

Effect of Ionic Liquids in CO₂ Capture from Natural Gas

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Abstract: This work presents a study to apply ionic liquids as potential industrial solvents for carbon dioxide capture. In order to obtain effective ionic liquid solvents, 3-(2-amino-ethyl)-1-methyl-1H-imidazol-3-ium-bis((trifluoromethyl)sulfonyl)amide(I), 3-(3-amino-propyl)-1-methyl-1H-imidazol-3-ium-bis((trifluoromethyl)sulfonyl)amide (II), 3-(2-amino-ethyl)-1-methyl-1H-imidazol-3-ium-tetrafluoroborate(III), and 3-(3-aminopropyl)-1-methyl-1H-imidazol-3-ium-tetrafluoroborate(IV) were synthesized and characterized by using elemental analysis, IR, ¹H-NMR, and Mass spectroscopy. The solutions of (I-IV) were prepared by dissolving with methanol. The absorption of CO₂ was obtained by gas chromatography. The results show that the synthesized ionic liquids have high efficiency for capture of CO₂ from natural gas.

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1. Introduction

Ionic liquids (ILs) are liquids that consist entirely of ions. In the last decade ILs have attracted the attention on scientific community due to their particular properties^[1] and their applications in organic synthesis^[2] catalysis^[3,4] biocatalysis^[5,6] liquid-liquid separations^[7], extraction^[8] and dissolution of cellulose in microwave^[9], petroleum asphaltenes in microwave^[10] processes, nanomaterials synthesis^[11], polymerization reactions^[12] and electrochemistry^[13]. ILs are excellent alternative to substitute volatile organic solvents in more environmental friendly technologies (green technologies), since their negligible vapor pressures, high thermal and chemical stability and their ability to act as catalysts, their non-flammability and non-corrosives properties. Most ILs reported in the literatures consist of organic cations and organic or inorganic anions. They can be designed with functionalized cations or anions that impart specific properties or reactivities^[14,15]. These ILs are called Task Specific Ionic Liquids or FILs which they have a wide range of potential applications.

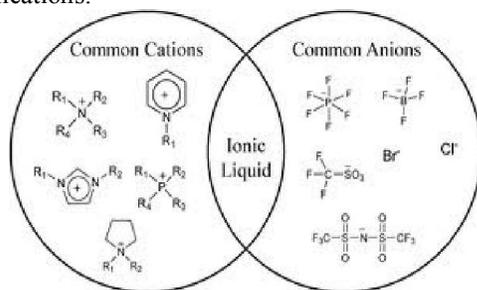


Figure (1): Most common cations and anions in ILs.

One of the most important applications of ionic liquids is removal of acid gases from natural gas. Natural gas is a mixture of combustible gases formed underground by the decomposition of organic materials in plant and animal. It is a mixture of various hydrocarbon molecules. Commercial-grade natural-gas compositions vary from 70% to 95% CH₄, with the balance composed of heavier hydrocarbons (primarily ethane, C₂H₆, and propane, C₃H₈) as well as diluents such as molecular nitrogen (N₂) and CO₂. There are also trace levels of sulphur compounds, often added as odorants, and other hydrocarbon species.

The use of natural gas (NG) as an alternative fuel has been growing in recent years. It has been actively promoted by industry as a pollution-free fuel; it costs less and has a proven safety record. Literatures^[16] indicate that automotive engines of current design can use natural gas satisfactorily as a fuel: world-wide, more than 700000 passenger cars, buses and trucks were running on natural gas in 1990. In addition, it is used in domestic appliances as well as in electric power stations.

In our work ionic liquids of the type 3-(2-aminoethyl)-1-methyl-1H-imidazol-3-ium bis((trifluoromethyl)-sulfonyl) amide(I), 3-(3-aminopropyl)-1-methyl-1H-imidazol-3-ium-bis((trifluoromethyl)sulfonyl)amide(II), 3-(2-aminoethyl)-1-methyl-1H-imidazol-3-ium tetrafluoroborate(III), and 3-(3-aminopropyl)-1-methyl-1H-imidazol-3-ium-tetrafluoroborate(IV) were synthesized to capture carbon dioxide from natural gas by chemical absorption using bubbling technique.

Removal of carbon dioxide increases the calorific value and transport ability of the natural gas. Carbon dioxide, which falls into the category of acid gases (as does hydrogen sulfide, for example) is commonly found in natural gas streams at levels as high as 80%.

2. Experimental:

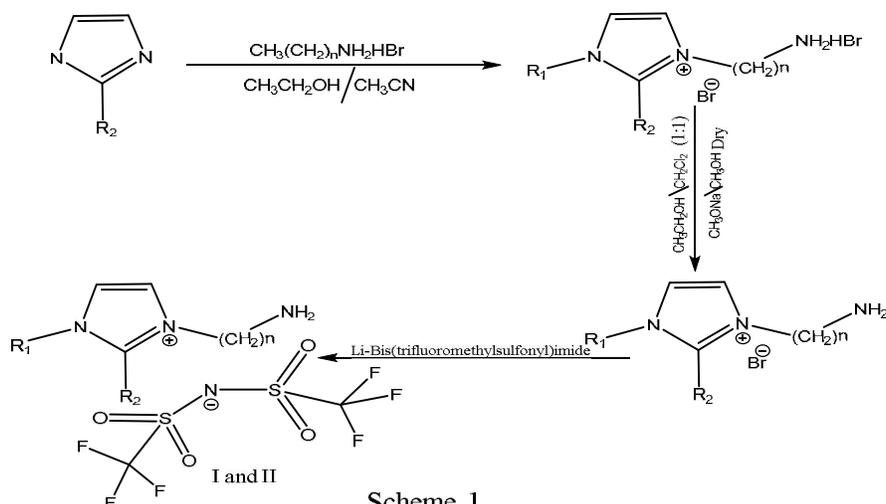
1.1. Materials:

1-Methyl imidazole (99%), 2-bromoethylaminehydrobromide (99%), 3-bromopropylaminehydrobromide (98%), sodium tetrafluoroborate (99%), and lithium bis(trifluoromethylsulfonyl) imide(99%) were purchased from Sigma-Aldrich. Sodium methoxide(99.98%), ethanol (99.99%), dry methanol (99.%), acetonitrile(98%), and methylene chloride(99%) were purchased from Merck chemicals company. PVDF membrane was obtained from Whatman incorporation.

1.2. Synthesis of Ionic liquids (ILs):

1.2.1. Synthesis of Imidazolium bistrifluoromethyl sulfonyl imides (I and II)^[17]:

Solution containing one equivalent of 1-methyl imidazole in acetonitrile (0.25 M) is added to stirring solution of one equivalent of n-bromoalkyl aminehydrobromide (ethyl- and propyl- respectively) dissolved in a minimal amount of ethanol, it is stirred at room temperature. Solvent is removed under vacuum yielding dark color. Add methylene chloride and ethanol (50:50) % to yield white precipitate and solvent is removed by evaporation. Deprotonating the amine moiety with 1.2 equivalence of sodium methoxide in dry methanol, solvent evaporation and methylene chloride is added to precipitate out the sodium bromide by-product which is filtered off. Methylene chloride solution is added with 1.1 equivalence of Lithiumbis(tri fluoromethyl sulfonyl) imide overnight and the organic layer repeatedly washed with water to remove bromide. Methylene chloride and water are removed under vacuum. The synthesized product is expressed in scheme 1:

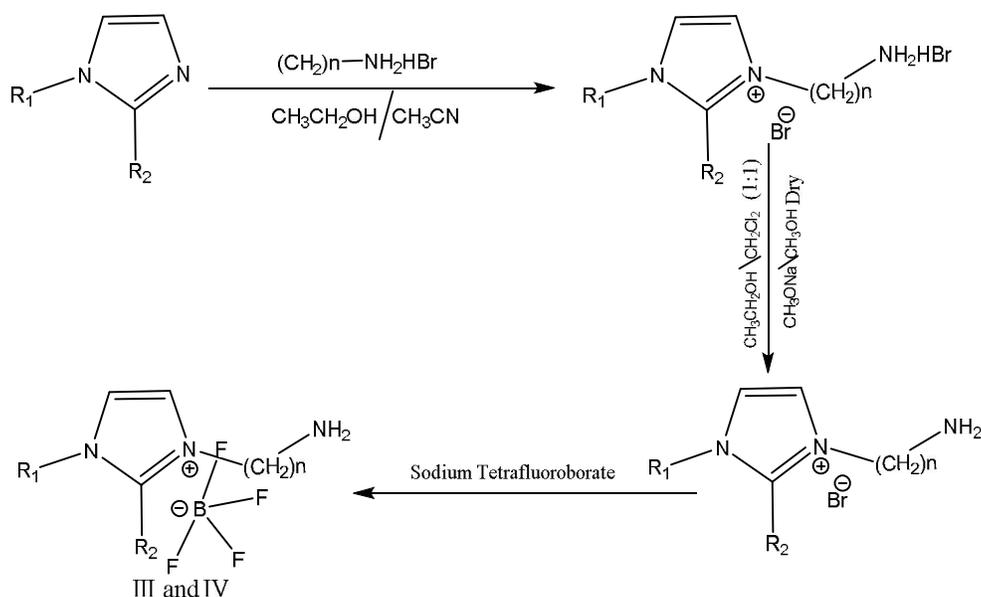


I=3-(2-aminoethyl)-1-methyl-1H-imidazol-3-iumbis((trifluoromethyl)sulfonyl)amide where ($n=2$, $R_1 = \text{CH}_3$, $R_2 = \text{H}$), II=3-(3-aminopropyl)-1-methyl-1H-imidazol-3-iumbis((trifluoromethyl)sulfonyl)amide where ($n=3$, $R_1 = \text{CH}_3$, $R_2 = \text{H}$).

2.2.2. Synthesis of Imidazolium tetrafluoroborate compounds (III and IV)^[17]:

Solution containing one equivalent of 1-methyl imidazole in acetonitrile (0.25 M) is added to stirring solution of one equivalent of n-bromoalkyl amine hydrobromide (ethyl- and propyl- respectively) dissolved in a minimal amount of ethanol, it is stirred at room temperature. Solvent removal under vacuum yields dark color. Add methylene chloride and ethanol (50:50) % to yield white precipitate, and solvent removal by evaporation. Deprotonating the

amine moiety with 1.2 equivalence of sodium methoxide in dry methanol, solvent evaporation and methylene chloride added to precipitate the sodium bromide as by-product which is filtered off. Methylene chloride solution is reacted with 1.1 equivalence of sodium tetrafluoroborate dissolved in water overnight and the organic layer is repeatedly washed with water. Methylene chloride and water were removed under vacuum. The synthesized reaction is expressed in scheme 2.



III=3-(2-aminoethyl)-1-methyl-1H-imidazol-3-iumtetrafluoroborate, (n=2, R₁=CH₃, R₂=H)

IV=3-(3-aminopropyl)-1-methyl-1H-imidazol-3-iumtetrafluoroborate, (n=3, R₁=CH₃, R₂=H)

2.3. Capture of CO₂:

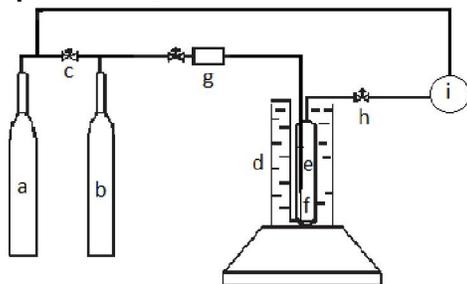


Figure (2): Flow sheet of CO₂ capture experimental apparatus.

Using methanol as a blank solution, prepare 0.1 mole solution of ionic liquid, put the solution in the bubbling cell and run the system as follows:

- Adjust the system as in figure (2) where: a) Cylinder of He, b) Cylinder of CO₂/CH₄, c) Valve, d) Water bath at 25°C, e) Bubbling cell, f) Needle,

g) Mass flow-meter, h) Sampling valve, i) Gas chromatography.

- Evacuate the system using He gas first.
- Flow CH₄/CO₂ gas to the system and pass to the solution through thin needle.
- Outlet gases go to gas chromatography to be measured.

3. Results and Discussions:

3.1. Characterization of the synthesized ionic liquids (I – IV):

3.1.1. Elemental analysis:

Elemental analysis for (I-IV) was performed via elemental analyzer Perkin Elmer 240° C and the obtained results are given in table (1), from the table we obtain that the found values are compatible to the calculated ones.

Table (1): Elemental analysis of (I-IV)

ILs	%C		%N		%H		%S	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
I	23.65	23.02	13.79	13.84	2.98	3.25	15.78	16.09
II	25.72	25.51	13.36	13.47	3.36	3.40	15.25	15.31
III	33.84	33.82	19.73	19.62	5.68	5.81	—	—
IV	37.04	37.33	18.51	18.38	6.22	6.06	—	—

3.1.2. ¹H-NMR Spectroscopy:

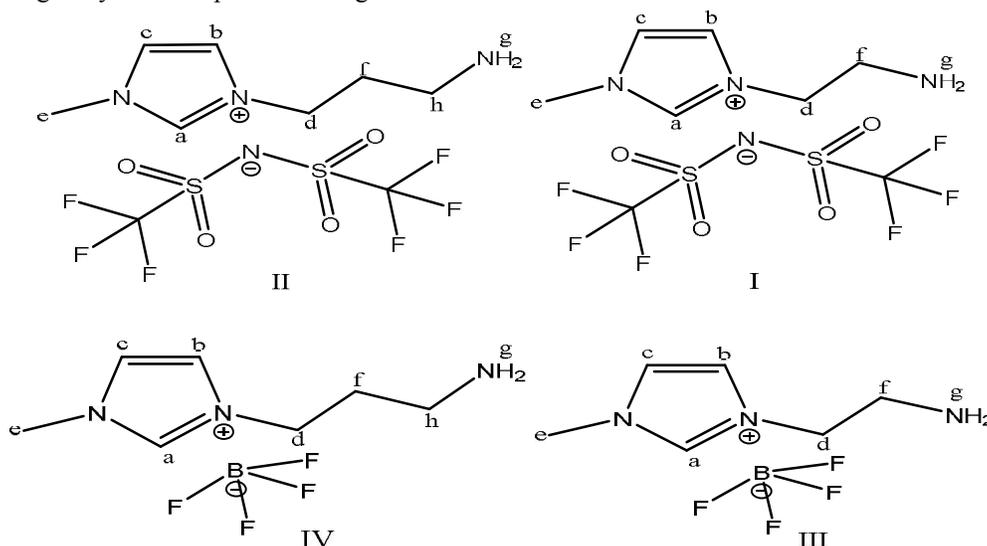
¹H-NMR for the synthesized ionic liquids (I-IV) was measured using Jeol-EX-270 MHz ¹H-NMR spectroscopy.

Table (2): ^1H -NMR spectroscopy of (I – IV)

Compound	Chemical Shift (ppm)							
	a Singlet	b Doublet	c Doublet	d Triplet	e Singlet	f Multiplet	g Triplet	h Multiplet
I	8.82	7.45	7.00	4.25	3.80	3.62	2.02	-
II	9.03	7.72	7.46	4.28	3.84	3.77	2.00	3.38
III	9.04	7.64	6.90	4.40	4.18	3.60	2.01	-
IV	9.02	7.50	6.80	4.22	3.78	3.52	2.02	3.42

The high value of δ for proton (a) (8.82-9.04) is due to the high electronegativity of the 2 nitrogen atoms that make this proton highly deshielded. Proton (b) and (c) are not similar, since (b) is affected greatly with the positive nitrogen atom

so that δ value of (b) (7.45-7.7) is greater than that of (c) (6.8-7.4). Proton (d) has great δ value (4.22-4.40 ppm) which means that it is affected by the neighbor positively charged nitrogen atom.



3.1.3. Mass spectroscopy:

Mass spectroscopy for the synthesized ionic liquids is measured using JEOL JMS- AX 500 Japan Spectrophotometer, we chose two of the four synthesized ionic liquids and made mass spectral analysis for them.

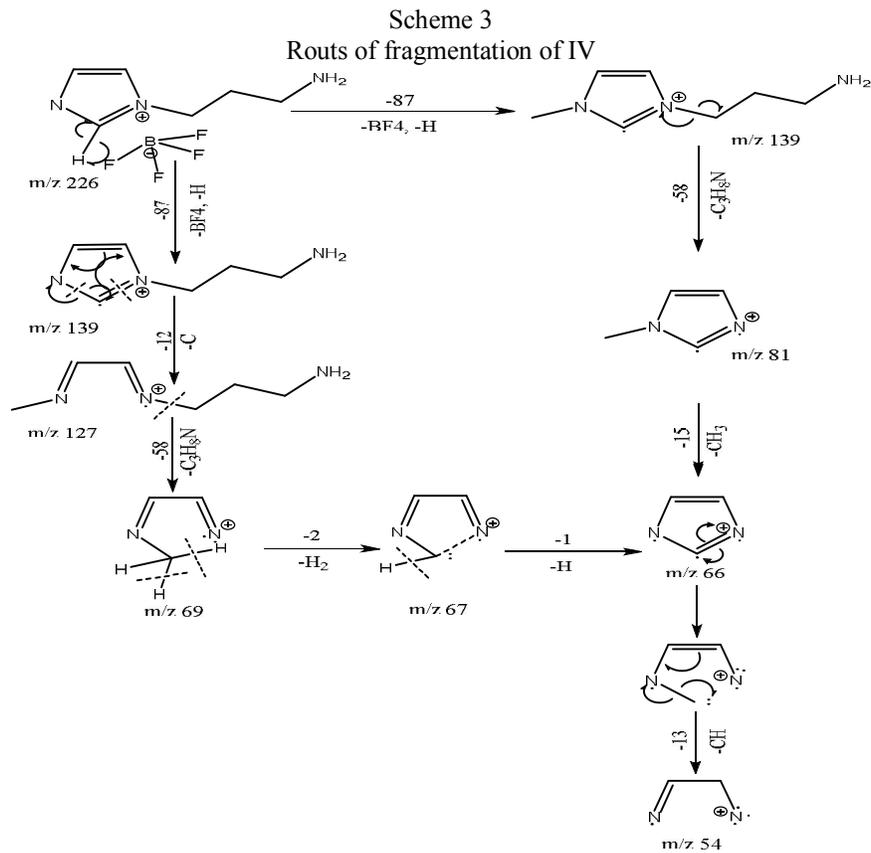
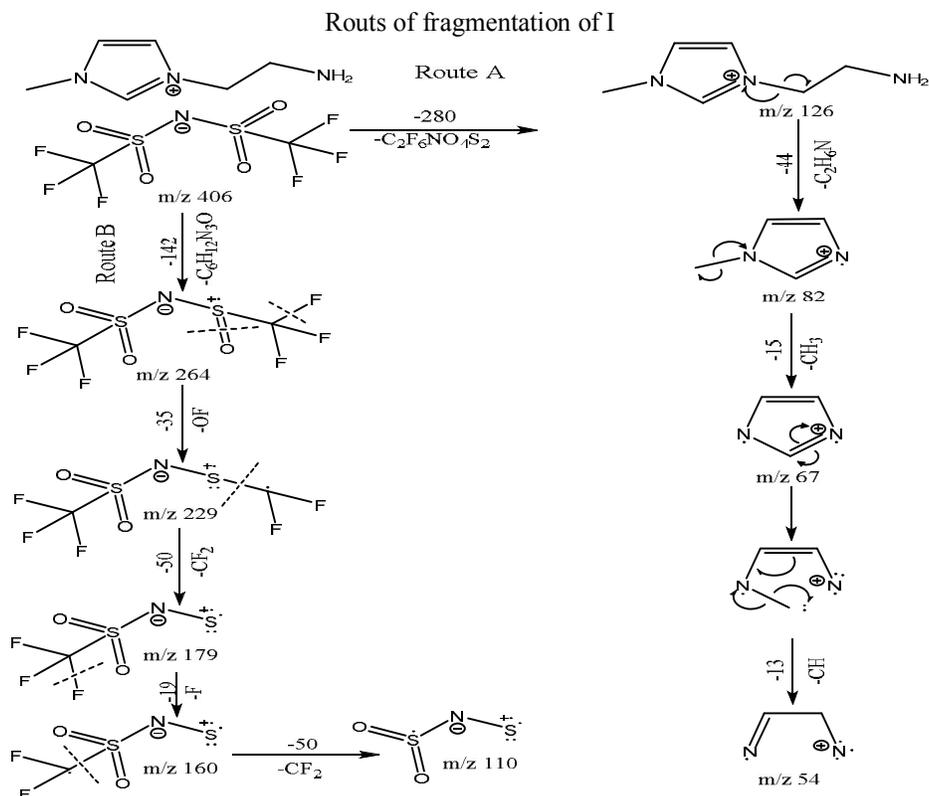
Table (3): Mass spectroscopy of synthesized ionic liquid I (m/z 406 ($\text{C}_8\text{H}_{12}\text{F}_6\text{N}_4\text{O}_4\text{S}_2$))

m/z	Molecular Formula	m/z	Molecular formula
406	$\text{C}_8\text{H}_{12}\text{F}_6\text{N}_4\text{O}_4\text{S}_2$ ⁺	126	$\text{C}_6\text{H}_{12}\text{N}_3$ ⁺
264	$\text{C}_2\text{F}_6\text{NO}_3\text{S}_2$ ⁺	110	NO_2S_2 ⁺
229	$\text{C}_2\text{F}_5\text{NO}_2\text{S}_2$ ⁺	82	$\text{C}_4\text{H}_6\text{N}_2$ ⁺
179	$\text{CF}_3\text{NO}_2\text{S}_2$ ⁺	67	$\text{C}_3\text{H}_3\text{N}_2$ ²⁺
160	$\text{CF}_2\text{NO}_2\text{S}_2$ ⁺	54	$\text{C}_2\text{H}_2\text{N}_2$ ³⁺

Table (4): Mass spectroscopy of synthesized ionic liquid IV (m/z 226 $\text{C}_7\text{H}_{14}\text{BF}_4\text{N}_3$)

m/z	Molecular Formula	m/z	Molecular formula
226	$\text{C}_7\text{H}_{14}\text{BF}_4\text{N}_3$ ⁺	69	$\text{C}_3\text{H}_5\text{N}_2$ ⁷⁺
139	$\text{C}_7\text{H}_{13}\text{N}_3$ ⁺	67	$\text{C}_3\text{H}_3\text{N}_2$ ³⁺
127	$\text{C}_6\text{H}_{13}\text{N}_3$ ⁶⁺	66	$\text{C}_3\text{H}_2\text{N}_2$ ³⁺
81	$\text{C}_4\text{H}_5\text{N}_2$ ³⁺	54	$\text{C}_2\text{H}_2\text{N}_2$ ³⁺

The schematic fragmentation of compounds I and IV are illustrated as follows:



3.1.4. IR Spectroscopy:

IR spectroscopy for the synthesized ionic liquids (I-IV) is shown in table (5), using Spectrum-One Perkin-Elmer. The spectra of the studied

samples were measured in the range of 400 – 4000 cm^{-1} with a suitable scan resolution 4 cm^{-1} and scan rate 32 cm/min .

Table (5): IR spectroscopy for the synthesized ionic liquids (I-IV).

Cpd.	$\nu \text{ Cm}^{-1}$					
	NH-	CH-Aromatic	CH ₂ & CH ₃	C=N	CH ₃ -C	C-C
I	3373	3161	2966	1645	1139	1057
II	3416	3050	2923	1617	1140	1084
III	3418	3070	2940	1621	1170	1083
IV	3418	3120	2923	1621	1144	991

3.2. CO₂ Capture Measurements:

In this work we started with measuring the percentage of CO₂ in CH₄/CO₂ cylinder using gas chromatography, then the percent of captured CO₂ is determined after using the four different synthesized ionic liquids (I-IV), (0.1 Mole). For every 4 minutes we calculated the carbon dioxide absorbed till the solution became saturated with CO₂. Finally we calculate the mmole absorbed of CO₂ per grams of the ionic liquids (I-IV) used according to the following equation:

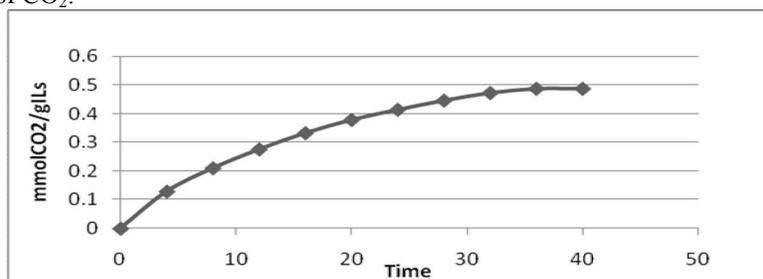
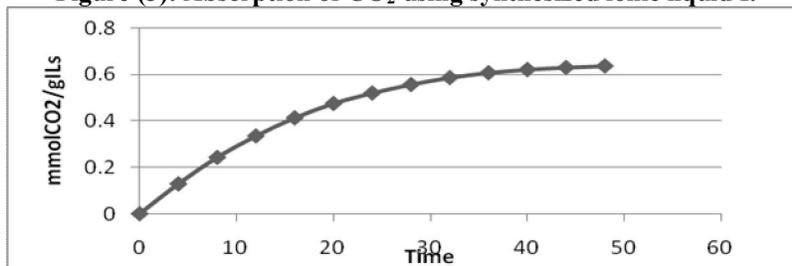
$$\left[\frac{\text{Time} \times \text{Rate} \times \text{CO}_2 \text{ absorption fraction}}{23760} \right] \div \text{Grams of ILs}$$

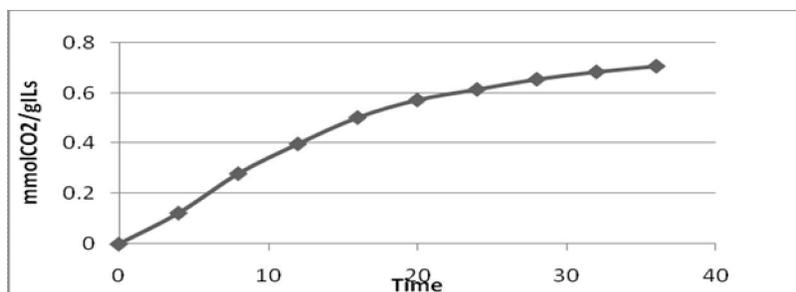
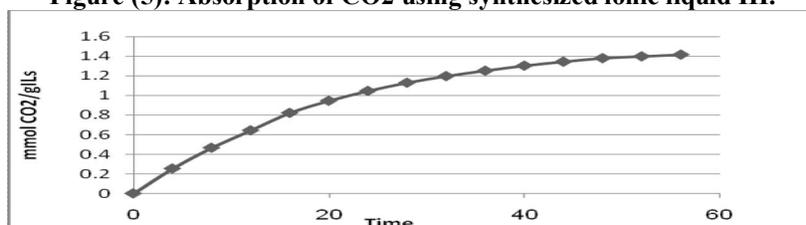
From the results obtained in tables (6-9) and figures (3-6) we found that:

- For (I), we note that the highest absorption % of CO₂ was after the first 4 minutes (about 72%). The solution is saturated by CO₂ after 40 minutes and each gram of (I) can capture 0.57 mmole of CO₂.

- For (II), the highest absorption % of CO₂ was after the first 4 minutes (about 75%). The solution is saturated by CO₂ after 48 minutes and each gram (II) can capture 0.638 mmole of CO₂.
- For (III), the greatest % of CO₂ absorbed was after 8 minutes (about 38%). Ionic liquid solution is saturated by CO₂ after 36 minutes and each gram of (III) can capture 0.74 mmole of CO₂.
- In case of (IV), the best absorption % of CO₂ was after the first 4 minutes (about 79%). Ionic liquid solution saturated by CO₂ after 60 minutes and each gram of ionic liquid IV can capture 1.4 mmole of CO₂.

Subsequently, from the above results, we notice that the efficiency order of the used ionic liquids (I-IV) will be as follows: IV > III > II > I.

**Figure (3): Absorption of CO₂ using synthesized ionic liquid I.****Figure (4): Absorption of CO₂ using synthesized ionic liquid II.**

Figure (5): Absorption of CO₂ using synthesized ionic liquid III.Figure (6): Absorption of CO₂ using synthesized ionic liquid IV.Table (6): Absorption of CO₂ using synthesized ionic liquid I.

Time min.	CO ₂ %	Remain CO ₂ %	CO ₂ absorbed	Accumulated CO ₂	Accumulated fraction	Mmol absorbed
0	21.482	21.482	0	0	0	0
4	21.482	5.98	15.502	15.502	0.15502	0.12855982
8	21.482	11.705	9.777	25.279	0.25279	0.20964157
12	21.482	13.569	7.913	33.192	0.33192	0.27526496
16	21.482	14.685	6.797	39.989	0.39989	0.33163325
20	21.482	15.934	5.548	45.537	0.45537	0.37764343
24	21.482	17.23	4.252	49.789	0.49789	0.41290574
28	21.482	17.652	3.83	53.619	0.53619	0.44466836
32	21.482	18.284	3.198	56.817	0.56817	0.47118973
36	21.482	19.716	1.766	58.583	0.58583	0.48583537
40	21.482	21.478	0.004	58.587	0.58587	0.48586854

Table (7): Absorption of CO₂ using synthesized ionic liquid II.

Time min.	CO ₂ %	Remain CO ₂ %	CO ₂ absorbed	Accumulated CO ₂	Accumulate fraction	Mmol Absorbed
0	21.482	21.482	0	0	0	0
4	21.482	5.38	16.102	16.102	0.16102	0.1290845
8	21.482	7.229	14.253	30.355	0.30355	0.24334616
12	21.482	9.926	11.556	41.911	0.41911	0.33598685
16	21.482	11.727	9.755	51.666	0.51666	0.41418951
20	21.482	13.738	7.744	59.41	0.5941	0.47627064
24	21.482	15.858	5.624	65.034	0.65034	0.52135642
28	21.482	16.878	4.604	69.638	0.69638	0.55826519
32	21.482	17.775	3.707	73.345	0.73345	0.587983
36	21.482	18.86	2.622	75.967	0.75967	0.60900273
40	21.482	19.747	1.735	77.702	0.77702	0.62291166
44	21.482	20.377	1.105	78.807	0.78807	0.63177008
48	21.482	20.656	0.826	79.633	0.79633	0.63839186

Table (8): Absorption of CO₂ using synthesized ionic liquid III.

Time min.	CO ₂ %	Remain CO ₂ %	CO ₂ absorbed	Accumulated CO ₂	Accumulate fraction	Mmol absorbed
0	21.482	21.482	0	0	0	0
4	21.482	13.315	8.167	8.167	0.08167	0.12276034
8	21.482	11.089	10.393	18.56	0.1856	0.27898028
12	21.482	13.64	7.842	26.402	0.26402	0.39685546
16	21.482	14.529	6.953	33.355	0.33355	0.50136785
20	21.482	16.847	4.635	37.99	0.3799	0.57103776
24	21.482	18.704	2.778	40.768	0.40768	0.61279461
28	21.482	18.802	2.68	43.448	0.43448	0.6530784
32	21.482	19.537	1.945	45.393	0.45393	0.68231421
36	21.482	19.979	1.503	46.896	0.46896	0.7049062

Table (9): Absorption of CO₂ using synthesized ionic liquid IV.

Time min.	CO ₂ %	Remain CO ₂ %	CO ₂ absorbed	AccumulateCO ₂	Accumulated fraction	Mmol CO ₂
0	21.482	21.482	0	0	0	0
4	21.482	4.496	16.986	16.986	0.16986	0.25306159
8	21.482	7.264	14.218	31.204	0.31204	0.46488484
12	21.482	9.564	11.918	43.122	0.43122	0.64244212
16	21.482	9.564	11.918	55.04	0.5504	0.8199994
20	21.482	13.186	8.296	63.336	0.63336	0.94359524
24	21.482	14.772	6.71	70.046	0.70046	1.04356247
28	21.482	15.86	5.622	75.668	0.75668	1.1273204
32	21.482	16.984	4.498	80.166	0.80166	1.19433271
36	21.482	17.751	3.731	83.897	0.83897	1.24991806
40	21.482	18.07	3.412	87.309	0.87309	1.30075087
44	21.482	18.759	2.723	90.032	0.90032	1.34131879
48	21.482	19.071	2.411	92.443	0.92443	1.37723846
52	21.482	20.259	1.223	93.666	0.93666	1.39545901
56	21.482	20.297	1.185	94.851	0.94851	1.41311344

4. Conclusion:

- 1- 3-(2-aminoethyl)-1-methyl-1H-imidazol-3-ium bis((trifluoromethyl)sulfonyl)amide(I), 3-(3-aminopropyl)-1-methyl-1H-imidazol-3-ium bis((trifluoromethyl) sulfonyl) amide(II), 3-(2-aminoethyl)-1-methyl-1H-imidazol-3-ium tetrafluoroborate (III), and 3-(3-aminopropyl)-1-methyl-1H-imidazol-3-ium tetrafluoroborate (IV) were synthesized and characterized by using elemental analysis, IR, ¹H-NMR, and Mass spectroscopy.
- 2- It was concluded that CO₂ capture capacity is relatively higher in IV than III, II and I respectively. The results showed that one gram of (I-IV) absorbed 0.49, 0.64, 0.7, 1.4 mmole of CO₂ Sequentially.
- 3- We can conclude that
 - i- Changing the anionic moiety of the synthesized ionic liquids affect their capture capacity for carbon dioxide.
 - ii- Also, the chain length of the n-alkyl- group (ethyl- and propyl- respectively) affect the percentage of carbon dioxide capture, so, IV > III and II > I.

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References:

- [1] S. A. Forsyth, J. M. Pringle, D. R. MacFarlane, Aust. J. Chem. 57(2004), 113-119.
- [2] H. Zhao, S. V. Malhotra, Aldrichimica Acta, 35(2002), 75-83.
- [3] D. Zhao, M. Wu, Y. Kou, E. Min, Catalysis Today, 74(2002), 157-189.
- [4] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K. J. Weaver, D. C. Forbes, J. H. Jr. Davis, J. Am. Chem. Soc., 124 (2002), 5962-5963.
- [5] S. G. Cull, J. D. Holbrey, V. Vargas-Mora, K. R. Seddon, G. J. Lye, Biotechnol. Bioeng., 69 (2000), 227-233.
- [6] K. R. Seddon, Green Chem. Ionic Liquid and Microwave-Assisted Organic Synthesis, 4(2002), 147-151.
- [7] R. P. Swatloski, A. E. Visser, W. M. Reichert, G. A. Broker, L. M. Facina, J. D. Holbrey, R. D. Rogers, Green Chem. 4(2002), 81-87.
- [8] S. Zhang, Q. Zhang, Z. C. Zhang, Ind. Eng. Chem. Res. 43(2004), 614-622.
- [9] R. P. Swatloski, S.K. Spear, J. D. Holbrey, R.D. Rogers, J. Am. Chem. Soc. 124(2002), 4974-4975
- [10] Y. Liu, Y. Hu, H. Wang, C. Xu, D. Ji, Y. Sun, T. Guo, Chinese J. Chem. Eng. 13(2005), 564-567.
- [11] J. M. Cao, B.Q. Fang, J. Wang, M.B. Zheng, S.G. Deng, X. J. Ma, Prog. Chem. 17(2005), 1028-1033.
- [12] Y. S. Vygodskii, A.S. Shaplov, E. I. Lozinskaya, O.A. Filippov, E.S. Shubina, R. Bandari, M.R. Buchmeiser, Macromolecules, 39(2006), 7821-7830
- [13] B. Q. Quinn, Z. Ding, R. Moulton, A. Bard, J. Lagmuir, 18(2002), 1734-1742.
- [14] J.H. Davis Jr., Chemistry Letters, 33 (2004), 1072.
- [15] M.A. Smiglak, R. D. Metlen, Rogers, Accounts of Chemical Research, 40(2007), 1182-1192.
- [16] G. T. Wolff, R.A. Frgsch, J. Air Waste Management Assoc., 41 (1991) 1616.
- [17] Christina Myers, Henry Pennline, David Luebke, Jeffery Ilconich, JaNeille k. Dixon, Edward J. Maginn, Joan F. Brennecke, Journal of Membrane science, 322(2008), 28-31.