

## 科学研究費助成事業 研究成果報告書

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研究成果の概要(和文)：地球温暖化の一因とされる二酸化炭素を発電所などの大規模発生源から分離回収する研究が進められている。中でも化学吸収法は、大規模発生源からの分離回収に最も適しており、実用化が進められているが、更に高性能な化学吸収剤の開発が求められている。本プロジェクトでは、所謂、Amine Functionalized Task Specific Ionic Liquids(TSILs)に着目し、種々の検討を進めた。その結果、コリンをカチオンとするいくつかのTSILsが二酸化炭素の吸収速度、吸収量他化学吸収液の基本性能としてこれまでにない高性能を示すことを見出した。

研究成果の概要(英文)：This project 15 novel TSILs was designed, synthesized, and their CO<sub>2</sub> capture performances were evaluated. These TSILs significantly increase in CO<sub>2</sub> capture performances such as, high absorption rate, highest gravimetric capacities (23.3%, which is obviously higher than previously reported task-specific ILs), high cyclic capacity, low temperature regeneration criteria, high CO<sub>2</sub> recovery (about 90% at 90 °C). All these results demonstrate the potential of this project TSILs as an absorbent for CO<sub>2</sub> capture.

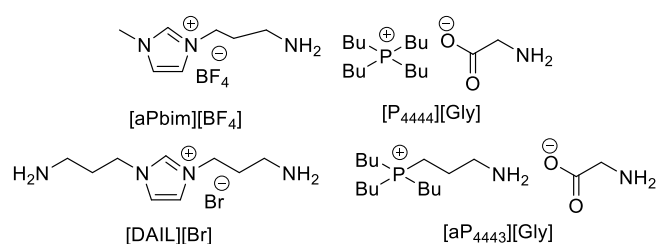
研究分野：Chemistry

キーワード：TSIL CO<sub>2</sub> Capture Absorption Rate CO<sub>2</sub> Loading Cyclic Capacity CO<sub>2</sub> recovery <sup>13</sup>C-NMR

## 1. 研究開始当初の背景

Development of innovative environmental control technologies for reducing greenhouse gas emissions is a key to maintaining fossil fuels as an affordable and environmentally sound energy sources. Most CO<sub>2</sub> is emitted as a byproduct of burning fossil fuels, and fossil fuels will still be the major source of energy for industrial activity in the coming decades. CO<sub>2</sub> capture and release by using aqueous organic amines is the most mature and widely applied technology for post-combustion CO<sub>2</sub> capture (PCC). Unfortunately, organic amines are highly volatile and corrosive, and solvent regeneration energy is estimated more than half of the capture cost arises.<sup>1</sup> To reduce solvent regeneration energy, our liquid amine based solvent development project, we modified organic amine chemical structure and developed energy efficient new organic amine based absorbents for PCC technology that can drastically reduce solvent regeneration energy.<sup>2-7</sup>

Ionic liquids (ILs) have attracted great attention for their potential as alternative media for CO<sub>2</sub> capture because of their unique properties such as wide liquid range, high thermal stability, extremely low volatility, and limitless chemical tunable properties. Subsequently, a great deal of research has been carried out on the solubilities of CO<sub>2</sub> RTILs<sup>8-10</sup> and TSILs.<sup>11-16</sup> RTILs are just limited to physical absorption, and the gravimetric absorption capacity is about 0.4 wt % at atmospheric pressure and room temperature.<sup>10</sup> Amine-functionalized TSILs has been specifically designed for high gravimetric CO<sub>2</sub> solubility. The highest CO<sub>2</sub> solubility has reached about 17.8wt% at 100kPa and 30 °C<sup>15</sup>. There are mainly three types of amino-functionalized TSILs for CO<sub>2</sub> capture: ILs in which the cations are functionalized with an appended amine group, for example [aPbim][BF<sub>4</sub>]<sup>12</sup>, ILs in which the anions are functionalized with an appended amine group, for example, [aP<sub>4444</sub>][Gly]<sup>13-14</sup> and dual amino-functionalized ILs in which the cation or both cation and the anion are functionalized with an appended amine group, for example [DAIL][Br]<sup>15</sup> and [aP<sub>4443</sub>][Gly]<sup>16</sup> are shown in Scheme 1.



**Scheme 1.** Structures of amino functionalized TSILs

This project we planned to develop novel new materials that are green and suitable for CO<sub>2</sub> capture, which can further reduce solvent regeneration energy. For example, a nonvolatile solvent that could facilitate CO<sub>2</sub> capture without the loss of solvent into the gas stream would be an advantageous compared to aqueous organic amines. The focus is on “tunable” materials, i.e., TSILs.

## 2. 研究の目的

Although significant progress has been made in the application of TSILs in the CO<sub>2</sub> capture process, still there are some inherent defects of ionic liquids, such as high cost and viscosity, low the gravimetric capacities limit their industrial applications. Integrating TSILs with other materials provides a platform for adjusting the physical

properties of ILs and makes them more feasible for industrial applications. This project we planned to design and synthesis novel new TSILs that will significantly increase in CO<sub>2</sub> capture performances such as, high absorption rate, high gravimetric capacities, high cyclic capacity, low regeneration temperature, high CO<sub>2</sub> recovery, and reduces of solvent regeneration energy.

## 3. 研究の方法

Commercially available conventional amines, room temperature ILs and solvents were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO), Wako Pure Chemical Industries (Osaka, Japan) or Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) used as received. The details chemical structures and shot names of the investigated TSILs are shown in Scheme 2-3.

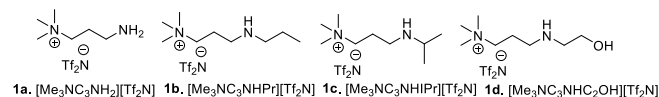
**Syntheses of TSILs:** 15 TSILs were produced in rapid and economic syntheses in our laboratory (Scheme 2 and 3) and their structures were established by nuclear magnetic resonance (NMR) spectroscopy.

**[Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br]HBr:** In a round bottomed flask, 3-bromopropan-1-amine hydrobromide (70.05 g, 0.32 mol) dissolved in 300 mL ethanol was added with 200 mL of a 3.2 M solution of trimethylamine in ethanol under magnetic stirring and at room temperature. After 4 days the white crystals formed were filtered and washed thrice with ethyl ether: the amount of the obtained product was 78.96 g (yield 89%). The preparation of other [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br]HBr, [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br]HBr, and [Me<sub>3</sub>NC<sub>3</sub>NHC<sub>2</sub>OH][Br]HBr followed the same procedure as described above using 3-bromo-N,N,N-trimethylpropan-1-aminium bromide and corresponding *iso*-propyl amine, propyl amine, and 2-aminoethanol.

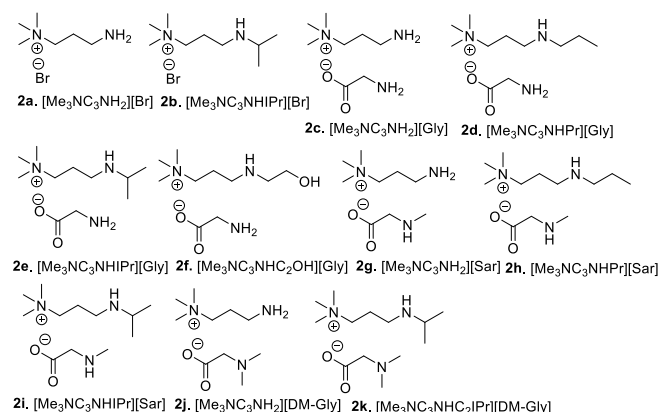
**[Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br]:** To a magnetically stirred solution of compound [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br]HBr (30.0 g, 0.108 mol) in MeOH (100 mL) was added KOH solution in methanol (6.05 g, 0.108 mol) at 0 °C. The mixture was stirred for 4 h and then solvent was removed under vacuum. This was followed by the addition of methanol (50 mL). The precipitated salts were filtered off, and the solvent was removed under vacuum. The obtained white powder like material was dried under vacuum at 60 °C for 24 h to give [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br] as white powder 20.78 g ( yield 98%). The preparation of other [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br], [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br], and [Me<sub>3</sub>NC<sub>3</sub>NHC<sub>2</sub>OH][Br] followed the same procedure as described above.

**[Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Tf<sub>2</sub>N]:** To a magnetically stirred solution of compound [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br] (10.0 g, 0.051 mol) in H<sub>2</sub>O (50 mL) was added aqueous solution of LiTf<sub>2</sub>N (14.63 g, 0.051 mol). An oily phase immediately separated. The mixture was subsequently vigorously stirred for 24 h to ensure thorough mixing in the reaction vessel. After this time, the oily phase was extracted into CH<sub>2</sub>Cl<sub>2</sub> (150 mL) and washed with deionized H<sub>2</sub>O (4 x 50 mL). The fifth aqueous washing was exposed to AgNO<sub>3</sub>, to confirm that residual bromide anion was no longer present via the lack of AgBr precipitate formation. The organic phase was then dried over anhydrous MgSO<sub>4</sub>. The solvent was then removed by rotary evaporation, and the final product was dried while stirring at 65 °C under dynamic vacuum (< 1 torr) for 24h. The product [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Tf<sub>2</sub>N] was obtained as a clear oil 18.24 g (yield 90%). The preparation of other [Me<sub>3</sub>NC<sub>3</sub>NHPr][Tf<sub>2</sub>N], [Me<sub>3</sub>NC<sub>3</sub>NHPr][Tf<sub>2</sub>N],

$[\text{Me}_3\text{NC}_3\text{NHC}_2\text{OH}][\text{Tf}_2\text{N}]$  followed the same procedure as described above.



**Scheme 2.** Amino-functionalized TSILs with  $\text{Tf}_2\text{N}$  anion



**Scheme 3.** Amino-functionalized TSILs with bromo and amino acid anion

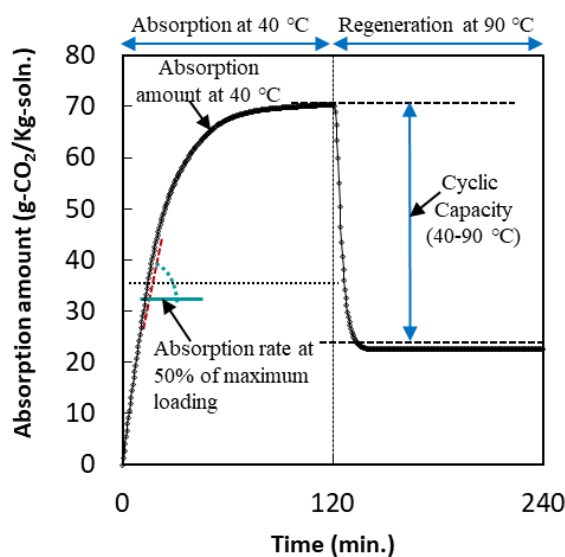
**$[\text{Me}_3\text{NC}_3\text{NH}_2][\text{Gly}]$ :** 20 g (0.072 mol) of  $[\text{Me}_3\text{NC}_3\text{NH}_2][\text{Br}]$  was diluted with a little water. Next, on passing through prewashed Amberlite IRN-78 (basic) resin column gave amine functionalized quaternary ammonium hydroxide solution of  $[\text{Me}_3\text{NC}_3\text{NH}_2][\text{OH}]$ . Neutralization of the  $[\text{Me}_3\text{NC}_3\text{NH}_2][\text{OH}]$  solution with equivalent amount amino acid [Gly] gave amine functionalized amino acid based ionic liquid  $[\text{Me}_3\text{NC}_3\text{NH}_2][\text{Gly}]$ . The obtained aqueous solution of  $[\text{Me}_3\text{NC}_3\text{NH}_2][\text{Gly}]$  were evaporated under reduced pressure at  $80^\circ\text{C}$  and then dried under vacuum at  $80^\circ\text{C}$  for 48 h. The preparation of other  $[\text{Me}_3\text{NC}_3\text{NHPr}][\text{Gly}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHIPr}][\text{Gly}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHC}_2\text{OH}][\text{Gly}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHNH}_2][\text{Sar}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHPr}][\text{Sar}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHIPr}][\text{Sar}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHPr}][\text{Sar}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHPr}][\text{DM-Gly}]$ , followed the same procedure as described above using [Gly], [Sar], and [DM-Sar].

**Gas Scrubbing Test:** The gas scrubbing tests of all ILs was performed according to our previous publication.<sup>4</sup> The gas screening test gives us information about absorption rate,  $\text{CO}_2$  loading capacities, cyclic capacities, and  $\text{CO}_2$  recovery. Figure 1 show typical results was obtained from the gas scrubbing test. The amount of absorbed  $\text{CO}_2$  in (amine + IL) or aqueous TSIL solution was calculated from the measured  $\text{CO}_2$  concentration in the outlet gas flow. The gradient of the curve at 50% of the 120 min  $\text{CO}_2$  loading was defined as the absorption rate. The difference between the maximum  $\text{CO}_2$  loading at  $40^\circ\text{C}$  and the minimum  $\text{CO}_2$  loading at  $90^\circ\text{C}$  was defined as the cyclic capacity.

**Viscosity:** All viscosity values of  $\text{CO}_2$ -loaded TSILs were determined using Brookfield digital LVDV-III ultra programmable viscometer. Ten viscosity measurements were taken and the mean values are used.

**$^{13}\text{C}$ -NMR Experiment:** All NMR sample were analyzed by Bruker Avance III 400 NMR spectrometer.  $\text{CO}_2$  equilibrated non-aqueous and aqueous amine sample approximately 0.4ml was taken into the 5-mm-o.d.NMR sample tube. After that a capillary sealed with internal standard [a 2 wt% 3-(trimethylsilyl)-propionic-2,2,3,3- $\text{d}_4$ -acid sodium salt in  $\text{D}_2\text{O}$ ] was poured into the NMR tube then it was closed by

using a rubber septum before measuring  $^{13}\text{C}$ -NMR spectra. Quantitative  $^{13}\text{C}$  spectra were recorded at 100 MHz using inverse-gated decoupling technique with a delay of 60 s and a pulse width of 10  $\mu\text{s}$  and 400 scans



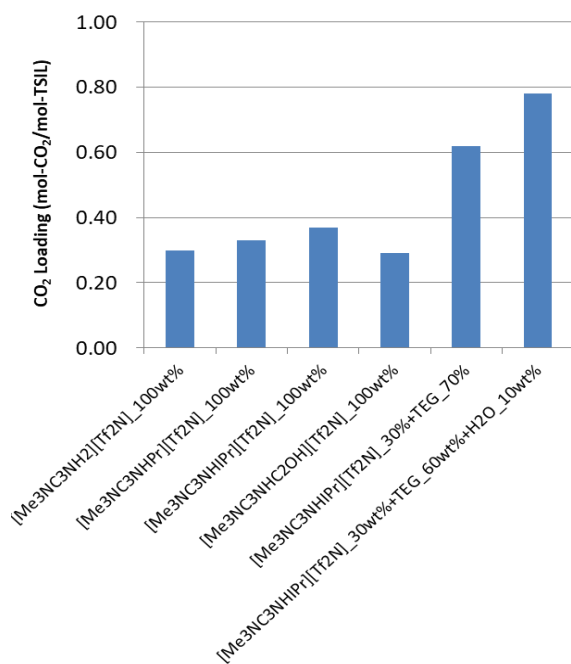
**Fig. 1.** Typical example of a gas scrubbing test

#### 4. 研究成果

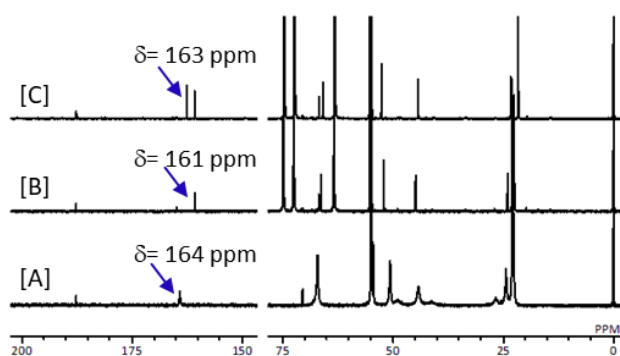
In this project, three classes of IL-based solvents were developed ① amino-functionalized TSILs with bis(trifluoromethylsulfonyl)imide anion ( $\text{Tf}_2\text{N}$ ), ② amino-functionalized TSILs with bromo anions, and ③ amino-functionalized TSILs with amino acid anions.

**4-1. Amino-functionalized TSILs with bis(trifluoromethylsulfonyl)imide anion ( $\text{Tf}_2\text{N}$ ):** Inspired from our liquid organic amine-based solvent, several amine-functionalized ILs has been specifically designed for  $\text{CO}_2$  capture. We designed and synthesis four amino functionalized TSILs in which the cations are functionalized with an appended primary ( $-\text{HN}_2$ ) and secondary amine group such as propyl, isopropyl and hydroxyethyl substituents shown in Scheme 2. The anionic part of these TSILs is  $\text{Tf}_2\text{N}$ . They are named as  $[\text{Me}_3\text{NC}_3\text{NH}_2][\text{Tf}_2\text{N}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHPr}][\text{Tf}_2\text{N}]$ ,  $[\text{Me}_3\text{NC}_3\text{NHIPr}][\text{Tf}_2\text{N}]$ , and  $[\text{Me}_3\text{NC}_3\text{NHC}_2\text{OH}][\text{Tf}_2\text{N}]$ . The  $\text{CO}_2$  capture performances of these amino functionalized TSILs with  $\text{Tf}_2\text{N}$  anions are summarized in Fig. 3. The neat TSILs  $\text{CO}_2$  solubility follows the trends  $[\text{Me}_3\text{NC}_3\text{NHIPr}][\text{Tf}_2\text{N}] > [\text{Me}_3\text{NC}_3\text{NHPr}][\text{Tf}_2\text{N}] > [\text{Me}_3\text{NC}_3\text{NH}_2][\text{Tf}_2\text{N}] > [\text{Me}_3\text{NC}_3\text{NHC}_2\text{OH}][\text{Tf}_2\text{N}]$ . The present amino-functionalized TSILs suffer from a dramatic increase in viscosity after they are complexed with  $\text{CO}_2$  as a result they suffers low  $\text{CO}_2$  solubility. A simple solution is to dilute amine-functionalized ILs with other solvents to form mixed absorbents. Among the various TSILs tested,  $[\text{Me}_3\text{NC}_3\text{NHPr}][\text{Tf}_2\text{N}]$  was identified as the most promising one. Reducing the viscosity of  $[\text{Me}_3\text{NC}_3\text{NHPr}][\text{Tf}_2\text{N}]$  was done by adding triethylene glycol (TEG). Mixtures of TEG and  $[\text{Me}_3\text{NC}_3\text{NHPr}][\text{Tf}_2\text{N}]$  dramatically lower the viscosity while increasing  $\text{CO}_2$  capture capacity 0.37 to 0.62 mol- $\text{CO}_2$ /mol-TSIL (Fig. 2). The viscosity further decreased by adding water. Adding 10wt%  $\text{H}_2\text{O}$  further decreased the viscosity and increasing  $\text{CO}_2$  capture capacity 0.62 to 0.78

mol mol-CO<sub>2</sub>/mol-TSIL (Fig. 2). Amino-functionalized TSILs work well in the presence of water, considering that water is a component of flue gas.

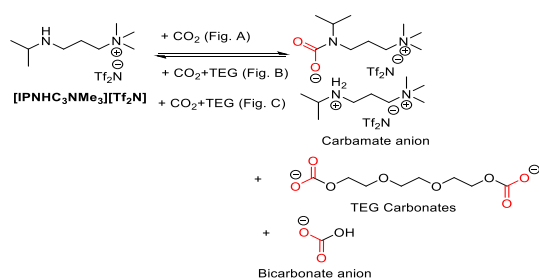


**Fig. 2.** CO<sub>2</sub> capture performances amino-functionalized TSILs with Tf<sub>2</sub>N anion



**Fig. 3.** <sup>13</sup>C-NMR species analysis of TSIL, [Me<sub>3</sub>NC<sub>3</sub>NHPr][Tf<sub>2</sub>N]; Fig. [A] = ([Me<sub>3</sub>NC<sub>3</sub>NHPr][Tf<sub>2</sub>N] + CO<sub>2</sub>); Fig. [B] = ([Me<sub>3</sub>NC<sub>3</sub>NHPr][Tf<sub>2</sub>N] + TEG + CO<sub>2</sub>) and Fig. [C] = (T [Me<sub>3</sub>NC<sub>3</sub>NHPr][Tf<sub>2</sub>N] + TEG + H<sub>2</sub>O + CO<sub>2</sub>)

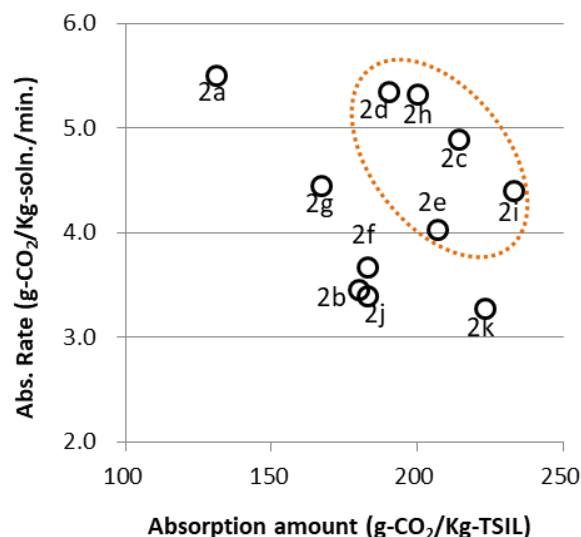
It is expected three interesting reaction may occurs when [Me<sub>3</sub>NC<sub>3</sub>NHPr] [Tf<sub>2</sub>N] + CO<sub>2</sub>, [Me<sub>3</sub>NC<sub>3</sub>NHPr] [Tf<sub>2</sub>N] TEG + CO<sub>2</sub>, and [Me<sub>3</sub>NC<sub>3</sub>NHPr] [Tf<sub>2</sub>N] TEG + H<sub>2</sub>O + CO<sub>2</sub> solutions reacted with CO<sub>2</sub>. <sup>13</sup>C-NMR species identification of these three pre-loaded CO<sub>2</sub> solutions with 0.37, 0.62, and 0.78 mol-CO<sub>2</sub>/mol-[Me<sub>3</sub>NC<sub>3</sub>NHPr] [Tf<sub>2</sub>N] were shown in Fig. 3. Scheme 4 shows the chemical reaction occurred in Fig. 4; [A], [B] and [C].



**Scheme 4.** <sup>13</sup>C-NMR species of identification from Fig. 3 [A], [B] and [C].

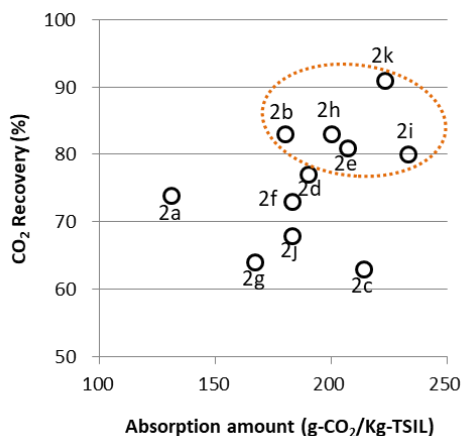
When [Me<sub>3</sub>NC<sub>3</sub>NHPr][Tf<sub>2</sub>N] reacted with CO<sub>2</sub> carbamate anion (COO<sup>-</sup>) is the only product shown in Fig. [A], and appeared at  $\delta = 164$  ppm. When [Me<sub>3</sub>NC<sub>3</sub>NHPr][Tf<sub>2</sub>N] + TEG reacted with CO<sub>2</sub> TEG carbonate is the major product (TEG-CO<sub>3</sub><sup>-</sup>), appeared at  $\delta = 161$  ppm plus minor carbamate anion (COO<sup>-</sup>) is shown in Fig. [B], and appeared at  $\delta = 164$  ppm. Interestingly when [Me<sub>3</sub>NC<sub>3</sub>NHPr] [Tf<sub>2</sub>N] + TEG + H<sub>2</sub>O reacted with CO<sub>2</sub> bicarbonate anion (HCO<sub>3</sub><sup>-</sup>) is the major product, appeared at  $\delta = 163$  ppm plus minor TEG-CO<sub>3</sub><sup>-</sup> as shown in Fig. [C].

**4-2. Amino-functionalized TSILs with bromo and amino acid anions:** In this project, 11 amino-functionalized TSILs are synthesized out of them 9 dual amino-functionalized ILs in which both cation and anion are functionalized with an appended amine group, and the rest two TSILs the cations are functionalized with bromo anion are shown in Scheme 3. All amino-functionalized TSILs are highly viscous or solid at room temperature. It is difficult to perform their CO<sub>2</sub> capture as it were. That is why TSILs were prepared as aqueous solution for CO<sub>2</sub> capture. Aqueous solutions of the TSILs (mass fraction 30%) were used to evaluate the performance for CO<sub>2</sub> capture.



**Fig. 5.** Absorption rate versus absorption amount values

For aqueous solution of TSILs performance evaluation (absorption rate, loading capacity, and cyclic capacity) two different temperatures (40 °C for absorption and 90 °C for regeneration) were investigated in detail. The findings are summarized in Table 1 and Fig. 5 and 6. In order to reduce high energy consumption of PCC process, it is necessary to develop new solutions which will be characterized by the best absorption rate and capacity. Fig. 5 illustrated the relation between absorption rates versus CO<sub>2</sub> loading capacities. All our synthesized TSILs show excellent CO<sub>2</sub> solubility (the gravimetric capacities are in between 13 to 23wt%) which reached the highest CO<sub>2</sub> capacity to the best of our knowledge. From Fig. 5 it can see that most of TSILs can absorb CO<sub>2</sub> at a faster rate. Higher absorption rate of solvent is an important parameter to reduce absorption column size when applied for practical application. The potential TSILs in terms of absorption rate versus capacity showed in yellow dotted cycle. Five such TSILs (2c, 2d, 2e, 2i, and 2e) were identified from Fig. 5. This means all of these TSILs can absorb CO<sub>2</sub> at a faster rate with very high gravimetric CO<sub>2</sub> loading capacities.



**Fig. 6.** CO<sub>2</sub> recovery versus absorption amount values

The recovery % of CO<sub>2</sub> versus absorption amount shown in Fig. 6. This work TSILs regeneration was done quite lower temperature 90 °C compared to conventional chemical absorption process (about 120-140 °C). The recovery of CO<sub>2</sub> calculated from (cyclic capacity divided by total absorption amount) will give CO<sub>2</sub> recovery percentage. Here the cyclic capacity is the rich-lean loading difference at temperature (40-90) °C. Five TSILs (2b, 2e, 2h, 2i, and 2k) gave very good CO<sub>2</sub> recovery in between 80 - 90% can be seen from Fig. 5. This means this work TSILs shows low temperature regeneration characteristics. High cyclic capacity at low regeneration temperature will increase net TSILs solvent recycling in the desorption tower that can decrease solvent regeneration energy. Lower temperature regeneration gives several benefits for TSILs such as reduce solvent degradation, equipment corrosion, and less environmental pollution.

**Table 1.** Screening result of TSILs (TSILs\_30wt% + H<sub>2</sub>O\_70wt%)

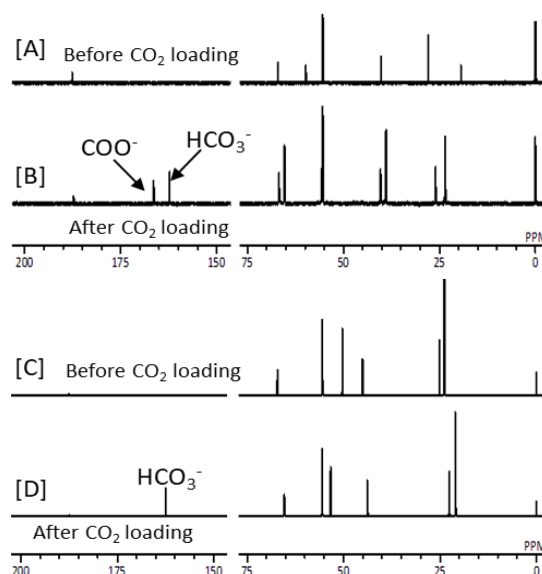
TSILs	M (g/mol) <sup>a</sup>	CO <sub>2</sub> loading <sup>b</sup>	CO <sub>2</sub> Wt. gain <sup>c</sup>	
[Me <sub>3</sub> NC <sub>3</sub> NH <sub>2</sub> ][Br]	197.12	0.59	13.1	this work
[Me <sub>3</sub> NC <sub>3</sub> NHPr][Br]	239.20	0.98	18.0	this work
[Me <sub>3</sub> NC <sub>3</sub> NH <sub>2</sub> ][Gly]	191.27	0.93	21.4	this work
[Me <sub>3</sub> NC <sub>3</sub> NHPr][Gly]	233.36	1.00	19.0	this work
[Me <sub>3</sub> NC <sub>3</sub> NHPr][Gly]	233.36	1.09	20.7	this work
[Me <sub>3</sub> NC <sub>3</sub> NHC <sub>2</sub> OH][Gly]	235.33	0.98	18.3	this work
[Me <sub>3</sub> NC <sub>3</sub> NH <sub>2</sub> ][Sar]	205.30	0.83	16.7	this work
[Me <sub>3</sub> NC <sub>3</sub> NHPr][Sar]	247.38	1.12	20.0	this work
[Me <sub>3</sub> NC <sub>3</sub> NHPr][Sar]	247.38	1.31	23.3	this work
[Me <sub>3</sub> NC <sub>3</sub> NH <sub>2</sub> ][DM-Gly]	219.33	0.91	18.3	this work
[Me <sub>3</sub> NC <sub>3</sub> NHPr][DM-Gly]	261.41	1.31	22.3	this work
[DAIL][Br] <sup>d</sup>	249.15	1.05	18.5	ref <sup>15</sup>
[aPbim][BF <sub>4</sub> ] <sup>e</sup>	269.09	0.50	7.4	ref <sup>12</sup>

<sup>a</sup>Molar mass of ILs. <sup>b</sup>Values in mol of CO<sub>2</sub> per mole of ILs. <sup>c</sup>Values in gram of CO<sub>2</sub> per gram of ILs. <sup>d</sup>Performed by pure IL.

The gravimetric capacities of TSILs are summarized in Table 1. The gravimetric capacities of this work TSILs are compared with the best result obtained from dual [DAIL][Br] amino-functionalized ILs. Five dual amino-functionalized TSILs shows higher gravimetric capacity 23.3, 22.3, 21.4, 20.7 and 20.0wt% compared with dual TSIL [DAIL][Br]<sup>15</sup>. TSILs from Table 1, [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br] and [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br] in which the cations are functionalized with an appended amine group

are compared with similar type TSILs [aPbim][BF<sub>4</sub>]<sup>12</sup>. [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br] and [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br] shows very high gravimetric capacities 13.1 and 18.0 wt% respectively in contrast with [aPbim][BF<sub>4</sub>], 7.4% only. At the absorption equilibrium state, the solution of seven TSILs, presented a molar CO<sub>2</sub> capture capacity about 1.0, (Table 1), three TSILs [Me<sub>3</sub>NC<sub>3</sub>NHPr][Sar], [Me<sub>3</sub>NC<sub>3</sub>NHPr][Gly], and [Me<sub>3</sub>NC<sub>3</sub>NHPr][DM-Gly] shows molar capacity 1.12, 1.31, and 1.31 respectively. Because all these TSILs cations and anions are functionalized with an appended secondary or tertiary amino group leads to higher CO<sub>2</sub> loading capacities by forming bicarbonate HCO<sub>3</sub><sup>-</sup> anion.

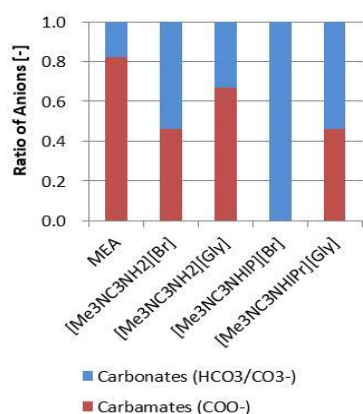
To gain a deeper insight into the absorption mechanism, the <sup>13</sup>C NMR spectrum of CO<sub>2</sub>-treated [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br] was compared with that [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br], as shown in Fig. 7. After absorption, [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br] shows two new resonance was observed at δ 166.4 and 162.3 ppm, corresponding to the formation of carbamate (-COO<sup>-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) anion respectively shown in Fig. 7 [B]. On the other hand after absorption, [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br] shows a new resonance was observed at δ 162.4 ppm, corresponding to the formation of a bicarbonate (HCO<sub>3</sub><sup>-</sup>) anion shown in Fig. 7 [D]. Introduction of medium hindered isopropyl group at the terminal end of TSIL [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br] completely alters the reaction product. Our experimental results showed a CO<sub>2</sub> absorption capacity of 0.98 mol CO<sub>2</sub> per mol of [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br], which is very close to the theoretical absorption capacity.



**Fig. 7.** <sup>13</sup>C-NMR spectra [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br] and [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br] before and after reaction with CO<sub>2</sub>. Fig. [A] & [B], [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br] before and after CO<sub>2</sub> loading. Fig. [C] & [D], [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br] before and after CO<sub>2</sub> loading.

Both carbamate and bicarbonate anions in a CO<sub>2</sub>-absorbed solvent were quantitatively analyzed from the <sup>13</sup>C NMR spectra of absorbed CO<sub>2</sub> and used to calculate the ratio of these two anions. Fig. 8 shows the results of <sup>13</sup>C NMR analysis. MEA mainly absorbed CO<sub>2</sub> as carbamate anion and ratio of the carbamate anion to total absorbed CO<sub>2</sub> was 82%. [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br] mainly absorbed CO<sub>2</sub> as bicarbonate anion. The structure of [Me<sub>3</sub>NC<sub>3</sub>NHPr][Br] contains steric hindrance and CO<sub>2</sub> was mostly absorbed as bicarbonate anions. [Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Br],

[Me<sub>3</sub>NC<sub>3</sub>NH<sub>2</sub>][Gly] and [Me<sub>3</sub>NC<sub>3</sub>NHPr][Gly] are TSILs in combination of primary and secondary amines and they all absorbed CO<sub>2</sub> as both carbamate and bicarbonate anions.



**Fig. 8.** Ratios of carbamate and bicarbonate anions obtained from <sup>13</sup>C-NMR analysis

In summary, this project 15 novel TSILs was designed, synthesized, and their CO<sub>2</sub> capture performances were evaluated. These TSILs significantly increase in CO<sub>2</sub> capture performances such as, high absorption rate, highest gravimetric capacities (23.3%, which is obviously higher than previously reported task-specific ILs), high cyclic capacity, low temperature regeneration criteria, high CO<sub>2</sub> recovery (about 90% at 90 °C). All these results demonstrate the potential of this project TSILs as an absorbent for CO<sub>2</sub> capture.

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#### 5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

[雑誌論文] (計 0 件)

[学会発表] (計 7 件)

- (Oral: O03.1): Chemically Tunable Ionic Liquid-Amine Solutions for CO<sub>2</sub> Capture. Firoz Alam Chowdhury and Tsuguhiko Kato. 3<sup>rd</sup> International Conference on Ionic Liquids in Separation and Purification Technology, Renaissance Kuala Lumpur, January 8-11, **2017**, Malaysia
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