Reversible Ionic Liquids as Double-Action Solvents for Efficient CO$_2$ Capture

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School of Chemistry and Biochemistry
Georgia Tech, Atlanta
Chemical Engineering and Chemistry
20-Year Collaboration at Georgia Tech

- Jointly Directed Students and Postdoctorals
  - Chemical Engineers
  - Chemists
  - > 50 PhDs Completed
- >50 Joint Research Grants
- >250 Publications and Presentations
- 2004 Presidential Green Chemistry Challenge Award
Project Goal – CO$_2$ Capture from Coal Fired Power Plants

• Long Term Goal
  ✓ Capture 90% of CO$_2$ with no more than a 35% increase in cost by 2020

• What We Seek to Contribute
  ✓ Novel Solvent for Absorption/Release of CO$_2$
  ✓ Design reversible ionic liquid with optimal physical and chemical properties
# Funding – $ in Thousands

*By Budget Period (BP), DOE and Cost Share*

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Overall Project Performance Dates

- Management, Planning, Reporting, 10/08-9/11
- 1-Comp. Silyl Amine-Based ILs, 10/08-6/10
- 1-Comp. Silyl Guanidine-Based ILs, 10/08-3/11
- Thermodynamics of IL Formation & CO$_2$ Reaction Rates, 7/09-6/11
- Optimize CO$_2$ Capture Solvent Structure, 10/09-9/11
- Process Design & Economic Analysis, 10/09-9/11
Project Participants

- Chemical Engineers and Chemists Supported on This Grant
  - Faculty – Charles Eckert, Charles Liotta
  - Postdocs – James Dong, Eduardo Vyhmeister
  - PhD Students – Ryan Hart, Kyle Flack, Ali Fadhel, Olga Dzenis
  - Undergraduate – Melissa Burlager

- Other Contributors
  - Postdocs – Pamela Pollet, Veronica Llopis Mestre
  - PhD Students – Tori Blasucci
  - Undergraduates – Sarah Lencenski, Katie Croft
**Background: Reversible Ionic Liquids – Amidine Absorbs and Releases CO₂**

\[
\text{DBU} (1,8\text{-diazabicyclo-[5.4.0]-undec-7-ene})
\]

- Absorbs CO₂ with Alcohol at Ambient T
- Releases CO₂ with Inert Gas Sparge or at Higher T
- All Done at Ambient Pressure – No High Pressure
- Many Other Examples

Turning the RevIL “On” = CO₂ Capture, and “Off” = CO₂ Release

![Graph showing conductivity over cycles with arrows indicating CO₂ bubble and heat release.](image)
Process Flow Diagram for Typical Solvent CO$_2$ Scrubbing System

- **Scrubbed Gas**
- **CO$_2$ Product Gas**
- **Flue Gas**
- **CO$_2$-Rich Solvent**
- **CO$_2$-Lean Solvent**
- **Absorber**
- **Stripper**

Heat Exchanger

Temperatures:
- $T_{low}$
- $T_{high}$
Common Mechanisms for CO₂ Capture

• **Chemical Absorption**
  - Chemical Reaction Affords Capture
  - High Efficiency
  - Thermally Driven Process
  - Large Heat for Regeneration
  - Thoroughly Researched
  - Proven Technology

• **Physical Absorption**
  - van der Waals Forces Give Separation
  - High Capacities and Selectivities Reported
  - Pressure Driven (Typically)
  - Low Heat for Regeneration
  - Economically Unfeasible
  - Not Effective…Alone
Limitations of 2-Component RevILs

• Too Complex
  ✓ Must Control Stoichiometry
• Light Alcohol will Evaporate with CO$_2$
• Heavy Alcohol Has Too Much Heat Capacity
• Too Hard to Control
• Large Energy Penalty
This Project: Develop and Apply A One-Component Reversible Ionic Liquid

Molecular Liquid $\xleftrightarrow{\pm \text{CO}_2}$ One-Component Ionic Liquid

\[
\begin{align*}
R & \quad Si \quad R \\
& \quad NH_2
\end{align*}
\]

\[
\begin{align*}
R & \quad Si \quad R \\
& \quad NH_3 \quad O \quad CO \quad O \\
& \quad R \quad R \quad R \quad R \quad R
\end{align*}
\]
1-Component Silyl RevILs: Advantages

- **Use Both Mechanisms**
  - ✔ Chemical Absorption – Reaction with RevILs
  - ✔ Physical Absorption – Dissolution in RevILs

- **Designer Solvents**
  - ✔ Modify Structure to Optimize Properties
  - ✔ Silylation Decreases Viscosity
  - ✔ Functions in Presence of Water

- **Increased Capacity, Less Energy Penalty**
1-Component Silyl RevILs: Challenges

- Design, Synthesize, and Characterize New Compounds
- Achieve Optimal Equilibria and Heats
- Achieve Rapid Reaction Rates
- Achieve Favorable Transport Rates
- Achieve Synergy of Results for New Process to Meet DOE Goals
## Project Objectives and Timing: Milestones

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<tr>
<th>Milestone/Title</th>
<th>Finish</th>
<th>Verification Method</th>
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<tr>
<td>A Complete Project Management Plan</td>
<td>10/1/08</td>
<td>PMP approved by DOE COR</td>
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<td>B, C, D, E One 1-Comp. Silyl RevILs</td>
<td>6/30/09 – 6/30/10</td>
<td>Successful Synthesis and Characterization</td>
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<td>F, G, H, I Thermo &amp; Rates of RevIL Formation</td>
<td>9/30/10 – 6/30/11</td>
<td>Successful Measurements</td>
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<td>J, K Optimize CO₂ Capture Solvent Structure</td>
<td>9/30/11</td>
<td>Optimal Solvent Identified and Produced</td>
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<tr>
<td>L Process Design and Economic Analysis</td>
<td>9/30/11</td>
<td>Design and Scaleup Completed</td>
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<tr>
<td>M Write Final Report</td>
<td>9/30/11</td>
<td>Final Report Submitted</td>
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Project Methodology

• Synthesis and Characterization of Novel Compounds
  ✓ 1-Comp. Silyl Amine-Based ILs
  ✓ 1-Comp. Silyl Guanidine-Based ILs
• Thermodynamics of IL Formation with CO$_2$
• Rates of Uptake/Release
• Optimize Solvent Structure for CO$_2$ Capture
• Process Design & Economic Analysis
Synthesis and Characterization of Novel Compounds -- Hydrosilation

- Synthesis of custom-made silylated amines precursors

\[
\begin{align*}
\text{R} & \quad \text{Si} & \quad \text{H} & \quad + \quad \text{NH}_2
\end{align*}
\]

\[
\begin{align*}
\stackrel{\text{DVDS-Pt}}{\longrightarrow}
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{Si} & \quad \text{NH}_2 \\
\text{R} & \quad \text{R}
\end{align*}
\]

R=Et, Pr, iPr, Hexyl etc…

- Characterized by \(^1\text{H}, ^{13}\text{C}\) NMR, Elemental Analysis, Mass Spectroscopy, DSC, TGA

DVDS-Pt: Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane
DSC Results for Reversal of Silylated One-Component RevIL

- **RevIL TESAC**
- **CO₂ removal**: 108°C
- **Molecular TESA Decomposition**: 237°C
Thermodynamics of IL Formation with CO$_2$ – What Do We Want?

- Low Heat Requirement for Regeneration
- Favorable Equilibrium at $T_{\text{low}}$ for Capture
- Favorable Equilibrium at $T_{\text{high}}$ for Release
- $T_{\text{low}}$ and $T_{\text{high}}$ as Close as Possible
  ✓ Reduces Losses in Cycling Solvent
  ✓ BUT, True only if High Heat of Regeneration
- **Bottom Line:** Optimize and Engineer
Assay Both Thermodynamics and Rates with Single-Pass Diamond ATR IR Cell

• Ample Adsorption in Single Pass
• Custom Cell, Small Volume – No Transport Limitations
• Temperature-Controlled
• Rapid and Accurate
Interface Structure with Properties (1)

- **Goal:** Optimize Thermodynamics and Kinetics for CO$_2$ Capture and Release
- **Systematic Modification Of Molecular Structure**
  - ✓ Adjust Basicity of Amine Functionality with Electron-donating and Withdrawing Substituents
  - ✓ Adjust Substituents Attached to the Silyl Group
  - ✓ Adjust Steric Environment Proximate to the Amine and to the Silyl Groups
  - ✓ Adjust the Length and Branching of the Carbon Chain Connecting the Amine to the Silyl Site
Interface Structure with Properties (2)

- New RevILs: Assay Effect on Properties
  - Measure Equilibrium Constant
  - Measure Heat of Reaction
  - Measure Rates of Reactions
  - Measure Transport Properties (Viscosity)
- Determine Key Structural Characteristics
  - (H-bond Donating/Accepting etc.)
- Synthesize Next Generation of RevILs
- Repeat Assay
Multifaceted Approach: Discovery and Use

- Synthesis of Amine Precursors
  - Investigation of Physical Properties
  - Thermodynamic Properties
  - New Molecule Characterization
  - Structure-Property Analysis and Simulation
  - Design and Application to Coal-Fired Power Plants
Final Process Optimization

- Solvent with Optimum Balance of Properties
  - Synthesize and Characterize
  - Use in Process Design
  - Determine Best by Energy, Economics
- Optimum Solvent
  - Demonstrate on Lab Scale
  - Design Pilot Scale Process
  - Develop Scalable Process for Synthesis
- **Bottom Line:** Superior Process for CO₂ Capture from Coal-Fired Power Plants
Economic Evaluation – Path Forward

- Setup complete process diagram
- Important variables
  - ✔ Input compounds/models
  - ✔ Setup general reaction in absorber
- Use to calculate targets
- Evaluate compounds synthesized in lab
  - ✔ Information communicated through website, http://www.chbe.gatech.edu/eckert/doeindex.html
Plans for Future Testing, Development, and Commercialization

• Seek Other Chemistries to Modify RevILs
• Assay SO$_2$ Removal with RevILs
• Work with Industrial Partner AMPAC on Scaleup/Production of RevILs
• Test New Solvent in Pilot Scale Facility
  ✓ Perhaps Existing Amine Scrubbing Unit
• Initiate Dialogs with Power Companies to Implement CO$_2$ Absorption by RevILs
Extra Slides for Questions

• Current Financial Figures
  ✓ DOE Funds, Cost Share Funds
• Traditional Ionic Liquids as Solvents
• CO₂ Capture by Absorption in ILs
• Dynamics of Ionic Liquid Formation
• Thermodynamic Relationships
• ASPEN Flow Sheet for Process
• Viscosity of RevILs
Current Financial Figures
Federal Funds

- Expended
  ✓ Pers. Services  72517
  ✓ Fringe  11829
  ✓ M&S  6740
  ✓ Travel  791
  ✓ Tuition  7488
- Direct, total  99365
- Indirect  46857
- Total To Date  146222

- Encumbered
  ✓ Pers. Services  34385
  ✓ Fringe  5446
  ✓ M&S  4290
  ✓ Travel  886
  ✓ Tuition  3744
- Direct, total  48751
- Indirect  22953
- Total To Date  71704
Current Financial Figures
Matching Funds

- Expended
  - Eckert 12379
  - Liotta 10832
  - Equipment 19649
- Total 42860

- Encumbered
  - Eckert 6266
  - Liotta 5416
  - Equipment 49072
- Total 60754
**Background:**
*Traditional Ionic Liquids as Solvents*

- Low-Melting Salts
  - Touted as “Green”
  - “Zero” Vapor Pressure, No Solvent Losses
- Many Organic Reactions Run Successfully
- Can Dissolve Gaseous CO₂
- Separation of Products are Challenging
- Many ILs are Expensive and/or Toxic
CO₂ Capture by Absorption in ILs

DOE, "Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO₂ Capture," Brennecke, Maginn and Schneider

CO₂ Solubility in [bmim]⁺-Based ILs at 333°K
Dynamics of Ionic Liquid Formation

\[ \nu_{\text{as}(\text{C=O})} \]
\[ \nu_{\text{s}(\text{C-H})} \]
\[ \nu_{\text{as}(\text{O=C=O})} \]

\[ \nu_{\text{(C=O)}} \]

\[ \nu_{\text{(O-H)}} \]

Carbonate
Alcohol

\[ \nu_{\text{as}(\text{C-H})} \]

Abs (A.U.)

\( \nu (\text{cm}^{-1}) \)

No CO2
20 bar (initial)
20 bar (10 min.)
20 bar (equil.)
**Thermodynamic Relationships**

Equilibrium Constant: \[ K = \frac{\text{conc}_{\text{IonicLiquid}}}{P_{CO_2} \cdot \text{conc}_{\text{TMBG}} \cdot \text{conc}_{\text{Alcohol}}} \]

Heat of Adsorption: \[ \frac{d(\ln K)}{dT} = \frac{\Delta H^{abs}}{RT^2} \]
The MEA Process: An Energy Hog

• Computer Simulation
  ✓ Flue Gas from 350 MW PC Plant
  ✓ Gives 90% Recovery
  ✓ Yields 95% CO₂ Product Stream

• Bottom Line: Solvent Regeneration
  Accounts for About 2/3 of Operating Costs
ASPEN Flow Sheet for Process

- Industry Standard Design Software
- Permits Process Alternatives, Optimization
Viscosity of RevILs

- Viscosity = Fluid Resistance To Flow
  - Higher Resistance → More Pump Power → Higher Energy Costs

- Viscosity = \( f \) (Size, Coordination Ability)
  - Smaller Ions Tend To Form Ion Pairs
  - More Coordination → More Ion Pairs → Higher Viscosity

Hydrodynamic radii of ions
Minimizing Viscosity of RevILs

• However, Minimizing Coordination Ability Requires Larger Ions
  ✔ ↑ Ion Size ↑ Viscosity

• Trade-off In Controlling Viscosity
  ✔ Between Ion Size And Coordination Ability

• Bottom Line: Find Optimal Balance
  ✔ Synthesize Relatively Small AND Weakly Coordinated Ions For The RevILs
  ✔ Effective CO₂ Capture; Minimum Pumping