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Review

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이온성 액체를 이용한 이산화탄소 분리막

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Ionic Liquid based Carbon Dioxide Separation Membrane

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요　약: 유기 양이온과 유기/무기 음이온을 포함하고 있는 이온성 액체는 저온 용융 염의 종류이며 이산화탄소 분리 기능에 대한 잠재력을 갖고 있다. 지구 온난화와 기후 변화의 문제점을 극복하기 위해 이온성 액체를 기반으로 한 막을 개발하여 연도가스에서 이산화탄소를 걸러내는 연구가 활발히 진행되고 있다. 본 리뷰에서는 홀로 설 수 있는 중합 이온성 액체(PIL), 이온성 액체와 이온성 액체 복합 막의 혼합의 기술이 논의될 것이다. 새로운 이온성 액체의 모노머 도입, 그리고 중합 이온성 액체 막과 복합 막의 미세구조변형은 막의 기계적 특성을 향상시켜 가스투과율과 선택도를 크게 향상 시키는데 시용되어 왔다. 이온성 액체 모너머의 양이온과 음이온의 다양한 변형은 막의 가스 분리성에 큰 영향이 있다.

Abstract: Ionic Liquid (IL) in the category of low-temperature molten salts with organic cation and organic/inorganic anion has shown great potentiality in CO_2 gas separation. CO_2 gas separation from flue gas by IL based membrane has been widely researched in recent years to overcome climate change and global warming. Membranes based on free standing polyionic liquid (PIL), blend of ionic liquid and composite ionic liquid membranes are discussed in this review. Introducing different IL monomers and tuning microstructure of PIL membrane and composite of PIL-IL to enhance mechanical properties of membranes with good CO_2 gas permeability and selectivity. Variations in cation and anions of monomer has great impact on the membrane gas separation performance.

Keywords: *ionic liquids (ILs), permeability, selectivity, membrane, carbon dioxide*

1. Introduction

Climate change and global warming due to high CO_2 gas concentration in atmosphere has been one of the crucial problems for humanity and environment. By separating CO_2 gas from immense flue gas of factory, one can capture the CO_2 gas from dispersing and utilize CO_2 gas as hyrdrocarbon fuel source. In order to achieve such results, advanced gas separating membrane has to be incorporated directly into power plants pipes and chimney. Gas separating membrane in such condition requires high mechanical stability, reusability, economical and high CO_2 gas selectivity[1-12].

Ionic Liquid (ILs), molten salt in low-temperature, is proved to be the ideal material for creating membrane due to its characteristics that allow high solubility and selectivity for CO_2 gas with low volatility[13]. Tuning the microstructure of crosslinked poly(ionic liquid) (PIL)

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Table 1. Summary of CO_2 Gas Separation Membrane

Membrane	CO_2 permeability (barrers)	Selectivity	References
SLIM (supported ionic liquid membranes) [C2mim][NTf_2] SILMs	589 ± 1.0	18.1 ± 0.3 (CO_2/CH_4)	[14]
PIL: poly([P_{888VB}][Tf_2N])-Phosphonium base	186	0.4 (H_2/CO_2)	[15]
Poly(RTIL)-RTIL composite: *Polymer2-[C_6mim][Tf_2N] Composite	19 ± 1	20 (CO_2/CH_4)	[17]
Cross-linked PIL- RTIL Gel membrane: cross-linked poly (vinylimidazolium)-([emim][Tf_2N])(75 wt%) Gel	520 ± 30	12 (CO_2/H_2)	[18]
Poly(RTIL) membrane: disiloxane functionalized vinyl poly(RTIL)	130	14 (CO_2/N_2)	[19]
PIL-IL membrane: supported Epoxy-amine based ion gel membrane (75 wt% of free [EMIM][Tf_2N])	525	18 (CO_2/CH_4)	[24]
Poly RTIL-RTIL composite membrane: poly([vbim][dca])-[emim][B(CN)4] (1 : 2)	340	42 (CO_2/N_2)	[25]

*Polymer 2: Imidazolium ionene with Tf_2N ion.

membranes and gels via a multicomponent reaction for improved CO_2 capture performance. The composition of ILs include organic cations and organic/inorganic anions which is used as monomers in polymer membrane can be tailored and modified to produce membrane with distinct property of gas separation. Supported Ionic Liquid membranes (SILMs) were the earliest apply of Ionic Liquids as CO_2 gas separation that showed excellent performance in CO_2 gas permeability and separation. Despite SILMs outstanding performance, it was not commercially used due to low mechanical strength in high pressure conditions such as power plants that displaced ILs from the membrane[14].

To enhance the mechanical stability and CO_2 gas separation property, IL based membrane was developed in various types: Room Temperature Ionic Liquid (RTIL), Poly Ionic liquid (PIL), PIL-IL composite membrane Each specific IL based membrane was finely tuned with different Ionic liquid materials, concentration and synthesis method that was tested for gas permeability and selectivity which was plotted on Robeson plot. Not all the IL based membrane was plotted on the upper bound of Robeson plot, representing high separation performance, each experiment result clearly shines light upon the potentiality and practicability of IL based membrane that can successfully capture CO_2 gas. Schematic diagram of the crosslinking behavior of the in PIL and IL is represented in Fig. 1.

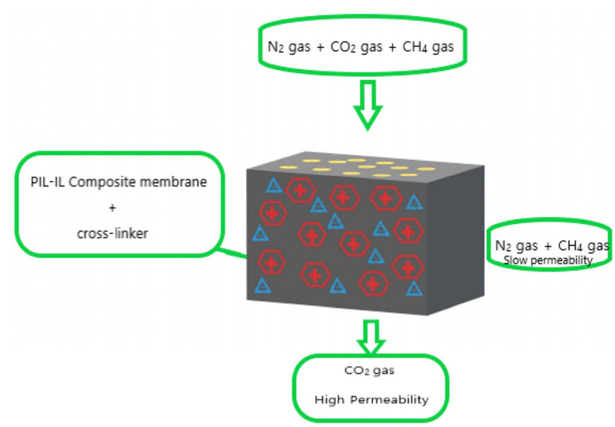


Fig. 1. Schematic diagram of gas separation PIL/IL membrane.

2. Ionic Liquid-based Gas Separation Membrane

2.1. Poly(ionic liquid) membranes

Poly ionic liquid is simply polymerization of ionic liquids to achieve advanced CO_2 sorption than room temperature Ionic Liquid. In order to discuss the different functionality and gas separation property, phosphonium-based PIL membrane, Styrene- based PIL membrane, modified Imidazolium- based PIL and cross-linked poly(vinylimidazolium) gel membrane will be discussed in detail.

Phosphonium-based poly ionic liquid (PIL) membrane is fabricated to obtain high CO_2 gas separation with high ion-conductive property[15]. Widely used imidazolium based PIL has limitations in chemical, thermal and biological conditions resulting membrane fouling property; however, phosphonium based PIL membrane's ion-conductive property enhances the prevention of membrane fouling in conditions referred above. The research by Cowan *et al.* carefully compares phosphonium based PIL by free radical polymerization with imidazolium and ammonium based PILs to obtain results of enhancements in thermal, chemical and fouling resistance. The phosphonium based PIL is synthesized by free radical polymerization of (tri-n-alkyl) vinyl benzyl phosphonium monomers and bis(trifluoromethylsulfonyl) with radical photo-initiator to prepare [P_{nnnVB}][Tf_2N] PIL. Obtained PIL is pressed between two quartz plates than irradiated at 365 nm to result free standing membrane. Tuning of alkyl chain length during the synthesis of [P_{nnnVB}][Tf_2N] showed linear relationship with permeation property while reducing selectivity property. The increased alkyl chain creates free volume in the PIL solid matrix which causes decrease in selectivity property and this value reaches plateau level at [P_{666VB}][Tf_2N]. Despite the loss in selectivity value, the [P_{888VB}][Tf_2N] PIL membrane showed highest CO_2 permeability value with 186 barrers by repeating three alkyl chains for every cation unit that greatly increased free-volume quantity. The ionic conductivity properties of [P_{nnnVB}][Tf_2N] membrane showed 10^{-8}~10^{-4} S cm^{-1} value at 25 to 105°C and when compared to imidazolium based PILs showed reduction of conductivity properties. The stability of [P_{nnnVB}][Tf_2N] PIL membrane material is tested at higher temperature than comparable PILs to prove the enhancement of membrane fouling resistance of thermal, chemical and biological conditions. In conclusion, the [P_{nnnVB}][Tf_2N] PIL membrane material has to be researched in more detail to find the optimum length of alkyl chain to achieve high quality selectivity level that can be incorporated in conditions that require high resistance to membrane fouling.

Styrene based Ionic Liquid monomer functionalized with branching and integrating cycloalkyl group to imidazolium ring showed improvements in gas separation properties compare to n-alkyl chain[16]. Modifying and branching the cyclic alkyl functionalized poly ionic liquid membrane showed 20% enhancement in selectivity property, but the membranes diffusivity decreased by 50% due to compact structural arrangement in cycloalkyl that resulted decrease in fractional free volume (FVV).

The research by Carlisle *et al.* on imidazolium ionene showed high selectivity for CO_2 gas which is polymerized withe three different membranes[17]. First polymer example is combination of imidazolium ionene with bromide counter ion and second polymer example is obtained by combining imidazolium ionene with Tf_2N ion. Composite film is also fabricated by blending polymer example 2 and RTIL. Three imidazolium-based polymer membranes gas permeability of single gases (CO_2, CH_4, N_2 and H_2) regarding to selectivity of CO_2/CH_4, CO_2/N_2 and H_2/CO_2 are plotted on Robeson plot. Polymer1 showed permeability values of CO_2 and H_2 gases around 0.13 barrer and 0.84 barrer accordingly. The permeability value of CH_4 and N_2 was not detected in polymer 1 due to small value of 0.01 barrer. The selectivity value of H_2/CO_2 was 6.0 despite having very low CO_2 diffusivity value. Polymer 1 membrane's counter-ion bromide ion created close dense packing that reduced free-volume resulting low diffusivity. Polymer 2 showed exceptional results of CH_4 and N_2 gas permeability to that of polymer 1 with 0.25 barrer and 0.20 barrer accordingly. The CO_2 and H_2 gas in polymer 2 showed permeability of around 5.3 barrer; however, the tradeoff relationship the selectivity level of H_2/CO_2 reduced to 1.00. Polymer 2 has higher CO_2 diffusivity than polymer 1 due to different counter ion, but polymer 2 resulted hindering when accessing CO_2 gas due to architect and ionic functionality of the membrane. Finally, the composite membrane showed the most increased permeability value by 360, 430 and 380% of CO_2, CH_4 and N_2 with slight loss of selectivity value. Composite membrane does not outperform the Poly(RTIL)-RTIL composite membrane with the decyl C_2 spacer composition due to the structure of the imidazolium ring that hinder structural functionality. The concept of chemical and functional modification of the imidazolium ionene membrane allows one to adapt modified spacer characteristics and functional groups to enhance permeability and selectivity level.

Room Temperature Ionic Liquids (RTILs) are also promising candidate in CO_2 gas separation due to tunable chemical characteristic and low flammability property compare to volatile organic compounds. Cross-linked poly (vinylimidazolium) gel membrane is synthesized through photo-polymerization of cross-linked functionalized oligo (ethylene glycol) and non-cross-linked vinylimidazolium RTIL monomers with free RTIL. Additional modification of cross-linked poly(vinylimidazolium) gel membranes includes the loading of free RTIL ([emim][Tf_2N]) by 45, 65 and 75 wt%, di-functional monomer for cross-linking from 5 to 100 mol% and substituting different functional RTIL monomer to test gas separation performance[18]. The membrane with 75% free RTIL component showed impressive CO_2 permeability level of 520 ± 30 barrers with high CO_2/H_2 selectivity level of 12. Decreased cross-linking monomer concentration showed high gas diffusivity value with minor enhancement of CO_2/H_2 gas selectivity value; however, when the cross-linking behavior dropped below critical value, the CO_2 permeability value was reduced by inhomogeneous structure and unsaturation of membrane. Modification of substituent monomers length and chemical composition showed minimal overall change. For example, the length change of the monomer showed very small reduction of CO_2 permeability and changing the chemical composition to apolar, n-hexyl resulted small reduction of CO_2 selectivity. By the experiment, it was clear that increased concentration of RTIL in poly (RTIL)-RTIL gel resulted excellent gas separation performance and modification of the membranes structural property can enhance mechanical strength. In the future study, the relationship between poly (RTIL)-RTIL gel and network formation of the membrane needs to be researched to generate RTIL gel membranes that can be modified to suit any environment and conditions; since, the work in this study is only possible at fixed high pressure that guarantees the liquid stability.

2.2. Poly(ionic liquid)/Ionic liquid blend (composite) membrane

PIL-IL composite membrane incorporates different loadings of free IL that results unique gas separation property. Research Carlisle *et al.* examines the effect of functionalization of polymer backbone that is integrated into PIL-IL composite membrane.

In previous research, the gas separation property of imidazolium based RTIL polymer membrane was conducted with little understanding of the polymer backbone[19]. Imidazolium- functionalized poly styrene and poly acrylate polymer backbone can be replaced with vinyl based poly(RTIL) with poly ethylene polymer backbone which is more accessible to create than styrene and acrylate based analogues. The vinyl poly(RTIL) membrane will be tested with various substituents including n-alkyl, ethylene glycol, fluoro-alkyl and disiloxane for gas transport behavior. Vinyl based poly(RTIL) showed increased gas transport effectiveness compare to styrene and acrylate based poly(RTIL) due to longer length of n-alkyl substituent; however, the CO_2 gas selectivity value showed lower trend, which was enhanced by modifying with ethylene glycol -ionefunctional group to vinyl poly(RTIL) membrane. CO_2 gas has fluorophilic conditions that can be adapted to enhance the selectivity nature of the membrane which is substituted to n-hexyl-functionalized poly(RTIL) that resulted increased CO_2 selectivity value. Disiloxane group was substituted to increase free volume of RTIL membrane and enhance gas permeability to maximum 130 barrers with little loss of CO_2 gas selectivity. The n-hexyl and disiloxane based vinyl poly(RTIL) showed highest gas permeability properties with 20 mol% of free (RTIL) to increase gas selectivity. Finally, it is crucial to prepare high gas selective and permeable poly(RTIL)-RTIL composite membrane with liquid and solid ion charged components held by ion-ion attraction.

Nellepalli *et al.* prepared poly(vinyl imidazolium) -polystyrene (Poly(vinylbenIm) NTf_2) homo and co-

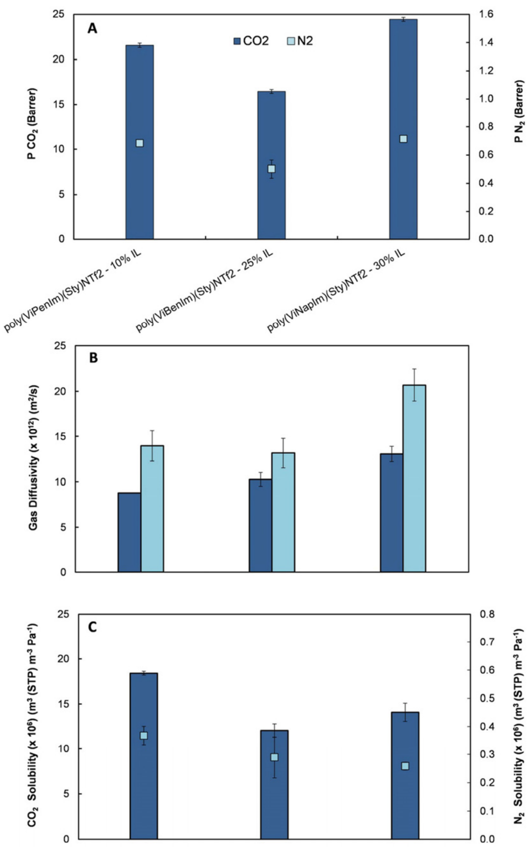


Fig. 2. Gas permeabilities (A), diffusivities (B), and solubilities (C) through the prepared imidazolium-based co-PIL-IL membranes. Error bars represent standard deviations based on three experimental replicas (Reproduced with permission from Nellepalli *et al.*, 20, Copyright 2019, American Chemical Society).

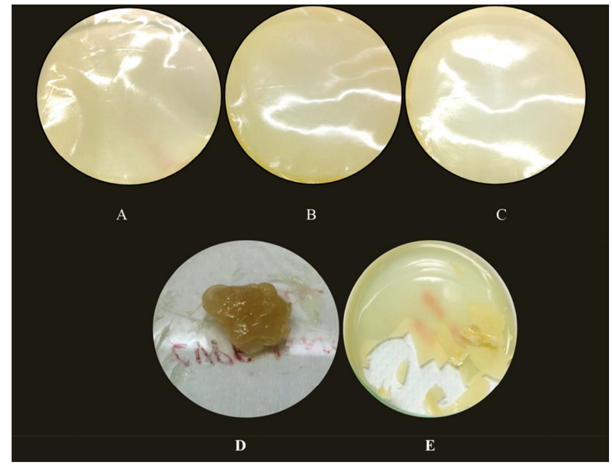


Fig. 3. Pictures of the PIL-IL membranes: (A) poly(ViPen-Im)-(Sty)NTf$_2$ with 10 wt% IL, (B) poly(ViBenIm)(Sty)NTf$_2$ with 25 wt% IL, (C) poly(ViPenIm)(Sty)NTf$_2$ with 30 wt% IL, (D) poly(ViBenIm)NTf$_2$ with 20 wt% IL, (E) poly(Vi-NapIm)NTf$_2$ with 20 wt% IL (Reproduced with permission from Nellepalli *et al.*, 20, Copyright 2019, American Chemical Society).

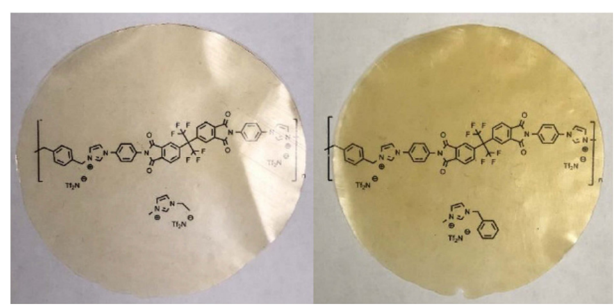
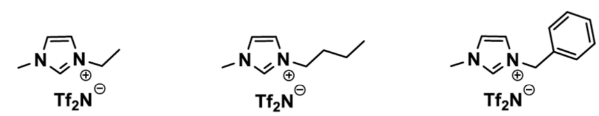


Fig. 4. Membranes (~300 in diameter) over their respective structures. [6FDA I4A Xy][Tf$_2$N] : [C2mim][Tf$_2$N] (left) and [6FDA I4A pXy][Tf$_2$N] : [Bnmim][Tf$_2$N] (right) (Reproduced with permission from O'Harra *et al.*, 22).



[C$_2$mim][Tf$_2$N] [C$_4$mim][Tf$_2$N] [Bnmim][Tf$_2$N]

Fig. 5. [Rmim][Tf$_2$N] ionic liquids (ILs) utilized to form polyimide-ionene + IL composites (Reproduced with permission from O'Harra *et al.*, 22).

polymer by random addition fragmentation chain transfer reaction (RAFT)[20]. Fabrication of membrane was possible by mixing it with various ionic liquid when the rigidity of the polymer was reduced (Figs. 2 and 3). Another new type of copolymer was prepared by O'Harra *et al.*[21]. Polyimide-ionene based on 6FDA with imdazolium moieties are prepared for CO_2 separation membrane. Ionic liquids like [C4mim][Tf$_2$N] and [Bnmim][Tf$_2$N] are mixed with the PIL to enhance the permeability of the composite membrane. Same group reported Troger's base containing ionene polymer to enhance carbon dioxide permeability (Figs. 4 and 5)[22]. McDanel *et al.* prepared epoxy amine PIL with cross-linking and PIL/IL ion gel membrane for CO_2 separation[23]. Ratio of amine to epoxide and the molecular weight of the monomer is critical for the gas separation properties. Comparison of primary and secondary

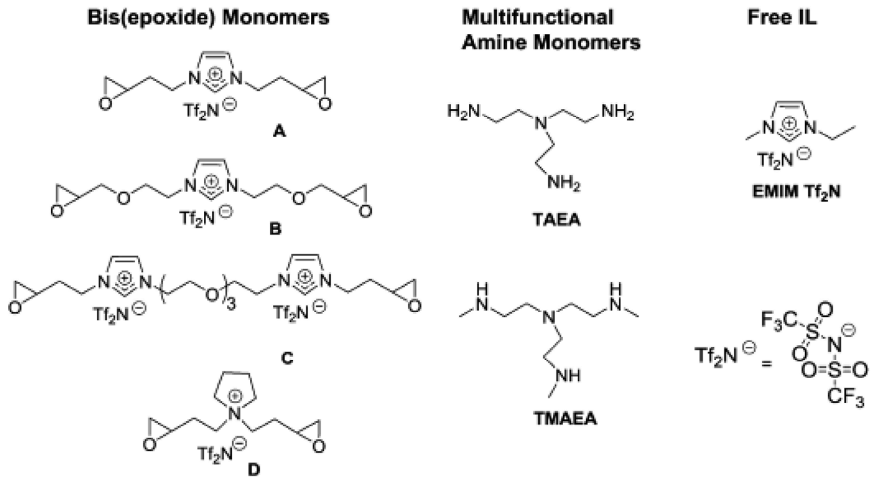


Fig. 6. Compounds utilized in this study. Compounds A~D are bis(epoxide)-functionalized IL monomers. TAEA and TMAEA are commercially available multifunctional amine monomers. EMIM Tf_2N is the free IL used to prepare the ion-gel membranes (Reproduced with permission from McDanel *et al.*, 23, Copyright 2015, American Chemical Society).

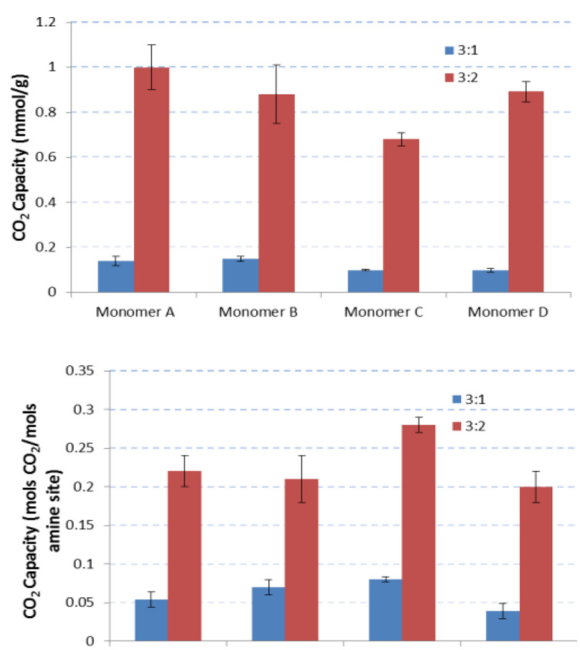


Fig. 7. Bar graphs displaying the CO_2 capacity for epoxy resins prepared with monomers A~D with TAEA at 3 : 1 and 3 : 2 monomer stoichiometries. The left plot displays CO_2 capacity in millimoles of CO_2 per gram of resin, while the graph on the right displays the data in units of moles of CO_2 per mole of amine binding sites (Reproduced with permission from McDanel *et al.*, 23, Copyright 2015, American Chemical Society).

amine group on the gas permeation properties and rate of reaction of the epoxy group was checked and conditions were optimized for tuning of CO_2 permeability and solubility (Figs. 6~8).

2.3. Modified Ionic liquid membrane

Friessa *et al.* reported the modification of ionic liquid-based gel membrane that performs in various conditions such as feeding pressure, humidity, fixed-site-carrier facilitated CO_2 transport mechanism and ionic liquid concentration[24]. Epoxy amine-based ion gel membrane exhibits high CO_2 permeability due to secondary and tertiary amine sites on PIL membrane and high gas diffusivity due to liquid like transport behavior of free IL. In single gas studies, the permeability and diffusivity properties are alternated by different concentration of [EMIM][Tf_2N]. When plotted in the Robeson Plot, the PIL-IL with 75 wt% of [EMIM][Tf_2N] resulted higher permeability than 50 wt% retaining comparable selectivity of 18 vs 20 (CO_2/CH_4). The diffusivity at PIL-IL 75 wt% showed rubbery polymer behavior of polydimethylsiloxane that penetrated large gas molecules such as CO_2 while 50 wt% was not capable. In mixed gas studies, the PIL-IL 75's permeation properties were tested in various feeding pressure of 0.27, 0.47 and 0.75 bar and humidity levels of 32 and 54%. At lowest feeding pressure, the separation maximum is achieved because CH_4 molecules did not

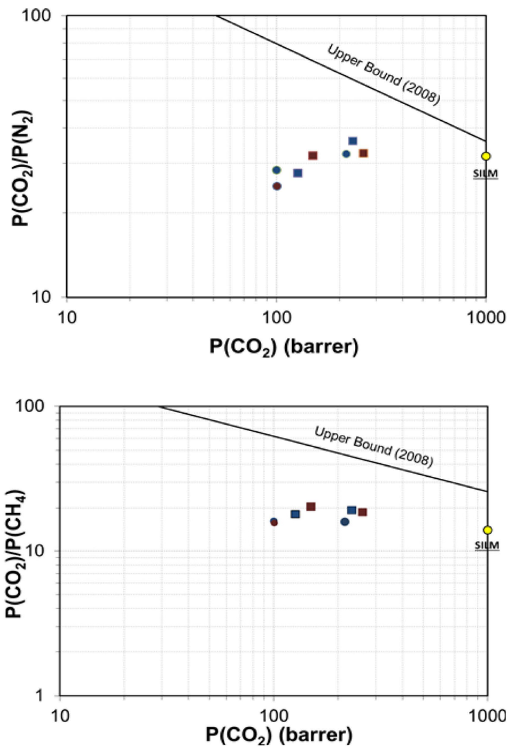


Fig. 8. CO_2/N_2 and CO_2/CH_4 Robeson plots for epoxy ion-gel membranes with either 50 or 60 wt% free IL and EMIM Tf_2N. The data points for ion-gel membranes prepared with monomer A are displayed in blue, and the data points for ion-gel membranes prepared with monomer B are in red. Membranes with 3 : 1 stoichiometries are depicted as squares, and membranes with 3 : 2 stoichiometries are displayed as circles (Reproduced with permission from McDanel *et al.*, 23, Copyright 2015, American Chemical Society).

hinder pathways for CO_2 and humidification which allowed CO_2 to be soluble in water while CH_4 was not. The advanced humid and IL content conditions allowed membranes to successfully apply separation of mixed biogas in high pressure feed. When separating CO_2 gas from natural gas (Flue gas) with pressure higher than atmosphere, the membrane system had to overcome the low partial pressure of CO_2 of 0.1 to 0.2 bar to obtain high permeability and CO_2/N_2 selectivity[25].

Room temperature ionic liquid is used widely due to its characteristics that involve negligible vapor pressure and high CO_2 gas solubility. Pure poly ionic liquids (PILs) are unstable to use in various conditions, so PIL-IL composite membrane is created to enhance gas selectivity and permeability behavior. The following study examines three different vinyl functionalized imidazolium RTILs [1-vinyl-3-ethylimidazoliumdicyanamide ([veim][dca]), 1-vinyl-3-butylimidazolium dicyanamide ([vbim][dca]) and 1-vinyl-3-heptylimidazolium dicyanamide ([vhim][dca])] to obtain 3 different Poly RTIL-RTIL composite membrane by UV polymerization with blend of three different free RTIL [1-ethyl-3-methylimidazolium dicyanamide ([emim][dca]), 1-ethyl-3methylimidazolium tetracyanoborate ([emim][B(CN)4])]. The result of the free RTILs show high permeability and selectivity value than poly RTIL. Second the increasing N-alkyl group in poly RTIL enhances overall permeation property, but the CO_2/N_2 selectivity value reduces. Third the composite membrane created from free RTIL and Poly RTIL enhances CO_2 gas permeability and CO_2/N_2 separation value. Among three different poly RTIL-RTIL composite membrane poly ([vbim][dca])-[emim][dca] (1 : 2) and poly ([vbim][dca])-[emim][B(CN)4] (1 : 2) has permeability value of 273 and 340 barrers and selectivity value of 53 and 42 at 1atm and 35°C respectively. Two composite membrane's gas separation result was very close to Robeson upper bound, denoting that the potential of quality CO_2 gas separation membrane.

2.4. Mixed ionic liquid membrane

Binary ionic liquid mixture's physical and chemical behavior is tested with different functional ionic liquid and viscosity behavior of CO_2 separation improvements [14]. Functional ionic liquid adapted with four different anions are controlled while maintaining 1-ethyl-3-methylimidazolium cation because CO_2 gas has high affinity to anions. Modified membranes gas separation property is tested at 293 and 100 KPA for permeability, solubility and diffusivity of natural gas. By the Robeson plot of [C2mim][Ac], [C2mim][Lac], [C2mim][DCA] and [C2mim][NTf_2] based SILM, one can clearly see the differences in gas diffusivities and permeability according to distinctive anions. [C2mim][Ac] and [C2mim][Lac] based SILMs had highest viscosity which decreased the gas permeability while [C2mim][DCA] showed highest CO_2/CH_4 permselectivity with lowest viscosity. Also by the camper model that examines the solubility selectivity property plotted [C2mim][NTf$_2$] SILMs at the highest among the functional anions which proved the importance of solubility when discussing permeability. As a result of achieving the highest CO_2 gas separation, it is crucial to find low viscosity ionic liquid mixture with functional anions for increased selectivity and permeability.

3. Conclusions

ILs used as monomers to CO_2 gas separation polymer membrane has clearly shown the potential to be widely used in industry that disperse flue gas to atmosphere. SLIMs, RTIL and PIL has each advantage but ultimately fail due to unstable IL containment and low mechanical stability of polymer membrane in high pressure and temperature. PIL-IL composite membrane with uniform structure with PIL and free-IL component has enhanced gas separation property and stability showing high potential with some limitations. The common limitation of gas separation membrane is the trade-off relationship between gas permeability and selectivity.

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