REVIEW ON CO_2 CAPTURE WITH IONIC LIQUIDS

Introduction:

Now a days, the world natural gas consumption has been increased significantly as the most important energy sources of the future. Compare to other fossil fuels like coal or oil, natural gas is more environment friendly. This is because natural gas produces relatively low amount of greenhouse gases (carbon di-oxide, sulfur di-oxide, nitrous oxide etc.) compare with other fossil fuels[1]. Recent world is suffering greatly from Global Warming. And Global Warming is mainly due to excess amount of different greenhouse gases, especially carbon di-oxide. Carbon di-oxide is produced naturally and consumed by the carbon cycle, which remains longer than other gases in the atmosphere and responsible for the Global Warming as well as the climate change. Now a days, the emission of greenhouse gases (majorly CO_2) increasing rapidly due to many human activities like fossil fuels burning, industrial processes and also including the deforestation. There are so many other sources of emission of CO_2 like different kind of agriculture processes and solid biomass burning for the generation of the heat and energy[2].

Moreover, world CO_2 energy-related emissions are expected to increase at a rate of 2.1% per year[3]. Thus, to control CO_2 emissions from these sources should be extremely important to minimize the emissions of GHGs that contribute to climate change without stifling economical and technological development. Although the characteristics of CO_2 capture from natural gas, for sweetening purposes, and from flue gas of conventional fossil-fuel-fired power plants (in which low CO_2 partial pressures, less than 0.15 atm, are common and with CO_2 concentrations of typically 3-13 vol%), are very different, it is clear that both problems are closely related, and thus, similar approaches are frequently used for both cases. Nevertheless, it should be remarked that the economics of CO_2 capture are strongly influenced by the partial pressure in the feed gas, with low partial pressures making their use as physical solvents difficult[1,4].

A number of CO_2 capture technologies have already been practiced on laboratory or industrial scale, for both natural gas sweetening and flue gases, that require various processes involving physisorption/chemisorption, membrane separation or molecular sieves, carbamation, amine physical absorption, amine dry scrubbing, mineral carbonation etc[4,5].

A very promising alternative for CO_2 capture, for both flue gases and gas sweetening purposes, is the use of ionic liquids (ILs) as absorbents[6,7]. Because the physical and chemical properties of room-temperature ILs could be enhanced and modified by both their cationic and anionic moieties, they serve a broad range of applications, such as solvents, sensors, solid-state photocells, thermal and hydraulic fluids, lubricants, and several analytical techniques, including mass spectrometry, separation techniques, and electrochemistry[8-11]. Therefore, considering that IL properties can be tailor-designed to satisfy the specific application such as the use of ILs for CO_2 capture.

PRINCIPAL
Dhruba Chand Halder College
P.O.- D. Barasat, P.S.- Jaynagar
South 24 Parganas. Pin- 743372

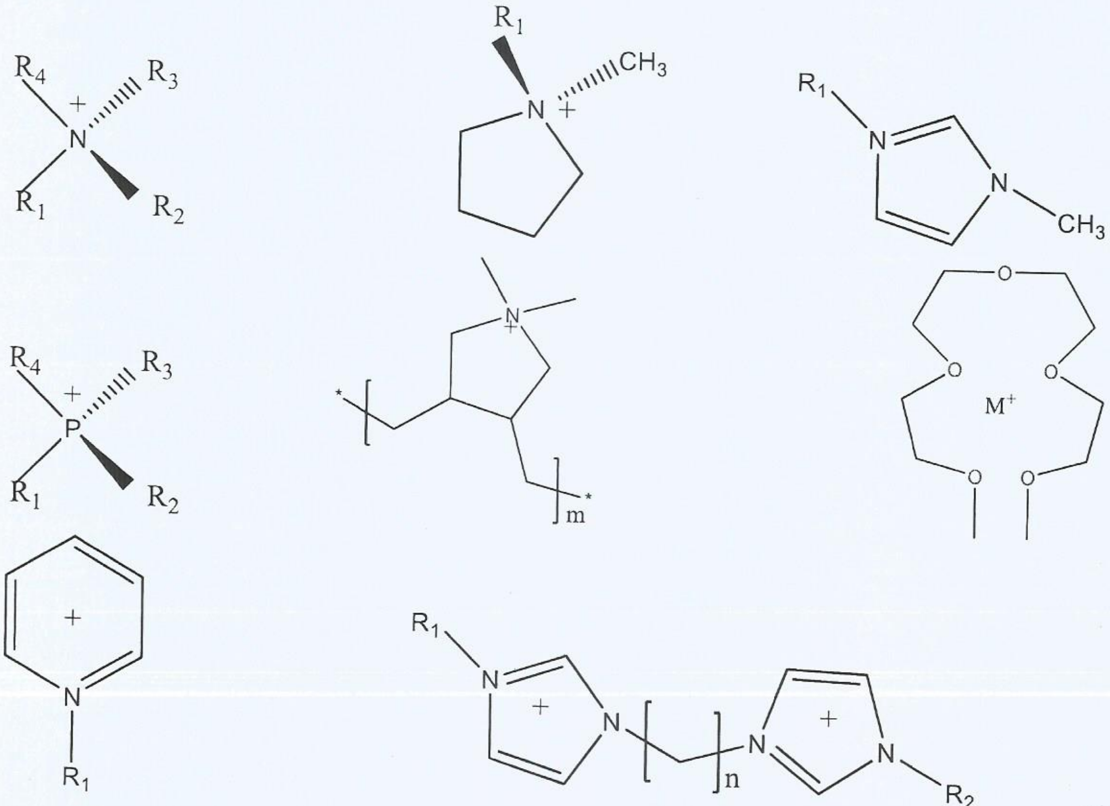
Project Investigator (4th Sem Hon)
Dr. Partha Biswas.

Ionic liquids, Their Composition and Properties:

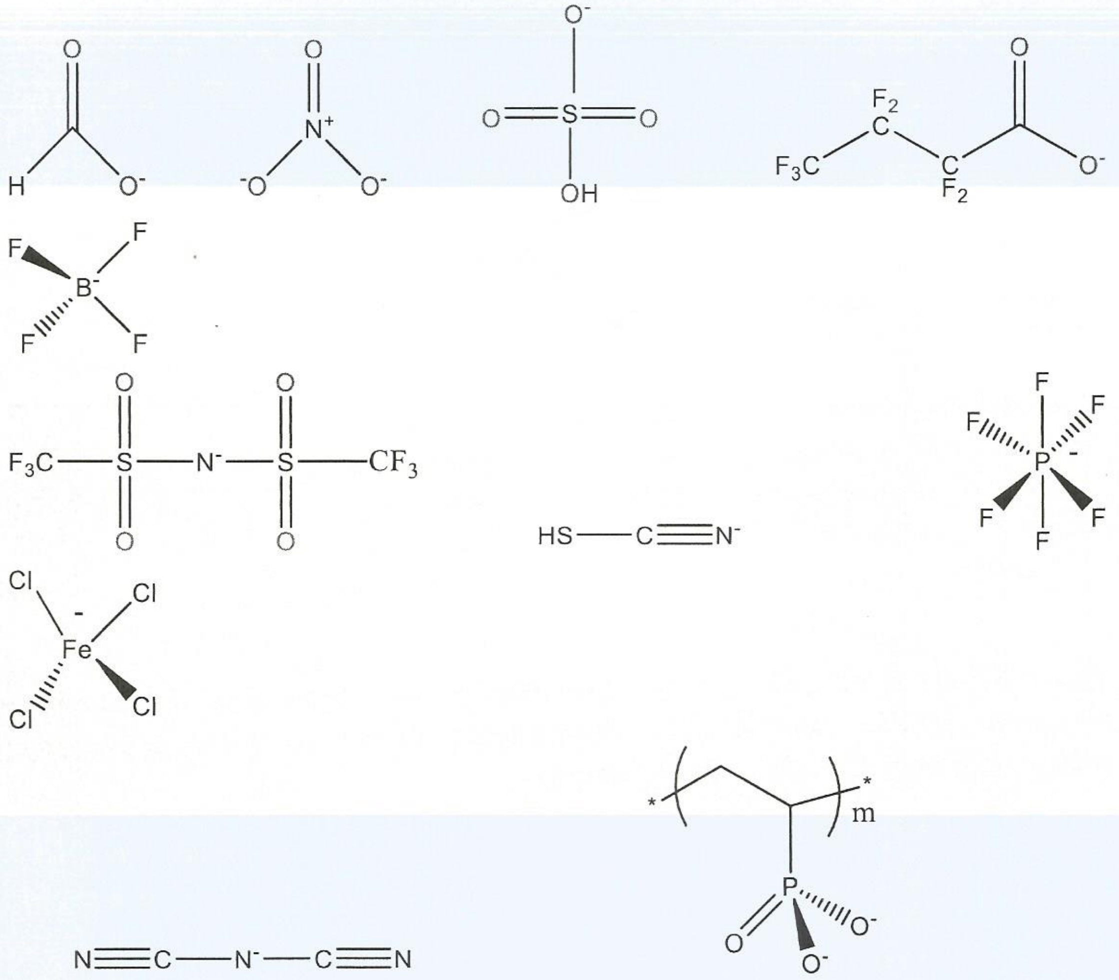
An ionic liquid (IL) is a liquid which contains only ions, but it is different from the classic definition of a molten salt. A molten salt is usually defined as a highly-melting, highly viscous and highly corrosive liquid, where as an ionic liquid is a liquid at low temperature (< 100°C) and has lower viscosity and very low vapour pressure. Based on the molecular structure, ILs are classified into proton-donating (protic ILs (PILs)) and nonproton-donating (aprotic ILs (AILs)) solvents[2].

Compositions of ionic liquids:

- In general, ionic liquids contain one nitrogen-containing organic cations and one inorganic anions in their basic skeleton.
- Tetraalkyl-ammonium cation, tetraalkyl-phosphonium cation, N,N′- dialkyl-imidazolium cation, N-alkyl pyridinium cations are used as cations mostly.
- On the other hand, hexafluoride sulphate, tetrafluoride borate, halide (chloride, bromide), trifluomethane sulfonate, ethyl sulfate etc. are used as anions in a wide number of ionic liquids[12].
- Structure of cations in most common ionic liquids[2]:



Structure of anions in most common ionic liquids[2]:



CO_2 capture processes:

CO_2 capture processes are divided into three main categories precombustion, post combustion and oxy combustion. Out of these three modes post combustion CO_2 capture was widely used, and post-combustion is easier to be implemented as a retrofit option in the existing power plants, compared to other two approaches[2,13,14]. the post-combustion carbon capture technique is divided into several main subcategories[2], As illustrated in Fig. 1.

PRINCIPAL
hruba Chand Halder College
.O.- D. Barasat, P.S.- Jaynagar
South 24 Parganas, Pin- 743372

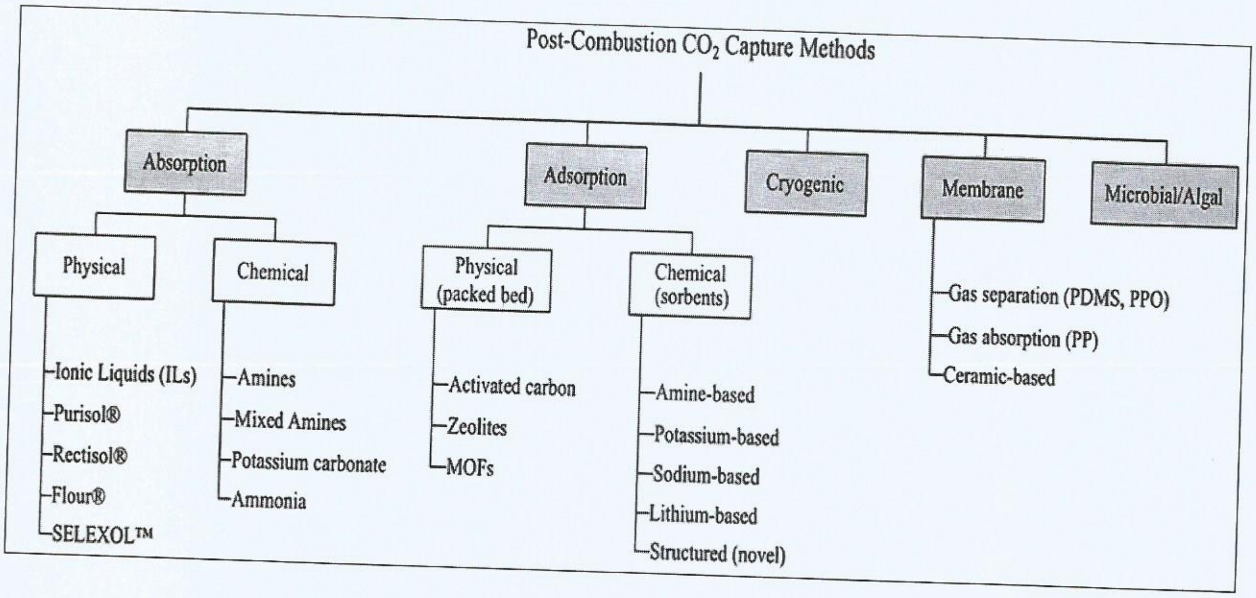


Fig. 1: Diagram of main carbon separation/capture methods in the post-combustion category. [MOFs: metal-organic frameworks; PDMS: polydimethylsiloxane; PPO: polyphenylene oxide; PP: polypropylene]

Among these techniques, absorption is more popular and is widely employed in the commercial post-combustion CO_2 capture plants. In this method, the flue-gas in the tall columns or towers (known as absorbers) is in contact with the solvent, which captures CO_2 from the flue-gas. The rate of CO_2 absorption with solvent is a crucial parameter in the chemical absorption processes. High absorption rate not only can reduce the capital costs of CO_2 capturing, but is also considered as an asset for an absorption process to be operated at the industrial scale[13,15]. s simple schematic diagram of CO_2 absorption and desorption columns in a typical carbon capture plant[2] as illustrate in figure 2.

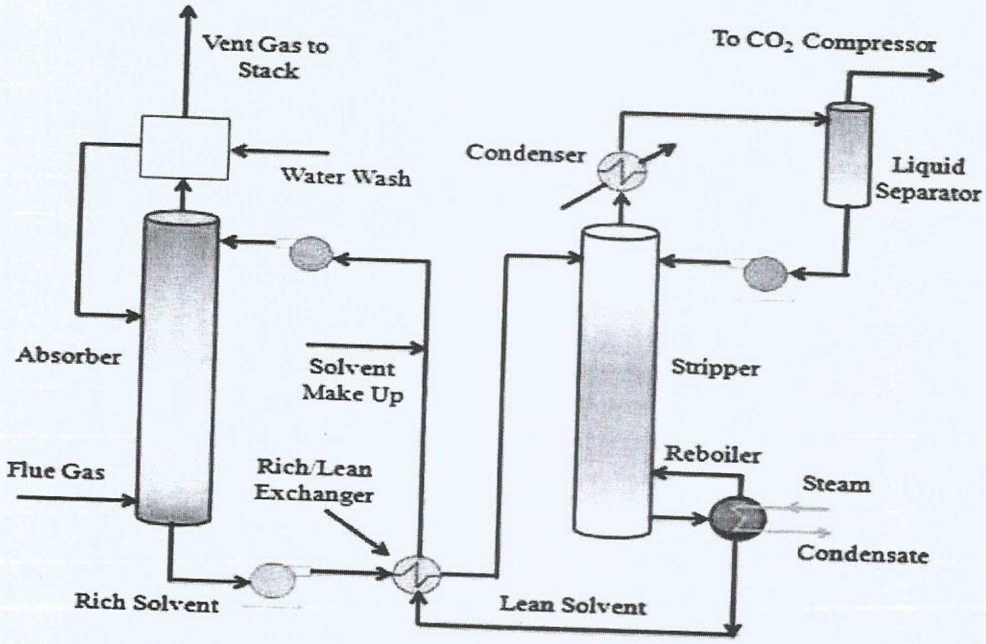


Fig. 2: Schematic figure of absorption/desorption columns in a CO_2 capture process

CO_2 capture with ionic liquids:

Ionic liquids usually consist of nitrogen-containing organic cations and inorganic anions[12]. A few examples of commonly used cations and anions of ILs are shown in Figure 3, where the Ri groups are often alkyl groups[16].

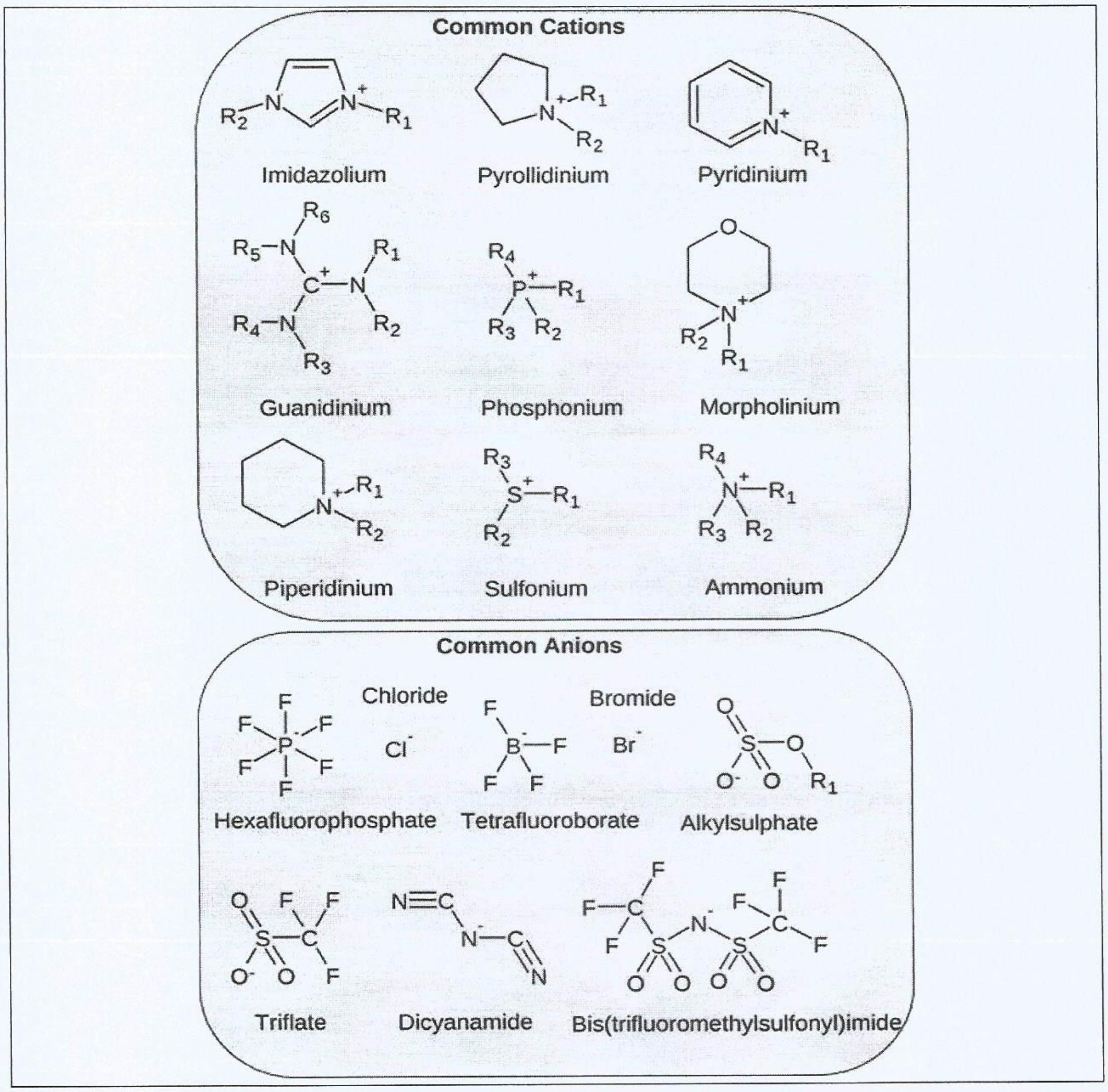


Fig. 3: Commonly used cations and anions of ionic liquids.

Conventional ILs capture the carbon through a physical absorption mechanism. Although adjusting cations/anions in the ILs can enhance the solubility of CO_2 in conventional ILs, compared to the current commercial carbon capture technologies such as amine-based solvents, their CO_2 capture capacity is still low[16].

CO_2 solubility in ILs:

Anions affect CO_2 solubility in ILs more than cations[17]. The CO_2 solubility in ten distinct imidazolium-based ILs was evaluated by Sudhir et al.[18]. They found that ILs with fluoroalkyl groups in the anion component (e.g., [methide] and [Tf_2N]) and nonfluorinated inorganic anions (e.g., [NO_3] and [DCA]) have the highest and lowest CO_2 solubility (table 4), respectively. Experiments indicated that solubility depends on anions. But CO_2 solubility is altered less by cation alkyls. When alkyl CO_2 solubility increases from butyl to octyl[19].

Table 1: Influence of anions in different ionic liquids[26]:

Anion	Nomenclature	Classification	Solubility of CO_2 in IL
Dicyanamide Nitrate	$[DCA]^-$ $[NO_3]^-$	Nonfluorinated anions	Low
Tetrafluoroborate	$[BF_4]^-$		
Hexafluorophosphate	$[PF_6]^-$		
Bis (trifluoromethyl sulfonyl) imide	$[TfO]^-$		
Trifuoromethanesulfonate	$[Tf_2N]^-$		
Tris (trifluoromethyl sulfonyl) methide	$[methide]^-$	Fluorinated anions	Relatively high

Molecular dynamic simulations show that the Imidazolium-based ILs have better CO_2 capture performance than phosphonium-based ILs with the same cation and anion. For example, [Tf_2N] is more efficient than [PF_6][20]. Zhang et al.[21] employed COSMO-RS to study IL CO_2 capture. They determined CO_2 Henry's law constants using cations and anions. [FEP] anion has the most CO_2 solubility, according to their studies. CO_2 is more soluble in [hmim][FEP] (imidazolium-based IL) than other ILs. Solubility, Henry's law constant, enthalpies, and entropies of nine gases dissolved in imidazolium-based IL ([bmim][PF_6]) were tested at up to 13 bar and at 10, 25, and 50°C. Carbon dioxide and oxygen have the highest solubilities in [bmim][PF_6]. [bmim] [PF_6] (relative to conventional organic solvents) is not a good solvent for industrial H_2, O_2, and CO processes (e.g., hydrogenation, oxidation, and hydroformylation) at high pressures[22].

CO_2 selectivity:

Due to the presence of gases and impurities in the flue-gas, the selectivity of CO_2 in ILs appears to be vital in carbon capture technique with ILs[23]. According to Zhang et al.[24], the large quadrupole moment of CO_2 provides traditional ILs with stronger CO_2 selectivity compared to other gases (such as CO, H_2, and O_2). Since flue-gas is a mixture of several gases, this high CO_2 selectivity is intriguing, since it suggests that ILs absorb CO_2 more readily than other gases. In general, CO_2 is more soluble in ILs than are N_2 and H_2. However, the solubility of H_2 and N_2 increases as the temperature increases[25,26]. In CO_2/H_2S systems, CO_2 selectivity is highly dependent on CO_2/H_2S feed ratio and CO_2 solubility is remarkably decreased in the presence of H_2S[27]. Ramdin et al.[28] showed that the selectivity of CO_2/CH_4 in different phosphonium and imidazolium-based ILs significantly decreases with increasing temperature. It seems important to optimise the CO_2 selectivity of ILs in terms of the gases they use and how they work. Most of the time, the selectivity of a CO_2 capture process makes it need more steps and, as a result, costs more to run and buy. For example, $CO_2/H_2S/CH_4$ systems that work at high temperatures need an extra step to separate H_2S and CH_4 from CO_2[29].

References:

1. F. Karadas, M. Atilhan and S. Aparicio, Energy Fuels 2010, 24, 5817–5828.

2. M. Aghaie, N. Rezaei and S. Zendehboudi, Renewable and Sustainable Energy Reviews 96 (2018) 502–525.

3. Energy Information Administration. International Energy Outlook; Energy Information Administration: Washington, D.C., 2008; http:// www.eia.doe.gov/oiaf/ieo.index.htm

4. Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. Advances in CO2 capture technology;The U.S. Department of Energy's carbon sequestration program. Int. J. Greenhouse Gas Control 2008, 2, 9–20.

5. Zelenak, V.; Badanicova, M.; Halamova, D. Amine-modified ordered mesoporous silica: Effect of pore size on carbon dioxide capture. Chem. Eng. J. 2008, 144, 336–342.

6. Bates, E. D.;Mayton, R. D.; Ntai, I.; Davis, J. H. CO2 capture by a task-specific ionic liquid. J. Am. Chem. Soc. 2002, 124, 926–927.

7. Anthony, J. L.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Feasibility of using ILs for carbon dioxide capture. Int. J. Environ. Technol. Manage. 2004, 4, 105–115.

8. Han, X.; Armstrong, D. W. ILs in separations. Acc. Chem. Res. 2007, 40, 1079–1086.

9. Berthod, A.; Ruiz-Angel, M. J.; Carda-Broch, S. ILs in separa- tion techniques. J. Chromatogr., A 2008, 1184, 6–18.

10. Rogers, R. D. Reflections on ILs. Nature 2007, 447, 917–918.

11. Brennecke, J. F.; Maginn, E. J. ILs: Innovative fluids for chemical processing. AIchE J. 2001, 47, 2384–2389

12. Hua Zhao et al, Physics and Chemistry of Liquids: An International Journal, 41:6, 545-557.

13. I. Sreedhara, Tanisha Nahara, A. Venugopalb, B. Srinivasc. Carbon capture by absorption – Path covered and ahead. Renewable and Sustainable Energy Reviews 76 (2017) 1080–1107,2017.

14. Chen Y, Mutelet F, Jaubert J-Nl. Modeling the solubility of carbon dioxide in imidazolium-based ionic liquids with the PC-SAFT equation of state. J Phys Chem B 2012;116(49):14375–88.

15. (a) C.A.T. Force, Advanced post-combustion CO2 capture, 2009.

(b) Freund H, Bauer J, Zeiser T, Emig G. Detailed simulation of transport processes in fixed-beds. Ind Eng Chem Res 2009;44(16):6423–34.

16. Ramdin M, de Loos TW, Vlugt TJ. State-of-the-art of CO2 capture with ionic liquids. Ind Eng Chem Res 2012;51(24):8149–77.

17. Cadena C, et al. Why is CO2 so soluble in imidazolium-based ionic liquids? J Am Chem Soc 2004;126(16):5300–8.

18. Aki SN, et al. High-pressure phase behavior of carbon dioxide with imidazolium based ionic liquids. J Phys Chem B 2004;108(52):2035.

19. Elena Torralba-Calleja, James Skinner, and David Gutiérrez-Tauste. CO2 Capture in Ionic Liquids: A Review of Solubilities and Experimental Methods. Hindawi Publishing Corporation Journal of Chemistry,2013.

20. YUE Z-g. et al., Molecular simulation on microstructure of ionic liquids in capture of CO2. 11(4); 2011.

21. Zhang X, Liu Z, Wang W. Screening of ionic liquids to capture CO2 by COSMO-RS and experiments. AIChE J 2008;54(10):2717–28.

22. Anthony JL, Maginn EJ, Brennecke JF. Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. J Phys Chem B 2002;106(29):7315–20.

23. Xu G, et al. An improved CO2 separation and purification system based on cryogenic separation and distillation theory. Energies 2014;7(5):3484–502.

24. Zhang X, et al. Carbon capture with ionic liquids: overview and progress. Energy Environ Sci 2012;5(5):6668–81.

25. Shifflett MB, Yokozeki A. Separation of carbon dioxide and sulfur dioxide using room-temperature ionic liquid [bmim][MeSO4]. Energy Fuels 2009;24(2):1001–8.

26. Kumełan J, Tuma D, Maurer G. Simultaneous solubility of carbon dioxide and hydrogen in the ionic liquid [hmim] [Tf 2 N]: experimental results and correlation. Fluid Phase Equilibria 2011; 311:9–16.

27. Shifflett MB, Yokozeki A. Separation of CO2 and H2S using room-temperature ionic liquid [bmim][PF6]. Fluid Phase Equilibria 2010;294(1):105–13.

28. Ramdin M, et al. Solubility of CO2 and CH4 in ionic liquids: ideal CO2/CH4 selectivity. Ind Eng Chem Res 2014;53(40):15427-35.

29. Ramdin M. CO2 Capture with ionic liquids: experiments and molecular simulations. TU Delft: Delft University of Tech 2015.

PRINCIPAL
Dhruba Chand Halder College
P.O.- D. Barasat, P.S.- Jo
South 24 Parganas, Pin- 743372