Ionic Liquids and CO$_2$ Capture

CRC REU Lunch Presentation

Zach Goldstein
7/1/11
CO₂ is a product of the burning of many types of fossil-fuels:

\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + \text{energy} \]
Worldwide CO2 emissions from fuel combustion were roughly 29.4 gigatons (Gt) in 2008.¹

In the U.S., IEA reported it as 5.6 Gt for 2008; roughly a third of this is from the burning of transportation fuels, a third is from power generation, and a third is from heating and cooling¹

Due largely to rapid growth in the developing world, this is expected to increase to 40.2 Gt by 2030¹

CO₂ is a green-house gas!

¹Joan F. Brennecke* and Burcu E. Gurkan, “Ionic Liquids for CO2 Capture and Emission Reduction”
Other gases are present in post-combustion flue gas

- The flue gas from a typical coal-fired power plant is
  - 13% CO₂
  - 68% N₂
  - 16% water
  - 3% O₂
  - And lower concentrations of other components

¹Joan F. Brennecke* and Burcu E. Gurkan, “Ionic Liquids for CO2 Capture and Emission Reduction”
We would like a way to separate CO$_2$ from the other gases produced.
Aqueous Amine solutions

i.e. monethanolamine

\[ \text{H}_2\text{N}\text{-}
\text{HOH} + \text{O} = \text{C} = \text{O} \rightleftharpoons \text{O} - \text{C-} \text{NH}_2^+ \text{-OH} \] (1)

\[ \text{H}_2\text{N}\text{-}
\text{HOH} + \text{C-} \text{NH}_2^+ \text{-OH} \rightleftharpoons \text{HO-} \text{N}\text{C-O}^-
\text{+H}_3\text{N}\text{-CH}_2\text{-OH} \] (2)

Two amines react with one molecule of CO₂
Aqueous amines have been used for many decades in the removal of CO₂ from natural gas and are even used to clean the air in submarines.

However, aqueous amines have never been deployed at the scale that would be necessary for a typical power plant.¹

¹Joan F. Brennecke* and Burcu E. Gurkan, “Ionic Liquids for CO2 Capture and Emission Reduction”
Schematic of an aqueous amine scrubbing operation

Cleaned flue gas

Absorber
\sim 40 \degree C

\text{CO}_2 < 0.2 \text{ bar}

\text{CO}_2\text{-lean}

Flue gas
68\% N_2
13\% \CO_2
16\% H_2O
3\% O_2
\sim 200 \text{ ppm SO}_2
\sim 60 \text{ ppm NO}_x
< 60 \text{ ppm hydrocarbons}

\text{CO}_2\text{-rich amine solution}

\text{Flash}

Regenerator
\sim 110 \degree C

\text{CO}_2\text{-lean}

Concentrate CO_2
Problems with current CO$_2$ separation techniques

The theoretical minimum energy requirement for the separation of CO$_2$ from flue gas and compression up to pipeline pressure is about 10% of the energy produced by the coal-fired power plant.\textsuperscript{1,2}

\textsuperscript{2}Fisher, K. S., Beitler, C. M., Myers, D. B. Systems Analysis Studies for CO$_2$ Capture Using Ionic Liquids; Trimeric Corp.: Buda, TX, July 2009
We need more efficient ways of capturing CO$_2$!
Most Ionic compounds are solid at room temperature

i.e. NaCl
Ionic Liquids are low-melting salts
<table>
<thead>
<tr>
<th>Substituent</th>
<th>$T_m$</th>
<th>$\rho$</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>92°C</td>
<td>1.98 g/cm$^3$</td>
<td>-54°C (g)</td>
</tr>
<tr>
<td>ethyl</td>
<td>67</td>
<td>1.69</td>
<td>-55 (g)</td>
</tr>
<tr>
<td>$n$-propyl</td>
<td>63</td>
<td>1.56</td>
<td>33</td>
</tr>
<tr>
<td>isopropyl</td>
<td>92</td>
<td>1.60</td>
<td>66</td>
</tr>
<tr>
<td>2-propenyl</td>
<td>62</td>
<td>1.59</td>
<td>-50 (g)</td>
</tr>
<tr>
<td>$n$-butyl</td>
<td>48</td>
<td>1.46</td>
<td>-50 (g)</td>
</tr>
<tr>
<td>methylcyclopropyl</td>
<td>73</td>
<td>1.58</td>
<td>56</td>
</tr>
<tr>
<td>$n$-pentyl</td>
<td>54</td>
<td>1.57</td>
<td>29</td>
</tr>
<tr>
<td>$n$-hexyl</td>
<td>76</td>
<td>1.34</td>
<td>0</td>
</tr>
<tr>
<td>$n$-heptyl</td>
<td>94</td>
<td>1.30</td>
<td>35</td>
</tr>
<tr>
<td>$n$-octyl</td>
<td>80</td>
<td>1.27</td>
<td>34</td>
</tr>
<tr>
<td>$n$-nonyl</td>
<td>81</td>
<td>1.26</td>
<td>53</td>
</tr>
<tr>
<td>$n$-decyl</td>
<td>90</td>
<td>1.23</td>
<td>51</td>
</tr>
</tbody>
</table>

ILs show great promise in efficient CO$_2$ capture

their most important property is their selectivity of CO$_2$ over other components in the gas mixture$^1$

Solubility of various gases in 1-hexyl-3-methylpyridiniumbis(trifluoromethylsulfonyl)imide. Anderson, J. L.; Dixon, J. K.; Brennecke, J. F. Solubility of CO$_2$, CH$_4$, C$_2$H$_6$, C$_2$H$_4$, O$_2$, and N$_2$ in 1-Hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: Comparison to Other Ionic Liquids. Acc. Chem. Res. 2007, 40, 1208–1216
Problems with IL Capacity

- Using the IL shown in the previous figure would require 33 mol of IL for every mole of CO2 captured if the CO2 pressure were 1 bar.

- Given the high molecular weight of the IL, this would require an inordinately large mass of IL in the system for separation of CO2 from the postcombustion flue gas, where the partial pressure is about 0.13 bar.

- Thus, capacity is as important as selectivity for practical postcombustion CO2 separation processes.