of poly(acrylate) or poly(styrene) backbone with imidazolium cations tethered as side chains where the anion is not chemically bonded to the main polymer chain as shown in Fig. 4 [100–102]. The gas transport mechanism in poly(RTIL) follows the solution-



**Fig. 4.** Poly(RTIL) structural overview where the blue circles represent the polymer bound cations, red circles represent the anions and the free cations (adapted from literature [95]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

diffusion mechanism which depends on the solubility and diffusivity of the gas molecules across the membrane.

While gas permeation across membrane is limited by thick membrane layer and viscous IL phase, poly(RTIL) membrane possess lower mass transport resistance due their flexible polymer backbone [94]. As Poly(RTIL) is able to absorb as twice as much for CO<sub>2</sub> compared to its respective IL, the membrane has been observed to give better separation performance [94,96]. In poly (RTIL) membranes, the polar components of RTILs are largely contributing to the high CO<sub>2</sub> solubility across the membrane. With the extension of alkyl chain, the cations are distributed across the polymer backbone thus increase sorption sites availability. The local immiscibility resulted from the immobilized alkyl chain has resulted in the formation of excess FFV in the polymer [93,96]. Therefore, with increasing n-alkyl substituent in the poly(RTIL) repeat units, the diffusion rate also increases, boosting the gas permeability as well [93].

Aside from their typical IL species, poly(RTIL) also contains ether substituent that facilitate the CO<sub>2</sub> transport [103–105]. Poly (RTIL) containing oligo(ethylene glycol) (OEG) has shown to improve the CO<sub>2</sub> permeability and selectivity. It is postulated that the presence of polar alkylether groups has increase the interaction with the quadrupole moment of CO<sub>2</sub>, resulting in improved CO<sub>2</sub> permeability [96]. Another study on poly(RTIL) membrane containing polar substituents oligo(ethylene glycol) (OEG<sub>p</sub>) and alkyl-terminated nitrile groups (C<sub>n</sub>CN) has also reported to improve gas permeability as the length of the substituents become longer [104], in par with the effect of alkyl chain length of poly(RTIL)s reported elsewhere [93,96]. As the OEG<sub>p</sub> substituents is made longer (increasing chain length, p), the volume of ether linkages becomes dominant likely due to the increasing in gas diffusion coefficient [105].

Although poly(RTIL) has shown attractive gas separation performance, it is also bounded by several limitations. The commonly reported drawback of poly(RTIL) is the reduction in gas diffusivity due to the restriction in chain mobility. Study has shown that poly (RTIL) with methyl group restricted the CO<sub>2</sub> diffusivity due to the tight polymer chain [106]. Although the gas selectivity (CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub>) is high, the CO<sub>2</sub> permeability of poly(RTIL) membranes are much lower than their IL counterpart. It was found that the deteriorated CO<sub>2</sub> permeability is due to the decrease in CO<sub>2</sub> diffusion through the membrane. The diffusion coefficient of poly(RTIL) depletes with contrast to the respective IL as gas diffusion through a dense, thin film will be less [95]. Further study on the matter shows that imidazolium based monomers can be tailored to overcome the reduction in gas diffusivity thus improving the gas selectivity in the poly(RTIL) membrane [94].

Furthermore, majority of the gas separation performance were often reported at low pressure of 1 to 2 bar. This is likely due to poly(RTIL) membranes are susceptible to plasticization at high pressure. Thermal analysis also indicates that poly(RTIL) membranes lies on the rubbery polymer region based on the low *T<sub>g</sub>* [96]. This suggests that poly(RTIL) possess high FFV and susceptible to plasticization even low pressure. Compared to other rubbery polymer which possess higher plasticization pressure (PSF at 34 bar, PI at 15 atm and CA at 54 atm) which indicates that poly (RTIL) is not suitable for high pressure gas separation application [107]. Since the CO<sub>2</sub> separation in natural gas industry occurs at high pressure (more than 30 bar), thus poly(RTIL) is more applicable in low pressure applications such as biogas treatment.

#### 4.3. Polymer-Ionic liquid blend membrane

Compared to Poly(RTIL) membrane and SILM, direct blending of IL into polymer is relatively a straightforward approach to utilize IL which provides high gas separation performance. Hence, this

approach has been emerging to optimize the high CO<sub>2</sub> affinity of IL into polymeric membrane [108–111]. The presence of IL improves the membrane performance via improving both solubility and diffusivity coefficient in solution-diffusion model by providing higher CO<sub>2</sub> affinity and improves polymer chain mobility, respectively. Therefore, the decreased in diffusivity by the chain mobility limitation in poly(IL) could be minimized by blending IL in the polymer while maximizing the high CO<sub>2</sub> affinity properties of IL.

As the solubility and diffusivity coefficient of gases are faster in IL compared to polymer, the CO<sub>2</sub> permeability in polymer/IL blend membranes can be improved with increasing IL loading [112–114]. As IL content increases, it creates excess FFV within the membrane resulting in higher gas diffusivity. Also, more sorption sites available with increasing IL to improves CO<sub>2</sub> solubility coefficient. The increase in CO<sub>2</sub> permeability is govern by the increase in CO<sub>2</sub> solubility in IL as the loading increase (Fig. 5) [114,115]. Combination of both effects simultaneously improve the CO<sub>2</sub> permeability and CO<sub>2</sub> selectivity with increasing IL content within the membrane [112]. For example, as much as 30 wt% of IL into polymer/IL blend membrane can increase the CO<sub>2</sub> permeability by 37 folds and 3 folds for CO<sub>2</sub>/CH<sub>4</sub> selectivity compared to pure polymer membrane. Supporting evidence from FESEM images also shows the increasing sorption sites with increasing IL loading. However, it is noted that both CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity depleted at IL loading of 40%. It is postulated that the depletion is due to the polymer aggregation [115].

Additionally, study on the influence of polymer interaction with IL (same polymer material on different IL) has proven that heterogeneous blend is preferable compared to homogeneous blend membrane [114,116]. In homogeneous blend, the chain flexibility may be restrained in molecular level interaction that could reduce the gas permeability. Therefore, the immiscibility between polymer and ionic liquid would lead to high gas permeability in polymer-IL blend membrane [116] as highlighted in Fig. 6. From the diagram, the heterogeneous blend membrane lies on the Maxwell prediction curve especially at higher IL loading, significantly above the homogenous blend membrane.

The homogeneity of IL-polymer membrane blend is also affected by polymer material used. Mannan *et al.* [117] reported that [EMIM][Tf<sub>2</sub>N] blended with PES creates homogenous membrane, whereas, blended with PVDF creates heterogeneous membrane. The gas separation performance has shown that the

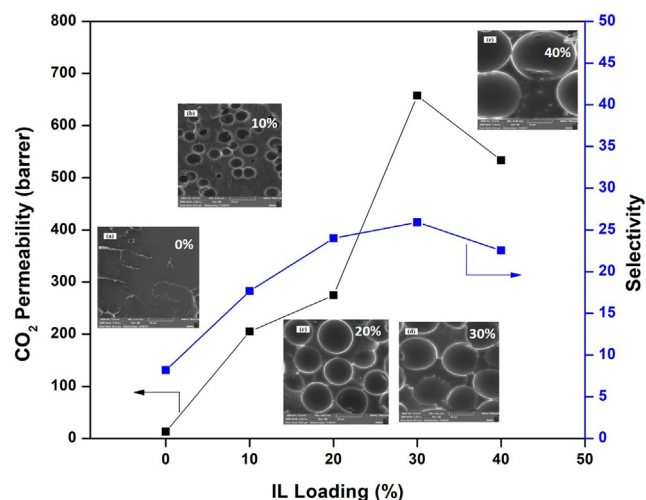


Fig. 5. Diagram shows the increase in CO<sub>2</sub> permeability and selectivity increase as the sorption site increase with increasing IL:Polymer ratio [114,115].

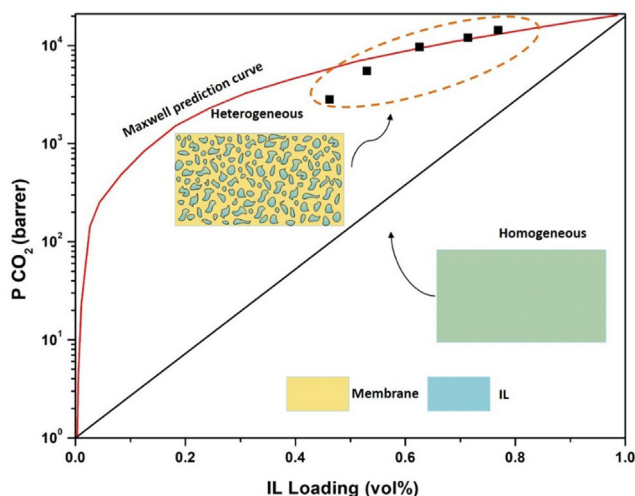


Fig. 6. Comparison of heterogeneous blend (experimental data), Maxwell prediction curve and homogenous blend shows the gas diffusivity through IL phase in heterogeneous blend is in good agreement with Maxwell prediction curve [116].

heterogeneous polymer-IL membrane gives higher CO<sub>2</sub> permeability (82% increment at 40% IL loading) compared to homogenous polymer-IL membrane [117]. While the separation performance can be correlated with their homogeneity, it should be noted that the study on the impact of polymer-IL homogeneity on gas separation performances is still limited to be discussed in detail.

Although polymer-IL membrane has shown improved performance compared to pure polymer membrane, it has always been reported that the mechanical strength of the membrane is reduced due to the IL-induced plasticization. The presence of IL would reduce the crystallinity of the membrane resulted in reduction of tensile strength [118–120]. The membrane is becoming more flexible with increasing CO<sub>2</sub> solubility but with the expense of reduce tensile strength [112,114,118,121–125]. For example, Jansen *et al.* [126] reported that increasing IL ([EMIM][TFSI]) in Poly(vinylidene fluoride-co-hexafluoropropylene) fluoroelastomer, p(VDF-HFP) up to 80% has reduces its tensile strength from 1800 MPa to 3 MPa (Fig. 7). The presence of IL swells the polymer chain by residing

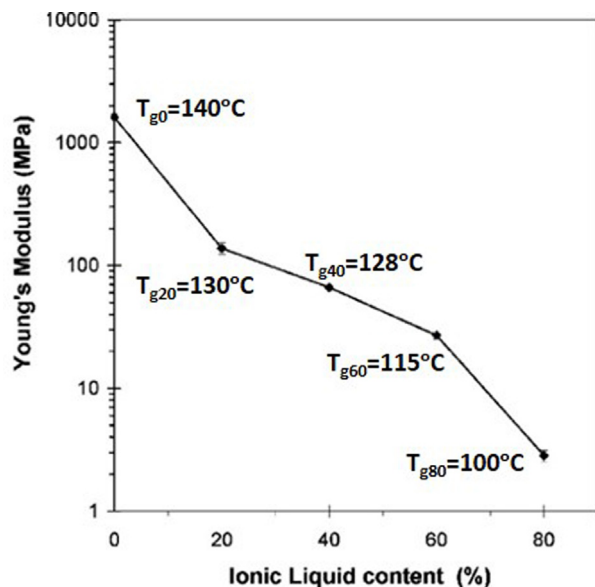


Fig. 7. Young's Modulus shows decreasing mechanical strength with increasing IL loading [126].

in between the polymer chain as can also be observed by the reduction in  $T_g$  as the IL loading increase. This resulted in formation of delicate structure upon applying stress and reducing the overall membrane strength [126,127].

Furthermore, the incorporation of IL could enhance the plasticization effect on polymer-IL blend membrane especially at high feed pressure. The presence of IL would swell the polymer membrane resulting in increasing gas diffusivity consequently leading to increase in gas permeability. Furthermore, the presence of IL has reduced the overall crystallinity of the polymer membrane which confirms the plasticization effect of the IL [128].

#### 4.4. Ionic liquid mixed matrix membrane

In general, Mixed matrix membrane (MMM) combined the excellent transport and selectivity properties of inorganic membrane and the fabrication properties of organic membrane resulting in the improved gas separation performance. However, the development of MMM for gas separation are often hindered by the limited compatibility and the adhesion problems at the organic-inorganic interface. Thus, studies have shown several approaches on overcoming the problems including modification of inorganic particles and the incorporation of interfacial agents [16,129,130]. Recently, interest in incorporation of IL in MMM has increased as the high solubility of CO<sub>2</sub> in IL could enhanced the gas separation performance of MMM and improve the adhesion problem between organic and inorganic phase in MMM [131].

##### 4.4.1. Direct Blending

The advantages of IL and MMM can be combined by 'blending' the IL into MMM. Over the years, research groups have been focusing on the effect of incorporating IL into MMM [122,132–134]. Inorganic fillers that often used in ILMMM includes SAPO-34 [122,134] MOFs [135] and ZIF-8 [132]. A three component mixed matrix membrane consist of poly(RTIL), RTIL and zeolites particles has also been studied [131]. Overall, the incorporation of IL has improved the interface between polymer and inorganic phase with the improved gas separation performance compared to that of MMM. The increased in performance was due to the addition of IL that has increased the free volumes in the membrane and act as wetting agent to increase the adhesion between organic/inorganic phase in the membrane thus increasing the gas permeability in the membrane [122,131].

For example, with the incorporation of 5–20 wt% of [EMIM][TF<sub>2</sub>N] in PES-SAPO34 MMM, the CO<sub>2</sub> performance increases up to 250% at 30 bar feed pressure while the selectivity increases by 202% compared to that of MMM. The separation enhancement is attributed by the improve interphase adhesion between PES and SAPO34 as can be seen from the FESEM images. The incorporation of [EMIM][TF<sub>2</sub>N] not only improved the interphase adhesion between polymer and fillers but also increase the CO<sub>2</sub> solubility resulted in the significant enhancement in both CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity [122]. Furthermore, the uniform dispersion of ZIF-8 fillers with addition of [EMIM][TF<sub>2</sub>N] and [EMIM][B(CN<sub>4</sub>)] has improved the CO<sub>2</sub> permeability by 2 folds and 3 folds, respectively [132].

Although high CO<sub>2</sub> permeability has been reported with the incorporation of IL in MMM, CO<sub>2</sub> selectivity is hardly being improved particularly when the loading of the inorganic fillers is increased [136]. For example, when the SAPO-34 loading increase in styrene based MMM, not enough IL was able to cover the fillers surface resulted in reduced CO<sub>2</sub>/CH<sub>4</sub> selectivity. Furthermore, residual water or solvents could remain in the pores of the fillers instead of IL which led to reduction in gas selectivity [34,136]. Filler's aggregation could have also been one of the factors of the stagnant CO<sub>2</sub> selectivity. This phenomenon may cause large void

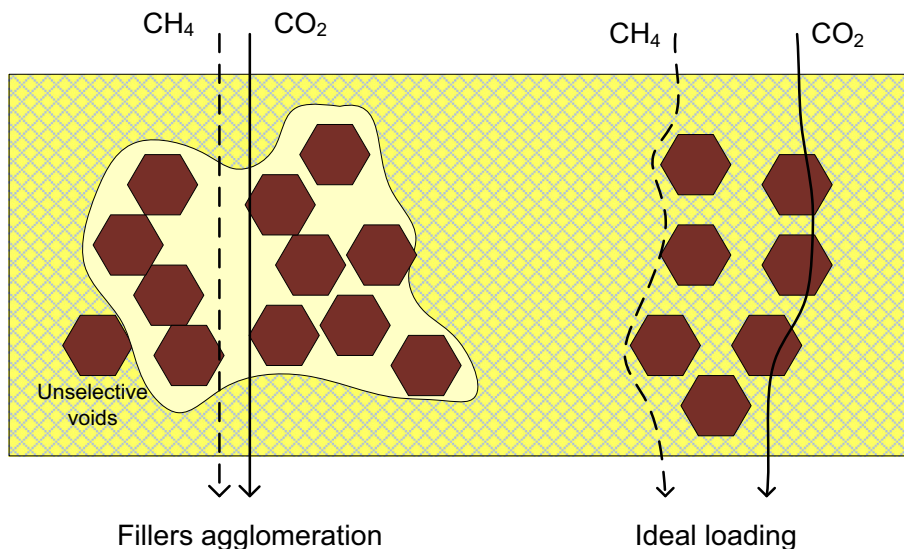


Fig. 8. Schematic diagram of the effect of fillers agglomeration on the formation of unselective voids [25,136].

space between polymer chain which favours non-selective gas molecules which then degrade the membrane selectivity (Fig. 8) [136].

4.4.2. Pore impregnation

Furthermore, studies have been conducted to impregnate IL into porous inorganic fillers, most notably when IL is confined within the pores or can be distributed at the filler-polymer interface instead of roaming freely inside the polymer matrix [137,138]. As a result, the effect of plasticization by IL can be controlled and the mechanical strength of the membrane would not be compromised while improving the CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. The presence of IL has also increased the diffusivity and the solubility coefficient. Furthermore, the addition of IL into MMM has shown no evidence of formation surface voids and hard agglomeration of the particle. In fact, the incorporation of IL has resulted in mixable mixing between polymer and fillers while

improving the interphase as IL acted as the wetting agent around the filler [131,139]. Single gas permeation has also showed improve CO<sub>2</sub> permeability compared to MMM owing to the presence of IL in the MMM [140].

Li et al. [141] demonstrate the interfacial toughening effect of IL resulted in improved gas separation performance and increase mechanical strength. During solidification of membrane in membrane fabrication, IL clusters were fixed in the interface of polymer/inorganic phase acting as the cross-linking agent, increasing and strengthening the interaction between both phases as shown in Fig. 9. As the result, the tensile strength increased by 20% at maximum loading of IL/filler of 15 wt% compared to that of pure PEBAX membrane. Consequently, the CO<sub>2</sub>/CH<sub>4</sub> selectivity also increases by 92% proving the enhanced effect of interfacial toughening of IL.

However, it should be noted that the aforementioned techniques are only applicable for porous fillers, wherein, the gas sep-

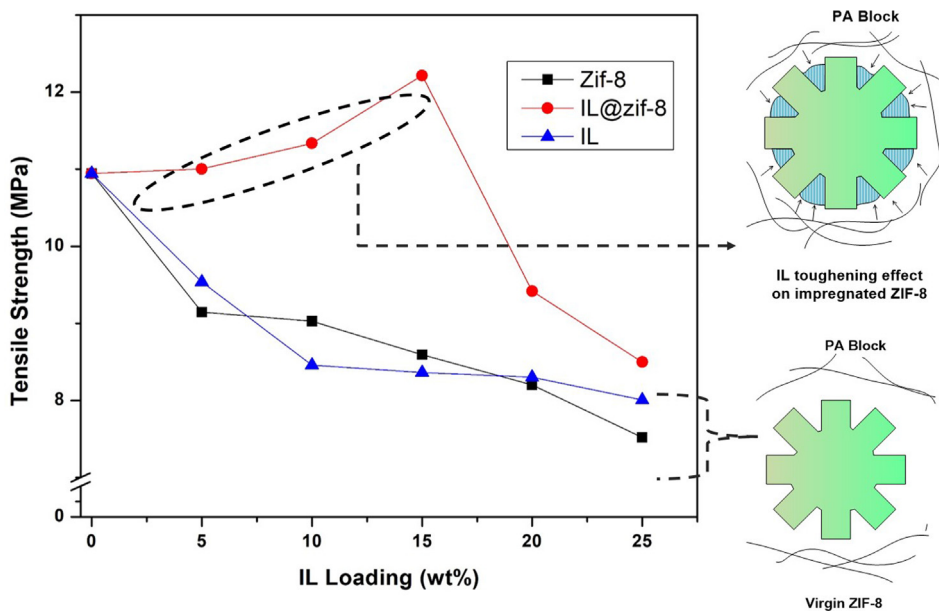


Fig. 9. Schematic diagram of interfacial toughening effect of IL and effect of IL toughening on membrane tensile strength [141].



**Table 1**  
Gas separation performance of selected studies on MMM-IL.

| Polymer    | Filler  | IL  | Remarks                  | Polymeric Membrane        |                      | MMM                       |                      | IL-MMM                    |                      | Ref.  |
|------------|---------|---|--------------------------|---------------------------|----------------------|---------------------------|----------------------|---------------------------|----------------------|-------|
|            |         |   |                          | P <sub>CO2</sub> (barrer) | $\alpha_{CO_2/CH_4}$ | P <sub>CO2</sub> (barrer) | $\alpha_{CO_2/CH_4}$ | P <sub>CO2</sub> (barrer) | $\alpha_{CO_2/CH_4}$ |       |
| PEBAX      | ZIF-8   | [BMIM][TF2N]                                  | Filler pore impregnation | 78                        | 19                   | 120                       | 19                   | 100                       | 36                   | [141] |
| PSf        | SAPO-34 | [EMIM][TF2N]                                  | Filler pore impregnation | 560                       | 3.24                 | 882                       | 3.47                 | 724                       | 20.35                | [142] |
| PSf        | ZIF-8   | [BMIM][TF2N]                                  | Direct Blending          | 200                       | 22                   | 400                       | 19                   | 560                       | 10                   | [138] |
|            |         |   | Filler pore impregnation | –                         | –                    | –                         | –                    | 300                       | 38                   |       |
| PEBAX      | Ag-NP   | [BMIM][BF4]                                   | Direct Blending          | 80                        | 15                   | 132                       | 22.8                 | 167                       | 57.6                 | [121] |
| PEBAX      | GO      | [EMIM][BF4]                                   | Direct Blending          | 57                        | 28 *                 | –                         | –                    | 98.1                      | 44 *                 | [143] |
| PEBAX      | GO      | 1-(3-aminopropyl)-3-methylimidazolium bromide | Surface Modification     | 92.4                      | 18.9                 | 113                       | 22.2                 | 127.6                     | 24.1                 | [144] |
| PES        | SAPO-34 | [EMIM][TF2N]                                  | Direct Blending          | 24                        | 0.004                | 30                        | 20                   | 18                        | 0.08                 | [139] |
| PSf        | Zeolite | [APTMS][Ac]                                   | Surface modification     | –                         | –                    | 18                        | 20                   | 16                        | 32                   | [145] |
| Pebax      | Zif-8   | (DnBMCI)                                      | Surface modification     | 150                       | 8                    | 250                       | 10                   | 250                       | 30                   | [146] |
| Chitosan   | Zif-8   | [EMIM][Ac]                                    | Direct Blending          | –                         | –                    | 1300                      | 32.3                 | 5413                      | 11.5                 | [147] |
| PSf        | PVBC    | [BMIM][tfsi]                                  | Polymer coating          | 27.9                      | 7.2 *                | 21                        | 9.5 *                | 27.3                      | 27.3 *               | [148] |
| Poly(RTIL) | SAPO-34 | [EMIM][TF2N]                                  | Direct Blending          | 9.2                       | 39                   | 13.9                      | 35                   | 72                        | 30                   | [131] |
| PES        | SAPO-34 | [EMIM][TF2N]                                  | Direct blending          | –                         | –                    | 85.69                     | 20.67                | 300                       | 62.58                | [122] |
| Chitosan   | ETS-10  | [EMIM][Ac]                                    | Direct blending          | 80                        | 2 *                  | 200                       | 4 *                  | 230                       | 11 *                 | [149] |
| Poly(RTIL) | SAPO-34 | [EMIM][TF2N]                                  | Direct Blending          | –                         | –                    | 44                        | 27                   | 240                       | 35                   | [150] |
| PSf        | SAPO-34 | [BMIM][Ac]                                    | Filler pore impregnation | 6                         | 5 <sup>b</sup>       | 12                        | 3 *                  | 2                         | 25 *                 | [134] |

\* Selectivity of CO<sub>2</sub>/N<sub>2</sub>.

eration mechanism is governed by molecular sieving. When IL is confined in the pores of the fillers, the gas separation would shift to the gas solubility in the respective IL in the pores. Therefore, the presence of IL would minimize the molecular sieving effect and the CO<sub>2</sub> permeability depends on the solubility of gases in IL only. The molecular sieving effect could also lead to the plasticization problem in the ILMMM which would be enhanced with the presence of IL as plasticizer. This could lead to deteriorating of membrane gas separation performance [138]. Table 1 compiled the CO<sub>2</sub> permeability and gas selectivity of MMM-IL.

## 5. IL based membranes gas separation performance on the Robeson's Upperbound

The gas separation performance of IL based membranes is compared with Robeson's upperbounds is shown in Fig. 10. The newly redefined upperbound includes the performance of PIMs [151]. Overall, IL based membranes are still performing below the upper-

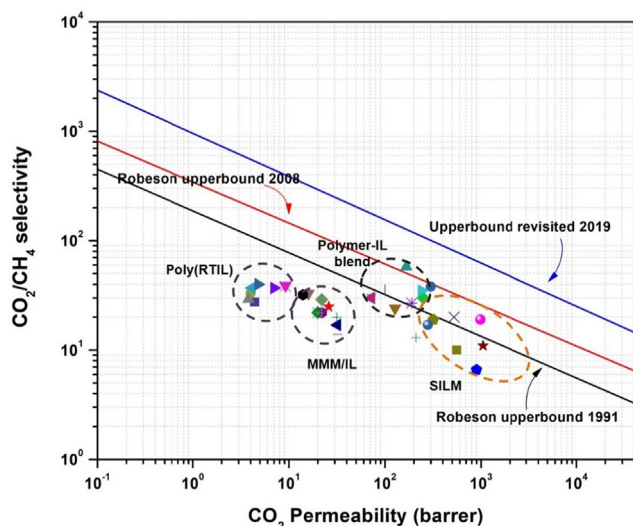
bound with the exception of SILMs. Although SILMs perform in par with the Robeson 1991 and 2008's upperbound, the lack of membrane stability and the low operation pressure would still be the drawback for the membrane to be applied in the industry. While Poly(RTIL), IL blend and MMM/IL membranes shows significantly high CO<sub>2</sub>/CH<sub>4</sub> selectivity, the CO<sub>2</sub> permeability still settles way lower compared to SILMs. Despite the aforementioned challenges of IL based membranes, the incorporation of IL leaves many opportunities for gas separation membranes to be further developed (Section 6).

## 6. Opportunities for future development

The application of IL in membrane for gas separation have been studied tremendously. Current application of IL based membrane for gas separation often faces challenges such as membrane stability, IL plasticization effect and reduction in tensile strength. Further research on the membrane properties and how to overcome those limitations should be explored. Some perspective for further development in IL based membrane will be suggested.

IL possess excellent tunability, with proper selection of both cation and anion, the optimum potential of the IL itself can be maximised for CO<sub>2</sub> separation. As anion plays the major role in CO<sub>2</sub> solubility in IL, selection of anion with high CO<sub>2</sub> solubility function would determine the effectiveness of the CO<sub>2</sub> separation in the IL based membrane. Furthermore, newly synthesised type of IL has been formulated in order to study the potential of IL in CO<sub>2</sub> separation. For instance, functional IL mixed with low viscosity IL ([Emim][BF<sub>4</sub>], [Bmim][BF<sub>4</sub>]) has shown to maintained the 80% CO<sub>2</sub> absorption with 5 cycles of regeneration [152]. This finding however has yet to be implemented in IL based membrane for CO<sub>2</sub> separation. With the high absorption capacity and additional of low viscosity property, the newly type of IL would be benefited to be incorporated in IL based membrane for high CO<sub>2</sub> separation performance.

Loss in mechanical strength is among the limitation faced by IL based membrane especially for IL blend membrane. The deteriorating strength of the membrane becomes more apparent when incorporating IL with high viscosity. The higher the viscosity of IL, the compact the polymer matrix thus reducing the overall membrane strength. Furthermore, with the incorporation of IL into polymer membrane, the plasticization effect becomes more prominent fur-



**Fig. 10.** Comparison of IL based membrane separation performance with Robeson's Upperbound.

ther reducing the mechanical strength. To utilize the high affinity of IL into polymer membrane, the introduction of fillers could minimize the plasticization effect and improve the mechanical strength by tightening effect. The incorporation of IL with the fillers before membrane fabrication can be studied such as pore impregnation or fillers surface modification in order to minimize the loss in mechanical strength [141]. While IL modified porous fillers has shown impressive gas separation performance, the effect of filler geometry (i.e. filler dimension, shape and size) can be further explored to further enhance the CO<sub>2</sub> solubility. Study shows that 3-dimensional fillers (ZIF-8) has better CO<sub>2</sub> adsorption capacity and is more selective towards CO<sub>2</sub> due to the increase surface area and porosity, compared to that of 2-dimensional fillers (ZIF-L) [153]. On the effect of particle size, it was found that larger particles (~500 nm) creates larger free volumes while disrupting the polymer chain resulted in higher gas permeation compared to smaller particles (~100 nm) [154]. Therefore, in order to maximize the IL potential to improve the gas permeability and selectivity, incorporation of IL (either via direct blending or fillers modification) on 3-dimensional fillers with size ranging from 100 nm to 500 nm would be an ideal way to improve CO<sub>2</sub> permeability in membrane.

Moreover, membrane properties and gas separation studies under extensive conditions should be considered. As most of the research on IL based membranes has been focusing on the application for CO<sub>2</sub> separation, it should be noted that other acid gases are also soluble in IL. For example, in flue gas process, it was demonstrated that SO<sub>2</sub> is highly soluble in pyridinium-based IL especially in [C4Py][SCN], attributed by the strong electrostatic force between the anion of the IL and SO<sub>2</sub> [155]. As IL interaction and SO<sub>2</sub> plays major role in gas solubility, studies have shown that the SO<sub>2</sub> solubility in IL is twice as high compared to that of CO<sub>2</sub>

in IL [156,157]. While the presence of H<sub>2</sub>O gives little to no effect on the SO<sub>2</sub> absorption capacity in IL, it was determined that low temperature condition is preferred to achieve optimal SO<sub>2</sub> absorption capacity [155]. Meanwhile, IL application in biogas upgrading has shown promising result with the improvement in CO<sub>2</sub> permeability by 170% with IL loading up to 75 wt% ([EMIM][TF<sub>2</sub>N] in membrane process). It was also found that dense membrane structure is preferred as H<sub>2</sub>O absorption is more apparent with the use of porous support [158]. Meanwhile, CH<sub>4</sub> is more likely to be soluble in ILs with higher molecular weight. Thus, in order to maximize the CO<sub>2</sub> solubility factor by IL, proper IL screening should always be considered first in order to minimize the effect of competitive sorption by other acid gases for an effective CO<sub>2</sub> separation performance.

On the other hand, membrane stability in particular for SILM should be further improved. SILM shows long stability at lower pressure but become unstable at higher pressure thus is suitable for biogas separation. This is due to the loss of IL from membrane pores when the transmembrane pressure exceeds the capillary force of IL in the membrane. To produce high stability membrane, extensive materials studies especially on the IL properties should be conducted. For example, low viscosity IL could penetrate through the membrane pores at the dipper part and stays longer and reduce the IL loss over time. As IL is a very tunable solvent [159,160], various combination of anion and cation could be studied in order to produce low viscosity IL with exceptional CO<sub>2</sub> adsorption performance [161,162]. Furthermore, small pores membrane and least interconnected pore network should minimize the loss of IL from membrane pores over time showing the potential of SILM to be explored for biogas separation.

Table 2 summarises the mechanism, advantages and challenges of IL based membrane for CO<sub>2</sub> separation. Overall, the incorpora-

**Table 2**  
Table of summary for IL based membranes.

| IL based membranes       | SILM   | Poly(IL)   | Polymer IL blend   | IL-MMM   |   |
|--------------------------|--|--|--|--|---|
|                          |  |  |  | Direct Blending  | Pore Impregnation   |
| How IL improve mechanism | Presence of IL increase the CO <sub>2</sub> solubility across the membrane since the gas transport mechanism is through the bulk of IL | Polymerization of IL increase the CO <sub>2</sub> absorption capacity compared to free IL with advanced absorption and desorption capacity.  | Act as wetting perimeter to improve the adhesion between polymer/inorganic phase resulting in enhance gas separation performance | IL as wetting agent improve the adhesion between polymer/inorganic phases                          |   |
| Advantages               | IL improve the SILM stability due to the negligible vapor pressure and high viscosity  | Low mass transfer resistance as compared to thick SILM   | The presence of free IL in the membrane increases the CO <sub>2</sub> solubility   | IL promotes the compatibility between polymer and inorganic phase                                  | Plasticization effect can be controlled without compromising membrane's mechanical strength |
|                          | Highly tunable. IL can be tuned to maximised membrane gas separation performance and stability (highly viscous IL)                     | Able to absorb twice as much CO <sub>2</sub> compared to free IL due to the increase in FFV created  | Increase in IL loading will increase the FFV of the membrane thus increasing the CO <sub>2</sub> permeability                    |  |   |
| Challenges               | Displacement of IL over time   | Reduce in gas diffusivity coefficient due to restriction of chain mobility   | Reduce mechanical strength due to the high viscosity of IL   | May aggregates fillers and create large void space leading to stagnant CO <sub>2</sub> selectivity | Minimize the molecular sieving effect<br>Plasticization effect                              |
|                          |  | Low pressure operation (time-lag method) which is unsuitable for NG separation<br><br>Plasticization is bound to happen even at low pressure | IL as plasticizer depletes the thermal stability of the membrane (reduce T <sub>m</sub> )  | Residual water or solvents could remain the pores and reduce the gas selectivity                   |   |

tion of IL into the membranes have shown to have improve the gas transport mechanism across the membrane thus improving the membrane CO<sub>2</sub> permeability and selectivity. By weighing both advantages and disadvantages for all IL based membranes, it is safe to say that these membranes are suitable for natural gas, flue gas and biogas separation. For instance, IL MMMs is suitable to be applied for natural gas separation based on the functionality of IL in improving the compatibility between fillers and polymer. Although in some cases, the presence of IL could minimize the mechanical strength loses, the plasticization effect could also take place thus further development in this area is crucial before IL MMMs can be adapted for industrial application for natural gas separation.

## 7. Conclusion

To summarize, this review gives critical intake on IL based membrane for CO<sub>2</sub> separation. The versatility of IL for CO<sub>2</sub> separation has given the opportunity for the application to be further developed. As CO<sub>2</sub> is highly soluble in IL, the development for IL based membrane in CO<sub>2</sub> capture industry is expected to keep expanding.

For SILM, the incorporation of IL has overcome the liquid displacement problem while enhancing the CO<sub>2</sub> solubility and diffusivity, CO<sub>2</sub> permeability as well as the gas selectivity. While the polymerization of IL (Poly(RTIL)) is able to absorb CO<sub>2</sub> twice as much compared to free IL, without compromising the absorption and desorption capacity further proving its potential in CO<sub>2</sub> separation. Moreover, IL was discovered to improve the adhesion between polymer/inorganic phase in MMM as the wetting agent. With the improve adhesion effect, the plasticization phenomenon could also been control while maintaining the overall membrane's mechanical strength.

Despite all the successful improvement, incorporation of IL in membrane still performs below the Robeson Upperbound. The main challenges that limit their full potential are the displacement of IL over time, reduction in mechanical strength due to the high viscosity nature of the IL and the plasticization effect in direct blending IL membrane. However, compared to other conventional membranes that performs above the Robeson Upperbound, there is still a great potential in IL to be applied in membrane for CO<sub>2</sub> separation. We believe that with proper understanding on the IL mechanism and properties, IL based membranes could offer various opportunity in membrane for CO<sub>2</sub> separation in order to overcome the current limitation in conventional technology.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgement

The authors would like to thank Universiti Teknologi PETRONAS (UTP) for providing financial assistance under Yayasan Universiti Teknologi PETRONAS–Fundamental Research Grant (YUTP-FRG/015LC0-031) and facilities necessary to complete the manuscript.

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