

Short Review: Different Type of Ionic Liquids for CO₂ Absorption

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Abstract— Carbon dioxide is the main greenhouse gas in the atmosphere. It is responsible for global warming. There are a number of technologies which have been developed that utilize the principle of CO₂ capture evolved via fossil fuel combustion and agricultural waste. There are three ways for capturing CO₂ from fossil fuel combustion: (a) after (post) combustion, (b) before (pre) combustion and (c) during combustion through modification (Oxy-fuel). Different technologies used for CO₂ capture include membranes, adsorption, absorption and other techniques such as reduction, cryogenic and mineralization methods. In this paper, we focus on different type of Ionic Liquids for CO₂ capture such as Conventional Ionic Liquids, Task-Specific Ionic Liquids (TSIL) & Poly (Ionic Liquids) (PILs) and discuss about advantages and disadvantages of the same against amine and ammonia solution.

Key words: Carbon Dioxide, Ionic Liquids, Absorption

I. INTRODUCTION

Carbon dioxide being the main greenhouse gas in the atmosphere is responsible for one of the most critical issues being faced by the world to-day i.e. global warming. This problem of global warming that everybody is concerned with since the initial spark of the industrial revolution is still an unresolved issue [1]. Weather change and severe environmental problems are seen as a direct result of the increased concentration levels of this greenhouse gas which disturbs the overall carbon cycle.

Greenhouse gas effect is increasing day by day in the atmosphere. This is proved by the fact that, the atmospheric concentration of carbon dioxide, was 280 ppm in 1750 which has increased to about 400 ppm in 2015. Global greenhouse gas emission data of 2015 reveals that CO₂ alone was responsible for around 77% emissions. CO₂ gas gets evolved from various different sources which include 56.6% from fossil fuels, 17.3% from deforestation and agriculture, 2.8% from other sources, with a further contribution from the production of methane and N₂O with an estimate of 14.3% and 7.9%, respectively.

The most noticeable greenhouse gas (GHG) is man-made “anthropogenic” emission of CO₂. Due to the increased utilization of energy and its production from fossil- or oil-based fuels, it left behind a negative impact on the overall ecosystem, what we call today as anthropogenic effect.

There are a number of technologies which have been developed that utilize the principle of CO₂ capture evolved via fossil fuel combustion and agricultural waste. The three main platforms for capturing CO₂ from a fossil fuel combustion system are: (a) after (post) combustion (b) before (pre) combustion and (c) during combustion through modification (Oxy-fuel). The different technologies used for CO₂ capture include membranes, adsorption, absorption and some other techniques such as reduction, cryogenic and mineralization methods [2]. Presently, amine and ammonia solutions are being used for CO₂ capture which gives high

absorption capacities due to the formation of chemical bonds [3].

Now a days, new technologies are being developed for CO₂ absorption utilizing Ionic Liquids. This is due to the limitations faced by amine and ammonia solutions which we will be discussing shortly. In ILs due to physical absorption mechanism, solvent recovery by heat require low energy for regeneration after absorption as compared to a mine and ammonia solutions. Further, efficiency is attained by their low vapor pressure, which allows them to regenerate and be reused with no appreciable losses into the gas stream [4, 5]. ILs are chemically stable and have high thermal stability. They degrade at temperatures greater than 300 °C [6]. Another advantage of ILs is that during their reaction, corrosion of the equipment as well as impurity formation is completely avoided. The flexible and tunable nature of ILs grant them with several chemical and physical properties superior than amine and ammonia solutions like better density and viscosity [7, 8], thermal decomposition temperature [9], heat capacity [10], surface tension [11] and lower toxicity & health effects [12, 13] and corrosion [14, 15]. The anions and cations combine to form IL for the capture of CO₂.

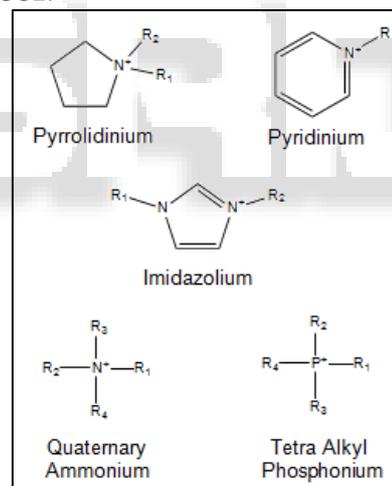


Fig. 1: Different cations

ILs are based on the combination of molten salts of cations and anions. Thus, it can be said that ILs are common salts. All ionic liquids have a melting point below 100 °C. Room temperature ionic liquids (RTIL) also called organic salts, fused salts, molten salts, non-aqueous ionic liquids, liquid organic salts are all liquid at room temperature [16]. ILs are defined as good green solvents due to their low vapor pressure. This lack of volatility essentially eliminates the possibility of solvent re-lease to the atmosphere [17]. ILs possess a number of excellent properties like gas solubility, hydrogen-bonding capability, conductivity, viscosity, density, Lewis acidity and hydrophobicity. The properties can be tuned by the alternative arrangement structure of the component ions which makes it possible for the solvent to have better properties.

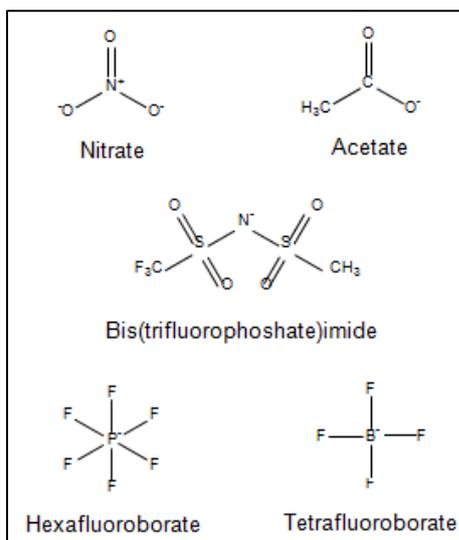


Fig. 2: Different anions

ILs mostly consist of phosphorus or nitrogen containing organic cations, with either non-cyclic or cyclic structures with attached medium-to-short length alkyl chains. Large number of cations combine with anions to form a compound which is liquid at room temperature. There are a number of different cations like pyridinium [Py], ammonium[N], sulfonium[S], imidazolium [IM], phosphonium [P] and inorganic & organic anions such as alkylsulfates [RSO₄]⁻, chloride [AlCl₄]⁻, bis(trifluoromethylsulfonyl) imide([Tf₂N]⁻), tetrafluoroborate [BF₄]⁻, alkylsulfonates [RSO₃]⁻, hexafluorophosphate [PF₆]⁻, aluminum as halides chloride [Cl]⁻, bromide [Br]⁻ or iodide [I]⁻, sulfate [SO₄]⁻, triflate ([TfO]⁻), nitrate [NO₃]⁻ and silver dicyanide [DCA]⁻ [17].

II. CONVENTIONAL IONIC LIQUIDS

The conventional ILs has been developed and specified after measuring the various effects like choice of cation and anion, temperature, and pressure. Results have shown high carbon dioxide solubility in what we now know as conventional ionic liquids. These type of Ionic Liquids do not have attached functional groups and consists of only cation and anion combination and thus, these behave as physical solvents [18, 19]. When low pressure CO₂ (1-2 bar) react with this IL, it results in decreased CO₂ concentration in the liquid phase. With increased pressure, absorption of CO₂ also increases. Gas solubility in this IL was measured with respect to the pressure difference. Thus, with increasing pressure CO₂ absorption in these ILs increases whereas with increase in temperature solubility or absorption decreases. The physical absorption mechanism is a result of the interaction between the CO₂ molecules with the IL, in which CO₂ generate a large “free space” with the ILs structure via van der Waals forces utilizing large quadrupole moment. CO₂ gas is highly soluble in these ILs than other gases such as H₂, CH₄, C₂H₄, C₂H₆, CO, O₂ and N₂ [20]. CO₂ demonstrate the strongest interactions and highest solubility with ILs followed by ethane and ethylene. Whereas, Oxygen and Argon show weak interactions and very low solubility with ILs.

A. Anion Effect on CO₂ Solubility

There are a number of fluorinate and non-fluorinate anions used for synthesizing ILs. The most important role of these anions is CO₂ capture via interaction between CO₂ and these anions. The interaction is proposed to be of Lewis acid-base type. In this process, CO₂ gas acts as a Lewis acid and the anion acts as Lewis base [21]. The axis of O=C=O molecules dissolved in ILs are perpendicularly oriented to the anion. CO₂ absorption is lower in nonfluorinated anions like [DCA]⁻ and [NO₃]⁻ [22], whereas it is highly soluble in fluorinated anions due to the presence of fluoroalkyl groups as in the case of [PF₆]⁻ and [BF₄]⁻ based ILs. The relatively high solubility CO₂ in [methide]⁻, [TfO]⁻, and [Tf₂N]⁻ have recently been reported due to the excellent interaction between CO₂ and these fluoroalkyl substituents consisting of the anion. CO₂ solubility increases with the increasing number of CF₃ groups in the anion [22].

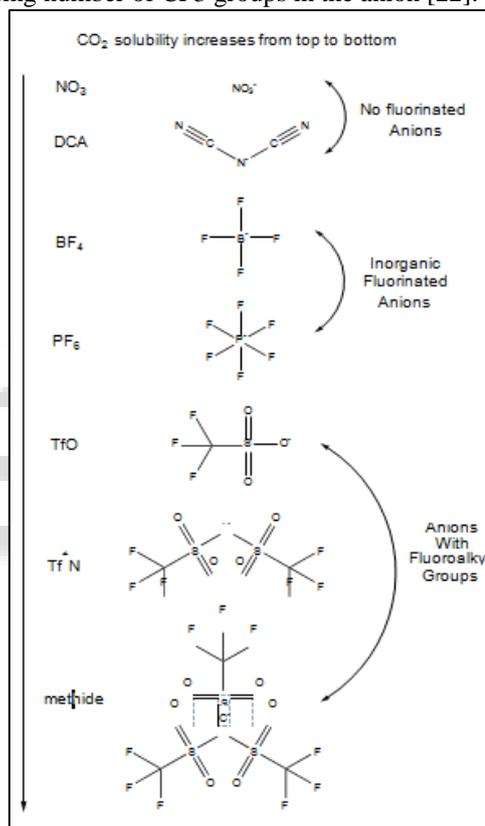


Fig. 3: CO₂ absorption capacity with different anions

B. Cation Effect on CO₂ Solubility

Mostly CO₂ absorbs on imidazolium based cation and these cations play a secondary role as compared with anions for CO₂ absorption. The most common cations based on imidazolium used for CO₂ absorption are Pyrrolidinium, Paridinium, Quaternary Ammonium and Tetra Alkyl Phosphonium. In imidazolium based cations, a long alkyl chain on the imidazolium ring is generally associated with better solubility. The long alkyl chain of the imidazolium ring is also associated with a more negative absorption entropy and a more negative absorption enthalpy [23]. The observed trend suggests a “free volume” mechanism, as the IL with a long alkyl chain exhibits a small density and a large “free volume” [24]. The effect of fluorination of a cation on CO₂ solubility in ionic liquids was examined with partially fluorinated alkyl chains on the cation. The cations

like [hmim][Tf2N] were directly compared to [C6H4F9mim][Tf2N] and it was concluded that fluorinating the last four carbons of the alkyl chain increases the CO₂ solubility [25].

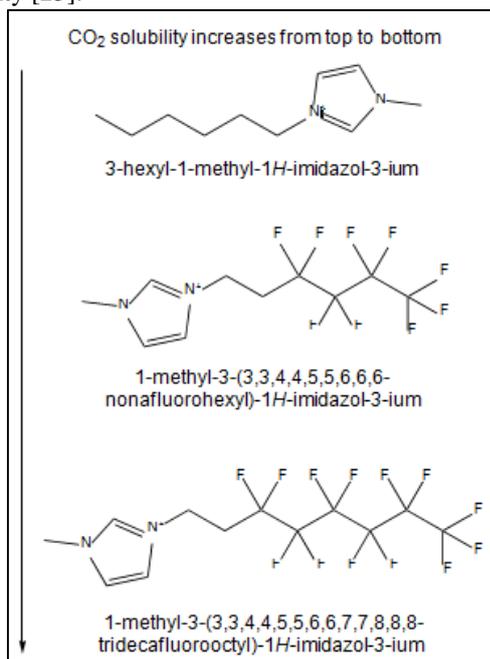


Figure 4: [hmim] cation with its fluorinated alkyl chain

III. TASK-SPECIFIC IONIC LIQUIDS (TSILs)

ILs are tailor-made solvents. It means their properties are arranged to suit the requirements of a particular process by tuning them for specific reactions via association of an anion with a cation [26]. These TSIL solvents mainly act as 'green' alternatives to several volatile organic solvents and allow us to produce environmental friendly technologies [27]. These ILs are synthesized specially for CO₂ absorption and demonstrate the concept of interaction of a solute with an IL in a specific fashion. The physical nature of TSILs allow for a high solubility of CO₂ as compared to organic conventional solvents such as benzene, cyclohexane, ethanol and heptane [28].

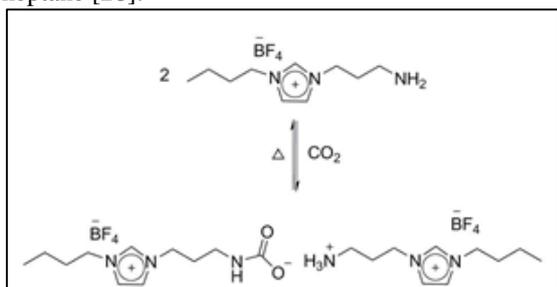


Fig. 5: Proposed reaction between TSIL and CO₂

In conventional ILs, the solubility of CO₂ is low due to their nature of physical interactions. Researchers have developed ILs functionalized with amine (-NH₂) groups which increase the solubility of CO₂. For example, a novel IL have been synthesized containing an amine-tethered, imidazolium-based IL that can absorb CO₂ with an efficiency of 7.4 wt%.

A. Functionalized Ionic Liquids

Functionalized ILs have high absorption capacity for CO₂. In these ILs, a physical absorption mechanism occurs.

Several research groups have developed a new concept reaping the advantages of ILs by combining them with functional groups to enable enhanced (chemical) binding of CO₂ to the absorbent. The functional groups intended for the anchoring should be carefully selected with respect to the thermodynamics and kinetics of a reversible process. First of all, CO₂ form bonds with functional groups according to the thermodynamics mechanism and the kinetics (K(T)abs) for the process should be sufficient to operate at a fast absorption rate. The absorption step is not highly exothermic, which allows the removal of CO₂ from the absorbent in the subsequent regeneration step without high energy requirements. Aqueous amine solutions attached to Conventional ILs have relatively large exothermic absorption enthalpies (-50 to -80 kJ mol⁻¹) [18, 29, 30]. Thus, functionalized ILs exhibiting lower exothermic absorption enthalpy seem very attractive from a thermodynamic point of view. There are a number of different functional groups that are attached to conventional ILs such as carboxylate, amine, combined (amine and acidic group) etc. Previous research on various alkanolamines show that, CO₂ undergoes a chemical interaction with amine function groups (-NH₂) when in alkanolamine solution, that gives a path for the designing of new kind of functional ionic liquids which contains -NH₂.

IV. POLY (IONIC LIQUIDS) (PILS)

Recent research has shown application of poly ILs as absorbents for CO₂ capture. In Poly (ionic liquids) (PILs) or polymerized ionic liquids, a chain of a polymer material is attached to ILs and this gives better stability and good absorption capacity [31–36]. Advantages of using PILs instead of conventional ILs are not only enhanced process ability, improved durability and mechanical stability, but also faster CO₂ absorption and desorption rates as compared to conventional ILs [37].

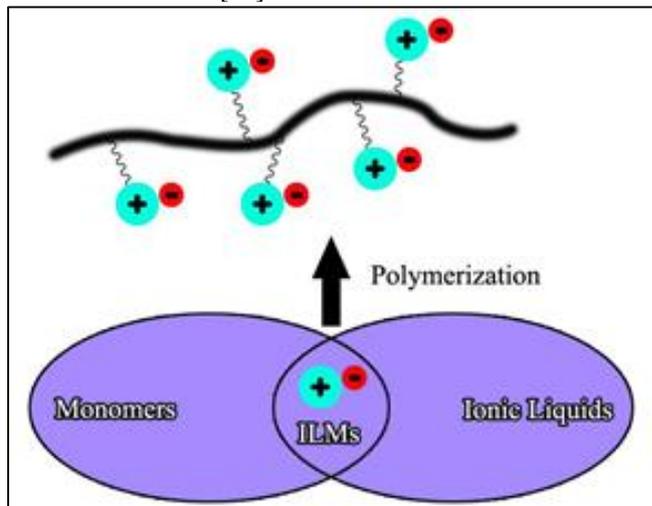


Fig. 6: Synthesis of Poly Ionic Liquids

PILs are polyelectrolyte type of ILs carrying IL as a functional group on the constitutional re-cycling unit (CRU), providing them with a combination of unique properties possessed by ILs along with the properties and flexibility of macromolecular structures. These enhanced novel properties and functions allow for large potential application of PILs as in the case of absorption of CO₂ [38].

PILs based on the combination of six different cations [MATMA]⁺, [VBBI]⁺, [BIEO]⁺, [VBMI]⁺, [MABI]⁺ and [VBTMA]⁺ with [BF₄]⁻ have been found. Another case which includes interaction of [VBBI]⁺ with different anions like [Tf₂N]⁻, o-benzoic sulfimide [Sac]⁻ and [PF₆]⁻ all demonstrate high absorption capacities [39].

V. CONCLUSION

Carbon dioxide as we saw being the main green-house gas in the atmosphere is responsible for global warming and thus its capture through physical absorption by ionic liquid is essential. Ionic liquids are nothing but a combination of cation and anion forming common salts. All ionic liquids have a melting point below 100 °C. They are defined as good green solvents because of their low vapor pressure. There are numerous excellent properties of ILs including gas solubility, hydrogen-bonding capability, conductivity, viscosity, density, Lewis acidity and hydrophobicity. In this overview, CO₂ capture by different type of ILs such as Conventional Ionic Liquids, Task-Specific Ionic Liquids (TSIL) and Poly (Ionic Liquids) (PILs) is compared. Conventional Ionic Liquids do not have attached functional groups and consist only of combination of cation and anion, thus, behaving as physical solvents. Conventional ILs give almost similar absorption capacity as compare to amine solutions. So, functionalized ILs were synthesized known as Task-Specific Ionic Liquids (TSIL) in which amine and alkyl chains are attached to conventional ILs. Hence, TSILs give good absorption capacity compared to amine solvents.

But, disadvantage of TSILs include high viscosity as compared to aqueous amine solutions, which slows absorption kinetics and increase the cost of operation. Poly Ionic Liquids (PILs) also give high CO₂ absorption rate but they are also very costly and environmentally not very suitable. Though all ILs are highly toxic, the toxicity depends on the toxicity of the cation present. Anion plays a secondary role as per toxicity of ILs is concerned. Toxicity trend for cations is: ammonium < pyridinium < imidazolium < triazolium < tetrazolium. Unfortunately sometimes in practical applications, pyridinium and ammonium based ILs have shown high toxicity as compared to imidazolium based ILs. Toxicity trend for anions is: [Br]⁻ < [DCA]⁻ < [Cl]⁻ < [BF₄]⁻ < [PF₆]⁻ < [Tf₂N]⁻. The fluorinated anions (Tf₂N and BF₄) thus are highly toxic.

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