

## Equimolar Carbon Dioxide Absorption by Ether Functionalized Imidazolium Ionic Liquids

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Received March 13, 2012, Accepted April 19, 2012

A series [C<sub>3</sub>Omim][X] of imidazolium cation-based ILs, with ether functional group on the alkyl side-chain have been synthesized and structure of the materials were confirmed by various techniques like <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, MS-ESI, FTIR spectroscopy and EA. More specifically, the influence of changing the anion with same cation is carried out. The absorption capacity of CO<sub>2</sub> for ILs were evaluated at 30 and 50 °C at ambient pressure (0-1.6 bar). Ether functionalized ILs shows significantly high absorption capacity for CO<sub>2</sub>. In general, the CO<sub>2</sub> absorption capacity of ILs increased with a rise in pressure and decreased when temperature was raised. The obtained results showed that absorption capacity reached about 0.9 mol CO<sub>2</sub> per mol of IL at 30 °C. The most probable mechanism of interaction of CO<sub>2</sub> with ILs were investigated using FTIR spectroscopy, <sup>13</sup>C NMR spectroscopy and result shows that the absorption of CO<sub>2</sub> in ether functionalized ILs is a chemical process. The CO<sub>2</sub> absorption results and detailed study indicates the predominance of 1:1 mechanism, where the CO<sub>2</sub> reacts with one IL to form a carbamic acid. The CO<sub>2</sub> absorption capacity of ILs for different anions follows the trend: BF<sub>4</sub> < DCA < PF<sub>6</sub> < TfO < Tf<sub>2</sub>N. Moreover, the as-synthesized ILs is selective, thermally stable, long life operational and can be recycled at a temperature of 70 °C or under vacuum and can be used repeatedly.

**Key Words** : ILs, CO<sub>2</sub> absorption, Ether, Imidazole, TSILs

### Introduction

The continuous increase in the concentration of carbon dioxide (CO<sub>2</sub>) which is one major green house gases (GHGs) responsible for global warming has become a world wide issue.<sup>1-5</sup> As long as coal, petroleum and natural gas are used as the primary source of fuel, the production of CO<sub>2</sub> is inevitable. Therefore, the global demand is the development of economically viable CO<sub>2</sub> capture and separation processes to reduce the concentration of CO<sub>2</sub> and achieve sustainable environment.

The current leading technology involves chemical separation of CO<sub>2</sub> by aqueous amine solutions.<sup>6-14</sup> Even though these amine-based methods are highly efficient for CO<sub>2</sub> capture, there are several concerns like; corrosion, loss of amine due to their volatile nature, degradation of amines by sulphur containing compounds and oxidative degradation of amines in presence of oxygen.<sup>15-17</sup> These drawbacks lying in the alkanolamine absorption process hinder the industrial application.

In this context, ionic liquids (ILs)<sup>18</sup> can be a promising nominee to replace the conventional candidates. Their negligible vapor pressure, wide range of polarities, broad liquid range, significant thermal and chemical stability and capability to dissolve CO<sub>2</sub> through a physical interaction make them an attractive candidate for CO<sub>2</sub> capture. The properties of ILs can be finely tuned by carefully selecting the cations and anions and specific properties can be achieved.<sup>19</sup> Due to this aptness for the fine tuning of their

properties through endless combination of cations and anions and functional moieties the ILs can be deemed as “designer solvent”. These promising strategy, leads to the synthesis and development of task specific ionic liquids (TSILs) for a specific requirement. They can be used as solvents for gas absorption operations in order to improve the process economy and general efficiency of gas separations. The separation of CO<sub>2</sub> through a physical interaction is particularly attractive since the stripping of CO<sub>2</sub> from ILs can be achieved at milder condition as compared to aqueous amine based solution. The class of imidazolium ILs is used in a wide variety of applications due to their attractive physical and chemical properties, like air and moisture stability, low flammability, thermal stability, negligible vapor pressure, being liquid over a wide range of temperature, wide electrochemical windows, high conductivities and ionic mobilities, easy recycling, tunable miscibility with water and organic solvents, and being a good solvent for a variety of organic and inorganic compounds.<sup>20-22</sup> More importantly, imidazolium based ILs have good aptency with CO<sub>2</sub>.<sup>23</sup>

Literature study reveal that Blanchard *et al.*<sup>24</sup> reported firstly that CO<sub>2</sub> was highly soluble in [bmim][PF<sub>6</sub>](1-butyl-3-methylimidazolium hexafluorophosphate), reaching a mole fraction of 0.6 at 8 MPa but IL didn't dissolve in CO<sub>2</sub>. Later a large number of results have been reported regarding the solubility measurement and prediction of CO<sub>2</sub> in ILs. Anthony *et al.*<sup>25</sup> reported the solubility of CO<sub>2</sub> in [bmim]-[BF<sub>4</sub>] (1-butyl-3-methylimidazolium tetrafluoroborate) and [bmim][Tf<sub>2</sub>N] (1-butyl-3-methylimidazolium bis(trifluoro-

methylsulfonylimide). Shiflett *et al.*<sup>26</sup> compared the energy requirement and economic investment of a commercial MEA post combustion CO<sub>2</sub> capture with a new process designed to use [bmim][Ac] (1-butyl-3-methylimidazolium acetate). Thereafter, Zhang *et al.*<sup>27</sup> reported four hundred and eight kind of ILs, with 24 cations and 17 anions, after screening to find promising candidates in CO<sub>2</sub> capture, by using the conductor-like screening model for real solvents (COSMO-RS) method. Huang *et al.*<sup>28</sup> proposed that in conventional ILs, CO<sub>2</sub> is absorbed by occupying the free space between the ions, high pressure is needed in the physical absorption, and the absorption capacity is relatively low. Bates *et al.*<sup>29</sup> acquired another tactic and modified cation by attaching an amine group to achieve so called task specific ionic liquid (TSIL) to improve the absorption capacity of ILs. Amine functionalized ILs, [aemim][BF<sub>4</sub>] (1-butyl-3-aminobutyl tetrafluoroborate), reported 0.5 mol of CO<sub>2</sub> per mol of IL. This report draw considerable attention and being inspired by this, Fukumoto *et al.*<sup>30</sup> synthesized ILs from 20 natural amino acids. Their prime goal was to replace amine group by easily available, bio-compatible, bio-degradable amino acids anions. Zhang *et al.*<sup>31,32</sup> synthesized a new TSIL, [P(C<sub>4</sub>)<sub>4</sub>][AA] (tetrabutyl phosphonium amino acid) and reported fast and reversible absorption of CO<sub>2</sub> with a capacity of 1 CO<sub>2</sub>/2[P(C<sub>4</sub>)<sub>4</sub>][AA]. Thereafter, they reported synthesis of 20 new dual amino functionalized phosphonium ILs, [aP<sub>443</sub>][AA] (3-aminopropyl)tributylphosphonium amino acid and claimed the capacity of chemical absorption of carbondioxide is 1 CO<sub>2</sub>/2[aP<sub>443</sub>][AA]. Gurkan *et al.*<sup>33</sup> reported synthesis of amino acid-based ILs, including [P<sub>6614</sub>][Pro] trihexyl(tetradecyl)phosphonium proline and [P<sub>6614</sub>][Met] trihexyl(tetradecyl)phosphonium methionine, which react with CO<sub>2</sub> in a ratio of one CO<sub>2</sub> per one amino acid (1:1 stoichiometry) achieving higher molar capacities than cation functionalized ILs or even aqueous amine absorbents. Wang *et al.*<sup>34-36</sup> used the intrinsic acidity of hydrogen at C-2 position in the imidazolium cation and reported equimolar CO<sub>2</sub> was captured under atmospheric pressure. Wappel *et al.*<sup>37</sup> carried out the experiments and compared the CO<sub>2</sub> absorption performance of 80 different ILs and blends of ILs and with a reference solution of 30 wt % MEA and water and proposed that the usage of ILs to replace MEA solution do have advantage in energy saving. Goodrich *et al.*<sup>38</sup> proposed 1:1 mechanism is predominating in amine functionalized anion tethered ILs as compared to 1:2 mechanism.

Although, imidazolium cation based some ether functionalized ILs have been synthesized with [Cl]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup>, [CH<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>, [CF<sub>3</sub>BF<sub>3</sub>]<sup>-</sup>, [C<sub>2</sub>F<sub>5</sub>BF<sub>3</sub>]<sup>-</sup> anions and their properties studied.<sup>39,40</sup> However, there is still some scope to develop new ether functionalized ILs with suitable properties like hydrophobic, low-melting, and low viscous ionic liquids by using anions like [NTf<sub>2</sub>]<sup>-</sup>,<sup>39,40</sup> [TfO]<sup>-</sup>,<sup>39,40</sup> and [DCA]<sup>-</sup><sup>39,40</sup> and they can be used as a potential absorbents for CO<sub>2</sub>. So finally we designed ether functionalized imidazolium based ILs with different anions to evaluate their combination effect on solubility of CO<sub>2</sub>.

Here in, we report the synthesis, characterization of a

series of ether functionalized ILs [C<sub>3</sub>Omim][X], based on the imidazolium cation that contains additional functional group, ether, on the alkyl group R and their application in capture of CO<sub>2</sub>. Till date, no report is available involving ether functionalized imidazolium based ILs in open literature with study of the solubility of CO<sub>2</sub>.

## Materials and Methods

**Materials.** Chloroethylmethylether (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>Cl), 1-methylimidazole, diethyl ether, acetone, sodium tetrafluoroborate (NaBF<sub>4</sub>), magnesium sulfate (MgSO<sub>4</sub>), potassium hexafluorophosphate (KPF<sub>6</sub>), Lithium bis[(trifluoromethyl)sulfonyl] amide Li(Tf<sub>2</sub>N), sodium trifluoromethylsulfonate Na(TfO), sodium dicyanamide (Na(DCA)) were supplied from Sigma-Aldrich and used without further purification.

**Synthesis of Ionic Liquids.** A previously reported methodology<sup>40</sup> was used for the synthesis of these ionic liquids. Alkylation of 1-methylimidazole with an alkyl halide is followed by halogen (Cl or Br) exchange with slight excess (1.1 equiv) of NaBF<sub>4</sub>, KPF<sub>6</sub>, Li(Tf<sub>2</sub>N), Na(TfO), Na(DCA) in order to reduce the amount of remaining halogen content.

**Synthesis of [C<sub>3</sub>Omim][Cl].** Chloroethylmethylether (85 mL, 0.93 mol) and 1-methylimidazole (50 mL, 0.63 mol) were added to a round-bottomed flask fitted with a reflux condenser for 24 h at 80 °C with stirring. The product was washed with diethyl ether (4 × 25 mL), heated at 80 °C and stirred under vacuum (0.5 mmHg) for 2 d. The product was obtained as a slightly yellow liquid which solidified on cooling (83% yield) with water content of 3.84 μg (H<sub>2</sub>O) mL<sup>-1</sup> (RTIL). <sup>1</sup>H NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C: δ 3.29 (s, 3H), 3.74 (t, 2H), 3.81 (s, 3H), 4.27 (t, 2H), 7.34 (s, 1H), 7.40 (s, 1H), 8.64 (s, 1H); <sup>13</sup>C NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C: δ 35.5, 48.73, 58.09, 69.72, 122.5, 123.5, 136.4; MS-ESI: *m/z* (%): 140 (100) [C<sub>3</sub>Omim]<sup>+</sup>, 35 (100) [Cl]<sup>-</sup>; FT-IR (neat): 3414, 3150, 3096, 2970, 2880, 1638, 1574, 1462, 1173, 1083, 1011, 970.3, 835.5, 761.2, 651.2 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>OCl (175): C 48.1, H 6.85, N 16.0; found: C 47.4, H 6.46, N 15.2.

**Synthesis of [C<sub>3</sub>Omim][BF<sub>4</sub>].** [C<sub>3</sub>Omim][Cl] (26.00 g, 0.152 mol) was transferred to a plastic Erlenmeyer flask (250 mL). Acetone (150 mL) was added followed by NaBF<sub>4</sub> (19.00 g, 0.17 mol). This mixture was stirred at room temperature for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 100 mL). The organic layer was collected, dried (MgSO<sub>4</sub>), filtered and the solvent removed in vacuum to give the product (91% yield) as a light brown liquid; water content of 2.68 μg (H<sub>2</sub>O) mL<sup>-1</sup> (RTIL). <sup>1</sup>H NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C: δ 3.28 (s, 3H), 3.73 (t, 2H), 3.80 (s, 3H), 4.28 (t, 2H), 7.35 (s, 1H), 7.41 (s, 1H), 8.65 (s, 1H); <sup>13</sup>C NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C: δ 35.2, 48.69, 58.01, 69.42, 122.1, 123.2, 136.9; MS-ESI: *m/z* (%): 140 (100) [C<sub>3</sub>Omim]<sup>+</sup>, 87 (100) [BF<sub>4</sub>]<sup>-</sup>; FT-IR (neat): 3400, 3140, 3090, 2969, 2885, 1642, 1570, 1469, 1169, 1079, 1059, 1010, 970, 835.5, 758.2 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>OBF<sub>4</sub> (227): C 37.0, H 5.28, N 12.33; found: C 36.2, H 4.92, N 12.0.

**Synthesis of [C<sub>3</sub>Omim][PF<sub>6</sub>].** [C<sub>3</sub>Omim][Cl] (26.00 g, 0.152 mol) was transferred to a plastic Erlenmeyer flask (250 mL). Acetone (150 mL) was added followed by KPF<sub>6</sub> (31.00 g, 0.168 mol). This mixture was stirred at room temperature for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 100 mL). The organic layer was collected, dried (MgSO<sub>4</sub>), filtered and the solvent removed in vacuum to give the product (87% yield) as a dark brown liquid; water content of 1.92 μg (H<sub>2</sub>O) mL<sup>-1</sup> (RTIL). <sup>1</sup>H NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C): δ 3.28 (s, 3H), 3.71 (t, 2H), 3.80 (s, 3H), 4.29 (t, 2H), 7.36 (s, 1H), 7.41 (s, 1H), 8.62 (s, 1H); <sup>13</sup>C NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C): δ 35.2, 48.6, 58.0, 69.4, 122.1, 123.3, 137.1; MS-ESI: *m/z* (%): 140 (100) [C<sub>3</sub>Omim]<sup>+</sup>, 145 (100) [PF<sub>6</sub>]<sup>-</sup>; FT-IR (neat): 3410, 3148, 3101, 2976, 2881, 1641, 1575, 1460, 1170, 1086, 1017, 967, 836, 833, 761, 558 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>OPF<sub>6</sub> (285): C 29.47, H 4.2, N 9.82; found: C 28.82, H 3.99, N 9.11.

**Synthesis of [C<sub>3</sub>Omim][Tf<sub>2</sub>N].** [C<sub>3</sub>Omim][Cl] (26.00 g, 0.152 mol) was transferred to a plastic Erlenmeyer flask (250 mL). Acetone (150 mL) was added followed by Li(NTf<sub>2</sub>) (49.00 g, 0.170 mol). This mixture was stirred at room temperature for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 100 mL). The organic layer was collected, dried (MgSO<sub>4</sub>), filtered and the solvent removed in vacuum to give the product (88.9% yield) as a light brown liquid; water content of 2.34 μg (H<sub>2</sub>O) mL<sup>-1</sup> (RTIL). <sup>1</sup>H NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C): δ 3.27 (s, 3H), 3.74 (t, 2H), 3.81 (s, 3H), 4.27 (t, 2H), 7.34 (s, 1H), 7.40 (s, 1H), 8.64 (s, 1H); <sup>13</sup>C NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C): δ 34.9, 48.11, 58.10, 69.52, 121.9, 123.0, 137.4; MS-ESI: *m/z* (%): 140 (100) [C<sub>3</sub>Omim]<sup>+</sup>, 280 (100) [NTf<sub>2</sub>]<sup>-</sup>; FT-IR (neat): 3414, 3150, 3096, 2979, 2970, 2880, 2876, 1638, 1574, 1462, 1348, 1336, 1181, 1173, 1135, 1083, 1055, 1013, 968.3, 833.5, 789, 760.2, 739 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>9</sub>H<sub>12</sub>N<sub>3</sub>O<sub>3</sub>F<sub>6</sub>S<sub>2</sub> (420): C 25.7, H 2.85, N 10.0, S 15.2; found: C 24.8, H 2.73, N 9.64, S 14.66.

**Synthesis of [C<sub>3</sub>Omim][TfO].** [C<sub>3</sub>Omim][Cl] (26.00 g, 0.152 mol) was transferred to a plastic Erlenmeyer flask (250 mL). Acetone (150 mL) was added followed by Na(TfO) (29.50 g, 0.171 mol). This mixture was stirred at room temperature for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 100 mL). The organic layer was collected, dried (MgSO<sub>4</sub>), filtered and the solvent removed in vacuum to give the product (89% yield) as a light brown liquid; water content of 2.38 μg (H<sub>2</sub>O) mL<sup>-1</sup> (RTIL). <sup>1</sup>H NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C): δ 3.28 (s, 3H), 3.72 (t, 2H), 3.79 (s, 3H), 4.29 (t, 2H), 7.35 (s, 1H), 7.41 (s, 1H), 8.63 (s, 1H); <sup>13</sup>C NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C): δ 35.5, 48.7, 58.9, 69.2, 122.0, 123.1, 136.9; MS-ESI: *m/z* (%): 140 (100) [C<sub>3</sub>Omim]<sup>+</sup>, 149 (100) [TfO]<sup>-</sup>; FT-IR (neat): 3410, 3155, 3100, 2976, 2879, 1642, 1569, 1458, 1422, 1363, 1253, 1223, 1170, 1089, 1021, 1060, 980, 965.3, 919, 844, 775, 763, 739, 717, 655, 636, 573, 529 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>F<sub>3</sub>S (289): C 33.2, H 4.15, N 9.68,

S 11.07; found: C 33.1, H 4.0, N 9.56, S 11.0.

**Synthesis of [C<sub>3</sub>Omim][DCA].** [C<sub>3</sub>Omim][Cl] (26.00 g, 0.152 mol) was transferred to a plastic Erlenmeyer flask (250 mL). Acetone (150 mL) was added followed by Na(DCA) (15.00 g, 0.168 mol). This mixture was stirred at room temperature for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 100 mL). The organic layer was collected, dried (MgSO<sub>4</sub>), filtered and the solvent removed in vacuum to give the product (90% yield) as a light yellow liquid; water content of 2.61 μg (H<sub>2</sub>O) mL<sup>-1</sup> (RTIL). <sup>1</sup>H NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C): δ 3.29 (s, 3H), 3.74 (t, 2H), 3.81 (s, 3H), 4.27 (t, 2H), 7.34 (s, 1H), 7.40 (s, 1H), 8.64 (s, 1H); <sup>13</sup>C NMR (500 MHz), acetone-*d*<sub>6</sub>, 25 °C): δ 35.4, 48.70, 58.19, 69.71, 122.45, 123.51, 136.44; MS-ESI: *m/z* (%): 140 (100) [C<sub>3</sub>Omim]<sup>+</sup>, 66 (100) [DCA]<sup>-</sup>; FT-IR (neat): 3400, 3138, 3089, 2971, 2876, 1643, 1575, 1459, 1168, 1077, 1011, 965, 830, 761.2 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>9</sub>H<sub>12</sub>N<sub>5</sub>O (206): C 52.42, H 5.8, N 33.98; found: C 51.94, H 5.1, N 33.14.

**Characterization.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker Avance-500 FT-NMR Spectrophotometer and acetone-*d*<sub>6</sub> was used as solvent. The Chemical shift values are reported in ppm with respect to TMS internal reference. The mass of the samples were measured on a Hewlett Packard 1100 Series, Mass Spectrophotometer, Agilent 1200 Series. The FT-IR spectra were recorded on Thermo, Model: Nicolet 6700. The elemental analysis (C, H, and N) was performed at the Thermo Finnigan Flash EA-2000 Elemental Analyzer (EA). The water content in the ILs was detected by Karl-Fischer titration (Mitsubishi Chem., model CA-07). All the salts were tested after vacuum drying at 70-100 °C for 24 h. The TGA was performed on a thermal analysis system (Mettler Toledo, Model: TGA/SDTA 85 1e). An average sample weight of 5 mg was placed in a platinum pan and heated at 10 °C/min from ca. 30 to 100 °C under a flow of N<sub>2</sub>. The density of the liquid salts was approximately determined by measuring the weight of 1.0 mL of the salt three times at 25 °C. The viscosity was measured with a viscometer (Brookfield, model DV-III+) using 0.6 mL sample at 10, 20 and 30 °C.

**CO<sub>2</sub> Absorption Isotherm Measurement.** The carbon dioxide absorption isotherm measurement was performed at 30 and 50 °C based on an isochoric saturation technique. The main composition of the apparatus includes a gas reservoir, a thermostat, a pressure gauge, an isochoric cell, a vacuum pump, and a magnetic stirrer. The temperature was determined with two calibrated platinum resistance thermometers placed in the heating jacket of the cell with an uncertainty below ± 0.1 °C. The uncertainty of the pressure gauge is approximately ± 0.001 bar in the experimental pressure range. In a typical experiment, about 2 mL ILs was loaded into the isochoric cell, the air in the system was eliminated by vacuum pump, then CO<sub>2</sub> was charged into the cell from the gas reservoir and the ionic liquid was stirred. The system was considered to have reached equilibrium if the pressure of the system had been unchanged within 2 h. The mass of the cell was determined with an electronic balance (Sartorius

BS224S) with an uncertainty  $\pm 0.0001$  g. The solubility of carbon dioxide in the ionic liquid was determined by the shifted quality of the isochoric cell.

**CO<sub>2</sub> Absorption Mechanism Verification.** The mechanism of CO<sub>2</sub> absorption in this report is investigated by FTIR spectroscopy and <sup>13</sup>C NMR spectroscopy of CO<sub>2</sub> absorbed ILs. The same instruments were used which were used for characterization of materials.

## Results and Discussion

The chemical structures of the ILs [C<sub>3</sub>Omim][X] synthesized and studied in the present work are presented in Figure 1. The various components of ILs, density and viscosity of ILs of the series [C<sub>3</sub>Omim][X] are reported in Table 1.

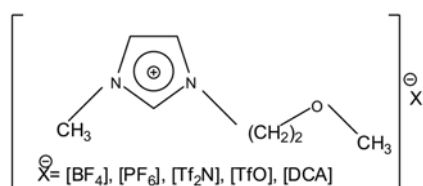
Generally, the density decreased with the length of 1-alkyl(alkyl ether) chain in cation increased, with a constant anion, for example, keeping the [CF<sub>3</sub>BF<sub>3</sub>]<sup>-</sup> constant, *i.e.*, (C<sub>1</sub> > C<sub>2</sub> > C<sub>3</sub> > C<sub>4</sub> > C<sub>6</sub>) and (C<sub>1</sub>O > C<sub>3</sub>O > C<sub>5</sub>O). The density of the [C<sub>m</sub>O<sub>n</sub>mim]<sup>+</sup> based ILs is a little higher than those of the similar [C<sub>m</sub>mim]<sup>+</sup> based ones *i.e.*, (C<sub>2</sub>O > C<sub>3</sub>) and (C<sub>3</sub>O > C<sub>4</sub>).<sup>39,40</sup> These trends are consistent with the reported observations in other ILs with imidazolium cations. On the other hand, with a constant cation, the density decreased with increasing the bulkiness of the anion. The density data for ILs are reported in Table 1.

The trend observed for the density of the [C<sub>3</sub>Omim][X] are as follows for different anions:



Therefore, the density values of ILs are in good agreement as expected. These results indicate that the densities of these ionic liquids can be fine-tuned with slight structural changes in cation and anion.

The viscosity of an ionic liquid is essentially determined by their tendency to form hydrogen bonds and by the strength of van der Waals interactions (dispersion and repulsion),



**Figure 1.** Chemical structures of the ILs [C<sub>3</sub>Omim][X].

being strongly dependent on the anion type.<sup>41</sup> For the imidazolium ILs, longer alkyl chains on the cation result in an increase in viscosity due to stronger van der Waals interactions whereas delocalization of the charge over the anion seems to favor lower viscosity by weakening hydrogen bonding with the cation.<sup>41-49</sup> In addition, an anion combined a good charge distribution and a flat shape (*e.g.*, [F(HF)<sub>2.3</sub>]<sup>-</sup>,<sup>50</sup> [N(CN)<sub>2</sub>]<sup>-</sup>,<sup>44,45</sup> and [C(CN)<sub>3</sub>]<sup>-</sup>,<sup>45,46</sup> or an irregular shape (*e.g.*, [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup>,<sup>43</sup> [(CF<sub>3</sub>SO<sub>2</sub>)(CF<sub>3</sub>CO)N]<sup>-</sup>,<sup>47</sup> and [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]<sup>-</sup>)<sup>42,48</sup> tends to form low-viscous ILs, while that with high symmetry (*e.g.*, BF<sub>4</sub><sup>-</sup>,<sup>41,48,49,51</sup> PF<sub>6</sub><sup>-</sup>,<sup>42,50,53</sup> AsF<sub>6</sub><sup>-</sup>,<sup>54</sup> SbF<sub>6</sub><sup>-</sup>,<sup>54</sup> TaF<sub>6</sub><sup>-</sup>,<sup>54</sup>) usually produces high-viscous and/ or high melting salts in spite of its weak coordinating ability. The viscosity data for ILs are reported in Table 1.

The trend observed for the viscosity of the ILs are as follows for different anions:

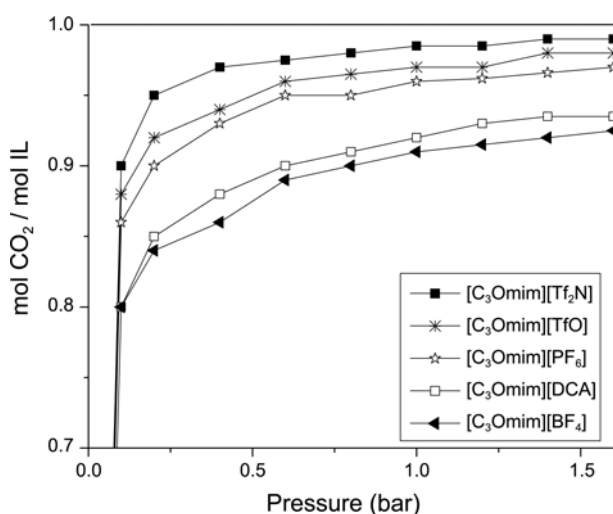


The trend obtained for viscosity of ILs are in good agreement with the earlier reported results and it shows that viscosity of ILs is mainly decided by anion. We observe that ILs containing [DCA]<sup>-</sup> anion are least viscous and [PF<sub>6</sub>]<sup>-</sup> containing ILs are most viscous. But there are enough study carried out by many research groups and it is concluded that the structure of the cation also influences the viscosity of ILs.<sup>39,40</sup> It is observed that ILs having alcoholic functional group are less viscous than ether functionalized ILs. While in case of ether functionalized ionic liquids, the ionic liquids having larger alkyl group having higher viscosity than ionic liquids having smaller alkyl group. The viscosity of ether functionalized ionic liquids having [CF<sub>3</sub>BF<sub>3</sub>] anion is higher than ionic liquids having [C<sub>2</sub>F<sub>5</sub>BF<sub>3</sub>] anion. It also states that the viscosity of these ionic liquids are less than [TfO]<sup>-</sup> anions. All this results suggest that, in search of low-viscous ILs, we should not only focus on weak coordinating ability of the anion, but the shape (symmetry) and size of the anion should also be taken into consideration.

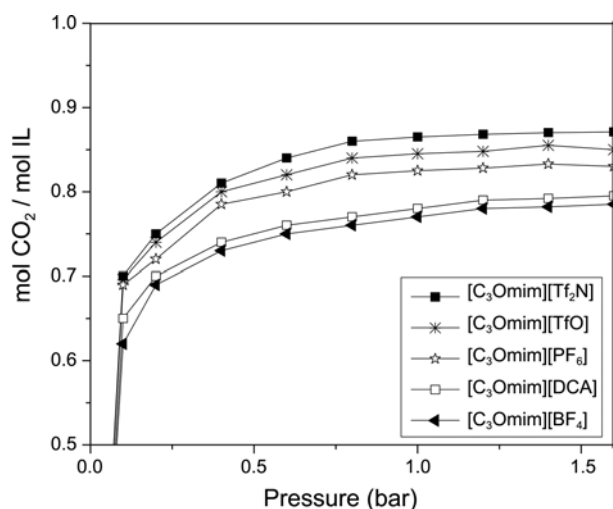
**CO<sub>2</sub> Absorption Isotherm Measurements.** The absorption isotherm of CO<sub>2</sub> in different ILs were determined at 30 and 50 °C at ambient pressure (Fig. 2 and Fig. 3). It was noted that ether functionalized ILs shows significantly high absorption capacity for CO<sub>2</sub>. The CO<sub>2</sub> absorption capacity of ILs increased with a rise in pressure and decreased when temperature was raised. Results showed that absorption capacity reached about 0.9 mol CO<sub>2</sub> per mol of ILs at at 30

**Table 1.** The various components of ILs, density and viscosity of ILs of the series [C<sub>3</sub>Omim][X]

Entry	Ionic liquid	Anion X <sup>-</sup>	Density (gmL <sup>-1</sup> ) at 25 °C	Viscosity (cP)		
				10 °C	20 °C	30 °C
1.	[C <sub>3</sub> Omim][Cl]	Cl <sup>-</sup>	1.16	602.6	409.6	219.5
2.	[C <sub>3</sub> Omim][BF <sub>4</sub> ]	BF <sub>4</sub> <sup>-</sup>	1.26	374.3	262.8	138.1
3.	[C <sub>3</sub> Omim][PF <sub>6</sub> ]	PF <sub>6</sub> <sup>-</sup>	1.40	607.5	283.6	148.2
4.	[C <sub>3</sub> Omim][Tf <sub>2</sub> N]	NTf <sub>2</sub> <sup>-</sup>	1.48	77.6	47.3	31.5
5.	[C <sub>3</sub> Omim][TfO]	TfO <sup>-</sup>	1.32	119.2	99.1	64.2
6.	[C <sub>3</sub> Omim][DCA]	DCA <sup>-</sup>	1.06	42.6	33.2	24.1



**Figure 2.** Mole fraction of CO<sub>2</sub> ( $\chi$ ) in different ILs as a function of pressure at 30 °C.



**Figure 3.** Mole fraction of CO<sub>2</sub> ( $\chi$ ) in different ILs as a function of pressure at 50 °C.

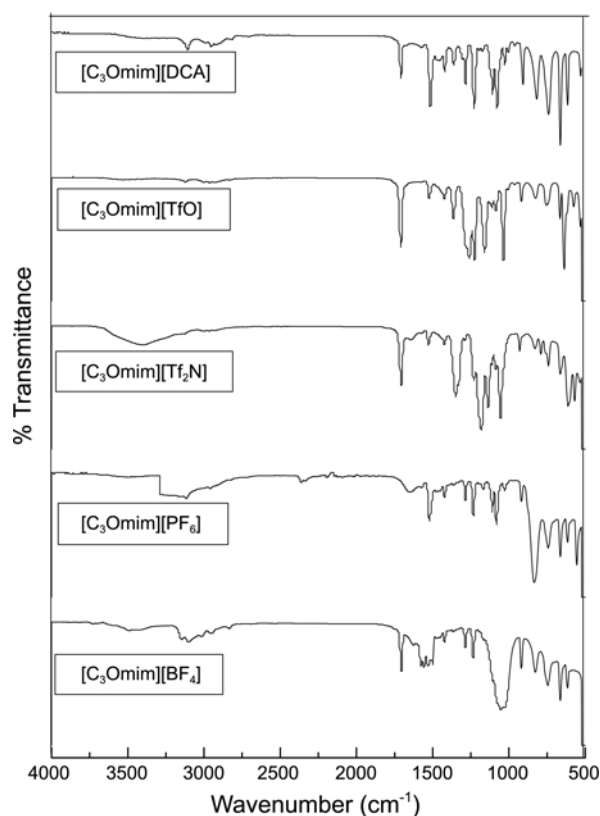
°C. The CO<sub>2</sub> absorption capacity of ILs for different anions follows the trend:



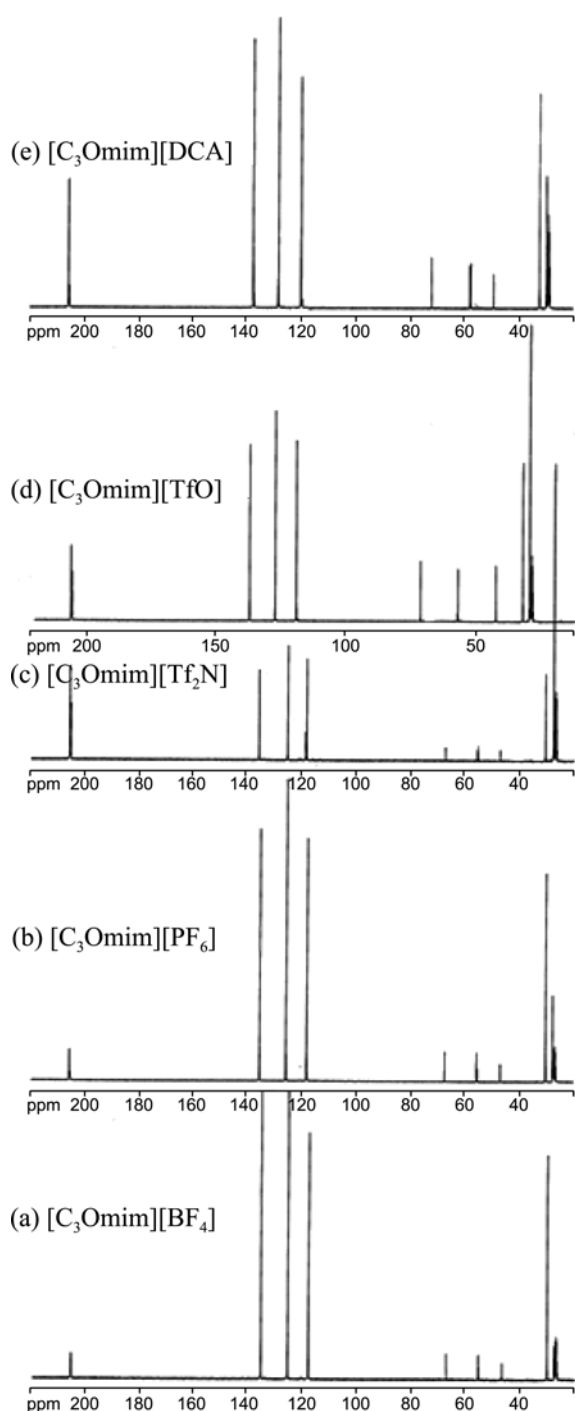
Until now, two views have been established to explain the effects of anion on the solubility of CO<sub>2</sub> in ILs. The first view states that anion played the major role in CO<sub>2</sub> solubility in ILs and anions that contain fluoroalkyl groups were found to have some of the highest CO<sub>2</sub> solubility.<sup>55,56</sup> Whereas, the second view states that the solubility of CO<sub>2</sub> in ILs is dictated by the cation-anion interaction, while CO<sub>2</sub>-anion interaction is secondary. Moreover, a good correlation between the cation-anion binding energy and CO<sub>2</sub> solubility indicates that weaker cation-anion interaction is the dominant factor responsible for the higher CO<sub>2</sub> solubility.<sup>57</sup> This conclusion seems reasonable since weaker cation-anion pair interactions allows easier expansion of the lattice and more CO<sub>2</sub> insertion into interstitial space (or free volume) is possible. Our result show that the anions that contain fluoro-

alkyl groups were found to have highest CO<sub>2</sub> solubility, and as the quantity of fluoroalkyl groups increased, the CO<sub>2</sub> solubility also increased. In Tf<sub>2</sub>N anion comprising IL, due to good charge distribution and irregular shape, Tf<sub>2</sub>N anion-cation interaction is very weak. Therefore maximum expansion of lattice takes place and highest CO<sub>2</sub> absorption capacity is reported. The CO<sub>2</sub> absorption capacity of TfO anion comprising IL is a little less than Tf<sub>2</sub>N anion comprising IL. Since the charge distribution is slightly less and due to its little regular shape the TfO anion - cation interaction is a little stronger, so a little less CO<sub>2</sub> absorption capacity is reported than Tf<sub>2</sub>N containing IL. But due to complete lack of any charge distribution and by virtue of its symmetrical structure, PF<sub>6</sub> anion - cation interaction is of moderate strength, shows lower CO<sub>2</sub> absorption capacity than Tf<sub>2</sub>N and TfO comprising ILs. And finally, a little higher CO<sub>2</sub> absorption capacity is obtained in DCA comprising IL as compared to BF<sub>4</sub> comprising IL. This is due to the reason that in DCA comprising IL, very good charge distribution occurs and its flat shape results a weak anion - cation interaction. In BF<sub>4</sub> anion comprising IL, the anion - cation interaction is a little stronger due to complete lack of charge distribution and symmetrical structure, hence minimum CO<sub>2</sub> absorption capacity is reported. These results and trend are in good agreement with previous reports.

**Mechanism of CO<sub>2</sub> Absorption.** The interaction of CO<sub>2</sub> with different ILs were investigated using FTIR and <sup>13</sup>C NMR spectroscopy and result shows that the absorption of CO<sub>2</sub> in ether functionalized ILs is a chemical process. The

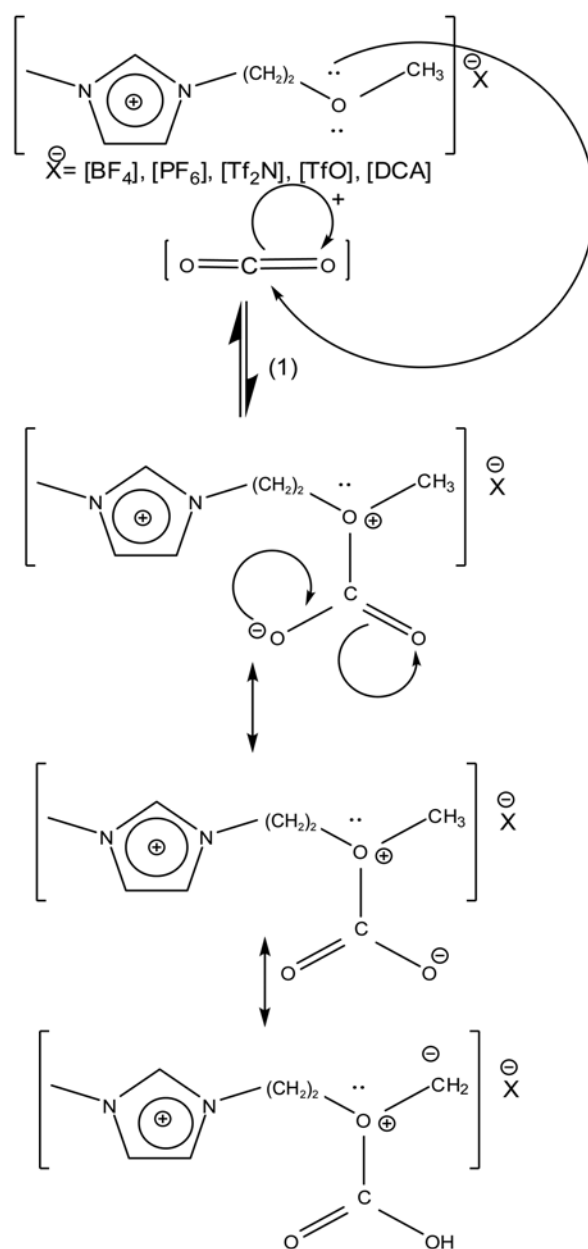


**Figure 4.** FTIR spectra of CO<sub>2</sub> absorbed different ILs.



**Figure 5.**  $^{13}\text{C}$  NMR spectra of carbon dioxide absorbed ILs; (a)  $[\text{C}_3\text{Omim}][\text{BF}_4]$ , (b)  $[\text{C}_3\text{Omim}][\text{PF}_6]$ , (c)  $[\text{C}_3\text{Omim}][\text{Tf}_2\text{N}]$ , (d)  $[\text{C}_3\text{Omim}][\text{TfO}]$  and (e)  $[\text{C}_3\text{Omim}][\text{DCA}]$ .

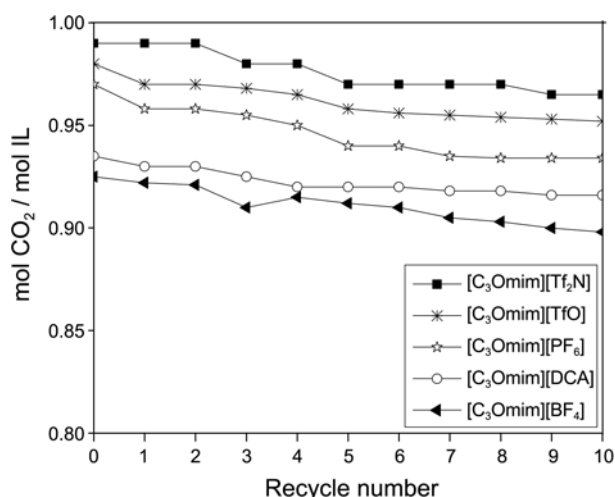
FTIR spectra of  $\text{CO}_2$  absorbed ILs (Fig. 4) shows two new peaks appeared around  $1700\text{ cm}^{-1}$  and  $1405\text{ cm}^{-1}$  for ( $=\text{C}=\text{O}_{\text{str}}$ ) and ( $-\text{O}-\text{H}$  in plane bend) of the carboxylic acid. The  $^{13}\text{C}$  NMR spectra of carbon dioxide absorbed ether functionalized ILs are shown in Figure 5(a-e). The NMR spectra of all the ILs shows a new peak is appeared around  $\delta$  200-210 ppm. This peak is attributed to carbonyl carbon atom of the formed carboxylic group after absorption of  $\text{CO}_2$  by ILs.



**Figure 6.** Proposed mechanism of  $\text{CO}_2$  absorption by ether functionalized ILs.

Based on this analysis, it can be concluded that absorption process of  $\text{CO}_2$  by ether functionalized ILs is a chemical process. This indicates that the lone pair of electrons on oxygen atom of the ether group attack as a nucleophile on the carbon atom of  $\text{CO}_2$  and leads to the formation of carboxylic acid. The detailed mechanism is presented in Figure 6. This indicates that one mole of  $\text{CO}_2$  reacts with one mole of ILs. This type of mechanism, also called 1:1 mechanism were also reported by previous researchers in case of amine tethered to anion of the ILs.<sup>33,38</sup>

One interesting point is to note that the maximum absorption of  $\text{CO}_2$  is 0.9 mol carbon dioxide per mol of ILs at  $30\text{ }^\circ\text{C}$  at 1.6 bar pressure. The maximum  $\text{CO}_2$  absorption capacity was not achieved here possibly due to the high viscosity of the ILs, which increased even further after  $\text{CO}_2$



**Figure 7.** Mole fraction of CO<sub>2</sub> ( $\chi$ ) in different recycled ILs as a function of pressure at 30 °C.

absorption. The viscosity of ILs decreases dramatically as the temperature increases. An important feature of the absorption process is that the viscosity of the liquid phase increases rapidly due to the formation of a hydrogen-bonded network. Previous studies also noted the non-ideal absorption properties of CO<sub>2</sub> in the TSILs due to the viscosity. Some researchers suggested that the viscosity during the absorption process could be controlled to a significant degree either by decreasing the number of hydrogen atoms available on the anion for hydrogen bonding, or by adding an organic solvent or water. Either approach would be expected to yield ideal absorption properties in ILs. From a practical perspective, the addition of organic solvents or water may not present the best option because these solvents are volatile. An alternative approach must be developed in an effort to address the viscosity problems. The other important reason underlying the failure of ILs to achieve a maximum CO<sub>2</sub> absorption capacity may be the presence of impurities.

**Thermal Stability and Recycle of ILs.** Thermal stability of the ether functionalized ILs have been studied by TGA in nitrogen environment (flow rate 20 mL/min), heating rate 10 °C/min. Results shows that there is no considerable weight loss upto 100 °C that means all ILs are stable under experimental conditions (30, 50 °C). The CO<sub>2</sub> saturated ILs were heated at 70 °C or under 20 Pa vacuum to desorb CO<sub>2</sub> and repeatedly used for 10 cycles continuously. The result shows (Fig. 7) that there was no significant change in the CO<sub>2</sub> capture capability of ILs.

### Conclusions

A series [C<sub>3</sub>Omim] [X] of hydrophobic, chemically-thermally stable ILs have been synthesized, characterized and the CO<sub>2</sub> absorption capacity were evaluated at ambient condition. The absorption capacity reaches 0.9 mol CO<sub>2</sub> per mol of ILs at ambient pressure. The maximum CO<sub>2</sub> absorption is shown by ILs having [Tf<sub>2</sub>N] anion. Since the extent of

fluoroalkylation is maximum in this anion as compared to the other anions, so maximum absorption is achieved. The absorption mechanism investigated by FTIR spectroscopy and <sup>13</sup>C NMR spectroscopy proved that the absorption is a chemical process. The absorbed CO<sub>2</sub> can be easily desorbed by heating at higher temperature or under vacuum and can be repeatedly used. Hence, these ether functionalized ILs are selective, thermally stable, long life operational, a promising candidate for CO<sub>2</sub> capture.

**Acknowledgments.** This work was supported by the Korea CCS R&D Center (KCRC) grant funded by the Korea government (Ministry of Education, Science and Technology). (No: 2011-0031969).

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