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Investigating the efficiency of newly prepared imidazolium ionic liquids for carbon dioxide removal from natural gas

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ABSTRACT

Four functionalized ionic liquids of the type 3-(*n*-aminoalkyl)-1,2-dimethyl imidazolium bis((trifluoromethyl)sulfonyl)imide (IL101 and IL102), and 3-(*n*-aminoalkyl)-1,2-dimethyl imidazolium tetrafluoroborate(IL103 and IL104) were synthesized and characterized via the conventional tools of analysis. The application of these compounds as potential industrial solvents for carbon dioxide removal from natural gas is studied. In our work we used bubbling technique, as chemical absorption one, for CO_2 removal by chemical means involves one or more reversible chemical reactions between CO_2 and another material to produce a liquid or solid species. The efficiency of synthesized ionic liquids for capturing carbon dioxide is ranked as follows, IL104 < IL103 < IL102 < IL101.

1. Introduction

Ionic liquids are compounds which attracted recognisable interest over the last few years and considered as green compounds. They contain charged organic cations and either organic or inorganic anions, combined together by strong coulombic attraction. The combinations of various cations and anions can significantly change the physicochemical properties of the ILs generated.

Referring to their properties [1], (which can be studied briefly), high thermal stability, solvating potential, non-flammability, non-volatility, non-corrosive melting point (below 100 °C) and recycling, they have wide range of applications. They are used in Organic synthesis [2,3], catalysis chemically [4,5], bio catalysis [6,7], liquid-liquid separations [8], extraction [9] and dissolution (cellulose in microwave [10] and petroleum asphaltenes in microwave [11]) processes, nanomaterial synthesis [12], polymerization reactions [13] and electrochemistry [14]. Room temperature ionic liquids (RT-ILs) were determined as lubricating fluids [15]. At the present, ILs are employed in different industrial processes [16]. Upon notification several ILs are commercially available at relatively high cost.

Acid gas removal has huge attention due to their global danger and their requirements in natural gas improvement. Generally acid gas removal occurred by chemical absorption using aqueous media or physical absorption in presence of substrate membrane. Particularly ionic liquids capture CO2 chemically and yield different carbon adducts on the other hands, physical absorption depends on gases dissolution according to Henry's law [17].

Natural gas composed chemically of mixture of hydrocarbons (C_1–C_4) [18], hydrogen sulfide, water vapor, carbon dioxide, and nitrogen [19]. In a contrary, the commercial natural gas is about 70–95% methane and molecular nitrogen and carbon dioxide, beside small traces of sulfur compounds used as odorants.

In our work we prepared specific ionic liquids and also studied them for carbon dioxide removal from natural gas using bubbling as a novel technique. Furthermore, we discussed the efficiency of using different anions and proved amine mechanism for carbon dioxide capture.

2. Experimental

2.1. Materials

1.2-Dimethyl imidazole (99%), 2-bromoethyl amine hydrochloride (98%), 3-bromopropyl amine hydrochloride (98%), sodium tetrafluoroborate (99%), lithium (bistrifluoromethyl sulfonyl) imide (99%), sodium methoxide (99.98%), ethanol (99.99%), methylene chloride (99), dry methanol (99%), acetonitrile (98%) were purchased from (Merck, Fluka and Sigma-Aldrich Chemical Co.) and used without further purification.

2.2. Synthesis of ionic liquids (ILs)

2.2.1. Synthesis of imidazolium(bistrifluoromethyl sulfonyl)imides (IL101 and IL102)

Solution containing (0.25 M) of 1,2-dimethyl imidazole, in acetonitrile, is added to a stirred solution of an equivalent amount of *n*-bromoalkyl amine hydrobromide (ethyl- and propyl- respectively), in minimal amount of absolute ethanol. The mixture is stirred at room

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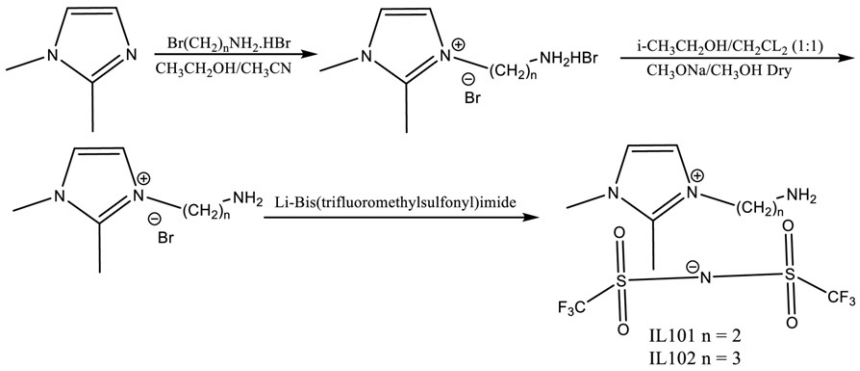


Scheme 1. IL 101: (n = 2), 3-(2-aminoethyl)-1,2-dimethyl-1H-imidazol-3-ium bis((trifluoromethyl)sulfonyl)imide. IL 102: (n = 3), 3-(2-aminopropyl)-1,2-dimethyl-1H-imidazol-3-ium bis((trifluoromethyl) sulfonyl)imide.

temperature. After 3 h of stirring, the solvent is removed under vacuum yielding dark solid precipitate. A mixed solvent of methylene chloride and ethanol (50:50) is added to yield white precipitate whereas the solvent removed by vaporization under vacuum. The product is deprotonated with 1.2 equivalence of sodium methoxide in dry methanol. Solvent vaporized and the sodium bromide, as bi-product, is salting out using methylene chloride. To the methylene chloride solution, 1.1 equivalence of lithium bis (trifluoromethyl sulfonyl) imide is added and the reaction left overnight at room temperature. The product is repeatedly washed with water so as to remove bromide. The solvent removed under vacuum and the final product (IL101 and IL102) obtained [20] (Scheme 1).

2.2.2. Synthesis of imidazolium tetrafluoroborates (IL103 and IL104)

Following the previous procedure [20], (using of 1.1 sodium tetrafluoroborate), IL103 and IL104 produced, Scheme 2.

The structure of the four prepared ionic liquids is elucidated, using the conventional tools of analysis, Elemental analysis (Elemental analyzer Perkin Elmer 240C), ^{1}H NMR (Jeol-EX-270 MHz) and Infra-Red (Spectrum-One Perkin-Elmer) spectroscopy.

2.2.3. Capture of carbon dioxide (bubbling technique)

We use 0.1 mol of the prepared ionic liquids in methanol, blank solvent, and the solution was put in the bubbling cell and the system run as follows:

- The system is adjusted as in Fig. 1: where: a) Cylinder of He, b) Cylinder of CO_2/CH_4, c) Valve, d) Water bath at 25 °C, e) Bubbling cell, f) Needle, g) Mass flow meter, h) Sampling valve, i) Gas chromatography.
- The system evacuated using Helium gas first.
- CH_4/CO_2 gas flowed to the system and passed to the solution through thin needle. Outlet gas is characterized by gas chromatography. The instrument used is Aglient7890 gas chromatography equipped with TCD column propack Q, 4 m length, 1/8 in. packed column.

3. Results and discussion

3.1. Characterization of the synthesized ionic liquids (IL101, IL102, IL103 and IL104)

3.1.1. Elemental analysis

The obtained results are shown in Table 1.

The data obtained in Table 1 show that the calculated values of the elements were in good compatibility with the found values.

3.1.2. ^{1}H NMR spectroscopy

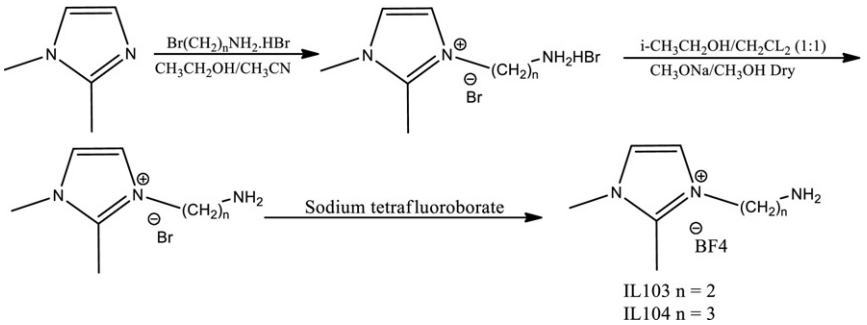
The data obtained in the Table 2 below illustrate the chemical shift (δ) of the different protons showed in Fig. 2.

Table 2 illustrates the following:

- Because of the high electronegativity of the positively charged nitrogen atoms, aromatic protons (a) have high (δ) values (7.48–7.78 ppm) i.e. highly deshielded protons.
- The aromatic protons (b) are affected by the positive nitrogen atoms, so that they have δ values of (6.82–7.18 ppm).
- Protons (c) have (δ) values of (4.23–4.54 ppm) which means that they are affected by the neighbor positively charged nitrogen atoms.
- The methyl protons (d and e), which are directly attached to the aromatic imidazolium nuclei have the (δ) values of (3.45–3.82 ppm).
- The aliphatic protons (f and h) have approximately similar (δ) values of (2.18–3.22 ppm).
- The (g) protons (-NH_2) have the lowest δ values of (1.67–1.84 ppm).

3.1.3. Infra-Red spectroscopy

IR spectroscopic bands for the prepared ionic liquids are shown in Table 3.



Scheme 2. IL 103: (n = 2), 3-(2-aminoethyl)-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate. IL 104: (n = 3), 3-(2-aminopropyl)-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate.