

Breaking boundaries in CO₂ capture: Ionic liquid-based membrane separation for post-combustion applications

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ABSTRACT

As a part of global warming reduction strategies, CO₂ capture and storage (CCS) is considered a promising and effective method, which can be classified as absorption and adsorption, chemical looping combustion and cryogenic distillation, hydrate-based separation, and membrane separation. But, the high energy requirement, solvent loss and degradation, corrosive nature, and toxicity of solvents can limit the applications. Developing novel techniques and materials are attracting high attention to achieve superior capacities. The supported ionic liquid membranes (SILMs) as a part of ionic liquids (ILs) have shown great potential for efficient and cost-effective separation of CO₂ from the gaseous flow. The present review demonstrates the mechanisms, advantages, difficulties, and disadvantages of CO₂ capture by SILMs and compares them with various conventional methods. A major part of this review covers the tunability of SILMs, experimental data of solubility, diffusivity, permeability, and selectivity of CO₂ in various combinations of ILs, membrane supports, and additives. Lastly, the stability of SILMs, reusability of ILs, membrane wetting, challenges, and future recommendations are presented.

1. Introduction

The rapid growth in industrialization is one of the major contributors to emissions of greenhouse gases which in turn causes an increase in average global temperature on earth. Carbon dioxide (CO₂) is a prime driver of climate change, accounting for almost 80% of all greenhouse gas emissions [1,2]. A recent IPCC report states that 62 million people have been directly affected by extreme weather anomalies due to climate change, attributed to the increased CO₂ level in the air [3]. To overcome this problem, the united nation framework convention on

climate change (UNFCCC) Conference of Parties (COP-26) has set an undertaking for all nations to keep the goal of limiting global warming to 1.5 °C in its meeting, which was held at London in April 2021 [4]. To meet this objective and overcome the problem of global warming, CO₂ capture and storage (CCS) technologies are the need of the hour, as it allows the huge adsorption of CO₂ from different point sources for its smooth transportation and storage to prevent its emission into the atmosphere [5].

Various CCS technologies, including post/pre-combustion and oxy-fuel combustion, are being investigated and are in place to combat global warming. The post-combustion CO₂ capture method is mostly

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Nomenclature

Glossary

C	Concentration of gas dissolving in the IL (mol mL ⁻¹).
D	Diffusion coefficient (m ² s ⁻¹).
$\Delta G_{i/s}^{\infty}$	Gibbs energy of solvation (kcal mol ⁻¹).
H_i	Henry's law constant (atm·m ³ mol ⁻¹).
J_i	Volume flux (m ³ s ⁻¹).
l	Thickness of membrane (μm).
n	Slope of the upper bound plot.
p	Pressure (bar).
P_i	Permeability of specie i Barrer. (1 Barrer=1 × 10 ⁻¹⁰ cm ³ _{STP} ·cm·cm ⁻² s ⁻¹ cmHg ⁻¹).
$P_{i,j}$	Permeability of species i (CO ₂) and j (N ₂) (Barrer).
S	Solubility coefficient (cm ³ _{STP} cm ⁻³ cmHg ⁻¹).
x_i, y_i	Mole fractions of the gas (mol).
y_i^{∞}	Infinite dilution activity coefficient.

Greek symbols

α_{ij}	Selectivity of species i (CO ₂) and j (N ₂).
Δp_i	Transmembrane pressure (cmHg ⁻¹).
θ	Time-lag intercept.
ϕ_i	Fugacity coefficient in the vapor phase.
γ_i	Activity coefficient in the liquid phase.

Acronyms

[APTMS][AC]	(3-aminopropyl) trimethoxysilane acetate.
[BMIM][Ala]	1-butyl-3-methylimidazolium alanine.
[BMIM][CF ₃ SO ₃]	1-butyl-3-methylimidazolium trifluoromethanesulfonate.
[BMIM][DCA]	1-butyl-3-methylimidazolium dicyanamide.
[BMIM][Gly]	1-butyl-3-methylimidazolium glycine.
[BMIM][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate.
[BMIM][SCN]	1-butyl-3-methylimidazolium thiocyanate.
[BMIM][NO ₃]	1-butyl-3-methylimidazolium nitrate.
[BMIM][Tf ₂ N]	1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide.
[BSMIM][tos]	1-butylsulfonate-3-methylimidazolium P-toluene sulfonate.
[C ₂ MIM][OAc]	1-ethyl-3-methylimidazolium acetate.
[C ₂ MIM][TfO]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate.
[C ₄ MIM][Tf ₂ N]	1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide.
[C ₆ MIM][Tf ₂ N]	1-Hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide.
[C ₈ mim][PF ₆]	1-octyl-3-methylimidazolium hexafluorophosphate.
CCS	CO ₂ capture and storage.
CO ₂	Carbon dioxide.
COP	Conference of parties.
C ₅ H ₆ NCl	Pyridinium.
CS	Chitosan.
Cu _x Mg _x	Copper and magnesium ions.
DAC	Direct air capture.
[Deme][TFSI]	(N,N-diethyl-N-(2-methoxyethyl)-N-methylammonium bis(trifluoromethylsulphonyl-imide).
DMAPAH	3-(dimethylamino)-1-propylammonium.
[DMEDAH]	Formate N,N-dimethylethylenediammonium formate.
[DMIM][Cl]	1-decyl-3-methylimidazolium chloride.
FD	Freeze drying.
EH	Ethanol hexane.

[EMIM][Ac]	1-ethyl-3-methylimidazolium acetate.
[EMIM][Ala]	1-ethyl-3-methylimidazolium alanine.
[EMIM][BF ₄]	1-ethyl-3-methylimidazolium tetrafluoroborate.
[EMIM][DCA]	1-ethyl-3-methylimidazolium dicyanamide.
[EMIM][EtSO ₄]	1-ethyl-3-methylimidazolium ethyl sulfate.
[EMIM][Gly]	1-ethyl-3-methylimidazolium glycine.
[EMIM][Tf ₂ N]	1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide.
GPU	Gas permeation unit.
H ₄ P ⁺	Phosphonium.
HFP	Hexafluoropropylene.
[HMIM][FEP]	Tris(pentafluoroethyl) trifluorophosphate.
HNIW	Hexaazaisowurtzitane.
IGCC	Integrated gasification combined cycle.
ILs	Ionic liquids.
ILMs	Ionic liquid membranes.
IPCC	Intergovernmental panel on climate change.
LMOG	Low molecular weight organic gelators.
MMMs	Mixed matrix membranes.
NF	Nanofiltration.
NH ₄ ⁺	Ammonium.
[OMIM][PF ₆]	1-octyl-3-methylimidazolium hexafluorophosphate.
PBI	Polybenzimidazole.
PES	Polyethersulfone.
[P ₂₂₂ VB][BF ₄]	Triethyl(4-vinylbenzyl)phosphonium tetrafluoroborate.
[P ₄₄₄ VB][BF ₄]	Tributyl(4-vinylbenzyl)phosphonium tetrafluoroborate.
[P ₆₆₆₁₄][Cl]	Trihexyltetradecylphosphonium chloride.
[P ₆₆₆₁₄][CoCl ₄]	Trihexyl(tetradecyl)phosphonium tetrachlorocobalt.
[P ₆₆₆₁₄][FeCl ₄]	Trihexyl(tetradecyl)phosphonium tetrachloroferrate.
[P ₆₆₆₁₄][MnCl ₄]	Trihexyl(tetradecyl)phosphonium tetrachloromanganese.
[P ₆₆₆₁₄][GdCl ₆]	Trihexyl(tetradecyl)phosphonium hexachlorogadolinium.
[P ₈₈₈ VB][BF ₄]	Trioctyl(4-vinylbenzyl)phosphonium tetrafluoroborate.
[P ₈₈₈ VB][Tf ₂ N]	Trioctyl(4-vinylbenzyl)phosphonium bis (trifluoromethane sulfonyl) imide.
PP	Polypropylene.
PS	Polysulfone.
PVDF	Polyvinylidene fluoride.
p(VDF-HFP)	Poly-vinylidene fluoride-co-hexafluoropropylene.
RTO	Room temperature oven.
[Set ₃][NTF ₂]	Triethylsulfonium bis(trifluoromethylsulfonyl)imide.
SILM	Supported ionic liquid membrane.
[Tespim][BF ₄]	1-(3-triethoxysyl propyl)- 3-methyl imidazolium hexafluorophosphate.
[TETA][Tfa]	Triethylenetetramine trifluoroacetate.
[THTDP][NTF ₂]	Trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) amide.
TNT	Trinitrotoluene.
TRLs	Technology readiness levels.
TSIL	Task specific ionic liquid.
UNFCCC	United nation framework convention on climate change.
VDF	Vinylidene fluoride.
WCA	Water contact angle.

retrofitted onto existing facilities [6,7]. Recently, ionic liquids (ILs) have gained huge attention in solvent-based post-combustion CO₂ capture because of their significant characteristic of being highly thermally stable, flammable, and low volatile with huge tunability in the selection of cations and anions, which make them able to achieve excellent CO₂ solubility and high separation for targeted gas molecule [8–10].

There are numerous studies on gas permeation using imidazolium [11,12], pyridinium (C₅H₆NCl) [13,14], phosphonium (H₄P⁺), and ammonium (NH₄⁺)-based ILs [15]. The pure ILs have limited surface area and low CO₂ capture capacity and are impregnated into porous polymer supports to overcome the mentioned limitations [16,17]. Supported ionic liquid membranes (SILMs) have been a preferred option due to the promising compatibility of polymer matrix with the ILs molecules, consequently leading CO₂/N₂ perm-selectivity close to or beyond the upper bound of Robeson's plot [18].

Highly technical and critical literature is available on CO₂ capture through different techniques, including ILs [19–22]. Fig. S1 shows the number of publications related to the post-combustion CO₂ capture and SILMs in the previous two decades indexed by scopus. Jiang et al. [23] comprehensively reviewed the phase change mechanism, energy consumption analysis and process flow behavior of ILs-based sorbents for CO₂ capture. Zheng et al. [24] presented a state-of-the-art review on the synthesis, functionalization, and absorption mechanism for conventional and task-specified ILs to enhance CO₂ capture. Chen et al. [25] presented a comprehensive discussion on the theoretical and experimental progress of thermal, electrochemical, and photochemical conversion of CO₂ mediated by ILs. Aghaie et al. [26] discussed the screening and economic concerns to developing effective ILs/CO₂ systems through proper optimization in design criteria. Elmobarak et al., [27] reviewed the toxicity and biodegradability of ILs used in CO₂ capture applications. The effect of cations/anions and functional groups on CO₂ capture was also discussed. Other recent notable reviews were presented by An et al. [28], Meylan et al. [29], Sood et al. [30], and Olabi et al. [31]. They reviewed the properties and mechanisms of various ILs used for CO₂ capture and discussed the background and limitations of membrane-based carbon capture technologies. However, the state-of-the-art review on types of ILs used in SILM, a theoretical study including solubility and diffusivity, and incorporation of additives in the polymer matrix of SILMs have not been broadly covered in a single review.

The current review aims to present the recently developed SILMs synthesized from various types of ILs, additives, and membrane supports. Experimental analysis and theoretical background for post-combustion CO₂ capture through SILMs are also presented. The ILs are comprehensively discussed based on CO₂ solubility and diffusivity. The polymer-inorganic filler matrix embodying IL as a part of SILMs is broadly reviewed in this study. Besides, technology readiness levels (TRLs) of different CO₂ capture technologies are critically analyzed and discussed. As well as the stability, reusability, and wetting of SILMs and challenges with SILMs are thoroughly investigated. The techno-economic analysis of post-combustion CO₂ capture through SILM is also described in detail.

2. CO₂ emissions and carbon capture

Worldwide anthropogenic gaseous emissions are predominantly related to human activities, including consumption of non-renewable energy resources, transportation, industrial processes, and emissions from forestry and other land use [32]. According to Fig. S2(a), in 2020, among various sources of anthropogenic emissions, the fuel combustion sectors, such as electricity and heat production, has the biggest commitment towards greenhouse gas emissions [33]. As reported by the Netherlands environmental assessment agency, in 2018, the development of altogether worldwide ozone-depleting substance emissions continued at a pace of 2.0%, reaching a CO₂ equivalent of 51.8 gigatons [34,35]. Fig. S2 (b) and (c) show the global CO₂ emissions and top CO₂ emission countries.

2.1. Carbon capture technologies

Selecting suitable methods for CCS from the feed streams mainly depends on the feed volume, CO₂ concentration in feed, and process conditions during combustion [36]. The CCS technologies are developed based on three routes: post-combustion, pre-combustion, and oxy-fuel combustion. The pre-combustion CO₂ capture route is restricted to the coal gasification plants, while the post-combustion technology is usually employed in the coal and gas-fired plants. In the oxyfuel combustion, the fuel is burned in pure oxygen with H₂O and CO₂ in flue gases. Post-combustion CO₂ capture is challenging because the emitted gas contains 3–20% CO₂ at 35–120 °C, 1 bar and 5–10% CO₂/N₂. [37,38]. Among post-combustion technologies, solvent-based absorption of CO₂ using amino-based solvents are most commonly applied in post-combustion CO₂ capture due to their fast kinetics and thermodynamics. However, corrosion potential, solvent degradation, solvent recovery, environmental hazards, and high capital cost are the main disadvantages that should be settled [39]. Solid sorbents such as activated carbon, MOFs, or zeolites were also used to selectively capture CO₂ [40]. However, less adsorption capacity of adsorbent, low selectivity towards CO₂, regenerative cost of adsorbents, and complex kinetics and thermodynamics decreased the overall effectiveness of the technology [41–43]. Membrane-based separation methods are regarded as the most rapidly growing separation processes for CO₂ capture [8]. Many researchers worked on the development of new processes and new materials to address the drawbacks of the conventional separation processes in CO₂ capture and to enhance the performance of membrane separation [44–47].

Various CO₂ capture technologies and separation routes are shown in Fig. 1(a, b). The pros and cons of each separation process are listed in Table 1. High energy consumption, solvent degradation, and limited selectivity towards CO₂ are the main disadvantages of the conventional methods of CO₂ separation, which limit its development and applications. Post-combustion CO₂ capture using amines-based chemical absorption is widely used due to the high reactivity and thermal stability of amines which facilitates their high absorption for CO₂. The adsorption based on amine solvents is usually performed through a tall absorption column which requires high capital expenses and maintenance. The major drawbacks of using amine-based absorption are the huge consumption and losses in solvent regeneration and degradation. Furthermore, most amine-based absorption research focused on separating CO₂/N₂ mixture. The cryogenic-based absorption of CO₂ also faces the restriction of excessive cooling duty requirement for CO₂ capture. The adsorption-based processes are normally used in natural gas industries for CO₂ capturing and are selected on the difference in affinities among various hydrocarbons. Adsorption-based processes usually face the limitations of higher operating costs and low adsorption capacity. Furthermore, the main challenges with CO₂ adsorption process include low CO₂ selectivity, limited adsorption capacity, lower capture efficiency, re-usability of the sorbent and regeneration, and the issue of fire hazard in the adsorption process. Membrane-based techniques are also used for CO₂ capture, but their major issues are associated with the permeability and selectivity of membranes and the higher cost required for the pretreatment of membranes. Nonetheless, hybrid mechanisms of separation, particularly incorporating membrane media in the conventional technique, is a viable option to address the constraints of a single separation procedure. Recent research indicated that SILM technology has an excellent potential for scale-up in an environmentally friendly manner for post-combustion CO₂ capture soon [48,49].

3. Supported ionic liquid membrane for post-combustion CO₂ capture

SILMs comprise the impregnation of ILs into the pores of membrane support through the action of capillary forces. Polymeric membranes are the most common support materials for SILMs. The gaseous species

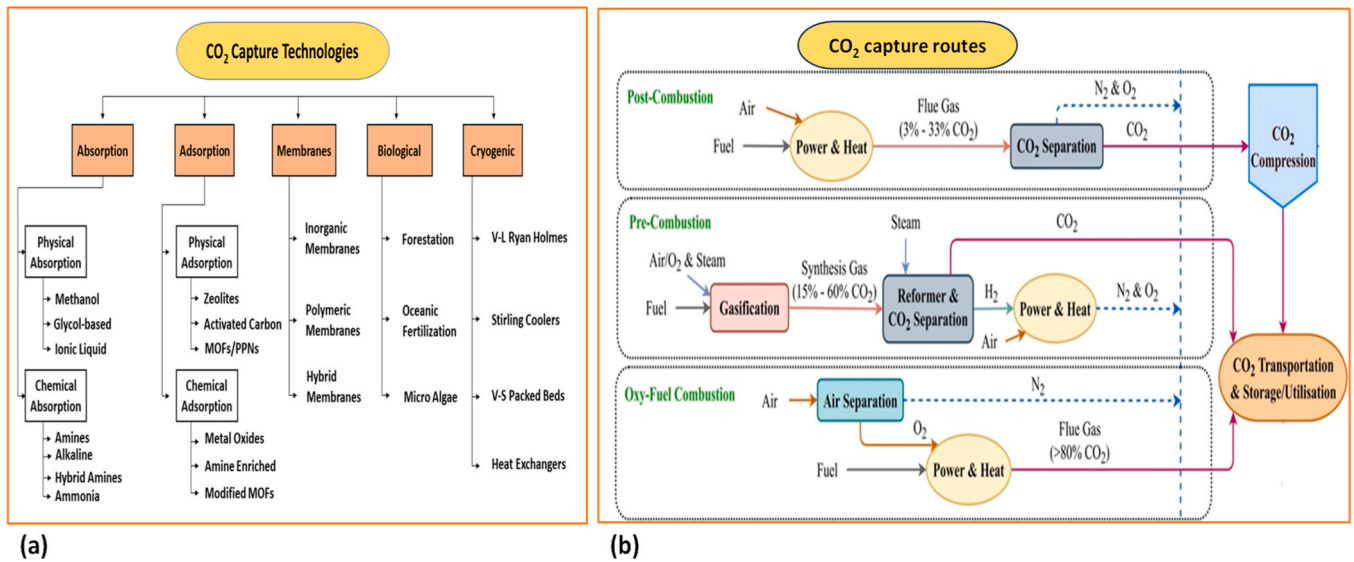


Fig. 1. (a) CO₂ capture technologies and (b) CO₂ capture routes. Reproduced with copyright permission from Ref. [54,55]. Copyright 2020, Elsevier.

diffuse/dissolve into the membrane facilitating the capture of gaseous specie either physically or chemically in IL and then stripped off on the other side of the membrane. The unique characteristics of ILs, such as high thermal stability, non-volatility, inflammability, tunability, high CO₂ solubility, and reusability, make them more appropriate solvents for SILMs than ordinary liquid membranes (Fig. 2) [56].

SILMs offer a large surface-to-volume ratio for the transmembrane transport of gaseous species. The tunable properties of embedded ILs have a greater impact on the separation performance of SILM, when compared with the membrane support. However, poor adhesion

between support and IL affects the settlement of IL into the pores of support, which also negatively affects their separation performance [57].

The transport model of gases through the SILM is assumed to be governed by the solution-diffusion mechanism described by the following equations [12,17],

$$P_i = S_i D_i \tag{1}$$

$$\alpha_{ij} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j} \right) \times \left(\frac{S_i}{S_j} \right) \tag{2}$$

Table 1
Advantages and disadvantages of CO₂ capture technologies [50–53].

CO ₂ separation processes		Advantages	Disadvantages
Single processes	Absorption	<ul style="list-style-type: none"> Appropriate for Manufacturing scale Functioning for small CO₂ feed concentration 	<ul style="list-style-type: none"> Excessive use of energy Corrosion caused by the breakdown of amines Emissions of hazardous by-products Costly regeneration
	Adsorption	<ul style="list-style-type: none"> Sustain high-pressure operation Large capacity for CO₂ adsorption High selectivity over other gases 	<ul style="list-style-type: none"> Excessive energy usage Trouble of restoration
	Chemical looping combustion	<ul style="list-style-type: none"> Mainly N₂ is released (harmless) Simply separation of CO₂ through condenser Lower capital cost than typical absorption 	<ul style="list-style-type: none"> Not recommended for cyclic operation Insufficient oxygen carrier stability Slow redox reaction
	Cryogenic	<ul style="list-style-type: none"> The product with high purity can be achieved 	<ul style="list-style-type: none"> High demand for energy
	Hydrate	<ul style="list-style-type: none"> High purity of the product 	<ul style="list-style-type: none"> Pre-processing is required to remove humidity from the mixed feed stream Only appropriate for feeds with a high CO₂ concentration (> 50%) Low temperature and High pressure Resulting the secondary pollution High initial investment cost
Hybrid processes	Membrane	<ul style="list-style-type: none"> Simply operating Simple installation Low usage of energy 	<ul style="list-style-type: none"> Membrane with a large surface area The permeability of feed gases, particularly polymeric membranes, is affected by humidity.
	Absorption- Membrane	<ul style="list-style-type: none"> Low capital cost Low regeneration energy Amine emissions can be reduced via a membrane process 	<ul style="list-style-type: none"> Operating conditions have an impact on performance. Corrosion caused by amines degradation Only appropriate for feeds with low CO₂ concentration (13% –23%)
	Absorption-adsorption	<ul style="list-style-type: none"> Low heat capacity Higher CO₂ carrying capacity 	<ul style="list-style-type: none"> Hazardous by-products are released. High sorbent regeneration energy
	Adsorption-Cryogenic	<ul style="list-style-type: none"> Minimal energy usage Rapid rate of recovery High purity 	<ul style="list-style-type: none"> Not mature enough to be used on a large scale. Only appropriate for low CO₂ feed concentrations (15%–36%)
	Membrane -Cryogenic	<ul style="list-style-type: none"> Improved process efficiency Low energy requirements Reduced equipment sizes 	<ul style="list-style-type: none"> High energy consumption High energy consumption A condensing agent must be chosen

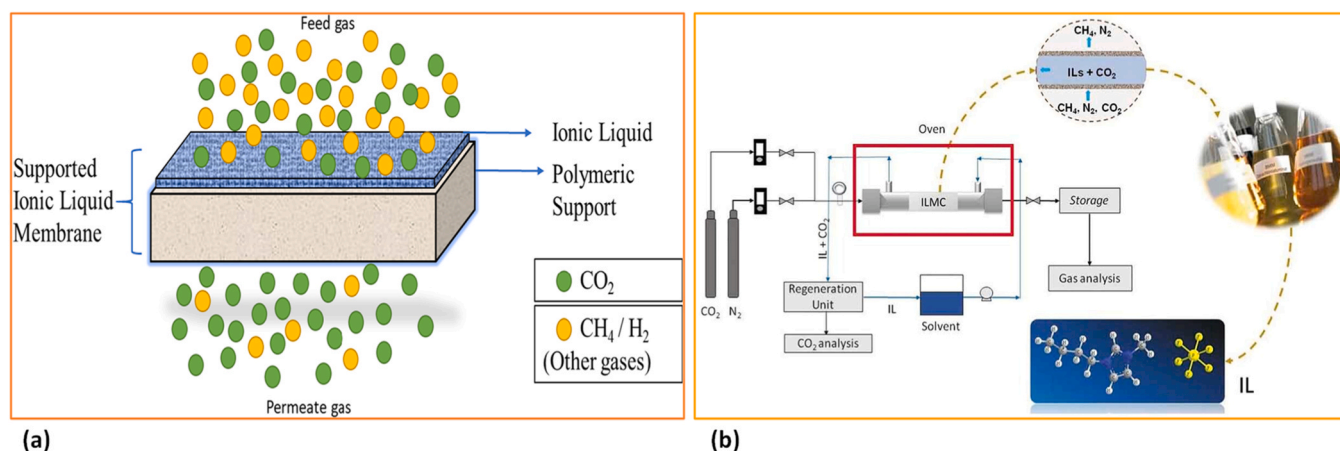


Fig. 2. (a) Schematic representation of CO₂ capture and CH₄/H₂ separation using SILM (b) Illustration of CO₂ separation using IL membrane contactor having regeneration unit.

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Here, P indicates the ideal permeability of gaseous specie i or j . S and D denote the solubility and diffusion coefficient, respectively of individual specie. α shows the ideal selectivity, defined as the ratio of the ideal gas permeabilities for a given gas pair. Selectivity, also termed separation factor, indicates separation media's ability (herein SILM) to separate two or more gaseous species. Selectivity is independent of membrane thickness and is concerned with the unique features of ILs and membrane support. Nevertheless, a trade-off exists between permeability and selectivity in gas separation. This trade-off relationship was described by Robeson, showing an upper bound in the log-log plot of selectivity versus permeability by the correlation Eq. (3) [59].

$$P_i = k \alpha_{ij}^n \quad (3)$$

Here n denotes the slope of the upper bound plot. Permeability as described by Eq. (3) is the steady-state flux (J) through the membrane under a trans-membrane pressure drop (Δp) and normalized to the unit thickness of the membrane (l).

$$P_{ij} = J_{ij} \frac{l}{\Delta p} \quad (4)$$

Barrer is a common unit to express the gas permeability, described by the following relationship,

$$1 \text{ Barrer} = \frac{10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}}{\text{cm}^2 \text{ s cmHg}} \quad (5)$$

Permeance is expressed as the ratio of permeability to the thickness of the membrane. The unit of permeance is GPU while GPU=Barrer/membrane thickness (μm).

A defect-free membrane is indispensable because of the closer size of gases in the feed. Alternatively, different physicochemical properties of species in gaseous feed promote the effective design of materials. The most common properties are surface tension, solubility, and diffusivity [12]. The detailed analysis of solubility and diffusion coefficient of CO₂ in IL will be presented later.

3.1. Types of polymer supports used for the fabrication of SILMs

One of the key drawbacks of SILMs is the possible loss or leaching of ILs when the transmembrane pressure increases from the capillary forces on IL inside the support pores [60]. The ILs must be properly embedded in a tight structure to achieve higher stability. To overcome the leaching of ILs from the porous supports, researchers have explored different polymer materials along with ILs to synthesize highly thermally and mechanically stable SILMs, which is critically summarized in the sub-sections below.

3.2. Low molecular weight organic gelators

One proposed higher-stability method is fabricating a gel by low molecular weight organic gelators (LMOG) [61]. However, the LMOG-based gels still need porous support for higher mechanical stability. Instead, highly elastic, soft, and mechanically robust solids can be produced from gels with low polymer concentrations. Such gels can be created using ABA triblock copolymers with a mesh size of 10–100 nm [62]. The mobility of such low polymer gels is comparable to that of pure ILs. Fig. 3(a). shows the thermally reversible ion gels based on ABA triblock copolymer. Self-assembly of the insoluble end-block upon evaporation or cooling of the solvents forms the physical cross-links in the polymer network containing IL and soluble mid-block. Ion gel membranes can be fabricated by soaking the existing polymer support in excess IL [63].

3.3. Glassy high-performance polymers

Glassy polymers maintain integrity and homogeneity if there is enough IL compatibility and do not plasticize the polymer too much, keeping the glass transition temperature higher than the operating temperature of the membrane. Numerous membranes have been fabricated using glassy polymers used for gas separation purposes in their neat form. For example, amorphous glassy-based polyethersulfone (PES) with 1-ethyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide [EMIM][Tf₂N] IL blend membrane were fabricated and remained homogeneous up to (50%) of the IL content [68]. However, the same IL underwent phase separation in the polyimide Matrimid®5218 [69]. Besides this, 1-methyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide [BMIM][Tf₂N] IL showed high compatibility with 6FDA and 2,3,5,6-tetramethyl-1,4-phenylene diamine-based polyimide (6FDA-TeMPD) [70], where the samples showed a distinct phase separation at 80 wt% IL and remained homogeneous up to 51 wt% of the IL. Additionally, [BMIM][Tf₂N] showed complete compatibility with polybenzimidazole (PBI) and poly(pyromellitimide-co-4,4'-oxydianiline) (PMDA-ODA) [71]. Fig. 3(b). shows the synthesis procedure and molecular structure of 6FDA-based polyimides.

3.4. Polymers of intrinsic microporosity (PIMs)

Polymers of intrinsic microporosity (PIMs) are a relatively new class of polymers and are represented as high-performance polymers. PIMs were first introduced by Budd and McKeown in 2004 [65] and possess high fractional free volume and gas solubility. Some researchers have synthesized blends with archetypal PIM-1 and

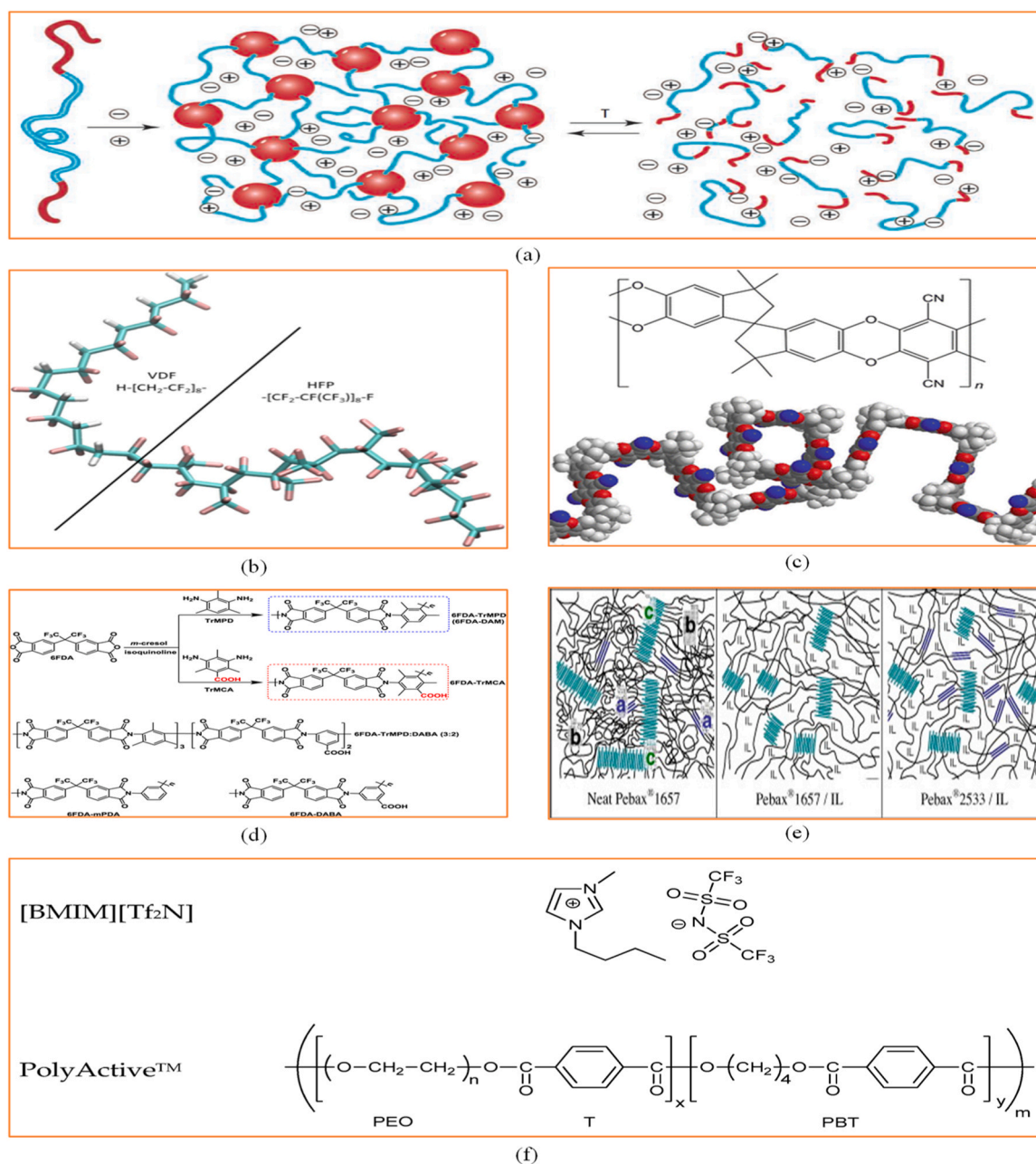


Fig. 3. (a) thermally reversible ion gels based on ABA triblock copolymer. Copyright 2008, American Association for the Advancement of Science. (b) Synthesis procedure and molecular structure of 6FDA-based polyimides. Copyright 2022 Elsevier. (c) Molecular structure and model of PIM-1. Copyright 2022, Royal society of chemistry. (d) Structure of vinylidene fluoride VDF and hexafluoropropylene (HFP). Copyright 2020, American chemical society. (e) Chemical structure of Pebax®1657 and Pebax®2533 with [TETA][TFA] IL and (f) chemical structure of [BMIM][TF₂N] IL and PolyActive™. Copyright 2020 MDPI. (a) With permission from Ref [62]. (b) With permission from Ref. [64]. (c) With permission from Ref. [65]. (d) With permission from Ref. [66]. (e) With permission from Ref [67].

1-ethyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide [C₂MIM][TF₂N], 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C₄MIM][TF₂N], and 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C₆MIM][TF₂N]. The CO₂ permeability with 5 wt% IL was gradually decreased from 7440 to 6650, 4590, and 2240 Barrer for the [C₂MIM], [C₄MIM], and [C₆MIM] cation, respectively. The increase in CO₂/N₂ and CO₂/CH₄ selectivity was noted as from 19 to 25 and 11–14, respectively, for [C₆MIM][TF₂N] [72]. The ILs partially separated into ellipsoidal domains because of the poor compatibility of the IL with the polymer. To increase the compatibility, the PIM-1 was copolymerized with a PEG functionalized anthracene maleimide comonomer, resulting in a CO₂ permeability of 812 Barrer

and a CO₂/N₂ and CO₂/CH₄ selectivity of 30 and 19, respectively, at a 10 wt% of [C₆MIM][TF₂N] [72]. Similarly, Guiver et al., [73] used PIM-1 structure with MeOH (PIM-1-MeOH) and ILs functional groups (PIM-1-ILs) to study the effect of ILs on the CO₂ separation performance. Their results revealed that pseudo-ILs functional groups in the PIM-1 structure increased the CO₂/N₂ selectivity while the CO₂ permeability was decreased. The CO₂ permeability and CO₂/N₂ selectivity using PIM-1-MeOH were 7340 Barrer and 15.1, respectively. Similarly, the CO₂ permeability and CO₂/N₂ selectivity using PIM-1-ILs were found 817 Barrer and 35.5, respectively. The molecular structure and model of PIM-1 is shown in Fig. 3(c).

3.5. Semi-crystalline fluoropolymers (SCFPs)

Crystalline fluoropolymers serve more commonly as porous supports and usually act as barrier materials for SILMs. The CO₂ permeability increases by blending SCFPs with IL, and the overall crystallinity reduces. Similarly, the amorphous phase and the overall flexibility increase by coupling SCFPs and IL. Song et al. [74] used PVDF support immobilized with 80% of 1-ethyl-3-methylimidazolium tetracyanoborate [EMIM][B(CN)₄] IL and the CO₂ permeability and diffusivity were increased four-fold, whereas the solubility was increased by more than 50%. The fluoroelastomer such as poly-vinylidene fluoride-co-hexafluoropropylene, p(VDF-HFP) is also used with different ILs to fabricate SILMs. Hong et al. [75] reported the gels of 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄] IL in p(VDF-HFP) with 67 wt% IL to synthesize a SILM and yielded the CO₂ permeability of 400 Barrer and CO₂/N₂ selectivity of about 60 which exceeded the Robeson 2008 upper bound. Similarly, Jung et al. [64] used p(VDF-HFP) with various amounts of 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [EMIM][TFSI]. Their results stated that embedding ILs into the polymer affects the properties and morphologies of the support. However, the polymer with 20 wt% of IL resulted in higher CO₂ diffusivity. The CO₂ diffusivity of p(VDF-HFP) at 20 wt% of IL was 10.6 (10⁻¹² m²/s) and reduced to 2.4 (10⁻¹² m²/s) at IL contents of 40 wt%, which indicated that the excess IL has a negative impact on the CO₂ diffusivity of p(VDF-HFP). Fig. 3(d). shows the structure of vinylidene fluoride (VDF) and hexafluoropropylene (HFP).

3.6. Thermoplastic elastomers

One of the largest membrane materials used to fabricate SILMs is the thermoplastic elastomers such as Pebax® and Polyactive® membranes. Various researchers have studied the effect of ILs on the transport properties of Pebax membranes. Bernardo et al. [76] studied the transport properties of Pebax®1657 and Pebax®2533 using 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF₃SO₃] IL up to 80 wt% loading. The crystallinity, young modulus of the supports, and melting point of the polyamide phase were reduced using [BMIM][CF₃SO₃] in Pebax®1657 while the CO₂ permeability was increased. The properties of Pebax®2533 were less affected by the IL, which was similarly observed by using Pebax®2533 composite membrane along with task-specific ionic liquid (TSIL) triethylenetetramine trifluoroacetate [TETA][Tfa] in dry conditions. However, the CO₂ permeability of the Pebax®2533 was increased three-fold using 30 wt% of TSIL, and the CO₂/N₂ selectivity was increased by 50% [77]. Sorption analysis in Pebax®1657 with 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄] IL showed a considerable increase in the CO₂ solubility by increasing the IL content [78].

PolyActive™ is a similar multi-block copolymer like Pebax®. It is made of polyester rather than polyamide. In a study on blends of PolyActive™ and [BMIM][Tf₂N] IL, Klepić et al. [67] examined how the composition of the copolymer and the amount of IL affected the morphological, thermal, mechanical, and transport properties of the blends for both pure and mixed gases. The IL showed almost no effect on the polyester phase, but it decreased the crystallinity and melting point of the polyether phase and the Young's modulus of the polymers. This resulted in increased permeability as a function of IL concentration due to increased diffusion coefficient. The CO₂/N₂ mixed gas selectivity was close to the ideal selectivity and was almost independent of the pressure up to 6 bar. The PolyActive™ grade with a high polyether content and a short block length revealed the maximum CO₂ permeability. Fig. 3(e) shows the structure of Pebax®1657 and Pebax®2533 with [TETA][TFA] IL. Fig. 3(f). shows the chemical structure of [BMIM][Tf₂N] IL and PolyActive™.

3.7. Drying/Pretreatment methods of membranes for post-combustion CO₂ capture

The membrane is the main component of the post-combustion CO₂ capture process, acting as a selective barrier between feed and permeate and conducting the separation of different gases. Membrane swelling and shrinkage are the main issues in post-combustion CO₂ capture applications [79]. Membrane pretreatment is an important factor to be considered to reduce the shrinkage and swelling of the membrane structure before use in post-combustion CO₂ capture. Thus, it is essential to understand the effect of the pretreatment procedure on the free-volume pore size as it determines the performance characteristics [80]. Albo et al. [81] pretreated different commercially available polyamide membranes (SWC5, ESPA2, CPA50) and evaluated the effect of each pretreatment technique on the separation performance of various gases such as CO₂/N₂, H₂/N₂, and He/N₂. The different membrane pretreatment procedures from their study are discussed as follows:

1. Room Temperature-Oven (RTO): In RTO method, the membranes are first rinsed 10 times in a pure water bath, then dry at room temperature for 24 h, and finally placed in an oven at 120 °C for 30 min
2. Ethanol-Hexane (EH): In the EH method, the membranes were rinsed 10 times in a pure-water bath, then immersed in pure ethanol for 5 min and then soaked in pure hexane for 1 min. Finally, the solvent evaporated at room temperature (25 °C) for 15 min
3. Freeze Drying (FD): In FD method, membranes were rinsed 10 times in a pure-water bath, then immersed in 50, 75, 90, 95, and 100 wt% t-butanol aqueous solutions for 15 min. Then, membrane coupons were placed in pure t-butanol in freeze-dried equipment under a vacuum (gradually decreasing from 533 to 0.4 Pa) for 2 h.

The CO₂ permeance and CO₂/N₂ selectivity of polyamide membranes (SWC5, ESPA2, CPA50) pretreated with RTO, EH, and FD methods are shown in Fig. 4(a), (b), (c), and (d). The gas permeation properties through the membranes changed depending on the pretreatment method applied to the membranes and the influence on the shrinkage/swelling of the selective layer. In particular, an increase of 1.8–9 and from 1.6 to 3.2 was observed when the membranes were pretreated with ethanol-hexane and freeze-drying, respectively, to samples dried at room temperature and in the oven. Gas permeability values did not correlate for freeze-drying and room-temperature-oven treatments, but there was a correlation for the ethanol-hexane pretreatment procedure. This was mainly attributed to avoiding the pore shrinkage during the ethanol-hexane procedure [81].

3.8. Experimental methods for SILMs preparation

Due to the high viscosity of IL, there are three techniques for preparing SILMs such as direct immersion, vacuum, and pressure methods, but the implementation of each of mentioned methods is a crucial factor in the efficiency of SILMs [82]. Table 2 shows the advantages and disadvantages of each technique. The direct immersion involves the in-situ immobilization of the ILs by soaping the support material in the ILs during the direct immersion process. The surplus IL will then be wiped away from the surface of the membrane material with a tissue after allowing it to drip overnight. This approach has created certain SILMs [83,84]. Eijiro Miyako et al. [85] reported the formation of a SILM by submerging a polypropylene (PP) support in IL [BMIM][PF₆]. Nosrati et al. [86] fabricated SILMs by impregnating using different support membranes with imidazolium, phosphonium, and ammonium-based ILs. They demonstrated that soaking membranes in IL, the membrane pores were properly filled with ILs with sufficient soaking time for synthesizing the composite membrane.

In the vacuum technique to synthesize SILMs, the support material is put inside a vacuum-tight container for a period to eliminate air through

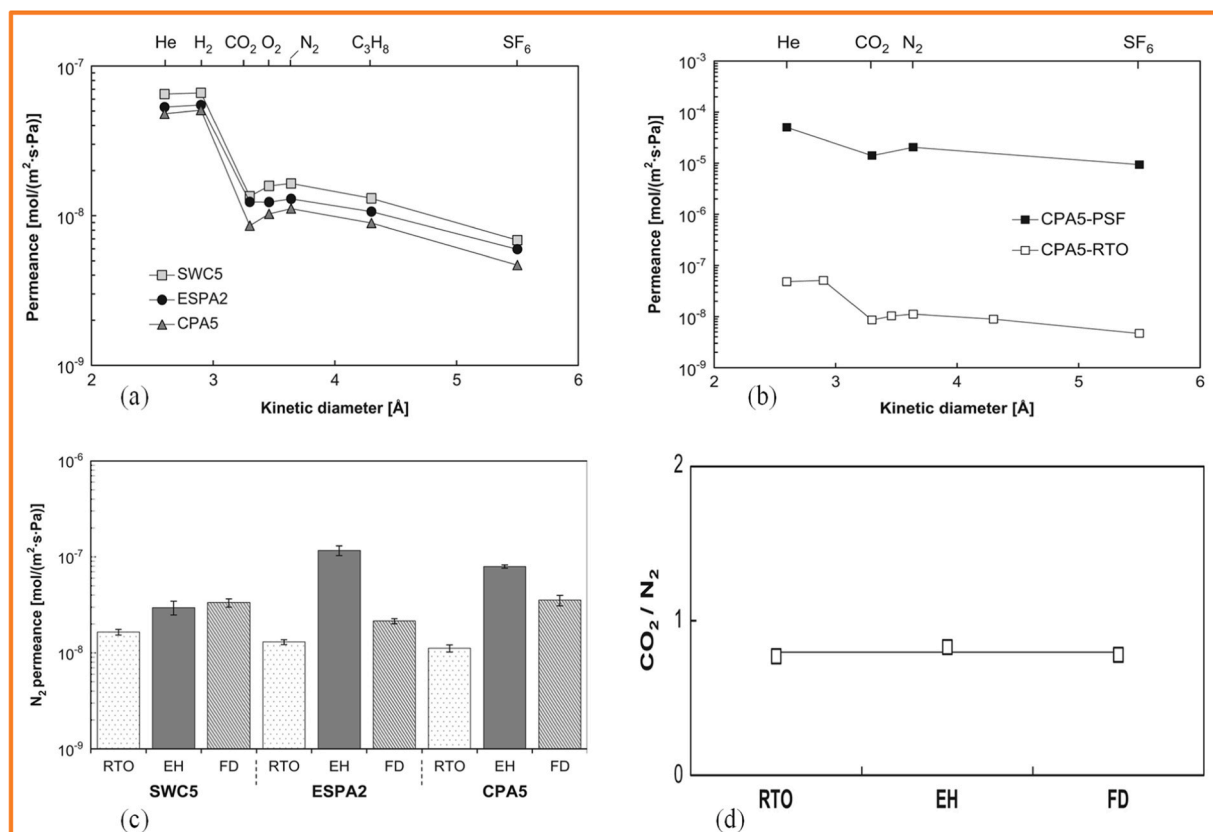


Fig. 4. (a) Single gas permeance of different PA membranes after drying at RTO ($16 \pm 3^\circ\text{C}$). (b) Single gas permeance of CPA5-RTO and CPA5-PSF samples at temperature ($16 \pm 3^\circ\text{C}$). (c) N_2 permeance of three PA membranes after different pretreatments. (d) CO_2/N_2 selectivity values for RTO, EH and FD procedures in CPA5 membrane.

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Table 2

Advantages and Disadvantages of different synthesis techniques for SILMs.

Properties	Process type		
	Direct Immersion method	Pressure immobilization method	Vacuum immobilization method
Advantages	<ul style="list-style-type: none"> Easiest method for the synthesis of SILM synthesis. Immobilization of IL involves soaping of the support materials in IL under ambient pressure and then removing the excess IL on the membrane by wiping up with tissue paper. The membranes synthesized via this technique are highly suitable and recommended for separating organic compounds from the mixture component. 	<ul style="list-style-type: none"> The amount of ILs which was immobilized was practically independent of the ILs used. The small losses in the ILs were experienced when it was immersed for a week after immobilization under pressure. High stability of membranes is achieved due to pores of membranes filled with IL through pressure. The SILMs synthesized using this procedure can be further utilized for experiments of pervaporation where high pressure is required. 	<ul style="list-style-type: none"> Suitable for the synthesis of SILMs, especially for low viscosity ILs. The small amount of the IL absorption experienced into the membranes in the case of high viscosity ILs. SILMs synthesized through this procedure could be further used for experiments of pervaporation where low pressure is required.
Disadvantages	<ul style="list-style-type: none"> The SILM synthesized with this method have less stability. The capillary forces have negative impact with viscosity of ILs. This refers to the behavior of IL pushed out inside the pores of SLM due to transmembrane pressure. 	<ul style="list-style-type: none"> The extremely high pressure in pressure immobilization method causes the dispersion of IL on the surface of membrane and may also causes the leaching of IL on support which reduces the separation performance of SILM. 	<ul style="list-style-type: none"> The high losses of ILs were experienced in carrying out immobilization under vacuum. The amount of immobilized IL reduced in correspondence with the viscosity of IL due to the decrease of the capillary force.

the pores of membranes. Then ILs are dispersed throughout the surface of the membrane. Finally, excess IL should be cleaned of membrane surface [87]. Fortunato et al. [88] studied two ILs, namely [BMIM][PF₆] and [OMIM][PF₆] used for synthesizing SILMs consisting of hydrophilic membranes such as PP, PVDF, nylon, and polyether sulfone (PES), and described that SILMs possess higher solubility and stability. To separate organic mixtures with this method, the SILMs should be used at low pressure [89,90].

In the pressure method, ILs are impregnated into the material's pores by placing it in an ultrafiltration unit, adding ILs, and applying N₂

pressure. After the membrane coating, the pressure is released [91]. Examples include SILMs containing [BMIM][Cl, BF₄, or NTf₂], which were produced using the pressure technique, which verified that the pores of the porous membrane support filled with ILs. As a result of this approach, it is possible to utilize SILMs for pervaporation studies even at higher pressures [92–94]. Fig. 5(a), (b), and (c) shows the SEM micrographs of nylon membrane impregnated with IL [Bmim⁺][PF₆⁻] using pressure and vacuum methods. Fig. 5(d) illustrates the preparation of SILM having PVDF polymer as support.

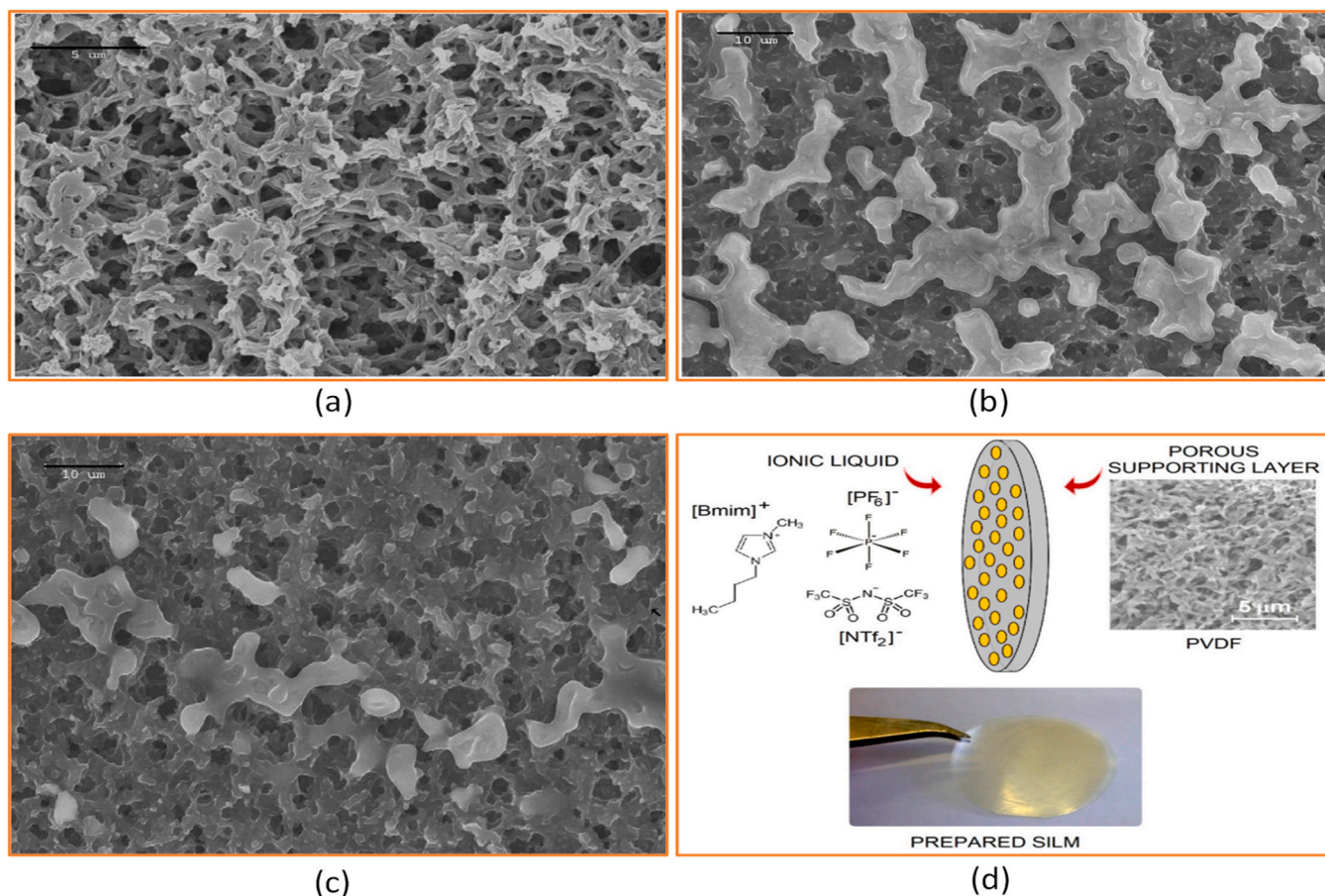


Fig. 5. Scanning electron micrographs of the (a) Nylon® membrane (scale bar = 5 μm), (b) the Nylon® membrane impregnated with [bmim⁺][PF₆⁻] by pressure (scale bar = 10 μm), and (c) by vacuum (scale bar = 10 μm). Copyright 2009 Elsevier (d) Illustration of SILM preparation. (a) With permission from Ref. [91]. (b) Reproduced with copyright permission from Ref. [95].

3.9. Tuning the IL properties in SILMs

The ILs are organic salts mainly composed of organic and inorganic anions with organic cations and exhibit various desirable properties, including low volatility, low vapor pressure above the liquid surface, and a melting point lower than 100 °C [96,97]. Lynette et al. [98] proposed ILs as a CO₂ separation medium. In addition, ILs could be used in various areas, including electrolytes [99–101], chemical solvents [102–104], and catalysts [105,106]. Furthermore, they have been effectively used in the removal of heavy metal ions from aqueous streams [107,108], treatment of greenhouse gases [109,110], and removal of volatile organic compounds [111,112]. An overview of some fields for utilizing SILMs is given in Fig. 6.

ILs have the most appealing features of being tailored in nature. The tailoring nature of ILs enables them to alter their properties via careful selection of anions and cations to give specific compounds for specific functions [113,114]. Due to their magical characteristics, the ILs are called green solvents. The ILs are nonvolatile because of their low vapor pressure and maintain their thermal stability over the high-temperature ranges and can both absorb and emit gases. Besides, the trends for the basicity and acidity of ILs can be tuned and adjusted, and ILs are usually hydrophilic and are rarely hydrophobic [115].

A complete database on the physicochemical properties of ILs has been compiled, and measurable data is available in the literature [116, 117]. Density, polarity, acidity, viscosity, vapor pressure, melting point, phase equilibria, conductivity, and many other notable properties are provided for ILs [118]. The presence of impurities such as H₂O or any organic solvent can substantially affect the physicochemical

characteristics of ILs. The small quantity of H₂O in the structure of ILs can significantly alter the acidity, density, viscosity, surface tensions, and molecular behavior of ILs [119,120]. Moisture contents in ILs result in strong intermolecular interactions including hydrogen bonds, van der Waals forces, electrostatic interactions, etc. At high quantities, the ILs begin to disintegrate into individual ions or ion pairs [120]. Rivera-Rubero et al., [121] used vibrational spectroscopy to study the surface orientation characteristics of ILs and H₂O. They concluded that ILs have many advantages over organic solvents, including high thermal conductivity and stability, high storage density, tunable properties, high heat capacity, negligible vapor pressure and low volatility, which have been used for many applications because of their attractive properties. Although ILs have limitations like aquatic toxicity, flammability, and high cost which need further attention.

The CO₂ gas can be captured and converted into useful products such as methanol and formic acid by ILs, which can help address the global carbon footprint [122]. Even though the inclusion of ILs has substantially improved the performance of CCS process, significant improvements in process optimization are still required. In most cases, the ILs utilized in the maturing binding process use imidazole, phosphonium, or pyridine as the basis, characterized by their biological toxicity [123–126]. In addition, the critical properties of CO₂ are predictable; however, finding the critical properties of ILs is challenging because it disintegrates close to the normal boiling point [26].

One of the core problems is related to the extra viscous nature of the ILs, which complicates the CO₂ absorption in the ILs. This property should be explored to devise and employ several approaches for their practical solution. One of the most common approaches is adding water

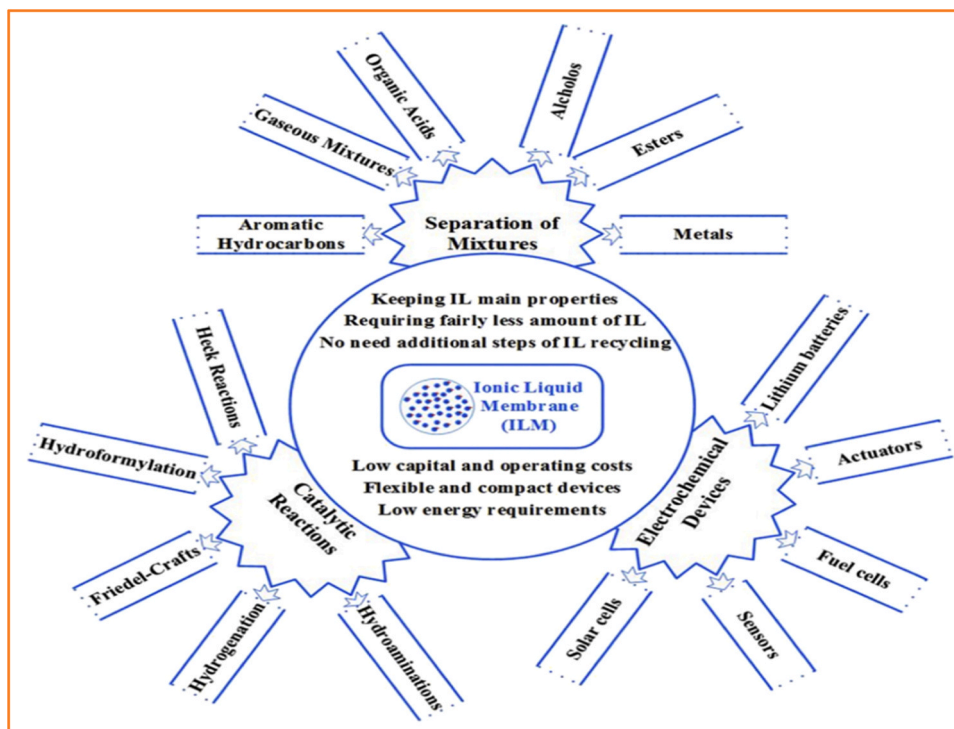


Fig. 6. Properties and applications of SILMs. With permission from Ref. [84]. Copyright 2016 Elsevier.

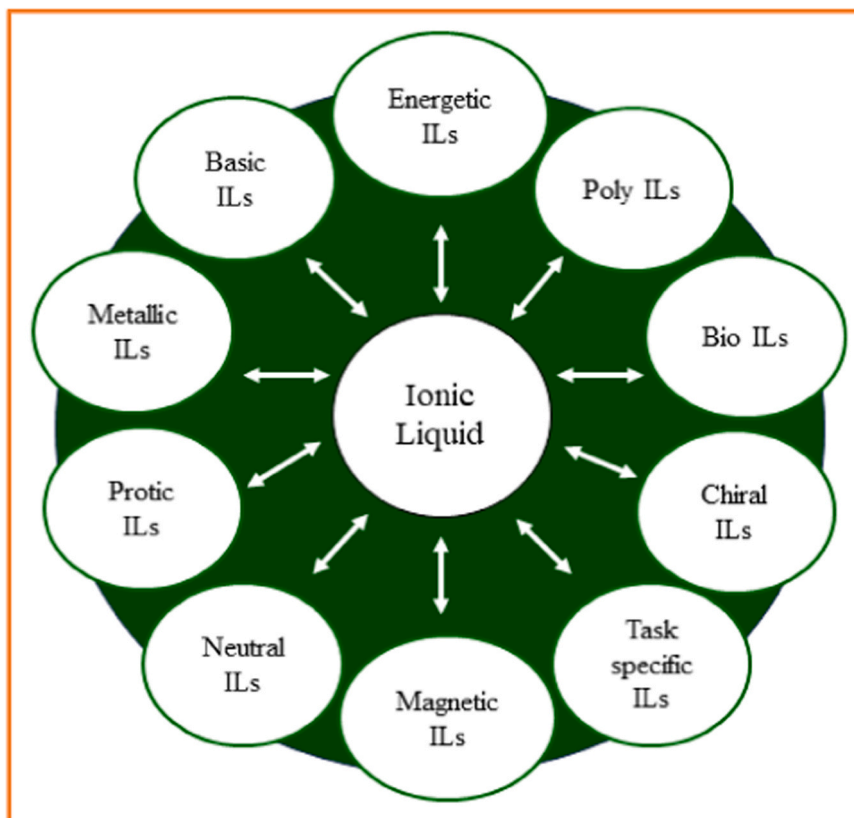


Fig. 7. Classification of various ILs. Reproduced with copyright permission from Ref. [115]. Copyright 2020 Elsevier.

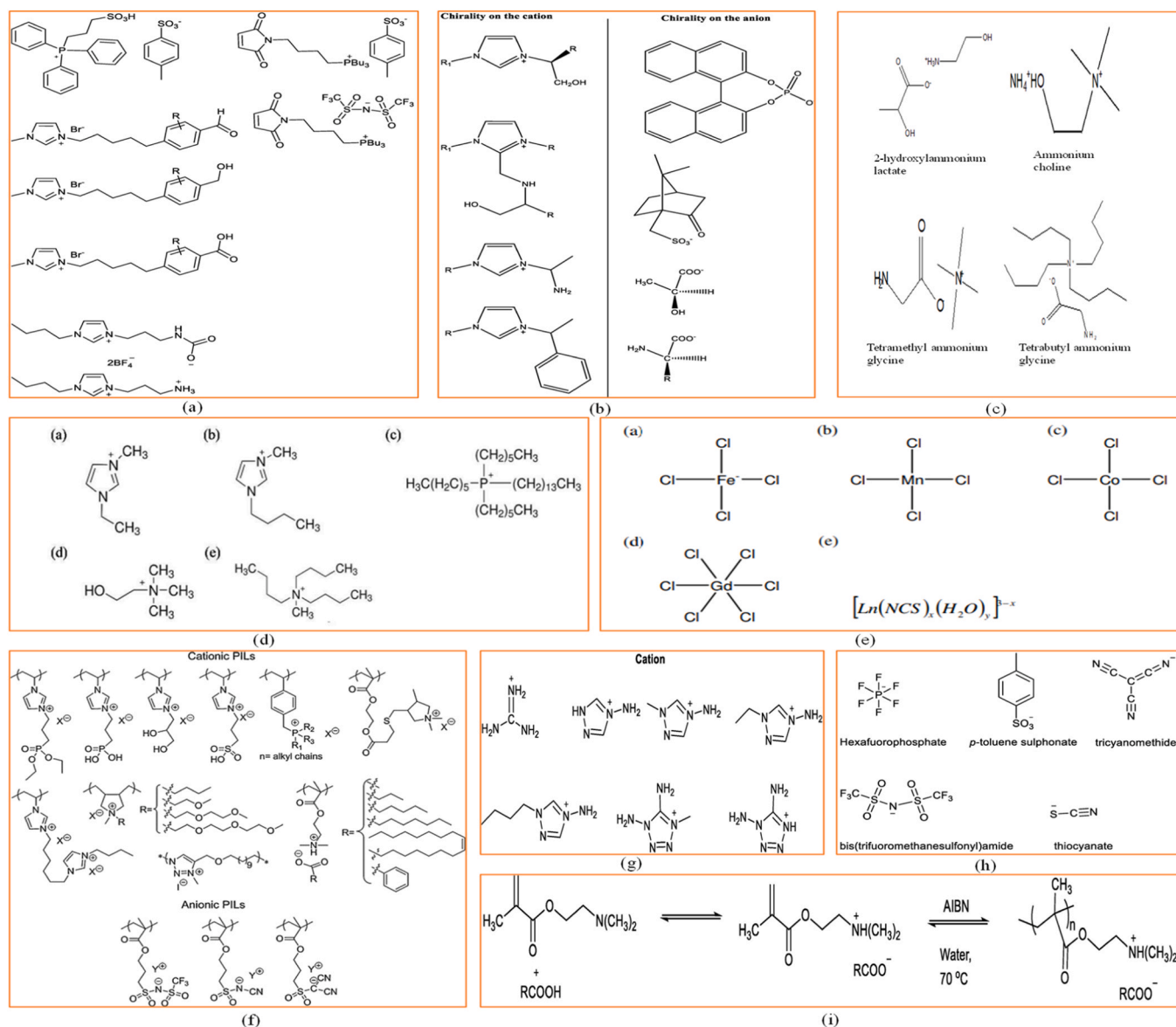


Fig. 8. (a) Structure of TSILs (b) Different cations and anions of C-ILs (c) Structure of ammonium-based BILs (d, e) Structures of different anions of M-ILs. (f) Structure of different cations and anions used for the synthesis of PILs (g) Structure of various cations used for the synthesis of EILs (h) Structure of commonly used neutral anions used for the synthesis of NILs (i) Synthesis procedure of PrILs (j) PrILs (k) MILs (l) BILs. (m) Structure of different cations. (n) Structure of different anions. (o) Imidazolium-based ILs used for gas separation.

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and amines in a suitable composition into ILs to drop their high viscosity. Another drawback in ILs utilization is their cost which restricts their extensive application over conventional solvents [26]. The continuous efforts by researchers are going on to develop an efficient and cost-effective strategy utilizing ILs as the medicated solvent CO₂ separation media. Zhang et al. [127] synthesized a surfacing-modified CO₂ sorbent from the mixture of a nonionic surfactant with the aqueous solution with imidazolium-based ILs. They achieved the lowest cost of sorption media. They demonstrated that the mentioned sorbent has low viscosity with the advantage of low consumption of IL and hasty regeneration, which made this system attractive as an advanced sorbent for CO₂ capture. They found that the surfactant polyethylene glycol sorbitan monooleate (Tween) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [C₂MIM][TfO] IL with the addition of water

[Tween 80 (surfactant) + 10% [C₂MIM][TfO] + H₂O], has the capacity to capture 0.798 mol/L CO₂ at low pressure (0.6 MPa) and at ambient temperature and is more resembled with the performance to alkanolamine solutions.

4. Types of ILs

The ILs can be classified based on their effective tunability in the selection of anions and cations and numerous physical, thermal, and chemical properties, including miscibility in both organic and aqueous solvents, relative acidity or basicity, and ionic conductivity [105,128]. Fig. 7 shows the classifications of different ILs.

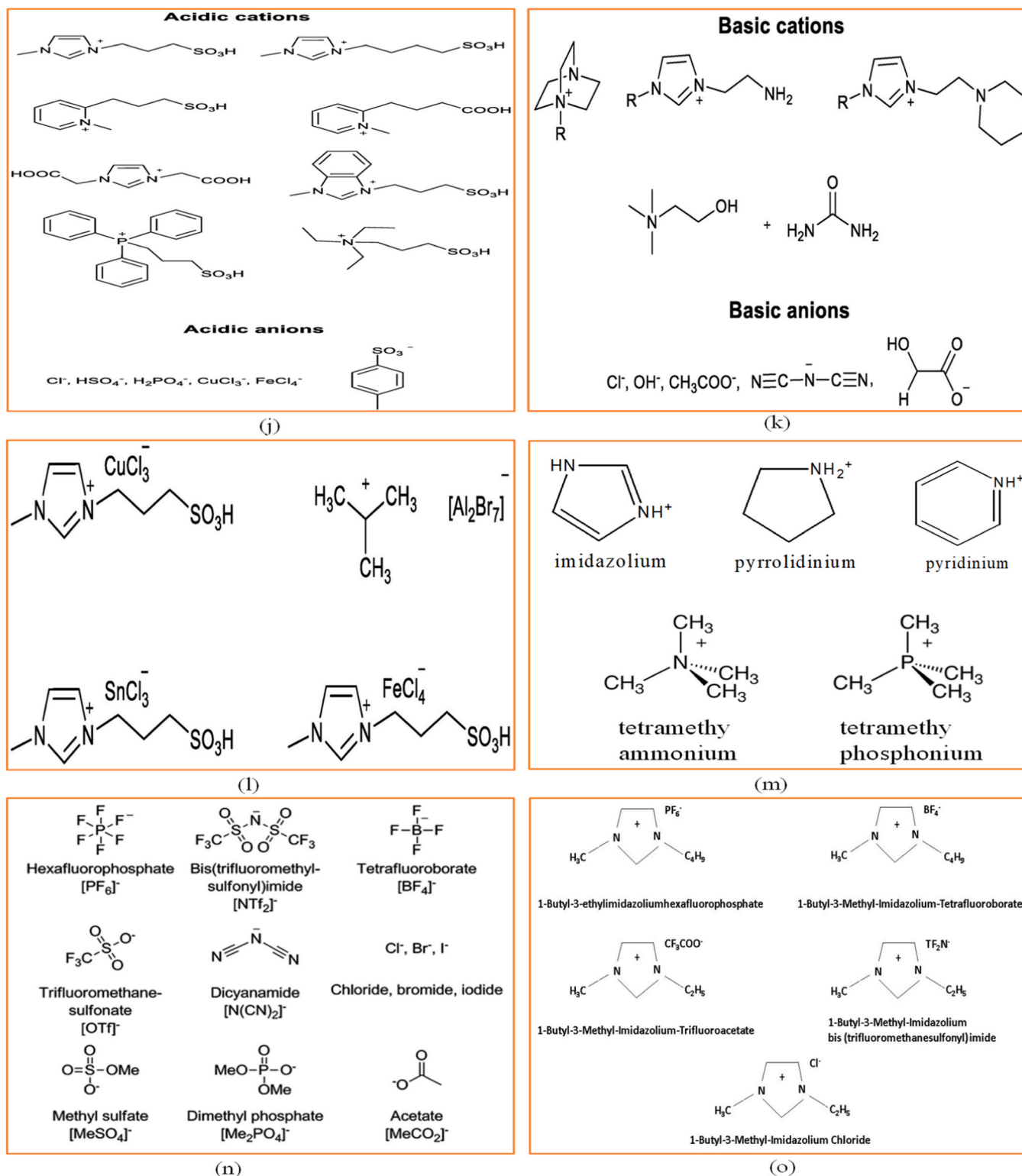


Fig. 8. (continued).

4.1. Task-specific ionic liquids (TSILs)

The TSILs are also called functionalized ILs [129]. Recently, TSILs have gotten more attention due to their unique features, which can be adjusted for a specific task by carefully selecting anionic and cationic moieties. The unique feature of TSILs was also studied to their

involvement in organic synthesis processes [130,131]. The molecular structures of different TSILs are shown in Fig. 8(a). Synthesis of TSILs is a little different and takes a long time, which might be owing to many active functional groups that are excessively reactive to various reactants [132].

4.1.1. Chiral ionic liquids (C-ILs)

Chiral ILs (C-ILs) are one of the most important classes of TS-ILs in the areas of liquid chiral chromatography, stereoselective polymerization, synthesis of potential active chiral compounds, liquid crystal, NMR chiral discrimination, and many other functional activities [138]. These ILs are promoted as catalysts or solvents for chiral chemical asymmetric synthesis. They associate with the chiral center inside the ILs at the cation, anion, or both [139]. Fig. 8(b) shows various examples of C-ILs. Furthermore, tetraethylammonium-based amino acid C-ILs showed strong ionic conductivity. Therefore, these ILs could be applied for specific applications such as bio-catalysts, chiral discriminations, electrolytes, and many more [140].

4.2. Bio ionic liquids (BILs)

The BILs are synthesized using recyclable bio-precursors with the advantage of being less toxic and more biodegradable. Green channels such as recyclable and sustainable bio-precursors make various hydroxide, choline cations, and other amino acid-based counter anions as non-toxic and sustainable bio-products with no chemical changes [141, 142]. The toxicity assessment of choline-based BILs based on the European standard revealed that all choline-based ILs had low toxicity and high biodegradability. The high bio-degradability of 95% was shown for 2-hydroxyethyl-ammonium lactate [143]. A schematic of a few ammonium-based BILs is shown in Fig. 8(c).

4.3. Magnetic ionic liquids (MILs)

MILs are a new class of ILs used in catalytic reactors such as flow battery systems. Magnetic properties are associated with incorporating a

metal ion in the structure of IL and applying an external magnetic field. Different MILs and their cations and anions structures are described in Fig. 8(d, e). In one of the recent studies by Santos et al. [133], synthesized magnetic phosphonium-based ILs such as [P₆₆₆₁₄][FeCl₄], [P₆₆₆₁₄][GdCl₆], [P₆₆₆₁₄][CoCl₄], and [P₆₆₆₁₄][MnCl₄] ILs and fabricated SILMs with their integration with the organic hydrophilic and hydrophobic PVDF porous support to utilize them for the separation of CO₂. Their results revealed that CO₂ permeability increases from 50 Barrer at temperature 312 K to 2000 Barrer at temperature 292 K. However, high driving conditions and functionalization are required to obtain high separation efficiency and stability with SILMs.

4.4. Poly ionic liquids (PILs)

The PILs are the critical component to form oligomers, dimers, trimers, and polymers with high molecular weight ($2.83 \times 10^5 - 5.25 \times 10^5$ Da) [144–146]. Furthermore, the synthesis of advanced PILs with the design selectivity of monomeric units has shown huge potential in numerous applications such as electrolytes for batteries [147], poly-electrolyte membranes for fuel cells [148], electrolytes for electrochemical supercapacitors [149], polymer electrolytes [150] CO₂ responsive gels [151], and CO₂ adsorbents and separation [152,153]. During the PILs synthesis, N-(2-(dimethylamino) ethyl) methacrylate (DMAEMA) and several carboxylic acids (RCOOH), including acetic acid, oleic acid, butyric acid, and hexanoic acid were used. These PILs were synthesized via a free radical polymerization process [154]. The synthesis procedure of PILs and different cations and anions for the synthesis of PILs is shown in Fig. 8(f, i).

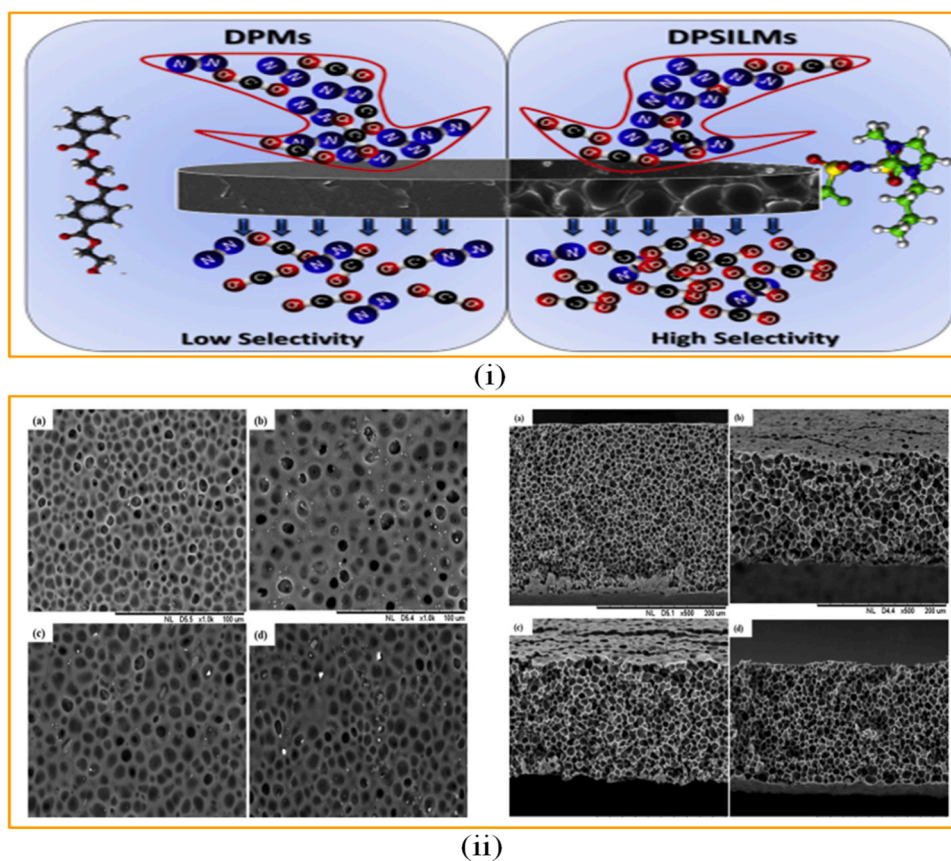


Fig. 9. (i) Dense polymer membrane and dense polymer SILM. Copyright 2016 Elsevier. (ii) Top & cross-sectional morphology of membranes (a) Pure Psf (b) TiO₂ modified Psf, (c) TiO₂/Psf@ [Dmim][Cl], and (d) TiO₂/Psf @ [Emim][PF₆].

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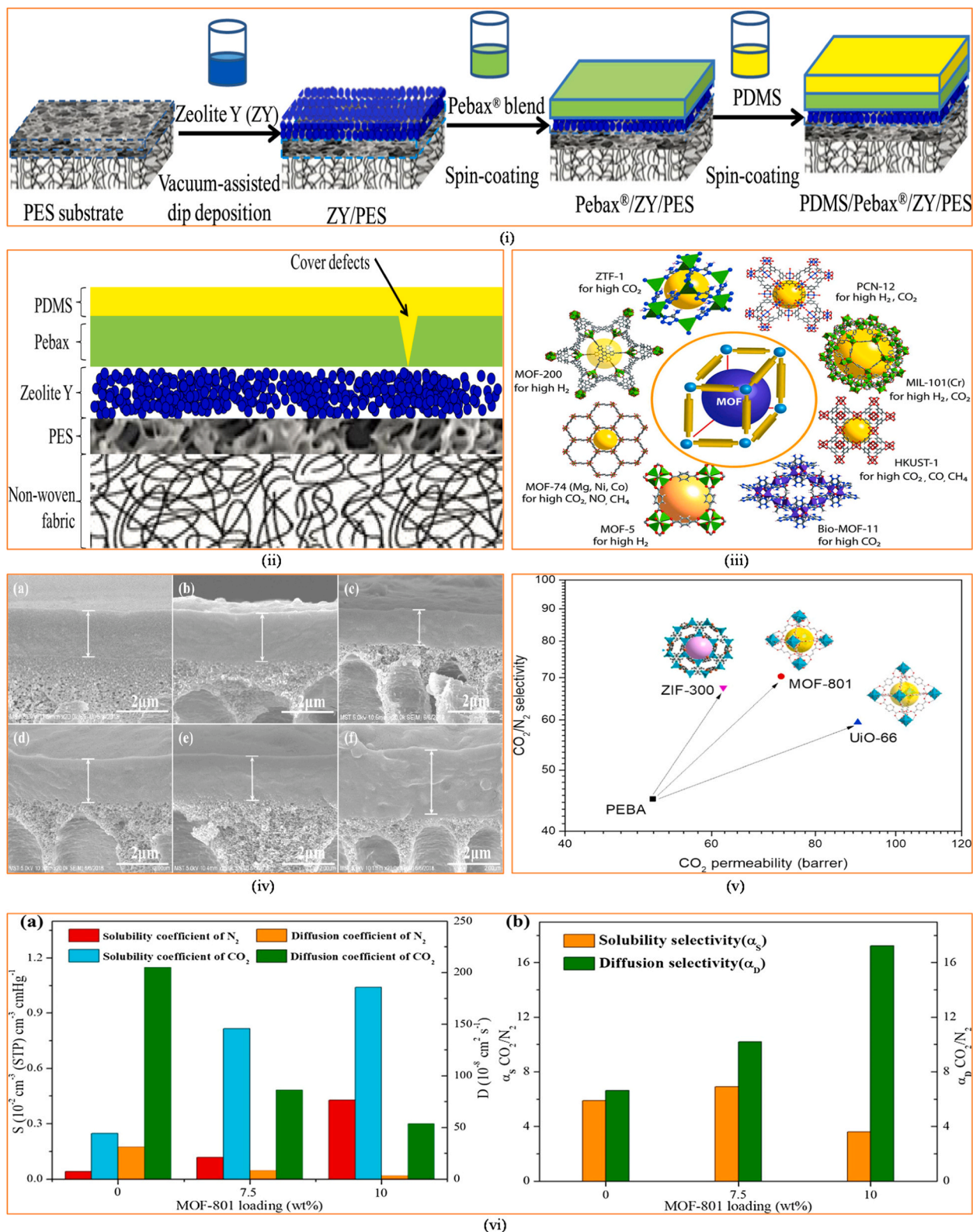


Fig. 10. (i) Schematic of the preparation procedure of the Pebax®/zeolite Y composite membrane. (ii) shows the schematic of Pebax®/zeolite Y composite membrane structure. Copyright 2015 Elsevier. (iii) 3D structures of different MOFs. Copyright 2021 Elsevier. (iv) Cross-section SEM images of pristine PEBA and MOF-801/PEBA at various loading. (v) comparison of the CO₂ permeability and CO₂/N₂ selectivity of PEBA mixed-matrix membranes with three types of MOF filler. (vi). (a) Sorption coefficient (S) and diffusion coefficient (D) and (b) sorption selectivity (α_s) and diffusion selectivity (α_d) of MOF-801/PEBA mixed-matrix dense films with different MOF-801 loading at $P = 3$ bar and $T = 20$ °C. Copyright 2019 Elsevier.

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Table 3
Comparison of CO₂ permeability and CO₂/N₂ selectivity of SILMs at different driving conditions.

Ionic Liquids	Support	Temp. (K)	Pressure (bar)	Permeability (barrer)		Selectivity CO ₂ /N ₂	Ref.
				CO ₂	N ₂		
[C ₆ mim][NTf ₂] 5 wt%	PIM-1	303	-	2240	90	25	[187]
[C ₂ mim][NTf ₂] 5 wt%				6650	332	20	
[Dems][TFSI] 50 wt%	PSF	308	7	5800	193	30	[179]
[Bdim][TFSI] 50 wt%				3600	130	27	
[Bmim][TFSI] 50 wt%				3000	107	28	
[N ₄₄₄₁][formate] 0.5 wt%	PSF	295	10	12	-	-	[176]
[P ₄₄₄₁][formate] 12.5 wt%				17.3	-	-	
Cyphos 102	PVDF	-	-	637	15.3	41.5	[188]
ECOENG™1111 P				127	11.6	10.9	
AMMOEN™100				93.9	1.79	52.6	
[Bmim][BF ₄]				93.9	5.04	52.3	
[Set ₃][NTf ₂]				747	18.4	26.2	
[Emim][OTf]				486	14.3	34	
[C ₈ mim][PF ₆]	PVDF	303	1.7	-	-	21	[11]
[C ₄ mim][NTf ₂]				-	-	30	
[C ₄ mim][BF ₄]				-	-	32	
[C ₄ mim][PF ₆]				-	-	20	
[MtdFHim][NTf ₂]	PES	296	1.85	210	13	16	[189]
[MnFHim][NTf ₂]				280	14	21	
[MpFHim][NTf ₂]				320	12	27	
[Bmim][NTf ₂]	PI	308	—	34.4	1.34	25.7	[190]
[C ₄ mim][NTf ₂]	PVDF	372	0.6	733.7	20.6	35.6	[191]
[Aemim][NTf ₂]	Ceramic	303	0.7	-	-	13	[192]
[Toma][An]				-	-	70	
[Bmim][NTf ₂]	Ceramic	303	2	-	-	127	[193,194]
[Emim][Ac]				-	-	34.7	
[Emim][NTf ₂]				-	-	21	
[BzPy][NTf ₂]	PTEF	298	0.35	518	18.4	27.9	[195]
[Bz ₂ Py][NTf ₂]				358	10.8	33.1	
[Bz ₄ Py][NTf ₂]				496	21.9	22.6	
[DMAPI][TFA]	PES	313	-	3028	20	151.4	[172]
[DMAPI][EoAc]				3352	26	129	
[Bmim][NTf ₂]	PVDF	313	0.1	1233	-	9.4	[173]
[Tespim][BF ₄]	zeolite	298	2	-	-	87	[174]
[Vbtma][Ac]	PVDF	-	-	1100	28.2	-	[193]
[C ₂ mim][NTf ₂]	Hydrophobic porous PVDF	-	-	589 ± 1.0	16.6 ± 0.11	-	[196]
[C ₆ mim][Tf ₂ N]	Carbon nanocomposite membranes	-	-	90	-	-	[197]
[C ₄ mim][Tf ₂ N]				140	-	-	
[DMAPI][TFA]				1500	-	90	[172]
[Bmim][PF ₆]	Hydrophobic PVDF	-	-	135–52	2220–530	-	[173]
[Bmim][BF ₄]							
[BMIM][BF ₄]		298	1.4	47.3 GPU	-	153	[198]
[bmim][TCM]	Nanoporous Silica Membrane	-	-	100–300	-	-	[199]
[emim][TCM]							
[APTMS][Ac]	P-84	298	10	—	-	38	[175]
[APTMS][Ac]	—	298	0.45	1100	-	39	[193]
[Emim][Ac]	—	313	0.45	1329	-	32	
[C ₂ py][Tf ₂ N]	—	293	1	20	-	20	[200]
[Bmpy][TFSI]	—	298	1	11.8	-	35	[171]
[Emim][Ac]	Al ₂ O ₃ /TiO ₂	298	4	-	-	30.72	[193]
[P ₈₈₈ VB][Tf ₂ N]	—	298	-	186	-	15	[201]
[Voim][PF ₆]	—	293	1.2	18	-	70	[168]
Pebax 1657/[bmim][NTf ₂]/@ZIF-8		298	1	104.9	1.25	83.9	[202]
[emim][B(CN) ₄]/P([vbim][dca])		308	1–2	340.1	8.10	42	[203]
[emim][dca]/P([vbim][dca])				272.9	5.1	53.5	
PSF/[bmim][NTf ₂]/@ZIF-8		303	6	350.7	2.18	161.1	[204]
[bmim][NTf ₂]/PI		308	0.1	510	18.4	27.6	[204]
[bmim][CF ₃ SO ₃]/Pebax 1657		298	1	320	8	40	[76]
[emim][NTf ₂]/SAPO-34/P(vinyl-IL)		296	1–1.5	527.2	20.2	26	[205]
(3-aminopropyl)trimethoxysilano acetate/@GO/Pebax 1657		298	4	118.6	1.67	71	[206]
[bmim][NTf ₂]/@ZIF-8/PSF		303	6	279	2.15	130	[204]
[Bmim][BF ₄] midblock-sulfonated multiblock polymer		308	1	153	-	64	[207]
Pebax 1657 [APMIm][Br]		298	4	900 GPU	-	45	[208]
Modified SAPO zeolites [Emim][Tf ₂ N]		298	3.75	7.24 GPU	-	19	[209]

4.5. Energetic Ionic liquids (EILs)

In recent decades, several EILs have been widely recognized to have several advantages over conventionally used energetic compounds such as trinitrotoluene (TNT) and hexanitro hexaazaisowurtzitane (HNIW) due to their thermal stability, ease of synthesis, insignificant vapor toxicity, safer transportation, and several other applications [155,156].

A variety of EILs have been synthesized using different cations such as 4-amino-1-methyltriazolium, 4-amino-1-ethyltriazolium, 4-aminotriazolium, guanidinium, and 4-amino-1-butyltriazolium [157]. The structure of various cations used to synthesize EILs is shown in Fig. 8(g). Furthermore, lanthanide-based EILs have high photochemical stability and luminous characteristics [158].

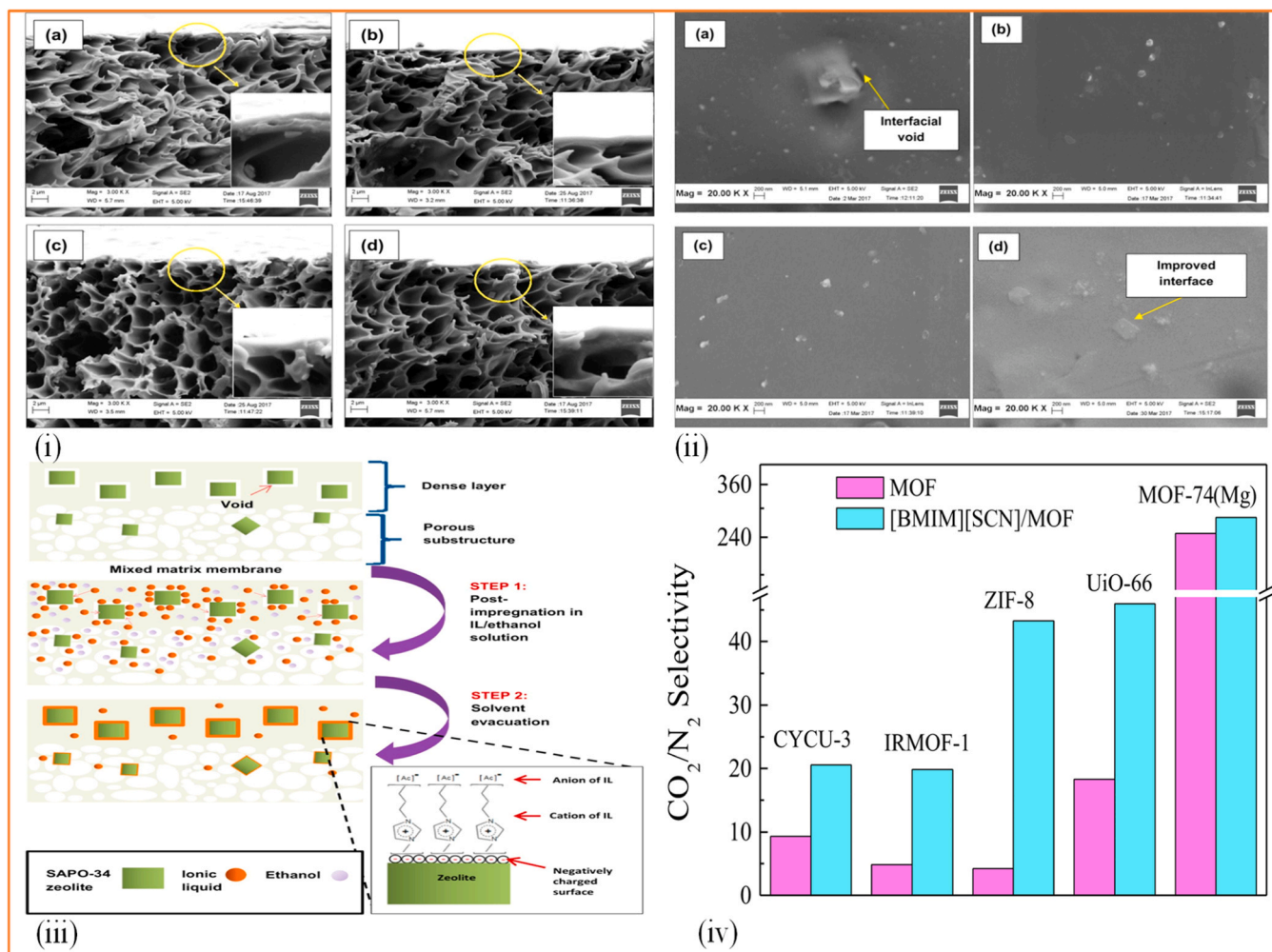


Fig. 11. (i, ii) SEM images showing cross-section and top surface of (a) PSf/SP5, (b) PSf/SP5-0.2 M, (c) PSf/SP5-0.4 M, and (d) PSf/SP5-0.6 M membranes. (iii). Post impregnation of MMM with [Bmim][Ac] IL. (iv). CO₂/N₂ selectivities of the MOFs and IL/MOF composites at 298 K. With permission from Ref [186]. Copyright 2017 Elsevier. With permission from Ref [219]. Copyright 2015 Elsevier.

4.6. Neutral Ionic liquids (NILs)

The NILs form equivalent anions with a weak electrostatic linkage to cations, resulting in low viscosity and melting temperatures which allow easy separation of the product but they possess high electrochemical and thermal stability [159]. As a result, these NILs are often used in various open windows [160]. Fig. 8(h) illustrates the commonly used neutral anions structure for NILs synthesis.

4.7. Protic ionic liquids (PrILs)

The exchangeable Bronsted acidic proton distinguishes PrILs from other acidic ILs. The PrILs may be used as a solvent or a catalyst in various processes such as dehydration, hydrolysis, and fuel cell chemistry [161]. Synthesis of PrILs is divided into two steps (i) the formation of zwitterions and (ii) its neutralization [162,163]. Fig. 8(j) shows the structure of various of PrILs [115,164].

4.8. Metallic Ionic liquids (MILs)

In many cases, the MILs are synthesized from pyridinium/imidazolium-based cations. As counter anions of ILs, chlorometalate or bromometalate salts (e.g., [CuCl₃]⁻, [Al₂Br₇]⁻, [AlCl₃]⁻, [FeCl₄]⁻, [SnCl₃]⁻, [NiCl₄]⁻) are used to improve their Bronsted and Lewis acidic characteristics. Because of their unique packing, metal halides are more

viscous than other ILs [165]. Fig. 8(k) shows the molecular structure of MILs.

4.9. Basic Ionic liquids (BILs)

The use of basic ILs has received a great deal in organic transformation like Markovnikov/Michael addition, aldol condensation, and many others to replace commonly used inorganic bases [166,167]. Furthermore, the basic ILs may provide an eco-friendly catalyst and benefit from inorganic bases. Overall, the basic ILs are flexible with the advantage of being non-corrosive/volatile in many organic solvents, they offer a larger potential weightage for substituting conventional inorganic bases [164]. Fig. 8(l) shows the structures of various anions and cations of basic ILs [129]. Different types of cations, anions, and structures of various ILs used for gas separation are shown in Fig. 8(m, n, and o), respectively.

5. Comparison of permeability and selectivity of different SILMs for CO₂ separation

5.1. Ionic liquid-based polymeric membranes for CO₂ separation

SILMs depict many benefits in CO₂ separation, but their weak mechanical properties and low stability under high pressure have limited their use on a large scale [168]. The ILs are kept stable in membrane

Table 4
CO₂ solubility in different ILs.

ILs	P (bar)	T (K)	Max Solubility (mol CO ₂ /mol IL)	Ref.
[hmim] [FEP]	0.297–18.1	283.15, 298.6, 323.2	0.517	[222]
[Bmim] [PF ₆]	0.97–92	313.15, 323.15, 333.15	0.729	[231]
[emim] [EtSO ₄]	-	-	0.579	
[Bmim] [NO ₃]	-	-	0.708	
[N-bupy] [BF ₄]	-	-	0.423	
[Bmim] [DCA]	1–120	298.15, 313.15, 333.15	0.550	[221]
[C ₂ mim] [Tf ₂ N]	10–43	301–344.4	0.761	[232]
[C ₆ mim] [Tf ₂ N]	-	-	0.845	
[THTDP] [NTf ₂]	1.06–375	293.2–363.2	0.879	[233]
[THTDP] [Cl]	-	-	0.800	[231]
[P ₍₁₄₎₆₆₆] [DCA]	-	-	0.033	
[N ₍₁₎₈₈₈] [Tf ₂ N]	-	-	0.034	
[hmpy] [Tf ₂ N]	1–10	283	0.200	[234]
[P ₆₆₆₁₄] [Gly]	< 1	303	0.574	[235]
[P ₆₆₆₁₄] [Ile]	-	303	0.5	
[P ₆₆₆₁₄] [Sar]	-	303	0.523	
[P ₆₆₆₁₄] [Ala]	-	303	0.66	
[Emim] [Gly]	1	313.15	0.49	[236]
[Emim] [Ala]	1	313.15	0.45	
[Bmim] [Met]	2	298.15	0.42	[237]
[Bmim] [Gly]	2	298.15	0.38	
[Bmim] [Ala]	2	298.15	0.39	
[P ₆₆₆₁₄] [Met]	1	295.15	0.9	[238]
[P ₆₆₆₁₄] [CoCl ₄]	-	298	0.40	[133]
[P ₆₆₆₁₄] [FeCl ₄]	-	298	0.50	
[P ₆₆₆₁₄] [MnCl ₄]	-	298	0.36	
[P ₆₆₆₁₄] [GdCl ₆]	-	298	0.25	
[P ₄₄₄₄] [Gly]	5	313.15	1.02	[239]
[P ₄₄₄₄] [Ala]	5	313.15	1.10	
[P ₄₄₄₄] [Val]	5	313.15	1.07	
[P ₆₆₆₁₄] [p-ANA]	1	303.15	0.78	[240]
[P ₆₆₆₁₄] [o-AA]	1	303.15	0.60	[241]

pores at high transmembrane pressure differences by various methods. It is also possible to fix the problem by synthesizing poly-IL membranes because it combines the high stability and CO₂ affinity of ILs with the mechanical and physical characteristics of polymeric materials [169]. A poly-IL membrane has been proposed by Tang et al. [170] as a viable alternative to IL monomers owing to their higher absorption capacity and rapid absorption/desorption rate.

The CO₂ separation performance of the individual poly-IL membranes is unsatisfactory. As a result, a mixture of PIL and free ILs is used to make SILMs [171]. Zhang et al. [172] inspected the CO₂ separation behavior using IL 1-butyl-3-methylimidazolium acetate [Bmim][Ac] with polymeric support of PVDF support at pressure 1 bar and 313 K, and reported that the CO₂ permeability of 2148 Barrer with CO₂/CH₄ selectivity of about 40 [173]. Also, Liu et al. [174] evaluated the selectivity (CO₂/N₂) and permeances (CO₂) of pure and modified membranes using RTIL [Tespimim][BF₄] and evaluated the selectivity (CO₂/N₂ = 17) using a pristine membrane. They reported that selectivity of CO₂/N₂ = 76 can be achieved under the same operating conditions for the modified membrane, compared to control SILM. A trade-off process was one significant feature identified in numerous studies and whenever the permeability is high, the selectivity decreases [175]. Fig. 9(i) shows the structure of dense polymer membrane and dense polymer SILM. The

surface and cross-sectional morphologies of different SILMs are shown in Fig. 9 (ii).

5.2. IL-based composite and mixed matrix membranes (MMMs) for CO₂ separation

The ILs use additives and a polymer matrix to make composite membranes with superior mechanical properties. It is divided into two categories: (i) ILs and polymers are used to make SILM, and (ii) membranes can be tuned via the integration of ILs with inorganic materials to fabricate mixed matrix membranes (MMMs) [178]. Halder et al. [72] stated that membranes integrated with IL [C₂mim][Tf₂N] and copolymer have higher CO₂ permeability with the CO₂/N₂ selectivity of about 6650 Barrer and 20, respectively [72]. In addition, Lu et al. [179] synthesized polysulfone (PS) membranes for CO₂ capture based on IL [Bmim][TFSI] and suggested that excellent selectivity was achieved due to the good solubility of CO₂ into ILs. MMMs have received more attention because of the benefits of both inorganic and polymeric membranes [180–182]. Through the interaction of the filler and matrix, the MMMs are composed of filler and a polymer phase [183].

It is possible to increase the selectivity of membranes by creating a membrane material by combining a minimum amount of ILs with other polymers [179]. Several CO₂ sorbents were mixed with Pebax membrane and found that CO₂ permeability increased by adding sorbents with Pebax [184]. Furthermore, silica, zeolites, molecular sieves, graphene oxide, and MOFs are examples of inorganic fillers used to synthesize MMMs [185]. With increasing the interaction between zeolite and PS, the ILs addition to composites and MMMs can improve selectivity and permeability [186]. Fig. 10 (i) shows the schematic of the preparation procedure of the Pebax®/zeolite Y composite membrane. Fig. 10 (ii) shows the schematic of Pebax®/zeolite Y composite membrane structure. Fig. 10 (iii) shows the 3D structures of different MOFs. Fig. 10 (iv) shows the cross-section SEM images of (a) pristine PEBA, (b) MOF-801/PEBA (2.5), (c) MOF-801/PEBA (5), (d) MOF-801/PEBA (7.5) membranes, (e) MOF-801/PEBA (10) membranes, and (f) MOF-801/PEBA (12.5) mixed-matrix membrane respectively. Fig. 10 (v) shows the comparison of CO₂ permeability and CO₂/N₂ selectivity of PEBA mixed-matrix membranes comprising three types of MOF filler with the same loading (7.5 wt%); 7.5 wt% ZIF-300/PEBA; 7.5 wt% UiO-66/PEBA. Fig. 10 (vi) shows the (a) Sorption coefficient (S) and diffusion coefficient (D) and (b) sorption selectivity (α_S) and diffusion selectivity (α_D) of MOF-801/PEBA mixed-matrix dense films with different MOF-801 loading for CO₂ and N₂. The CO₂ permeability and selectivity of different SILMs are summarized in Table 3.

5.3. Types of fillers in mixed matrix supported ionic liquid membranes (MM-SILMs) and their performance on CO₂ separation

In recent decades, interest has increased in mixed matrix (MM) SILMs, where blending organic and inorganic materials coupled with ILs is an exciting way of combining and increasing the properties of both phases [94]. The separation performance of SILMs for targeted gas molecules can be improved by adding inorganic fillers such as (i.e., MOFs, nanoparticles, graphite etc.) [193].

MMMs coupled with room-temperature ionic liquids (RTILs) and polymerizable ILs (PILs) will enhance the performance of SAPO-34-based membranes for CO₂/N₂ separation. However, the selectivity was still low [212]. By incorporating a small amount of 1-ethyl-3-methylimidazolium acetate [Emim][Ac] IL into the chitosan (CS) matrix, a hybrid solid IL-CS membrane has been synthesized to increase the mechanical and thermal stability of MMM. A good adhesive capability with improved flexibility and CO₂ permeability was achieved [213].

MOFs have been considered as suitable fillers in MMMs for gas separation because of their partly organic nature and high compatibility with polymer chains [6,214]. Chen et al. [215] synthesized IL/MOF composite by incorporating MOF-5 (Zn₄O(BDC)₃) as a filler with [Bmim][PF₆] IL

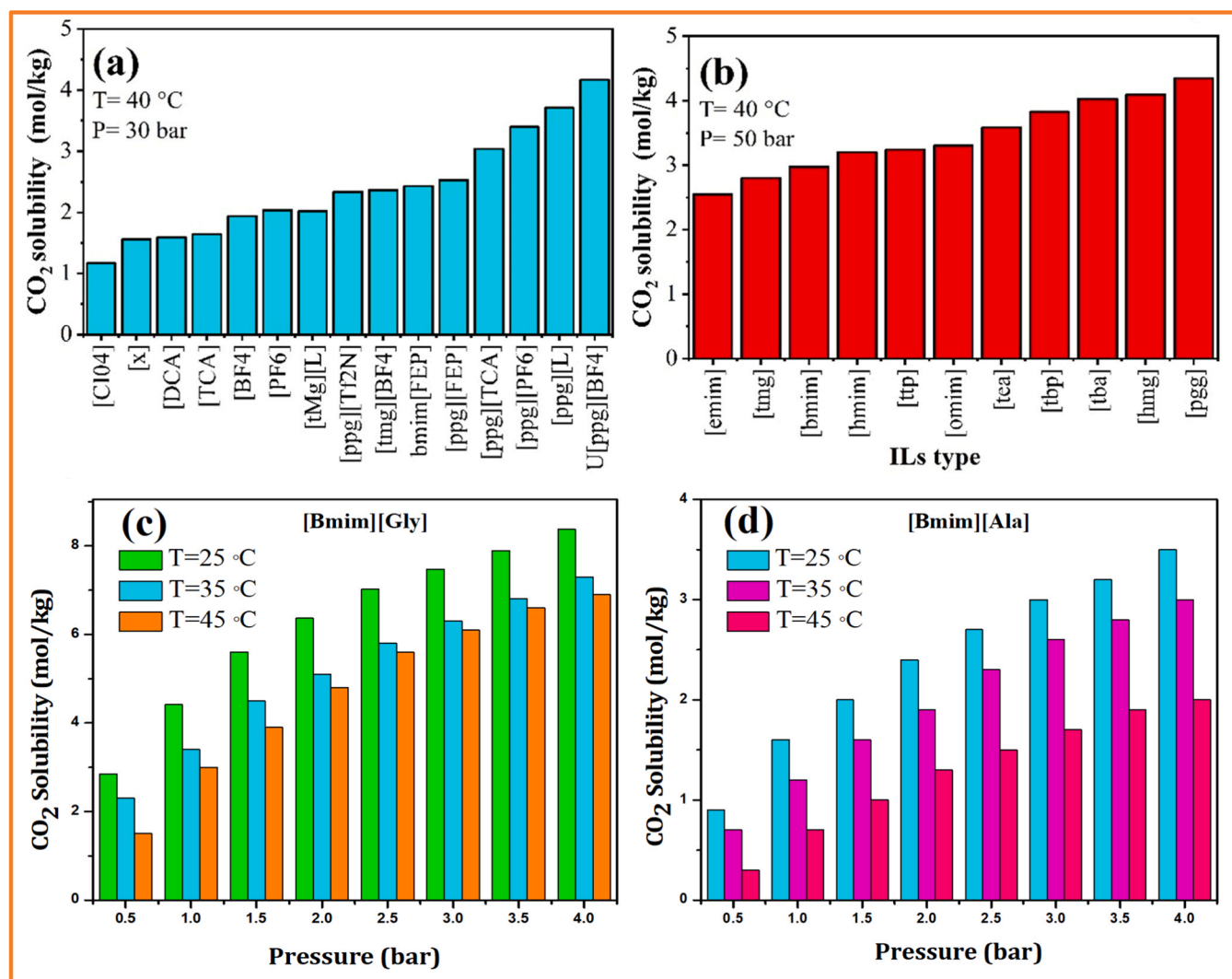


Fig. 12. CO₂ solubility of different ILs having (a) Bmim cation, and (b) having TF₂N anion. Copyright 2009 John Wiley and Sons. (c) CO₂ solubility in [Bmim][Gly] IL (d) CO₂ solubility in [Bmim][Ala] IL at different pressure and temperature.

(a) Reproduced with copyright permission from Ref. [242]. (b) Adapted from Ref. [243].

and found the highest CO₂/N₂ selectivity of 70 at 100 kPa. Ahmad et al. [216] used unmodified MMM and modified with 1-butyl-3-methylimidazolium acetate [Bmim][Ac] IL and polysulfone (PSF) as membrane support and SAPO-34 zeolite as filler to synthesize MM-SILM. Compared to unmodified MMM, the interfacial sealing using IL further improved CO₂/N₂ selectivity of IL-modified MMM. The maximum selectivity of 39.60 was achieved using PSf membrane incorporating 5 wt% of SAPO zeolite loading and 0.4 M of IL. Ali et al. [217] fabricated PTFE-based SILM incorporated with bimetallic MOF of copper and magnesium ions (Cu_xMg_x) and Trihexyltetradecylphosphonium chloride [P₆₆₆₁₄][Cl] IL. Single gas permeation tests of membranes loaded with 0.2/0.8 wt/wt% MOF/IL solution showed the highest CO₂ permeability of 2937 Barrer and CO₂/N₂ selectivity of 33.26. Gupta et al. [218] used 1-butyl-3-methylimidazolium thiocyanate [Bmim][SCN] IL and hydrophobic ZIF-71 and hydrophilic Na-rho-ZMOF based membranes to examine the CO₂/N₂ selectivity at various feed pressures. The CO₂/N₂ selectivity ranges within 13–15 and 110–315 in [Bmim][SCN]/ZIF-71 and [Bmim][SCN]/ZMOF, respectively. Among different MM-SILMs, [Bmim][SCN]/ZMOF achieved the highest CO₂/N₂ selectivity. Fig. 11 (i, ii) shows the SEM cross sectional and surface micrographs of PSF/SP5 membranes and (iii and iv) shows the post impregnation of MMM with IL and CO₂/N₂ selectivity of the MOFs and IL/MOF composite membranes, respectively.

6. CO₂ solubility and diffusivity in ILs

6.1. CO₂ solubility in ILs

Gas solubility in liquid solvent (cm³ (STP) cm⁻³ cmHg⁻¹) is a thermodynamic property described by Henry's law. It demonstrates the concentration/dissolution of gaseous specie in IL-impregnated membrane under equilibrium. It was reported that, compared to the cations, the anions play a key role in the solubility of CO₂ in ILs [220]. Sudhir et al. [221] reported the CO₂ solubility for various imidazolium-based ILs and revealed that ILs attached with fluoroalkyl groups in anion showed the highest solubility for CO₂. Zhang et al. [222] investigated Henry's law constants of CO₂ gas using several cations and anions combinations and demonstrated that anion [FEP] has the highest CO₂ solubility. Similarly, nine different gases were tested to investigate the solubility with imidazolium-based IL [Bmim][PF₆] and found that [Bmim][PF₆] has the highest CO₂ solubility. Additionally, it was shown that under extreme pressure, [Bmim][PF₆] is not a suitable solvent for industrial processes involving H₂, O₂, and CO as opposed to conventional organic solvents. The increasing order of CO₂ solubilities with the cation [BMIM] with the different anions are [NO₃] < [SCN] < [MeSO₄] < [BF₄] < [DCA] < [PF₆] < [TF₂N] < [Methide] < [C₇F₁₅CO₂]. The anions containing fluorine are reported to have high CO₂ solubilities; for

Table 5
CO₂ diffusivity in various ILs.

ILs	P (bar)	T (K)	Max CO ₂ diffusivity (10 ⁻⁸ cm ² s ⁻¹)	Ref.
[EMIM] [Dca]	0.2	298	3.2	[252]
[BENZ] [Ac]	10	298	3.45	[253]
[APTMS] [Ac]	10	298	4.23	[254]
[BSmim] [tos]	5	293	3.04	[22]
[EMIM] [Tf ₂ N]	5	303	8.7	[255]
[BMIM] [BF ₄]	1.4	303	2.2	[256]
[BMIM] [BF ₄]	2.06	303	2.3	
[OMIM/BMIM] [PF ₆]	0.7	303	0.6	[257]
[DMIM/BMIM] [BF ₄]	0.7	303	0.6	
[BMIM] [SCN]	1	298	6.25	[258]
[NH ₂ ebim] [PF ₆]	1	303	1.02	[259]
[BSMPY] [tos]	1	298	3.79	[260]
[Im-TB(o)-Xy] [Tf ₂ N]	3	293	0.78	[261]
[Im-TB(o)-C ₁₀] [Tf ₂ N]	3	293	0.95	
[Im-TB(p)-Xy] [Tf ₂ N]	3	293	0.79	
[Im-TB(p)-C ₁₀] [Tf ₂ N]	3	293	0.80	
[Voim] [PF ₆]	1.2	303	4.96	[168]
[APTMS] [Ac]	-	-	3.6	[246]
[BMIM] [SCN]	1	298	0.55	[218]
[BMIM] [SCN]	2	298	0.83	
[BMIM] [SCN]	6	298	0.93	
[BMIM] [PF ₆]	-	293	5.0	[262]
[EMIM] [EtSO ₄]	0.2	288	4.9	[263]

example, in the decreasing order, [BF₄] < [TfO] < [TfA] < [PF₆] < [Tf₂N] < [methide] < [C₇F₁₅CO₂] < [eFAP] < [bFAP]. However, fluorine-containing anions is non-biodegradable and more toxic than non-halogen anions [223]. On the other hand, cations do not have as much impact on CO₂ solubility as anions. However, if cations are

functionalized with specific moieties such as fluorine or long alky-chain, the CO₂ solubility may marginally enhance. For example, the increasing order of CO₂ solubility is found as follows: [OMIM] > [HMIM] > [PMIM] > [BMIM] > [EMIM] [224].

The solubility of CO₂ in ILs is a critical consideration for selecting appropriate solvents and designing an effective absorption system for CO₂ capture [225]. Henry's law constant is an important thermodynamic parameter to determine the solubility of a gas in a solvent at infinite dilution. Henry's law states that the amount of a gas dissolved in a liquid is proportional to its fugacity in the gas phase at equilibrium with the liquid. The solubility of a gas in a solvent is determined from the equality of fugacity of the gas in both phases [226]. The fugacity (*f*) of a pure gas can be calculated by using (Eq. 6),

$$y_i P \phi_i = P_i = S_i \gamma_i(p, T, x) f_i(T, p) \quad (6)$$

where *y_i* and *x_i* are the mole fraction of the gas in the vapor and the liquid phases, *p* is the pressure of the system, *φ_i* is the fugacity coefficient in the vapor phase, *γ_i* is the activity coefficient in the liquid phase, and *f_i* is the fugacity of the gas molecule (e.g., CO₂, N₂) in the liquid state at pressure *p* and temperature *T*.

When the vapor phase is regarded ideal (i.e., *φ_i* = 1), then the solubility (*S_i*) of gas in the liquid phase can be calculated at given *P*, *T*, and partial pressure of the gas *p_i* (= *y_ip*) using (Eq. 7),

$$P_i = x_i \gamma_i(p, T, x) f_i(T, p) \quad (7)$$

For cases where the solubility in a liquid is low, then Henry's law is often used as described in (Eq. 8),

$$P_i = x_i H_{i/s}(P, T) \quad (8)$$

where *H_{i/s}* is Henry's law constant of gas (*i*) in the solution and is related to the infinite dilution activity coefficient and the pure gas fugacity. Infinite dilution activity coefficient can be calculated using (Eq. 9),

$$H_{i/s}(p, T) = \lim_{x_i \rightarrow 0} \left(\frac{f_i(p, T, x)}{x_i} \right) = y_i^\infty f_i(p, T) \quad (9)$$

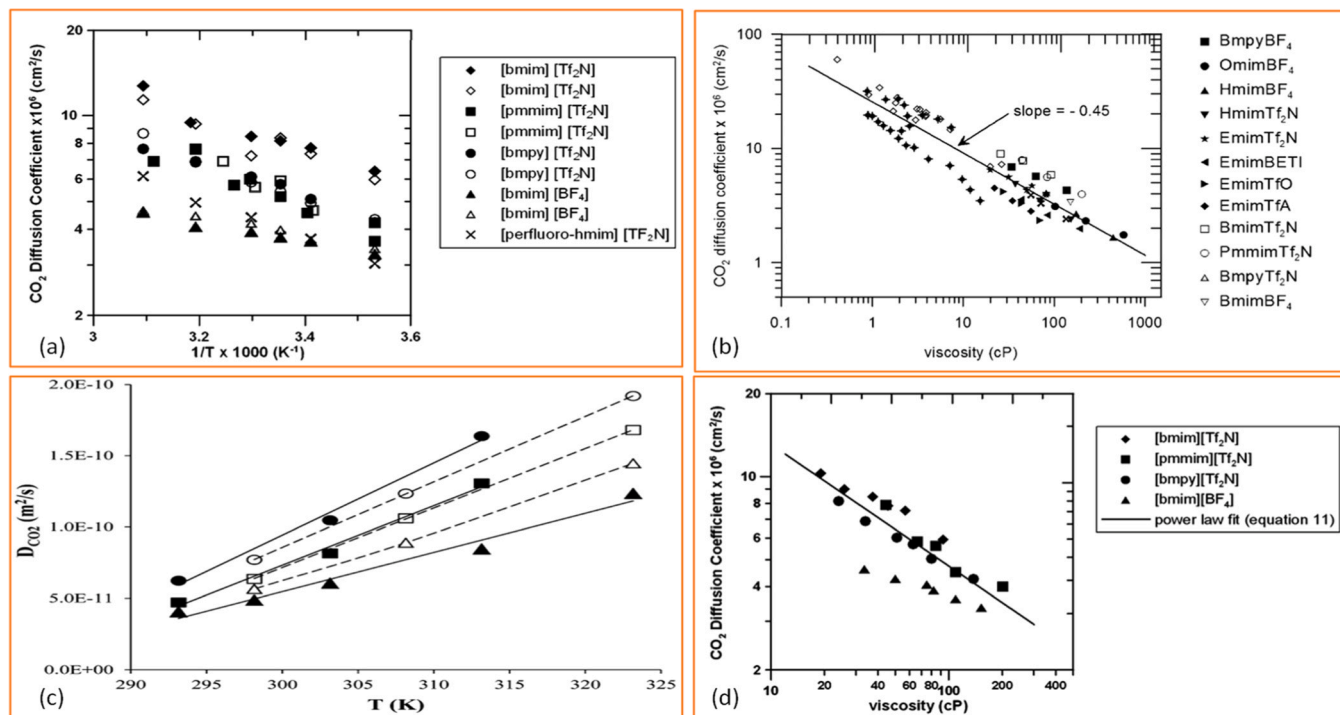


Fig. 13. CO₂ diffusivity of different ILs at (a) various operating temperatures (b) different viscosities (c) Comparison of diffusion coefficients of CO₂ in ILs obtained from experiments (open symbols) and estimated by Wilke–Chang correlation (filled symbols): ● [HMIM][Tf₂N]; ■ [OMIM][Tf₂N]; and ▲ [DCMIM][Tf₂N] (d) at different viscosities. With permission from Ref. [245,264,265]. Copyright 2007, 2010 and 2014 American Chemical Society.

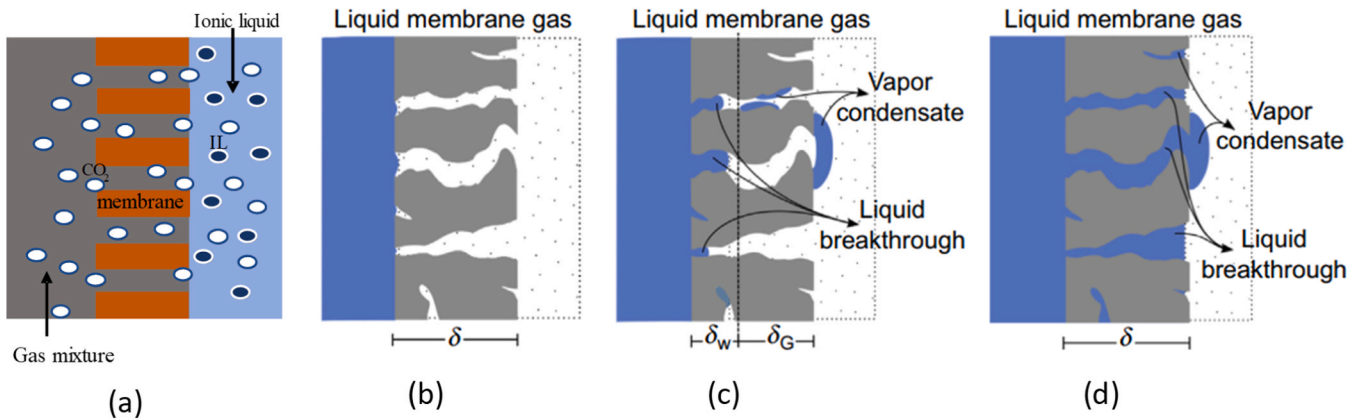


Fig. 14. (a) SILM schematics, (b) non-wetted SILM structure, (c) partially wetted SILM structure, (d) fully wetted SILM structure, Reproduced with permission from Ref. [9].

Table 6

LEP values per different ILs and contactors in the two modes before and after (240 hrs) the absorption process, Reproduced with permission from Ref. [9].

Membrane	LEP (± 14 kPa)													
	Water		[EMIM][EtSO ₄]		[EMIM][Ac]		[EMIM][TFA]		[EMIM][Tf ₂ N]		[BMIM][PF ₆]		[OMIM][BF ₄]	
	Pristine	Used	Pristine	Used	Pristine	Used	Pristine	Used	Pristine	Used	Pristine	Used	Pristine	Used
PES	323.0	302.0	203.0	184.0	189.0	168.0	176.0	163.0	172.0	160.0	163.0	148.0	156.0	148.0
PP	276.0	259.0	224.0	202.0	218.0	205.0	209.0	186.0	194.0	180.0	186.0	168.0	168.0	136.0
PVDF	376.0	361.0	257.0	226.0	248.0	223.0	234.0	217.0	227.0	216.0	208.0	186.0	184.0	154.0
PTFE	478.0	464.0	287.0	263.0	268.0	247.0	246.0	232.0	238.0	228.0	216.0	204.0	200.0	176.0

where y_i^∞ is the infinite dilution activity coefficient of the gas in the solution. Henry's law constant can be used as a quick estimate for the solubility of a gas in a solution at a partial pressure of 1 bar, e.g., $x_i = 1$ (bar)/ $H_{i/s}$.

Similarly, the selectivity of gases (particularly CO₂, N₂) over a membrane e.g., the SILM [227], can also be estimated from the ratios of Henry's law constant as the selectivity is the ratio of permeability, which can be calculated by the product of solubility (x_i) and diffusivity (D_i) of two gases [228] as stated in Eq. 10.

$$S_{1/2} = \frac{p_1}{p_2} = \frac{X_1 D_1}{X_2 D_2} = \frac{H_{2/s} D_1}{H_{1/s} D_2} \approx \frac{H_2}{H_1} \quad (10)$$

The last equality sign indicates that the diffusion has a relatively very low effect on the selectivity of gases and is nearly unity in certain ILs compared to the solubility of gases which is supported by some experiments [229].

In addition, Henry's law constant is directly related to the Gibbs energy of solvation (ΔG_{sol}^∞), which is defined as the free energy of

transfer of a gas molecule from a pure gas state at a certain pressure ($P^\circ = 1$ bar) to the solution [230]. Gibbs energy of solvation is described in (Eq. 11),

$$\Delta G_{i/s}^\infty = RT \ln \frac{H_{i/s}}{P^\circ} \quad (11)$$

Hence, the enthalpic and entropic contributions to the solvation process can be estimated from the temperature dependence of Henry's law constant as described in (Eqs. 12 and 13),

$$\Delta H_{sol}^\infty = -T^2 \frac{\partial}{\partial T} \frac{\Delta G_{sol}^\infty}{T} = -RT^2 \frac{\partial}{\partial T} \left[\ln \frac{H_{12}}{P^\circ} \right] \quad (12)$$

$$\Delta S_{sol}^\infty = \frac{\Delta H_{sol}^\infty - \Delta G_{sol}^\infty}{T} = -RT \frac{\partial}{\partial T} \left[\ln \frac{H_{12}}{P^\circ} \right] - R \ln \left(\frac{H_{12}}{P^\circ} \right) \quad (13)$$

These parameters provide useful information regarding the interaction of solute and the molecular structure of the solution, including the enthalpy and entropy. Since enthalpy and entropy indicate the interaction of gas molecules with IL and the structure of solvent molecules surrounding the solute.

The CO₂ solubility of various ILs is summarized in Table 4. In addition, Fig. 12 (a), (b), (c), and (d) shows the CO₂ solubility of different ILs at various pressure and temperature.

6.2. CO₂ diffusivity in ILs

Gas diffusivity is important for the design of gas separation processes involving ILs. It demonstrates the transport of gaseous specie through the IL-immobilized membrane pores and is expressed as cm² s⁻¹. Because of the large and expanding number of ILs used in the CO₂ separation processes, there is a need for effective experimental measurement and the development of theoretical expressions for estimating gas diffusivities in ILs. There are four general theoretical approaches used for developing diffusivity correlations in solvents [244]: (i) hydrodynamic theories, (ii) kinetic theory of liquids, (iii) Eyring's absolute reaction rate theory, and (iv) semiempirical equations based on these theories. Based on these approaches, several empirical correlations for predicting

Table 7
Water Contact Angle data of SILMs [177,269–276].

Ionic Liquid	Membrane	Contact angle, ($\theta \pm \sigma$)/deg
[EMIM][PF ₆]	Psf/TiO ₂	78.2
[DMIM][Cl]	Psf/TiO ₂	75.7
[C ₄ C ₁ im][Ac]	PTFE	98.03 ± 0.02
[C ₄ C ₁ im][DMP]	PTFE	90.48 ± 0.16
[C ₄ C ₁ im][TFA]	PTFE	83.43 ± 0.36
[C ₄ C ₁ im][N(CN) ₂]	PTFE	82.38 ± 0.30
[C ₄ C ₁ im][EtSO ₄]	PTFE	80.32 ± 0.32
[C ₄ C ₁ im][MeSO ₄]	PTFE	79.54 ± 0.26
[C ₄ C ₁ im][CF ₃ SO ₃]	PTFE	76.43 ± 0.17
[C ₄ C ₁ im][SCN]	PTFE	74.77 ± 0.19
[C ₄ C ₁ im][C(CN) ₃]	PTFE	72.74 ± 0.06
[C ₄ C ₁ im][NTf ₂]	PTFE	66.76 ± 0.06
[C ₄ C ₁ im][BF ₄]	PTFE	65.07 ± 0.07
[C ₄ C ₁ im][PF ₆]	PTFE	60.11 ± 0.07
[C ₂ C ₁ im][NTf ₂]	PTFE	66.93 ± 0.01
[C ₃ C ₁ im][NTf ₂]	PTFE	66.82 ± 0.06
[C ₅ C ₁ im][NTf ₂]	PTFE	66.53 ± 0.03
[C ₆ C ₁ im][NTf ₂]	PTFE	66.10 ± 0.38
[C ₇ C ₁ im][NTf ₂]	PTFE	65.95 ± 0.15
[C ₈ C ₁ im][NTf ₂]	PTFE	65.60 ± 0.17
[C ₉ C ₁ im][NTf ₂]	PTFE	64.14 ± 0.33
[C ₃ C ₁ pip][NTf ₂]	PTFE	71.97 ± 0.78
[C ₄ C ₁ pip][NTf ₂]	PTFE	67.21 ± 0.02
[C ₄ -4-C ₁ py][NTf ₂]	PTFE	68.88 ± 0.80
[BMIM][BF ₄]	PTFE	92
[C ₂ O ₂ HMIM][BF ₄]	PTFE	100
[EMIM][EtSO ₄]	PTFE	90
[OMIM][BF ₄]	PTFE	80
[EMPy][EtSO ₄]	PTFE	92
[DMIM][Cl]	PTFE	105.951 ± 1.295
[Emim][Ac]	PTFE	131 ± 3
[C ₂ mim][OAc]	PTFE	128 ± 3
[C ₂ mim][O ₂ CH]	PTFE	125 ± 0.3
[C ₄ mim][Cl]	PTFE	121
[DMEDAH] formate	PTFE	100 ± 3
HFP/[Cl]	PVDF	92
HFP/[TfO]	PVDF	59
HFP/[NTf ₂]	PVDF	30
[Emim][Ac]	PVDF	118 ± 3
[C ₂ mim][OAc]	PVDF	47 ± 2
[C ₂ mim][O ₂ CH]	PVDF	127 ± 2
[EMIM][Tf ₂ N]	PVDF	66
[EMIM][TfO]	PVDF	67
[BMIM][Tf ₂ N]	PVDF	71
[BMIM][TfO]	PVDF	37
[C ₄ mim][Cl]	PVDF	135
[EMIM][Tf ₂ N]	PP	61
[EMIM][TfO]	PP	46
[BMIM][Tf ₂ N]	PP	68
[BMIM][TfO]	PP	47
C ₁₁ H ₂₁ NO ₅ S	PP	138.0 ± 1.0
[Emim][BF ₄]	PP	96 ± 2
[Emim][DCA]	PP	100 ± 2
[Bmim][BF ₄]	PP	95 ± 2
[P ₆₆₆₁₄][Phos]	PP	64 ± 2
[P ₆₆₆₁₄][Br]	PP	67 ± 2
[DMEDAH] formate	PP	103 ± 15
Poly[P ₂₂₂ VB][BF ₄]+ acrylates	-	100
Poly[P ₄₄₄ VB][BF ₄]+ acrylates	-	98
Poly[P ₈₈₈ VB][BF ₄]+ acrylates	-	105
Poly[P ₈₈₈ VB][Tf ₂ N]+ acrylates	-	115
Poly[P ₈₈₈ VB][PF ₆]+ acrylates	-	110

diffusivities in infinitely dilute liquid solutions have been developed [245]. The diffusion coefficient is determined using the time-lag intercept as described in (Eq. 14) [246]:

$$D = \frac{l^2}{6\theta} \quad (14)$$

Where (D) is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), (l) is the thickness of membrane (μm) and (θ) is the time lag intercept.

Similarly, the CO₂ diffusion coefficients can be estimated by applying an effective mass diffusion model reported by Shifflet and Yokozei [247] for CO₂ –IL systems. The proposed model has been used previously for gas absorption in lubricant oils [248] and later has also been applied for other solute (NH₃, toluene)–IL systems [249,250]. This model is developed based on the following assumptions: (i) gaseous species dissolve through a one-dimensional (vertical) diffusion method, in which there is no convective flow in the liquid; (ii) a thin boundary layer between the gas and liquid phases exists, where the thermodynamic equilibrium is established with the saturation concentration and where the concentration is constant all the time at a given pressure and temperature; (iii) pressure and temperature are kept constant; (iv) the gas-dissolved liquid is a highly dilute solution, and so the relevant thermophysical properties of the solution do not change. The process may be described by one-dimensional mass diffusion due to the local concentration difference. The CO₂ mass balance in the diffusivity model is expressed in Eq. (15) below,

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial z^2} \quad (15)$$

with an initial condition $C = C_0$ when $t = 0$ and $z < 0 < L$ and boundary conditions (i) $C = C_s$ when $t > 0$ and $z = 0$ and (ii) $\partial C/\partial z = 0$ at $z = L$. C is the concentration of gas dissolving in the IL as a function of time, t , and vertical location, z . L is the depth of IL in the container [obtained using the sample container diameter (1.0 or 1.5 cm), the IL mass sample, and the experimentally determined density by the buoyancy measurements], and C_0 is the CO₂ initial concentration at each temperature and pressure. However, since the obtained CO₂ solutions in IL are not highly dilute, the diffusion coefficients must be taken as “effective” diffusion constants [247]. A detailed description of the procedure followed to apply the diffusion model to find the diffusivity values in ILs is given elsewhere [251]. The CO₂ diffusivity of various ILs is summarized in Table 5. In addition, Fig. 13 (a), (b), (c) and (d) shows the CO₂ diffusion coefficient in different ILs.

7. Stability, wetting, regeneration, and biodegradability of supported ionic liquid membranes

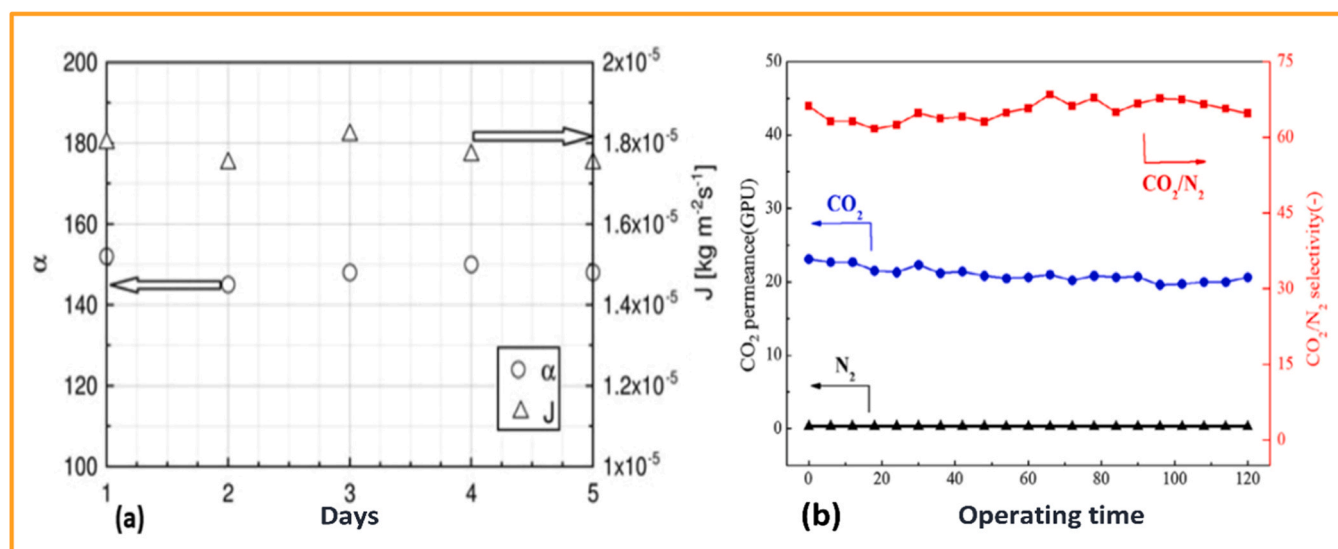
Despite SILMs having better CO₂ separation performance, their stability is a significant challenge in their evolution [266,267]. The interfacial tension between the membrane and aqueous phase determines a SILM’s stability. The leaching of ILs from large pores of membrane support and membrane compression were identified by Zhao et al. [268] as the two mechanisms responsible for solvent loss in SILMs. However, for the smaller membrane pore sizes, less wetting is observed. But a much smaller pore size causes a decrease in mass transfer coefficient. Membranes with 100–200 nm pore diameters were acceptable and exhibited non wetting phenomena [193]. The schematics of gas-liquid diffusion process and wetting phenomena in SILM are better described in Fig. 14. In SILM, a certain pressure is required to stabilize the IL within the pores of porous membrane. Instead, pressure is also needed to allow the gaseous species to pass through. However, when the operating pressure reaches a point where the IL begins to penetrate across the membrane pores, this pressure is termed as liquid entry pressure (LEP). Thus, selecting the IL with the highest surface tension is envisaged. Swati et al. [9] immobilized various commercial ILs into the pores of hydrophobic polymeric supports for post-combustion CO₂ capture and closely observed the changes in LEP after the extended period of experimentation (240 h). These results are presented in Table 6. It was observed that as the LEP values were higher, membrane wetting was lesser, and a more stable system was guaranteed. Water contact angle (WCA) is another parameter indicating membrane wetting. WCA values for various SILMs are shown in Table 7. However, these WCAs lose their values as long as the absorption experiment continues. This loss might be due to irregular pore size distribution, pore

Table 8

Contact angle values per different ILs and contactors in the two modes before and after (240 h) the absorption process. [9].

Membrane	Contact Angle ($\theta \pm 3$)													
	Water		[EMIM] [EtSO ₄]		[EMIM] [Ac]		[EMIM] [TFA]		[EMIM] [Tf ₂ N]		[BMIM] [PF ₆]		[OMIM] [BF ₄]	
	Pristine	Used	Pristine	Used	Pristine	Used	Pristine	Used	Pristine	Used	Pristine	Used	Pristine	Used
PES	123	103	76	71	79	72	86	78	92	83	95	84	97	87
PP	110	98	84	76	83	75	92	85	94	87	96	87	101	91
PVDF	128	117	89	81	93	84	96	89	98	91	98	90	99	93
PTFE	142	125	95	85	98	88	100	94	102	95	105	94	102	95

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**Fig. 15.** (a) Long-term stability of the prepared PDMS SILM at 1.5 bar and 20°C. Copyright 2021 Taylor and Francis, and (b) Long-term operation test on MOF-801/PEBA MMM. Copyright 2019 Elsevier.

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geometry, high surface tension, surface degradation, severe operating conditions, and low roughness of polymer support. Swati et al. [9] tabulated the experimentally measured values of WCAs for fresh and used SILM, as shown in Table 8.

So far as the stability of SILMs on hydrophobic and hydrophilic supports is concerned, the hydrophobic support was more stable than hydrophilic support because hydrophobic ILs and hydrophilic supports interact poorly. Nanofiltration (NF) membranes have been demonstrated to minimize IL loss even at high transmembrane pressures up to 10 bar, indicating the importance of membrane support and pore size selection when limiting IL loss [266].

Several factors affect the stability of SILMs, such as the type and size of membranes, porosity, and pore size. To increase the stability of SILMs, the appropriate selection of ILs is crucial. In addition to surface tension and hydrophobicity, the viscosity of ILs plays a critical role in the stability of SILM [9]. The high viscosity of ILs and strong Van der Waals forces interaction makes the ILs challenging to remove from membrane pores compared with ILs with low viscosity with the disadvantage of being pushed from the pores [277]. Fig. 15 (a) and (b) show the long-term stability of PDMS SILM and MOF-801@PEBA MMM.

The cations, anions, and alkyl-chain length of ILs play their part in the regeneration and biodegradability of SIMs. In general, an increase in alkyl-chain length causes an increase in biodegradability. Imidazolium-based ILs are not readily biodegradable. However, the pyridinium-based ILs with long alkyl-chain length are more readily biodegradable. Biodegradation further increases if the ILs are functionalized with a moiety such as ester. But ether, acetal or carbamate functionalities do not have gross impact on the biodegradation of ILs. On the other hand, anions play a minor role in the degradation of ILs. Nevertheless,

halogens, and extensive chain branching cause poor degradation of ILs and should be avoided in SILM [224].

8. Techno-economic assessment and environmental viability of SILMs for post-combustion CO₂ capture

Economic and environmental aspects are the major barriers to commercializing post-combustion CO₂ capture technologies. Gas-liquid membrane contactors are highly effective hybrid separation systems that use porous membranes as an interface between a flue gas stream and an absorption liquid (such as amine, ILs etc.) [21]. In general, SILMs that combine membranes and ILs for the selective separation of gases have received growing attention in recent years [279]. However, SILMs have not been commercialized because of the following reasons.

The current prices of ILs are ~1000 \$/kg (lab scale), but economy of scale should apply, and the cost for a large-scale process will certainly drop to < 40 \$/kg; however, the cost is still 100–1000 times higher than the conventional solvents [224]. Due to negligible volatility, ILs are not assumed to pollute the air, but most of the ILs are water soluble, which may contaminate the hydrosphere through industrial effluents or accidental leakages [27]. Although significant work is being done regarding the physical, thermodynamic, and kinetic aspects, very limited data is available on the toxicity of ILs. The longer alkyl chains ILs showed higher toxicity. However, cation type did not contribute to toxicity [280, 281].

The significant interest in membrane technology for CO₂ separation from flue gas contrasts with its market position, with the fact that membrane separation only accounts for 10% of the worldwide CO₂ separation technology market, whereas amine absorption accounts for

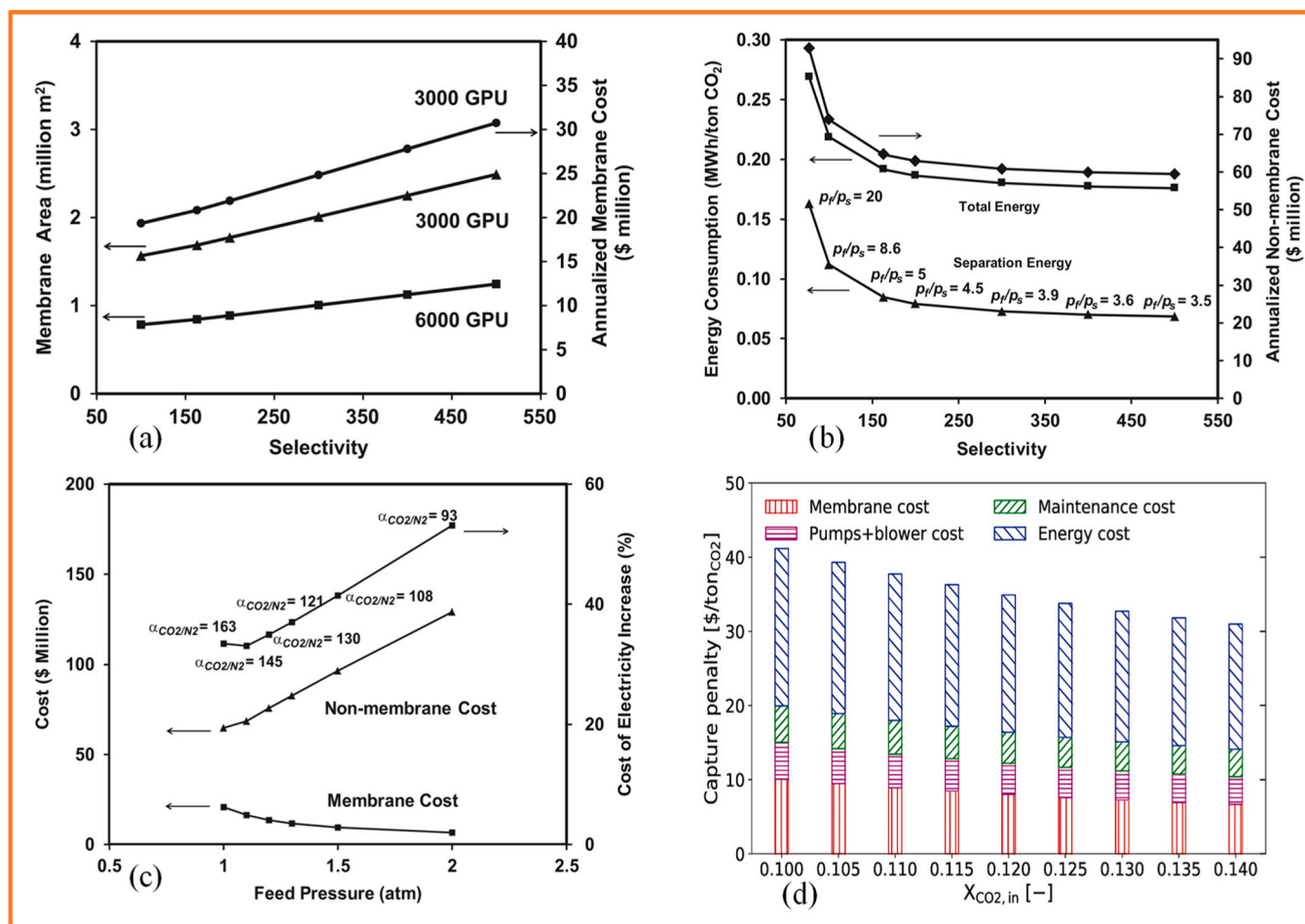


Fig. 16. (a) Effects of CO₂/N₂ selectivity on membrane area and annualized membrane cost for XCO₂ = 22.5% and P = 1 bar. (b) Effects of CO₂/N₂ selectivity on energy consumption and annualized non-membrane cost for XCO₂ = 22.5%. (c) Effects of feed pressure on overall costs for XCO₂ = 22.5% and P = 1 bar. (d) Capture penalty (\$/tonCO₂) at various inlet CO₂ concentrations, at P = 0.05 and 0.10 bar for both 1st and 2nd stages. With permission from Ref. [283,285]. Copyright 2012 and 2021 Elsevier.

90% of the share [200]. The versatility of membranes for bulk separation is widely accepted but typically is not an economical choice for low feed concentration or high-purity product requirements. Therefore, post-combustion CO₂ capture is very challenging for membrane technology because it contains flue gases with a dilute 3–20% CO₂ at low pressure (up to 1 bar), temperature (35–120 °C), and moisture contents of (5–10%) [282,283].

A cost analysis of various strategies for increasing membrane driving force under post-combustion CO₂ capture conditions has been conducted, and several researchers have reported the possible use of a sweep gas on the permeate side. Specifically, Merkel et al. [284] showed the potential of air sweep method to meet the cost targets. A two-stage membrane process was used with a feed pressure of 2 bar and membrane with a CO₂ permeance of 1000 GPU, a CO₂/N₂ permselectivity of 50 and a proposed membrane cost of \$50 per m² to achieve CO₂ purity of 83% and a capture cost of \$23 per ton of CO₂. Similarly, Ramasubramanian et al. [285] used a two-stage membrane process for CO₂ capture with air sweeping. They observed that a \$24 per ton CO₂ captured along with 33% increase in the cost of electricity were required to achieve CO₂ recovery and purity of 90% and 95% respectively. To obtain these results a CO₂/N₂ selectivity of 140, CO₂ permeance of 3000 GPU and membrane cost of \$27 per m² are required at a feed pressure of about 1 bar. These results highlight again the importance of highly CO₂ permeable membranes operating at low pressure (1 bar). Fig. 16 (a), (b), and (c) shows the membrane and electricity cost of a two-stage membrane process for CO₂ capture under fixed conditions. Fig. 16 (d) shows

the membranes and pumps investment costs, energy, and maintenance cost of two stage membrane-based technology for CO₂ capture.

9. Technology readiness level (TRL) of different CO₂ capture technologies

As the separation process is part of the capture technology, technology readiness levels (TRLs) depend mainly on their combination, the type of CO₂ generating plant, and the fuel used. The current development progress of CO₂ capture technologies in terms of TRL, exhibited three scale-up stages: (i) research (TRLs 1–3), (ii) development (TRLs 4–6) and (iii) demonstration (TRLs 7–9) as shown in Fig. 17. It is typical for the technical advancement of CCS to proceed through a series of scaling phases, which correspond to the respective levels of TRL. These include the initial concept and basic principles (TRL 1), followed by the formulation of the application (TRL 2), starting with laboratory scale (TRL 3–5), progressing to pilot scale operation (TRL 6), demonstration scale (TRL 7), the need for commercial refinement requirements (TRL 8), and finally commercial scale (TRL 9) [286]. To summarize, TRL 1–3 describes the research, TRL 4–6 the development, and TRL 7–9 the demonstration phase [287]. Currently, only a few CO₂ capture technologies have reached a commercial level (TRL 9) in pre-combustion capture (widely used in natural gas processing plants) and post-combustion capture (power plants/aqueous amines). Pre-combustion capture (IGCC - integrated gasification combined cycle + CCS), oxy-fuel combustion (coal power plant), and post-combustion (solid

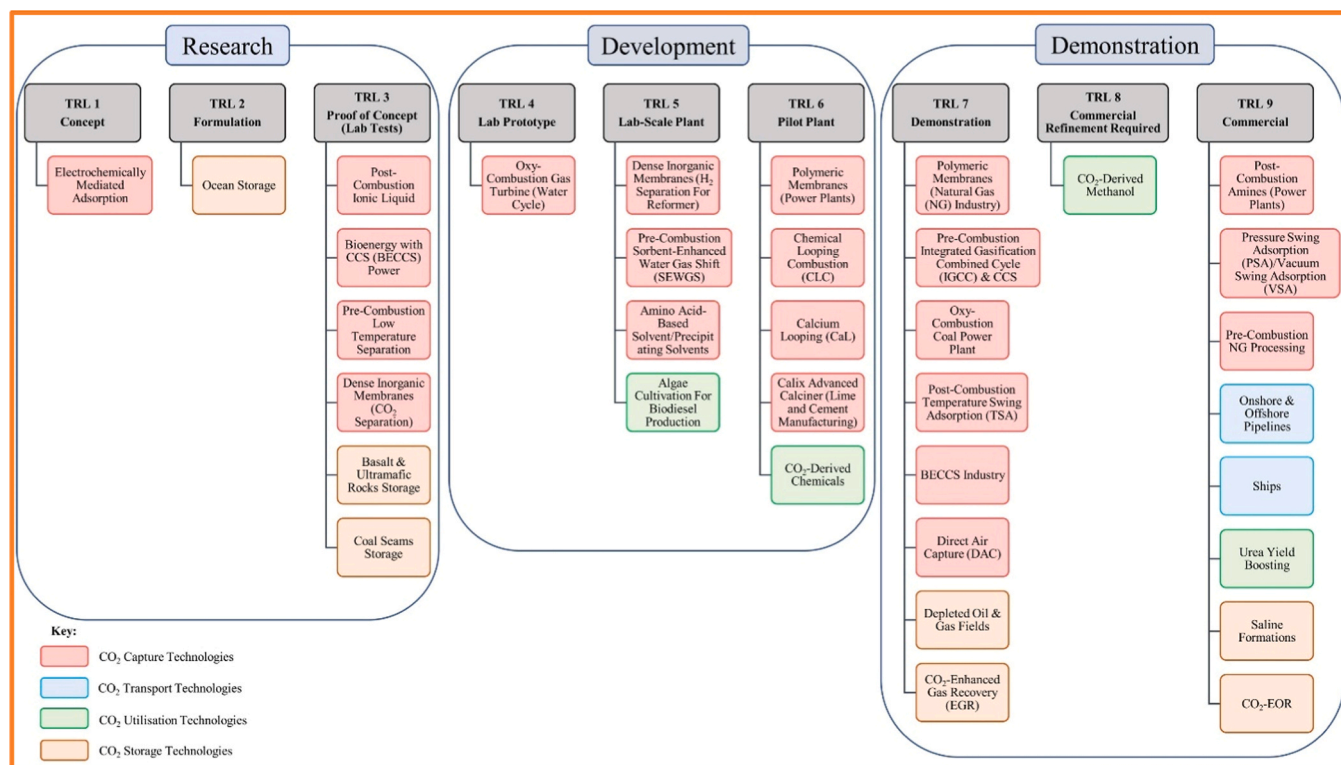


Fig. 17. Technology readiness level (TRL) of CCUS technologies. With permission from Ref [55]. Copyright, 2022 Elsevier.

sorbent) and direct air capture (DAC) are in the demonstration scale (TRL 7). They might also reach the stage of commercialization in the near future. Post-combustion capture (calcium looping, polymeric membranes, and chemical looping combustion) are in the pilot plant scale (TRL 6). Dense inorganic membranes, pre-combustion sorbent enhanced water gas shift (SEWGS), and amino acid-based solvents are in lab-scale plant (TRL 5). Oxy-fuel combustion gas turbine (water cycle) is in the lab prototype (TRL 4). Post-combustion (Ionic liquids) and pre-combustion with low-temperature separation are in proof of concept (TRL 3). Ocean storage and electrochemically mediated adsorption are in formulation (TRL 2) and concept (TRL 1), respectively [55].

10. Conclusions and outlook

The immobilization of ionic liquids (ILs) in membrane pores as supported ionic liquid membrane (SILM) has been extensively investigated as promising technology for post-combustion CO₂ capture. Because of the unique features of ILs (negligible volatility, ionic tunability, generatability) and membranes (compact unit size, easy operation, low energy consumption and operating costs), SILM is the emerging field in carbon capture and storage (CCS). Different types of ILs, their characteristics, properties, pros and cons, and CO₂ solubility of several ILs have been reported in recent years. ILs with higher CO₂ solubility and diffusivity in SILM have been identified.

A detailed perspective on SILM was presented, which considered the evolution of the chemistry of different types of ILs and incorporating various fillers and additives in the membrane supports. Recent reports provided insight into supported configurations on SILMs using MMMs, IL gel membranes and functionalized IL membranes. Appropriately selecting porous support, task-specific IL and additive substantially improves the thermal, mechanical, and surface properties for SILM and CO₂/N₂ permeability and selectivity, represented by the Robeson upper bound, showing great potential of SILM technology for industrial applications. Proper choice of cationic, anionic moieties, and length of

alkyl chain in the polymer matrix define the toxicity, degradability, and economic viability of the SILM technology for large scale applications in CCS.

Applying ILs in the large point sources is the primary drawbacks in SILMs. Despite the rapid advancements in ILs, and polymer matrices including fillers and additives, SILM technology is still looking for real-time applications. The CO₂ capture experiments are carried out by lab scale SILMs under ideal conditions or by changing the parameter over time. However, in real-based conditions, the parameters vary instantaneously, which makes the practice highly complex. For example, when CO₂ is released from large point sources like industries, power plants, and waste heat recoveries, the conditions are severe compared with lab-scale conditions. This mainly consists of flue gases like CO₂, N₂, O₂, SO₂, H₂O, CO, NO_x, with ash and other harmful particles. Regarding flue gas streams, pressure loss is one of the most challenging issues in their treatment. As a result of a pressure decrease, the ILs disperse, diffuse, or evaporate, resulting in poor performance of the membranes.

The following points have been analyzed from the recent developments on post-combustion CO₂ capture using SILMs;

- Functionalized ILs in SILMs have improved CO₂ absorption performance.
- CO₂ solubility and selectivity are important parameters in industrial applications.
- Physico-chemical properties of ILs and support membranes, including viscosity, molecular weight, molar volume, free volume, and surface characteristics, play important role in CO₂ absorption.

The following recommendation is drawn from the recent development.

- The development and testing methods for SILMs must be improved and upgraded. A new development demonstrates that

hybrid composites, particularly nanoscale composites, can improve SILMs' separation efficiency and stability. Furthermore, the advantage of biobased ILs, with the magical features of non-volatility, polarity, and miscibility can be a successful addition that may improve the stability of SILMs.

- (ii) Theoretical and experimental analysis and validation of physico-chemical and thermodynamics data should be investigated further. These include density, viscosity, surface tension, diffusion coefficient etc.
- (iii) Phenomenological studies on adsorption/desorption studies, regeneration, recyclability of ILs and membrane supports, and engineered and systematic approach-based analysis need more in-depth analysis.
- (iv) More scale-up studies need to be conducted to assess the feasibility of SILM technology for commercial applications.
- (v) Environment-health-safety (EHS) including biodegradability and toxicity of SILM technology, should be assessed thoroughly.

Conclusively, though several barriers, including mainly the cost of ILs curtails the commercial applications of SILMs, extensive research is being carried out in diverse directions to overcome these challenges and to improve the CO₂ absorption performance.

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.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2023.102555.

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