REVIEW

Progress and Development of Capture for CO$_2$ by Ionic Liquids

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Ionic liquids have attracted considerable attention used as green solvents because they have excellent properties, such as no volatility, stability, good solubility and adjustable structures. This review describes the recent development of ionic liquids for CO$_2$ capture and separation, including room-temperature ionic liquids, task-specific ionic liquids, supported ionic-liquids membranes and polymerized ionic liquids and discusses the mechanism of the absorption and introduced combined technologies of room temperature ionic liquid and other solvents for CO$_2$ capture. Finally, the application outlook of ionic liquids is prospected.

Key Words: Ionic liquids, CO$_2$, Separation, Absorption, Mechanism.

INTRODUCTION

With population growth, improved standards of living and expanding economies, the amount of CO$_2$ generated and emitted into the atmosphere continues to rise. Carbon dioxide is one of the major contributors to the greenhouse effect, which has become the focus everybody cares. Almost every country is committed to control and reduce the emission of CO$_2$, paying more and more attention to the researches on capture of carbon dioxide by various techniques in recent years. The main CO$_2$ separation technologies from gas mixtures are currently: adsorption, absorption, cryogenic methods and separation with membranes[1,2].

Among the different technologies to capture post-combustion carbon dioxide, those based on chemisorptions by aqueous alkanolamines are still considered the most efficient and the relatively least expensive[3-5]. However, amine-based aqueous processes have several drawbacks. These include loss of the amino compounds and their decomposition products through evapouration and oxidative degradation, resulting in reduced CO$_2$ absorption capacity and potential toxic byproduct release, operational instability caused by foaming and altered viscosity and frequent equipment maintenance due to excessive corrosion of the amine system.

The discovery of materials that selectively and efficiently absorb CO$_2$ from flue gases is essential to realizing practical carbon capture and sequestration (CCS). Ionic liquids are promising in this regard because of their negligible vapour pressures, high thermal stability and virtually limitless chemical tunability. These properties made ionic liquids a good potential to replace these conventional organic solvents (aqueous solutions of alkanolamines). These ionic liquids are also termed designer solvents because they can be custom-fitted for specific applications, which has aroused extensive concern from domestic and alien scholars.

In order to better use of the ions liquid, development and progress on the ionic liquids for CO$_2$ capture will be summarized from the scientific literature in this review.

CO$_2$ capture by room-temperature ionic liquids: In 1999 Blanchard and co-workers first investigated that CO$_2$ could be soluble in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim]-[PF$_6$]) but [bmim]-[PF$_6$] could hardly be soluble in CO$_2$[6]. Since then, research on capture of CO$_2$ using ionic liquid caused widespread concern.

Considerable research work is being done showing high carbon dioxide solubility in certain room-temperature ionic liquids, especially in those having imidazolium-based cations[6-10]. It is found that the anion dominates the interactions with the CO$_2$, with the cation playing a secondary role[11-13]. The origin of this high solubility could be related more to the anion moiety that enhances interactions by favouring particular distributions of CO$_2$ molecules around the cation[13]. It is found that the *bis*-(trifluoromethylsulfonyl)-imide anion has the greatest affinity for CO$_2$, while there is little difference in CO$_2$ solubility between ionic liquids having the tetrafluoroborate or hexafluorophosphate anion. Besides, alkyl-side chain length of the

imidazolium-based cation of the ionic liquids also affects CO_2 solubility to a certain extent. Fluorine substituted side chains greatly augment the uptake of CO_2 with respect to the corresponding non-substituted side chains but at the expense of an increase in viscosity[14-17].

Anthony *et al.*[18] studied the solubility of carbon dioxide, ethylene, ethane, methane, argon, oxygen, carbon monoxide, hydrogen and nitrogen in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6] and found there was obvious difference. The results indicated that there was potential value for ionic liquid as the separate media of CO_2 mixtures. Room-temperature ionic liquids approach to CO_2 capture is mostly physical absorption so the absorb volumes is less. To make room-temperature ionic liquids more workable, Camper *et al.*[19] mixed room-temperature ionic liquids with commercial amines and found reactive solvents can be tailored to capture CO_2 in a variety of conditions and processes. These room-temperature ionic liquid-amine solutions behave similarly to their water based counterparts but may offer many advantages, including increased energy efficiency, compared to current aqueous amine technologies[19].

CO_2 capture by task-specific ionic liquids: As discussed earlier, CO_2 is sufficiently soluble in room-temperature ionic liquids. However, the CO_2 capture ability can be enhanced by introducing basic character in the ionic liquids. It is well known that the ammonia, the alkaline group, takes the main role in the absorption of organic amines for CO_2. So the CO_2 capture ability can be enhanced by introducing amine moiety in the ionic liquids.

Taking a clue from the chemistry of aqueous organic amines reacting with CO_2[20], Bates *et al.*[21] first synthesized [NH_2p-bim], ionic liquid with a amine moiety BF_4 and proposed a one-step CO_2 reaction mechanism in accordance with that of Crooks and Donnellan[22]. The first reported example contained an amine group on an imidazolium cation, which reacted with CO_2 in a manner similar to aqueous amines, by forming carbamate and ammonium ions in a stoichiometry of one CO_2 to two amines as shown in Fig. 1. The molar uptake of CO_2 per mole of task-specific ionic liquid during the 3 h exposure period approaches 0.5, the theoretical maximum for CO_2 sequestration as an ammonium carbamate salt. This permole uptake of CO_2 by the amine-appended task-specific ionic liquid is comparable to those of standard sequestering amines such as monoethanolamine. The process of CO_2 uptake is reversible and CO_2 can be extruded from the ionic liquid upon heating. The recovered ionic liquid has been repeatedly recycled for CO_2 uptake (five cycles) with no observed loss of efficiency.

Afterwards, the study of task-specific ionic liquids widely appeared. A number of groups have explored other amine-functionalized ionic liquids, including functionalized sulfones[23] and amino acids anions with imidazolium[24] and phosphonium[25] cations. Zhang *et al.*[26] synthesized dual amino-functionalized phosphonium ionic liquids for CO_2 capture. The chemical absorption of CO_2 by some dual amino-functionalized ionic liquids was found to approach 1 mol CO_2 per mol ionic liquid, which is a factor of two greater than that reported before. The loss of absorption rate and capacity was not very significant for five absorption cycles.

The above-all systems have been assumed to produce 1:2 stoichiometry, although some of the evidence points to higher capacities and may warrant revisiting in light of the findings presented in this paper. Nonetheless, Gurkan *et al.*[27] found a different result in the latest research. They reported the synthesis and characterization of amino acid based ionic liquids, including trihexyl(tetradecyl)phosphonium prolinate-([P66614][Pro]) and methioninate ([P66614][Met]), that react with CO_2 in a ratio of one CO_2 per one amine (1:1 stoichiometry). Reaction schematics are shown in Fig. 2.

Above all, a series of task-specific ionic liquids containing amine functional groups have been demonstrated to have much higher capacities for CO_2 due to their reactivity with CO_2, as well unusually high viscosities in both the neat and complexed states, in spite of the tunable approach towards task-specific ionic liquids[28]. Yu and co-workers[29] used molecular simulations to help to explain the high viscosity of the neat task-specific ionic liquids. They found that the anions prefer to interact strongly with the -NH_2 tails of the cations *via* hydrogen bonding, which they suggest leads to the high viscosity. The dramatic increase in viscosity upon contacting these materials with CO_2 greatly impacts the way these materials might be used for CO_2 capture. The mechanism for the viscosity increase in the amine-functionalized task-specific ionic liquids has not been thoroughly investigated, although strong evidence exists for the formation of salt bridges.

High viscosities pose serious complications to be applicable on industrial scale. An alternative to decrease viscosites is the use of mixtures of ionic liquids. Binary mixtures of reactive task-specific ionic liquids with nonreactive ionic liquids, such as 1-butyl-3-methylimidazolium *bis*-(trifluoromethanesulfonyl)imide, offer not only the promise of lower viscosities but also lower costs associated with the conservation
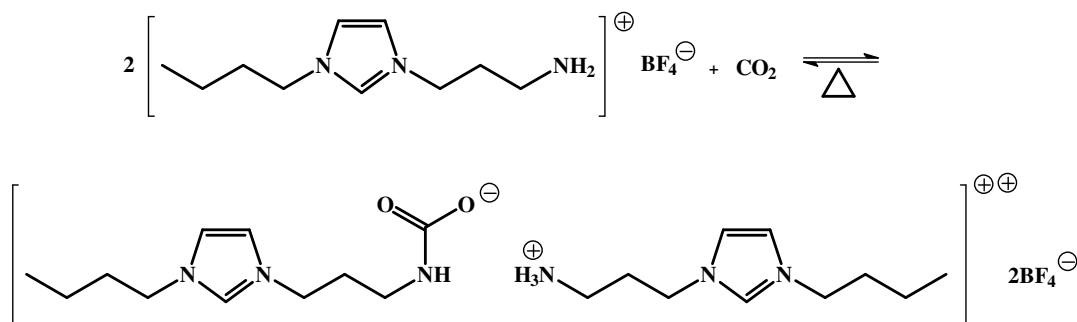

Fig. 1. Possible mechanism for the capture of CO_2 by [NH_2p-bim][BF_4][21]
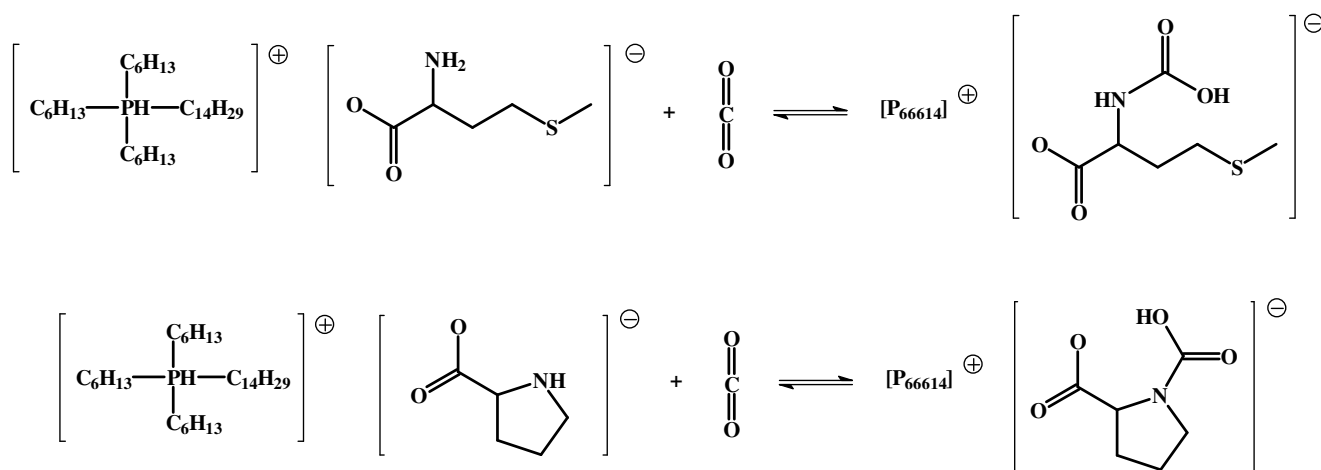
Fig. 2. Proposed mechanism for the capture of CO_2 by [P66614][Met] (top) and [P66614][Pro] (bottom)[27]

of expensive, specialized task-specific ionic liquid materials. Likewise, binary or ternary mixtures that involve task-specific ionic liquids combined with organic diluents, such as in ionic liquid-liquid clathrate systems[30], offer a plethora of alternatives and potential solutions. Besides, another solution may be that task-specific ionic liquids were adsorbed onto porous membranes.

CO₂ capture by supported ionic-liquid membranes: In spite of many demerits, the high viscosity of amine-tethered task-specific ionic liquids before and after complexation with CO_2 is not entirely a hindrance. Task-specific ionic liquids have been deposited or supported on a porous matrix within a membrane, also known as supported ionic liquid membranes, have been shown to exhibit high permeability and selectivity for CO_2[31]. Room-temperature ionic liquid, [bmim][Tf₂N], supported on porous alumina membrane revealed very optimistic results in favour of CO_2 capture ability[32].

In another study[33,34], [bmim][BF₄] was adsorbed onto poly vinylidene fluoride polymeric membrane. Zhang *et al.*[35] synthesized tetrabutylphosphonium amino acid [P(C₄)₄][AA] supported on porous silica gel effected fast and reversible CO_2 absorption when compared with bubbling CO_2 into the bulk of the ionic liquid. No changes in absorption capacity and kinetics were found after four cycles of absorption/desorption. The CO_2 absorption capacity at equilibrium was 50 mol % of the ionic liquids. In the presence of water (1 wt %), the ionic liquids could absorb equimolar amounts of CO_2.

In practice, supported ionic-liquid membranes have several major shortcomings. Typically, supported ionic-liquid membranes reported in the literature are quite thick, perhaps 150 μm or more[36-38]. CO_2 capture from flue gas occurs at atmospheric pressure[39,40] and is perhaps a more realistic target separation for supported ionic-liquid membranes. Regardless of their future viability in industrial processes, supported ionic-liquid membranes will remain a valuable research tool for understanding gas separations in room-temperature ionic liquids. Supported ionic-liquid membranes should also prove useful for analyzing the properties of hazardous, reactive, rare and noble gases in ionic liquids.

CO₂ capture by polymerized ionic liquids: To reduce the CO_2 sorption and desorption time of ionic liquids, Tang and co-workers[41-43] polymerized novel sorbent and membrane materials for CO_2 separation, poly(ionic liquid)s made from ionic liquid monomers, poly[*p*-vinylbenzyltrimethyl ammonium tetrafluoroborate](P[VBTMA] [BF₄]) and poly[2-(methacryloyloxy)ethyltrimethylamnonium tetrafluoroborate] (P[MATMA][BF₄]), which have absorption capacities 7.6 and 6.0 times of those of room temperature ionic liquids, *e.g.* [bmim][BF₄]. Moreover sorption/desorption rates of the polymerized ionic liquid is quite fast as compared to room-temperature ionic liquids. These polymers are very prospective as sorbent and membrane materials for CO_2 separation. In the reseach of others room-temperature ionic liquids containing polymerizable entities show higher permeability, solubility and diffusivity values for CO_2, N_2 and CH_4[44].

Afterwards Tang and co-worker made a progressive research on polymerized ionic liquids[45]. They probed structure effects on the CO_2 sorption. An ammonium cation with short alkyl group, BF₄ anion and polystyrene backbone was found to favour CO_2 sorption in polymerized ionic liquids. The results suggested that the CO_2 sorption consists of dissolution in the polymer matrix and Langmuir sorption in the microvoids. Furthermore Bara *et al.*[46] reported the membranes made up of polymerizable ionic liquids may be a better option for CO_2 separation.

Conclusion

This brief survey on the current trends on the ionic-liquid mediated CO_2 capture suggests that CO_2 capture by ionic liquids is a feasible practice. A variety of ionic-liquid techniques involving room-temperature ionic liquids, task-specific ionic liquids or supported ionic-liquid membranes can be employed for CO_2 capture. At present, the lack of availability of inexpensive and diverse ionic liquids is the major cause of hesitation in employing ionic liquid systems for CO_2 capture on large scales.

Serious consideration is clearly warranted for the use of room-temperature ionic liquids in industrial CO_2 separation processes, owed to their low viscosities, nonvolatility, robust stability and compatibility with other organic solvents and reagents. While a great deal of applied research will certainly be needed for room-temperature ionic liquids to realize commercial viability, the nonvolatile nature of room-temperature

ionic liquids should allow for significant improvements to current processes and the development of new approaches to CO_2 separation and capture. In the long term, the beneficial qualities that room-temperature ionic liquids can impart on CO_2 separation processes will far outweigh the expense of producing significant volumes of room-temperature ionic liquid solvents. Greater availability of room-temperature ionic liquids is needed to drive industrial innovation and commercial application of these unique solvents.

REFERENCES

1. M.L. Srivastava, N.K. Shukla, S.K. Sungh and M.R. Jaiswal, *J. Membr. Sci.*, **117**, 39 (1996).
2. C. Moreno and M. Valiente, *J. Membr. Sci.*, **155**, 155 (1999).
3. A. Jamal, A. Meisen and C. Lim, *J. Chem. Eng. Sci.*, **61**, 6590 (2006).
4. B.A. Oyenekan and G.T. Rochelle, *Ind. Eng. Chem. Res.*, **45**, 2457 (2006).
5. A. Henni, J. Li and P. Tontiwachwuthikul, *Ind. Eng. Chem. Res.*, **47**, 2213 (2008).
6. L.A. Blanchard, D. Hancu, E.J. Beckman and J.F. Brennecke, *Nature*, **399**, 28 (1999).
7. L.A. Blanchard, Z.Y. Gu and J.F. Brennecke, *J. Phys. Chem. B*, **105**, 2437 (2001).
8. J.L. Anthony, E.J. Maginn and J.F. Brennecke, *J. Phys. Chem. B*, **106**, 7315 (2002).
9. A.P.S. Kamps, D. Tuma, J. Xia and G. Maurer, *J. Chem. Eng. Data*, **48**, 746 (2003).
10. P. Husson-Borg, V. Majer and M.F. Costa Gomes, *J. Chem. Eng. Data*, **48**, 480 (2003).
11. S.G. Kazarian, B.J. Briscoe and T. Welton, *Chem. Commun.*, 2047 (2000).
12. L. Cammarata, S.G. Kazarian, P.A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, **3**, 5192 (2001).
13. C. Cadena, J.L. Anthony, J.K. Shah and T.I. Morrow, *J. Am. Chem. Soc.*, **126**, 5300 (2004).
14. E.K. Shin and B.C. Lee, *J. Chem. Eng. Data*, **53**, 2728 (2008).
15. J. Palgunadi, J.E. Kang, D.Q. Nguyen, J.H. Kim, B.K. Min, S.D. Lee, H. Kim and H.S. Kim, *Thermochim. Acta*, **494**, 94 (2009).
16. E.K. Shin, B.C. Lee and J.S. Limb, *J. Supercrit. Fluids*, **45**, 282 (2008).
17. R.E. Baltus, B.H. Culbertson, S. Dai, H. Luo and D.W. DePaoli, *J. Phys. Chem. B*, **108**, 721 (2004).
18. J.L. Anthony, E.J. Maginn and J.F. Brennecke, *J. Phys. Chem. B*, **106**, 7315 (2002).
19. D. Camper, J.E. Bara, L.G. Douglas and R.D. Noble, *Ind. Eng. Chem. Res.*, **47**, 8496 (2008).
20. A.M. Wolsky, E.J. Daniels and B. Jody, *J. Environ. Prog.*, **13**, 214 (1994).
21. E.D. Bates, R.D. Mayton, L. Ntai and J.H. Davis Jr., *J. Am. Chem. Soc.*, **124**, 926 (2002).
22. J.E. Crooks and J.P. Donnellan, *J. Chem. Soc. Perkin Trans.*, 331 (1989).
23. M.D. Soutullo, C.I. Odom, B.F. Wicker, C.N. Henderson, A.C. Stenson and J.H. Davis Jr., *Chem. Mater.*, **19**, 3581 (2007).
24. K. Fukumoto, M. Yoshizawa and H. Ohno, *J. Am. Chem. Soc.*, **127**, 2398 (2005).
25. K. Fukumoto, Y. Kohno and H. Ohno, *Chem. Lett.*, **35**, 1252 (2006).
26. Y.Q. Zhang, S.J. Zhang, X.M. Lu, Q. Zhou, W. Fan and X.P. Zhang, *Chem. Eur. J.*, **15**, 3003 (2009).
27. B.E. Gurkan, J.C. de la Fuente, E.M. Mindrup, L.E. Ficke, B.F. Goodrich, E.A. Price, W.F. Schneider and J.F. Brennecke, *J. Am. Chem. Soc.*, **132**, 2116 (2010).
28. K.E. Gutowski and E.J. Maginn, *J. Am. Chem. Soc.*, **130**, 14690 (2008).
29. G. Yu, S. Zhang, G. Zhou, X. Liu and X. Chen, *AICHE J.*, **53**, 3210 (2007).
30. J.D. Holbrey, W.M. Reichert, M. Nieuwenhuyzen, O. Sheppard, C. Hardacre and R.D. Rogers, *Chem. Commun.*, 476 (2003).
31. C. Myers, H. Pennline, D. Luebke, J. Ilconich, J.K. Dixon, E.J. Maginn and J.F. Brennecke, *J. Membr. Sci.*, **322**, 28 (2008).
32. R.E. Baltus, R.M. Counce, B.H. Culbertson, H. Luo, D.W. DePaoli, S. Dai and D.C. Duckworth, *Sep. Sci. Technol.*, **40**, 525 (2005).
33. S.H. Lee, B.S. Kim, E.W. Lee, Y.I. Park and J.M. Lee, *Desalination*, **200**, 21 (2006).
34. Y.I. Park, B.S. Kim, Y.H. Byun, S.H. Lee, E.W. Lee and J.M. Lee, *Desalination*, **236**, 342 (2009).
35. J.M. Zhang, S.J. Zhang, K. Dong, Y.Q. Zhang, Y.Q. Shen and X.M. Lu, *Chem. Eur. J.*, **12**, 4021 (2006).
36. J.E. Bara, C.J. Gabriel, T.K. Carlisle, D. Camper, A. Finotello, D.L. Gin and R.D. Noble, *Chem. Eng. J.*, **147**, 43 (2009).
37. J. Ilconich, C. Myers, H. Pennline and D. Luebke, *J. Membr. Sci.*, **298**, 41 (2007).
38. P. Scovazzo, J. Kieft, D.A. Finan, C. Koval, D. DuBois and R. Noble, *J. Membr. Sci.*, **238**, 57 (2004).
39. L. Zhao, E. Riensche, R. Menzer, L. Blum and D. Stolten, *J. Membr. Sci.*, **325**, 284 (2008).
40. M.T. Ho, G.W. Allinson and D.E. Wiley, *Ind. Eng. Chem. Res.*, **47**, 1562 (2008).
41. J.B. Tang, H.D. Tang, W.L. Sun, H. Plancher, M. Radosz and H.Q. Shen, *Chem. Commun.*, 3325 (2005).
42. J.B. Tang, W.L. Sun, H.D. Tang, M. Radosz and Y.Q. Shen, *Macromolecules*, **38**, 2037 (2005).
43. J.B. Tang, H.D. Tang, W.L. Sun, M. Radosz and Y.Q. Shen, *Polymer*, **46**, 12460 (2005).
44. J.E. Bara, S. Lessmann, C.J. Gabriel, E.S. Hatakeyama, R.D. Noble and D.L. Gin, *Ind. Eng. Chem. Res.*, **46**, 5397 (2007).
45. J.D. Tang, Y.Q. Shen, M. Radosz and W.L. Sun, *Ind. Eng. Chem. Res.*, **48**, 9113 (2009).
46. J.E. Bara, D.E. Camper, D.L. Gin and R.D. Noble, *Acc. Chem. Res.*, **43**, 152 (2010).