

Review Article

CO₂ Capture in Ionic Liquids: A Review of Solubilities and Experimental Methods

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The growing concern of climate change and global warming has in turn given rise to a thriving research field dedicated to finding solutions. One particular area which has received considerable attention is the lowering of carbon dioxide emissions from large-scale sources, that is, fossil fuel power. This paper focuses on ionic liquids being used as novel media for CO₂ capture. In particular, solubility data and experimental techniques are used at a laboratory scale. Cited CO₂ absorption data for imidazolium-, pyrrolidinium-, pyridinium-, quaternary-ammonium-, and tetra-alkyl-phosphonium-based ionic liquids is reviewed, expressed as mole fractions (χ) of CO₂ to ionic liquid. The following experimental techniques are featured: gravimetric analysis, the pressure drop method, and the view-cell method.

1. Introduction

In recent years, increasing attention has been paid towards the worldwide climate change. Moreover, the exponential increase of carbon dioxide emissions into the atmosphere from the combustion of fossil fuels, making up the 86% of greenhouse gases [1], does not reflect a sustainable energy model. Entry into the Kyoto protocol has brought about the need to reduce anthropogenic emissions of CO₂. Thus carbon capture and storage (CCS) proves to be one of the most important initiatives to mitigate this global warming effect.

CCS is a concept based on the reduction of CO₂ emissions into the atmosphere from industrial processes, such as ammonia production, natural gas processing, or cement manufacture, to name a few. This review however will focus on CO₂ emissions from fossil fuel power plants, which is seen to be the main contributor to this effect [2]. It has been approximated that, if CCS is fully implemented, its potential by 2050 could be the total capture and storage of 236 billion tons of CO₂ [3]. An approach to CCS that holds the greatest promise is the sequestration of captured carbon dioxide, in suitable deep sedimentary formations, for example, oil and depleted gas reservoirs, coal beds, and saline deposits [4–7].

The challenge is to develop a technology which will allow us to accomplish this task in an environmental, economic, and efficient way in the next years [8–10]. However the need to assess the environmental impact is great. The potential risks of geological storage to humans and ecosystems are abundant and need to be carefully monitored. Leakage of sequestered CO₂ would be the main concern. This could happen along fault lines, ineffective confining layers, abandoned wells, and so forth. The pollution of groundwater and mineral deposits is also a problem and could have lethal effects on plant life and animals. A recent review by Manchao et al. [11] offers a detailed risk assessment of the CO₂ injection process and storage in geological formations, with a main focus on abandoned coal mines and coal seams.

An alternative to geological storage of CO₂ would be the direct conversion of CO₂ into a high-valued product after the initial capture; this is sometimes referred to as carbon capture and usage (CCU). CO₂ is used in many industries such as the food industry (carbonation of beverages), electronics industry (surface cleaning and semiconductor manufacture), and the chemical industry (polymers, plastics, and fertilizers). CCU is yet to be a mainstream technology so that many process aspects and methods are being published and reviewed [12, 13].

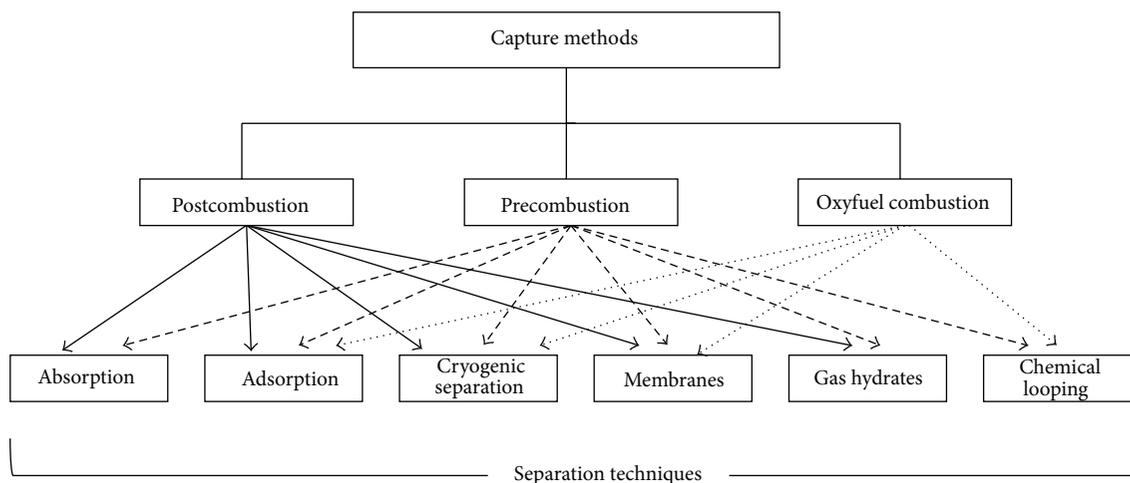


FIGURE 1: Possible techniques that can be used in conjunction with the processes of postcombustion, precombustion, and oxyfuel combustion.

2. State-of-the-Art CO₂ Capture Technologies

The capture of CO₂ is achieved through the use of specific materials that interact with the gas in one form or another. The materials that are used depend on the processes in which the flue gas is conditioned (Figure 1) [14].

There are three processes, each of which conditions the CO₂ for capture in different ways.

Postcombustion. The separation of CO₂ from the flue gas after the combustion of fuel. Air is typically used as the oxidant in this process; therefore the flue gas becomes largely diluted with nitrogen.

Precombustion. The hydrocarbon fuel (in this case gasified coal) is converted into carbon monoxide (CO) and hydrogen (H₂). This forms a synthesis gas. By using water shift conversion, CO is converted into CO₂. Finally the CO₂ is then separated from the H₂.

Oxyfuel CO₂ Combustion. It uses pure oxygen as the oxidant instead of air, creating a flue gas mainly consisting of high-concentrated CO₂ and steam.

Although CO₂ capture and separation is a well-known technology, this technology is just applied in a small scale, so that right now it is not commercially available for being used in large power stations. The most challenging obstacle to overcome in CCS and CCU is finding an effective technique that satisfies environmental and economic factors. Some of the currently studied techniques for capturing CO₂ from the three conditioning processes are as follows (Figure 1).

Absorption occurs within the bulk of the material via a chemical or physical interaction. Chemical absorbents react with the CO₂, forming covalent bonds between the molecules. The solvent can be habitually regenerated through heating and captured CO₂ is released. This mechanism can also be made highly selective by the introduction of specific chemical complexes. Typical compounds used in this process are amines, or ammonia-based solutions. Physical absorbents obey Henry's law, where gas solubility is directly proportional

to the partial pressure of the said gas in equilibrium, at a constant temperature. Typically this is at high CO₂ partial pressures and low temperatures. The interaction between CO₂ and the solvent is by nonchemical surface forces, that is, Van der Waals interaction. Regeneration of the solvent is achieved by increasing the temperature and lowering the pressure of the system [15]. Selexol and Rectisol are examples of physical absorbents that have been used in natural gas sweetening and synthesis gas treatment.

Adsorption, as opposed to absorption, takes place at the surface of the material. This interaction can also occur chemically (covalent bonding) or physically (Van der Waals). Typical adsorbents are solid materials with large surface areas, such as zeolites, activated carbons, metal oxides, silica gel, and ion-exchange resins. These can be used to capture CO₂ by separation, so that flue gas is put in contact with a bed of these adsorbents, allowing the CO₂ capture from the other gases which pass through. When the bed is fully saturated with CO₂, the flue gas is directed to a clean bed and the saturated bed is regenerated [16]. Three techniques can be employed to the adsorption mechanism: pressure swing adsorption (PSA) introduces the flue gas at high pressure until the concentration of CO₂ reaches equilibrium, then the pressure is lowered to regenerate the adsorbent, temperature swing adsorption (TSA) increases the temperature to regenerate the adsorbent, and electric swing adsorption (ESA) is where a low-voltage electric current is passed through the sorbent to regenerate. Adsorption is not yet considered practical for large-scale applications as the CO₂ selectivity in current sorbents is low. However, recently new sorbents are being investigated such as metal-organic frameworks and functionalised fibrous matrices that show some promise for the future of this particular technique.

Membrane separation technology is based on the interaction of specific gases with the membrane material by a physical or chemical interaction. Through modifying the material, the rate at which the gases pass through can be controlled. There are wide varieties of membranes available for gas separation, including polymeric membranes, zeolites,

and porous inorganic membranes, some of which are used in an industrial scale and have the possibility of being implemented into the process of CO₂ capture. However achieving high degrees of CO₂ separation in one single stage has so far proved to be difficult; therefore, having to rely on multiple stages has led to increasing energy consumption and cost. An alternative approach is to use porous membranes as platforms for absorption and stripping. Here a liquid (typically aqueous amine solutions) provides the selectivity towards the gases. As the flue gas moves through the membrane, the liquid selects and captures the CO₂ [17].

Cryogenic Separation is a technique based on cooling and condensation. This has the advantage of enabling the direct production of liquid CO₂, benefiting transportation options. Although a major disadvantage of cryogenic technology in this respect is the high amounts of energy required to provide cooling for the process, this is especially prominent in low-concentration gas streams [18]. This technique is more suited to high-concentration and high-pressure gases, such as in oxyfuel combustion and precombustion.

Within these techniques lie the materials with which research pathways aim to develop more effective CO₂ capture mechanisms. Currently the postcombustion process is the most widely researched area for reducing CO₂ emissions from power stations. This is mainly because it can be retrofitted to existing combustion systems without a great deal of modification, unlike the other two processes. The flue gas emitted, from the postcombustion of fossil fuels in power stations, has a total pressure of 1-2 bars with a CO₂ concentration of approximately 15%. As this process creates low CO₂ concentration and partial pressures, strong solvents have to be used to capture the CO₂, resulting in a large energy input to regenerate the solvent for further use. This creates the technical challenge of finding an efficient, cost-effective, and low-energy-demanding capture mechanism using novel materials.

2.1. Aqueous Amines Used in Postcombustion. The conventional technologies used in this postcombustion process are solvent-based chemical absorbers. The common chemical solvents used for separation are aqueous amines, which are ammonia derivatives, where one or more of the hydrogen atoms have been replaced by alkyl groups. Some common amines used in this process are (Table 1) monoethanolamine (MEA) [19], methyldiethanolamine (MDEA) [20], and diethanolamine (DEA) [21]. Aqueous amines are stated as “conventional absorbers” because they are well-known solvents used in the oil and gas industries, dating back to the 1930s; for example, Gregory and Scharmann investigated the implementation of amine CO₂ scrubbers in a hydrogenation plant of the Standard Oil Company of Louisiana in 1937. Today the aqueous amine absorption technology is still used in natural gas sweetening (removal of acidic gases, for example, hydrogen sulphide and carbon dioxide) and has also been applied to some small-scale fossil fuel power plants [22, 23], for example, Fundación Ciudad de la Energía (CIUDEN), Alstom power plant, and so forth.

Briefly, post-combustion capture with amines, seen in Figure 2, involves the CO₂ being removed by circulating a

flue gas stream into a chamber containing an aqueous amine solution. In the case of primary amines like MEA, the CO₂ is captured by a chemical absorption process in which the CO₂ reacts with the amine in the form of a carbamate [24]. With secondary and tertiary amines, which do not possess a hydrogen atom attached to a nitrogen atom, they react with CO₂ in the form of bicarbonate through hydrolysis. This is a reversible reaction, and at high temperatures the captured CO₂ is released and the amine solution recycled. Piperazine (PIPA) is commonly used to improve reaction kinetics of secondary and tertiary amines in the form of an additive; this is because the heat of reaction to form a bicarbonate is low, causing more heat being needed for regeneration and thus higher costs [25].

Amines are so effective for CO₂ capture thanks to some of their properties such as high reactivity with CO₂, high absorbing capacity (in terms of mass of CO₂), relatively high thermal stability, and CO₂ selectivity [26]. However there are inherent disadvantages linked with amines, which need to be addressed in order to make a valid and efficient process for CO₂ capture. These disadvantages come in the form of high vapour pressure, corrosive nature, and high-energy input for regeneration. The high vapour pressure allows emission of amine gases into the air upon heating. These gases are unstable in nature thus giving them the possibility of producing dangerous toxins such as nitrosamines, nitramines, and amides. Nitrosamines are of the most concern as they are carcinogenic and toxic to humans even at low levels [27]. Amines are also corrosive, especially MEA. They take part in reactions in which waste forms and can eventually corrode the equipment, Kittel et al. [28] investigated the effects of MEA operating pilot plants and found that areas made of carbon steel had corrosion rates of 1 mm year⁻¹; so besides environmental impacts, expense on a large industrial scale is another issue. The recycling/regeneration process leads to high-energy consumption in order to break the chemical bonds formed between the CO₂ and amine [29]. This process also causes degradation of the amine which limits its CO₂ capture rate, causing them to be replaced frequently.

Much research has gone into developing new solvents with the foresight of being superior to amines. The factors that would allow new solvents to perform better than amines are lower cost, lower volatility, better thermal stability, less degradation, low corrosive nature, and low energy needed for regeneration and adaptability to an existing system. Although amines have high CO₂ solubility and selectivity, environmental and economic effects are taken into consideration when selecting the criteria for the most suited CO₂ capture mechanism. While continued research into improving the performance of these mature technologies is expected, research into novel materials and technologies could produce the significant breakthroughs required to minimise the environmental and energy penalties of capture.

2.2. Ionic Liquid Media for CO₂ Capture. One of these advanced R&D pathways currently conveying great potential in the field of alternative technologies is ionic liquids (ILs). ILs are commonly defined as materials that are comprised of large organic cations and organic/inorganic anions, which

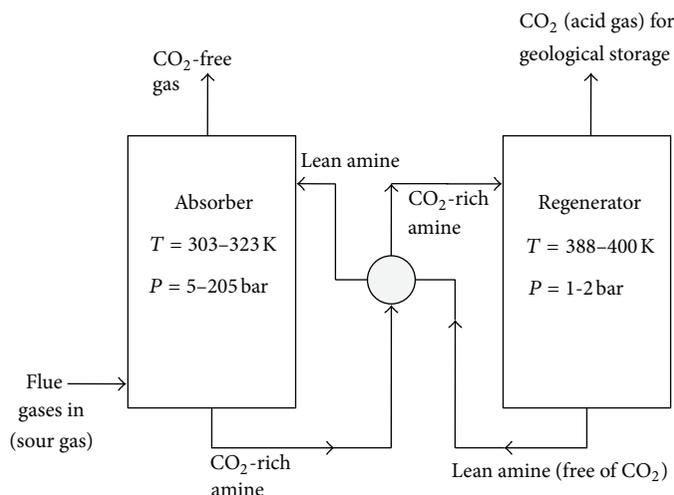


FIGURE 2: Conceptual scheme for CO₂ absorption using amine-based chemical absorption.

TABLE 1: Chemical structures of commonly used amines.

| Amine | Acronym | Structure |
|----------------------|---------|---|
| Monoethanolamine | MEA | $\begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ |
| Methyldiethanolamine | MDEA | $\begin{array}{c} \text{HO}-\text{H}_2\text{C}-\text{H}_2\text{C}-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH} \\ \\ \text{CH}_3 \end{array}$ |
| Diethanolamine | DEA | $\begin{array}{c} \text{HO}-\text{H}_2\text{C}-\text{H}_2\text{C}-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH} \\ \\ \text{H} \end{array}$ |
| Piperazine | PIPA | $\begin{array}{c} \text{H} \\ \\ \text{N} \\ \\ \text{C}_4\text{H}_8 \\ \\ \text{N} \\ \\ \text{H} \end{array}$ |

demonstrate melting points below 100°C [30]. To date a wide range of ILs has been synthesised through different combinations of anions and cations. It has been stated that the theoretical number of potential ILs is to the order of 10¹⁸ [31]. An example of some of the common cations and anions used in IL synthesis can be seen in Table 2.

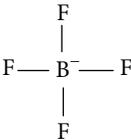
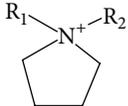
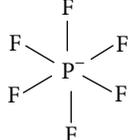
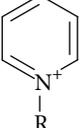
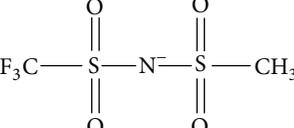
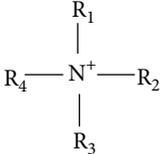
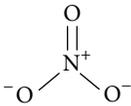
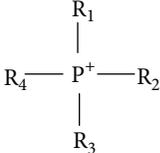
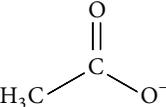
ILs possess several unique and diverse characteristics such as high thermal and chemical stability, low vapour pressure, large electrochemical window, tuneable/designer nature, and excellent solvent properties for a range of polar and nonpolar compounds. It is due to these characteristics that research into developing and implementing ILs over the past decade has spanned into many sectors of industry [32], for applications such as electrolytes [33], solar cells [34], lubricants [35], electropolishing and electroplating [36], and biomass processing [37], to name a few. This has become possible due to the large number of ILs that can be synthesised

in the lab [38–40] and purchased commercially. Companies like BASF, Merck, Sigma-Aldrich, Solvionic, Sachem, and IoLitec provide basic ILs and can also aid in the design and development of ILs for specific tasks. Therefore these compounds have created exciting new media for emerging technological applications already commercially available.

2.3. Ionic Liquids in the Scope of CO₂ Capture. The aforementioned characteristics are particularly advantageous when applying ILs as solvents for CO₂ capture in comparison to current aqueous amine technology:

- (i) less energy is required when regenerating ILs to remove the captured CO₂ [41] due to their physical absorption mechanism,
- (ii) further efficiency is attained by their low vapour pressure, which allows them to be regenerated and

TABLE 2: Structures of common IL cations and anions.

| Cation | Structure | Anion | Structure |
|-------------------------|--|------------------------------|--|
| Imidazolium |  | Tetrafluoroborate |  |
| Pyrrolidinium |  | Hexafluoroborate |  |
| Pyridinium |  | Bis(trifluorophosphate)imide |  |
| Quaternary Ammonium |  | Nitrate |  |
| Tetra Alkyl Phosphonium |  | Acetate |  |

reused with no appreciable losses into the gas stream [42, 43],

- (iii) ILs have a high thermal and chemical stability; typically they degrade at temperatures $>300^{\circ}\text{C}$ [44] avoiding their reaction with impurities and causing corrosion to the equipment,
- (iv) the tuneable and designer nature of ILs offers many options concerning the physicochemical properties (viscosities and densities [45–47], heat capacities [48], thermal decomposition temperatures [49], surface tension [50], toxicity and health issues [51, 52], and corrosion [53, 54]) in the sense that the anions and cations can be manipulated to create an IL for a specific task.

This designer aspect can also be applied to the anion or cation in the sense that various chemical functionalities and structures can be attached, allowing properties such as absorption and viscosity to be controlled. These are commonly referred to as task-specific ionic liquids (TSILs). Generally ILs fulfil many of the major requirements stated in the green-chemistry principles stated by Anastas and Warner [55], in that they offer a new approach to industrial/chemical processes whereby steps are taken to eliminate hazardous waste in a system before a by-product is formed, thus neglecting the use of volatile organic solvent.

Most development concerning ILs for CO_2 capture is at present conducted at laboratory scale, while other technological applications are already in use as it was mentioned before. Conversely, their industrial application and implementation is being constantly investigated in areas of post-combustion [56]. For industrial-scale integration, it is necessary to achieve extensive knowledge of their physical and chemical properties. Therefore the need for experimental techniques and data is critical in enabling the ionic liquid to be the green, viable, and economic carbon capture technique of the future.

The solubility of CO_2 in ILs compared to other gases such as methane and nitrogen enables ILs to separate CO_2 from the source, be it a power plants' flue gas or natural gas. Even when there are low concentrations of CO_2 in a mixed gas, the IL can be designed to incorporate a functional group, such as an amine, thus rendering it task specific. The capacity for CO_2 solubility in ILs originates from the asymmetrical combination of the anion and cation, which results from short-range repulsive forces between their ionic shells. Therefore the more incompatible the ionic constituents are the greater the solubility is.

2.4. Conventional Ionic Liquids. Over the past decade, and at present, research has been built upon measuring the effects of variables such as pressure, temperature, and anion/cation choice. Results have shown high carbon dioxide solubility in what have become known as conventional ionic liquids. They

TABLE 3: Influence of anions in different ionic liquids.

| Anion | Nomenclature | Classification | Solubility of CO ₂ in IL |
|---------------------------------------|----------------------------------|-----------------------|-------------------------------------|
| Dicyanamide | [DCA] ⁻ | Nonfluorinated anions | Low |
| Nitrate | [NO ₃] ⁻ | | |
| Tetrafluoroborate | [BF ₄] ⁻ | Fluorinated anions | Relatively high |
| Hexafluorophosphate | [PF ₆] ⁻ | | |
| Trifluoromethanesulfonate | [TfO] ⁻ | | |
| Bis(trifluoromethylsulfonyl) imide | [Tf ₂ N] ⁻ | | |
| Tris(trifluoromethylsulfonyl) methide | [methide] ⁻ | | |

are defined as ILs that do not possess an attached functional group and have been reported by many as portraying the typical behaviour of physical solvents [57–59]. This is evident when low-pressure CO₂ (1-2 bars) is put in contact with the IL, resulting in low CO₂ concentrations in the liquid phase. As the increment of pressure increases, typically to up to 100 bar, the concentration of absorbed CO₂ increases. Thus displaying the general characteristics of a physical absorber. As a rule, the solubility of CO₂ in ILs increases with increasing pressure and decreases with increasing temperature. The physical absorption mechanism is a result of the interaction between the CO₂ molecules and the IL, in which the CO₂ occupies the “free space” within the ILs structure through a large quadrupole moment and Van der Waals forces.

2.4.1. Anion and Cation Effects. In order to create an optimal process for capturing CO₂ in ILs, assessment of the essential building blocks, that is, cation/anion combinations, needs to be investigated. Synthesising ILs that encompass CO₂-philic groups on the anion such as carbonyls or fluorines has proven to increase CO₂ capture [60]. In the past decade studies have shown that the origin of high solubility is strongly dependent on the choice of anion [61]. Aki et al. [62] investigated the influence of the anion with seven ILs. They all contained the 1-butyl-3-methylimidazolium [Bmim] cation. The results are shown in Table 3.

Aki and coworkers also systematically investigated the effects of the cation on CO₂ solubility; they found that, in general, the increase of the alkyl chain on the cation resulted in a slight increase in solubility, which became more apparent at higher pressures. The effect of increasing the alkyl chain results in the increased volume available for CO₂ interaction. Muldoon et al. [60] concluded that adding partially fluorinated alkyl chains on the imidazolium cation does increase CO₂ solubility. They compared [hmim][Tf₂N] directly to [C₆H₄F₉mim][Tf₂N] and found that this increased solubility was due to fluorinating the last four carbons of the alkyl chain. Research on IL CO₂ solubility, in general, has focused intensively on imidazolium-based structures. However some groups have focused on using different cations. Recently Carvalho et al. [63] reported CO₂ solubilities in two phosphonium-based ILs, [THTDP][Tf₂N] and [THTDP][Cl]. They found exceptionally high solubility measurements exceeding those of current imidazolium-based ILs; they go on to conclude that their study shows the highest

recorded solubility observed without chemical interactions in the absorption process. Although imidazolium is the most stable and commercially available cation of choice, it is evident that there are further enhancements and possibilities that can be developed from other bases.

To provide further insight into the interactions between CO₂ and the constituent anions and cations of RTILs, researches using spectroscopic approaches and molecular simulations have been made. Of which has broadened our understanding of absorption mechanisms and structure-property relationships, Kazarian et al. [64] used ATR-FTIR spectroscopy to analyse the specific interactions of CO₂ and ILs [Bmim][BF₄] and [Bmim][PF₆]. They saw evidence of chemical interactions between the anion [PF₆]⁻ and CO₂. They concluded that they observed weak Lewis acid-base interactions, where the anion acts as a Lewis base. ILs by their nature have intrinsic acid-base properties. These properties can be enhanced with the addition of acidic functions like carbonic or halide acids; likewise, basic functions like amino and fluorine groups can be added. This has shown to create specific Lewis acid-base chemical interactions between CO₂ and the IL.

As it can be seen in Tables 4 and 5, fluorination of the anion and in some cases the cation can improve CO₂ solubility in RTILs. However the associated disadvantages are cost increase, poor degradability, and a negative environmental impact [65]. Therefore paths to develop ILs with enhanced CO₂ solubility without fluorination are also being investigated.

Due to certain limitations of conventional ionic liquid systems, where physical absorption takes place and high solubility is only seen at high pressures, numerous research groups have been developing the ILs designer character, by covalently tethering a functional group to either or both anion or cation. This resulting functionalized IL is capable of chemically binding to CO₂, adding chemical absorption to the capture mechanism.

[Bmim][Ac] has been found to be one of these RTILs in which a chemical complexation with CO₂ occurs [66]. In 2008, Yokozeki et al. [67] completed CO₂ solubility tests for 18 RTILs, eight of which showed chemical absorption mechanisms. They found that RTILs that show strong chemical absorption with CO₂ all contain the anion [X-COO]⁻, that is, [Bmim][Ac], [Emim][Ac], [Bmim][PRO], [Bmim][IBS], [Bmim][TMA], and [Bmim][LEU]. Their results can be seen

TABLE 4: CO₂ solubility data for imidazolium-based ionic liquids.

| Ionic liquid | Acronym | T (K) | P (bar) | χ_{CO_2} | References |
|---|---------------------------------------|--------|---------|----------------------|----------------------------|
| 1-N-Octyl-3-methylimidazolium hexafluorophosphate | C ₈ mim[PF ₆] | 313 | 92.67 | 0.7550 | Blanchard et al. 2001 [86] |
| 1-N-Butyl-3-methylimidazolium nitrate | Bmim[NO ₃] | 323 | 92.62 | 0.5300 | Blanchard et al. 2001 [86] |
| 1-N-Octyl-3-methylimidazolium tetrafluoroborate | C ₈ mim[BF ₄] | 313 | 92.90 | 0.7080 | Blanchard et al. 2001 [86] |
| 1-Ethyl-3-methylimidazolium ethyl sulfate | Emim[EtSO ₄] | 333 | 94.61 | 0.4570 | Blanchard et al. 2001 [86] |
| 1-Butyl,3-methyl-imidazolium hexafluorophosphate | Bmim[PF ₆] | 313 | 96.67 | 0.7290 | Blanchard et al. 2001 [86] |
| 1-Butyl-3-methylimidazolium acetate | C ₄ mim[Ac] | 333.3 | 12.75 | 0.2510 | Carvalho et al. 2009 [87] |
| | | 323.09 | 755.26 | 0.5990 | Carvalho et al. 2009 [87] |
| 1-Butyl-3-methylimidazolium trifluoroacetate | C ₄ mim[TFA] | 293.43 | 9.79 | 0.2250 | Carvalho et al. 2009 [87] |
| | | 293.59 | 436.25 | 0.6790 | Carvalho et al. 2009 [87] |
| 1-Butyl,3-methyl-imidazolium tetrafluoroborate | Bmim[BF ₄] | 303 | 10 | 0.1461 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0895 | Galan-Sanchez 2008 [88] |
| 1-Octyl,3-methyl-imidazolium tetrafluoroborate | Omim[BF ₄] | 303 | 10 | 0.1873 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.1213 | Galan-Sanchez 2008 [88] |
| 1-Butyl,3-methyl-imidazolium dicyanamide | Bmim[DCA] | 303 | 10 | 0.1434 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0997 | Galan-Sanchez 2008 [88] |
| 1-Butyl-3-methylimidazolium thiocyanate | Bmim[SCN] | 303 | 10 | 0.0978 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0664 | Galan-Sanchez 2008 [88] |
| 1-Butyl,3-methyl-imidazolium hexafluorophosphate | Bmim[PF ₆] | 303 | 10 | 0.1662 | Galan-Sanchez 2008 [88] |
| 1-Butyl,3-methyl-imidazolium hexafluorophosphate | Bmim[PF ₆] | 333 | 10 | 0.1012 | Galan-Sanchez 2008 [88] |
| 1-Butyl-3-methylimidazolium methylsulfate | Bmim[MeSO ₄] | 303 | 10 | 0.1190 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0733 | Galan-Sanchez 2008 [88] |
| 1-N-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | Emim[NTf ₂] | 303 | 10 | 0.2257 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.1446 | Galan-Sanchez 2008 [88] |
| 1-Butyl,3-methyl-imidazolium hexafluorophosphate | Bmim[PF ₆] | 298.15 | 6.66 | 0.122 | Kim et al. 2005 [89] |
| 1-Hexyl-3-methylimidazolium hexafluorophosphate | C ₆ mim[PF ₆] | 298.15 | 9.27 | 0.167 | Kim et al. 2005 [89] |
| 1-Ethyl-3-methylimidazolium tetrafluoroborate | Emim[BF ₄] | 298.15 | 8.75 | 0.106 | Kim et al. 2005 [89] |
| 1-Hexyl-3-methylimidazolium tetrafluoroborate | C ₆ mim[BF ₄] | 298.15 | 8.99 | 0.163 | Kim et al. 2005 [89] |
| 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | Emim[Tf ₂ N] | 298.15 | 9.03 | 0.209 | Kim et al. 2005 [89] |
| 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | C ₆ mim[Tf ₂ N] | 298.15 | 8.59 | 0.236 | Kim et al. 2005 [89] |
| 1-Ethyl-3-methylimidazolium trifluoromethane-sulfonate | C ₂ mim[TfO] | 303.85 | 149 | 0.6260 | Shin and Lee 2008 [90] |
| | | 303.85 | 15 | 0.2610 | Shin and Lee 2008 [90] |
| 1-Butyl-3-methylimidazolium trifluoromethane-sulfonate | C ₄ mim[TfO] | 303.85 | 160 | 0.6720 | Shin and Lee 2008 [90] |
| | | 303.85 | 11.5 | 0.2730 | Shin and Lee 2008 [90] |
| 1-Hexyl-3-methylimidazolium trifluoromethane-sulfonate | C ₆ mim[TfO] | 303.85 | 180 | 0.7170 | Shin and Lee 2008 [90] |
| | | 303.85 | 12.5 | 0.2880 | Shin and Lee 2008 [90] |
| 1-Octyl-3-methylimidazolium trifluoromethane-sulfonate | C ₈ mim[TfO] | 303.85 | 180 | 0.7410 | Shin and Lee 2008 [90] |
| | | 303.85 | 15.8 | 0.3440 | Shin and Lee 2008 [90] |
| 1,3-Dimethylimidazolium methylphosphonate | Dmim[MP] | 313.35 | 95 | 0.4750 | Revelli et al. 2010 [91] |
| | | 313.45 | 34 | 0.1620 | Revelli et al. 2010 [91] |
| 1-Butyl,3-methyl-imidazolium tetrafluoroborate | Bmim[BF ₄] | 293.65 | 73 | 0.6100 | Revelli et al. 2010 [91] |
| | | 293.25 | 10.5 | 0.1410 | Revelli et al. 2010 [91] |
| 1-Butyl-3-methylimidazolium thiocyanate | Bmim[SCN] | 313.65 | 99 | 0.4300 | Revelli et al. 2010 [91] |
| | | 292.35 | 10.5 | 0.1260 | Revelli et al. 2010 [91] |
| 1-Ethyl-3-methylimidazolium trifluoroacetate | Emim[TFA] | 298.1 | 19.99 | 0.2820 | Yokozeki et al. 2008 [67] |
| 1-Ethyl-3-methylimidazolium acetate | Emim[Ac] | 298.1 | 19.99 | 0.4280 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium trifluoroacetate | Bmim[TFA] | 298.1 | 19.99 | 0.3010 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium acetate | Bmim[Ac] | 298.1 | 19.99 | 0.4550 | Yokozeki et al. 2008 [67] |

TABLE 4: Continued.

| Ionic liquid | Acronym | T (K) | P (bar) | χ_{CO_2} | References |
|---|-------------------------------|---------|-----------|----------------------|---------------------------|
| 1-Ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide | Emim[Tf_2N] | 298.1 | 19.99 | 0.3900 | Yokozeki et al. 2008 [67] |
| 1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate | Hmim[FAP] | 298.1 | 19.99 | 0.4930 | Yokozeki et al. 2008 [67] |
| 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | Hmim[Tf_2N] | 298.1 | 19.74 | 0.4330 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate | Bmim[TFES] | 298 | 19.9 | 0.2850 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium propionate | Bmim[PRO] | 298.2 | 19.9 | 0.3900 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium isobutyrate | Bmim[ISB] | 298.2 | 20 | 0.4030 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium trimethylacetate | Bmim[TMA] | 298.1 | 19.9 | 0.4310 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium levulinate | Bmim[LEV] | 298.1 | 19.9 | 0.4600 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium succinamate | Bmim[SUC] | 298.1 | 19.9 | 0.2320 | Yokozeki et al. 2008 [67] |
| Bis(1-butyl-3-methylimidazolium) iminodiacetate | Bmim ₂ [IDA] | 298.1 | 19.9 | 0.3950 | Yokozeki et al. 2008 [67] |
| 1-Butyl-3-methylimidazolium iminoacetic acid acetate | Bmim[IAAc] | 298.1 | 19.9 | 0.1910 | Yokozeki et al. 2008 [67] |
| 1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate | Hmim[FEP] | 283.5 | 17.99 | 0.5170 | Zhang et al. 2008 [92] |

TABLE 5: CO_2 solubility for ammonium ionic liquids.

| Ionic liquid | Acronym | T (K) | P (bar) | χ_{CO_2} | References |
|---|----------|---------|-----------|----------------------|-------------------------|
| Bis(2-hydroxyethyl)-ammonium acetate | (BHEAA) | 298.15 | 15.15 | 0.1076 | Kurnia et al. 2009 [78] |
| | | 298.15 | 5.48 | 0.0391 | Kurnia et al. 2009 [78] |
| 2-Hydroxy-N-(2-hydroxyethyl)-N-methylethanaminium acetate | (HHEMEA) | 298.15 | 15.42 | 0.0761 | Kurnia et al. 2009 [78] |
| | | 298.15 | 6.15 | 0.0300 | Kurnia et al. 2009 [78] |
| Bis(2-hydroxyethyl)-ammonium lactate | (BHEAL) | 298.15 | 15.12 | 0.0835 | Kurnia et al. 2009 [78] |
| | | 298.15 | 3.46 | 0.0192 | Kurnia et al. 2009 [78] |
| 2-Hydroxy-N-(2-hydroxyethyl)-N-methylethanaminium lactate | (HHEMEL) | 298.15 | 15.23 | 0.0776 | Kurnia et al. 2009 [78] |
| | | 298.15 | 3.48 | 0.0179 | Kurnia et al. 2009 [78] |
| 2-Hydroxy ethyl ammonium formate | (HEF) | 303 | 78.9 | 0.3083 | Yuan et al. 2007 [93] |
| | | 303 | 4.4 | 0.0340 | Yuan et al. 2007 [93] |
| 2-Hydroxy ethyl ammonium acetate | (HEA) | 303 | 90.1 | 0.4009 | Yuan et al. 2007 [93] |
| | | 303 | 8.9 | 0.0687 | Yuan et al. 2007 [93] |
| 2-Hydroxy ethyl ammonium lactate | (HEL) | 303 | 82 | 0.2422 | Yuan et al. 2007 [93] |
| | | 303 | 7.8 | 0.0410 | Yuan et al. 2007 [93] |
| Tri-(2-hydroxyethyl)-ammonium acetate | (THEAA) | 303 | 82.5 | 0.2561 | Yuan et al. 2007 [93] |
| | | 303 | 10.3 | 0.0534 | Yuan et al. 2007 [93] |
| Tri-(2-hydroxyethyl)-ammonium lactate | (THEAL) | 303 | 70.9 | 0.4617 | Yuan et al. 2007 [93] |
| | | 303 | 9.6 | 0.1006 | Yuan et al. 2007 [93] |
| 2-(2-Hydroxyethoxy)-ammonium formate | (HEAF) | 303 | 72.8 | 0.1907 | Yuan et al. 2007 [93] |
| | | 303 | 6.6 | 0.0300 | Yuan et al. 2007 [93] |
| 2-(2-Hydroxyethoxy)-ammonium acetate | (HEAA) | 303 | 65.7 | 0.4860 | Yuan et al. 2007 [93] |
| | | 303 | 7.6 | 0.0889 | Yuan et al. 2007 [93] |
| 2-(2-Hydroxyethoxy)-ammonium lactate | (HEAL) | 303 | 73.2 | 0.2640 | Yuan et al. 2007 [93] |
| 2-(2-Hydroxyethoxy)-ammonium lactate | (HEAL) | 303 | 12.4 | 0.0704 | Yuan et al. 2007 [93] |

in Table 4. In general it is assumed that conventional RTILs with acidic or basic functionalities strongly influence the absorption of CO_2 .

As discussed, RTILs sufficiently absorb CO_2 especially those containing CO_2 -philic groups like fluorine. These are

known as TSILs (task-specific ionic liquids). Widely researched TSILs are those with appended amine group, examples of which can be seen in Table 5. Bates and coworkers [68] synthesized the amine functionalized IL [pNH₂Bim][Pf₆] and found it to chemically react with the CO_2 . The CO_2 reacts

with the amine on the IL, this then reacts with another amine and forms an ammonium carbamate double salt. This form of capture results in one CO₂ captured for every two ILs. This 1:2 capture mechanism is also observed on the molecular level with traditional aqueous amines. It is theoretically suggested that, when amines are tethered to the anion only, a 1:1 ratio can be met allowing a more efficient process.

Evidence has shown that TSILs have the ability to absorb CO₂ both chemically and physically. At low pressures (typically below 2 bars) chemical absorption takes place, in the same way as aqueous amines. After the majority of the chemical bonding have taken place, physical absorption dominates the capture mechanism; this is especially relevant at high pressures, whereas aqueous amines reach their absorption limits at low pressure. This shows how the absorption performances of TSILs with amine functionalities merge the characteristics of physical solvents with the attractive features of chemical solvents. In spite of TSILs showing greater CO₂ solubility than conventional RTILs, they tend to exhibit high viscosity in comparison to other commercially available absorbents. This poses a large problem for their implementation into large-scale platforms, as the heat required for absorption and regeneration would be a lot larger and energy intensive. In order to reduce the viscosity, some groups have combined mixtures of TSIL and RTIL. Bara et al. [69] dissolved their TSIL in a common RTIL, [C₆mim][Tf₂N]. Although the solution was stable and capable of absorbing in a 1:2 molar ratio, the viscosity was still high. As a whole TSILs and TSILs + RTILs are robust and have a high absorption capacity; however, they are limited by the intensive synthesis that is required, high viscosity, and the fact that the TSIL serves as both the capture material and the dispersant.

Instead of the direct incorporation of amino-functionalized anions and cations, some recent groups have reported using imidazolium-based RTILs with amines added in solution to act as the capture reagent. Camper and coworkers [70] first investigated this concept. They synthesized an [Rmim][Tf₂N] RTIL solution containing 16% v/v of MEA and found that this is capable of rapid and reversible capture of one mole of CO₂ per two moles of MEA at low CO₂ partial pressures. An MEA-carbamate was found to precipitate from the RTIL solution; this helps to drive the capture reaction. They have currently seen that this MEA-carbamate seems to be a consequence of the [Tf₂N] anion and does not occur in other [C_nmim][X] RTILs.

2.5. CO₂ Solubility Results Reported by Various Experimental Groups. Tables 4, 5, 6, and 7 aim to provide a range of experimental data cited by various experimental groups, for peak CO₂ absorption values for different cation-based ILs. This can then be used to characterise an experimental system to ensure correct implementation and method. T (K) represents the system's temperature when measurements were recorded. P (bar) is the corresponding pressure of CO₂. χ_{CO_2} is the solubility of CO₂ expressed as a mole fraction, that is, moles of CO₂ to moles of IL. The tables also attempt to show the effects of temperature and pressure on ILs as well as different cation and anion combinations.

3. Experimental and Measurement Techniques

In order to integrate CO₂ separation techniques into large industrial systems, one needs to experimentally determine the ILs gas solubility in order to characterise the carrying capacity and selectiveness. These measurements can be accumulated via a number of experimental techniques, in which factors such as pressure and temperature can be controlled. The variety of techniques used for measuring solubility for high- and low-pressure phase equilibrium is vast and the naming of these techniques tends to vary from author to another. However all the techniques fall into two categories both of which are dependent on the equilibrium phases and mixture composition. If these two factors are unknown, measurements can be carried out analytically (analytical method); if the mixture is prepared with a precisely known composition, the synthetic method can be used. The experimental and measurement techniques reviewed here are gravimetric analysis, pressure drop method, and view-cell method and gas chromatography. All of which are being specifically applied to pure CO₂ solubility in ionic liquids. It is important to remember that impurities can occur in the gas and liquid, affecting the accuracy and precision of the results. Therefore degassing the liquid fully before analysis allows an accurate determination of the true solubility of the gas. This also relies on allowing true equilibrium conditions to be met between the gas and the liquid.

3.1. Gravimetric Analysis. Gravimetric analysis is an analytical method which describes the quantitative determination of, in this case, gas solubility by measuring the overall weight change of a sample during absorption. The gravimetric method is most commonly applied when the analyte is converted into a solid; however, as ILs are nonvolatile in nature and exhibit properties such as low vapour pressure, they can be used to a great effect with this method of analysis. Gravimetric gas analysers are used in laboratories conducting both fundamental studies into the physical properties of ILs and applications where the ability to measure gas solubility is of interest. The basic components of a typical gravimetric instrument can be seen in Figure 3.

High-precision gravimetric instruments are commercially available, in the form of thermogravimetric microbalances. These allow in situ measurements of gas absorption that record the mass gain of a sample with a high-precision electrobalance, which is capable of taking readings at high temperature and pressure. Also available are analysers which use magnetic suspension balances rather than an electrobalance [71]. The main difference between these two weighing systems is that, in magnetic suspension, the sample is weighed from the outside. Therefore the balance is not in physical contact with the high temperature and pressures subjected to the sample. This particular system is helpful when working with samples under extreme conditions. Petermann et al. [72] show the use and experimental setup of a magnetic suspension balance in conjunction with a volumetric determination method. The advantages of using magnetic suspension balances are also discussed by Dreisbach and Löscher [73].

TABLE 6: CO₂ solubility for phosphonium, pyridinium and pyrrolidinium ionic liquids.

| Ionic liquid | Acronym | <i>T</i> (K) | <i>P</i> (bar) | χ_{CO_2} | References |
|---|--------------------------|--------------|----------------|----------------------|----------------------------|
| N-Butylpyridinium tetrafluoroborate | N-BuPy[BF ₄] | 323 | 92.35 | 0.5810 | Blanchard et al. 2001 [86] |
| Trihexyltetradecylphosphonium chloride | THTDP[Cl] | 302.55 | 149.95 | 0.8000 | Carvalho et al. 2010 [94] |
| | | 313.27 | 5.17 | 0.2000 | Carvalho et al. 2010 [94] |
| Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide | THTDP[NTf ₂] | 296.58 | 721.85 | 0.8790 | Carvalho et al. 2010 [94] |
| | | 293.2 | 6.12 | 0.3080 | Carvalho et al. 2010 [94] |
| N-Butyl-4-methylpyridinium tetrafluoroborate | MeBuPy[BF ₄] | 303 | 10 | 0.1443 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0961 | Galan-Sanchez 2008 [88] |
| N-Butyl-3-Methylpyridinium dicyanamide | MeBuPy[DCA] | 303 | 10 | 0.1436 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0683 | Galan-Sanchez 2008 [88] |
| N-Butyl-4-Methylpyridinium thiocyanate | MeBuPy[SCN] | 303 | 10 | 0.0962 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0632 | Galan-Sanchez 2008 [88] |
| 1-Butyl-1-methylpyrrolidinium dicyanamide | MeBuPyr[DCA] | 303 | 10 | 0.1204 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0613 | Galan-Sanchez 2008 [88] |
| 1-Butyl-1-Methylpyrrolidinium thiocyanate | MeBuPyr[SCN] | 303 | 10 | 0.0971 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.0608 | Galan-Sanchez 2008 [88] |
| 1-Butyl-1-methylpyrrolidinium trifluoroacetate | MeBuPyr[TFA] | 303 | 10 | 0.1674 | Galan-Sanchez 2008 [88] |
| | | 333 | 10 | 0.1030 | Galan-Sanchez 2008 [88] |
| Tetrabutylphosphonium formate | TBP[FOR] | 298.1 | 19.9 | 0.3480 | Yokozeki et al. 2008 [67] |
| 1-Butyl-1-methylpyrrolidinium tri(pentafluoroethyl)trifluorophosphate | BmPyr[FEP] | 283.5 | 18.00 | 0.4980 | Zhang et al. 2008 [92] |

TABLE 7: CO₂ Solubility data for functionalized ionic liquids (TSILs).

| Acronym | Functionalization | Anion | Cation | <i>T</i> (K) | <i>P</i> (bar) | χ_{CO_2} | References |
|---|-------------------------|------------------|--------|--------------|----------------|----------------------|-------------------------|
| APMim[NTf ₂] | NH ₂ -cation | NTf ₂ | Im | 303 | 10.00 | 0.27 | Galan-Sanchez 2008 [88] |
| | | | | 343 | 10.00 | 0.18 | |
| APMim[DCA] | NH ₂ -cation | DCA | Im | 303 | 10.00 | 0.29 | Galan-Sanchez 2008 [88] |
| APMim[BF ₄] | NH ₂ -cation | BF ₄ | Im | 303 | 10.00 | 0.32 | Galan-Sanchez 2008 [88] |
| | | | | 343 | 10.00 | 0.36 | |
| AEMPyr[BF ₄] | NH ₂ -cation | BF ₄ | Pyr | 303 | 10.00 | 0.28 | Galan-Sanchez 2008 [88] |
| | | | | 333 | 10.00 | 0.24 | |
| MeImNet ₂ [BF ₄] | NR ₃ -cation | BF ₄ | Im | 303 | 4.00 | 0.09 | Galan-Sanchez 2008 [88] |
| Bmim[Tau] | NH ₂ -Anion | Taureate | Im | 333 | 10.00 | 0.43 | Galan-Sanchez 2008 [88] |
| Bmim[Gly] | NH ₂ -Anion | Glycinate | Im | 333 | 10.00 | 0.39 | Galan-Sanchez 2008 [88] |

Gravimetric analysis systems often measure gas solubility by recording isotherms, isobars, and kinetic sorption data, which can be output through a computer from which the system can be controlled. Hence when a sample is loaded, the operation of the instrument can be fully automated and programmed to carry out isothermal absorption and desorption measurements.

Due to gravimetric balances undergoing constant changes in temperature and pressure during measurements and the high sensitivity in which they operate, readings must be corrected for the changes in buoyant forces on the sample. In some apparatus, a counterweight side, which is symmetrical to the sample side, is used to minimise these effects.

However they still need to be considered. Liu et al. [74] show a concise approach to calculate this.

A detailed experimental procedure using the gravimetric balance can be seen in [67]. Also measurements of CO₂ solubility for two imidazolium-based ILs using a thermogravimetric microbalance can be found in [75].

3.2. The Pressure Drop Method. The pressure drop method is a synthetic technique that is widely used in this scientific community and is also known as the isochoric method. In this instance the volume of the system is held constant, as well as the temperature, and the pressure difference is recorded during gas absorption into the sample. This method for

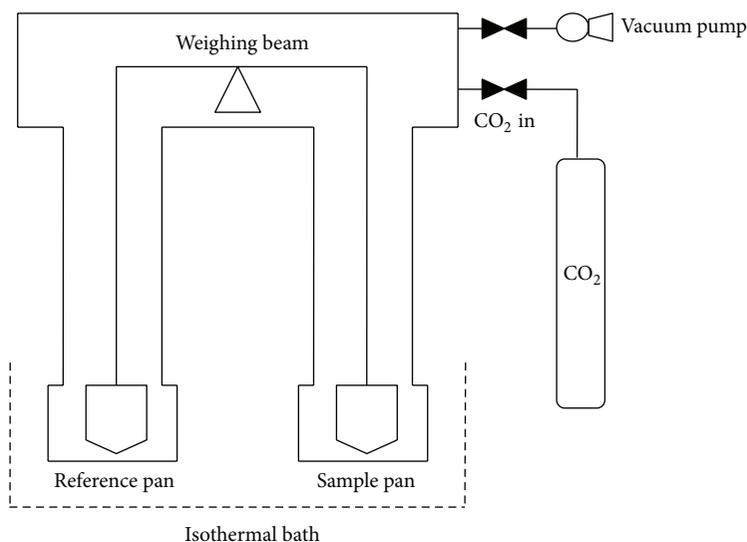


FIGURE 3: Basic components of a gravimetric system.

working out gas solubility is practically suited for ILs as they have negligible vapour pressure, therefore ensuring that the gas phase remains pure, and therefore the assumption can be made that changes in pressure are due to gas sorption. From an initial measurement of pressure, temperature, and volume, and a final measurement of these variables at equilibrium, the amount of gas absorbed by the IL can be calculated. This calculation can be performed using an equation of state to convert all three variables into moles of gas.

The basic principles of this method are as follows: CO_2 gas is transferred into a reservoir of known volume and brought to a constant system temperature. An initial reading of pressure is measured. By using a PVT relation, the moles of CO_2 in the reservoir are calculated. The IL is loaded into an equilibrium cell/stainless steel reactor and equalized to system temperature. The CO_2 is then introduced to the ionic liquid and the pressure drop is recorded when the cell's pressure remains stable; this is the equilibrium point. From the pressure drop measured, the number of moles of CO_2 left in the gas phase can be calculated. The difference between CO_2 mole values corresponds to the amount of gas absorbed in the IL. A typical setup for the pressure drop method can be seen in Figure 4.

The moles of dissolved CO_2 in the ionic liquid can be calculated by (1).

Number of CO_2 moles dissolved in the ionic liquid

$$n_{\text{CO}_2} = \frac{P_{\text{initial}} V_{\text{GR}}}{Z_{\text{CO}_2}(P_{\text{initial}}, T_{\text{initial}}) RT_{\text{initial}}} - \frac{P_{\text{eq}} (V_{\text{tot}} - V_{\text{IL}})}{Z_{\text{CO}_2}(P_{\text{eq}}, T_{\text{eq}}) RT_{\text{eq}}}, \quad (1)$$

P_{initial} and T_{initial} are the initial pressure and temperature in the gas reservoir. P_{eq} and T_{eq} are the pressure and temperature at equilibrium in the equilibrium cell. V_{tot} is the total volume

of the entire apparatus. V_{IL} is the volume of the ionic liquid, assumed to be constant. R is the ideal gas constant. Z_{CO_2} is the compressibility factor for CO_2 ; this modifies the ideal gas to account for real gas behaviour. A detailed experimental procedure and full calculations for CO_2 solubility measurements using the pressure drop method can be seen in [76, 77].

Further investigations that utilize this pressure drop method to derive gas solubility can be found where alternative experimental setups are shown [78–80].

3.3. View-Cell Methods. These involve the preparation of a mixture with a precisely known composition and then the observation of phase behavior inside an equilibrium cell, where measurements are recorded in the equilibrium state, that is, temperature and pressure. Synthetic methods consist of two main techniques, one being with a phase transition, and the other without. In synthetic methods with a phase transition a known amount of gas and IL is loaded into the equilibrium cell. The pressure is then varied at a constant temperature (or vice versa) until a second phase is formed, where the gas dissolves in the ionic liquid causing the vapor phase to diminish, whereby using different gas pressures, solubility can be worked out at various pressure, and temperatures.

In synthetic methods without a phase transition, equilibrium properties like temperature, pressure, density, cell volume, and gas/liquid phase volumes are measured, and the composition of the phase mixtures can be calculated in terms of moles or by a mass balance equation.

As can be seen in Figure 5, a pump releases CO_2 at a constant selected pressure and monitors the volume of CO_2 flowing into the system. The CO_2 is also heated to a constant temperature. By monitoring the volume, a known amount of CO_2 is then introduced to the high-pressure view cell, which contains a known amount of IL. In the case of non-phase transition, the amount of CO_2 absorbed is calculated by the difference in the amount of gas delivered to the cell and the amount of gas in the vapor phase. The amount of gas in the

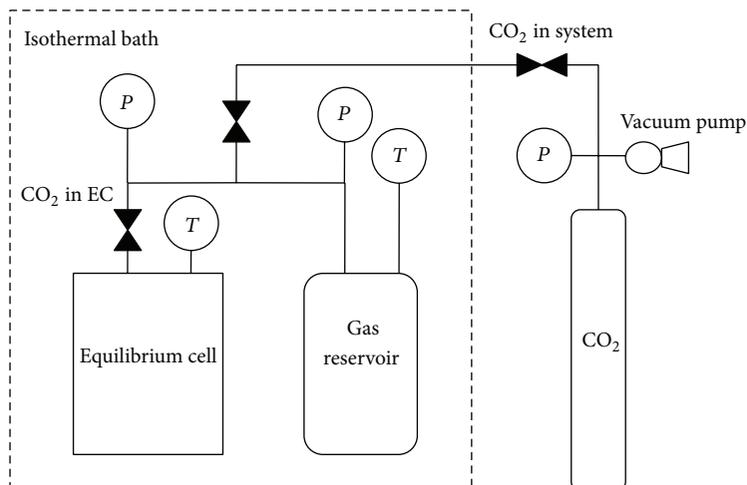


FIGURE 4: The pressure drop apparatus, where P and T correspond to pressure and temperature sensors.

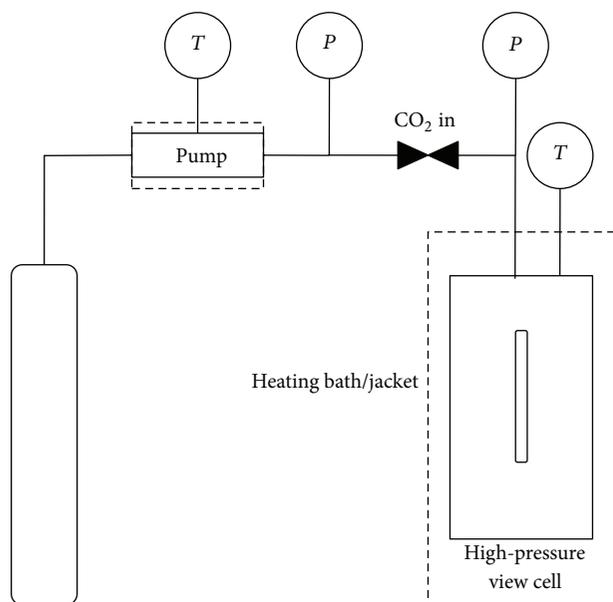


FIGURE 5: Scheme of a synthetic method setup.

vapor phase can be calculated using a mass balance, shown in (2), coupled with an equation of state.

Equation to calculate amount of gas in the vapor phase:

$$m_g = m_{\text{pump}} - m_{\text{lines}} - m_{\text{headspace}} + m_{\text{lines}}^0 + m_{\text{headspace}}^0, \quad (2)$$

where m_g is the mass of CO_2 in the liquid phase, m_{pump} is the mass of CO_2 injected into the system, m_{lines} is the mass of CO_2 in the gas lines, connecting the pump to the equilibrium cell, $m_{\text{headspace}}$ is the mass of the gas in the headspace of the cell, m_{lines}^0 is the mass of the gas in the lines after venting the system, and $m_{\text{headspace}}^0$ is the mass of gas in the headspace, initially in the system after venting.

A full experimental procedure using a synthetic method without phase transition and demonstrating the use of mass balancing to determine gas solubility is explained in the literature [30, 81, 82].

3.4. Further Techniques. Gas chromatography is an analytical method that boosts high precision and accuracy. When applied to measuring gas solubility in absorption media, the gas chromatograph is usually coupled with a high-pressure reactor cell in which a synthetic or pressure drop method is applied, and at equilibrium, a sample is taken and analyzed [83]. Solubility data from gas chromatography can be achieved by using an extractive technique; here the solvent (IL) is saturated with the solute (CO_2) and then coated on a column. Nitrogen, or any other nonabsorbing carrier gas, is directed on to the column in order to extract the CO_2 from the IL. The nitrogen is then analyzed in the gas chromatograph. This determines the amount of CO_2 removed (per amount of coating). A detailed method for applying gas chromatography can be found in the thesis by Wilbanks [84].

Other analytical techniques can be used in some cases to determine the solubility of specific gases; this may be in the form of a titration; this was demonstrated by Shen and Li [85] with aqueous amine solutions. However this has so far not been applied to ILs. Inline gas sensors also have the potential to be used. A possible scenario could involve linking an electrochemical sensor to measure the difference in CO_2 concentration of the vapor phase before and after equilibrium conditions.

Many advantages come from using gravimetric microbalances for solubility measurements. The ability to measure mass change to a high precision is helpful for a variety of reasons. When initially degassing the ionic liquid sample, being able to measure mass decrease allows the experimentalist to see when a constant mass value has been reached, thus allowing the assumption that full degassing has occurred. Also, the mass reading is very important to ensure equilibrium conditions once the CO_2 has been introduced.

Equilibrium is reached when the mass change is zero. In situ gravimetric balances, that is, when the balance is enclosed in the measuring gas, are limited to lower pressures and temperatures. Disadvantages of gravimetric systems are mainly due to their high retail price, making them impractical for small projects where the funding is restricted.

In comparison to the gravimetric analysis, the pressure drop and synthetic methods are much simpler in design. As samples of any size can be investigated with these methods, a high sensitivity can generally be achieved, however, not a high accuracy. The most significant errors in the pressure drop and synthetic methods are the error calculations of dead space; for gravimetric methods, it is the determination of buoyancy forces. In pressure drop and synthetic methods, the two variables, pressure and gas absorbed, are determined by the pressure sensors and calibrated volumes; this can result in measuring error which is added on each step of the absorption isotherm. With the gravimetric method, all of the variables, temperature, gas pressure, and absorbed gas, are measured independently and the absorption pressure is monitored at each step of the isotherm.

4. Conclusion

The versatility and inherent advantages of ionic liquids in the process of CO₂ capture are giving rise to a promising and expansive field. Their potential as physical absorbents is highly attractive, although at present their capture rate is not to the same scale as current aqueous amine technologies; the fact that amines for CO₂ capture have been developed through many years and that ILs are a new research field leaves room for further research and improvement.

Solubility data of CO₂ in different imidazolium-based ionic liquids are the most often found in the literature. This is especially the case for bmim[BF₄] and bmim[PF₆], because these ionic liquids were among the first ones commercially available. Therefore an abundant amount of previous data is available and allows the validation of subsequent experimental procedures. Although commercially available, the price of these ionic liquids remains high. Quaternary ammonium and tetra alkylphosphonium bases provide a cheaper alternative. In comparison the synthesis process of these ionic liquids is simpler and the raw materials are accessible. However the lack of experimental data with these solvents means that they are constantly overshadowed.

Although experimental data on CO₂ solubility in ionic liquids is available in the literature, more is needed for process design. Here several different methods have been presented in order to obtain this data. These include gravimetric analysis, pressure drop, and synthetic methods, all of which are particularly well suited for the measurement of gases in nonvolatile liquids. In terms of solubility data measurements, gravimetric balances offer the simplest and most precise route; however, their general high prices make them impractical for small research groups conducting initial experiments with ionic liquids. Pressure drop and synthetic methods provide a cheaper alternative and do not need sampling. However these methods depend on the models used to calculate the thermodynamic properties and phase equilibrium. It is

important to observe that for some thermodynamic properties, such as excess molar enthalpy, research groups use a test system to check their equipment and methods accuracy. In the case of gas-liquid solubility, however, there is no test system, especially at elevated temperatures and pressures.

The main challenges affecting ionic liquids as green solvent for CO₂ capture are availability, cost, purity, and compatibility. These challenges are faced at present on a laboratory scale and must have solutions before expanding to industry. At present the advantages and disadvantages of ionic liquids and amines seem to be equally balanced. The main criteria for ideal CO₂ capture mechanisms are high CO₂ solubility, low energy input for regeneration, low cost, long-term reusability, and being environmentally benign. At the moment amines have the advantage of having high CO₂ solubility and being of low cost. However due to the vast number of ionic liquids that can be developed and different ways in which they can be synthesized, the potential is there. Moreover through increasing research and commercialization of ionic liquids in other areas of industry, the cost is set to decrease.

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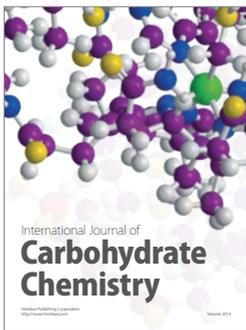
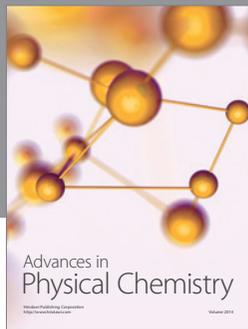
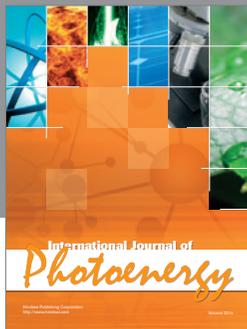
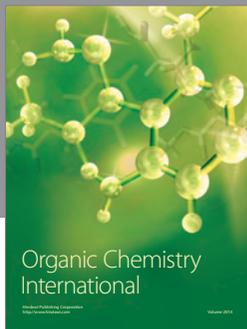
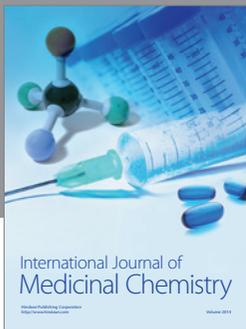
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