The Research Progress of CO_2 Capture with Ionic Liquids[*]

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Abstract Due to their negligible volatility, reasonable thermal stability, strong dissolubility, wide liquid range and tunability of structure and property, ionic liquids have been regarded as emerging candidate reagents for CO_2 capture from industries gases. In this review, the research progresses in CO_2 capture using conventional ionic liquids, functionalized ionic liquids, supported ionic-liquids membranes, polymerized ionic liquids and mixtures of ionic liquids with some molecular solvents were investigated and reviewed. Discussion of relevant research fields was presented and the future developments were suggested.
Keywords CO_2, capture, absorption, separation, ionic liquids, desorption, solubility, selectivity

1 INTRODUCTION

The emission of carbon dioxide (CO_2) from utilization of fossil fuels has received worldwide attention due largely to the rapid growth in worldwide CO_2 emissions predicted to 40.2 Gt by 2030 [1]. Therefore, there is a growing interest in developing technologies for efficient capture and sequestration of large quantities of CO_2. By far, a number of CO_2 capture technologies which have already being practiced on laboratory scale or industrially are processes based on physisorption/chemisorption, membrane separation or molecular sieves, carbamation, amine physical absorption, amine dry scrubbing, mineral carbonation [2]. The traditional technology for CO_2 capture in industry is chemical adsorption by an aqueous solution of amine, which has some advantages such as its maturity, stable operation, good reactivity, and high capacity [3]. However, using aqueous amines like monoethanolamine (MEA) CO_2 capture consumes almost 30% of the energy that is needed to run a power plant [4], in addition to other drawbacks like insufficient CO_2 capture capacity, high solvent losses caused by evaporation, degradation and poor thermal stability, as well as the equipment corrosion [5, 6]. Therefore, developing the economical and energy efficient CO_2 capture technologies is urgently needed.

Ionic liquids (IL) with a low melting point (<373.15 K) have been emerging as nonvolatile and reversible absorbents for CO_2 capture. Compared to traditional organic solvents, the non-volatile ILs are more environmentally friendly [7, 8]. This paper reviews the latest research progress of CO_2 capture with ILs, and also proposes some research prospects.

2 RESEARCH PROGRESS OF CO_2 CAPTURE WITH IONIC LIQUIDS

2.1 CO_2 capture with conventional ionic liquids (CIL)

Blanchard *et al.* [9] reported firstly that CO_2 is highly soluble in ionic liquid of 1-butyl-3-methyl-imidazolium hexafluorophosphate ([C_4mim][PF_6]), reaching a mole fraction of 0.6 at 8 MPa (Fig. 1), while the solubility of [C_4mim][PF_6] in CO_2 is less than 10^{-5} mole fraction at 13.8 MPa and 40 °C. In six ILs such as 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]), 1-*n*-octyl-3-methylimidazoliumhexafluorophosphate ([C_8mim][PF_6]), 1-*n*-octyl-3-methylimidazoliumtetrafluoroborate ([C_8mim][BF_4]), 1-*n*-butyl-3-methylimidazoliumnitrate ([C_4mim][NO_3]), 1-ethyl-3-methylimidazolium ethyl sulfate ([C_2mim]
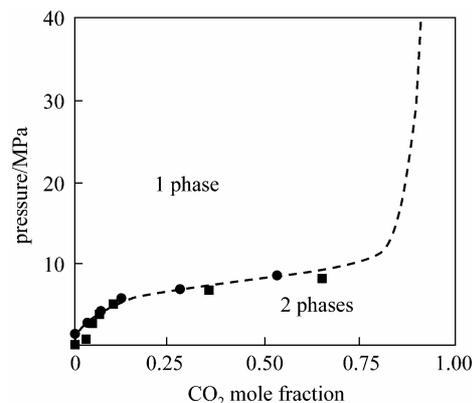

Figure 1 CO_2 solubility in [C_4mim][PF_6] at 25 °C [9]

[EtSO$_4$]), and *N*-butylpyridiniumtetrafluoroborate ([*N*-bupy][BF$_4$]) at high-pressure, a large quantities of CO$_2$ was found to dissolve in the ionic liquid phase, while no appreciable amount of ionic liquid solubilized in the CO$_2$ phase [10]. At present, the CO$_2$ capture by ILs received much attention.

The solubility of CO$_2$ in a series of imidazolium-based IL at low pressure has been determined by Baltus *et al* [11]. It was found to increase with the length of the alkyl side chain on the imidazolium ring but the solubility in IL with phenyl groups was lower when compared to that with alkyl groups. The CO$_2$ solubility is greater in ionic liquids with Tf$_2$N$^-$ anions than that in ILs with PF$_6^-$ anions. And the imidazolium-based ionic liquids with a fluorine-substituted C$_8$ side chain are higher than the corresponding ILs having a non-fluorinated C$_8$ side chain. Chen *et al*. [12] studied the CO$_2$ solubility in 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$]) and 1,1,3,3-tetramethylguanidium lactate (TMGL) at 297 K to 328 K under 0 to 11 MPa. The experimental results showed that the solubilities of CO$_2$ in TMGL are slightly higher than those in [C$_4$mim][PF$_6$]. The solubility of CO$_2$ in TMGL is 2.77 mol·kg^{-1} and in [C$_4$mim][PF$_6$] is 2.65 mol·kg^{-1} at 319 K and 5.73 MPa and the selectivity of TMGL toward CO$_2$ is much more favorable than other gases such as N$_2$, O$_2$, CH$_4$ and H$_2$ [13]. Anderson *et al*. [14, 15] studied the impact of fluorination of the cation on CO$_2$ solubility with the conclusion the CO$_2$ solubility was higher in [C$_8$H$_4$F$_{13}$mim][Tf$_2$N] than [C$_6$H$_4$F$_9$mim][Tf$_2$N], and lowest in [C$_6$mim][Tf$_2$N]. In all, the CO$_2$ solubility increases as the numbers of fluorine in the alkyl side chain but this tendency is not very visible.

Experimental and the molecular dynamics simulation results from Cadena *et al*. [16] indicated that the nature of anion has the greatest influence on the solubility of CO$_2$ and the bis(trifluoromethylsulfonyl)-imide anion ([Tf$_2$N]$^-$) has the greatest affinity for CO$_2$. Aki *et al*. [17] studied the CO$_2$ solubility in ILs with cation [C$_4$mim]$^+$ but different anions, and found CO$_2$ solubility increases in the order of [NO$_3$]$^-$<[DCA]$^-$<[BF$_4$]$^-$< [PF$_6$]$^-$<[CF$_3$SO$_3$]$^-$<[Tf$_2$N]$^-$<[methide]$^-$. Therefore, the more fluorine atoms in the anions, the higher CO$_2$ solubility is, due to the strong coulombic interactions responsible for the organization of the liquid, which also proved by other groups [18–20].

In order to study the selectivity of separating CO$_2$ from mixture gases, Anthony *et al*. [21] measured the solubilities of CO$_2$, C$_2$H$_4$, C$_2$H$_6$, CH$_4$, CO, O$_2$, H$_2$ and N$_2$ in [C$_4$mim][PF$_6$], and found that CO$_2$ is the most soluble among these gases, and [C$_4$mim][PF$_6$] can absorb CO$_2$ selectively (Fig. 2). Regarding the purification of natural gas, certain hygroscopic imidazolium-based ionic liquids like [C$_4$mim][PF$_6$], [C$_8$mim][BF$_4$] and [C$_8$mim][PF$_6$] have ability of dehydration as well [22, 23]. Shiflett *et al*. [24] developed a ternary equation of state (EOS) model for the N$_2$O/CO$_2$/[C$_4$mim][BF$_4$] system. With this EOS model, for both large and small N$_2$O/CO$_2$ feed ratios, the N$_2$O/CO$_2$ gas selectivity *a* is predicted
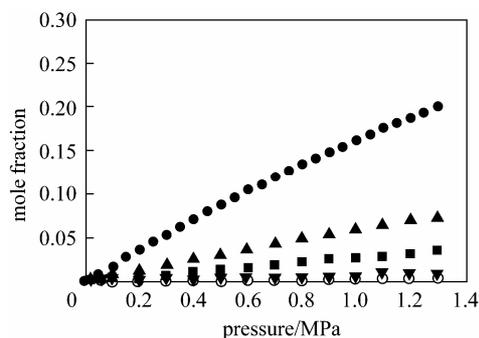
Figure 2   CO$_2$, C$_2$H$_4$, C$_2$H$_6$, CH$_4$, Ar and O$_2$ solubility in [C$_4$mim][PF$_6$] at 25 °C [21]
● CO$_2$; ▲ C$_2$H$_4$; ■ C$_2$H$_6$; ▼ CH$_4$; ○ Ar; + O$_2$

to be 1.4−1.5, compared with (*a* = 0.96−0.98) in the absence of ionic liquid. Anderson *et al*. [14] measured the solubility of CO$_2$, C$_2$H$_4$, C$_2$H$_6$, CH$_4$, O$_2$ and N$_2$ in [C$_6$mpy][Tf$_2$N], they also found this IL is a potential CO$_2$ absorbent with high selectivity.

Thus far, some CIL (especially imidazolium-based) have diminished corrosion of the equipment, and the heat capacity of CIL is almost one-third of that of aqueous systems, which may have profound effect in reducing the high investment and operation cost [25−28]. As for the regeneration, CIL based materials can be easily recycled either by pressure sweep process coupled with vacuum treatment, or by applying heat or by bubbling nitrogen through the absorbent [29, 30].

In short, fluorination of the cation and anion is an effective way to improve CO$_2$ solubility in conventional IL, but the anion got more attention. Though the conventional IL can absorb and separate CO$_2$ effectively to a certain extent, it is just by mechanism of physical adsorption. The drawback is that the CO$_2$ absorption capacity of these ILs, even in the fluorinated ILs, is far below that of the traditional alkanolamine solutions.

2.2   CO$_2$ capture with functionalized ionic liquids (FIL)

As discussed above, the solubility of CO$_2$ in the CIL is not satisfying, and the CO$_2$ absorption capacity can be further improved by functionalization of IL with a suitable moiety (like amine) [31, 32]. Bates *et al*. [33] firstly synthesized [NH$_2$p-bim][BF$_4$] consisting of an imidazolium ion to which a primary amine moiety is covalently bonded, and gave the proposed reaction mechanism between FIL and CO$_2$, similar to the reaction between traditional organic amine and CO$_2$ (Scheme 1). In 3 h, the CO$_2$ capacity in [NH$_2$p-bim][BF$_4$] approached the theoretical maximum (0.5 mol CO$_2$ per mol IL), similar to the CO$_2$ capacity of alkanolamine (Fig. 3). The process of CO$_2$ uptake is reversible, and CO$_2$ being depleted from IL upon heating (80−100 °C) in several hours under vacuum. The recovered IL can be recycled for CO$_2$ uptake (five cycles) with no detectable loss of efficiency.
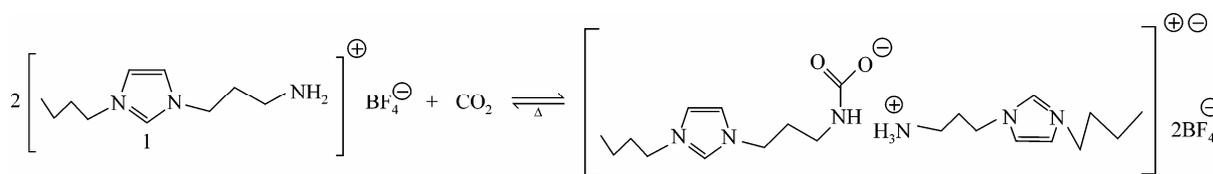
Scheme 1   Proposed reaction mechanism between FIL and CO_2 [33]
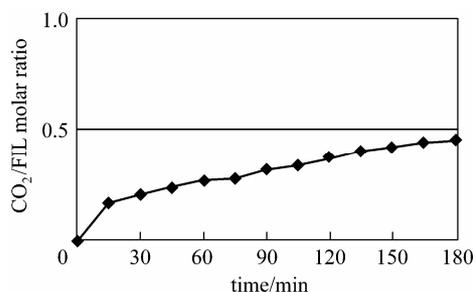
Figure 3 CO_2/ FIL molar ratio as a function of time [33]

More and more FILs appeared by utilizing two techniques. The first one is to functionalize the anion with alkaline group-NH_2 such as [NH_2p-bim][BF_4], and the other is to attach the functional group to the anion.

2.2.1   Functionalize the anion of IL with alkaline group-NH_2

Zhang et al. [34] functionalized the anion with alkaline group-NH_2, and tetrabutylphosphonium amino acid ([$P(C_4)_4$][AA]) was synthesized by reaction of tetrabutylphosphonium hydroxide [$P(C_4)_4$][OH] with amino acids, including glycine, l-alanine, l-b-alanine, l-serine, and l-lysine. The CO_2 absorption capacity of this IL is similar with that of the [NH_2p-bim][BF_4] (0.5 mol CO_2 per mol IL).

Meindersma et al. [35] studied the kinetics of CO_2 absorption in amino-functionalized IL such as 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate ([APmim][BF_4]) at concentrations between 45 and 253 mol·m^{-3} at 303 K and 333 K. The experimental enhancement factors based on the fluxes of CO_2 absorbed are between 1.2 and 2.3, depending on the [APmim][BF_4] concentration. Han et al. [36] evaluated firstly the basicity of IL choline chloride/urea and 1-aminoethyl-3-methyl imidazolium tetrafluoroborate ([AEMIM][BF_4]), and 1,1,3,3-tetramethylguanidinium perchlorate ([TMG][ClO_4]). Their results suggested that adding CO_2 of ambient pressure to IL could reduce their basicity significantly, and the basicity of ILs was readily recovered after removing CO_2 by bubbling N_2 through the solutions, which can help to understand the reaction mechanism between IL and CO_2.

Zhang et al. [37] functionalized both the anion and cation with alkaline group such as —NH_2. The (3-aminopropyl)tributylphosphonium amino acid ([aP_{4443}][AA]), a dual amino-functional IL, were obtained by neutralizing (3-aminopropyl) tributylphosphonium hydroxide ([aP_{4443}]-[OH]) with 20 natural amino acids. [aP_{4443}][OH] was prepared from (3-aminopropyl)tributyl phosphonium bromide ([aP_{4443}]Br) using an anion-exchange resin. In order to improve the absorption rate, ([aP_{4443}][AA] was then supported on the porous SiO_2 and their CO_2 absorption was investigated. The results showed that the ratio of chemical absorption of CO_2 by [aP_{4443}[Gly], [aP_{4443}][leu], [aP_{4443}][Ala], [aP_{4443}][Val] was close to 1 mol CO_2 per mol IL within 80 min, which is consistent with the absorption mechanism proposed in [33, 34]. Although the CO_2 absorption capacity and the rate of this IL decreased steadily, the recovered IL can be repeatedly recycled with out detectable loss for five cycles.

Mu et al. [38] synthesized a new dual amino IL [aemmim][Tau] with amino-functionalized imidazolium cation and taurine anion. The CO_2 absorption capacity of this IL reaches 0.9 mol CO_2 per mol IL at 303.15 K and 0.1 MPa. The dissolved CO_2 can be easily desorbed at higher temperature or under vacuum, so [aemmim][Tau] can be reused and no significant loss of capability was observed after six recycles.

2.2.2   Attach the anion of IL with functional group

Gurkan et al. [39] found a case of intra molecular proton transfer by using one larger phosphonium cations with steric hindrance to block the intermolecular proton transfer process and synthesized [P_{66614}][Pro] and [P_{66614}][Met]. The proposed reaction mechanism between these ILs and CO_2 is different (Scheme 2). The CO_2 capacity in these ILs approached the theoretical maximum (1.0 mol CO_2 per mol IL) (Fig. 4). Then they synthesized six amine-functionalized anion-tethered ILs, trihexyl(tetradecyl)phosphonium glycinate ([P_{66614}] [Gly]), alanate ([P_{66614}][Ala]), sarcosinate ([P_{66614}][Sar]), valinate ([P_{66614}][Val]), leucinate ([P_{66614}][Leu]), and isoleucinate ([P_{66614}][Ile]), and showed the capacity of these four ILs was above 0.5 mol CO_2 per mol IL at CO_2 pressures of less than 0.1 MPa. This indicated that the predominance of the 1 ∶ 1 mechanism, where the CO_2 reacts with one IL to form a carbamic acid, over further reaction with another IL to make a carbamate (the 1 ∶ 2 mechanism). The chemically absorbed CO_2 increased dramatically the viscosity of the IL, but this can be mitigated to some extent by decreasing the number of hydrogens on the anion available for hydrogen bonding [40]. Furthermore, from temperature dependent isotherms, they estimated the heat of absorption is −63 kJ·mol^{-1} CO_2 for the 1 ∶ 1 reaction of CO_2 with [P_{66614}][Pro], whose viscosity was not increased, likely due to its ring structure limiting hydrogen atoms to form a hydrogen bonding network.

In short, the FIL can enhance the CO_2 absorption capacity with ascending pressure, while the aqueous
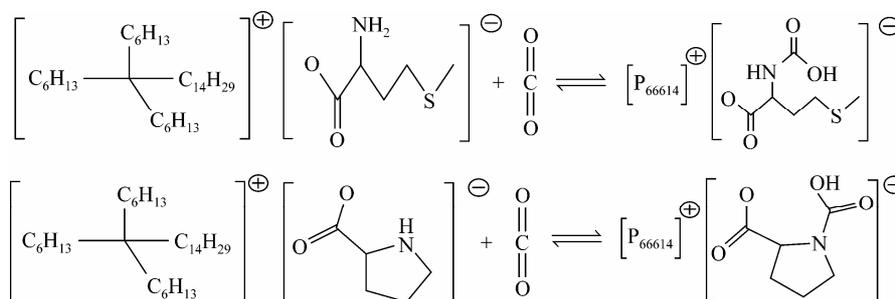
Scheme 2   Reaction mechanism of CO$_2$ with [P$_{66614}$][Met] (top) and [P$_{66614}$][Pro] (bottom) [39]
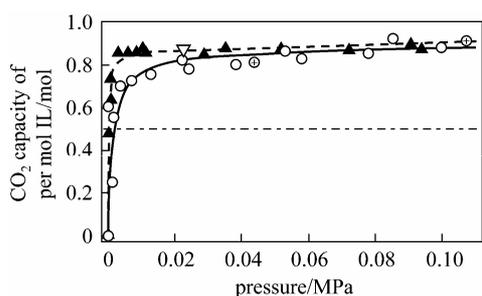
Figure 4   CO$_2$ absorption by [P$_{66614}$][Pro] and [P$_{66614}$)][Met] at 22 °C [39]
○ [P$_{66614}$][Met]; ⊕ [P$_{66614}$][Met] React-IR; —— [P$_{66614}$][Met] calc.
▲ [P$_{66614}$][Pro]; ▽ [P$_{66614}$][Pro] React-IR; ‑ ‑ ‑ [P$_{66614}$][Pro] calc.

amine solutions reached their maximum capacity at about 0.2 MPa [41, 42]. But the viscosity was increased sharply after CO$_2$ absorption by these ILs [43, 44], which seriously limited their application on industrial scale. Yu and Zhang [45] studied the structure and inter-ionic interaction of the IL by molecular orbital simulation and showed the intermolecular —NH$_2$ associated hydrogen bonds can substantially increase the cation-anion interaction which increased the viscosity of the IL, but the in-deep reaction mechanism is still worthwhile to study.

2.3   CO$_2$ capture with supported ionic liquids membranes (SILM)

In order to get better absorption efficiency, some studies explored the prospects of supported ionic liquid on membranes. The supported ionic liquids membranes (SILM) are made by using IL as liquid phase of membrane. The properties of IL such as viscosity and non-volatility can stop the membrane solvent flowing out from porous membrane, which prolongs the life of the SILM greatly without diminishing the ability and selectivity of separation. The high-thermal stability and non-flammation of IL is suitable for capturing CO$_2$ from the flue-gases at high temperature, and SILM can enhance the contact area between gas and IL [46, 47].

2.3.1   *Supported ionic liquids membranes based with conventional IL*

Scovazzo *et al*. [48] supported ILs on the porous hydrophilic polyethersulfone (PES) and evaluate the penetrability and selectivity of this CIL-membranes towards CO$_2$, N$_2$ and CH$_4$. They also studied the influence of the CIL-membranes having the following four water stable anions: bis(trifluoromethanesulfonyl) amide [Tf$_2$N]$^-$, trifluoromethanesulfone [CF$_3$SO$_3$]$^-$, chloride [Cl]$^-$, and dicyanamide [Dca]$^-$. The experimental results showed CO$_2$ permeabilities of 2.6×10^{-8} cm$^3 \cdot$cm$\cdot$cm$^{-2} \cdot$s$^{-1} \cdot$kPa^{-1} (for [Cl]$^-$) to 7.5×10^{-8} cm$^3 \cdot$cm$\cdot$cm$^{-2} \cdot$s$^{-1} \cdot$kPa^{-1} (for [Tf$_2$N]$^-$) together with ideal CO$_2$/N$_2$ selectivities of 15 (for [Cl]$^-$) to 61 (for [DCA]$^-$), and the CO$_2$/C$_2$H$_4$ ideal selectivities ranged from 4 (for [Cl]$^-$) to 20 (for [DCA]$^-$). Note that these permeability/selectivities of above CIL-membranes were relatively good and even better in comparison to polymer membranes. Baltus *et al*. [49] achieved good CO$_2$ absorption capacity by fixing [C$_4$min][Tf$_2$N] to porous Al$_2$O$_3$. Moriya *et al*. [50] supported IL like [C$_4$mim][PF$_6$] to a porous (ceramic or zeolite) material for CO$_2$ separation by putting pressurized gas on one side and collecting the CO$_2$-depleted gas stream downstream of the porous medium. Then Park *et al*. [51] supported [C$_4$min][BF$_4$] on the PVDF (poly-vinylidene fluorolide) as polymer materials for membrane to absorb and separate the mixture gases of CO$_2$ and CH$_4$. To investigate the permeation properties, the SILMs were tested with CO$_2$, H$_2$S and CH$_4$ at various operating conditions. Since CO$_2$ and H$_2$S have higher affinity toward CIL than CH$_4$, the permeability coefficients of these two acidic gases were found to be considerably high at $(0.225-1.35) \times 10^{-8}$ cm$^3 \cdot$cm$\cdot$cm$^{-2} \cdot$s$^{-1} \cdot$kPa^{-1} and $(0.12-0.825) \times 10^{-7}$ cm$^3 \cdot$cm$\cdot$cm$^{-2} \cdot$s$^{-1} \cdot$kPa^{-1}, respectively. Moreover, the selectivity of CO$_2$/CH$_4$ and H$_2$S/CH$_4$ were found to be 25−45 and 130−260, respectively.

Neves *et al*. [52] studied the potential of using supported IL membranes (SILM) for CO$_2$/N$_2$ and CO$_2$/CH$_4$ gas separations. Their results showed that the SILMs prepared with the most hydrophobic support are more stable than those based on the hydrophilic support, and had a high affinity for CO$_2$ over other gases. It also indicated that the presence of water vapour in gas stream increases the SILMs gas permeability but decreased their CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivity significantly. This decrease in selectivity was due to the formation of water clusters inside the membrane, because this effect is more significant for the less hydrophobic CIL.

The permeability coefficient of CO_2 and CH_4 increased dramatically with the CIL content in the membrane. It also increased with the increase in operating temperature which enlarged the free volumes inside the polymer membranes. But the selectivity of CO_2/CH_4 decreased with the increasing temperature because the permeability coefficient of CH_4 was more likely to depend on the membrane structure rather than interaction between CH_4 and membrane.

Furthermore, the new SILMs demonstrated the selectivity of CO_2/CH_4 increased with increasing pressure and maintained mechanical stability at the same time. Kim et al. [53] supported $[C_2mim][Tf_2N]$ on the polymeric hollow fiber, and found the structure of the support has a large impact on membrane stability, and the sponge-like structure has higher stability than a finger-like one. Compared to a cylindrical void structure, the support with a structure consisting of dense polymer chains, i.e., a torturous structure, showed stronger resistance to pressure.

Gonzalez-Miquel et al. [54] found the $[SCN]^-$ based ILs have generally low gas solubilities but it is possible to increase the CO_2 solubility by enhancing the van der Waals intermolecular interactions of CO_2 with the ILs. While exhibiting no affinity for N_2. The reason was the CO_2/N_2 selectivity also depends on the counter anion structure, which makes it possible to select the cation family and its alkyl substitute to tune CO_2/N_2 selectivity and other properties of interest of the ILs, such as density or viscosity, to optimize the CO_2/N_2 separation in SILMs.

However, the CIL-membranes were found to be unsuitable for gas separation at high pressures because of decreased gas solubility. The properties of CIL membranes were found to be enhanced significantly by the addition of an organic salt with an amine group functionality [55].

2.3.2 Supported ionic liquids membranes based with functionalized IL

Haniola et al. [56] and Shishatskiy et al. [57] supported 1-butyl-3-methylimidazoliumbis (trifluoromethyl-sulfonyl)-imide ($[C_4mim][Tf_2N]$), N-aminopropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_3NH_2mim][Tf_2N]$) and N-aminopropyl-3-methylimidazolium trifluoromethanesulfone ($[C_3NH_2mim][CF_3SO_3]$) on the porous hydrophilic polytetrafluoro-ethylene (PTFE) membrane to separate the mixture gas of CO_2 and CH_4. The experimental results suggested the permeability coefficients of CO_2 in $[C_3NH_2mim][Tf_2N]$ and $[C_3NH_2mim][CF_3SO_3]$ are higher than that in $[C_4mim][Tf_2N]$. The reason was that CO_2 permeated across the SILM by the simple solution-diffusion mechanism in $[C_4mim][Tf_2N]$ while CO_2 permeated by chemical reaction mechanism in the case of $[C_3NH_2mim][Tf_2N]$ and $[C_3NH_2mim][CF_3SO_3]$, which worked as transport-carrier in the CO_2 permeation. These SILMs had high stability, without detectable loss, after performance of 260 days. The high temperature prevented the reaction between CO_2 and amine moiety, so the permeability coefficient of CO_2

decreased with the increasing temperature [58]. The combination of SILMs with FIL may be a better choice for capture at elevated temperatures and pressures [59]. The CH_4 permeation was based on the simple solution-diffusion mechanism, the permeability coefficient of CH_4 in $[C_3NH_2mim][Tf_2N]$ and $[C_3NH_2mim][CF_3SO_3]$ was lower than that in $[C_4mim][Tf_2N]$. The reason was that the viscosities of $[C_3NH_2mim][Tf_2N]$ and $[C_3NH_2mim][CF_3SO_3]$ were too high (2180 mPa·s and 3760 mPa·s respectively). The CO_2/CH_4 selectivity was quite high even at low CO_2 partial pressure. At 2.5 kPa of CO_2, the SLMs based on $[C_3NH_2mim][Tf_2N]$ and $[C_3NH_2mim][CF_3SO_3]$ achieved the selectivity of approximately 100 and 120, respectively.

Meanwhile, the supported IL membranes were made by placing cross-linked nylon supports in a container and depositing $[H_2NC_3H_6mim][Tf_2N]$ on top of the membrane with a pipette [62]. The separation of CO_2 from H_2 in this amino-functional IL ($[C_6mim][Tf_2N]$ as reference) was studied. The results suggested when the temperature rises above 85 °C, this IL based facilitated transport membrane will have lower permeability of CO_2, which was similar to the Hanioka's results [56]. The reason was that the high temperature impacts the stability of carbonate, which made the diffusion phenomenon start to dominate. Considering the selectivity and permeability together, the properties of $[C_6mim][Tf_2N]$ was relatively good but lower than $[H_2NC_3H_6mim][Tf_2N]$. In case of hydrophilic composite membranes, the presence of moisture in flue gas affected the CO_2 separation performance. Moist feed seemed to increase permeability up to 35-fold without any detectable loss in CO_2/H_2 or CO_2/N_2 selectivity as compared to dry feed [57].

From the above results, we find that though the supported IL membrane has several drawbacks such as the thick membrane (150 μm or even thicker [48, 61, 62]), unapplicability in separating CO_2 from the flue-gases at high pressures, it is regarded as a potential technology for CO_2 capture. To develop more efficient and cost-effective SILMs requires in-depth study into the role of anion/cation in optimization of molar volume of constituent ILs and the structure of the support materials, so as to produce more stable, more permeable but thinner membranes [63].

2.4 CO_2 capture with polymerized ionic liquids (PIL)

One of the disadvantages of SILM is to leach the liquid through membrane pores when the pressure drop surpasses the liquid stabilizing forces within the matrix. In order to reduce the time of absorption/desorption and overcome this disadvantage, Tang et al. [64] firstly made IL into polymeric form which significantly increased the CO_2 sorption capacity compared with conventional IL. The experiment showed that the polymers of tetraalkylammonium-based IL (e.g. poly[p-vinylbenzyltrimethylammonium tetrafluoroborate] ($P[VBTMA][BF_4]$) has CO_2 sorption capacity 7.6 times

than those conventional IL *e.g.* [C₄mim][BF₄]. The CO_2 absorption and desorption by these polymers are much faster than in IL. The polymers can also absorb selectively CO_2 in N_2/CO_2 mixed gas and did not absorb N_2 or O_2 at 78.97 kPa and 22 °C [64, 65]. They also found when polyethylene glycol (PEG) was grafted onto ionic polymers, such as P[VBTMA][BF₄], it can produce thermally, chemically and mechanically stable CO_2-selective membranes [66]. Bara *et al.* [67] found the solubility, permeability and diffusion of CO_2 CH_4 and N_2 in both types of poly-CIL increased dramatically, and the sorption/desorption was completely reversible, which made these poly-ILs very promising as sorbent and membrane materials for CO_2 separation.

Tang *et al.* [68–72] studied the CO_2 solubility in an ammonium-type ionic and other type polymers, and probed the structure effects on the CO_2 sorption. They showed the CO_2 sorption capacities of the PILs with different cations decreased in the order: ammonium>pyridinium>phosphnium>imidazolium, and those of the PILs with different anions were in the sequence of BF_4^->PF_6≫Tf_2N. P[VBTMA][BF₄] with a polystyrene backbone had a higher CO_2 absorption capacity than P[MATMA][BF₄] with a polymethylmethacrylate backbone. Long alkyl substituents on the cation and cross-linking decreased the CO_2 sorption capacity. The results also illustrated that the CO_2 sorption process consists of dissolution in the polymer matrix and Langmuir sorption inside the microvoid.

Bara *et al.* [67, 73] tethered oligo(ethylene glycol) or nitrile-terminated alkyl substituents to CIL monomers and these polymer membranes were found to exhibit 50% greater CO_2/N_2 and CO_2/CH_4 separation factors than those with comparable length *n*-alkyl substituents, but with similar CO_2 permeability. The OEG-functionalized poly-CIL exhibited several times higher permeability than those with C*ₙ*CN functional groups. They mixed CIL and poly-CIL as a composite gas separation membrane to absorb CO_2 and showed that incorporation of an appropriate amount of CIL and introducing free ion pairs into the polymer membrane, the CO_2 permeability and CO_2/N_2 selectivity increased up to 300%–600% and with 25%–33%, respectively, relative to the analogous poly-CIL membrane lacking any free ion pairs [74, 75].

The polymerized-ILs are very viscous at room temperature and easy to be applied as membrane

materials, so if the techniques of combing the polymerized IL and supported IL membranes were used, it will produce higher CO_2 absorption capacity than the small molecular ILs. Bara *et al.* [76] summarized the using of polymerized-ILs as membrane materials in the CO_2 capture and they agreed that this kind of membranes is a relatively good option for separating and absorbing CO_2.

2.5　CO_2 capture with mixture solvent of ionic liquids and molecular solvents

The viscosity of the conventional IL at 33 °C is forty time higher than that of aqueous alkanolamine solutions such as MEA (30%), which brought great influence on the CO_2 absorption capacity and rate of the absorption of IL [77]. Some scientists synthesized the absorbent by mixing IL with organic solvents or water.

2.5.1　*IL mixing with water or methanol*

Zhang *et al.* [34] reported that in the presence of water (1%), the IL with one amino group could absorb equimolar amounts of CO_2 and formed the product of carbonate, which is different from the product of carbamate without water (Scheme 3).

Ventura *et al.* [78] studied systematically the impact of water content on the viscosity of IL and the CO_2 absorption capacity. The results suggested the addition of water can reduce the viscosity but decrease the CO_2 absorption capacity. Li *et al.* [29] compared [Choline][Pro] with or without the poly-ethyleneglycol at temperature between 35–80 °C at normal pressure. Their conclusion, similar to Ventura *et al.* [78]: the addition of poly ethyleneglycol can reduce the viscosity of IL and improve the CO_2 absorption or desorption rate, but the solubility of CO_2 decreased with added poly ethyleneglycol.

Han *et al.* [79] studied the phase behavior of CO_2-methanol-[C₄mim][PF₆] system under different conditions by a static method. It showed the three-phase region exists only in the temperature range from 35 to 44.5 °C at 7.6 MPa. Increase of pressure and decrease of temperature were favorable to enlarging the distribution coefficients of IL and methanol. They also studied the phase behavior of CO_2-water-[C₄mim][BF₄] system at different conditions [80], and the results suggested
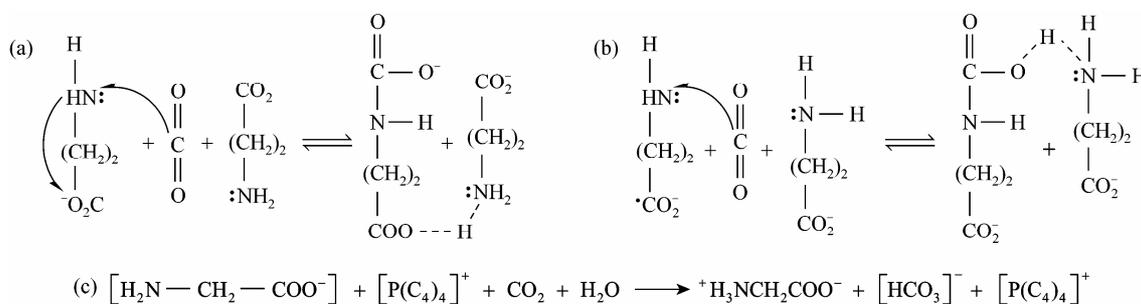
Scheme 3　Proposed mechanism for the CO_2 capture by IL: (a) , (b) without water and (c) with water[34]

the concentrations of CO_2 in the IL-rich phase and water-rich phase increase as the pressure rises and decreases with increasing temperature. The phase behavior of CO_2-acetone-[C_4mim][PF_6] systems at 313.15 K and at pressures up to 15 MPa was also studied, which illustrated CO_2 distribution coefficient decreased with increasing pressure while acetone distribution coefficient increased with pressure [81].

2.5.2 *IL mixing with alkanolamines*

In recent years, some researchers proposed a more practical absorbent of mixing IL with aqueous alkanolamine to absorb CO_2, and the experimental results showed the non-volatility of IL can restrain the volatility of the aqueous alkanolamine solvent to some degree. Meanwhile, the compound absorbent can provide more physical properties than single absorbent. Camper *et al*. [82] mixed MEA and [C_6mim][Tf_2N] to investigate the CO_2 solubility. They found that the CO_2 solubility in this compound absorbent approached the maximum 0.5 mol CO_2 per mol amine and it also can reduce the energy of desorption effectively. This compound absorbent really shed light to a new way to the CO_2 capture.

Zhang *et al*. [83] synthesized four ILs: tetramethylammonium glycinate ([Gly]), tetraethylammonium glycinate ([N_{2222}][Gly]), tetramethylammonium lysinate ([N_{1111}][Lys]) and tetraethylammonium lysinate ([N_{2222}][Lys]) and mixed with water or *N*-methyldiethanolamine (MDEA) aqueous solutions to form new solvents for the uptake of CO_2. The results indicated that IL enhanced greatly the absorption and raised the absorption rate of CO_2 in aqueous MDEA solutions. The CO_2 absorption capacity in the pure [N_{2222}][Gly] is very small and the absorption rate is slow which cannot reach equilibrium in 100 min, but the CO_2 absorption capacity and rate are improved after the addition of MDEA.

Zhang *et al*. [84] studied three compound absorbents such as amines-IL-H_2O, IL-H_2O, and amines-H_2O at temperature ranging from 303.15 to343.15 K with different IL mass fractions. The results indicated the absorbent of amines-IL-H_2O shows the best performance on CO_2 capture. Zhao *et al*. [85] investigated the solubilities of CO, H_2, N_2, O_2 and CO_2 in IL ([MDEA][Cl]) at different pressures from 1.22 to 8.62 MPa and temperature from 313.15 to 333.15 K, showing that the solubility of CO_2 was much higher than the other four gases. And 1 g solvent of MCHP (MDEA-[MDEA][Cl]-H_2O-PZ) could absorb approximately 0.1584 g of CO_2 [86], while 0.15 g of CO_2 for 1 g solvent of MCHP (MDEA-[MDEA][PF_6]-H_2O-PZ) at 303.15 K and 1.50 MPa [87]. Their research on mechanism of CO_2 capture in [MDEA][Cl] and [MDEA][PF_6] indicated that both of them could capture CO_2 by physisorption and chemisorption.

Aroua *et al*. [88] found that the CO_2 loading in IL-MDEA (MEDA 4.0 mol·L^{-1}) mixtures increased with increasing CO_2 partial pressure and decreased with increasing temperature and the CO_2 loading decreases significantly as the IL concentration increases,

but this reduction in solutions contained [C_4mim][BF_4] was less than other types of imidazolium-based ILs.

2.5.3 *IL mixing with super-base or other organic solvents*

Wang *et al*. [89, 90] combined bicyclic amidine (DBU) with hydroxyl modified IL as a superbase to trap the proton produced during sorption process of CO_2, which proved to be an effective way in achieving an equimolar of sorption (Fig. 5). Superbase-derived protic ILs were further synthesized with the equilibrium sorption molar ratio approached 1 ∶ 1. The sorption mechanism between CO_2 and anions with proton trapped by the superbase to form cations is shown in Scheme 4.
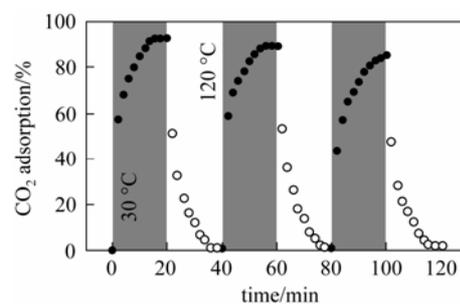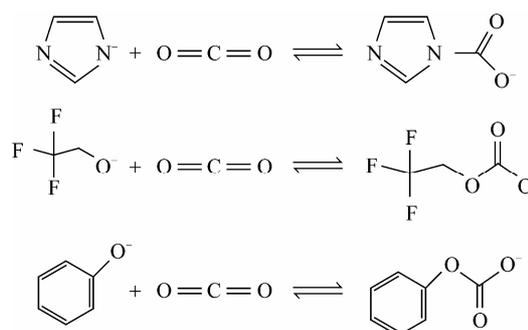

Figure 5   Three consecutive cycles of CO_2 absorption (grey, 30 °C) **and release** (white, 120 °C) **by the [$Im_{21}OH$][Tf_2N]-DBU system** (100% CO_2 uptake denotes 1.0 mol CO_2 per mol IL [89]

Scheme 4   The sorption mechanism of CO_2 absorption by the anions of superbase-derived protic ILs [90]

Zhang *et al*. [91] mixed IL 1-butyl-3-methylimidazolium chloride ([C_4mim][Cl]) with chitin or chitosan as a mixed solvent to capture CO_2. Chitin has two hydroxyl groups in the cellulose-like polymeric structure, whereas chitosan has an additional amine group. For the chitosan/IL mixture, the measured absorption capacity exceeds the theoretical capacity due to the physical absorption of CO_2 in these liquids. Physical absorption is also observed for the chitin/IL mixture. Although this approach can not provide as high absorption capacities as pure FIL, it really has the advantage of bringing a fully recyclable, less corrosive and non-volatile CO_2 absorbent.

In summary, the viscosity of this kind of solvent is lower than that of pure IL and easier to regenerate

than the traditional alkanolamines. So it maybe another potential option to CO_2 capture in the future.

3   CONCLUSIONS AND OUTLOOK

The unique properties of IL such as non-volatility, high thermal stability, strong solubility capacity, and tunability of structure and property made it be potential candidate materials for CO_2 capture. This paper summarized the current research progress on the ionic liquids and IL-based materials which are used in CO_2 capture. It showed that functionalized IL, supported IL membranes, polymerized IL and the mixtures of IL with molecular solvents have good prospects for CO_2 capture. Some companies in the world have intended to use the IL-based materials for industrial-scale separating CO_2 from natural gas or flue gas CO_2 [92, 93]. The future research should be focused on the following issues.

(1) Understanding the mechanism of the CO_2 capture with IL combing molecular simulation and experimental characteristics, and revealing the relationships between structures of IL and the performance of CO_2 capture;

(2) Developing the new IL with low cost, low viscosity and high absorption capacity with high selectivity, which will reduce the absorption rate and decrease the energy demand for desorption. The CO_2 desorption process is also crucial with respect to the energy consumption required by industries;

(3) Studying the transport phenomena which will be very important for the suitable design and operation of industrial unit, especially at low pressure and high temperature (like flue gas from coal-fired power plants) used for CO_2 capture with ionic liquids.

Though there are lots of problems in using ILs to capture CO_2, we believe all the problems will be resolved one by one with in depth investigation and then it is possible to use ILs to capture CO_2 on large scales in the future.

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