VOLUME 13 NO.1 JUNE 2016 ISSN 1675-7009

SCIENTIFIC RESEARCH JOURNAL

Institute of Research Management & Innovation (IRMI)

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SCIENTIFIC RESEARCH JOURNAL

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Research Trends of Carbon Dioxide Capture using Ionic Liquids and Aqueous Amine-Ionic Liquids Mixtures

Siti Nabihah Jamaludin^{1,a*} and Ruzitah Mohd Salleh^{1,b}

¹Faculty of Chemical Engineering, Universiti Teknologi MARA 40450 Shah Alam, Selangor, Malaysia ^actnabihahjamaludin@gmail.com, ^bruzitah@salam.uitm.edu.my

ABSTRACT

Anthropogenic CO_2 emissions has led to global climate change and widely contributed to global warming since its concentration has been increasing over time. It has attracted vast attention worldwide. Currently, the different CO_2 capture technologies available include absorption, solid adsorption and membrane separation. Chemical absorption technology is regarded as the most mature technology and is commercially used in the industry. However, the key challenge is to find the most efficient solvent in capturing CO_2 . This paper reviews several types of CO_2 capture technologies and the various factors influencing the CO_2 absorption process, resulting in the development of a novel solvent for CO_2 capture.

Keywords: chemical absorption, amine, ionic liquids, CO, solubility

INTRODUCTION

Generally, major sources of carbon dioxide (CO_2) emission are from industries such as natural gas treatments, fossil fuel power plant and petroleum industries. Flue gas from coal combustion contains hazardous pollutants such as CO_2 , mercury (Hg) and sulfur dioxide (SO₂), at different compositions and percentages. Carbon dioxide has been considered a major contributor to greenhouse gases since its concentration in the atmosphere has been increasing over time. Excessive CO_2 emission has a negative impact that leads to global climate change and disruption of the ecosystem. In order to maintain a safe and secure environment, CO_2 emissions can alternatively be controlled by carbon capture and storage (CCS) [1], whereby CO_2 is separated from flue gas and permanently stored in large subsurface geologic reservoirs.

Various technologies that have been developed for CO₂ capture are gas membrane separation, solid adsorption, and absorption by chemical/physical solvents[1][2][3]. Table 1 shows a comparison of three different CO₂ capture methods. These methods utilize different approaches which can be adapted to the treatment of industrial effluents. In the chemical industry, the use of separation technologies correlate directly with operational confidence [4]. The absorption technology is the most common method for capturing CO₂, since it is applicable to industry demands and scale. Efficiency of the carbon dioxide absorption technology can be as high as 98%. The source of energy penalty in absorption-based methods is from thermal regeneration, h leads to high-energy consumption. This may be because a large amount of water is vaporized during solvent regeneration. Compared to other CO, capture methods, adsorption requires a slightly lower amount of energy for the regeneration process. This is because there is low steam loss during CO₂ desorption [5]. Energy penalty in the adsorption process comes from either thermal or vacuum regenerations. In the membrane separation methods, energy penalty is from feed compression or/and vacuum on the permeate. Membrane separation technology is seldom used as the operating flexibility of the membrane system is strongly affected by flue gas conditions, making it difficult to apply the technology [6].

Absorption processes are commonly employed in chemical industries, where they are significantly utilized for CCS applications, and in the treatment of natural gases. One of the most effective methods for CO_2 capturing is by the use of amine solvents in gas absorption. However, the use of alkanolamines for CO_2 capture has several drawbacks, such as high incidence of corrosion, volatility and proneness to thermal and oxidative degradation [7][8]. These limitations cause extra energy consumption and require more investment on equipment [9]. Therefore, the detriment of using amine solvents for CO_2 capture drives researchers to find alternative solvents with improved absorption performance.

	Absorption	Adsorption	Membrane	Ref	
Commercial usage in CPIª	High Moderate Low		Low	[4]	
Operational Confidence	High	High but complex	Low to moderate	ate ^[4]	
Operating Flexibility	Moderate Moderate C 2		[10]		
Energy Requirement			[10]		
CO ₂ Recovery 90-98% 80-95% 80-9		80-90%	[6] [10]		
Scale Industrial Pilot Expe		Experimental	[11]		
Primary source of energy penalty	Solvent Regeneration (Thermal)	Sorbent Regeneration (Thermal/ Vacuum)	Compression on feed and/ or vacuum on permeate	[4]	
Development trends	New chemistry, thermal integration	New chemistry, process configuration	New membrane, process configuration	[4]	

Table I: Comparison of Post-Combustion CO, Capture Methods

^a Chemical Process Industry

The use of amines and ionic liquid mixtures as improved solvents has been suggested to overcome these drawbacks[12]. Ionic liquids (ILs) are the organic salts that form stable liquids below 100°C, or even at room temperature. The recent concept of using ILs for CO₂ capture has became attractive when it was discovered that they had CO₂ absorption properties [3][13][14]. The advantages of ILs are that they have low vapor pressure and are thermally stable over a wide range of temperature. However, most ILs are not cost effective compared to commercial amines. Thus, developing economical and energy efficient CO₂ capture technologies is urgently required.

With respect to this, the desirable properties of ILs and alkanolamines may be integrated, so that energy can be saved during the regeneration process. The aim of this short review is to summarize research trends in CO_2 capture, and the factors influencing the CO_2 capture when using ionic liquids and aqueous amine-ionic liquids mixtures.

RESEARCH PROGRESS ON CO, CAPTURE

Ionic Liquid

In the recent decade, ionic liquids have been considered as good absorbents for CO_2 capture. Zubeir *et al.*,[15] studied the solubility of CO_2 in low viscous ILs; 1-butyl-3-methylimidazolium tricyanomethanide [bmim][tcm] for the first time, using it as a solvent for capturing CO_2 . They performed the experiment at 288.15K to 363.15K with pressure of 0.01 to 10 MPa using two different methods (gravimetric and volumetric). The authors discovered that [bmim][tcm] had good solubility performance compared to other non-fluorinated ionic liquids. This indicated that [bmim] [tcm] was a suitable and promising solvent candidate for carbon capture.

In a subsequent research, three ionic liquids; Methyl Trioctyl Ammonium Bis (trifluoromethylsulfonyl)imide $[MOA][Tf_2N)$, 1-butyl-3-Methylimidzolium Bis (trifluoromethylsulfonyl)imide $[bmim][Tf_2N]$ and 1-butyl-3-Methylimidazolium Methyl Sulfate $[bmim][MeSO_4]$ were used by Bahadur et al., [16] to capture CO₂. They used gravimetric analysis to measure CO₂ solubility and found that absorption increased with pressure and decreased with temperature. $[MOA][Tf_2N]$ was noted to have the highest CO₂ solubility, followed by $[bmim][Tf_2N]$ and $[bmim][MeSO_4]$.

Most CO₂ absorption performance studies were carried out using imidazolium ionic liquids. Pinto et al., [17] investigated CO₂ solubility performance using pyridinium-based ionic liquid, 1-ethylpyridinium ethylsulfate [C2Py][EtSO₄]. The temperature was set at 298.2 K and pressure up to 1.6 MPa. They compared the CO₂ loading performance between [C2Py][EtSO₄] and an equivalent imidazolium-based ionic liquids, 1ethylimidazoliumethylsulfate [C2mim][EtSO₄] [18]. The authors found that pyridinium ionic liquids exhibited slightly lower CO₂ absorption. This may due to greater steric effects on [C2mim][EtSO₄] that led to the generation of more free volume. Pyridinium-based ionic liquids were considered more biodegradable and cheaper compared to imidazolium ionic liquids, and much more promising when used in real scaled-up CO₂ absorption. The CO₂ solubility performance using six hydroxyl ammonium ionic liquids; 2-hydroxyethanaminium acetate [hea], bis (2-hydroxyethyl) ammonium acetate [bheaa], 2-hydroxy-N-(2-hydroxyethyl)-N-methylethanaminium acetate [hhemea], 2-hydroxyethanaminium lactate [hel], bis (2-hydroxyethyl) ammonium lactate [bheal] and 2-hydroxy-N-(2-hydroxyethyl)-N-methylethanaminium lactate [bheal] and 2-hydroxy-N-(2-hydroxyethyl)-N-methylethanaminium lactate [hhemel] were studied by Kurniaet al., [19]. They observed the CO₂ solubility results in the sequences of [hea] > [bheaa] \approx [hel] > [bheal] > [hhemel] > [hhemea]. Enthalphy and entrophy from estimated Henry's constant showed that solubility increased with pressure and decreased with temperature.

AQUEOUS AMINE-IONIC LIQUID MIXTURES

Recently, Lv *et al.*, [20] forwarded the idea of mixing Monoethanolamine (MEA) and hydrophilic amino acid ionic liquid $[C_2OHmim][Gly]$ in order to study CO₂ capture performance. They found that the CO₂ absorption capacity of the mixed solution was higher compared to the total absorption of MEA single solution. The MEA/ $[C_2OHmim]$ system tend reacts with CO₂ as zwitterions They act as a base to participate in the carbamate formation.

This is in agreement with the findings of Taib and Murugesan [21] which compared the CO₂ absorption performance of ionic liquids [bmim] [BF₄] and [bheaa], to MEA solution. Both amine ionic liquid mixtures were found to have higher CO₂ loading compared with single amines or ionic liquid solutions. In subsequent research, Feng *et al.*, [22] found that the addition of ionic liquids ([N₁₁₁₁][Gly]), ([N₂₂₂₂][Gly]), ([N₁₁₁₁][Lys]) and ([N₂₂₂₂][Lys]) to amine mixtures greatly reinforced CO₂ absorption.

In contrast, Fu and Zhang [23] found that CO_2 loading decreased significantly when 1-butyl-3-methylimidazolium glycinate [bmim][Gly] was added to the methyldiethanolamine MDEA aqueous solution. However, the absorption rate increased with the addition of ILs into MDEA aqueous solution. Results from the study of Xu *et al.*, [24] supported the findings, where the addition of ionic liquids in amine solution was shown to decrease CO_2 absorption efficiency. They conducted the experiment using two low viscous ionic liquids; [C₂OHmim][DCA] and [bmim][DCA], mixed with an aqueous MEA solution. The authors reported that both [C₂OHmim]

[DCA] and [bmim][DCA] gave slightly reduced solubility, due to salting out effects that inhibited CO₂ absorption.

Ahmady *et al.*, [25] also found that the amount of CO_2 loading declined with the addition of [bmim][DCA], [bmim][BF4] and [bmim][Ac], into MDEA solution. Similarly, results from Sairi *et al.*, [26] demonstrated that the use of MDEA and [gua]⁺[OTf]⁻ mixtures resulted in less CO_2 absorption, as [gua]⁺[OTf]⁻ hindered the tertiary amine of MDEA.

Table 2 shows summarizes recent research findings in CO_2 capture using amine and ionic liquid mixtures.

Table 2:	Summary	of the	Effects	of	Various	Aqueous	Amine-Ionic
		Liquic	Mixtures	on	CO ₂ Load	ing	

Amine	Ionic Liquids	CO ₂ Loading	Ref
MEA	 hydrophilic amino acid ionic liquid [C₂OHmim][Gly] 	Increase	[20]
MEA	 bis(2 hydroxyethyl)ammonium acetate (bheea) 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] 	Increase	[21]
MDEA	 tetramethylammonium glycinate [N₁₁₁₁][Gly], tetraethylammonium glycinate [N₂₂₂₂][Gly] tetramethylammonium lysinate [N₁₁₁₁][Lys] tetraethylammonium lysinate [N₂₂₂₂][Lys] 	Enhance	[22]
MDEA	 1-butyl-3-methylimidazolium glycinate [bmim][Gly] 	Decrease	[23]
MEA	 1-(2-hydroxyethyl)-3-methyl- imidazolium dicyanamide [C₂OHmim][DCA] 1-butyl-3-methylimidazolium [Bmim][DCA] 	Decrease	[24]
MDEA	 1-butyl-3-methyl-imidazolium tetrafluoroborate [bmim][BF4] 1-butyl-3-methyl-imidazolium acetate [bmim][Ac] 1-butyl-3-methyl-imidazolium dicyanamide [bmim][DCA] 	Decrease	[25]

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Amine	Ionic Liquids	CO ₂ Loading	Ref
MDEA	• Guanidium trifluoromethanesulfonate [gua]⁺[OTf]⁻	Decrease	[26]
MDEA	• Guanidium tris(pentafluoroethyl) trifluorophosphate [gua]*[FAP]⁻	Decrease	[27]the solubility of CO 2 in aqueous blends of N-methyldiethanolamine (MDEA
AMP	 N-butyl-3-methylpyridinium tetrafluoroborate, [B₃MPYR][BF₄] 	Decrease	[28]

FACTORS AFFECTING ABSORPTION PERFORMANCE

In recent years, several experimental works have been carried out to investigate the efficiency of CO_2 capture. Details on the effect of temperature, pressure, absorbent/solvent concentration, anion types, and alkyl chain length in cations, on the performance of CO_2 capture is further discussed in following subsections.

Effects of Temperature and Pressure

Gas absorption theories by chemical reaction have assumed in isothermal conditions to facilitate the experimental procedure. Generally, liquid phase temperature can increase due to the heat given off by the solution, or even by the reaction itself. In CO_2 removal with alkanolamine solution, high thermal effects have been recorded.

The study of CO_2 solubility using aqueous mixtures of MEA + Ionic liquids; bis (2-hydroxylethyl) ammonium acetate [bheaa] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim] [BF₄] was conducted by Taib and Murugesan [21]. They discovered that the solubility of CO_2 increased linearly with pressure, for both aqueous bheaa and in addition of MEA solution. A similar trend was also reported when they used aqueous [bmim] [BF₄]. The addition of ionic liquid was expected predominated the process by physical solubility of CO_2 . In terms of temperature effects, they found that there was not much change in CO_2 absorption when temperature was increased in the range of 298.15K-313.15K.

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This CO₂ solubility pattern is in agreement with findings of other researchers. Feng *et al.*, [22] used four amino acid based ILs: tetramethylammonium glysinate [N₁₁₁₁][Gly], tetraethylammonium glysinate [N₂₂₂₂][Gly], tetramethylammonium lysinate [N₁₁₁₁][Lys], and tetraethylammonium lysinate [N₂₂₂₂][Lys] to investigate the effect of temperature ranging 298K to 318K towards the absorption of CO₂ in ILs + MDEA aqueous solutions. They found that raising the temperature increased the absorption rate only during the first 20 minutes. This is due to the larger reaction rate and might be attributed to the solution becoming less viscous at higher temperature resulted in less CO₂ amount being absorbed.

This similar trend was also seen by Xu *et al.*, [24] in their work where CO_2 solubility decreased with an increase in temperature. The authors used two low viscous ionic liquids; [C₂OHmim][DCA] and [Bmim][DCA] mixed with aqueous 30 wt% MEA. In terms of pressure effects toward CO_2 absorption, results showed that CO_2 solubility was directly proportional to the increase in CO_2 partial pressure.

The study of the effects of temperature and pressure on CO_2 absorption in aqueous N-methyldiethanolamine (MDEA) and guanidinium trifluoromethanesulfonate, $[gua]^+$ [OTf]⁻ ionic liquid system at elevated pressures and various temperatures were conducted by Sairi *et al.*, [26]. Their finding is in agreement with the expected general trend. Equilibrium loading was found to decrease with temperature and increase with pressure. This indicated that more gas was present in the solution with a lower temperature, compared to a solution of higher temperature. This trend can be explained by the fact that vapor pressure increases with temperature. Based on Henry's law, the solubility of a gas in a liquid is proportional to the partial pressure of the gas above the surface of the liquid [29]. The same phenomenon was also reported by Anthony *et al.*, [30] and Husson-Borg *et al.*, [31].

In 2012, Aziz *et al.*, [27] demonstrated the effects of temperature and pressure on absorptionby conducting an experiment, using aqueous mixtures of MDEA and [gua]+[FAP]-. They concluded that the solubility of carbon dioxide was inversely proportional to an increase in temperature and pressure.

Effects of Anions and Cations of Ionic Liquids

Anions and cations also provide significant impact on absorption systems and CO, solubility.

With respect to the influence of anion and cation, the effect of length of the alkyl chain was evaluated by Gonzalez-Miquel *et al.*,[32]. They compared three different imidazolium based ionic liquids; 1-hexyl-3methylimidazolium bis (trifluoromethylsulfonyl) imide [hxmim][Tf₂N], 1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [omim] [Tf₂N] and 1-decyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [dcmim][Tf₂N] in CO₂ capture. They found that CO₂ absorption in ILs slightly increased with increasing length of cation alkyl chain. This solubility pattern was supported by evaluating the Henry's law constant (K_H) of CO₂, where K_H values decreased with increasing length of the alkyl chain, indicating higher CO₂ solubility.

Yunus *et al.*, [33] investigated the effect of alkyl chain length in four of pyridinium based ionic liquids toward CO_2 capture where the CO_2 solubility in [C4py][Tf2N], [C8py] [Tf2N], [C10py][Tf2N], and [C12py] [Tf2N] were measured at 3 different temperatures of 298.15 K, 313.15 K and 333.15 K. They found that [C12py] [Tf2N] had the greatest total of CO_2 absorbed compared to others, since the absorption performance depends on the length of chain. Aki *et al.*, [34] reported that increasing the cation alkyl chain length of the ionic liquid will decrease the density of the ionic liquid and subsequently increase free volume. Space filling allows for greater absorption of CO_2 . Thus, it was concluded that an increase in the cation alkyl chain length, slightly increases the CO_2 solubility in the ionic liquid [35].

Most studies have proved that the solubility of CO₂ was far more influenced by the nature of anions, compared to cations of the ILs [36] [37][38]. Bahadur *et al.*, studied the effect of anions and cations of ionic liquids on CO₂ solubility. They used Methyl Trioctyl Ammonium Bis (trifluoromethylsulfonyl) imide [MOA][Tf₂N], 1-butyl-3-Methylimidzolium Bis (trifluoromethylsulfonyl) imide [bmim][Tf₂N] and 1-butyl-3-Methylimidazolium Methyl Sulfate [bmim][MeSO₄] as the solvent to absorb CO₂. The authors reported that CO₂ solubility is in the sequence of [MOA] $[Tf_2N > [bmim] [Tf_2N] > [bmim] [MeSO_4]$. The increasing fluorination of the ionic liquids resulted in higher absorption. Solubility was influenced by the strong interaction between anion gas and the molar volume of the ionic liquid. When the molar volume of the ILs increases, the void space eventually increases, allowing for more gas to be dissolved.

Similar solubility trends was also reported by Ramdin *et al.*, [39] using inexpensive solvents; tributylmethylammonium methylsulfate [TBMN] [MeSO₄] and tributylmethylphosphonium methylsulfate [TBMP][MeSO₄] for capturing CO₂ The authors compared the solvents with with commonly used industrial ILs. Their findings revealed that both [TBMN][MeSO₄] and [TBMP][MeSO₄], had slightly higher solubility compared to 1-butyl-3-methylimidazolium methylsulfate [bmim][MeSO₄] [40]. However, by comparing with 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [bmim][Tf₂N] [41], obviously fluorinated anion has a much larger effect on solubility. This explanation was strongly supported by the sequences of CO₂ solubility reported by Sharma *et al.*, [42] where; BF⁻₄ < DCA⁻ < PF⁻₆ < TfO⁻ < Tf₂N. The anion effect on CO₂ solubility was attributed to the presence of the fluoroalkyl group, which led to highest CO₂ solubility [43][44][45][46], and due to the weaker ILs cation-anion interactions. Table 3 lists anion classification and CO₂ solubility.

Anion	Nomenclature	Classification	CO ₂ solubility	
Tetrafluoroborate BF ₄				
Hexafluorophosphate	PF ₆		High	
Trifluoromethanesulfonate	TfO			
Bis (trifluoromethylsulfonyl) imide	Tf ₂ N	Fluorinated		
Tris (trifluoromethylsulfonyl) methide	methide			
Dicyanamide	DCA	Non fluoringted	1	
Nitrate	NO ₃	Non fluorinated Low		

Table 3: Influence of Anions in [Different Ionic Liquids
-----------------------------------	-------------------------

Effects of Ionic Liquids / Amines Concentrations

Recently, Lv *et al.*, [7] compared the CO_2 capture into different mole ratios of MEA / [C₂OHmim] [Gly] mixtures. They found that the absorption capacity of aqueous MEA solution was lower than pure ionic liquid. The absorption capacity increased with increasing [C₂OHmim] [Gly] concentration for mixed solutions of MEA and [C₂OHmim] [Gly].

Nordin *et al.*, [28] evaluated the interaction of 2- amino-2-methyl-1 propanol (AMP) with N-butyl-3-methylpyridinuim tetrafluoroborate, $[B_3MPYR][BF_4]$. The amount of CO₂ absorbed was found to decrease with increasing of $[B_3MPYR][BF_4]$ concentrations. The acidity of the ionic liquid reduced the alkalinity of aqueous AMP in the mixtures, causing the driving force for the mass transfer to decrease and inhibit CO₂ absorption [27]. Blends of methyldietanolamine (MDEA) with three different types of ionic liquids, 1-butyl-3-methyl-imidazolium tetrafluoroborate [bmim] $[BF_4]$, 1-butyl-3-methyl-imidazolium acetate [bmim][Ac] and 1-butyl-3-methyl-imidazolium dicyanamide [bmim][DCA] have been extensively studied by Ahmady *et al.*, [25] who observed similar trends.

CONCLUSION

Generally, the addition of ionic liquids into aqueous amine solution enhanced CO_2 absorption and CO_2 loading performance. However, in some cases there is still contrasting trends found by researchers. Absorption was seen to decrease with increasing temperatures, and linearly increased with increasing pressure. Carbon dioxide solubility was found to decrease with increased concentrations of amine or ionic liquids, due to the increase in viscosity and decresed presence of water molecules in the solution. Anions and cations significantly affects CO_2 absorption. Solubility is more affected by the nature of anions, compared to cations. Ionic liquids with fluoroalkyl groups absorb a high amount of CO_2 compared to non-fluorinated ionic liquids. Cation alkyl chains impart a slight effect on CO_2 solubility. Increasing the chain length will slightly increase CO_2 solubility. Selecting the right combination of amine-ionic liquid mixtures can improve the performance of CO_2 absorption.

ACKNOWLEDGEMENT

Financial Support from Fundamental Research Grant Scheme (600-RMI/ FRGS 5/3 (91/2014)) for this project is gratefully acknowledged. The authors also would like to thank Universiti Teknologi MARA (UiTM) for supporting the completion of this research work.

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