FTIR Study of Carbon Dioxide Interaction with some Room Temperature Ionic Liquids

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Abstract

Four ionic liquids were investigated for abilities to capture CO_2 alone or with added catalyst at room temperature and atmospheric pressure. Hydrated aluminum nitrate Al $(NO_3)_3.9H_2O$-urea with added CaO, hydrated ammonium aluminum sulfate NH_4Al $(SO_4)_2.12H_2O$-urea with added solid NaOH did not show in FTIR chart sign of either physical or chemical absorption of CO_2, however hydrated ammonium aluminum sulfate NH_4Al $(SO_4)_2.12H_2O$-urea with added $NaOH_{aq}$ or few water showed a chemical absorption of CO_2 at 1666 cm^{-1} as in aluminum chloride-urea ionic liquid while aluminum chloride-acetamide showed weaker or no ability to capture CO_2.

Keywords: Ionic liquids, Carbon dioxide capture, Catalysts, FTIR.

Introduction

One of the interesting gases which represent important problem in the atmosphere is carbon dioxide. Its concentration has been increased from 280 ppm at the beginning of the industrial (Ca.1750) to 390 ppm in 2010 [1]. The increased concentration of CO_2 in atmosphere influences the balance of incoming and outgoing energy in the atmosphere system, leading to raise the average surface temperature of earth. Thus, CO_2 has often been cited as the primary anthropogenic greenhouse gas (GHG) as well as the leading culprit in climate change. The reasons for this skewed reliance on fossil fuels as our primary energy source is due to the inherent energy density, abundance and the economic dependence of modern society on the acquisition and trade of these resources [1,2].

One of the mostly studied solvent used to capture CO_2 is monoethanolamine (MEA) which has some advantages such as its maturity, stable operation, good reactivity, and high capacity[3]. (MEA) CO_2 capture consumes almost 30% of the energy that is needed to run a power plant[4], in addition to other drawbacks like, high solvent losses caused by evaporation, degradation and poor thermal stability, as well as equipment corrosion [4,5]. Therefore, developing an economical and energy efficient CO_2 capture technologies is highly needed. Ionic liquids ILs constitute a new class of solvents which are also known to be selective for CO_2 absorption[6,7].

Carbon dioxide was reported to have solubility commonly higher in ILs with fluoroalkyl groups such (tris (trifluoromethylsulfonyl) methide, [methide], and bis (trifluoromethylsulfonyl) imide, $[Tf_2N]^-$) and lower in ILs with non-fluorinated inorganic anions such as (nitrate, $[NO_3]^-$, and dicyanamide, $[DCA]^-$)[8].

The general mechanism of CO_2 absorption in ionic liquids could be described as physical or chemical process. Ionic liquids comprise combinations of large organic cations and smaller inorganic anions and are typically viscous liquids near room temperature[9].

In addition to their extremely low vapor pressures, they are non-flammable, environmentally benign, and can exhibit exceptional thermal stability. The mechanism for CO_2 capturing is often based on physisorption, and involves weak association between the ionic liquid and CO_2 molecules (rather than chemical bonds), with heats of adsorption of around (11 $kJmol^{-1}$)[10,11]. In view of this low heat of reaction, the obvious benefit for CO_2 capture is the minimal energy required for solvent regeneration. The capacity is directly proportional to the partial pressure of CO_2 and improves at pressures above 1–2 bar. For this reason, ionic liquids were initially proposed for pre -combustion applications. Some ionic liquids react with CO_2 in a chemisorption mechanism. This is an additional benefit as that ionic liquids can simultaneously serve to remove CO_2 [12].

In amine functionalized ionic liquids, the mechanism considered as chemical process. Therefore it was found that the careful choice of the ionic liquids and its properties and profound knowledge of the molecular features seem to be the way to proceed in order to find ionic liquids appropriate for carbon dioxide selective absorption [9].

The work of this paper covered the ability of some ionic liquids to absorb CO_2. The investigation of CO_2 absorption was followed by FTIR technique. Ionic liquids containing urea were found to be good solvent for some metal oxides particularly those of room temperature ionic liquids with aluminum chloride, aluminum sulfate, aluminum nitrate or containing choline chloride. Additionally, aluminum chloride- acetamide ionic liquid was also used in this study to elucidate its capability to absorb CO_2.

Experimental Work

Materials. $NH_4Al(SO_4)_2.12H_2O$ 99% BDH, $Al(NO_3)_3.9H_2O$ 97% BDH, $AlCl_3$ 98% Fluka, $(NH_2)_2CO$ 99.5% THOMAS BAKER, NaOH 99% BDH, CaO 99% BDH, NH_2COCH_3 98% Fluka chemical were used.

Instrument

The main instrument used throughout this study was FTIR (Fourier Transform Infrared Spectrophotometer, 2006, Shimadzu, IR-Prestige 21).

1-Preparation of ionic liquids

a- Hydrated ammonium aluminum sulfate $NH_4Al(SO_4)_2.12H_2O$ and urea NH_2CONH_2 in a mole ratio of (1:5) respectively were milled, well mixed and heated gradually to (85°C) in a closed glass tube with continuous gentle stirring until the solid salts changed to colorless liquid[13].

b- Solid mixture of hydrated aluminum nitrate $Al(NO_3)_3.9H_2O$ and urea NH_2CONH_2 in a mole ratio of (1:1.3) was milled, well mixed and heated gradually to (85°C) in a close container with continuous gentle stirring until both solid components melted together producing colorless liquid.

c- Aluminum chloride with either urea or acetamide were used to prepare the ionic liquid in a mole ratio of (1.4:1) by direct mixing of solid components which gave a clear faint liquids[14].

2- Added chemical compounds to ionic liquids.

Some chemical compounds were added to ionic liquids as powder or aqueous solution:-

a- Sodium hydroxide pellet (0.04 g) was crashed and added to 10 ml of $NH_4Al(SO_4)_2.12H_2O$ –urea ionic liquid.

b- Three drops of sodium hydroxide aqueous solution (0.002 M) was added to 10 ml of $NH_4Al(SO_4)_2.12H_2O$ –urea ionic liquid.

c- Calcium oxide (0.01g) was added to 10ml of both $NH_4Al(SO_4)_2.12H_2O$ –urea and $Al(NO_3)_3.9H_2O$-urea ionic liquids (0.0178 M) in its powder form.

3-Carbon dioxide gas flow

Carbon dioxide was bubbled in to 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 and at the end of experiment the liquid was examined by FTIR.

Result and Discussion

Added sodium hydroxide pellet to 10 ml of $NH_4Al(SO_4)_2.12H_2O$ –urea IL formed a clear liquid mixture at room temperature (17 C^o) which showed the vibration bands as in Fig.(2) that appeared to have no difference frequency from the vibration bands of the ionic liquid alone Fig.(1) which might indicate an absorption of CO_2 in ionic liquid alone or with added NaOH. To enhance the absorption of CO_2 by ionic liquid, NaOH was also added but as aqueous solution. This was though to decrease the viscosity of the mixture due to the presence of water and expected to increase the dissolution of CO_2. The FTIR of this mixture shown in Fig.(3) indicated a change in the higher frequencies, particularly of the N-H stretching vibrational bands of the urea amine group above (3000 cm^{-1}) and in the lower frequencies in the carbonyl vibrational bands at 1647 cm^{-1} and 1666-1627 cm^{-1} as listed in Table (1). This might be related to an interaction of carbon dioxide CO_2 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_2 with amine group where gas diffusion is more feasible.

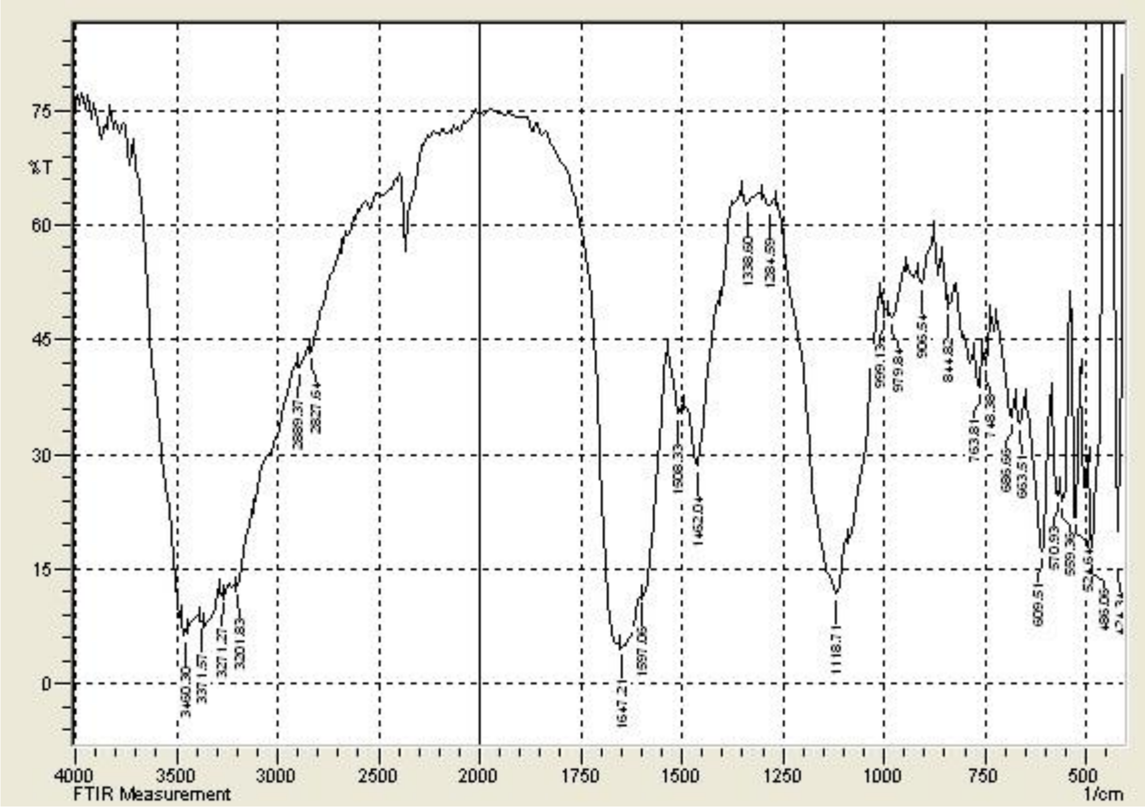

Fig.(1) FTIR spectra of $NH_4Al(SO_4)_2.12H_2O$ –urea IL.

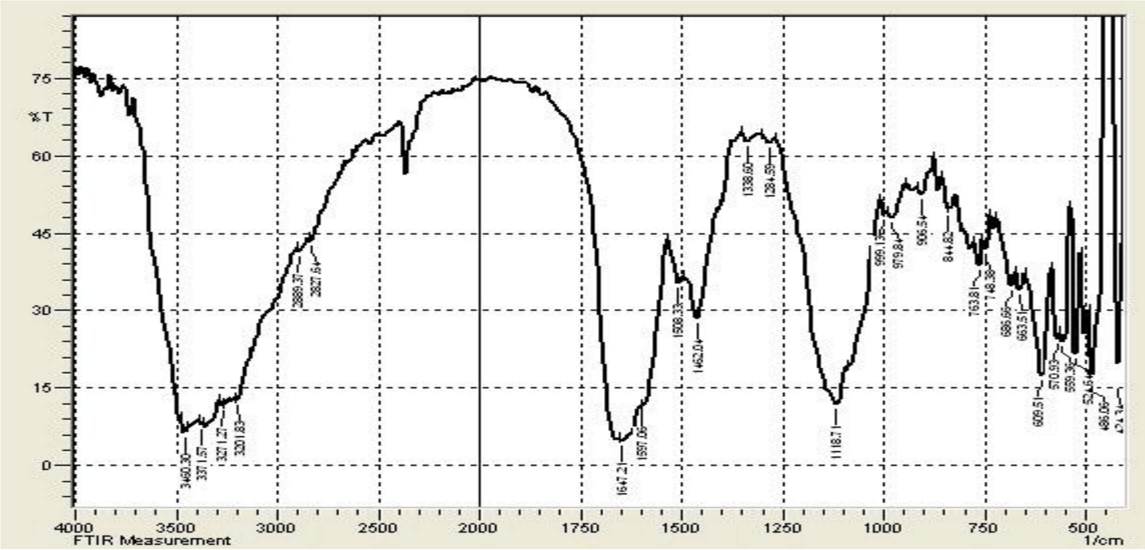

Fig.(2) FTIR spectra of $NH_4Al(SO_4)_2.12H_2O$ –urea IL with added solid NaOH.

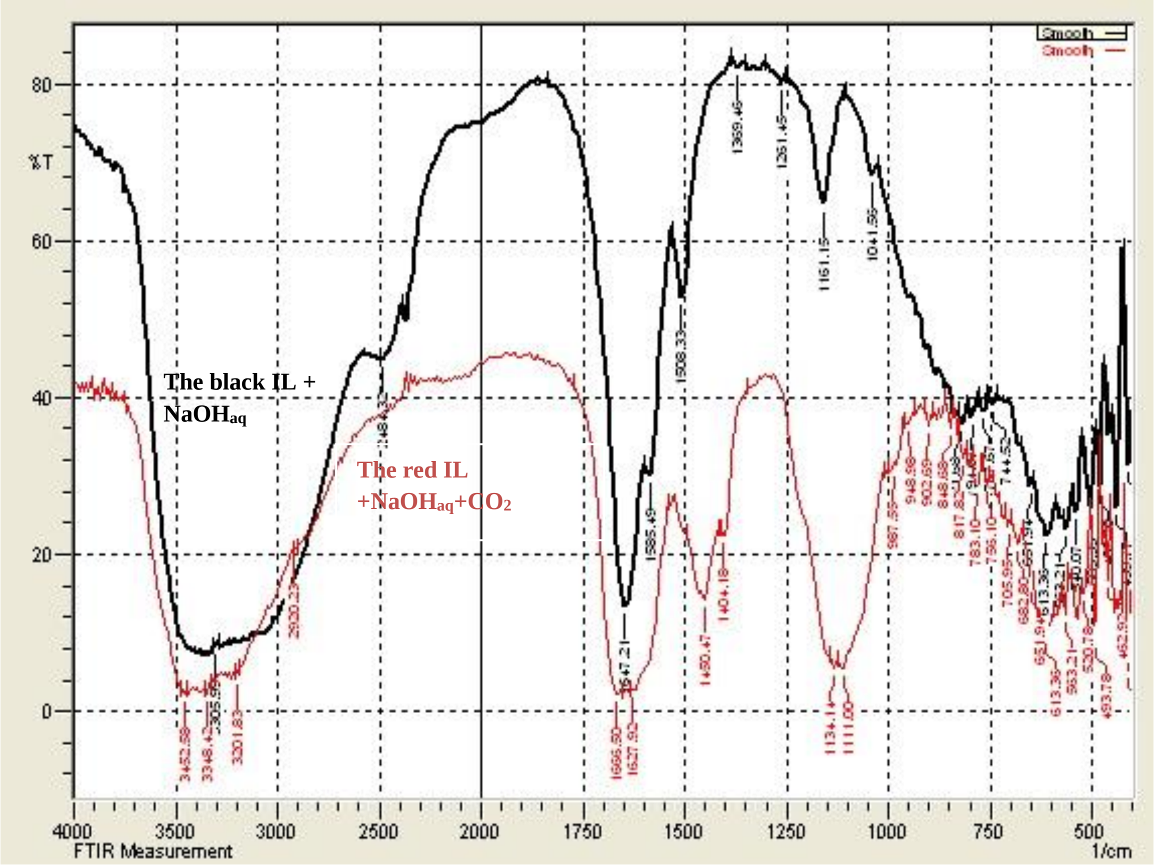

Fig.(3) FTIR spectra of $NH_4Al(SO_4)_2.12H_2O$ –urea IL with NaOH$_{aq}$, the black IL with NaOH$_{aq}$, the red IL with NaOH$_{aq}$ after bubbling CO$_2$.

Table (1)
Vibrational bands of the ionic liquid $NH_4Al(SO_4)_2.12H_2O$-urea alone; with added NaOH $_{aq}$ and with capturing CO$_2$.

IL	υ(N-H) cm^{-1}	δ(N-H) cm^{-1}	υ (C=O) cm^{-1}	υ $_s$(N-C-N) cm^{-1}	υ $_{as}$(N-C-N) cm^{-1}
$NH_4Al(SO_4)_2.12H_2O$.Urea. NaOH$_{aq}$	3305	1595 1508	1647	1161	1404
$NH_4Al(SO_4)_2.12H_2O$.Urea. NaOH$_{aq}$ + CO$_2$	3452 3348 3201	1450	1666 1627	1134 1111	1404

This enhancement of CO$_2$ absorption in this work is in the same trend as number of catalyst systems has also been developed by other workers to increase the efficiency of carbon dioxide absorption by the amine group including added alkali metal salts, ammonium salts, metal oxides, transition metal and main group complexes [15].

Powdered calcium oxide when added made a clear solution with $NH_4Al(SO_4)_2.12H_2O$ – urea ionic liquid and showed no visible changes until the end of the experiment. The solution showed the FTIR vibration bands as shown in Fig.(4). 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 similar effect as their frequencies decreased from 1649 cm^{-1} to 1626 cm^{-1} Table (2). Both might be considered as an indication of an interaction of carbon dioxide with amine group forming carbamate (N-carbxy urea).

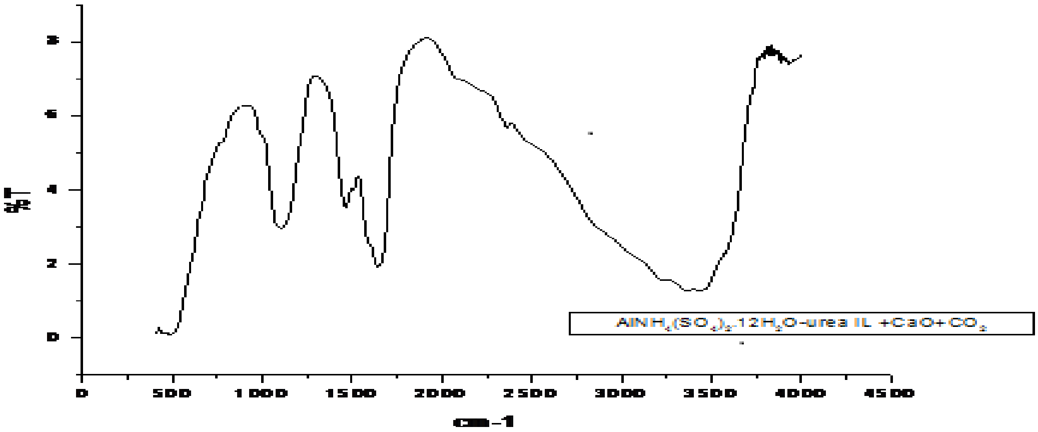

Fig.(4) FTIR vibration bands of $NH_4Al(SO_4)_2.12H_2O$ –urea IL containing CaO.

Table (2)
FTIR vibration bands of $NH_4Al(SO_4)_2.12H_2O$.urea containing CaO before and after bubbling CO_2.

IL	υ(N-H) cm^{-1}	δ(N-H) cm^{-1}	υ (C=O) cm^{-1}	$υ_s$(N-C-N) cm^{-1}	$υ_{as}$(N-C-N) cm^{-1}
$Al(SO_4)_2.NH_4.12H_2O$.urea. CaO	3230	1550	1645	1132	1396
$Al(SO_4)_2.NH_4.12H_2O$.urea. CaO + CO_2	3244	1540	1626	1107	1462

Powdered calcium oxide when added to Al $(NO_3)_3.9H_2O$-urea ionic liquid formed clear solution and after bubbling carbon dioxide showed the vibrational bands as in Fig.(5). 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 might be taken as indicator for carbon dioxide absorption in agreement with other report[11].

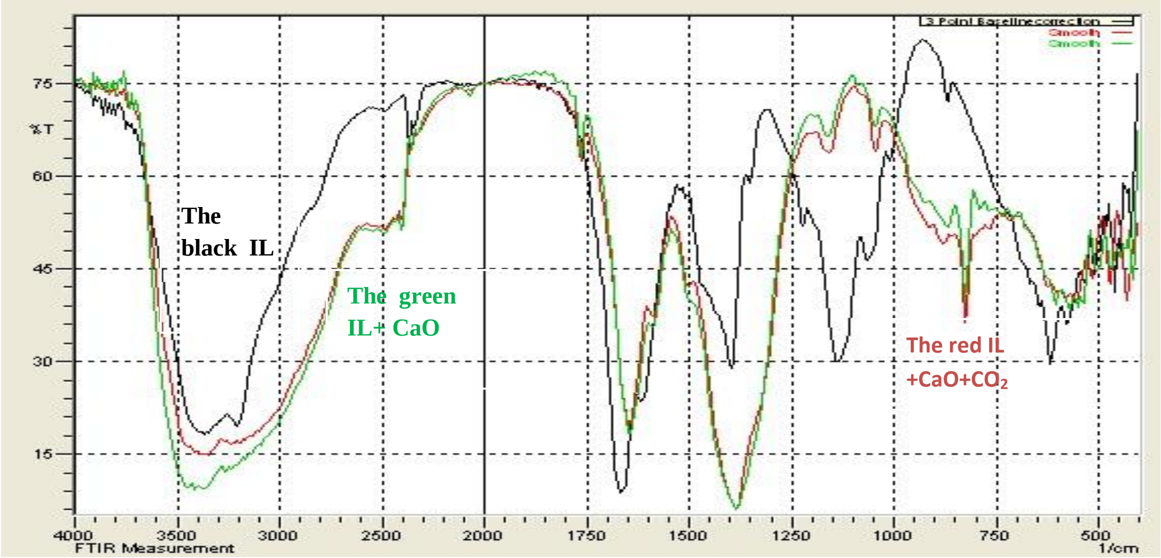

Fig.(5) FTIR spectra overlay to compare between vibrational bands of Al $(NO_3)_3.9H_2O$-urea, the black IL alone, the green with CaO and the red with capturing CO_2.

Aluminum chloride - urea ionic liquid [14] bubbled with carbon dioxide observed to have some changes in the vibrational mode of the amide and carbonyl groups in addition to the appearance of a new band at (1655 cm^{-1}, Fig.(6). The latter frequency could be arise from a splitting in the carbonyl group vibrational mode. Amide bending vibration band at 1504 cm^{-1} Table (3) showed an increase in its intensity with similar increase in the intensity of C=O. The changes in the backbone vibrational mode of urea molecule (N-C-N). The changes would indicate an interaction of carbon dioxide with urea of the ionic liquid.

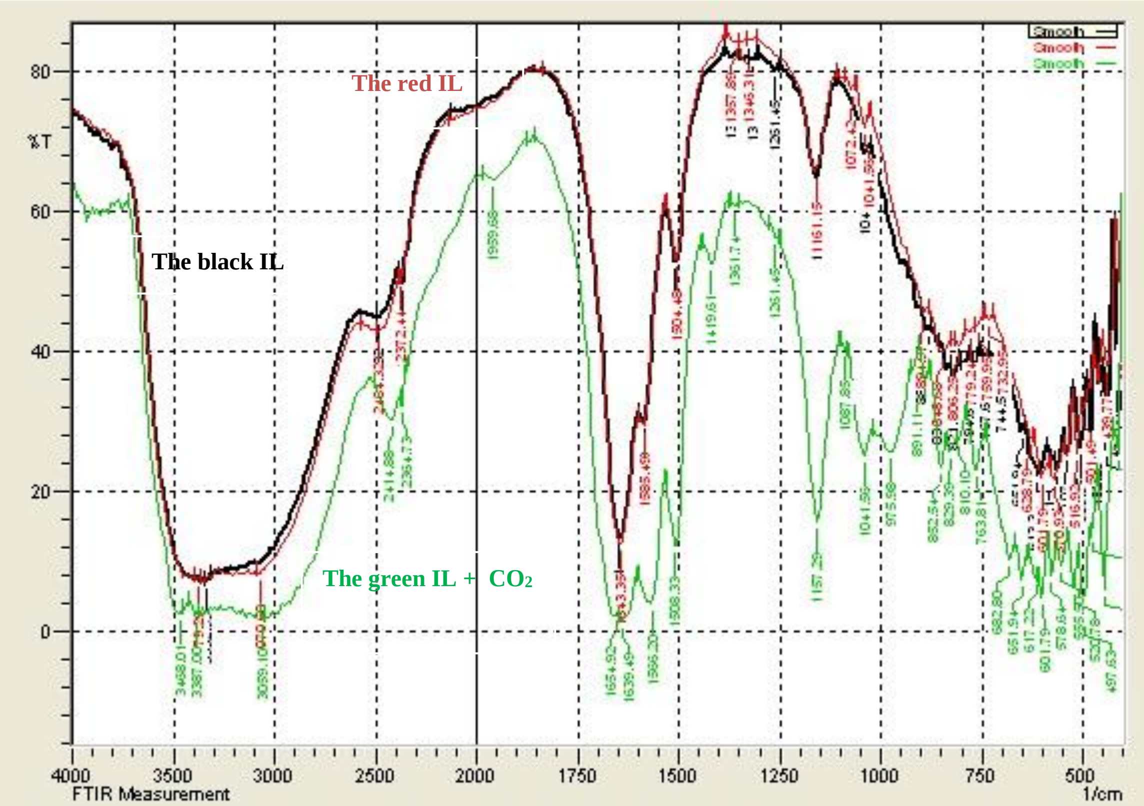

Fig.(6) FTIR spectra of $AlCl_3$-urea IL, (black) IL alone ,(red) before bubbling CO_2 and (green) after bubbling CO_2.

Table (3)
FTIR vibrational bands of $AlCl_3$ - urea IL and with capturing CO_2.

IL	υ(N-H) cm^{-1}	δ(N-H) cm^{-1}	υ (C=O) cm^{-1}	$υ_s$(N-C-N) cm^{-1}	$υ_{as}$(N-C-N) cm^{-1}
$AlCl_3$ - urea	3333 3270	1585 1504	1643	1161	1320
$AlCl_3$ - urea + CO_2	3498 3387 3059	1566 1508	1655 1639	1157	1350

Aluminum chloride–acetamide ionic liquid [14] bubbled with carbon dioxide showed FTIR Fig.(7) without an effect on the vibration modes of $AlCl_3$-acetamide ionic liquid indicating no interaction of carbon dioxide with amide nor dissolved carbon dioxide in ionic liquid.

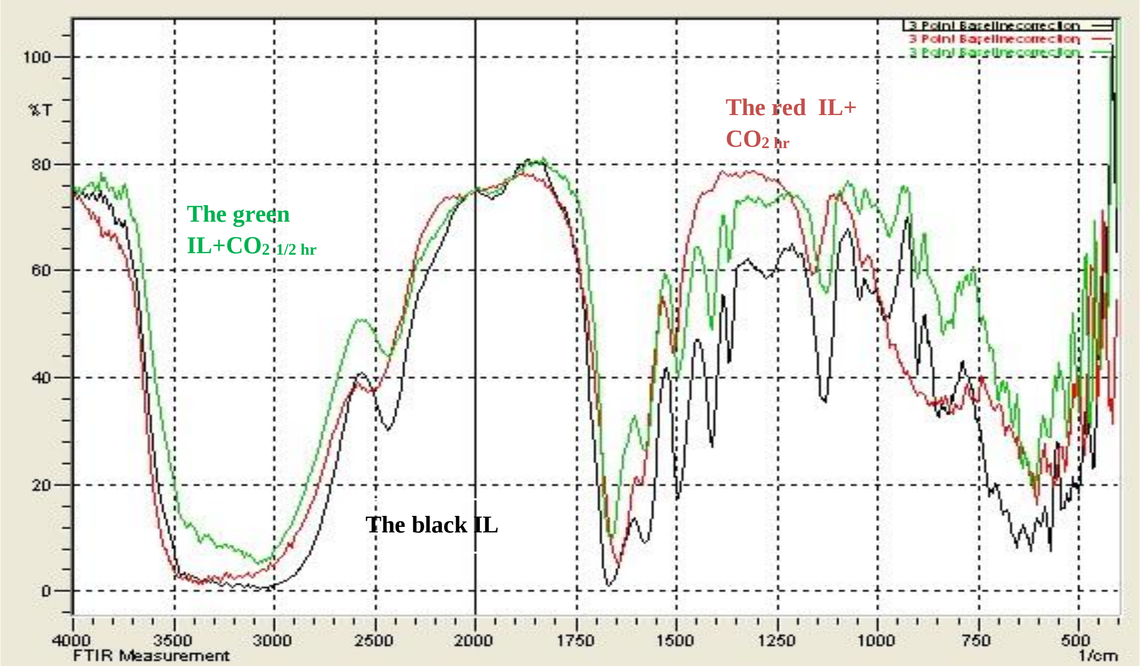

Fig.(7) FTIR vibrational bands of $AlCl_3$-acetamide IL,(black) IL alone, (green)after bubbling CO_2 for half an hour and (red) bubbling CO_2 for an hour.

To differentiate between the effect of water in the added $NaOH_{aq}$ to $NH_4Al(SO_4)_2.12H_2O$ – urea IL and solid NaOH effect ,an equivalent amount of water (3 drops) were added to the above IL. Examination of FTIR Fig.(8) vibrational modes before and after bubbling CO_2indicated a broaden effect on the high vibrational bands above 2500 cm^{-1}. This broad band returned its shape (as in IL alone) after bubbling CO_2 gas in the same trend as with mixture of added $NaOH_{aq}$ with IL. However, the carbonyl group vibrational band 1662 cm^{-1} seems to have no clear effect by the addition of water nor the vibrational band of sulfate group at 1103 cm^{-1}. These two bands showed clear effect in the case of the mixture of $NaOH_{aq}$ with IL Fig.(9) which indicate that both water and NaOH have affected the vibrational band of IL while the IL returned its initial vibrations after bubbling CO_2 which indicate an interaction of added water or $NaOH_{aq}$ to IL. This interaction could result in forming carbonic acid as follow:-

$$H_2O + CO_2 \rightarrow H_2CO_3 \text{ ....} (1)$$

$$OH^- + CO_2 \rightarrow HCO_3^- \text{ ....} (2)$$

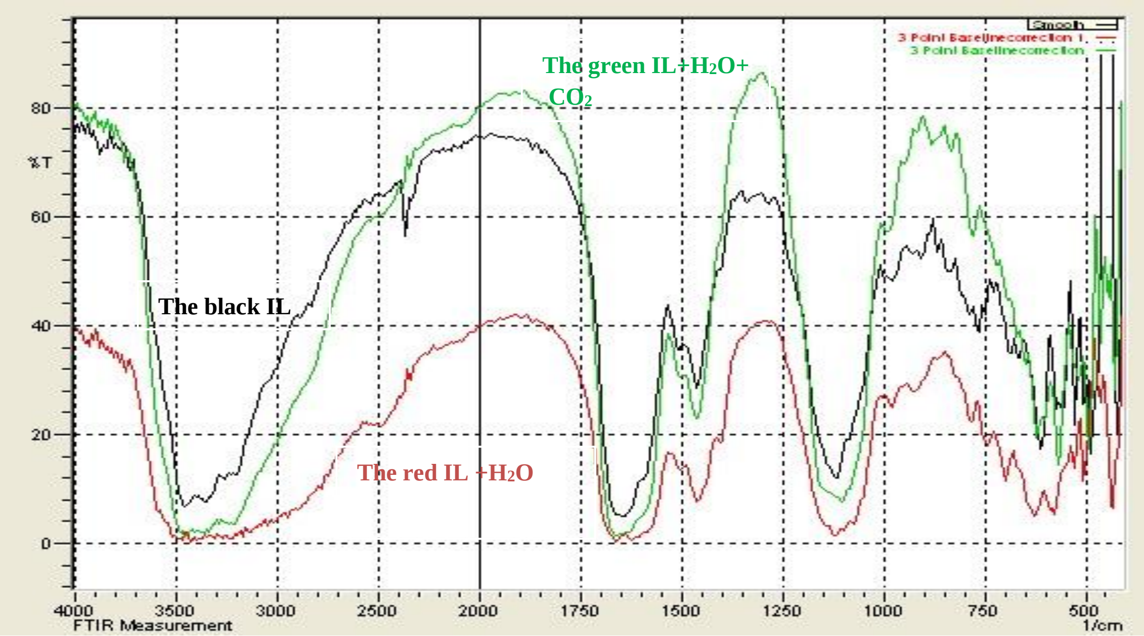

Fig.(8) FTIR vibrational bands of $NH_4Al(SO_4)_2.12H_2O$ –urea IL, (black) IL alone, (red) with added H_2O and (green) after bubbling CO_2.

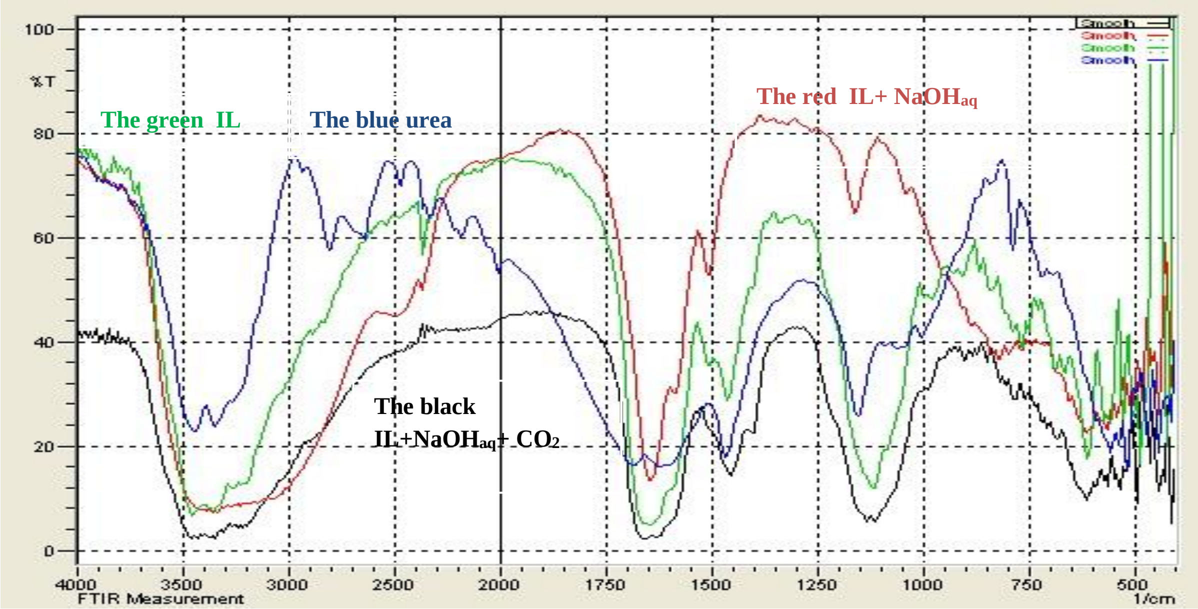

Fig.(9) FTIR vibrational bands of $NH_4Al(SO_4)_2.12H_2O$ –urea IL, (green) IL alone, (red) with $NaOH_{aq}$, (blue) urea alone and (black) IL with $NaOH_{aq}$ after bubbling CO_2.

Conclusion

Carbon dioxide was observed to be absorbed by $NH_4Al(SO_4)_2.12H_2O$ –urea ionic liquid containing aqueous sodium hydroxide solution ,as indicated by the new band at 1666 cm^{-1} for the carbon dioxide of the carbamate and the disappearance of broad band resulted from the addition of aqueous sodium hydroxide solution to this ionic liquid of the OH^{-1} stretching indicating the absence of free water molecule in ionic liquid. The resulted bands at the high frequency region related to N-H stretching at (3201 cm^{-1},3348 cm^{-1} and 3452 cm^{-1}) which appeared originally in the ionic liquid before the addition of aqueous sodium hydroxide solution. While in absence of added water the active absorption of carbon dioxide was not observed as no FTIR changes were recorded in the vibration frequencies. Similar new band of a carbon dioxide carbamate vibration was also observed in $AlCl_3$-urea alone at 1655 cm^{-1} similar to the reported frequency in [mim] PF_6 ionic liquid [16] and accepted as an indication of carbon dioxide absorption in ionic liquid. Similarly dissolved carbon dioxide was not observed in the FTIR bands. However, with ($AlCl_3$-Acetamide) the weak absorption of carbon dioxide could be related to the less basic amide group as the lone pair is closely withdraw to the carbon atom to enhance its electronic density due to the interaction of oxygen atom of its carbonyl group with Aluminum in the $[AlCl_2\text{-Acetamide}]^+$ cationic species of the ionic liquid [14]. This is not the case with $AlCl_3$-urea, as two amide group are bonded to carbonyl group of urea, thereby providing good electron density on the amide group than on the amide group of acetamide. This will afford a reaction of more basic amide group with carbon dioxide forming carbamate (N-carboxy urea).

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الخلاصة

تم دراسة اربعة انواع من السوائل الايونية لغرض دراسة قابليتها على امتصاص ثاني اوكسيد الكربون لوحدها او مع أضافة مواد محفزة كيميائيا عند درجة حرارة الغرفة والضغط الجوي. وقد وجد بأن السائل الايوني نترات الامونيوم الالمنيوم المائية – يوريا مع اضافة اوكسيد الكالسيوم او كبريتات الامونيوم الالمنيوم المائية – يوريا مع اضافة هيدروكسيد الصوديوم لم يظهر تغير في تحليل طيف الاشعة تحت الحمراء قد يشير الى وجود امتصاص ثاني اوكسيد الكربون بالطريقة الكيميائية او الفيزيائية. ولكن اظهر السائل الايوني كبريتات الامونيوم الالمنيوم المائية – يوريا مع اضافة هيدروكسيد الصوديوم المائي اظهر تغير في طيف الاشعة تحت الحمراء يشير الى وجود امتصاص كيمياوي لثاني اوكسيد الكربون. بالأضافة الى ذلك فقد وجد بأن السائل الايوني كلوريد الالمنيوم – يوريا ذو قابلية على امتصاص ثاني اوكسيد الكربون وقد اظهر طيف جديد عند $1655\ cm^{-1}$ لطيف الاشعة تحت الحمراء. وكانت قابلية هذا السائل اكبر من قابلية السائل الايوني كلوريد الالمنيوم – اسيتامايد في قنص ثاني اوكسيد الكربون.