

Republic of Iraq  
Ministry of Higher Education  
And Scientific Research  
Al-Nahrain University  
College of Science  
Department of Chemistry



# INVESTIGATION OF CO<sub>2</sub> GAS CAPTURING BY ROOM TEMPERATURE IONIC LIQUIDS

A Thesis  
Submitted To The College of Science Al-Nahrain University  
As a Partial Fulfillment of The Requirements For The  
Degree of M. Sc. In Chemistry

**By:**

**EVON AKRAM ABD-ALJABAR**

**Supervised by**

**Dr. HADI M. A. ABOOD**

## Committee certification

We, examining committee, certify that we have read this thesis and examined the student in its content, and that in our opinion it is adequate with standing as a thesis for the Degree of M. Sc. in Chemistry.

### Chairman

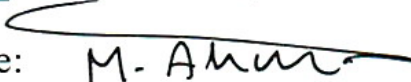
Signature: 

Name: **Prof.**

**Dr. F. H. Musa**

Date: / / 2014

### Member

Signature: 

Name: **Prof.**

**Dr. Mahasin F. Alias**

Date: / / 2014

### Member

Signature: 

Name: **Assist. Prof.**

**Dr. Emad Yousif**

Date: / / 2014

### Supervisor

Signature:

Name: **Assist. Prof.**

**Dr. Hadi M. A. Abood**

Date: / / 2014

---

Approved for the College of Graduate Studies

**Signature:**

Name: **Assist. Prof. Dr. Hadi M. A. Abood**

Dean of the College of Science, Al-Nahrain University

Date: / / 2014

## **Supervisor Certification**

I certify that this thesis was prepared under my supervision in the Department of Chemistry, College of Science, Al-Nahrain University as a partial requirements for the Degree of Master of Science in Chemistry.

### **Signature:**

**Name:** Assistant Prof.

Dr. Hadi M. A. Abood

**Date :** / /2014

In view of the available recommendations, I forward this thesis for debate by the Examining Committee.

### **Signature:**

Assistant Prof.

Dr. Nasreen Raheem Jber

Head of Chemistry Department,

College of Science,

Al-Nahrain University.

**Date:** / /2014

## **Abstract**

Some ionic liquids were investigated for abilities to capture CO<sub>2</sub> alone or with added some catalysts at room temperature under atmospheric pressure to increase the capacity of ionic liquids to capture carbon dioxide gas some catalysts were found effective such as :-

Hydrated aluminum nitrate/urea ionic liquid with added CaO and NaOH , monoethanolamine and ammonium chloride were added to hydrated ammonium aluminum sulphate/urea ionic liquid did not show in FTIR sign of either physical or chemical absorption of CO<sub>2</sub> .

The addition of NaOH<sub>aq</sub> to hydrated ammonium aluminum sulphate/urea ionic liquid showed a new vibration absorption at 1666 cm<sup>-1</sup> and changing the frequencies in the amine group vibrational bands above 3000 cm<sup>-1</sup> . While the distilled water when added to the ionic liquid hydrated ammonium aluminum sulphate/urea showed a broaden effect on the high vibrational bands above 2500 cm<sup>-1</sup> and the carbonyl group vibrational band at 1662 cm<sup>-1</sup> was not effected .

Calcium oxide was added to hydrated ammonium aluminum sulphate/urea showed a new splitting vibration absorption bands at 1666 cm<sup>-1</sup> ,1618 cm<sup>-1</sup> .

Aluminum chloride-urea ionic liquid very effective to capture carbon dioxide gas without add any catalysts showed a chemical absorption of CO<sub>2</sub> 1655 cm<sup>-1</sup> while aluminum chloride-acetamide showed weaker or no ability to capture CO<sub>2</sub> .

## ACKNOWLEDGEMENTS

*I would like to express my special appreciation and thanks to my supervisor Dr. Hadi M. A. Abood , you have been a tremendous mentor for me. I would like to thank you for encouraging my research and for allowing me to grow as a research scientist. Your advice on both research as well as on my career have been priceless.*

*I want to thank my guardian angel that paved the way for me to take the flag to the spirit of Dr. Shahbaz Ahmed .*

*A special thanks to my family. Words cannot express how grateful I am to my mother , my father , my sister only , my brother only and all my family for all of the sacrifices that you 've made on my behalf. Your prayer for me was what sustained me thus far. I would also like to thank all of my friends who supported me in writing , and incited me to strive towards my goal. Special thanks to Dr. Nasreen Raheem Ibr.*

*Evon Akram*

# CONTENTS

## Abstract

## Chapter One Introduction

<b>1.1</b> Historical background	<b>1</b>
<b>1.2</b> Carbon dioxide capture by monoethanolamine	<b>2</b>
<b>1.3</b> Room temperature ionic liquids	<b>4</b>
<b>1.4</b> Room temperature ionic liquids used for carbon dioxide capture	<b>11</b>
<b>1.5</b> Mechanisms of ILs for CO <sub>2</sub> capture	<b>13</b>
<b>1.5.1</b> Designer solvents	<b>16</b>
<b>1.5.2</b> Task-specific ionic liquids (TSILs)	<b>16</b>
<b>1.6</b> Measurements of gas solubility	<b>18</b>
<b>1.6.1</b> The stoichiometric technique	<b>18</b>
<b>1.6.2</b> The gravimetric technique	<b>19</b>
<b>1.6.3</b> spectroscopic technique	<b>19</b>
<b>1.6.4</b> Gas chromatography	<b>20</b>
<b>1.7</b> CO <sub>2</sub> solubility in ionic liquids	<b>20</b>
<b>1.7.1</b> Low –pressure CO <sub>2</sub> solubility	<b>20</b>
<b>1.7.2</b> High –pressure CO <sub>2</sub> solubility	<b>21</b>
<b>1.8</b> carbon dioxide capture storage (CCS)	<b>21</b>
<b>1.9</b> The process carbon dioxide capture storage	<b>23</b>
<b>1.10</b> Technologies/methods and materials in CO <sub>2</sub> capture	<b>23</b>
<b>1.11</b> Advances and challenges in CO <sub>2</sub> capture	<b>29</b>
<b>1.12</b> Thermogravimetric Analysis (TGA)	<b>32</b>
<b>1.12.1</b> General description	<b>33</b>
<b>1.12.2</b> TGA example	<b>33</b>
<b>1.12.3</b> DTA changes in heat / temperature (endo- or exothermic)	<b>34</b>
<b>1.13</b> Thermal stability of ionic liquids	<b>35</b>
<b>1.14</b> Aim of The Present Work	<b>37</b>

## Chapter Two

### Experimental Part

<b>2.1</b> Chemicals	<b>38</b>
<b>2.2</b> Instrument	<b>39</b>
<b>2.3</b> Preparation of solutions	<b>39</b>
<b>2.3.1</b> Preparation of ionic liquids	<b>39</b>
<b>a-</b> Aluminum chloride- urea and aluminum chloride- acetamide ILs	<b>39</b>
<b>b-</b> Choline chloride -urea IL - Hydrated aluminum nitrate- urea IL	<b>39</b>
<b>c-</b> Hydrated ammonium aluminum sulphate- urea ionic liquid	<b>39</b>
<b>d-</b> Aluminum chloride- urea and aluminum chloride- acetamide	<b>40</b>
<b>2.4</b> Addition of some chemical compounds to ionic liquids	<b>40</b>
<b>2.5</b> Carbon dioxide gas flow	<b>41</b>

## Chapter three

### Result & discussion

<b>3.1</b> the preparation of a number of room temperature ionic liquids	<b>42</b>
<b>3.2</b> CO <sub>2</sub> capture by ionic liquids	<b>42</b>
<b>3.2.1</b> Aluminum chloride – urea IL	<b>42</b>
<b>3.2.2</b> Aluminum chloride – acetamide IL	<b>44</b>
<b>3.2.3</b> Choline chloride – urea IL	<b>45</b>
<b>3.3</b> Enhancement chemical compound to ionic liquids to capture CO <sub>2</sub>	<b>46</b>
<b>3.3.1</b> Addition sodium hydroxide to hydrated ammonium aluminum sulphate-urea	<b>46</b>
<b>3.3.2</b> Addition of calcium oxide to hydrated ammonium aluminum sulphate-urea , hydrated aluminum nitrate-urea ILs	<b>48</b>
<b>a-</b> Addition of calcium oxide to hydrated ammonium aluminum sulphate-urea IL	<b>48</b>
<b>b-</b> Addition of calcium oxide to hydrated aluminum nitrate-urea IL	<b>51</b>
<b>3.3.3</b> Added H <sub>2</sub> O and compared it with the addition of NaOH <sub>aq</sub> ionic liquid	<b>52</b>
<b>3.3.4</b> Addition of monoethanolamine to ionic liquid	<b>55</b>
<b>3.3.5</b> Addition of ammonium chloride to hydrated ammonium aluminum sulphate NH <sub>4</sub> Al (SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O –urea IL	<b>56</b>

## List of Figures

No.	Figures	Page
1.1	FTIR spectra of each IL, (a) before CO <sub>2</sub> absorption, (b) after CO <sub>2</sub> absorption	14
1.2	Atmospheric CO <sub>2</sub> concentration during 1958–2010 (at Mauna Loa Observatory), showing the continuing and accelerating increase of CO <sub>2</sub> in atmosphere	22
1.3	Ex. Decomposition of calcium oxalate monohydrate	34
1.4	Decomposition temperatures of the different branched and linear imidazolium-based ionic liquids, bearing chloride and tetrafluoroborate as counter-ions	36
3.1	FTIR spectra of AlCl <sub>3</sub> -urea IL, ( black) IL alone ,(red) before bubbling CO <sub>2</sub> and ( green ) after bubbling CO <sub>2</sub>	43
3.2	FTIR vibrational bands of AlCl <sub>3</sub> -acetamide IL,( black) IL alone ,(green)after bubbling CO <sub>2</sub> for half an hour and ( red) bubbling CO <sub>2</sub> for an hour	44
3.3	FTIR vibrational bands of choline chloride-urea IL, ( red) IL alone, ( black) after bubbling CO <sub>2</sub> .	45
3.4	FTIR vibrational bands of NH <sub>4</sub> Al (SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O -CO(NH <sub>2</sub> ) <sub>2</sub> IL , ( red) IL alone, ( black) with added solid NaOH after bubbling CO <sub>2</sub> .	47
3.5	FTIR spectra of NH <sub>4</sub> Al (SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O –urea IL and with NaOH <sub>aq</sub> after bubbling CO <sub>2</sub>	47
3.6	FTIR vibration bands of NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O –urea IL containing CaO	49
3.7	FTIR vibration bands of NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O –urea IL containing CaO after bubbling CO <sub>2</sub>	50
3.8	FTIR spectra overlay to compare between vibrational bands of Al (NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O-urea IL, the black IL alone , the green with CaO and the red with capturing CO <sub>2</sub>	52
3.9	FTIR vibrational bands of NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O –urea IL , (black) IL alone , ( red) with H <sub>2</sub> O addition and ( green ) after CO <sub>2</sub> bubbling	54
3.10	FTIR vibrational bands of NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O –urea IL , (green) IL alone , ( red ) with NaOH <sub>aq</sub> , ( blue ) urea alone and ( black ) IL + NaOH <sub>aq</sub> after bubbling CO <sub>2</sub>	54
3.11	FTIR vibrational bands of hydrated ammonium aluminum sulphate NH <sub>4</sub> Al (SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O- CO(NH <sub>2</sub> ) <sub>2</sub> IL, ( black) IL with MEA ,(red) after bubbling CO <sub>2</sub> .	55



<b>3.12</b>	FTIR vibrational bands of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ - $\text{NH}_4\text{Cl}$ IL, (black) IL, (red) after bubbling $\text{CO}_2$ .	<b>57</b>
-------------	--	-----------

## List of Schemes

<b>No.</b>	<b>Schemes</b>	<b>Page</b>
<b>1.1</b>	Mechanisms of an aqueous solution of amine for $\text{CO}_2$ capture	<b>3</b>
<b>1.2</b>	The first publication and first patent of ionic liquids	<b>5</b>
<b>1.3</b>	Examples of simple room-temperature ionic liquid	<b>6</b>
<b>1.4</b>	the $\text{CO}_2$ reacted with two IL molecules to form a carbamate group	<b>15</b>
<b>1.5</b>	Three options for $\text{CO}_2$ capture from power generation plants	<b>24</b>
<b>1.6</b>	Different technologies and associated materials for $\text{CO}_2$ separation and capture	<b>27</b>
<b>2.1</b>	The system of $\text{CO}_2$ capture by ionic liquids	<b>41</b>

## List of Tables

<b>No.</b>	<b>Table</b>	<b>Page</b>
<b>2.1</b>	The chemicals used with their purities and suppliers	<b>38</b>
<b>3.1</b>	Major FTIR vibrational bands of $\text{AlCl}_3$ - urea IL and with capturing $\text{CO}_2$	<b>43</b>
<b>3.2</b>	Vibrational bands of the ionic liquid $\text{NH}_4 \cdot \text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .urea alone; with added $\text{NaOH}_{\text{aq}}$ and with capturing $\text{CO}_2$	<b>48</b>
<b>3.3</b>	FTIR vibration bands of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ -urea IL containing CaO before and after bubbling $\text{CO}_2$	<b>50</b>
<b>3.4</b>	FTIR main vibration bands of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ -urea containing CaO before and after bubbling $\text{CO}_2$	<b>51</b>
<b>3.5</b>	FTIR vibration bands of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ -urea. $\text{H}_2\text{O}$ before and after bubbling $\text{CO}_2$	<b>53</b>
<b>3.6</b>	FTIR vibrational bands of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ -ammonium chloride IL before and after bubbling $\text{CO}_2$	<b>56</b>

# List of Abbreviations

Abbreviations	Name
<b>RTILs</b>	<b>Room temperature ionic liquids</b>
<b>GHG</b>	<b>Greenhouse gas</b>
<b>IPCC</b>	<b>Intergovernmental Panel on Climate Change</b>
<b>CCS</b>	<b>carbon dioxide capture and storage</b>
<b>MEA</b>	<b>Monoethanoamine</b>
<b>MDEA</b>	<b>Methyldiethanolamine</b>
<b>DIPA</b>	<b>Diisopropanolamine</b>
<b>RPy<sup>+</sup></b>	<b>Alkylpyrimidinium</b>
<b>EtNH<sub>3</sub>NO<sub>3</sub></b>	<b>Ethyl ammonium nitrate</b>
<b>C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>NO<sub>3</sub></b>	<b>Ethyl ammonium nitrate</b>
<b>AlCl<sub>3</sub></b>	<b>Aluminum(III) chloride</b>
<b>BMI.BF<sub>4</sub></b>	<b>1-n-butyl-3-methylimidazolium tetrafluoroborate</b>
<b>BMI.PF<sub>6</sub></b>	<b>hexafluorophosphate</b>
<b>[emim]- [BF<sub>4</sub>]</b>	<b>Ethylmethylimidazolium tetrafluoroborate</b>
<b>[hmim][HSO<sub>4</sub>]</b>	<b>1-hexyl-3-methyl-imidazolium hydrogen sulphate</b>
<b>[bmim][H<sub>2</sub>PO<sub>4</sub>]</b>	<b>1-butyl-3-methyl- imidazolium dihydrogen phosphate</b>
<b>[heemim][HSO<sub>4</sub>]</b>	<b>1-[2-(2-hydroxy-ethoxy)ethyl]-3-methyl-imidazolium hydrogen sulphate</b>
<b>[bmim]Cl . ) (2AlCl<sub>3</sub></b>	<b>1-butyl-3- methyl-imidazolium chloroaluminate</b>
<b>EMIM</b>	<b>Ethylmethylimidazolium</b>
<b>[R<sub>4</sub>N] [RSO<sub>3</sub>]</b>	<b>Tetraalkylammonium sulphonates</b>

<b>[R<sub>4</sub>N] [OH]</b>	<b>Tetraalkylammonium hydroxide</b>
<b>[THTDP][Cl]</b>	<b>Trihexyltetradecylphosphonium chloride</b>
<b>[THTDP][NTf<sub>2</sub>]</b>	<b>Trihexyltetradecylphosphonium bis(trifluoromethylsulphonyl)imide</b>
<b>([C<sub>2</sub>mim][Tf<sub>2</sub>N])</b>	<b>1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide</b>
<b>([C<sub>5</sub>mim][Tf<sub>2</sub>N])</b>	<b>1-methyl-3-pentyl-imidazolium bis(trifluoromethyl -sulphonyl)imide</b>

# *Chapter one*

## *Introduction*

## **Chapter One**

### **Introduction**

#### **1.1 Historical background**

Since the beginning of the industrial age in eighteenth century, the CO<sub>2</sub> concentration in the atmosphere had increased from (280 to 390 ppm) in 2010<sup>[1]</sup>. The increase of the CO<sub>2</sub> concentration in atmosphere influences the balance of incoming and outgoing energy in the atmosphere system, leading to the raise of average surface temperature of earth. Thus, CO<sub>2</sub> has often been cited as the primary anthropogenic greenhouse gas (GHG) as well as the leading culprit in climate change. Although there are many uncertainties, it is beyond all doubts that strategies to reduce CO<sub>2</sub> emissions are urgently required to minimize climate change<sup>[1,2]</sup>. CO<sub>2</sub> capture from flue gas since 1978, longer than any other such plant in the world. CO<sub>2</sub> is separated from flue gas of a coal-fired boiler, which is used to produce electricity<sup>[3,4]</sup>.

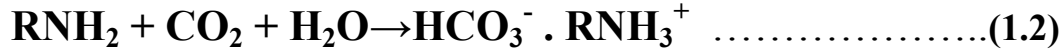
The prospect of a worsening climatic situation due to global warming is a subject of widespread public concern with annual global emissions of CO<sub>2</sub> having escalated by approximately 80 % between 1970 and 2004. This drastic rise has been attributed to an increasing dependence on the combustion of fossil fuels (coal, petroleum, and natural gas which account for 86% of anthropogenic greenhouse gas emissions, the remainder arising from land use change primarily deforestation) and chemical processing<sup>[5-7]</sup>.

Carbon dioxide, CO<sub>2</sub>, is one of the greenhouse gases and its atmospheric concentration had increased at an annual rate of about ( 2 ppm ), and thus, the development of efficient CO<sub>2</sub> capture technologies is essential for the future of carbon-based energy [8-10]. Therefore, there is a growing interest in developing technologies for efficient capture and sequestration of large quantities of CO<sub>2</sub>. By far, a number of CO<sub>2</sub> capture technologies which have already being practiced on laboratory scale or industrially are processes based on physisorption - chemisorption, membrane separation or molecular sieves, carbamation, amin physical absorption, amine dry scrubbing and mineral carbonation [11]. Amine-functionalized ILs displayed high absorption capacities toward CO<sub>2</sub>. The CO<sub>2</sub> absorption capacities of the ILs increased with increasing pressure and decrease with increasing temperature [12].

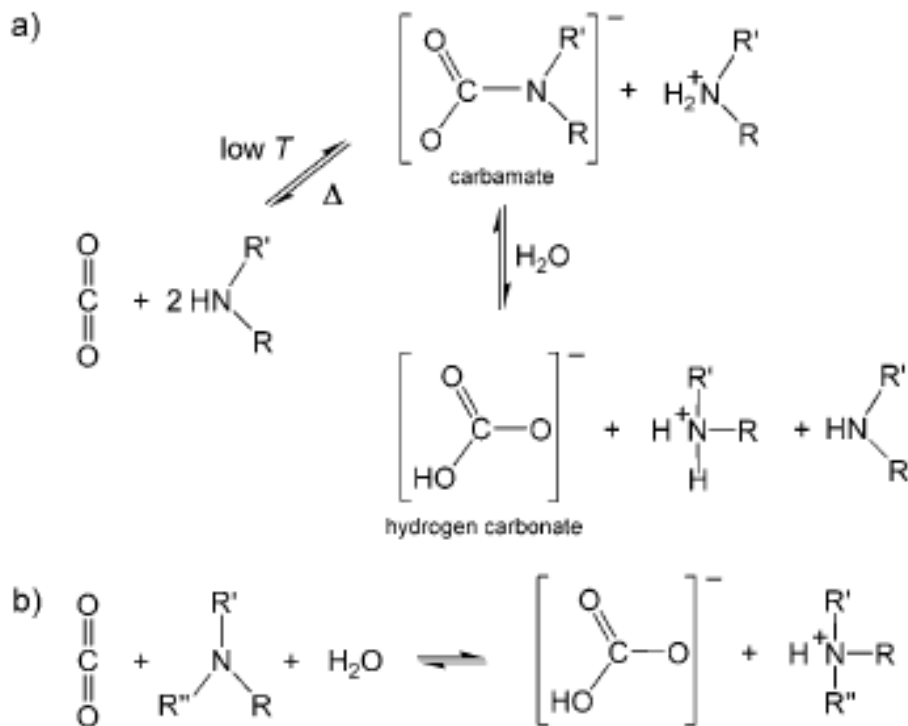
## **1.2 Carbon dioxide capture by monoethanolamine**

The traditional technology for CO<sub>2</sub> capture in industry is chemical adsorption by an aqueous solution of amine, which has some advantages such as its maturity, stable operation, good reactivity, and high capacity [12,13]. However, using aqueous amines like monoethanolamine (MEA) CO<sub>2</sub> capture consumes almost 30% of the energy that is needed to run a power plant [14], in addition to other drawbacks like insufficient CO<sub>2</sub> capture capacity, high solvent losses caused by evaporation, degradation and poor thermal stability, as well as the equipment corrosion [15]. Therefore, developing the economical and energy efficient CO<sub>2</sub> capture technologies is urgently need. An aqueous amine solution which reacts with the CO<sub>2</sub> in the

gas by an acid-base neutralization reaction to form a soluble carbonate salt showed in scheme (1.1) <sup>[16]</sup>.



The amine used in this process is most commonly one of several alkanolamines including monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), or diisopropanolamine (DIPA) <sup>[17]</sup>.



**Scheme (1.1): Mechanisms of an aqueous solution of amine for CO<sub>2</sub> capture.**

The concentration of MEA has to be limited to (15-30) wt % and this makes the CO<sub>2</sub> capture and the solvent regeneration processes complicated and costly <sup>[18,19]</sup>.

One of the most commercially utilised technologies for CO<sub>2</sub> recovery is the chemical absorption of CO<sub>2</sub> by aqueous amine solutions which has been shown to have many disadvantages, for example, the uptake of water into the gas stream requires an additional drying process. The evaporation of water increases the energy demand and cost of the procedure and the loss of volatile amines can cause environmental pollution<sup>[19]</sup>.

### **1.3 Room temperature ionic liquids RTILs**

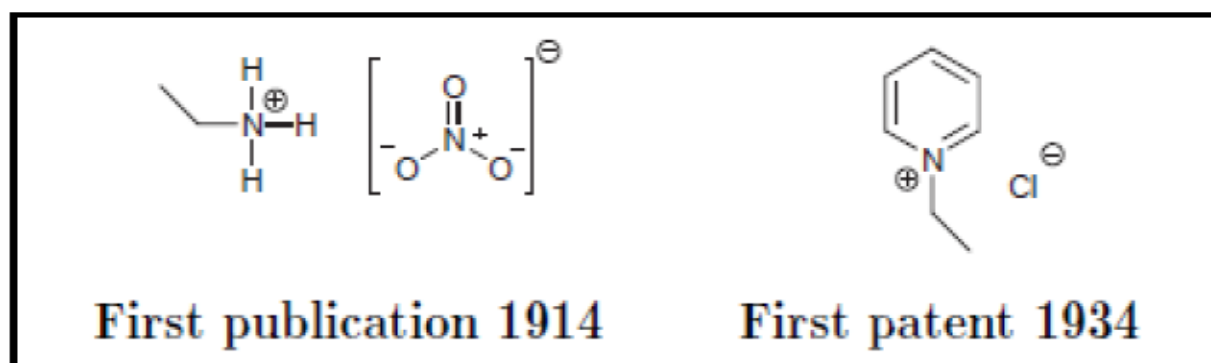
Room temperature ionic liquids exhibit many interesting properties:- extremely low vapor pressure, a broad range of liquid temperature, high thermal and chemical stability, tune able physicochemical characteristics. High intrinsic CO<sub>2</sub> solubility, selectivity and huge chemical diversity<sup>[20]</sup>.

RTILs are liquid organic salts, which generally consist of an organic cation and either an inorganic or organic anion considered as designer solvents. The nature of the cation and the anion determine the physical and chemical properties of the ionic liquid. As a result of the existing dependence of properties on the nature of the constituent ions, it is possible to achieve specific properties by choosing the right combination of anion and cation. Using this tailoring process, functional groups can be added to the structure to provide a better performance of the RTIL when chemical reaction or specific affinity and selectivity are required<sup>[21]</sup>.

The discovery date of the "first" ionic liquid is disputed, along with the identity of its discoverer. Ethanol ammonium nitrate (m.p. 52-55 °C) was reported in 1888 by S. Gabriel and J. Weiner<sup>[22]</sup>.



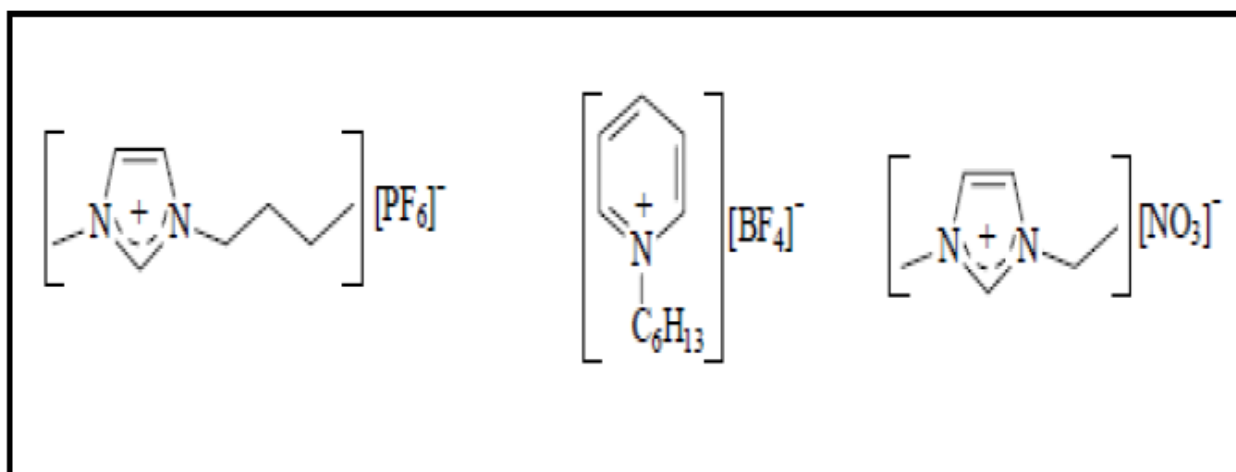
The first room-temperature ionic liquid in scheme (1.2) ethyl ammonium nitrate [ $C_2H_5NH_3 NO_3$ ] (m.p. 12 °C) was synthesized in 1914<sup>[23]</sup> by Paul Walden, this organic salt already was a room temperature ionic liquid, but didn't prompt any significant interest at that time. This was surprising as this discovery brought out a new class of solvents. It took about two decades (1934)<sup>[24]</sup> before the next ionic liquid was presented to the public in a patent. In this patent it was claimed that certain organic salts have the ability to dissolve cellulose and alter its reactivity<sup>[24]</sup>, later on, in 1948 this ionic liquid was followed by chloroaluminate base ionic liquids<sup>[25]</sup>, but interest did not develop until the discovery of binary ionic liquids were made from mixtures of aluminum(III) chloride and *N*-alkylpyridinium chloride<sup>[26]</sup> or 1,3-dialkylimidazolium chloride<sup>[27]</sup>. In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point<sup>[28]</sup>.



Scheme (1.2): The first publication and first patent of ionic liquids<sup>[23,24]</sup>.

Alkylpyridinium (RPy<sup>+</sup>) chloroaluminate based ionic liquids were first reported in the early 1950s <sup>[29]</sup>. However, the report by Wilkes and co-workers <sup>[27]</sup> of 1,3-dialkylimidazolium-based chloroaluminate ionic liquids in scheme (1.3), that possess favorable physical and electrochemical properties, provided the impetus for a dramatic increase in activity in this area <sup>[30]</sup> by Chauvin and co-workers <sup>[31]</sup>.

Ionic liquids come in two main categories, namely simple salts (made of a single anion and cation) and binary ionic liquids (salts where an equilibrium is involved). For example, [EtNH<sub>3</sub>][NO<sub>3</sub>] is a simple salt whereas mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, and their melting point and properties depend upon the mole fractions of the aluminum(III) chloride and 1,3-dialkylimidazolium chloride present.



**Scheme (1.3): Examples of simple room-temperature ionic liquid<sup>[21]</sup>.**

Ionic liquid was published by Parshall in 1972<sup>[32]</sup>, but other scientists had chosen to focus more on their electrochemical properties like Swain and co-workers<sup>[33]</sup>. they used tetraalkylammonium ionic liquid to describe kinetic and electrochemical effects. In 1975 the Osteryoung<sup>[26]</sup> group and Gilbert co-workers<sup>[34]</sup> studied the physical properties of pyridinium-based chloroaluminate ionic liquid, an ionic liquid that raised hope to be applicable in batteries, especially by the United States air force. This hope had to be abandoned due to the easy reducibility of the pyridinium moiety, a real constraint for application in batteries. The chemical behavior of Franklin acidic chloroaluminate(III) ionic liquids (where  $X(\text{AlCl}_3) > 0.50$ ) is that of a powerful Lewis acid. As might be expected, it promotes reactions that are conventionally promoted by aluminum(III) chloride, without suffering the disadvantage of the low solubility of aluminum(III) chloride in many solvents. Indeed, chloroaluminate(III) ionic liquids are exceptionally powerful solvents, being able to dissolve kerogen<sup>[35]</sup>,  $\text{C}_{60}$  and many polymers<sup>[36]</sup>. The preparation of these ionic liquids is straightforward. Simply by mixing the appropriate organic halide salt with aluminum(III) chloride results in the two solids melting together to form the ionic liquid. However, this synthesis must be performed in an inert atmosphere<sup>[37]</sup>.

The stable room temperature ionic liquids (RTILs) 1-n-butyl-3-methylimidazolium tetrafluoroborate ( $\text{BMI}.\text{BF}_4$ ), hexafluorophosphate ( $\text{BMI}.\text{PF}_6$ ) and their analogues has begun in the middle of the 1990s a renaissance of the rich chemistry of molten salts and continued to flourish. 1,3-Dialkylimidazolium cations associated with relatively weak coordinating anions such as tetrafluoroborate, hexafluorophosphate, trifluoromethane sulphonate which are compounds with unique physical-chemical properties: they are liquids over a large range of temperatures (down to  $-80\text{ }^\circ\text{C}$ ), possess

high thermal and chemical stability, large electrochemical window (up 7V), high density, relatively low viscosity and negligible vapor pressure <sup>[38]</sup>.

Another important property that changes with structure is the miscibility of water in these ionic liquids. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts are miscible with water at 25 °C where the alkyl chain length is less than 6, but when  $C \geq 6$  carbon atoms in the alkyl, they form a separate phase when mixed with water <sup>[37]</sup>.

In 1992 the first of the new ionic liquids, [emim]- [BF<sub>4</sub>], was prepared via metathesis of [emim]I with Ag[BF<sub>4</sub>] in methanol <sup>[42]</sup>. This salt has a melting point of 12 °C and may be prepared considerably more cheaply using [NH<sub>4</sub>][BF<sub>4</sub>] in acetone <sup>[39]</sup>. This ease of preparation, together with its relative moisture stability and its immiscibility with a number of organic solvents leads to increasing use in biphasic catalysis. The preparation of [emim][PF<sub>6</sub>] shortly followed; this time it was prepared by reaction of [emim]Cl with HPF<sub>6</sub> <sup>[40]</sup>, its melting point is 60 °C, which makes it slightly less attractive than the [BF<sub>4</sub>] - salt, if room temperature working is desired.

Since then, thiocyanate, nonafluorobutanesulphonate, bis((trifluoromethyl)sulphonyl)imide, tris((trifluoromethyl)sulphonyl)methide, trifluoroacetate, and heptafluorobutanoate salts have all been prepared by metathesis reactions <sup>[41-43]</sup>. These metathesis reactions are good candidates for those preparing new ionic liquids for the first time. However, they can leave the ionic liquids contaminated with a small amount of halide ions that may react with solute materials <sup>[44]</sup>.

Other ionic liquids are made by the quarternerization of the appropriate amine. This has been used to prepare a number of 1-alkyl-3-methylimidazolium trifluoromethanesulphonate salts. Methyl triflate is reacted with a stoichiometric amount of the 1-alkylimidazole in 1,1,1-trichloromethane. Since the methyl triflate is sensitive to moisture, the reaction must be carried out under anhydrous conditions.

Ionic liquids with acidic counterions like in 1-hexyl-3-methylimidazolium hydrogen sulphate ([hmim][HSO<sub>4</sub>]), 1-butyl-3-methylimidazolium dihydrogen phosphate ([bmim][H<sub>2</sub>PO<sub>4</sub>]), 1-[2-(2-hydroxyethoxy)ethyl]-3-methylimidazolium hydrogen sulphate ([heemim][HSO<sub>4</sub>]) and 1-butyl-3-methylimidazolium chloroaluminate ([bmim]Cl . 2AlCl<sub>3</sub>) can be used as good acid catalysts<sup>[30]</sup>.

Abbott and co-workers<sup>[45]</sup> prepared a new class of air and moisture stable ionic liquids based on choline chloride, a green chemistry of such ionic liquids were demonstrated particularly in the metal process such as metal winding coating, this process offered much safer conditions and good quality for the manufacture .

Different types of choline chloride based ionic liquids with metal chlorides (hydrated or anhydrous) were synthesized and each could be used in particularly for their constituent, metal coating such as chrome, nickel, copper, zinc ....etc<sup>[46,47]</sup> .

Development of chloroaluminate was not halted at replacing the imidazolium or pyridinium by the less sensitive boron tetrafluoride or phosphate hexafluoride ions.

New ionic liquids based on aluminum chloride when it combined with either urea or acetamide or trimethyl urea were prepared by Abood and co-workers<sup>[48]</sup>. These ionic liquids are much stable than chloroaluminate ionic liquids, offering relatively cheaper, easily prepared ionic liquids with promising similar properties in at least its catalytic properties for organic reactions and aluminum metal coating on copper substrate .

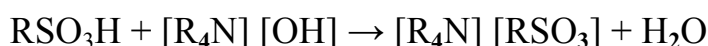
Another type of ionic liquids were prepared from alum sulfate instead of alum chloride for its ease of handling, cheaper, greener and availability of these compounds in variable industrial applications such as water purification. Alum of the type  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{XH}_2\text{O}$ ,  $\text{AlNH}_4(\text{SO}_4)_2 \cdot \text{XH}_2\text{O}$  and  $\text{AlK}(\text{SO}_4)_2 \cdot \text{XH}_2\text{O}$  with urea or acetamide offered room temperature ionic liquids with highly moisture and air stable characterization. This is a green ionic liquid as it was expected to be used in variable process such as metal coating since it offers good media for some insoluble compounds in aqueous media to dissolve easily this ionic liquid such as silver sulphate<sup>[49]</sup> .

There are many ways to prepare different types of ionic liquids such as:

1- Metathesis reactions: which are good candidates for the preparing of new ionic liquids for the first time. However, they can leave the ionic liquids contaminated with a small amount of halide ions that may react with solute materials<sup>[50]</sup> .



2- Acid-base neutralization reaction: tetraalkylammonium sulphonates have been prepared by mixing equimolar amounts of the sulphonic acid and the tetraalkylammonium hydroxide, the excess water was removed in vacuum [50].

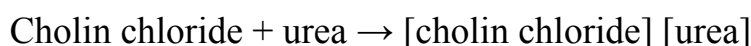


3- The final method is the direct combination of a halide salt with a metal halide [50], such as:



Using a large amount of  $\text{AlCl}_3$  gives  $[\text{Al}_2\text{Cl}_7]^-$ , this considered as (acidic part), and add excess from  $\text{AlCl}_3$  gives  $[\text{Al}_3\text{Cl}_{10}]^-$ , this reaction must occur in dry and high purity conditions.

-Another example for this type of reaction is:



#### **1.4 Room temperature ionic liquids used for carbon dioxide capture**

Many room temperature ionic liquids were investigated as potential absorbents for  $\text{CO}_2$  capture.

Ferguson and Scovazzo [51] showed that imidazolium and phosphonium-based ILs have similar solubilities for several gases, while Anthony and co-workers [52] suggested that the nature of the anion has the most significant influence on the gas solubility. Hutchings and co-workers [53] have reported that, at subcritical temperatures, several phosphonium ionic liquids would completely dissolve as soon as all the  $\text{CO}_2$  condensed and that the isopleths for these systems follow the vapor pressure curve of the pure  $\text{CO}_2$ .

Rhone-Poulenc used a tetrabutylphosphonium chloride to stabilize zero-valent palladium catalysts for carbonylation <sup>[54]</sup>. Eastman Chemical Company used a Lewis basic phosphonium iodide ionic liquid along with a Lewis acid catalyst for the isomeration of 3,4-epoxybut-1-ene to 2,5-dihydrofuran <sup>[55]</sup>.

Trihexyltetradecylphosphonium chloride, [THTDP][Cl], and trihexyltetradecylphosphonium bis(trifluoromethylsulphonyl)imide [THTDP][NTf<sub>2</sub>], ionic liquids were chosen for CO<sub>2</sub> capture. The structure of the phosphonium cation minimizes any specific interactions between the IL cation and the carbon dioxide. Furthermore, the chloride anion of the [THTDP][Cl] allows also to minimize any anion interaction with the CO<sub>2</sub> <sup>[56]</sup>.

1-ethyl-3-methylimidazoliumbis(trifluoromethylsulphonyl)imide ([C<sub>2</sub>mim][Tf<sub>2</sub>N]) and 1-methyl-3-pentyl-imidazolium bis(trifluoromethylsulphonyl)imide ([C<sub>5</sub>mim][Tf<sub>2</sub>N]) were studied to investigate the CO<sub>2</sub> solubility in ionic liquids.

The ionic liquids ; 1-n-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF<sub>4</sub>]<sub>2</sub> and 1-n-butyl-3-methylimidazolium dicyanamide, [bmim][DCA]<sub>2</sub> were used for CO<sub>2</sub> solubility <sup>[57]</sup>.

The Tf<sub>2</sub>N anion-based ILs 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide ([C<sub>2</sub>mim][Tf<sub>2</sub>N]), 1-methyl-3-pentyl-imidazolium bis(trifluoromethylsulphonyl)imide ([C<sub>5</sub>mim][Tf<sub>2</sub>N]) were the ones presenting the highest CO<sub>2</sub> solubility <sup>[58]</sup>.

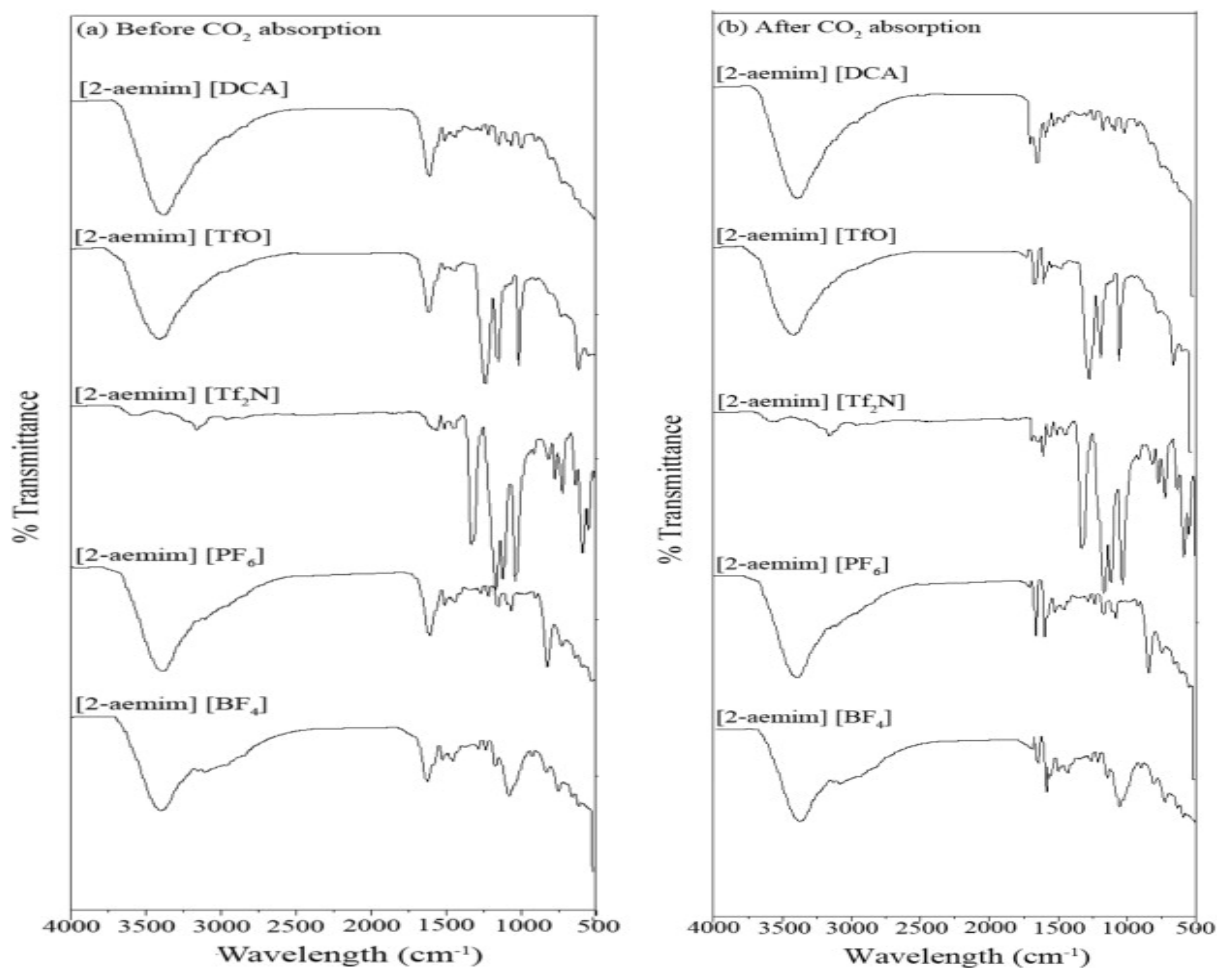


The CO<sub>2</sub> solubility into different room temperature ionic liquids (RTILs) was measured at temperatures between (298 - 343 K) and pressures up to about (1 MPa) . A chemical enhancement of the CO<sub>2</sub> absorption was observed when functionalized RTILs were used as absorption solvents. It was possible to increase the ionic liquid volumetric gas load almost threefold by attaching functional groups to the ionic liquid, whereas for the traditional amine solutions the maximum gas load is stoichiometrically limited <sup>[57]</sup>.

### **1.5 Mechanisms of ILs for CO<sub>2</sub> capture**

Ionic liquids for CO<sub>2</sub> capture requires an appropriate knowledge of the mechanisms involved in the gas absorption, both in the case of physical absorption or chemical reaction, and of the relations between the molecular structure and the properties of the ionic liquids the absorption of CO<sub>2</sub> in the amine-functionalized ILs could be described as a chemical process . In this context, systematic studies of different families of ionic liquids have only a limited utility. The careful choice of the ionic liquids and the properties to study, with the aim of building up a profound knowledge of the molecular features responsible for the behaviors found , seem to be the way to proceed in order to find ionic liquids appropriate for carbon dioxide selective absorption <sup>[59]</sup>.

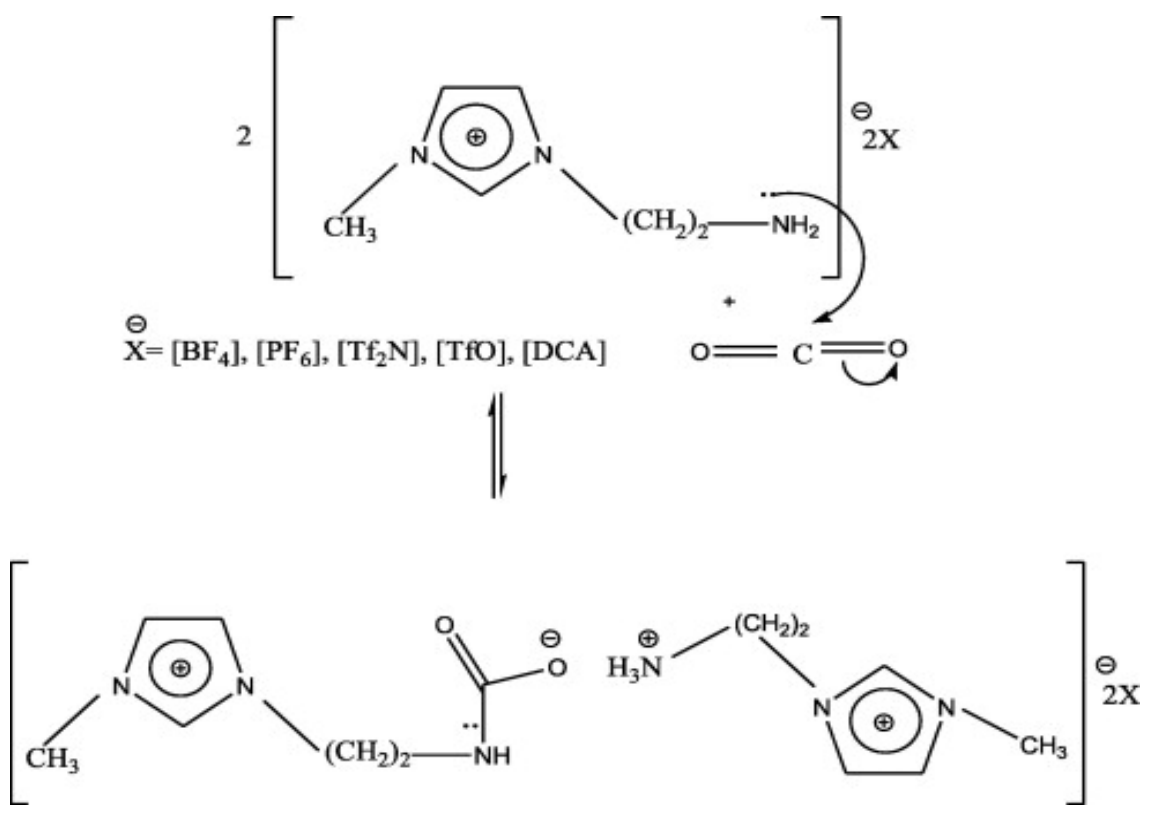
A series of amine-functionalized imidazolium cation-based ionic liquids (ILs) with different anions were synthesized to be potential absorbents for CO<sub>2</sub> capture .The absorption capacities of the ILs for CO<sub>2</sub> were investigated at (30 and 50 °C) at ambient pressures (0-1.6 bar).



**Fig. (1.1) : FTIR spectra of each IL, (a) before CO<sub>2</sub> absorption, (b) after CO<sub>2</sub> absorption<sup>[60]</sup>.**

Spectrum of the CO<sub>2</sub> as shown in Fig.(1.1) treated material manifests a new absorption at 1666 cm<sup>-1</sup>, consistent with a carbamate C=O stretch, it has characteristic peaks of dissolved CO<sub>2</sub> at 2380 and 2400 cm<sup>-1</sup>. Centered at 3238 cm<sup>-1</sup> a broad amide N-H band with considerable fine structure is present. Another broad, but similarly notable new band is centered around 3623 cm<sup>-1</sup> is assigned as an ammonium N-H stretch. Perhaps equally noteworthy is the virtual absence of bands associated with dissolved CO<sub>2</sub><sup>[61-63]</sup>.

The CO<sub>2</sub> absorption results and detailed study indicated the predominance of a 1:2 mechanism, whereby the CO<sub>2</sub> reacted with two IL molecules to form a carbamate group for example as shown in scheme (1.4). The CO<sub>2</sub> absorption capacity of the ILs toward each anion followed the trend: . BF<sub>4</sub><sup>-</sup> < DCA<sup>-</sup> < PF<sub>6</sub><sup>-</sup> < TfO<sup>-</sup> < Tf<sub>2</sub>N<sup>-</sup>. The as-synthesized ILs were selective, thermally stable, provided long-lived operational stability, could be recycled at 70 °C or under vacuum conditions, and could be used repeatedly [60].



Scheme (1.4) : The reacted CO<sub>2</sub> with two IL molecules to form a carbamate group [60].

### **1.5.1 Designer solvents**

Ionic liquids can be modified, for example, by changing the size of their side chains or by adding different functional groups, allowing the synthesis of a huge number of ionic liquids. By controlling these modifications on the ions, it is possible to control certain physico-chemical properties of ionic liquids. For example, properties like melting point, viscosity, density or hydrophobicity can be controlled by adjusting the structure of the ions that constitute an ionic liquid. For this reason, ionic liquids have been regarded as “designer solvents”, because they can be precisely designed for a specific application. Because of the mentioned advantages associated with certain properties of ionic liquids, this class of solvents has been the subject of different areas of investigation in the recent years. For instance, ionic liquids have been studied for applications like chemical synthesis, catalysis, analytical chemistry, electrochemistry, liquid-liquid extraction or biotechnology<sup>[64-66]</sup>.

### **1.5.2 Task-specific ionic liquids (TSILs)**

Ionic liquids (low-temperature molten salts) have been proposed as solvent reagents for gas separations<sup>[67,68]</sup>. Due to the Coulombic attraction between the ions of these liquids, they exhibit no measurable vapor pressure up to their thermal decomposition point, generally  $>300$  °C. This lack of vapor pressure makes these materials highly attractive for gas processing. Indeed, for these purposes they may be thought of as “liquid solids”, incorporating some of the most useful physical properties of both phases. Despite the general promise of ionic liquids (IL) in gas treatment, the molten salts used so far for CO<sub>2</sub> separation are generally “off the shelf” materials

such as  $(\text{CH}_3)_4\text{NF} \cdot 4\text{H}_2\text{O}$  that are not optimized for this purpose, frequently depending upon another volatile reagent - water- to function<sup>[69,70]</sup>. For instance the very weakly basic bi-fluoride ion to drive the net generation of bicarbonate from  $\text{CO}_2$  and water. In this light, the development of new ionic liquids designed for  $\text{CO}_2$  capture is clearly desirable. Recent work suggests that the chances for preparing a broad array of ionic liquids with ions incorporating functional groups are rather good<sup>[71]</sup>. Moreover, certain of these new “task-specific” ionic liquids have proven useful in both synthetic and separations applications<sup>[72,73]</sup>.

The cation of a new task-specific ionic liquid consists of an imidazolium ion to which a primary amine moiety is covalently tethered. This novel salt readily and reversibly sequesters  $\text{CO}_2$ .

Task-specific ionic liquids (TSILs) containing amine functional groups have been synthesized and demonstrated to have much higher capacities for  $\text{CO}_2$  due to their reactivity with  $\text{CO}_2$ , as well as unusually high viscosities in both the neat and complexed states.

Semiquantitative estimates of the cation and anion self-diffusion coefficients and rotational time constants, as well as detailed hydrogen bond analysis, are consistent with the experimentally observed formation of glassy or gel-like materials upon contact with  $\text{CO}_2$ . This has significant implications for the design of new approaches or materials involving ILs that take advantage of these preconceived limitations in the synthesis or manipulation of new TSIL frameworks for  $\text{CO}_2$  capture, and in novel experimental studies of chemistries and dynamics in persistent heterogeneous environments<sup>[74]</sup>.

## **1.6 Measurements of gas solubility**

There are many experimental techniques to measure gas some which are :-

### **1.6.1 The stoichiometric technique:-**

It is the simplest method to measure gas solubility can be done either at constant pressure or with a constant volume of gas. For the constant pressure technique a given mass of ionic liquid is contacted with the gas at fixed pressure. The liquid is stirred vigorously to enhance mass transfer and allow approach to equilibrium. The total volume of gas delivered to the system is used to determine the solubility. For the constant volume technique a known volume of gas is contacted with the stirred ionic liquid sample. Once equilibrium is reached , the pressure is noted and the solubility is determined as before.

The advantage of this technique is that ; it is extremely simple. Care has to be taken to remove all gases dissolved in the ionic liquid sample initially, but this is easily accomplished because one does not have to worry about volatilization of the ionic liquid sample.

The disadvantage of this technique is that it requires relatively large amounts of ionic liquid to get accurate measurements for gases that are only sparingly soluble<sup>[75]</sup>.

### **1.6.2 The gravimetric technique**

The gravimetric technique involves the measurement of the weight gain of an ionic liquid sample when gases are introduced into a sample chamber at a given pressure. The main advantage of this technique, it requires a much smaller sample than the stoichiometric technique. There are two main disadvantages for this technique. First, the sample is placed in a static sample container there is no possibility of stirring. Thus, equilibrium is reached solely by diffusion of the gas into the ionic liquid sample. For the more viscous samples this can require equilibration times of as much as several hours. Second, the weight gain must be corrected for the buoyancy of the sample in order to determine the actual gas solubility<sup>[76]</sup>.

### **1.6.3 spectroscopic technique**

Various spectroscopic techniques can also be used to measure gas solubilities in ionic liquids. For instance, Welton and co-workers have used proton NMR spectroscopy<sup>[77]</sup> to determine the solubility of hydrogen in a series of ionic liquids. Since hydrogen exhibits low solubility in ionic liquids and has such a low molecular weight, it is difficult to measure gravimetrically or by any of the stoichiometric techniques. As a result, it is particularly well suited to determination by spectroscopy. In addition, Kasarian and co-workers have measured CO<sub>2</sub> solubility by infrared spectroscopy. In general, spectroscopic techniques are quite attractive, as long as extinction coefficients do not vary significantly with temperature and pressure, since they can be performed<sup>[78]</sup>.

### **1.6.4 Gas chromatography**

This technique has been used to measure the infinite dilution activity coefficients of a wide variety of liquid solutes in ionic liquids and could conceivably be used to get the infinite dilution activity coefficients of condensable gases, as well. This technique would work for condensable gases that are retained by the ionic liquid more strongly than the carrier gas (usually helium), which may well be the case for many of the alkanes and alkenes of interest<sup>[79-83]</sup>.

### **1.7 CO<sub>2</sub> solubility in ionic liquids**

CO<sub>2</sub> solubility is of a particular importance due to its use in industrial mixtures and its significance for green engineering. CO<sub>2</sub> has one of the highest solubilities in ionic liquids and most solubility measurement techniques can quantify CO<sub>2</sub> sorption. The ionic liquids appearing most often include [BMIM][PF<sub>6</sub>] and [BMIM][BF<sub>4</sub>]<sup>[84]</sup>. Unfortunately, [BMIM][PF<sub>6</sub>] is particular concern as it degrades to HF in the presence of water. Products which result from this degradation can also affect the solubility measurement. The published solubility results include both high and low pressure measurements that utilize numerous apparatus based on gravimetric, stoichiometric, and spectroscopic techniques<sup>[85-86]</sup>.

#### **1.7.1 Low –pressure CO<sub>2</sub> solubility**

The ability to "tune" ionic liquid properties has led to an increase in the number of ionic liquids synthesized in recent years. There are several trends that appear in the CO<sub>2</sub> solubility<sup>[87]</sup>. The first is that the influence of changing the anion is much larger than making changes in the cation.



Secondly, the substitution of a methyl group on the C<sub>2</sub> carbon of the imidazolium ring does not largely affect the solubility at low pressure<sup>[88,89]</sup>.

### **1.7.2 High –pressure CO<sub>2</sub> solubility**

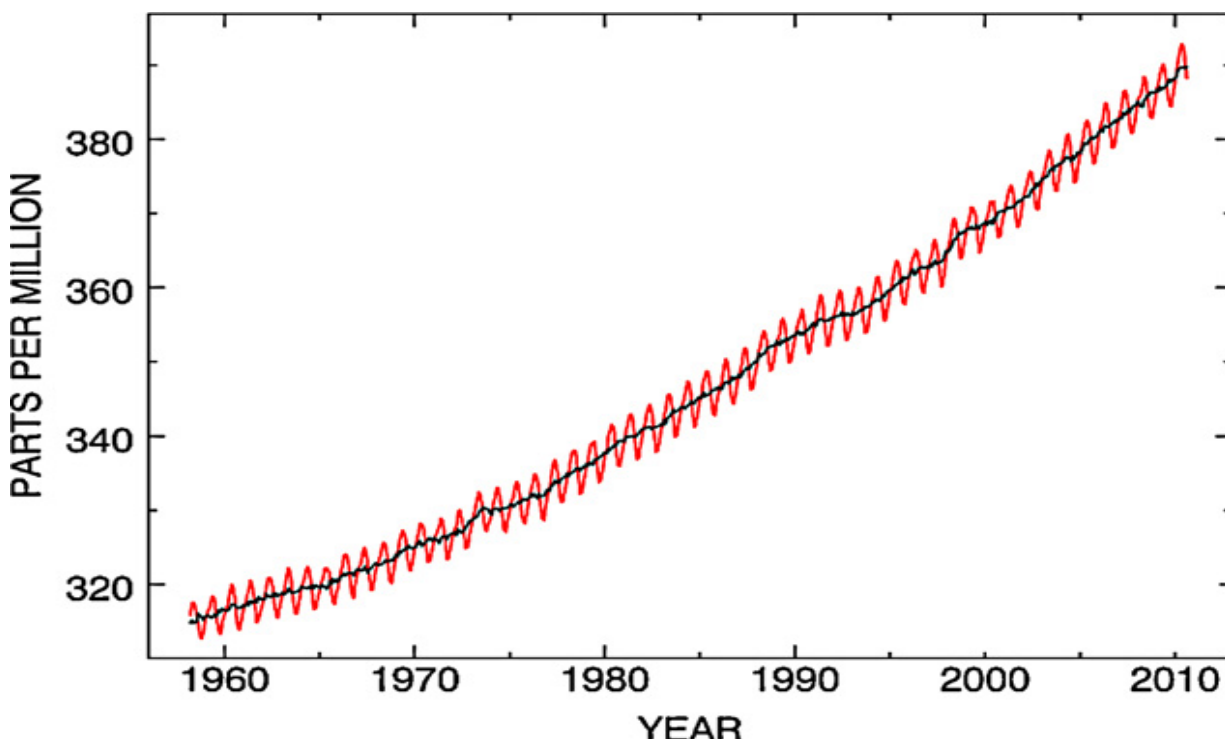
High pressure CO<sub>2</sub> gas solubility in ionic liquids is of a particular interest for supercritical CO<sub>2</sub> extraction and biphasic reactions. Many groups have published phase behavior which was needed to design extraction and reaction processes necessary for these applications<sup>[90-93]</sup>. The imidazolium ionic liquids helped to study the majority of ionic liquids with very few exceptions. Results from the imidazolium ionic liquids suggest that the solubility of CO<sub>2</sub> is strongly dependent on the choice of anion, with the solubility increasing with increasing fluorination on the anion. The cation also affects solubility with increasing alkyl chain length marginally increasing its CO<sub>2</sub> solubility<sup>[94]</sup>.

### **1.8 carbon dioxide capture storage (CCS)**

Fossil fuels will continue to play an important role in the foreseeable future, mainly in power generation and industrial manufacturing. The burning of these fossil fuels releases large amounts of CO<sub>2</sub> into the atmosphere; this disturbs the carbon balance of our planet which has been steady over hundreds millions of years. Although anthropogenic CO<sub>2</sub> emissions are relatively small compared to the natural carbon fluxes, such as photosynthetic fluxes, the increased release has had obvious influences on the global climate in a very short period of time. Since the beginning of the industrial age in ca. 1750, the CO<sub>2</sub> concentration in atmosphere has increased (Fig. 1.2)<sup>[95]</sup>. The increase of the CO<sub>2</sub> concentration in atmosphere influences the balance of incoming and outgoing energy in the

atmosphere system, leading to the raise of average surface temperature of earth<sup>[96]</sup>.

The ultimate goal of a green society will only be achieved when the dependence on fossil fuels is relinquish in favor of clean energy sources such as hydrogen fuel or solar energy. In the interim period to a low-carbon society, however, it is imperative to reduce anthropogenic CO<sub>2</sub> emission . The estimation from the Intergovernmental Panel on Climate Change (IPCC) has shown that CO<sub>2</sub> emissions could be reduced by 80-90% for a modern power plant that is equipped with suitable carbon dioxide capture and storage (CCS) technologies <sup>[97]</sup> . The use of CCS will also complement other crucial strategies, such as switching to less carbon fuels, improving energy efficiency, and phasing in the use of renewable energy resources <sup>[95]</sup>.



**Fig. (1.2) : Atmospheric CO<sub>2</sub> concentration during 1958-2010 (at Mauna Loa Observatory), showing the continuing and accelerating increase of CO<sub>2</sub> in atmosphere <sup>[95]</sup>.**

## **1.9 The process carbon dioxide capture storage (CCS)**

CCS is a three-step process including CO<sub>2</sub> capture, a process consisting of separating CO<sub>2</sub> from other emissions before it enters the atmosphere; CO<sub>2</sub> transportation to a storage site; and its permanent storage. The transportation and storage of CO<sub>2</sub> are relatively mature technologies and a growing number of fully integrated CCS projects have reached the pilot-stage prior to commercialization [98]. However, the considerable cost of capture, approximately two thirds of the total cost for CCS (primarily separating CO<sub>2</sub> from other gases), is slowing down the deployment of commercial CCS projects. In the majority of the proposed technologies, one significant contributor to lower cost is the maximum separation efficiency that can be achieved by a given capture material. Thus, the discovery of new materials with high separation ability becomes one of the biggest challenges. Several monographs have been published on this topic, where basic knowledge, progress, and perspective for CCS were presented by experts in this field [96-98].

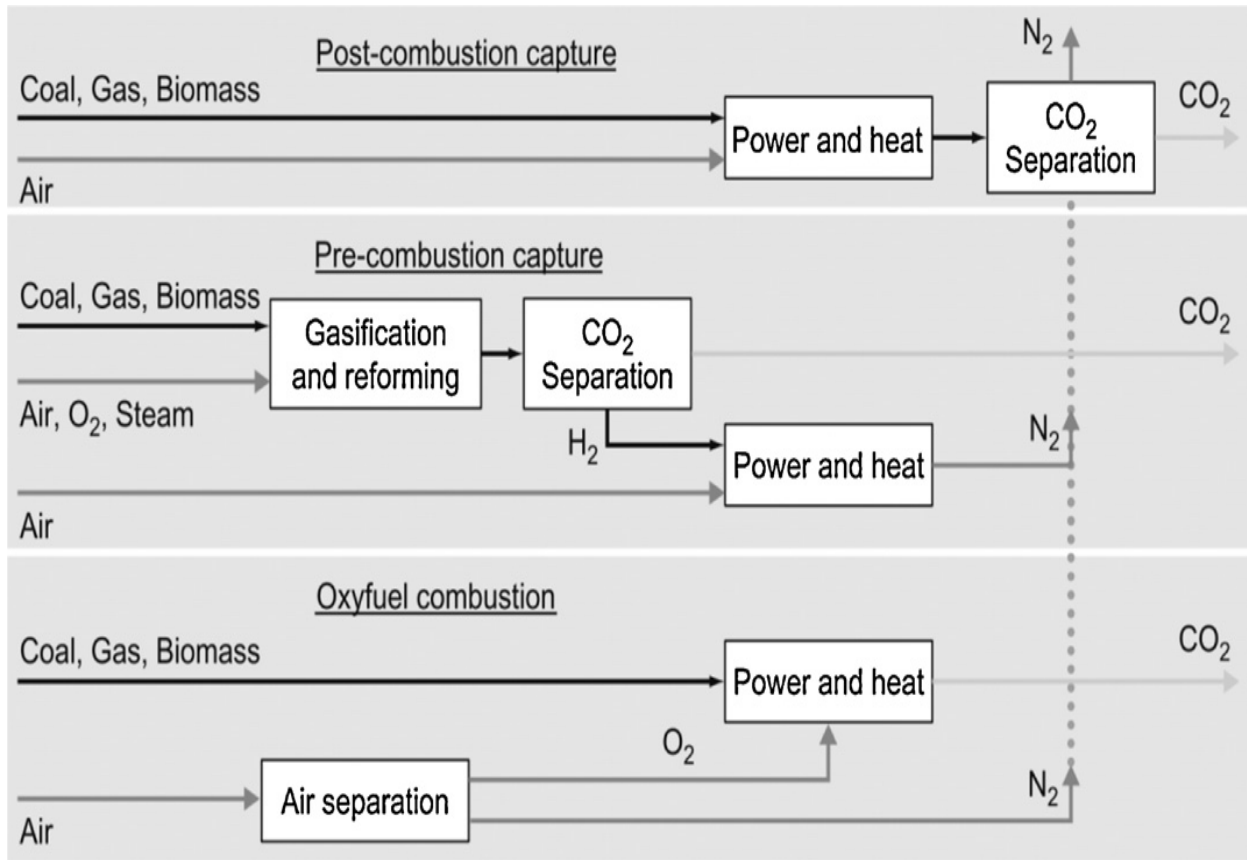
## **1.10 Technologies, methods and materials in CO<sub>2</sub> capture**

Exploring cost-effective, scalable technologies and methods for CO<sub>2</sub> capture from power generation and industrial operation where CO<sub>2</sub> is produced on the combustion of fossil fuels are regarded as the most effective strategies in controlling anthropogenic CO<sub>2</sub> emissions. Depending on the generation of CO<sub>2</sub>, several capture options and tendentious technologies have been suggested and implemented [99].

Generally, based on the fundamental chemical process involved in the combustion of fossil fuels, three basic CO<sub>2</sub> separation and capture options were adopted [99-101].-

- (1) Pre-combustion capture;
- (2) Oxy-fuel combustion
- (3) Post-combustion capture .

As an example, the three options for CO<sub>2</sub> capture from power generation plants are illustrated in scheme (1.5).



Scheme (1.5) : Three options for CO<sub>2</sub> capture from power generation plants<sup>[101]</sup> .

Pre-combustion capture involves the reaction of a primary fuel with oxygen or air to produce H<sub>2</sub>. In some cases the produced gas mixture is mainly composed of CO and H<sub>2</sub>, which is known as synthesis gas (syngas). The CO formed is further reacted with steam in a catalytic reactor, called a shift converter, to give CO<sub>2</sub> and more H<sub>2</sub>. The separation of CO<sub>2</sub> and H<sub>2</sub> then

can be achieved by a number of technologies. Pre-combustion has the advantage of lower energy requirements, but the temperature and efficiency associated with H<sub>2</sub>-rich gas turbine fuel is a big problem. More challenging issues are the enormous capital cost and the public resistance for new construction <sup>[99]</sup>.

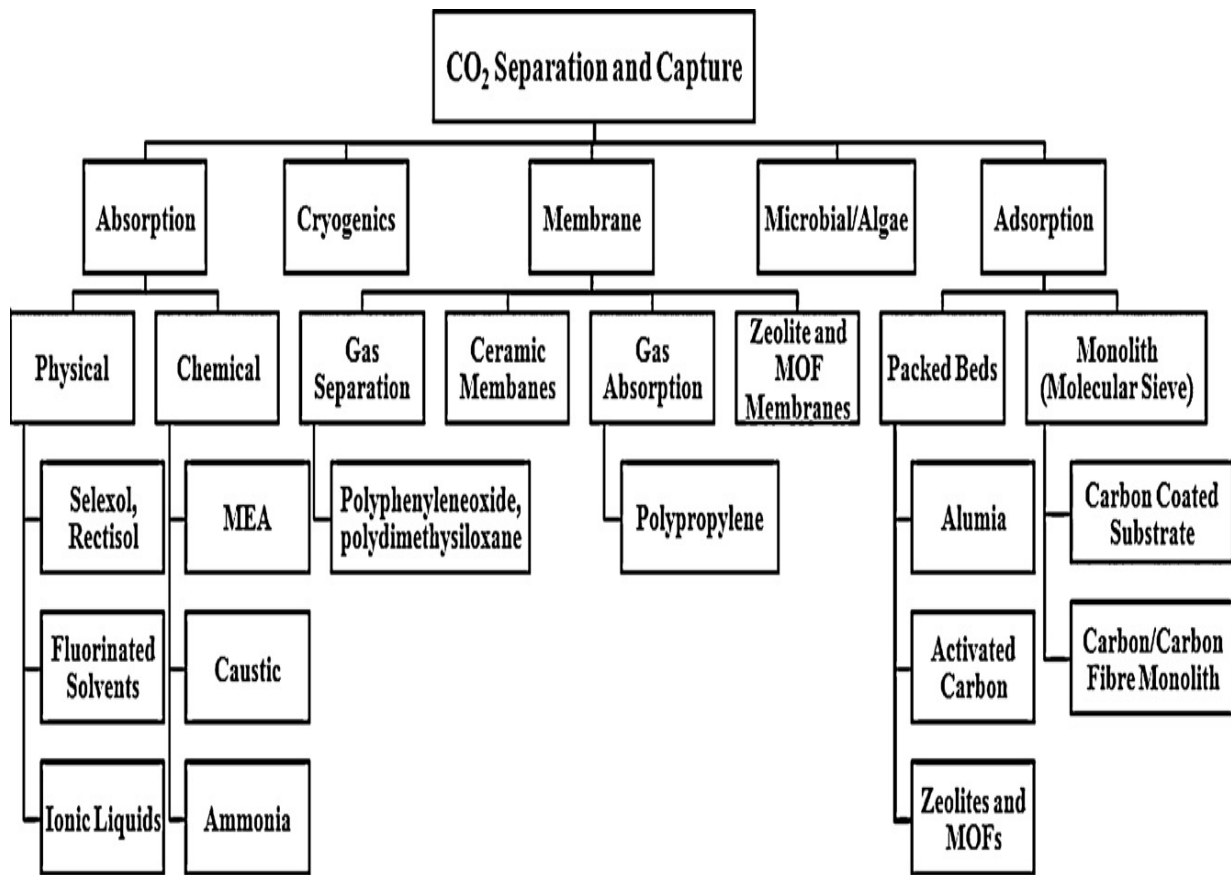
Oxy-fuel combustion has the stringent requirement of nearly pure oxygen, rather than air, for the combustion of fuels; the advantage here being that the gaseous product is nearly pure CO<sub>2</sub>, which can be directly stored. The drawback of this option is the requirement of pure oxygen, which can usually be obtained by the separation of air or by other novel techniques that are available. However, the conventional cryogenic air separation to produce O<sub>2</sub> contributes to the high capital cost for this option <sup>[100]</sup>.

Post-combustion capture requires removing CO<sub>2</sub> from flue gas, comprised mainly of N<sub>2</sub> and CO<sub>2</sub>, before emission into the atmosphere. Post-combustion capture is the most feasible on a short time scale because many of the proposed technologies can be retrofitted to existing fossil fuel consuming power plants. One such new approach involves also using cooled and CO<sub>2</sub>-rich flue gases to feed bioreactors to produce micro algal biomass that would be used as a biofuel. An additional advantage of post-combustion capture is that even if when the CO<sub>2</sub> capture unit is shut down for an emergency, one can still generate electricity, which is not possible with the other more integrated capture methods. Post combustion methods have been deployed commercially, primarily for the removal of minor contaminants such as Hg and SO<sub>x</sub>/NO<sub>x</sub> gas, but the materials for the CO<sub>2</sub> separation require modification, especially those with high preparation and regeneration costs <sup>[101]</sup>.

A further advantage of developing CO<sub>2</sub> separation techniques is their application in the purification of natural gas (mainly CH<sub>4</sub>), which is typically sourced with over 40% CO<sub>2</sub> and N<sub>2</sub> and is only useable at low concentrations of CO<sub>2</sub>. One of the challenges in this separation is the special technologies and materials that are required to withstand the high pressures that are present during the mining of natural gas. Scheme (1.5) <sup>[102]</sup> illustrates the technologies and method usually used in CO<sub>2</sub> separation in each case, except focryogenic separation, different materials are required as the carriers. Absorption (i.e. solvent scrubbing) is a well-established CO<sub>2</sub> separation approach used in the chemical and petroleum industries today <sup>[103]</sup>.

Absorption falls into two categories: (1) physical, which is temperature and pressure dependent (absorption occurs at high pressures and low temperatures) and (2) chemical where absorption of CO<sub>2</sub> depends on the acid–base neutralization reaction(in this case caustic solvents are required).

Some of the preferred solvents are amines (such as monoethanolamine), ammonia solutions, Selexol, Rectisol, and fluorinated solvents. The most recent addition is ionic liquids which have exhibited great potential in absorption of CO<sub>2</sub> and are also environmentally benign <sup>[104]</sup>.



**Scheme (1.6) : Different technologies and associated materials for CO<sub>2</sub> separation and capture <sup>[102]</sup> .**

Cryogenic distillation uses a principle of separation based on cooling and condensation, and has been used in liquid separations for a long time. This technique is theoretically sound for CO<sub>2</sub> separation, however, the considerable energy demand deems it unreasonable for practical application. This method is more effective when the gas stream contains high CO<sub>2</sub> concentration and it can be adopted in oxygen production for oxyfuel combustion. It is presently the most widely used system for the large-scale production of O<sub>2</sub> from the separation of air.

Membrane-based separation is based on the differences in physical and/or chemical interactions between gases and the membrane material, which can be modified to allow some components to pass preferentially through the membrane based on size (kinetic) and/or affinity

(thermodynamics). Membranes have great potential in CO<sub>2</sub>/H<sub>2</sub> separation in pre-combustion capture and post-combustion CO<sub>2</sub>/N<sub>2</sub> separation. A wide variety of different membrane materials and processes are available, some of which already on an industrial scale, and potentially applicable in CO<sub>2</sub> separation. The performance and associated cost of these membrane-based technologies in large scale CO<sub>2</sub> capture mainly relies on the membrane materials themselves. Inorganic ceramic membranes and organic polymeric membranes have been used in CO<sub>2</sub> separation from flue gas in post-combustion. However, reaching a high degree of CO<sub>2</sub> separation by using single-stage ceramic or polymeric membrane is difficult as of yet (although it is feasible in terms of cost). New materials are still required to achieve the desired effectiveness in CO<sub>2</sub> separation by membranes<sup>[105]</sup>.

Gas separation based on adsorption has been well developed, in which the selection of a sound adsorbent is the key for specific separation. Although materials for gas adsorptive separation have been established and a diverse range of useful sorbents are available for CO<sub>2</sub> separation, there is still plenty of room to optimize the performance of these materials and investigate a wider range of new sorbents. These adsorbents can then be combined with a broad range of process options yielding a fertile field for the optimization of separation performance. Conventional solid adsorbents include activated carbons, silica gel, ion-exchange resins, zeolites, and mesoporous silicates, activated alumina, metal oxides, and other surface-modified porous media. In recent years, a few new adsorbents such as carbon fibres and their composites as well as metal-organic frameworks have been developed for gas separation<sup>[106]</sup>.



A recent review has comprehensively described the adsorbent materials for CO<sub>2</sub> capture from large anthropogenic point sources . Depending on the regeneration methods, several adsorption processes can be adopted to achieve CO<sub>2</sub> separation, including <sup>[107]</sup>:-

- (1) Vacuum and pressure swing adsorption (VSA and PSA)
- (2) Temperature swing adsorption (TSA)
- (3) Electric swing adsorption (ESA)
- (4) Simulated moving bed (SMB)
- (5) Purge displacement <sup>[107]</sup> .

A part from physical and chemical methods mentioned before, biological methods have also been proposed for CO<sub>2</sub> separation <sup>[105 -107]</sup> . Algal bio-fixation of CO<sub>2</sub> in photo-bioreactors has, for example, recently gained great interest in CO<sub>2</sub> capture. In addition, attempts using chemoautotrophic microorganisms which use inorganic chemicals instead of light energy for CO<sub>2</sub> removal have also been investigated <sup>[105 -108]</sup> . It is evident that the progress and achievement of almost all of these technologies relies heavily on the development of materials. The challenges that arise in the development of these materials and techniques lies in being able to transfer the technology from the lab to the harsh conditions that it will be subjected to while maximizing efficiency and minimizing costs<sup>[108]</sup> .

### **1.11 Advances and challenges in CO<sub>2</sub> capture**

CCS is a fast growing field of research and a broad range of technologies are being explored and developed on a daily basis. Few technologies have already reached the deployment stage, but most require

further improvements to the technical capabilities and reduction in the associated costs.

The most mature technology, post-combustion amine absorption, has been employed in industry for a long time. Simultaneously, a number of materials are available for different technologies and some new materials are emerging. However, the commercialization of any one these technologies still faces substantial challenges not only in the final technological and processes aspects but also in the capabilities of the capture materials themselves<sup>[109]</sup>.

Up to date, three options have developed to a stage commercially viable, namely post-combustion CO<sub>2</sub> capture using amine solvents based on chemical absorption, oxyfuel combustion, and calcium looping. The membrane-based separation and adsorption of CO<sub>2</sub> into advanced sorbents, such as zeolites and metal-organic frameworks (MOFs), have become intense research subjects in the last ten years. Tuning the properties of traditional adsorbents can be quite challenging which is why these new, advanced sorbents have become such a hot topic. Since separation is a combination of a kinetic (diffusion selectivity) and a thermodynamic (adsorption) properties, the materials of tomorrow will have to account for both the size and electronic properties of the gas molecules.

The relatively small difference in kinetic diameters between CO<sub>2</sub> (3.30Å<sup>o</sup>), CH<sub>4</sub> (3.76Å<sup>o</sup>), and N<sub>2</sub> (3.64Å<sup>o</sup>) makes exclusion based purely on size very challenging, but the differences in electronic properties such as quadrupole moment and polarization can be used to accomplish the tasks at hand<sup>[110]</sup>.

Challenges and shortcomings in terms of the three basic capture options for CO<sub>2</sub> are outlined briefly below. For pre-combustion capture<sup>[111]</sup>:-

- (1) Poor availability and operability is the primary deficiency;
- (2) No single process is responsible for the overall operational performance;
- (3) High cost remains
- (4) Systems are not mature for large-scale application.

For oxy-fuel combustion capture:

- (1) The technology is only at a developmental stage without commercial experience.
- (2) The air-separation that supplies pure oxygen consumes a lot of energy.

For post-combustion capture:

- (1) Low pressure and dilute CO<sub>2</sub> concentration of the flue gas requires a high volume of gas to be treated.
- (2) Compression of the captured CO<sub>2</sub> requires additional energy.
- (3) The regeneration of the sorbent (the amine solution) requires a high energy input. Most of these problems can be solve with the implementation of advanced Materials.

The three basic technologies for CO<sub>2</sub> separation: (absorption, adsorption, and membrane processes), have been extensively studied, using the amine-based absorption process as the current bench mark . Despite the intensive investigation, however, no single technology has been demonstrated to be capable of meeting the requirements set by the DOE/NETL: 90% CO<sub>2</sub> capture at less than 35% increase in the cost of

electricity <sup>[111]</sup>. In almost all absorption and chemical adsorption processes, the capture and separation steps consist of the formation of CO<sub>2</sub>-based molecular complexes via chemical interactions and subsequent regeneration of CO<sub>2</sub> through significant increases in temperature.

This regeneration accounts for the majority of the parasitic power requirement <sup>[112]</sup>. There is therefore a critical need to develop transformative CO<sub>2</sub> capture materials and processes that can drastically lower the operation cost by addressing the regeneration cost. In this regard, CO<sub>2</sub> capture by physical sorbents and membranes can provide promising energy-efficient alternatives to the current amine-based absorption systems if the following challenges can be addressed.

Membrane-based CO<sub>2</sub> separation is one of the most energy efficient ways to capture CO<sub>2</sub> <sup>[112]</sup>. However, the traditional polymer membranes suffer from low CO<sub>2</sub>/N<sub>2</sub> selectivity (less than 100). For the membrane-based separation to be commercially viable, the CO<sub>2</sub>/N<sub>2</sub> selectivity must be in the range of 200 <sup>[113]</sup>. Despite the potential of molecular sieve membranes, conventional molecular sieves (i.e. zeolites) are limited for their use for CO<sub>2</sub>/N<sub>2</sub> separation due to the similarity of the kinetic diameters of CO<sub>2</sub> (3.3Å) and N<sub>2</sub> (3.64Å). Therefore, it is highly desirable to develop advanced molecular sieve membranes with high CO<sub>2</sub>/N<sub>2</sub> selectivity.

## **1.12 Thermogravimetric Analysis (TGA)**

Thermal Analysis (TA) is a group of techniques that study the change in mass properties of materials with temperature change <sup>[114]</sup>.

### 1.12.1 General description

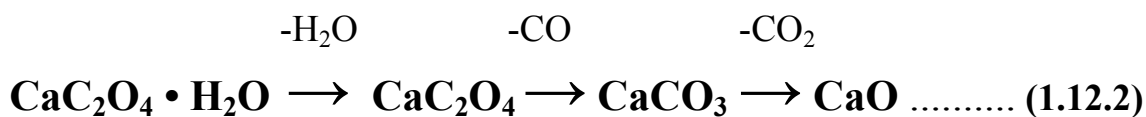
Thermogravimetric analysis (TGA) is an analytical technique used to determine the thermal stability of any solid material and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% O<sub>2</sub> in N<sub>2</sub> or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) <sup>[114]</sup>.

The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process. In practice thermal analysis gives properties like; enthalpy, thermal capacity, mass changes and the coefficient of heat expansion. Solid state chemistry uses thermal analysis for studying reactions in the solid state, thermal degradation reactions, phase transitions and phase diagrams <sup>[114]</sup>.

### 1.12.2 TGA example

#### **- Ex. Decomposition of calcium oxalate monohydrate**

Calcium oxalate monohydrate, a standard material often used to demonstrate TGA performance. Exhibits three weight losses with temperature in an inert atmosphere (e.g. N<sub>2</sub>) <sup>[115]</sup>.



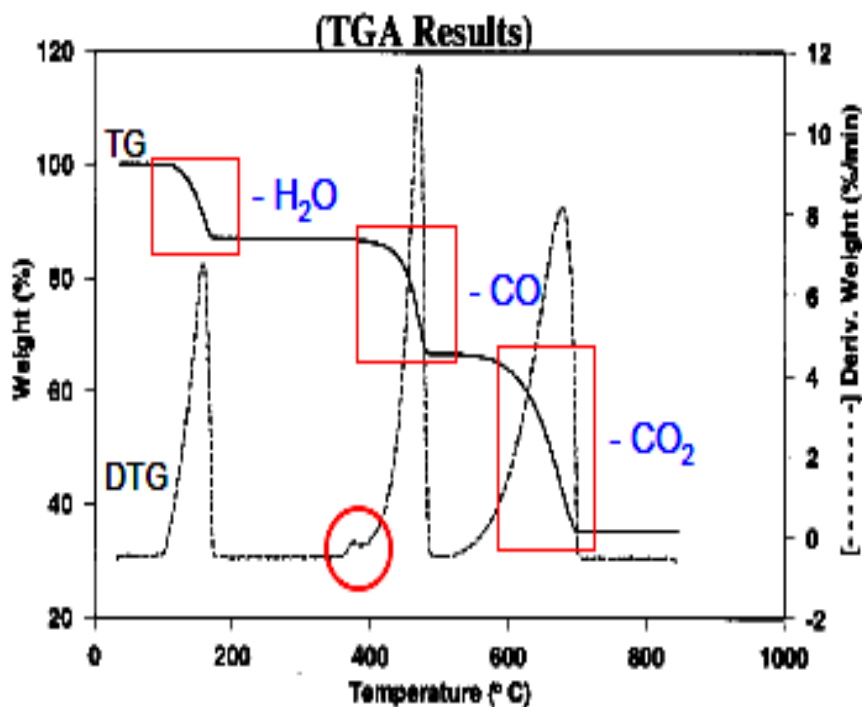


Fig. (1.3) : Decomposition of calcium oxalate monohydrate <sup>[115]</sup> .

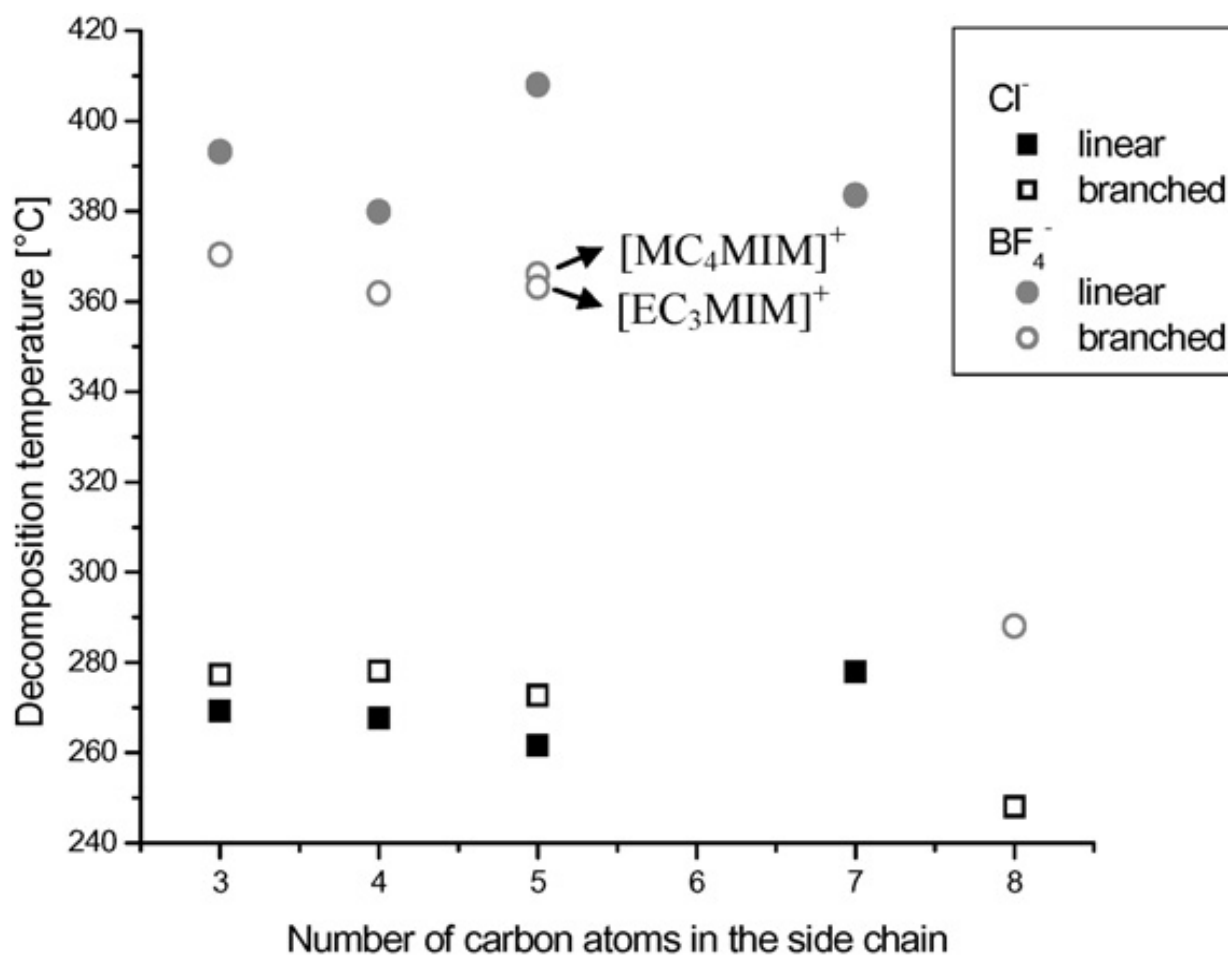
### 1.12.3 DTA changes in heat / temperature (endo- or exothermic)

DTA can measure some physical changes in heat / temperature due to adsorption (exothermic), desorption (endothermic), a change in crystal structure , (endo - or exothermic) , melting (endothermic) , vaporization (endothermic) or sublimation (endothermic) and it can measure some chemical changes due to oxidation (exothermic), reduction (endothermic) , break down reactions ,(endo - or exothermic), chemisorption (exothermic), solid state reactions,(endo - or exothermic)<sup>[114]</sup>.

### **1.13 Thermal stability of ionic liquids**

The heat of combustion of ionic liquids is one of the chemical properties that is influenced by structure of ionic liquids. Ionic liquids was developed by increase the branched alkanes that have a slightly lower heat of combustion and therefore they are more stable than their linear analogues<sup>[116]</sup>. The thermogravimetric analysis (TGA), depicted in (Fig.1. 4) revealed that the degree of branching has a small, but not significant influence on the decomposition temperature of the chloride - containing ionic liquids of the imidazolium types. The branched ionic liquids were found to be on average 10 C more stable than their linear analogues.

Anion thermal stability of ionic liquids decreases in the order  $\text{BF}_4^- > \text{H}_3\text{CSO}_3^- > \text{PF}_6^-$ <sup>[117]</sup>. The improvements in thermal stabilities of ionic liquids by polymeric chains were used to investigate  $\text{CO}_2$  capture at elevated temperatures of flue gas. All polyetheramine samples synthesized showed excellent thermal stabilities with no weight drop until the onset of their thermal decomposition, indicating negligible vapor pressure over a wide range of operating temperatures. Therefor the thermal stability of ionic liquids can be further optimized by selecting different polymers and linkers<sup>[118]</sup>.



**Fig. (1.4) Decomposition temperatures of the different branched and linear imidazolium-based ionic liquids, bearing chloride and tetrafluoroborate as counterions<sup>[117]</sup>.**



### **1.15 Aim of The Present Work**

Since ionic liquids offering a new class of green solvent media , it is worthy to investigate their ability and capability to capture carbon dioxide .

The aims of the present work are :-

1- Prepare some known ionic liquids hydrated ammonium aluminum sulfate  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and urea  $\text{NH}_2\text{CONH}_2$ , hydrated aluminum nitrate  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and urea  $\text{NH}_2\text{CONH}_2$  , aluminum chloride with either urea or acetamide ( $\text{CH}_3\text{CONH}_2$ ) , choline chloride  $\text{OH}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3$  and urea  $\text{NH}_2\text{CONH}_2$ .

2- Study the capturing of  $\text{CO}_2$  at room temperature and atmospheric pressure using FT-IR to demonstrate the interaction between carbon dioxide and some selected ionic liquids.

3- Study the enhancement of these ionic liquids in the presence of some catalysts like sodium hydroxide, Calcium, oxide, monoethanolamine and ammonium chloride as a solid or aqueous.

# *Chapter two*

## *Experimental part*

## Chapter two

### Experimental part

#### 2.1 Chemicals:

All chemicals in this work were used with highest purity available without further purification table (2-1) .

**Table (2.1):- The chemicals used with their purities and suppliers.**

Chemical compounds	Chemical formula	Purity %	Company
Hydrated ammonium aluminum sulfate	$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	99	BDH
Hydrated ammonium aluminum nitrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	97	BDH
Aluminum chloride	$\text{AlCl}_3$	98	Fluka
Urea	$\text{NH}_2\text{CONH}_2$	99.5	THOMAS BAKER
Sodium hydroxide	$\text{NaOH}$	99	BDH
Calcium oxide	$\text{CaO}$	99	BDH
Choline chloride	$\text{OH}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3$	98	BDH
ammonium chloride	$\text{NH}_4\text{Cl}$	97	BDH
Monoethanolamine	$\text{OH}(\text{CH}_2)_2\text{NH}_2$	99	THOMAS BAKER
Distilled water	$\text{H}_2\text{O}$	99	
Acetamide	$\text{CH}_3\text{CONH}_2$	98	Fluka

## 2.2 Instrument

The main instrument used throughout this study was FTIR .

**FTIR:-** (Fourier Transform Infrared Spectrophotometer , 2006 , Shimadzu , IR-Prestige 21, Shimadzu 8000) .

## 2.3 Preparation of solutions

### 2.3.1 Preparation of ionic liquids :-

#### **a- Aluminum chloride- urea and aluminum chloride- acetamide ILs<sup>[119]</sup>.**

Aluminum chloride  $\text{AlCl}_3$  with either urea  $\text{CO}(\text{NH}_2)_2$  or acetamide  $\text{NH}_2\text{COCH}_3$  were used to prepare the ionic liquid in a mole ratio of (1.4:1) by direct mixing of solid components giving a clear faint liquids.

#### **b- Choline chloride -urea IL<sup>[120]</sup>.**

Solid choline chloride  $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OH Cl}^-$  and urea  $\text{NH}_2\text{CONH}_2$  in a mole ratio of (1:2) were mixed and heated gradually to  $85^\circ\text{C}$  in a closed container with continuous gentle stirring until both solid components melted together producing colorless liquid .

#### **c- Hydrated ammonium aluminum sulfate- urea ionic liquid<sup>[121]</sup>**

Hydrated ammonium aluminum sulfate  $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$  and urea  $[\text{NH}_2\text{CONH}_2]$  in a mole ratio of (1:5) were milled, well mixed and heated gradually to  $85^\circ\text{C}$  in a closed glass tube with continuous gentle stirring until the solid salts changed to colorless liquid.

**d- Hydrated aluminum nitrate- urea IL<sup>[122]</sup>**

Solid mixture of hydrated aluminum nitrate  $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$  and urea  $[\text{NH}_2\text{CONH}_2]$  in a mole ratio of (1:1.3) was milled, well mixed and heated gradually to  $85^\circ\text{C}$  in a closed container with continuous gentle stirring until both solid components melted together producing colorless liquid.

**2.4 Addition of some chemical compounds to ionic liquids.**

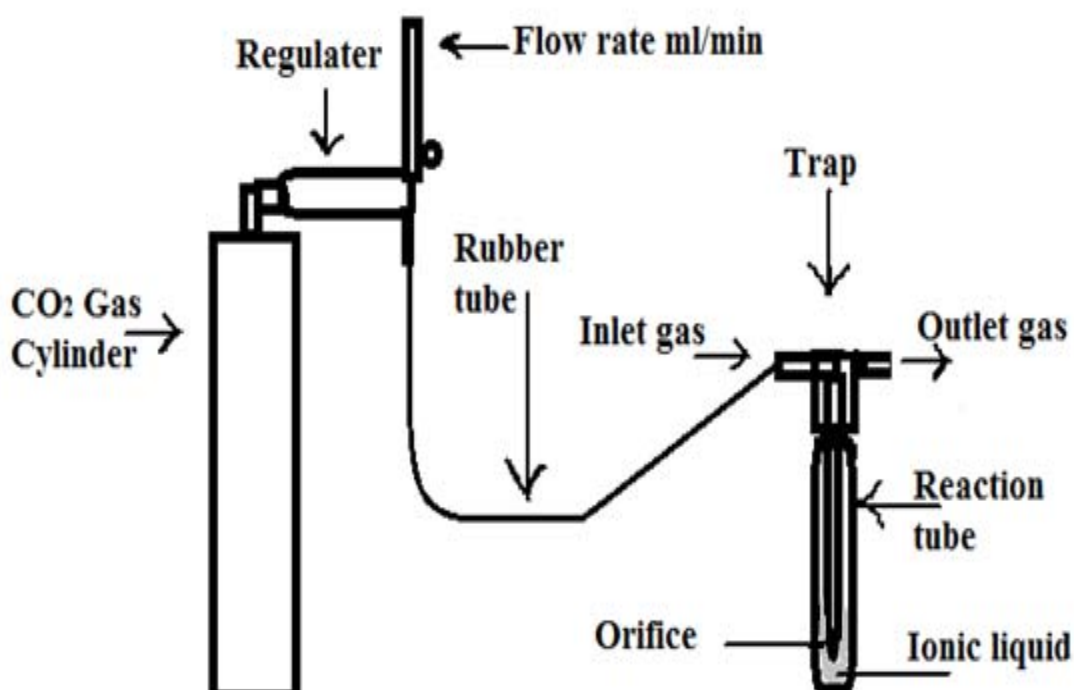
Some chemical compounds were added to ionic liquids as powders or aqueous solutions as stated bellow :-

- a-** Sodium hydroxide pellet (0.04 g) was crashed and added to 10 ml of  $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}] - \text{CO}(\text{NH}_2)_2$  ionic liquid in its powder form to make a solution of (0.001 M) .
- b-** Three drops of sodium hydroxide aqueous solution (0.002 M) were added to 10 ml of  $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}] - \text{CO}(\text{NH}_2)_2$  ionic liquid .
- c-** Calcium oxide (0.01g) was added to both  $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}] - \text{CO}(\text{NH}_2)_2$  and  $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] - \text{CO}(\text{NH}_2)_2$  ionic liquids in its powder form to make a solution of (0.0178 M) .
- d-** 1 ml of monoethanolamine was added to (10 ml) of  $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$  and urea  $[\text{NH}_2\text{CONH}_2]$  ionic liquid , heated gradually to ( $60^\circ\text{C}$ ) with continuous gentle stirring until it completely dissolved after half an hour .
- e-** Ammonium chloride (0.001g) was added to (10ml) hydrated ammonium aluminum sulfate -urea ionic liquid (0.00187 M) .

- f- Addition of few drops of distilled water to  $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$  and urea  $[\text{NH}_2\text{CONH}_2]$  ionic liquid.

## 2.5 Carbon dioxide gas flow

Carbon dioxide was bubbled into ionic liquids at flow rate of 500 ml/min. for half an hour through mesh orifice ended glass tube immersed down the bottom of the reaction tube (scheme 2.1) . At the end of the experiment the liquid was examined by FT-IR.



Scheme ( 2.1):- The system of CO<sub>2</sub> capture by ionic liquids.

# *Chapter Three*

## *Results and Discussion*

## Chapter Three

### Results and Discussion

#### 3.1 The preparation of a number of room temperature ionic liquids

The ionic liquids of aluminum chloride  $\text{AlCl}_3$  with either urea  $\text{NH}_2\text{CONH}_2$  or acetamide  $\text{CH}_3\text{CONH}_2$ <sup>[119]</sup>, choline chloride  $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OHCl}^-$  and urea  $\text{NH}_2\text{CONH}_2$ <sup>[120]</sup>, hydrated ammonium aluminum sulphate  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and urea  $\text{NH}_2\text{CONH}_2$ <sup>[121]</sup> and hydrated aluminum nitrate  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and urea  $\text{NH}_2\text{CONH}_2$ <sup>[122]</sup>, were prepared. These ionic liquids were used to investigate their ability to absorb carbon dioxide gas with or without catalysts in an attempt to enhance their capacity for  $\text{CO}_2$  gas absorption.

#### 3.2 $\text{CO}_2$ capture by ionic liquids

Prepared ionic liquids bubbling with carbon dioxide were analyzed using FTIR to verify the reaction between the functional amine group and carbonyl group of ionic liquids with carbon dioxide.

##### 3.2.1 Aluminum chloride – urea IL

Aluminum chloride - urea ionic liquid previously was<sup>(119)</sup> bubbled with carbon dioxide, there were some changes in the vibrational mode of the amide and carbonyl groups in addition to the appearance of a new band at  $1655\text{ cm}^{-1}$  (Fig. 3.1). The latter frequency could be arise from a splitting in the carbonyl group vibrational mode. Amide bending vibration band at  $1508\text{ cm}^{-1}$  (Table 3.1) showed an increase in its intensity with similar increase in the intensity of  $\text{C}=\text{O}$ . These changes may indicate qualitatively an interaction of carbon dioxide with urea of the ionic liquid.



Table-(3.1):- Major FTIR vibrational bands of AlCl<sub>3</sub> - CO(NH<sub>2</sub>)<sub>2</sub> IL and with capturing CO<sub>2</sub> in cm<sup>-1</sup>.

Ionic liquid	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{C=O})$	$\nu_s(\text{N-C-N})$	$\nu_{as}(\text{N-C-N})$	Fig
AlCl <sub>3</sub> -urea	3333 3270	1585 1504	1643	1161	1320	3.1(black and red)
AlCl <sub>3</sub> -urea + CO <sub>2</sub>	3498 3387 3059	1566 1508	1655 1639	1157	1350	3.1 (green)

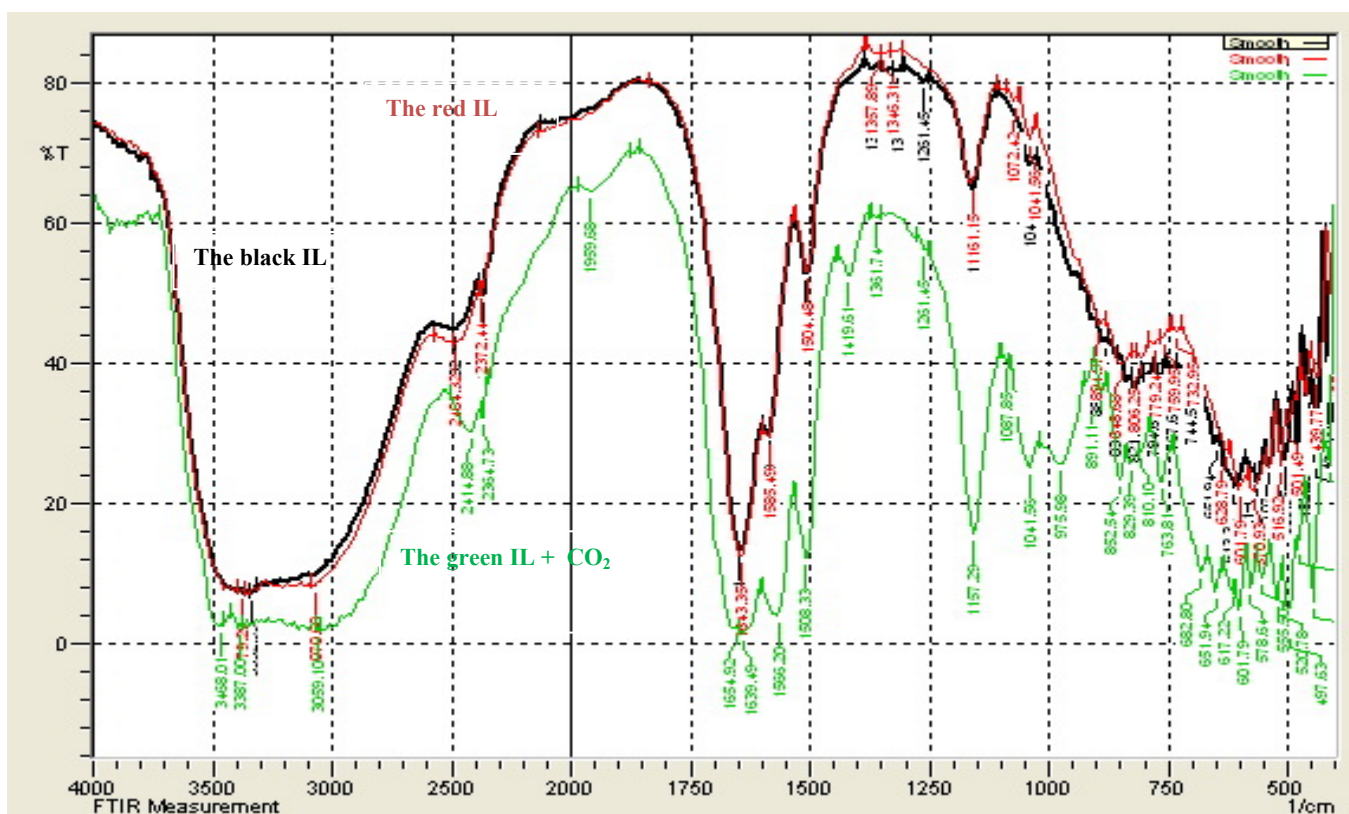


Fig.(3.1):- FTIR spectra of AlCl<sub>3</sub>- CO(NH<sub>2</sub>)<sub>2</sub> IL, ( black) IL alone ,(red) before bubbling CO<sub>2</sub> and ( green ) after bubbling CO<sub>2</sub> .

### 3.2.2 Aluminum chloride – acetamide IL

Aluminum chloride – acetamide IL ionic liquid <sup>(119)</sup> was bubbled with carbon dioxide showed FTIR, ( Fig. 3.2) without an effect on the vibration modes of  $\text{AlCl}_3\text{-CH}_3\text{CONH}_2$  ionic liquid indicating no obvious interaction of carbon dioxide with amide nor a dissolved carbon dioxide in the ionic liquid which would show a band around  $2300\text{ cm}^{-1}$  particularly when bubbling  $\text{CO}_2$  for half an hour. Yet, for one hour bubbling  $\text{CO}_2$ , the ionic liquid indicated a slight vibrational bands differences, but not at the main functional group of amide or carbonyl where the interacted  $\text{CO}_2$  was expected.

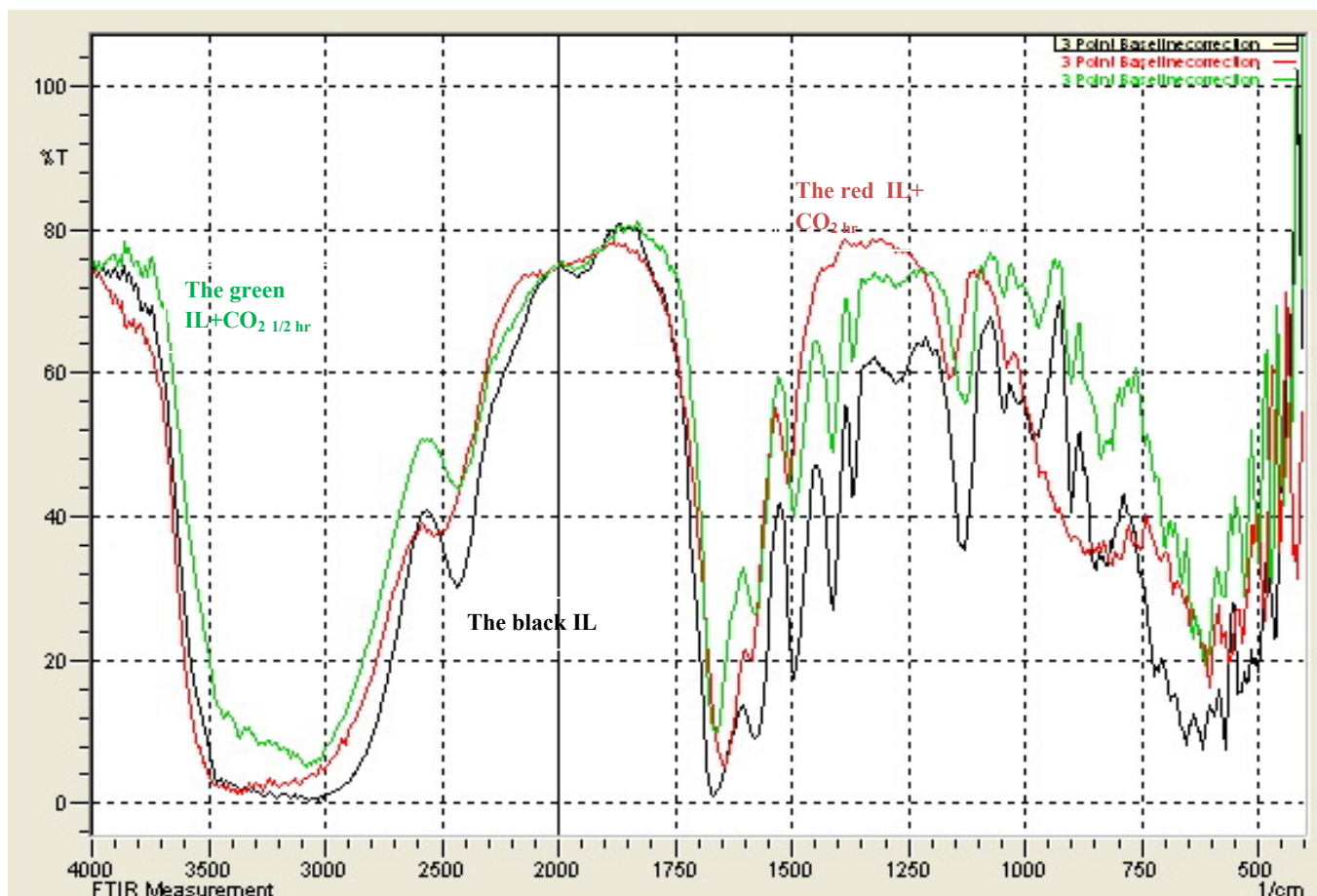


Fig. (3.2) :- FTIR vibrational bands of  $\text{AlCl}_3\text{-CH}_3\text{CONH}_2$  IL, (black) IL alone, (green) after bubbling  $\text{CO}_2$  for half an hour and (red) bubbling  $\text{CO}_2$  for an hour.

### 3.2.3 Choline chloride – urea IL

Choline chloride-urea IL bubbled with carbon dioxide showed FTIR bands, (Fig. 3.3) . There was no obvious effect on the vibration modes despite changing the reaction conditions ( time and temperature) both at atmospheric pressure. This refers to bad capturing of carbon dioxide by choline chloride- urea ionic liquid . This might indicate the weak capturing ability of this ionic liquid such conditions probably due to the weak lewis acid – base interaction .

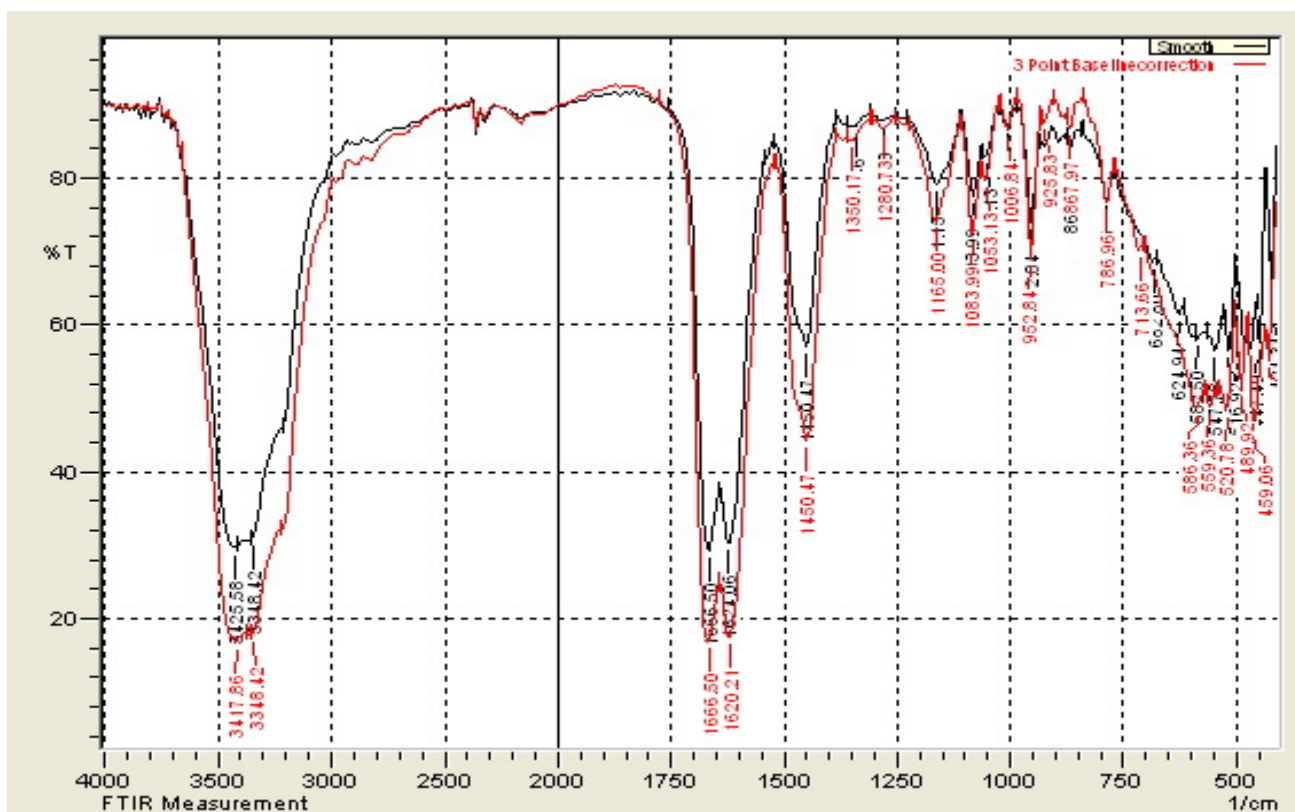


Fig. (3.3):- FTIR vibrational bands of choline chloride-urea IL, ( red) IL alone, ( black) after bubbling CO<sub>2</sub> .

### 3.3 Enhancement chemical compound to ionic liquids to capture CO<sub>2</sub>

Some chemical compounds were added to ionic liquids in the form of powder or aqueous solutions as catalysts to increase the capability of ionic liquids to capture carbon dioxide in comparison with ionic liquid alone when no differences were observed at the functional group of the ionic liquids of hydrated ammonium aluminum sulphate-urea and hydrated aluminum nitrate-urea ionic liquids.

#### 3.3.1 Addition of sodium hydroxide to hydrated ammonium aluminum sulphate-urea ionic liquid

The addition of sodium hydroxide pellets to 10 ml of  $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}] - \text{CO}(\text{NH}_2)_2$  IL formed a clear liquid mixture at room temperature. This mixture was examined by FTIR which showed vibration bands, (the black Fig. 3.4). It appeared to have no difference from the vibration bands of the ionic liquid alone, (the red Fig. 3.4) indicated no CO<sub>2</sub> absorption in ionic liquid alone or with NaOH addition. NaOH was also added but as aqueous solution to enhance the absorption of CO<sub>2</sub> by ionic liquid (chapter 2.4.b). This was to decrease the viscosity of the mixture due to the presence of distilled water expecting an increase in the dissolution of CO<sub>2</sub>. The FTIR of this mixture, ( Fig. 3.5) after bubbling CO<sub>2</sub> as stated in (chapter 2.5) indicates a change in the higher frequencies, particularly of the N-H stretching vibrational bands of the urea amine group (above 3000 cm<sup>-1</sup>) and in the lower frequencies in the carbonyl vibrational bands at 1647 cm<sup>-1</sup> and 1666-1627 cm<sup>-1</sup>, (Table - 3.2). This might be related to an interaction of carbon dioxide with the amine groups affecting their vibration mode and there by influencing the vibrational mode of the carbonyl group of urea. It also indicated the importance of reducing viscosity of ionic liquid to improve the interaction of CO<sub>2</sub> with amine group where gas diffusion factor is more effective.

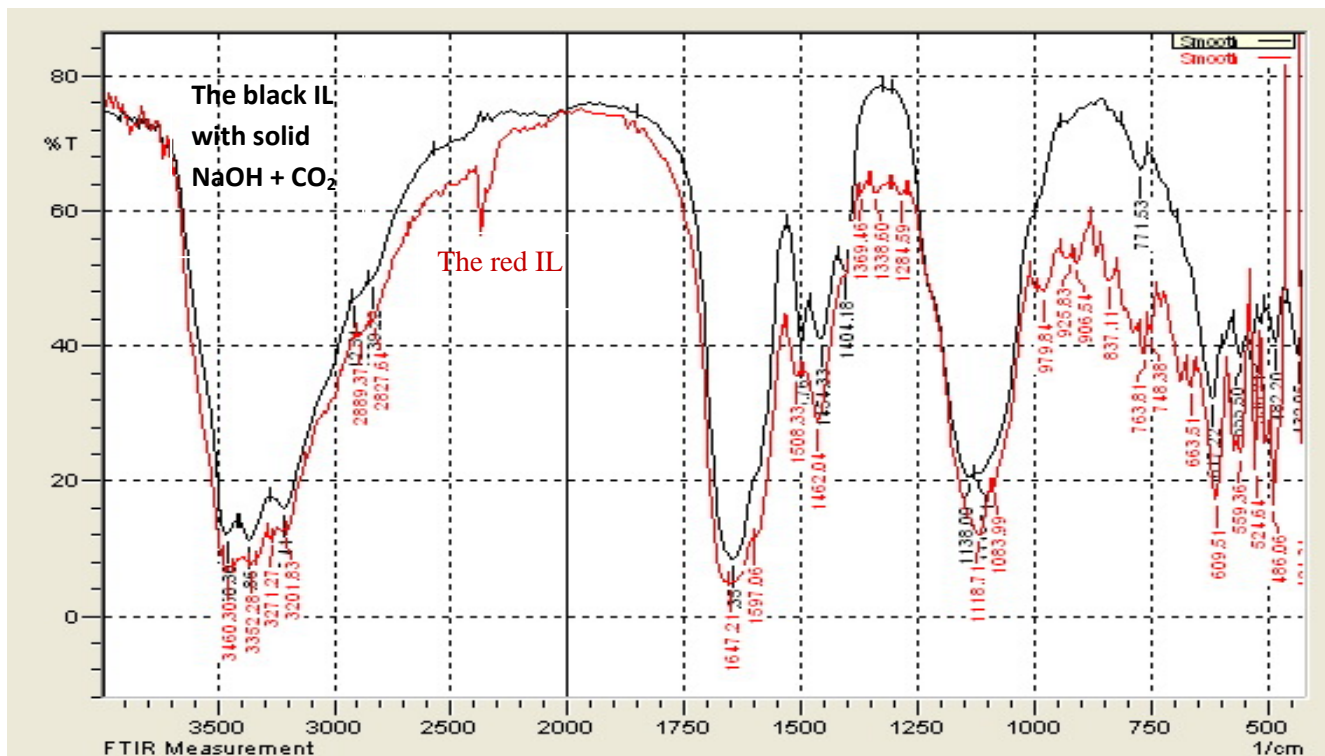


Fig. (3.4):- FTIR vibrational bands of NH<sub>4</sub>Al (SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O - CO(NH<sub>2</sub>)<sub>2</sub> IL , ( red) IL alone, ( black) with added solid NaOH after bubbling CO<sub>2</sub> .

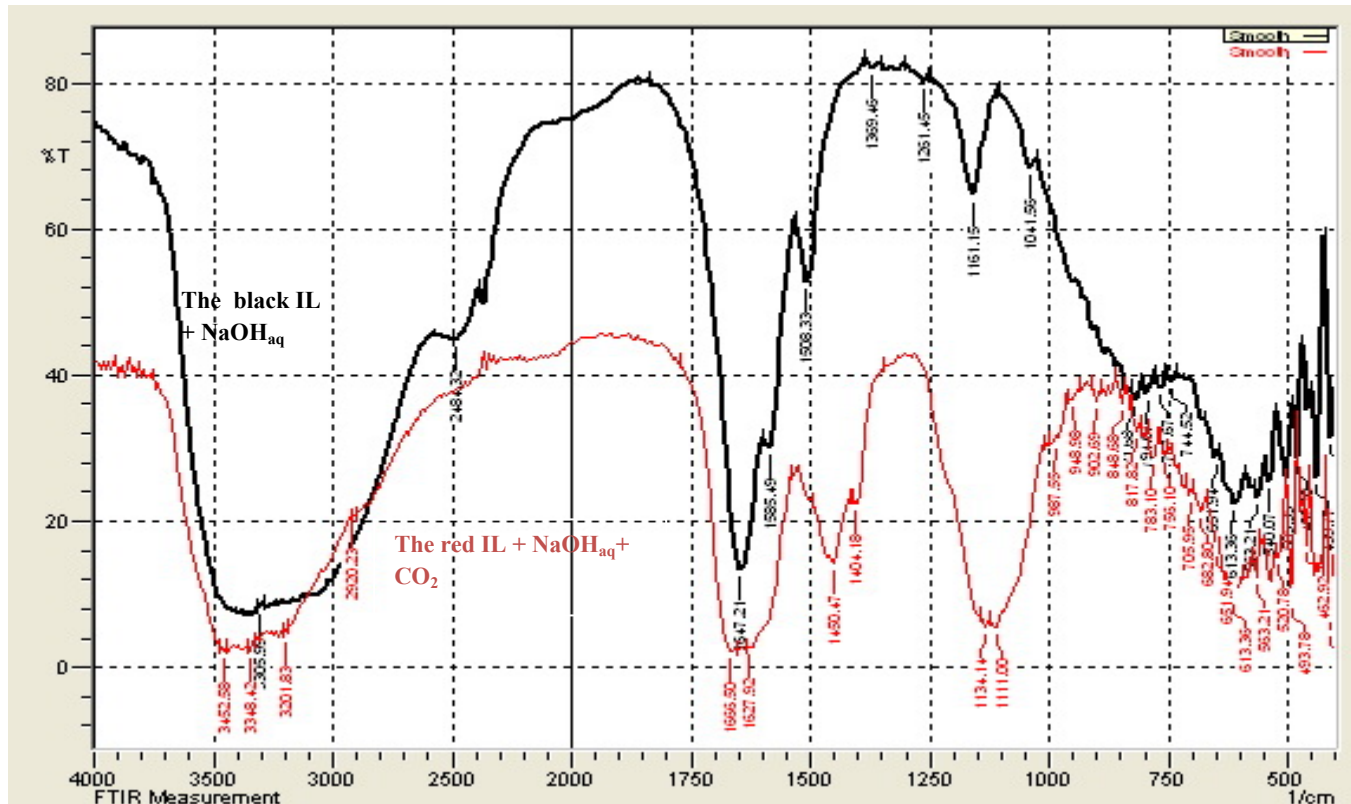


Fig. (3.5):- FTIR spectra of NH<sub>4</sub>Al (SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O – CO(NH<sub>2</sub>)<sub>2</sub> IL and with NaOH<sub>aq</sub> before and after bubbling CO<sub>2</sub> .



Table (3.2) :- Vibrational bands of the ionic liquid  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2$  alone, with added  $\text{NaOH}_{\text{aq}}$  and with capturing  $\text{CO}_2$  in  $\text{cm}^{-1}$ .

Ionic liquid	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{C=O})$	$\nu_s(\text{N-C-N})$	$\nu_{\text{as}}(\text{N-C-N})$	Fig
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \cdot \text{Urea}$ $\text{NaOH}_{\text{aq}}$	3305	1595 1508	1647	1161	1404	3.5(black)
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \cdot \text{Urea}$ $\text{NaOH}_{\text{aq}} + \text{CO}_2$	3452 3348 3201	1450	1666 1627	1134 1111	1404	3.5 ( red)

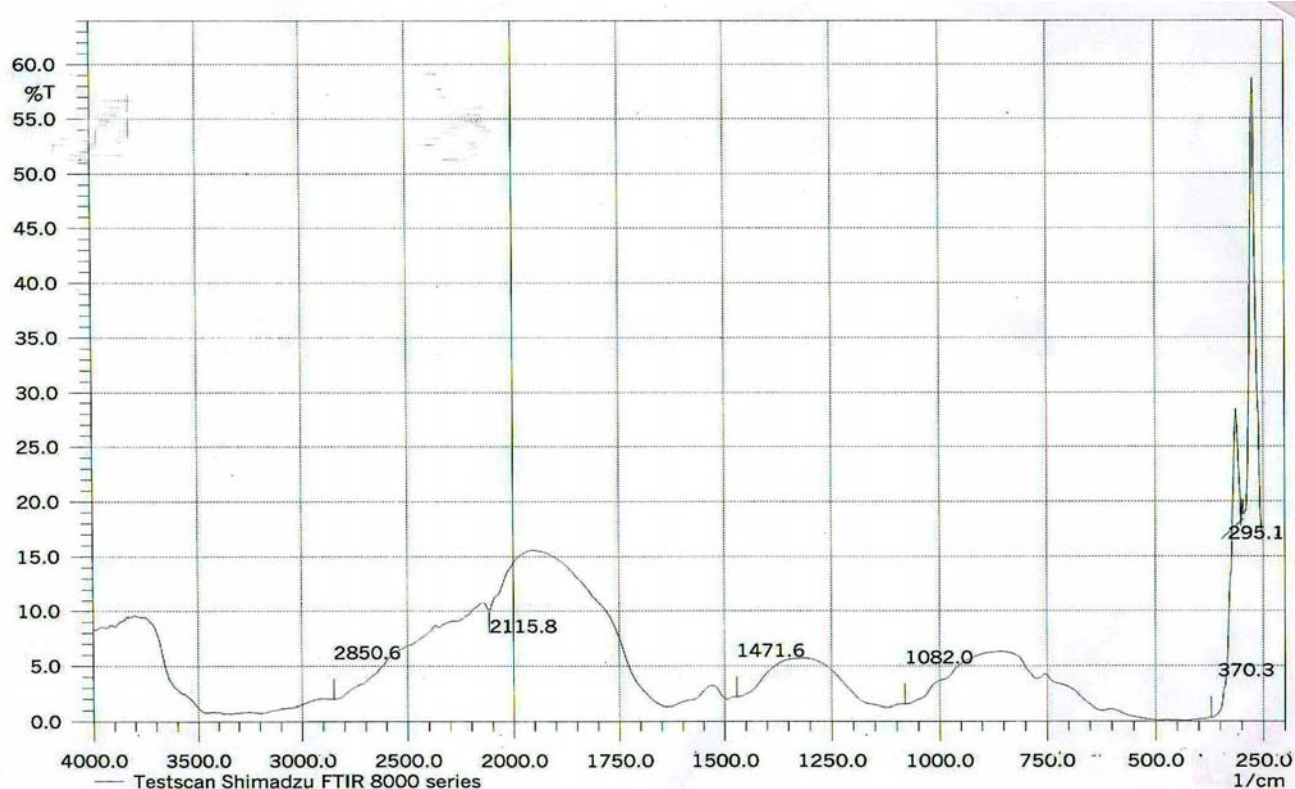
This enhancement of  $\text{CO}_2$  absorption in this work is in the same trend as number of catalysts systems have also been developed by other workers to increase the efficiency of carbon dioxide absorption by the amine group including the addition of alkali metal salts, ammonium salts, metal oxides, transition metal and main group complexes<sup>(123)</sup>.

### 3.3.2 Addition of calcium oxide to hydrated ammonium aluminum sulphate-urea, hydrated aluminum nitrate-urea ILs

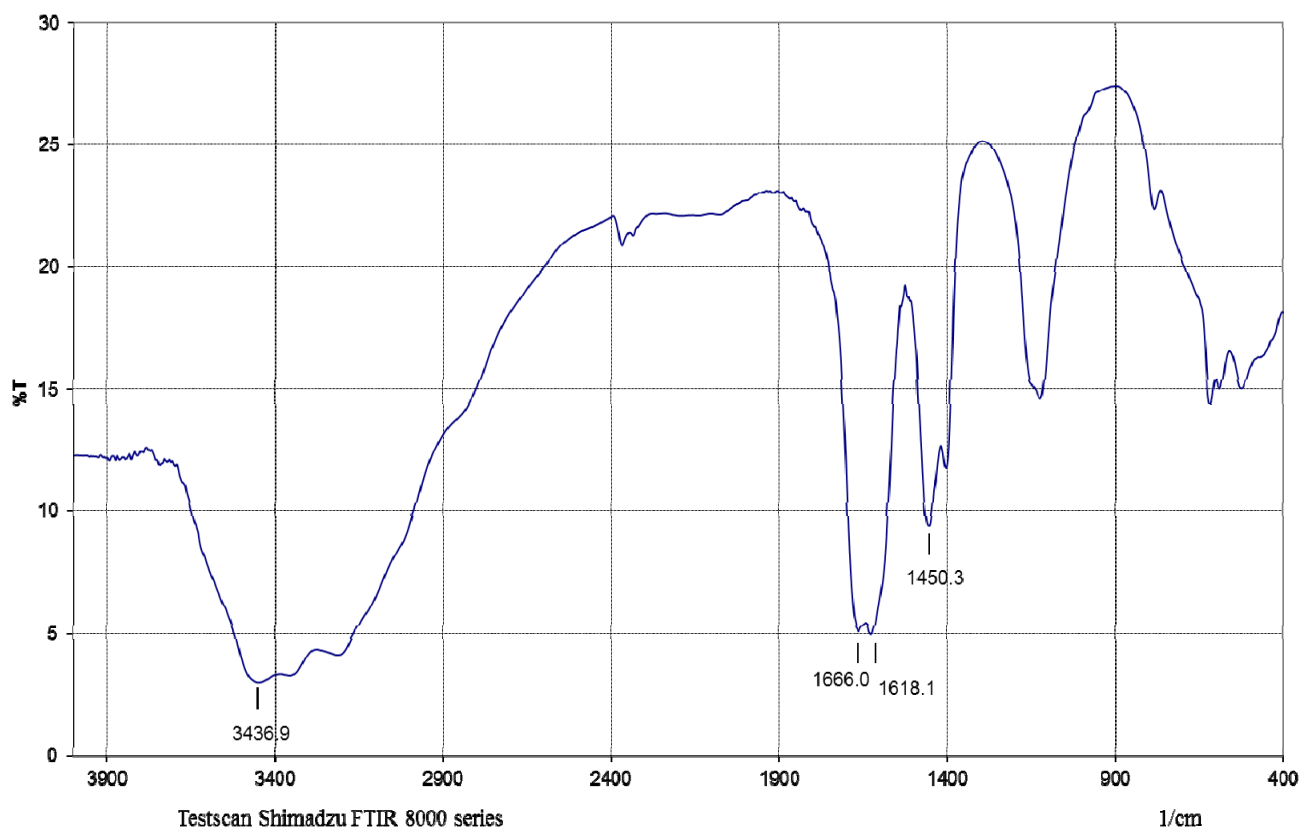
#### a- Addition of calcium oxide to hydrated ammonium aluminum sulphate-urea IL

A powdered calcium oxide made a clear solution when added to  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2$  ionic liquid showed no visible changes until the complete dissolution of calcium oxide. After bubbling carbon dioxide gas, the solution showed clear changes in the FTIR vibration bands as shown in (Fig. 3.7).

The N-H stretching frequencies showed an increase in their frequencies when compared with those before bubbling carbon dioxide in ionic liquid. Additionally the carbonyl group also showed new and sharp splitting vibration bands at  $1666\text{ cm}^{-1}$  to  $1618.3\text{ cm}^{-1}$ , (Table-3.3), both might be considered as an indication of an interaction of carbon dioxide with amine group forming carbamate (N-carboxy urea)<sup>(97)</sup>.



**Fig.(3.6):**FTIR vibration bands of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2$  IL containing CaO before bubbling  $\text{CO}_2$ .



**Fig. (3.7) :- FTIR vibration bands of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2$  IL containing CaO after bubbling  $\text{CO}_2$  .**

**Table (3.3):- FTIR vibration bands of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2$  IL containing CaO before and after bubbling  $\text{CO}_2$  in  $\text{cm}^{-1}$ .**

Ionic liquid	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{C=O})$	$\nu_s(\text{N-C-N})$	$\nu_{as}(\text{N-C-N})$	Fig
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \cdot \text{urea}$ CaO	3230	1471	1645	1132	1396	3.6
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \cdot \text{urea}$ CaO + $\text{CO}_2$	3436.9	1450.3	1666 1618.1	1107	1408	3.7



### b- Addition of calcium oxide to hydrated aluminum nitrate-urea IL

A powdered calcium oxide formed clear solution when added to Al (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O- CO(NH<sub>2</sub>)<sub>2</sub> ionic liquid and after bubbling carbon dioxide, the FTIR showed vibrational bands as in ( Fig. 3.8). In contrast to the observed frequencies of N-H stretching in ionic liquids alone, this ionic liquid mixture showed no changes in both N-H or C=O frequencies which may be taken as an indicator for carbon dioxide absorption in agreement with other reported value <sup>(124)</sup> (Table 3.4) which also claimed the weakens of ionic liquid containing nitrate to capture carbon dioxide gas, while the changes in the stretching bands above 3000 cm<sup>-1</sup> could be related to intensities which broaden the bands and make it to appear at lower frequencies when carbon dioxide gas was bubbled.

**Table (3.4) :- FTIR main vibration bands of Al (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O - CO(NH<sub>2</sub>)<sub>2</sub> containing CaO before and after bubbling CO<sub>2</sub> in cm<sup>-1</sup>.**

Ionic liquid	v(N-H)	δ(N-H)	v(C=O)	v <sub>s</sub> (N-C-N)	v <sub>as</sub> (N-C-N)	Fig
Al (NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O.urea. CaO	3441 3263	1589	1643	1161	1384	3.8(green)
Al (NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O.urea. CaO + CO <sub>2</sub>	3371 3080	1585	1647	1157	1484	3.8 (red)

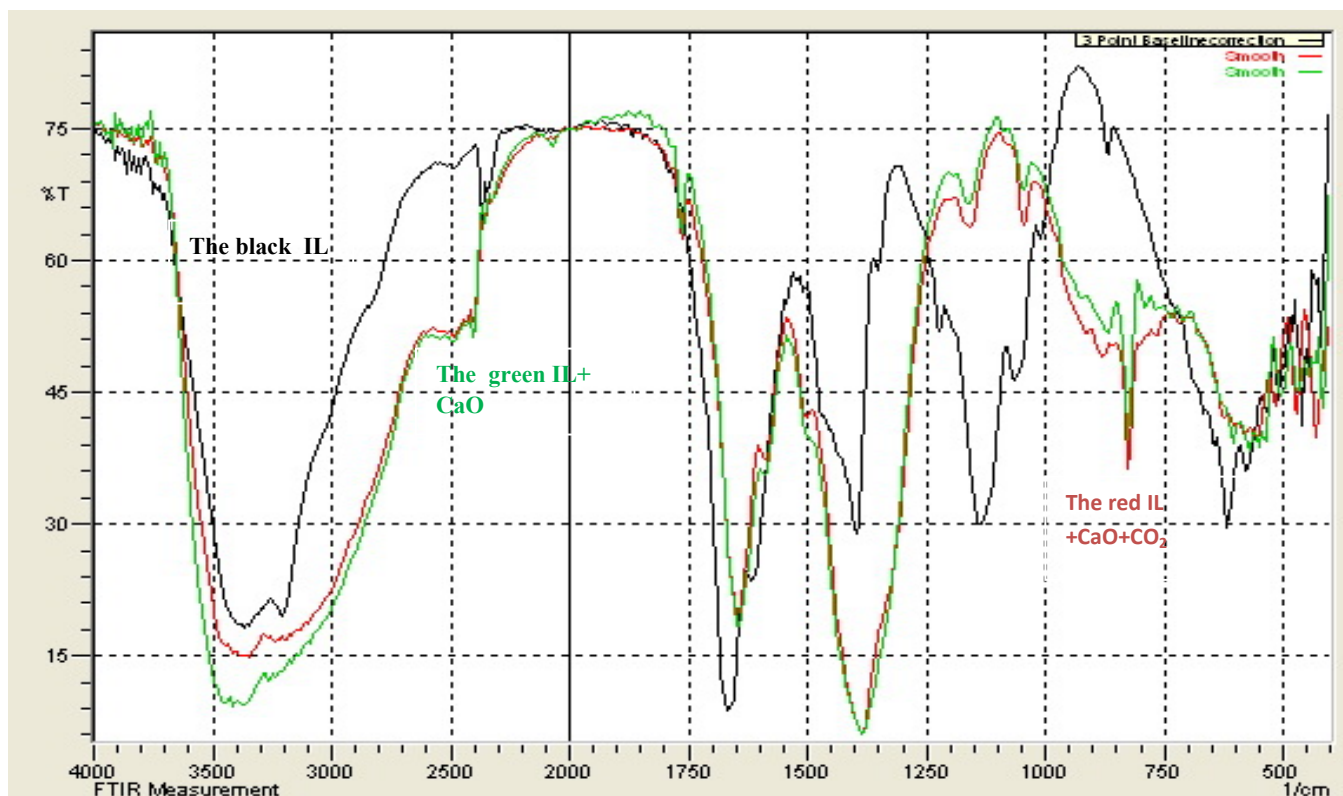
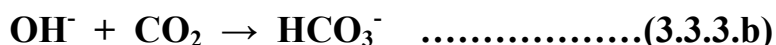


Fig. (3.8) :- FTIR spectra overlay to compare between vibrational bands of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \cdot \text{CO}(\text{NH}_2)_2$  IL, the black IL alone , the green with CaO and the red with capturing  $\text{CO}_2$ .

### 3.3.3 Addition of distilled $\text{H}_2\text{O}$ and compared with the addition of $\text{NaOH}_{\text{aq}}$ ionic liquid

To differentiate between the effect of distilled water in  $\text{NaOH}_{\text{aq}}$  added to  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2$  IL and the addition drops of water alone , an equivalent amount of distilled water (3 drops ) were added to the IL alone. Examination of FTIR , ( Fig. 3.9 ) vibrational modes before and after bubbling  $\text{CO}_2$  indicated a broaden effect on the high vibrational bands above  $2500 \text{ cm}^{-1}$ . This broad band returned its shape (as in IL alone) after bubbling  $\text{CO}_2$  gas in the same trend as with added  $\text{NaOH}_{\text{aq}}$  to IL . However , the carbonyl group vibrational band  $1662 \text{ cm}^{-1}$  seems to have no clear effect by the addition of distilled water nor the vibrational band of sulphate group at  $1103 \text{ cm}^{-1}$  , ( Table 3.5).

These two bands showed a clear effect in the case of the mixture of  $\text{NaOH}_{\text{aq}}$  with IL, (Fig. 3.10) after bubbling  $\text{CO}_2$  gas which indicate that both distilled water and  $\text{NaOH}_{\text{aq}}$  have affected the vibrational band of IL, while the IL returned its initial vibrations after bubbling  $\text{CO}_2$  this Indicate an interaction of water to IL. This interaction could result in forming carbonic acid when passing carbon dioxide gas as follows :-



**Table (3.5) :- FTIR vibration bands of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$  before and after  $\text{CO}_2$  bubbling in  $\text{cm}^{-1}$ .**

Ionic liquid	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{C=O})$	$\nu_s(\text{N-C-N})$	$\nu_{\text{as}}(\text{N-C-N})$	Fig
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \cdot \text{urea}$	3491	1504	1662	1122	1319	3.9( red)
$\text{H}_2\text{O}$	3235		1624			
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \cdot \text{urea}$	3456	1504	1662	1103	1319	3.9(green)
$\text{H}_2\text{O} + \text{CO}_2$	3352		1627			

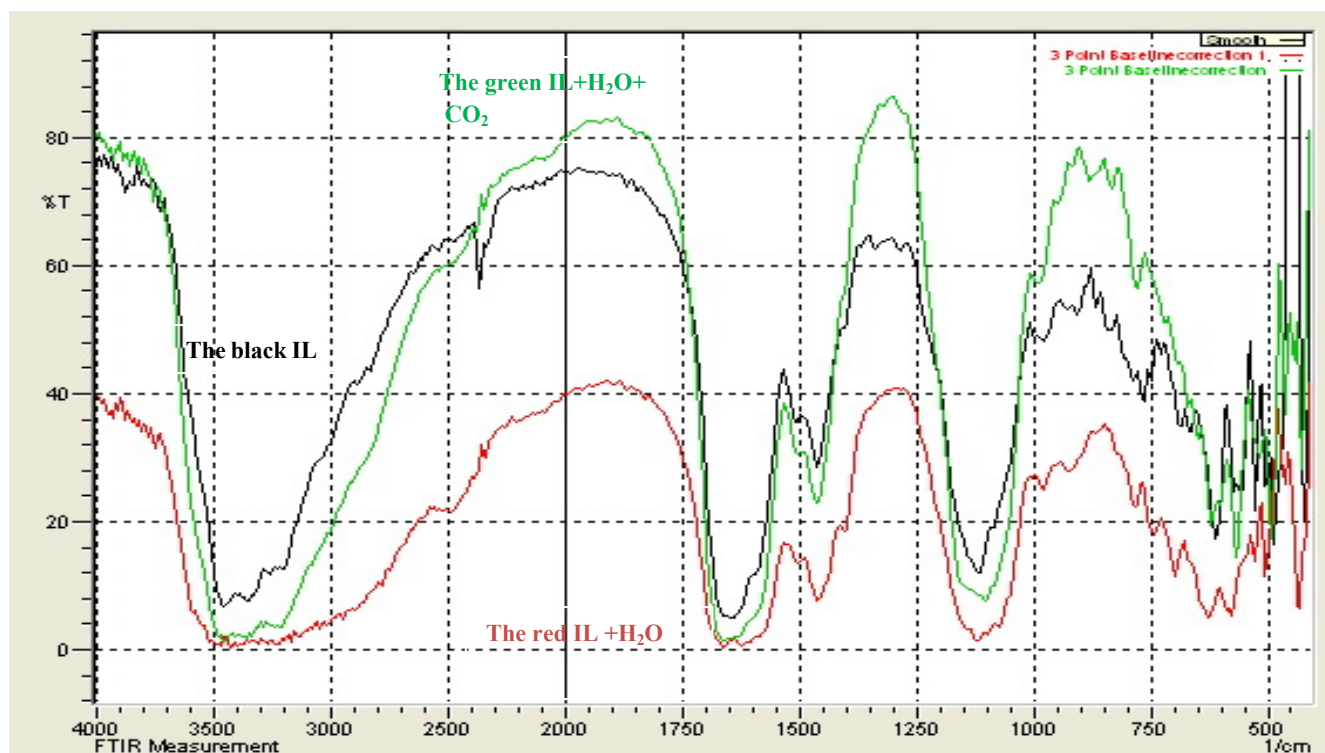


Fig. (3.9) :- FTIR vibrational bands of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2$  IL, ( black) IL alone , ( red) with  $\text{H}_2\text{O}$  addition and ( green ) after  $\text{CO}_2$  bubbling .

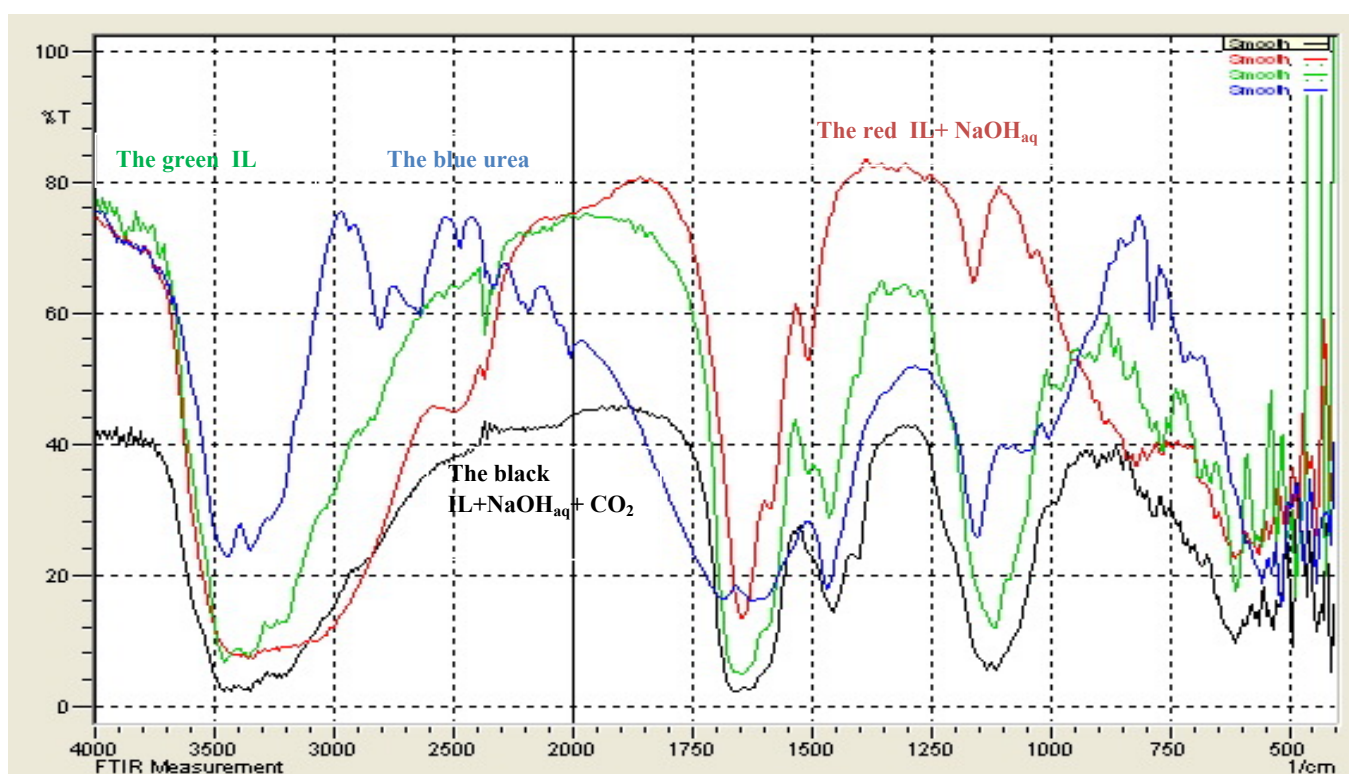


Fig. (3.10) :- FTIR vibrational bands of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} - \text{CO}(\text{NH}_2)_2$  IL, ( green) IL alone , ( red) with  $\text{NaOH}_{\text{aq}}$  , ( blue)  $\text{CO}(\text{NH}_2)_2$  alone and ( black ) IL+  $\text{NaOH}_{\text{aq}}$  after  $\text{CO}_2$  bubbling .

### 3.3.4 Addition of monoethanolamine to ionic liquid

The addition of monoethanolamine to hydrated ammonium aluminum sulphate  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ -urea IL (chapter 2.4.d), bubbled with carbon dioxide showed a similar vibrations to the vibrational modes before bubbling  $\text{CO}_2$  which indicate that MEA does not effect to increase the activity of the amine functional group to capture carbon dioxide FTIR Fig. 3.11(black),3.11(red), this is surprising that monoethanolamine alone has been used for many times as a good carbon dioxide capturing liquid. This behavior may be related to the small concentration of monoethanolamine present in the ionic liquid or to an veiled side reaction with ionic liquid preventing it to react with  $\text{CO}_2$ .

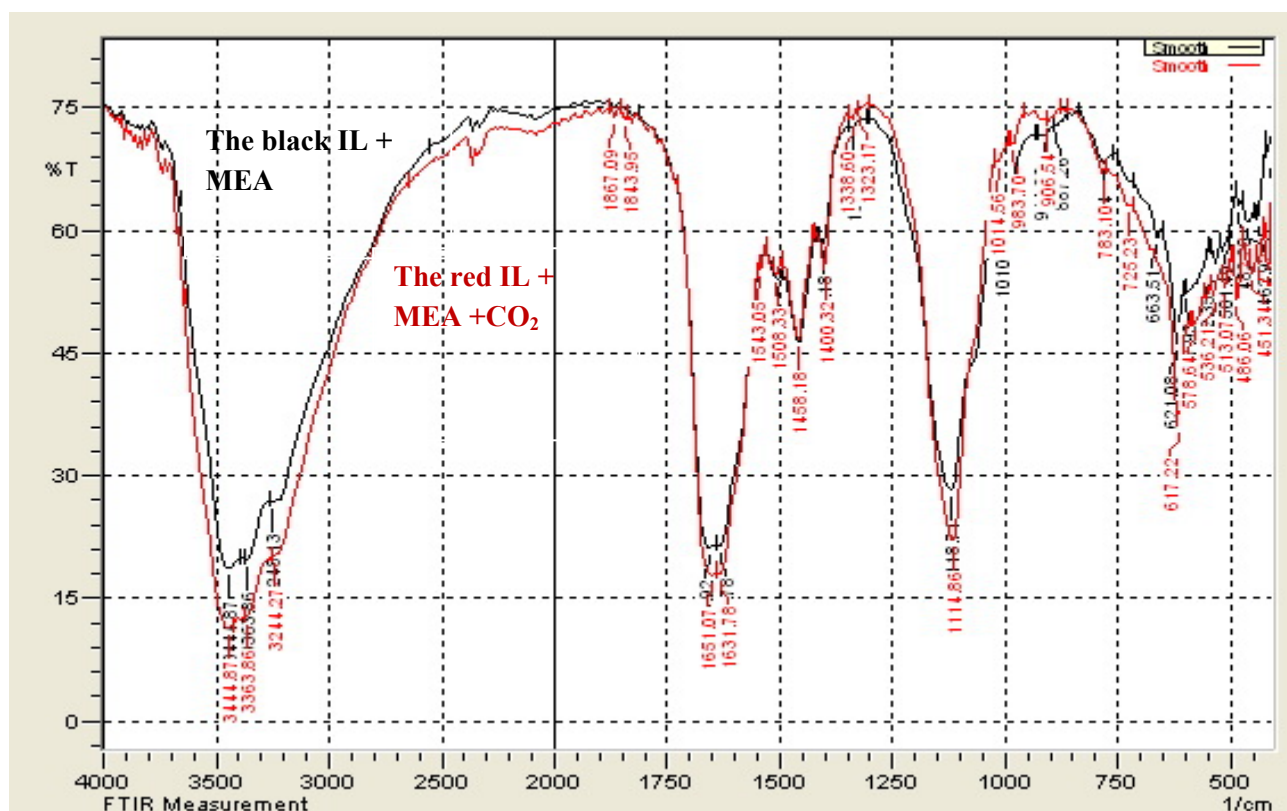


Fig. (3.11) :- FTIR vibrational bands of hydrated ammonium aluminum sulphate  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ -  $\text{CO}(\text{NH}_2)_2$  IL, ( black) IL with MEA ,(red) after bubbling  $\text{CO}_2$ .

### 3.3.5 Addition of ammonium chloride to hydrated ammonium aluminum sulphate $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ – urea $\text{CO}(\text{NH}_2)_2$ IL

The spectra of hydrated ammonium aluminum sulphate  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  -  $\text{CO}(\text{NH}_2)_2$  ionic liquid (chapter 2-4-e) with ammonium chloride  $\text{NH}_4\text{Cl}$  after bubbling  $\text{CO}_2$  are shown, Fig. (3.12). There was small changes in the vibration modes as it showed an increase in the intensity of the vibrational bands especially the N-H bending of the urea amine group ( $1500\text{ cm}^{-1}$ ), Table (3.6). This may be related to captured  $\text{CO}_2$ .

Table (3.6) :- FTIR vibrational bands of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ -  $\text{NH}_4\text{Cl}$  IL before and after bubbling  $\text{CO}_2$  in  $\text{cm}^{-1}$ .

Ionic liquid	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{C=O})$	$\nu_s(\text{N-C-N})$	$\nu_{as}(\text{N-C-N})$	Fig.
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ -urea. $\text{NH}_4\text{Cl}$	3444 3340 3221	1504	1658	1138 1122	1458	3.13(black)
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ -urea. $\text{NH}_4\text{Cl} + \text{CO}_2$	3460 3363 3205	1500	1647	1118	1458	3.13(red)



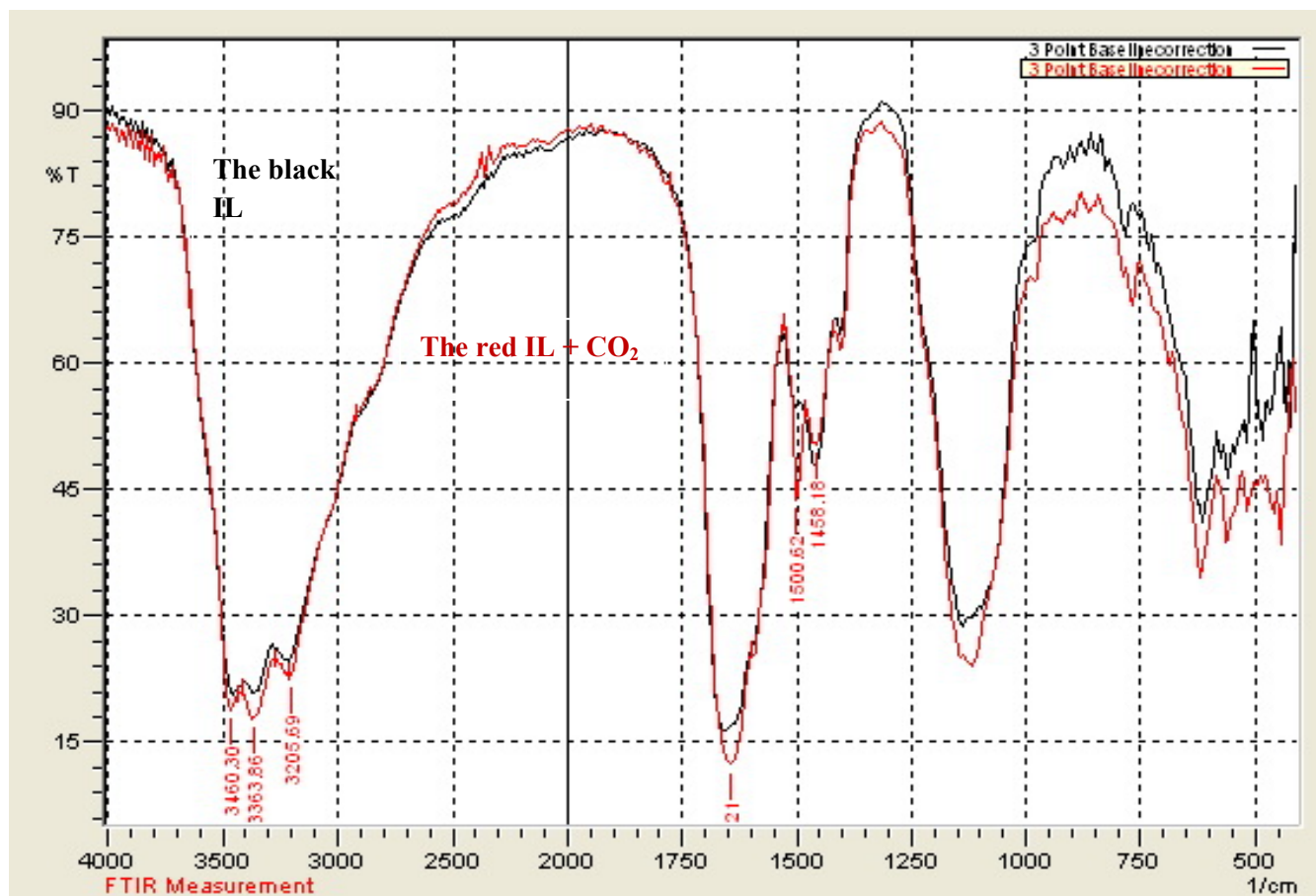


Fig. (3.12) :- FTIR vibrational bands of  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \cdot \text{NH}_4\text{Cl}$  IL, ( black) IL, (red) after bubbling  $\text{CO}_2$ .

## Conclusions

Four ionic liquids were investigated with or without some catalysts. Hydrated aluminum nitrate/urea ionic liquid did not show an ability to dissolve carbon dioxide with it neither alone nor with calcium oxide addition.

The negative observation was concluded from the FTIR absorptions of hydrated ammonium aluminum sulphate/urea ionic liquid either alone or with solid sodium hydroxide addition, monoethanolamine or ammonium chloride. However aqueous sodium hydroxide addition showed a clear interaction of carbon dioxide with the latter ionic liquid hydrated ammonium aluminum sulphate/urea as indicated by a band at  $1666\text{ cm}^{-1}$  which was not observed when only distilled water was added to the same ionic liquid.

Similarly in the same trend, calcium oxide showed the same band  $1666\text{ cm}^{-1}$  when used with this ionic liquid after bubbling carbon dioxide indicating the capture of carbon dioxide.

A more clear and strong effect of capturing carbon dioxide was observed by aluminum chloride-urea ionic liquid as a new frequency at  $1655\text{ cm}^{-1}$  was related to the captured carbon dioxide while aluminum chloride-acetamide ionic liquid did not show such evidence.

The weak capturing of the latter ionic liquid was related to its weaker basicity compared with aluminum chloride-urea ionic liquid.



## **Future work**

1- The qualitative results obtained in this work requires an additional research work to establish the quantitative capability of the investigated ionic liquids with or without some catalysts addition . This investigation depends on thermogravimetric studied .

2- It is important to compare the obtained results in this work with the suggested thermogravimetric studies to make use of many techniques in this field.

3-The physical absorption of carbon dioxide gas by using gas chromatographytechnique and applying further methods to study the absorption carbon dioxide, such as NMR, UV, Mass spectroscopy, Atomic Absorption, etc.

### References:

- 1- A. Costello ; M. Abbas ; A. Allen and S. Ball ;"Managing the Health Effects of Climate Change"; *The Lancet Commissions*.Vol. 373, pp. 1659-1663 , **2009**.
- 2- J. Rong Li ; Y. Ma ; M. Colin Mc Carthy; J. Sculley ; J. Yu ; H. Kwon Jeong ; Perla B. Balbuena and H. Cai Zhou ; "Carbon Dioxide Capture-Related Gas Adsorption and Separation in Metal-Organic Frameworks" ;*coordination chemistry review* ; Lett. Vol. 255 , pp .1791-1823 , **2011**.
- 3- D. S. Arnold ; D. A. Barrett and R. H. Isom ;" Carbon dioxide can be Produced from Flue Gas"; *Oil Gas J.*, Vol. 80 , pp. 130-136 , **1982**.
- 4- R. Brian Strazisar ; R. Richard Anderson and M. Curt White ; "Degradation Pathways for Monoethanolamine in a CO<sub>2</sub> Capture Facility" ; *energy and fuels*,Vol.17, pp. 1034-1039 , **2003**.
- 5- W. D. Nordhaus ; " Stern Review on the Economics of Climate Change" ; *New Haven* , Vol. 28 , pp. 12741 , **2006**.
- 6- B. Metz ; O. Davidson ; H. de Coninck ; M. Loos and L. Meyer ; "Carbon Dioxide Capture and Storage"; *Cambridge University Press*, pp. 442 , **2005**.
- 7-M. Deanna ; D. Alessandro ; Berend Smit and R. Jeffrey Long ;"Carbon Dioxide Capture: Prospects for New Materials" ; *Angew. Chem.*,Vol. 49, pp. 6058 - 6082 , **2010**.
- 8- E. F da Silva and H. F. Svendsen ; "Ab Initio Study of the Reaction of Carbamate Formation from CO<sub>2</sub> and alkanolamines" ; *Chem. Res.*,Vol. 43, pp. 3413-3418 , **2004**.

## References

---

- 9-** J. Gabrielsen ; M. L. Michelsen ; E. H. Stenby and G. M. Kontogeorgis ; "A model for Estimating CO<sub>2</sub> Solubility in Aqueous alkanolamines" ; *Chem. Res.*, Vol. 44, pp. 3348-3354 , **2005**.
- 10-** K. Yi Andrew Lin and A. Alissa Park ; "Effects of Bonding Types and Functional Groups on CO<sub>2</sub> Capture using Novel Multiphase Systems of Liquid-like Nanoparticle Organic Hybrid Materials", *Environ. Sci. Technol.*, Vol. 45, pp. 6633-6639 , **2011**.
- 11-** M. Hasib-ur-Rahman ; M. Siaj and F. Larachi ; "Ionic liquids for CO<sub>2</sub> Capture-Development and Progress"; *Chem. Eng. Process.* , Vol. 49 (4) , pp. 313-322 , **2010**.
- 12-** Z. Zhijun ; D. Haifeng and Z. Xiangping ; "The Research Progress of CO<sub>2</sub> Capture with Ionic Liquids"; *Chinese journal of chemical engineering*, Vol. 20(1) , pp. 120-129 , **2012**.
- 13-** B. A. Oyenekan ; G.T. Rochelle ; "Energy Performance of Stripper Configurations for CO<sub>2</sub> Capture by Aqueous Amines" ; *Chem. Res.* , Vol. 45 (8), pp. 2457-2466 , **2006**.
- 14-** K.S. Fisher ; G.T. Rochelle ; S. Ziaii and C. Schubert ; "Advanced Amine Solvent Formulations and Process Integration for Near-term CO<sub>2</sub> Capture Success" ; *Trimeric Corporation, Pennsylvania* , pp. 102-105, **2007**.
- 15-** O.F. Dawodu and A. Meisen ; "Degradation alkanolamine Blends by Carbon Dioxide" ; *Can J . Chem. Eng.* , Vol. 74 (6), pp. 960-966 , **1996**.
- 16-** S. Ahn ; H.J. Song ; J.W. Park ; J.H. Lee ; I.Y. Lee and K.R. Jang ; "Characterization of Metal Corrosion by Aqueous Amino Acid Salts for the Capture of CO<sub>2</sub>"; *Kor. J. Chem. Eng.*, Vol. 27 (5) , pp. 1576-1580 , **2010**.

## References

---

- 17-** F. Karadas ; M. Atilhan and S. Aparicio ;"Review on the Use of Ionic Liquids (ILs) as Alternative Fluids for CO<sub>2</sub> Capture and Natural Gas Sweetening"; *Energy Fuels* ,Vol. 24 (11) , pp. 5817-5828 , **2010**.
- 18-** Y. D. Liu ; L. Z. Zhang and S. Watanasiri ;" Representing Vapor-Liquid Equilibrium for an Aqueous MEA-CO<sub>2</sub> System using the Electrolyte Nonrandom-two-Liquid Model" ; *Ind. Eng. Chem. Res.*, Vol. 38 (5), pp. 2080-2090 , **1999**.
- 19-** J. Zhang ; S. Zhang ; K. Dong ; Y. Zhang ; Y. Shen and X. Lv ; "Supported Absorption of CO<sub>2</sub> by tetrabutylphosphonium Amino Acid Ionic Liquids" ; *Chem.—Eur. J.*, Vol. 12, pp. 4021-4026 , **2006**.
- 20-** F. Joan Brennecke ; J. Edward Maginn ; F. William Schneider and J. Mark McCready ; "Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO<sub>2</sub> Capture"; *DOE energy*, pp. 22-26, **2011**.
- 21-**T. Welton ; " Review Ionic liquids in Catalysis"; *Coord. Chem. Rev.*, Vol. 248 , pp. 2459-2477, **2004**.
- 22-** S. Gabriel and J. Weiner; "Ueber einige Abkmmlinge des Propylamins". *Ber.* Vol. 21 (2), pp. 2669-2679, (**1888**).
- 23-** S. Sugden and H.Wilkins ;" CLXVII.-The Parachor and Chemical Constitution. Part XII. Fused Metals and Salts " ; *J. Chem. Soc.*, pp.1291-1298, **1929**.
- 24-** C. Granacher ;" Cellulose solution" ; *Claims*.Vol. 6 , pp. 152-260 , **1934**.

## References

---

- 25-** F. Hurreley and T. Wier ;" The Electrodeposition of Aluminum from Nonaqueous Solutions at Room Temperature "; *Electrochem. Soc.*, Vol. 98 , pp. 207-212, **1951**.
- 26-** H. Chum; V. Koch; L. Miller and R. Osteryoung;" Electrochemical Scrutiny of Organometallic iron complexes and hexamethylbenzene in a room temperature molten salt"; *J. Am. Chem. Soc.*, Vol. 97, pp. 3264-3267, **1975**.
- 27-** J. Wilkes; J. Levisky; R. Wilso and C. Hussey ;" Dialkylimidazolium chloroaluminate Melts: a new Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy and Synthesis"; *Inorg. Chem.*, Vol. 21, pp. 1236-1264, **1982**.
- 28-** K. R. Seddon;" In Molten Salt Forum: Proceedings of 5th International Conference on Molten Salt Chemistry and Technology"; *H. Wendt* , Vol. 5-6 , pp. 53-62 ,**1998**.
- 29-** F. H. Hurley and T. P. Wier ; *J. Electrochem. Soc.*, Vol. 98, pp. 203 , **1951**.
- 30-** J. S. Wilkes and M. J. Zaworotko ;" Air and Water Stable 1-Ethyl-3-methylimidazolium Based Ionic Liquids "; *J. Chem. Soc., Chem. Commun.*, Vol.13 , 965-967, **1992**.
- 31-** H. Zhao and S. V. Malhotra ;" Applications of Ionic Liquids in Organic Synthesis"; *Aldrichimica ACTA* , VOL. 35, pp. 75-83, **2002** .
- 32-** F. N. Tebbe ; G. W. Parshall; G. S. Reddy ; " Olefin Homologation with titanium methylene Compounds "*J. Am. Chem. Soc.*, Vol. 100, pp. 3611-3613, **1978**.

## References

---

- 33-** C. Swain; A. Ohno; D. Roe; R. Brown and T. Maugh;" Tetrahexylammonium benzoate, a Liquid Salt at 25.degree., a solvent for kinetics or Electrochemistry"; *J. Am. Chem. Soc.*, Vol. 89, pp. 2648-2649, **1967**.
- 34-** R. Gale; B. Gilbert and R. Osteryoung;" Raman Spectra of Molten Aluminum Chloride: 1-butylpyridinium chloride Systems at Ambient Temperatures"; *Inorg. Chem.*, Vol.17, pp. 2728-2729, **1978**.
- 35-** L. Dutta, A. Fleet, Y. Patell, K. R. Seddon, unpublished results.
- 36-** M. Earle and K. R. Seddon, unpublished results.
- 37-** M. J. Earle and K. R. Seddon; " Ionic liquids. Green Solvents for the Future"; *Pure Appl. Chem.*, Vol. 72, pp. 1391–1398, **2000**.
- 38-** J. Braz. "On the Solid, Liquid and Solution Structural Organization of imidazolium Ionic Liquids" ; *Chem. Soc.*, vol.15 pp. 3, **2004**.
- 39-** D. Sheng; Y. H. Ju and C. E. Barnes; *J. Chem. Soc., Dalton. Trans.* 1201, **1999**.
- 40-** A. G. Fadeev; M. M. Meagher;" Opportunities for Ionic Liquids in Recovery of Biofuels"; *Chem. Commun.*, pp. 295-296, **2001**.
- 41-** J. F. Brennecke and E. J. Maginn; "Ionic liquids : Innovative Fluids for Chemical Processing"; *AIChE J*, Vol. 47, 2384, . **2001** .
- 42-** F. J. Carlin, R. T. De Long and H. C. Haworth, *D. J. Chem. Soc., Chem. Commun.*, 299, **1994** .
- 43-** Y. Chauvin; "Non aqueous Ionic Liquids as Reaction Solvents"; Olivier-Bourbigou, H. *CHEMTECH*, 25(9), 26-30, **1995**.

## References

---

- 44-** W. Keim ; W. Korth and P. Wasserscheid , Intl. Patent 0016,902, Mar 30,*Chem.*, **2000**.
- 45-** A. P. Capper; G. Davies; D. L. Munro; H. Rasheed; A. Abbott and R. K. Tambyrajah; *V. Chem. Commun*, **2010**.
- 46-** A. P. Eardley; C. A. Farley; A.P. Abbott and N. R. S. Pratt; *A. Trans. Inst. Met. Finish*, 77, 26, **1999**.
- 47-** R . C. Tambyrajah; V. Jenkins; Morales; P. R. Davies and A. P. Abbott;" The Regiospecific Fischer in dole Reaction in Choline Chloride·2ZnCl<sub>2</sub> with Product Isolation by Direct Sublimation from the Ionic Liquid "; *A. P. Chem. Commun*, pp. 158-159, **2004**.
- 48-** H. M. A. Abood ; A. P. Abbott; A. D. Ballantyne and K. S. Ryder;" Do all Ionic Liquids need Organic Cation? Characterisation of [AlCl<sub>2</sub> nAmide]<sup>+</sup>AlCl<sub>4</sub><sup>-</sup> and Comparison with imidazolium Based System"; *Chem., Commun.*,Vol. 47, pp. 3523, **2011**.
- 49-** S. B. Sapkal; K. F. Shelke; B. R. Madje; B. B. Shingate; and M. S. Shingare;" 1-Butyl-3-Methyl Imidazolium Hydrogen Sulphate Promoted One-Pot Three-Component Synthesis of Amidoalkyl Naphthols"; *Bull. Korean Chem. Soc*, Vol. 30, No. 12, pp. 2887-2889, **2009**.
- 50-** T. Welton; "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis"; *Chem. Rev.*,Vol. 99(8), pp.2071-2084, **1999**.
- 51-** L. Ferguson and P. Scovazzo;" Solubility, Diffusivity, and Permeability of Gases in phosphonium-based Room Temperature Ionic Liquids: Data and Correlations"; *Ind. Eng. Chem. Res.*Vol. 46,pp.1369-1374, **2007**.

## References

---

- 52-** J. Anthony; J. Anderson; E. Maginn and J. Brennecke;" Anion Effects on Gas Solubility in Ionic Liquids"; *J. Phys. Chem.* ,Vol. 109 ,pp. 6366-6374, **2005**.
- 53-**J.W. Hutchings; K. L. Fuller; M. P. Heitz and M. M. Hoffmann;"Surprisingly high solubility of the ionic liquid trihexyltetradecylphosphonium chloride in dense carbon dioxide"; *Green Chem.* Vol.7,pp. 475-478 , **2005**.
- 54-** J. F. Jenck; F. Agterberg and M. J. Droescher;" Products and Processes for a Sustainable Chemical Industry: a Review of Achievements and Prospects"; *Green Chem.*Vol. 6 , pp. 544-556 , **2004**.
- 55-** N.V. Plechkova and K.R. Seddon;" Applications of Ionic Liquids in The Chemical Industry"; *Chem. Soc. Rev.*Vol. 37,pp. 123-150 , **2008** .
- 56-** J. Pedro Carvalho ; H. Victor Alvarezb; M. Isabel Marruchoa; Martin Aznarb and A.P. Joao Coutinho ;" High Carbon Dioxide Solubilities in trihexyltetradecylphosphonium-based Ionic Liquids " ; *J. of Supercritical Fluids* ,Vol. 52,pp. 258-265 , **2010** .
- 57-** L. M. Galan Sanchez ;G. W. Meindersma and A. B. de Haan ;" Solvent Properties of Functionalized Ionic Liquids for CO<sub>2</sub> Absorption " ; *Chemical Engineering* , Vol 85 , pp. 3-39 , **2007** .
- 58-** A. M. Schilderman ; S. Raeissi and C. J. Peters ; " Solubility of Carbon Dioxide in the Ionic Liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide"; *Fluid Phase Equilib.*,Vol. 260 ,pp. 19-22, **2007**.
- 59-**D. Almantariotis ; O. Fandino ; J.-Y. Coxam and M.F. Costa Gomes ;"Direct Measurement of the Heat of Solution and Solubility of Carbon Dioxide in 1-hexyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide and 1-octyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide" ; *International Journal of Greenhouse Gas Control*, Vol.10 , pp. 329-340, **2012**.



## References

---

- 60-** P. Sharma ; S. Do Park ; K. Tae Park ; S. Chan Nam ; S. Kwan Jeong ; Y. Yoon and H. Baek ;"Solubility of Carbon Dioxide in Amine-Functionalized Ionic Liquids: Role of The Anions "; *Pankaj sharmaa*, pp.193-194 , **2012**.
- 61-**D. Eleanor Bates ; D. Rebecca Mayton ; I. Ntai and H. James Davis ; "CO<sub>2</sub> Capture by a Task-Specific Ionic Liquid"; *J. AM. CHEM. SOC* , Vol. 6, pp.124 , **2002**.
- 62-** A. Lynnette Blanchard ; Z. Gu and F. Joan Brennecke ; "High-Pressure Phase Behavior of Ionic Liquid/CO<sub>2</sub> Systems"; *J. Phys. Chem.* ,Vol. 105,pp. 2437-2444 , **2001**
- 63-** L. A. Blanchard ; D. Hancu ; E. J. Beckman ; Brennecke ;" Green Processing Using Ionic Liquids and CO<sub>2</sub>" ;*J. F. Nature* ,Vol. 399, pp. 28-29 ,**1999**.
- 64-** H. Ohno ;" Functional design of ionic liquids"; *Bull. Chem. Soc. Jpn.* Vol. 79, pp. 1665-1680, **2006**.
- 65-** R. Sheldon ; " Catalytic Reactions in Ionic Liquids ";*Chem. Commun.*Vol.37 , pp. 2399-2407, **2001**.
- 66-** C. Chiappe and D. Pieraccini;" Ionic Liquids : Solvent Properties and Organic Reactivity "; *J. Phys. Org. Chem.* Vol.18 , pp. 275-297, **2005**.
- 67-** Y. Xiao Luo; F. Ding and J. Wen Lin; "Efficient and Energy-Saving CO<sub>2</sub> Capture through the Entropic Effect Induced by the Intermolecular Hydrogen Bonding in Anion-Functionalized Ionic Liquids"; *Phys. Chem.*, Vol.5 (2), pp. 381-386 , **2013**.

## References

---

- 68-** D. Eleanor Bates ; D. Rebecca Mayton ; I. Ntai and H. James Davis; "CO<sub>2</sub> Capture by a Task-Specific Ionic Liquid"; *AM. CHEM. SOC.* Vol.124, pp. 926-927, **2002**.
- 69-** H. James and JR. Davis; "Anionic-Sweetener-Based Ionic Liquids and Methods of Use Thereof" *United State*, Vol. 26 , pp. 286-333, **2005**.
- 70-** Jr. Davis and J. Hillard ;" Functionalized Ionic Liquids, and Methods of use Thereof "; *G. P. J. Am. Chem. Soc.* , pp. 117-329, **1995**.
- 71-** M. Erbedinger ; J. Anita Mesiano and J. Alan Russell ;" Enzymatic Catalysis of Formation of Z-Aspartame in Ionic Liquid -An Alternative to Enzymatic Catalysis in Organic Solvents"; *Biotechnol. Prog.*, Vol.16, pp. 1129-1131 , **2000**.
- 72-** A. E. Visser ; J. D. Holbrey and R. D. Rogers ;"Hydrophobic Ionic Liquids Incorporating N-alkylisoquinolinium Cations and their Utilization in Liquid-Liquid Separations", *Chem. Commun.*, Vol. 4, pp. 2484-2485 , **2001**.
- 73-** C. Amanda Cole ; L. Jessica Jensen ; I. Ntai ; K. Loan Tran ; K. Weaver ; D. Forbes and J. Davis ;" Novel Brønsted Acidic Ionic Liquids and Their Use as Dual Solvent-Catalysts"; *J. AM. CHEM. SOC.*, Vol.124 , pp. 5962-5963 , **2002**.
- 74-** E. Keith Gutowski and J. Edward Maginn ;" Amine-Functionalized Task-Specific Ionic Liquids: A Mechanistic Explanation for The Dramatic Increase in Viscosity upon Complexation with CO<sub>2</sub> from Molecular Simulation"; *American Chemical Society*, Vol.130, pp. 14690-14704 , **2008**.

## References

---

- 75-** F. Endra ; D. MacFarlane and A. Abouott ; " Electrodeposition in Ionic Liquids"; *ISNB*. Vol. 9, pp. 527-31565 , **2007**.
- 76-** R. E. Baltus ; B. H. Culbertson ; S. Dai ; H. M. Luo and D.W. DePaoli ;"Room Temperature Ionic Liquids for Separating Organics from Produced Water"; *Phys.Chem.B*,Vol.108(2) , pp. 721-727, **2004**.
- 77-** P. J. Dyson ; G. Laurency ; C. A. Ohlin ; J. Vallance and T. Welton; "Coordination Chemistry Review"; *Chem.Commun.*, Vol.19, pp. 2418-2419, **2003**.
- 78-** S. G. Kazarian, B. J. Briscoe, T. Welton, *Chem.Comm.*,2047-2048, **2000**.
- 79-** A. Heintz ; D.V. Kulikov and S. P. Verevkin ;" Thermodynamic Properties of Mixtures Containing Ionic Liquids. Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkylbenzenes in 4-Methyl-n-butylpyridinium Tetrafluoroborate Using Gas-Liquid Chromatography"; *Chem. Eng. Data* ,Vol. 46, pp. 1526-1529 , **2001**.
- 80-** A. Heintz ; D.V Kulikov and S.P. Verevkin;" Thermodynamic Properties of Mixtures Containing Ionic Liquids Activity Coefficients at Infinite Dilution of Hydrocarbons and Polar Solutes in 1-Methyl-3-ethyl-imidazolium Bis(trifluoromethyl-sulfonyl) Amide and in 1,2-Dimethyl-3-ethyl-imidazolium Bis(trifluoromethyl-sulfonyl) Amide Using Gas-Liquid Chromatography"; *Chem. Eng.Data*,Vol.47, pp. 894-899, **2002**.
- 81-** A. Heintz ; D.V Kulikov and S.P. Verevkin ;" Thermodynamic Properties of Mixtures Containing Ionic Liquids. Activity Coefficients at Infinite Dilution of Polar Solutes in 4-methyl- N-butyl-pyridinium tetrafluoroborate Using Gas-Liquid Chromatography";*Chem.Thermodyn.*,Vol.43, pp.1341-1347, **2002**.

## References

---

- 82-** T. M. Letcher ; B. Soko ; P. Reddy and N. Deenadayalu ;" Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid 1-Hexyl-3-methylimidazolium Tetrafluoroborate Using Gas-Liquid Chromatography at the Temperatures 298.15 K and 323.15 K"; *Chem. Eng. Data*, Vol. 48, pp. 1587-1590 , **2003**.
- 83-** T. M. Letcher ; B. Soko ; P. Reddy ; D. Ramjugernath ; N. Deenadayalu ; A. Nevines and P. K. Naicker ; "Ionic liquids in Separation Processes " ; *J. Chem. Eng. Data*, Vol. 48, pp. 708-711, **2003**.
- 84-** K. R. Seddon ; A. Stark and A. J. Torres ; " Use of Capillary Electrophoresis (CE) for Characterization of Ionic Liquids (IL) and IL Interest as New Environments Separation EC " ; *Pure. Appl. Chem.*, Vol. 72 , pp. 2275-2287, **2000**.
- 85-** J. A. Widegren ; A. Laesecke and J. W. Magee ; " The Effect of Dissolved Water on the Viscosities of Hydrophobic Room-Temperature Ionic Liquids " ; *Chem. Commun.*, Vol. 12, pp. 1610-1612 , **2005**.
- 86-** R. P. Swatloski ; J. D. Holbery and R. D. Rogers ;" Halogen-Free Ionic Liquid for Extraction And simultaneous Determination of Cu(II), Pb(II), Cd(II), and Hg(II)"; *Green Chem.*, Vol. 5, pp. 361, **2003**.
- 87-** A. Shariati and C. J. Peters ;"Solubility of Gases in Ionic Liquids"; *J. Supercrit. Fluids*, Vol. 34, pp. 171-176 , **2005**.
- 88-** C. Cadena ; J. L. Anthony; J. K. Shah ; T. I. Morrow ; J. F. Brennecke and E. J. Maginn; "Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids"; *J. Am. Chem. Soc.*; **2004**.
- 89-** M. J. Muldoon ; S. N. V. K. Aki ; J. L. Anderson ; J. K. Dixon and J. F. Brennecke ; "Improving Carbon Dioxide Solubility in Ionic Liquids"; *J. Phys. Chem. B*, pp. 9001- 9009 , **2007**.

## References

---

- 90-** S. N. V. K. Aki ; B. R. Mellein ; E. M. Saurer and J. F. Brennecke ; "Probing Anion-Carbon Dioxide Interactions in Room Temperature Ionic Liquids: Gas Phase Cluster Calculations"; *J.Phys.Chem.B*,**2004**.
- 91-** M. F. C. Gomes and A.A.H. Padua ;" Ionic Liquids: Promising Media for Gas Separations"; *Pure Appl. Chem.*, Vol.77, pp. 653-665 , **2005** .
- 92-** A.P.S. Kamps ; D. Tuma ; J. Z. Xia and G. Maurer;" Synthesis of New Cross Linked Porous Ammonium-Based Poly(Ionic Liquid) and Application in CO<sub>2</sub> Adsorption" ; *J. Chem.Eng.Data*,Vol.48 ,pp. 746-749, **2003**.
- 93-** M. Costantini ;V. A. Toussaint ; A. Shariati ; C. J. Peters and I. Kikic ;" High-Pressure Phase Behavior of Systems with Ionic Liquids: Part IV. Binary System Carbon Dioxide + 1-Hexyl-3-methylimidazolium Tetrafluoroborate"; *J. Chem. Eng.Data*,Vol.50 , pp. 52-55, **2005**.
- 94-** A. Shariati and C. J. Peters;" High-Pressure Phase Behavior of Systems with Ionic Liquids: Part III. The Binary System Carbon Dioxide + 1-hexyl-3-methylimidazolium hexafluorophosphate"; *J. Supercrit. Fluids*, Vol.25, pp.109-117, **2003**.
- 95-** Y. Liu ; Z. U. Wang and H. Cai Zhou ;"Recent Advances in Carbon Dioxide Capture with Metal-Organic Frameworks"; *Greenhouse Gas Sci Technol*. Vol. 2 , pp. 239-259 , **2012**.
- 96-** S. A. Roosa and A.G. Jhaveri;" Carbon Reduction: Policies. Strategies and Technologies"; *The Fairmont Press*, Vol.10, pp. 603-604, **2009**.
- 97-** S. Edward Rubin ;" IPCC Special Report on Carbon Dioxide Capture and Storage"; *February* , 20, **2006**.
- 98-** E. J. Wilson and D. Gerard;" Carbon Capture and Sequestration: Integrating Technology, Monitoring, Regulation;" *Wiley*, **2007**.

## References

---

- 99-** J. Bolhar-Nordenkamp ; "Chemical Looping for Syngas and Power Generation with CO<sub>2</sub> Capture: Pilot Plant Study and Process Modeling"; *Suedwestdeutscher Verlag fuer Hochschulschriften* , **2009**.
- 100-** S. Mokhatab ; W. A. Poe and J. G. Speight ;"Handbook of Natural Gas Transmission and Processing"; *Gulf Professional Pub*, **2012**.
- 101-** M . Tagliabue ; D. Farrusseng ; S. Valencia ; S. Aguado ; U. Ravon ; C. Rizzo ; A. Corma and C. Mirodatos ;" Natural Gas Treating by Selective Adsorption: Material Science and Chemical Engineering Interplay"; *Chem. Eng. J.* ,Vol.155, pp. 553-566 , **2009**.
- 102-** R. Thiruvengkatahari, S. Su and H. An, X.X. Yu;" Post Combustion CO<sub>2</sub> Capture by Carbon Fibre Monolithic Adsorbents" *Prog. Energy Combust. Sci.* Vol.35 , pp. 438-455 , **2009**.
- 103-** M. Hasib-ur-Rahman ; M. Siaj and F. Larachi ;" Ionic Liquids for CO<sub>2</sub> Capture-Development and Progress"; *Chem. Eng. Process.* Vol.49 , pp.313-322 , **2010**.
- 104-**D. Wappel ; G. Gronald ; R. Kalb and J. Draxler;" Ionic Liquids for Post-Combustion CO<sub>2</sub> Absorption"; *Int. J. Greenhouse Gas Control* , Vol.4, pp. 486-494 , **2010**.
- 105-** S. Choi ; J. H. Drese and C.W. Jones ;" Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources"; *ChemSusChem* ,Vol. 2 , pp.796-854 , **2009**.
- 106-** J. R. Benemann ;" Utilization of Carbon Dioxide from Fossil Fuel – Burning Power Plants with Biological Systems"; *Energy Convers. Manage.*,Vol. 34 , pp.999 , **1993**.

## References

---

- 107-** K. Maeda ; M. Owada ; N. Kimura ; K. Omata and I. Karube ;" CO<sub>2</sub> Fixation from The Flue Gas on Coal-Fired Thermal Power Plant by Microalgae"; *Energy Convers. Manage.* Vol.36 , pp. 717-720 , **1995**.
- 108-** K.O. Kwak ; S. Jung ; S.Y. Chung ; C. M. Kang ;Y.I. Huh and S.O. Bae ;"A Study about Different Strategies in Risk Elicitation"; *Biochem. Eng. J.*, Vol.31, pp. 20-22 , **2006**.
- 109-** G.T. Rochelle;" Amine Scrubbing for CO<sub>2</sub> Capture"; *Science.*; Vol. 325 ,pp.1652 , **2009** .
- 110-** J. R. Li ; R. J. Kuppler and H.C. Zhou ;" Selective Gas Adsorption and Separation in Metal-Organic Frameworks";*Chem. Soc. Rev.* ,Vol.38, pp.1477-1504 , **2009**.
- 111-** A. D. Ebner and J. A. Ritter ;" State-of-the-art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries"; *Sep. Sci. Technol.* Vol.44, pp.1273-1421, **2009**.
- 112-** H. Herzog ; J. Meldon and A. Hatton ;"Advanced Post-Combustion CO<sub>2</sub> Capture Massachusetts Institute of Technology"; *Boston, MA*, **2009**.
- 113-** M.T. Ho ; G. Leamon ; G.W. Allinson and D. E. Wiley;" Economics of CO<sub>2</sub> and Mixed Gas Geosequestration of Flue Gas Using Gas Separation Membranes"; *Ind. Eng. Chem. Res.* ,Vol.45 , pp. 2546-2552 , **2006**.
- 114-** R. Bruce Prim ; H. E. Bair ; S. Vyazovkin ; P. K. Gallagher and A. Riga ;"Thermogravimetric Analysis (TGA)"; *Wiley*,Vol.3, pp. 241-314 , **2009**.
- 115-** L. Fröberg ;"Thermal Analysis TGA / DTA"; *Process Chemistry Center*.
- 116-** T. Erdmenger ; J. R. Vitz ; F. Wiesbrock and U. S. Schubert ; "Influence of Different Branched Alkyl Side Chains on The Properties of Imidazolium-Based Ionic Liquids "; *J. Mater. Chem.*, Vol. 18, pp. 5267-5273 , **2008**.

## References

---

- 117-** S. Henri Schrekker ; O. Dagoberto Silva ; A. Marcos Gelesky ; P. Marcelo Stracke ; M. L. Clarissa Schrekker ; S. Reinaldo Gonçalves and Jairton Dupont ; "Preparation, Cation-Anion Interactions and Physicochemical Properties of Ether-Functionalized Imidazolium Ionic Liquids"; *J. Braz. Chem. Soc.*, Vol. 19, No. 3, pp. 426-433 , **2008**.
- 118-** D. J. Heldebrant ; C. R. Yonker ; P. G. Jessop; L. Phan ;"Organic Liquid CO<sub>2</sub> Capture Agents with High Gravimetric CO<sub>2</sub> Capacity"; *Energy Environ. Sci.*, Vol.1 , pp. 487-493 , **2008** .
- 119-** H. M. A. Abood ; A.P. Abbott ; Ballantyne and Ryder K. ;"AlCl<sub>3</sub>-Amid Systems-Ionic Liquids with Metal Containing Cations" ; *Chem. Commun.* Vol. 47, pp. 3523-3525 , **2011**.
- 120-**A. P. Abbott ; David Boothby ; Glen Capper ; David Davies and Raymond Rasheed ; "Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids" *J. Am. Chem. Soc.*, Vol. 126 (29), pp. 9142-9147, **2004**.
- 121-**Z. N. Al-Qudsi and H. M. A. Abood;" The Electronic Transition Behavior Cr (III), Fe (III), Fe (II) and Ni (II), Transition Metal Cations In Ammonium Alum-Urea Room Temperature Ionic Liquid"; *Journal of Al-Nahrain University*; Vol.16 (3) , pp. 46-55 , **2013**.
- 122-** A. C. Taş; P. J. Majewski and F. Aldinger;" Synthesis of Gallium Oxide Hydroxide Crystals in Aqueous Solutions with or without Urea and Their Calcination Behavior"; *American Ceramic Society*, Vol.85, pp. 1421-1429, **2004**.
- 123-** A. Binin; "Metal Organic Frameworks (MOFs) for CO<sub>2</sub> capture"; *New Orleans.* ;Vol.38, pp.7-9 , **2008**.



## *References*

---

**124-** J. Brennecke and E. Maginn ;" Why Is CO<sub>2</sub> So Soluble in Imidazolium-Based Ionic Liquids?"; *J. AM. CHEM. SOC.* Vol.126 , pp.5300-5308 , **2004**.

## الخلاصة

تم دراسة مجموعة من السوائل الايونية المحضرة لغرض دراسة قابليتها على امتصاص غاز ثاني اوكسيد الكربون لوحدها او بوجود بعض المحفزات وذلك عند درجة حرارة الغرفة والضغط الجوي.

ولزيادة سعة السوائل الايونية في قابليتها لقمص غاز ثاني اوكسيد الكربون تم اضافة بعض محفزات بعضها كانت فعالة . وقد وجد بأن كل من السائل الايوني نترات الالمنيوم المائية – يوريا مع اضافة اوكسيد الكالسيوم ، و اضافة كل من هيدروكسيد الصوديوم وكلوريد الالمنيوم واحادي ايثانول الامين الى السائل الايوني كبريتات الالمنيوم – يوريا لم يظهر تغير في تحليل طيف الاشعة تحت الحمراء قد يشير الى وجود امتصاص لغاز ثاني اوكسيد الكربون بالطريقة الكيميائية او الفيزيائية .

ولكن مع اضافة هيدروكسيد الصوديوم المائي الى السائل الايوني كبريتات الالمنيوم – يوريا اظهر تغير في طيف الاشعة تحت الحمراء عند  $1666\text{ cm}^{-1}$  يشير الى وجود امتصاص كيميائي لغاز ثاني اوكسيد الكربون . وكذلك تم اضافة الماء المقطر الى السائل الايوني كبريتات الالمنيوم – يوريا وقد ظهر في طيف الاشعة تحت الحمراء توسع في الحزمة فوق  $2500\text{cm}^{-1}$  ولم يظهر اي تغير واضح عند مجموعة الكربونيل .

اما اوكسيد الكالسيوم الذي اضيف الى السائل الايوني كبريتات الالمنيوم – يوريا فقد اظهر تغير في طيف الاشعة تحت الحمراء عند  $1666\text{ cm}^{-1}$  و  $1618\text{ cm}^{-1}$  حيث كانت منفصلة وحادة والذي يشير الى وجود امتصاص لغاز ثاني اوكسيد الكربون .

كما وجد ان السائل الايوني كلوريد الالمنيوم – يوريا ذو قابلية على امتصاص غاز ثاني اوكسيد الكربون بدون اضافة اي من المحفزات حيث اظهر طيف جديد عند  $1655\text{ cm}^{-1}$  لطيف الاشعة تحت الحمراء . وكانت قابلية وفعالية هذا السائل الايوني اكبر من السائل الايوني كلوريد الالمنيوم – استاميد في قمص غاز ثاني اوكسيد الكربون الذي لم يظهر تغير واضح في طيف الاشعة تحت الحمراء .

## {الاهداء}

الى من تعهداني بالتربية في الصغر ، وكانا لي نبراساً يضيء  
فكري بالنصح والتوجيه في الكبر امي وابي .

الى من شملوني بالعطف و امدوني بالعون وحفزوني للتقدم  
اخوتي واخي .

الى روح استاذي الفاضل الدكتور شهباز احمد " رحمه الله " .

الى كل من علمني حرفاً واخذ بيدي في سبيل تحصيل العلم  
والمعرفة صديقاتي وزميلاتي وبالانص الدكتور نسرين رحيم  
جبر .

## شكر وتقدير

اشكر الله مولاي وخالقي الذي منّ عليّ بأتمام هذا العمل المتواضع مع رجائي ان يتقبله مني ويجعله خالصاً لوجهه الكريم انطلاقاً من قوله تعالى " ومن يشكر فأنا ما يشكر لنفسه " ومن قول رسول الله ( ص ) " لا يشكر الله من لا يشكر الناس " وإيماناً بفضل الاعتراف بالجميل وتقديم الشكر والامتنان لأصحاب المعروفه فأني اتقدم بالشكر الجزيل والثناء العظيم الى استاذي ومشرفي الدكتور هادي محمد علي عبود علي قبوله الاشراف علي هذا البحث ومتابعته له منذ الخطوات الاولى وعلى ما منحني من صدر واسع ونصح وارشاد ساعد علي اخراج هذا العمل بهذه الصورة واسأل الله أن يجزيه عني خير الجزاء .

ولا أنسى من شكري الجزيل لزميلاتي وزملائي في العمل وكذلك زميلاتي وزملائي في دراسة الماجستير وكل من أمان علي إنجاز هذا البحث بإسداء معروفه أو بتقديم خدمة مهما كانت أو بدعاء لي في ظهر الغيب، فجزى الله الجميع عني خير الجزاء.

ايثون أكرم

2014

# بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

{ اللَّهُ نُورٌ السَّمَاوَاتِ وَالْأَرْضِ مِثْلُ نُورِهِ كَمِشْكَاةٍ فِيهَا  
مِصْبَاحٌ الْمِصْبَاحُ فِي زُجْجَةٍ الزُّجْجَةُ كَأَنَّهَا كَوْكَبٌ  
كَارِيٌّ يُوقَدُ مِنْ شَجَرَةٍ مُبَارَكَةٍ زَيْتُونَةٍ لَا شَرْقِيَّةٍ وَلَا غَرْبِيَّةٍ  
يَكَادُ زَيْتُهَا يُضِيءُ وَلَوْ لَمْ يَمْسَسْهُ نَارٌ نُورٌ عَلِيُّ نُورٌ بِهَيْكَلٍ  
اللَّهُ لِنُورِهِ مِنْ بَشَاءٍ وَيَضْرِبُ اللَّهُ الْأَمْثَالَ لِلنَّاسِ وَاللَّهُ بِكُلِّ  
شَيْءٍ عَلِيمٌ }

## حِكَايَةُ اللَّهِ الْعَظِيمِ



جمهورية العراق  
وزارة التعليم العالي والبحث العلمي  
جامعة النهرين / كلية العلوم  
قسم الكيمياء

# تحريي قنص غاز ثاني اوكسيد الكربون بواسطة السوائل الايونية عند درجة حرارة الغرفة

رسالة مقدمه إلى

كلية العلوم - جامعة النهرين

وهي جزء من متطلبات نيل درجة ماجستير في الكيمياء

من قبل

ايثون أكرم عبد الجبار

بأشراف

الدكتور هادي محمد علي عبود

2014