CO₂-Binding Organic Liquids (CO₂BOLs) For Acid Gas Capture

David J. Heldebrant* Phillip K. Koech James E. Rainbolt Feng (Richard) Zheng Tricia Smurthwaite

Water Limits Aqueous Chemically-Selective CO₂ Absorption

- Solid CO₂ carriers (Carbamate and bicarbonate)
  - High hydrogen bonding
- Exogenous solvent to dissolve CO₂ carrier
- Highly corrosive
- Large Regeneration penalty
  - High specific heats
  - Large volumes of water needed
  - Dilution needed
- Amine chemistry limited to CO₂
  - Nucleophilic amines form heat stable salts with COS, SO₂ etc…
Avoid Water, Make it Organic…
Design The CO₂ Carrier to be a Liquid Salt

- CO₂BOLs are not conventional ionic liquids that either physically dissolve CO₂ or are chemically modified to chemically capture CO₂
- Switchable Ionic liquids discovered in 2004 with Dr. Phillip Jessop
- CO₂ acts as a chemical trigger with amidine bases and alcohols
- Alternatively switchable carbamates-Georgia Tech (Eckert and Liotta)
- Tunable physical and thermodynamic properties by changing components


CO₂BOLs vs. Aqueous Amines

- 7% by wt. and 108 g/L
- Chemically tolerant only for CO₂
- Stripping 121 °C
- Corrosive
- High specific heat
- Large volumes
- 20 % by wt. 147 g/L
- Chemically compatible for CO₂, COS, CS₂, SO₂
- Stripping as low as 25 °C, commonly 90 °C
- Less corrosive
- Low specific heat
- Smaller volumes

Amidine and Guanidine are non-nucleophilic bases with high boiling points

\[ \text{H}_3\text{C}-\text{N}^+\text{N}^-\text{N}^-\text{CH}_3 \quad \text{(Guanidine)} \]
\[ \text{H}_3\text{C}-\text{N}^+\text{N}^-\text{N}^-\text{CH}_3 \quad \text{(Resonance stabilized)} \]

\[ \text{H}_3\text{C}-\text{N}^+\text{N}^-\text{N}^-\text{CH}_3 \quad \text{(Amidine)} \]
\[ \text{H}_3\text{C}-\text{N}^+\text{N}^-\text{N}^-\text{CH}_3 \quad \text{(Resonance stabilized)} \]

### pKa’s of Alkylcarboxylic Acids Are Key

<table>
<thead>
<tr>
<th>Alkylcarboxylic acid</th>
<th>COSMO-RS</th>
<th>DBU</th>
<th>TMG</th>
<th>Ph-TMG</th>
<th>NEt\textsubscript{3}</th>
<th>Hünig’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{3}CO\textsubscript{2}H</td>
<td>18.3\textsuperscript{a}</td>
<td>24.3</td>
<td>25.3</td>
<td>20.3</td>
<td>18.8</td>
<td>18.6</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}CO\textsubscript{2}H</td>
<td>19.8</td>
<td>4.5</td>
<td>3.5</td>
<td>1</td>
<td>4</td>
<td>-1.2</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CO\textsubscript{2}H</td>
<td>19.7</td>
<td>4.6</td>
<td>3.6</td>
<td>1.1</td>
<td>4.9</td>
<td>-1.1</td>
</tr>
<tr>
<td>((\text{CH}_3)\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CO\textsubscript{2}H)</td>
<td>20.0\textsuperscript{b}</td>
<td>4.3</td>
<td>3.3</td>
<td>0.8</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>CH\textsubscript{3}(\text{CH}_2)\textsubscript{2}CO\textsubscript{2}H</td>
<td>19.7</td>
<td>4.6</td>
<td>3.6</td>
<td>1.1</td>
<td>4.9</td>
<td>-1.1</td>
</tr>
<tr>
<td>CH\textsubscript{3}(\text{CH}_2)\textsubscript{3}CO\textsubscript{2}H</td>
<td>19.7</td>
<td>4.6</td>
<td>3.6</td>
<td>1.1</td>
<td>4.9</td>
<td>-1.1</td>
</tr>
</tbody>
</table>

\(\Delta\text{pK}_\text{a} = \text{experimental pK}_\text{a}(\text{base}) - \text{computationally estimated pK}_\text{a}(\text{acid})\). In the case of the alkylcarboxylic acids, the average pKa value of correlations 1 and 2 (Table 1) was used.
Thermodynamics Are Tunable By Changing Base and Alcohol Components

First Generation
- DBU/Linear ROH: ΔH = -136 kJ/mol, ΔS = -425 J/mol, ΔG = -8.6 kJ/mol
- TMG/Linear ROH: ΔH = -180 kJ/mol, ΔS = -610 J/mol, ΔG = 1.7 kJ/mol
- Barton’s/Linear ROH: ΔH = -72 kJ/mol, ΔS = -210 J/mol, ΔG = -9.2 kJ/mol

Second Generation:
ΔH = -87.0 kJ/mol and ΔS = -293 J/mol, ΔG = 0 kJ/mol

K = \frac{[\text{baseH}][\text{ROCO}_2]}{[\text{PCO}_2][\text{base}][\text{ROH}]}$

K’ = \frac{[\text{TMG-OCO}_2]}{[\text{PCO}_2][\text{TMG-OH}]}$

Estimated Regeneration Energy

- CO₂BOLs
  - 16 wt.% CO₂ capacity
  - No stripping steam required for CO₂BOLs
  - Absorber
    - CO₂BOLs Tᵢn = 31°C (88°F)
  - Stripper
    - CO₂BOLs T = 90°C (194°F)

- 30 wt.% MEA
  - DOE/EPRI Case 7A
    - Coal fired supercritical steam plant with CO₂ removal and recovery (1000316)
  - Absorber
    - Tᵢn = 55°C (131°F)
  - Stripper
    - T_reboiler > 100°C

Total Regeneration Energy = Q_{\text{sensible}} + Q_{\text{reaction}} + Q_{\text{strip}}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ΔH_{\text{fan}} (kJ/mol CO₂)</th>
<th>ΔH_{\text{fan}} (kJ/kg CO₂)</th>
<th>Q_{\text{Sensible}} (kJ/kg CO₂)</th>
<th>Q_{\text{Reaction}} (kJ/kg CO₂)</th>
<th>Q_{\text{Strip}} (kJ/kg CO₂)</th>
<th>Total Regeneration Energy (kJ/kg CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBU-HexOH</td>
<td>-140</td>
<td>-3,182</td>
<td>502</td>
<td>3,182</td>
<td>-</td>
<td>3,684</td>
</tr>
<tr>
<td>TMG-BuOH</td>
<td>-180</td>
<td>-4,091</td>
<td>502</td>
<td>4,091</td>
<td>-</td>
<td>4,593</td>
</tr>
<tr>
<td>30 wt% MEA</td>
<td>-85</td>
<td>-1,932</td>
<td>4,069</td>
<td>1,918</td>
<td>1860</td>
<td>7,847</td>
</tr>
</tbody>
</table>
CO₂BOLs Under Investigation

- **Dual components**
  - separate base and alcohol
  - Amidinium or guanidinium alkylcarbonates
  - Uptake influenced by bulk polarity

- **Single components**
  - Conjoined alcohol and base
  - Zwitterionic alkylcarbonate
  - Uptake influenced by bulk polarity

Green Chem., 2010, 12, 713–721

Making 2nd Generation CO₂BOLs VOC-Free

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass Recovery After 10 Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dual component</td>
<td></td>
</tr>
<tr>
<td>TMG/ PrOH</td>
<td>0% H₂O</td>
</tr>
<tr>
<td></td>
<td>10% H₂O</td>
</tr>
<tr>
<td>TMG/ HexOH</td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td>17.2</td>
</tr>
<tr>
<td>t-Bu-TMG/ PrOH</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>36.6</td>
</tr>
<tr>
<td>t-Bu-TMG/ HexOH</td>
<td>48.2</td>
</tr>
<tr>
<td></td>
<td>56</td>
</tr>
<tr>
<td>Single component</td>
<td></td>
</tr>
<tr>
<td>DBU-(CH₂)₅-OH</td>
<td>95.6</td>
</tr>
<tr>
<td></td>
<td>92.6</td>
</tr>
<tr>
<td>DBU-(CH₂)₆-OH</td>
<td>95.1</td>
</tr>
<tr>
<td></td>
<td>98.7</td>
</tr>
<tr>
<td>DBU-CH(OH)-Bu</td>
<td>94.4</td>
</tr>
<tr>
<td></td>
<td>86.5</td>
</tr>
<tr>
<td>TMG-(CH₂)₆-OH</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>90.7</td>
</tr>
<tr>
<td>Me-DHI-(CH₂)₅-OH</td>
<td>95.6</td>
</tr>
<tr>
<td></td>
<td>96</td>
</tr>
<tr>
<td>Me-DHI-(CH₂)₆-OH</td>
<td>94.9</td>
</tr>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Pr-DHI-(CH₂)₆-OH</td>
<td>80.9</td>
</tr>
<tr>
<td></td>
<td>74.4</td>
</tr>
</tbody>
</table>

- **Dual-component CO₂BOLs are high-boiling but still volatile due to vapor pressure**
- **Single-component CO₂BOLs are less-volatile and estimated to have a small vapor pressure**

*This material was not analyzed with 10 mol% H₂O. 10 cycles absorption (50 psi) / desorption (85 °C)*
**Chemical Tolerance To Water**

Water can react in place of alcohols in CO\textsubscript{2}BOLs making a more thermodynamically stable bicarbonate salt.

Water is in direct competition with alcohol but can be diluted out.

---

**Performance With and Without Water**

<table>
<thead>
<tr>
<th>Dual component</th>
<th>Anhydrous Avg CO\textsubscript{2} wt. %</th>
<th>10 mol % H\textsubscript{2}O Avg CO\textsubscript{2} wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 TMG/ PrOH</td>
<td>25.5</td>
<td>25.7</td>
</tr>
<tr>
<td>2 TMG/ HexOH</td>
<td>17.1</td>
<td>15.2</td>
</tr>
<tr>
<td>3 t-Bu-TMG/ PrOH</td>
<td>12.2</td>
<td>5.9</td>
</tr>
<tr>
<td>4 t-Bu-TMG/ HexOH</td>
<td>11.8</td>
<td>9.4</td>
</tr>
</tbody>
</table>

**Single component**

<table>
<thead>
<tr>
<th>Single component</th>
<th>Anhydrous Avg CO\textsubscript{2} wt. %</th>
<th>10 mol % H\textsubscript{2}O Avg CO\textsubscript{2} wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 DBU-(CH\textsubscript{2})\textsubscript{2}-OH</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>6 DBU-(CH\textsubscript{2})\textsubscript{3}-OH</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>7 DBU-CH(OH)-Pr</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>8 TMG-(CH\textsubscript{2})\textsubscript{3}-OH</td>
<td>5.6</td>
<td>6.4</td>
</tr>
<tr>
<td>9 Me-DHI-(CH\textsubscript{2})\textsubscript{2}-OH</td>
<td>8</td>
<td>7.4</td>
</tr>
<tr>
<td>10 Me-DHI-(CH\textsubscript{2})\textsubscript{2}-OH</td>
<td>9.2</td>
<td>--</td>
</tr>
<tr>
<td>11 Pr-DHI-(CH\textsubscript{2})\textsubscript{2}-OH</td>
<td>6.1</td>
<td>7.9</td>
</tr>
</tbody>
</table>

10 cycles absorption (50 psi) /desorption (85 °C)
Chemical Tolerance to COS, CS₂, SO₂

*Thermally reversible liquid alkylcarbonate, alkylthiocarbonate, alkylxanthate and alkylsulfite anions

Weight Capacities @ S.T.P.
20% CO₂, 19% COS, 23% CS₂, 43% SO₂


2nd Generation SO₂BOLs Are Potential FGD Replacements

1-(N,N-Di-n-butylamino)-1-undecanol (DBUA)

► Selective for SO₂
► 43% by weight SO₂ at STP
► Non-volatile
► Inexpensive
► 5 cycles of capture and release of SO₂ With no loss in activity
► Stripping of SO₂ at 70 °C (compare to CANSOLV at 160 °C)
► Possible pretreatment to decant water upstream to CO₂BOLs

Energy Environ. Sci., 2010, 3, 111–113
**Highlights**

- CO$_2$BOLs are chemically selective for acid gas capture without the limitations of water
  - Low specific heat
  - High weight capacities for each acid gas
  - Tunable thermodynamics and physical properties

- Post-combustion
  - Captures acid gases selectively at < 1 ATM
  - Compatible with CO$_2$, COS and SO$_2$
  - Chemically tolerant to water
  - Non-volatile

- Desulfurization
  - SO$_2$BOLs can capture up to 3 equivalents of SO$_2$ selectively over CO$_2$
  - Potential FGD replacement
  - Potential water decanting pre treatment for CO$_2$BOL

**Future Work**

- Isotherms for 2nd generation materials
- Continuous flow testing on pure gas streams using wetted wall contactors
- Integrated SO$_2$ and CO$_2$ removal

**Acknowledgment**

**Funding:** PNNL Energy Conversion Initiative

- John C. Linehan (PNNL)
- Lam Phan (Queen’s University)

- Philip Jessop (Queen’s University)
- Ivo Leito & Merit Oss (Tarto University)
- Mark Bearden & Corrine Valkenburg (PNNL)
Supplementary Slides

CO₂BOL Physical Properties

*All specific Heats below 2 J g⁻¹ K⁻¹
- H₂O = 4 J g⁻¹ K⁻¹
- MEA = 3.7 J g⁻¹ K⁻¹

CO₂ loading:
- 0% = 8.4 cP
- 100% = 3000 cP

*Operating at 100% capacity is undesired for 1:1:1 (Base, ROH, CO₂)
  Operating envelope is below 90% capacity

*Viscosity can be modified using less viscous components,
  slight excess alcohol
Removal of acid gases from 1-hexanol and varied bases at 140 °C. Heating begins at 1 min.