Development of Amino-Functionalized New Task Specific Ionic Liquids (TSILs) for Efficient CO₂ Capture

Firoz A. Chowdhury¹, Kazuya Goto¹

¹Research Institute of Innovative Technology for the Earth (RITE), 9-2 Kizugawadai, Kizugawa-shi, Kyoto 619-0292, Japan

Abstract

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. CO₂ capture and release by using aqueous amine solution is the most mature and widely applied technology for post-combustion CO₂ capture (PCC). Unfortunately, organic amines are highly volatile and corrosive, and solvent regeneration energy is estimated more than half of the capture cost arises.¹ Recently, ionic liquids (ILs) have attracted great attention for their potential as alternative media for CO₂ 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 solubility of CO₂ room temperature ionic liquids (RTILs)²-⁴ and TSILs⁵-¹⁰. RTILs are just limited to physical absorption, and the gravimetric absorption capacity is about 0.4 wt % at atmospheric pressure and room temperature.⁴ Amino-functionalized TSILs has been specifically designed for high gravimetric CO₂ solubility. The highest CO₂ solubility with [DAIL][Br] has reached about 17.8wt% at 100kPa and 30 °C⁹. There are mainly three types of amino-functionalized TSILs for CO₂ capture: ILs in which the cations are functionalized with an appended amine group, for example [aPbim][BF₄]⁶, ILs in which the anions are functionalized with an appended amine group, for example, [P₄₄₄₄][Gly]⁷-⁸ 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]⁹ and [aP₄₄₄₃][Gly]¹⁰ are shown in Scheme 1.

Scheme 1. Structures of amino functionalized TSILs
Although significant progress has been made in the application of TSILs in the CO₂ capture process, still there are some inherent defects of ionic liquids, such as high cost and viscosity, low gravimetric capacities limit their industrial applications. Modifying cationic and anionic part of TSILs with other materials provides a platform for adjusting their chemical and physical properties and makes them more feasible for industrial applications. To increase amine based absorbents CO₂ capture performances, our aqueous amine based absorbent project, we modified organic amine based absorbent project, we modified organic amine chemical structure and developed energy efficient new amine based absorbents for PCC technology that can drastically reduce solvent regeneration energy.11-16 Similarly, this project we modified cationic and anionic part of ILs and synthesized 11 novel new TSILs shown in Scheme 2.

Scheme 2. Amino-functionalized TSILs with bromo and amino acid anion

![Scheme 2: Amino-functionalized TSILs with bromo and amino acid anion](image)

Fig. 1. Absorption rate versus absorption amount values
This work, TSILs are highly viscous or solid at room temperature. It is difficult to perform their CO₂ capture as it were. Aqueous solutions of the TSILs (mass fraction 30%) were used to evaluate their CO₂ capture performances. TSILs, gas scrubbing tests were done according to our previous work. CO₂ capture performances of two different temperatures (40 °C for absorption and 90 °C for regeneration) were investigated in detail. The findings are summarized in Table 1, Fig. 1 and 2. Fig. 1 illustrated the relation between absorption rates versus CO₂ absorption capacities. The potential TSILs in terms of absorption rate versus absorption amount showed in yellow dotted circle. Five such TSILs (2c, 2d, 2e, 2h, and 2i) were identified from Fig. 1.

TSILs CO₂ regeneration efficiency verses absorption amount shown in Fig. 2. The regeneration efficiency of CO₂ calculated from cyclic capacity divided by total absorption amount. Here the cyclic capacity is the rich-lean loading difference at temperature 40 °C and 90 °C. From Fig. 2, five potential TSILs (2b, 2e, 2h, 2i, and 2k) were identified (yellow dotted circle) which CO₂ regeneration efficiency is in between 80 - 90%. High cyclic capacity at low regeneration temperature (this work 90 °C) will increase net TSILs solvent recycling in the desorption tower that can decrease solvent regeneration energy. Lower regeneration temperature also give several benefits for TSILs such as reduce solvent degradation, equipment corrosion, and less environmental pollution.

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 amino-functionalized ILs [DAIL][Br]. This work, six dual amino-functionalized TSILs shows higher gravimetric capacities 23.3, 22.3, 21.4, 20.7, 20.0 and 19.0 wt% compared with [DAIL][Br]9, 17.8 wt%. TSILs [Me₃NC₃NH₂][Br] and [Me₃NC₃NHIPr][Br] in which the cations are functionalized with an appended amine group are compared with similar type of TSILs [aPbim][BF₄]6. [Me₃NC₃NH₂][Br] and [Me₃NC₃NHIPr][Br] shows very high gravimetric capacities 13.1 and 18.0 wt% respectively in contrast with [aPbim][BF₄], 7.4% only. All our synthesized TSILs show excellent CO₂ solubility (the gravimetric capacities are in between 13 to 23 wt%) out of them [Me₃NC₃NHIPr][Sar] reached the highest CO₂ capacity (23.3 wt%) to the best of our knowledge.
Table 1. CO₂ absorption by TSILs (TSILs _30wt% + H₂O _70wt%) and reported ILs

<table>
<thead>
<tr>
<th>TSILs</th>
<th>M (g / mol)ᵃ</th>
<th>CO₂ loadingᵇ</th>
<th>Gravimetric Capacities (wt %)ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me₃NC₃NH₂][Br]</td>
<td>197.12</td>
<td>0.59</td>
<td>13.1</td>
</tr>
<tr>
<td>[Me₃NC₃NHP][Br]</td>
<td>239.20</td>
<td>0.98</td>
<td>18.0</td>
</tr>
<tr>
<td>[Me₃NC₃NH₂][Gly]</td>
<td>191.27</td>
<td>0.93</td>
<td>21.4</td>
</tr>
<tr>
<td>[Me₃NC₃NHP][Gly]</td>
<td>233.36</td>
<td>1.00</td>
<td>19.0</td>
</tr>
<tr>
<td>[Me₃NC₃NHP][Gly]</td>
<td>233.36</td>
<td>1.09</td>
<td>20.7</td>
</tr>
<tr>
<td>[Me₃NC₃NHC₂OH][Gly]</td>
<td>235.33</td>
<td>0.98</td>
<td>18.3</td>
</tr>
<tr>
<td>[Me₃NC₃NH₂][Sar]</td>
<td>205.30</td>
<td>0.83</td>
<td>16.7</td>
</tr>
<tr>
<td>[Me₃NC₃NHP][Sar]</td>
<td>247.38</td>
<td>1.12</td>
<td>20.0</td>
</tr>
<tr>
<td>[Me₃NC₃NHP][Sar]</td>
<td>247.38</td>
<td>1.31</td>
<td>23.3</td>
</tr>
<tr>
<td>[Me₃NC₃NH₂][DM-Gly]</td>
<td>219.33</td>
<td>0.91</td>
<td>18.3</td>
</tr>
<tr>
<td>[Me₃NC₃NHP][DM-Gly]</td>
<td>261.41</td>
<td>1.31</td>
<td>22.3</td>
</tr>
<tr>
<td>[DAIL][Br]ᵈ</td>
<td>249.15</td>
<td>1.05</td>
<td>17.8</td>
</tr>
<tr>
<td>[aPbim][BF₄]ᵉ</td>
<td>269.09</td>
<td>0.50</td>
<td>7.4</td>
</tr>
</tbody>
</table>

ᵃMolar mass of ILs.ᵇValues in mol of CO₂ per mole of ILs.ᶜValues in gram of CO₂ per gram of ILs.ᵈPerformed at 30 °C in 30 wt% aqueous solution of IL.ᵉPerformed by pure IL.

Fig. 3. Ratios of carbamate and carbonate anions obtained from ¹³C-NMR analysis

Both carbamate (COO⁻) and carbonate (HCO₃⁻/CO₃²⁻) anions in a CO₂-absorbed solvent were quantitatively analyzed from the ¹³C NMR spectra of absorbed CO₂ and used to calculate the ratio of these two anions. Fig. 3 shows the results of ¹³C NMR analysis. MEA mainly absorbed CO₂ as carbamate anion and ratio of the carbamate anion to total absorbed CO₂ was 82%.
[Me₃NC₃NHIPr][Br] mainly absorbed CO₂ as bicarbonate anion. Introduction of medium hindered isopropyl group at the terminal end of [Me₃NC₃NHIPr][Br] completely alters the reaction product. TSILs [Me₃NC₃NH₂][Br], [Me₃NC₃NH₂][Gly] and [Me₃NC₃NHIPr][Gly] are in combination of primary and secondary amines and all they absorbed CO₂ as both carbamate and bicarbonate anions.

In summary, this work 11 novel TSILs was designed, synthesized, and their CO₂ capture performances were evaluated. These TSILs significantly increase in CO₂ 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, and high CO₂ regeneration efficiency (about 90% at 90 °C). All these results demonstrate the potential of this work TSILs as an efficient absorbent for CO₂ capture.

Acknowledgement
This work was carried out under the JSPS KAKENHI project (Grant Number 26410202).

References: