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

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Chemical Engineering and Chemistry
Two Decades of Collaboration

• Jointly Directed PhD Students and Postdoctorals
  ✓ Chemical Engineers
  ✓ Chemists
  ✓ > 50 Completed
• >50 Joint Research Grants
• >250 Publications and Presentations
• 2004 Presidential Green Chemistry Challenge Award
Outline of Presentation

• Introduction – the Need for CO$_2$ Capture
• Background – Existing Reversible Two-Component Ionic Liquids (RevILs)
• Path Forward – The Upcoming Project
  ✓ Synthesize and Characterization of New Single-Component RevILs
  ✓ Determine Reaction Thermodynamics and Rates
  ✓ Optimize CO$_2$ Capture Solvent Structure
  ✓ Process Design and Economic Analysis
Electricity Generation from Coal Expected to Rise

• Summary of U.S. Electricity Generation:

- 2003 - 3.662 trillion kWhrs

- 2030 - 5.5 trillion kWhrs (projected)
Coal Combustion is the Leading Contributor to CO$_2$ Emissions in U.S.

Wyodak 500 MW PC Power Plant – Gillette, WY

- 2003 CO$_2$ Emissions - 6300 Mt: 1/3 from coal
Power Plant Flue Gas:
A Technically Challenging Feed Stream

- 350 MW PC power plant flue gas characteristics:
  - Temp = 185°C
  - Flow = 78 MMscf/hr
  - CO₂ = 6000 t/day

- Must Produce a High Purity Product Stream
Basis for Comparison: Monoethanolamine (MEA)

- MEA uses chemical absorption
  - Similar process design
- Well researched, proven
- Problem:
  - Dilute solvent streams
  - High operating costs
- Can validate simulation
- Provides efficiency and economic targets

NewPoint Gas MEA Process
The MEA Process: An Energy Hog

- Computer Simulation
  - ✔ Flue Gas from 350 MW PC Plant
  - ✔ Gives 90% Recovery
  - ✔ Yields 95% CO$_2$ Product Stream

- Bottom Line: Solvent Regeneration Accounts for About 2/3 of Operating Costs
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
CO$_2$ Capture by Absorption in ILs
DOE, "Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO$_2$ Capture," Brennecke, Maginn and Schneider

CO$_2$ Solubility in [bmim]$^+$-Based ILs at 333ºK
Mechanisms for CO$_2$ 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
The Path to Dual-Mechanism Capture: Two-Component RevILs

$\text{CO}_2$ (1 atm.) Acts as “Switch”

Guanidine-Based RevIL

$\text{CO}_2 (1 \text{ atm.})$ Acts as “Switch”

- TMBG (tetramethyl-butyl guanidine)

Turning the RevIL “On” and “Off”

- Equimolar methanol/TMBG diluted in chloroform
Thermodynamic Relationships

Chemical Reaction:

\[
\text{N-N} + \text{R-OH} + \text{CO}_2 \leftrightarrow \text{R-H} + \text{O-CO}_2\text{OR}
\]

Equilibrium Constant:

\[
K = \frac{\text{concentration}_{\text{IonicLiquid}}}{P_{\text{CO}_2} \times \text{concentration}_{\text{TMBG}} \times \text{concentration}_{\text{Alcohol}}}
\]

Heat of Adsorption:

\[
\frac{d(\ln K)}{dT} = \frac{\Delta H_{\text{abs}}}{RT^2}
\]
Thermodynamics – 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 to Each Other as Possible
  - Reduces Losses in Cycling Solvent
  - BUT, true only for High Heat of Regeneration
- Bottom Line: Optimize and Engineer
Preliminary Thermo Measurements

- High-pressure ATR-FTIR cell
  - Attenuated Total Reflection
  - IR reflected from sample surface
  - Pathlength: ~ a few μm

![Diagram of ATR-FTIR cell with ZnSe Crystal]
Dynamics of RevIL Formation

![Graph showing dynamics of RevIL Formation](image)
Reaction of $CO_2 +$ Alcohol Results in Formation of a Carbonyl
Phases of New DOE Project

- Synthesize and Characterize Single-Component Silyl RevILs
  - Amine-Based and Guanidine-Based
  - Structure/Property Relationships
    - Both Empirical and Theoretical
  - Directed Design of Molecules for CO₂ Capture
- Thermodynamics, Rates of RevIL Formation
- Optimize CO₂ Capture Solvent Structure
- Process Design and Economic Analysis
Limitations of 2-Component RevILs

• Too Complex
  ✓ Must Control Stoichiometry
• Light Alcohol will Evaporate with CO₂
• Heavy Alcohol Has Too Much Heat Capacity
• Too Hard to Control
• Too Much Energy Penalty
Synthesize and Characterize Single-Component RevILs

- Example Based on Guanidine Molecule
Synthesize and Characterize Single-Component Silyl RevILs

- Example Based on Silylated Amine
- Structures are Completely Adjustable
- Eliminates Need for Alcohol
Synthesize and Characterize Single-Component Silyl RevILs

- Example Based on Silylated Guanidine
- Structures are Completely Adjustable
- Eliminates Need for Alcohol

![Chemical Structure](image)
Must Choose Chemistry That Works Well in Presence of Water

- Also Example Based on Silylated Amine
- Change Alkoxy Group to Alkane Group
Single-Component Silyl RevILs

- Our Designer Solvents Use Both Mechanisms
- Chemical Absorption
  - By Reaction of CO$_2$ with RevILs
- Physical Absorption
  - By Dissolution of CO$_2$ in RevILs
- Increases Capacity
  - Better Separation with Less Energy Penalty
Interface Structure with Properties

- Measure Equilibrium and Heat of Reaction
- Use Structure/Property Methods to Upgrade
  - ✓ Empirical Methods
  - ✓ Theoretical Methods
- Synthesize Next Generation of RevILs
  - ✓ Improved Properties
- Repeat
Thermodynamics and Rates

• Use Single-Pass Diamond Cell
• Effect of Structure
  ✓ On Chemical Equilibrium
  ✓ On Heat of Reaction
  ✓ On Rates
• Effect of Temperature
• Effect of CO$_2$ Pressure
• Effect of Water
Single-Pass Diamond ATR IR Cell

- Ample Adsorption in Single Pass
- Small Volume – No Transport Limitations
- Temperature-Controlled
- Rapid and Accurate
Sample Cell for ATR on RevILs

- Ease of Assembly, Operation
- Low Volume, High Surface RevIL
- Facile Flow of CO₂
But What About Viscosity?

- Viscosity of ILs Can be Quite High
- Rate of Transport of CO\(_2\) Will Depend on Viscosity
- But, Viscosity Can Be Greatly Reduced
Viscosity Change for RevIL Formation is Highly Nonlinear

Increasing Viscosity → Increasing Conversion → Molecular Liquid Viscosity

Ionic Liquid Viscosity
Dealing with Liquid Viscosity

- RevIL Viscosity Can Be Greatly Reduced
- Viscosity Change vs. Conversion is Nonlinear
  - Viscosity High Only for >95% Conversion
- Impurities Cut Viscosity Drastically
  - Water, Dissolved Gases
- Silylation Reduces Viscosity
- Goal: Viscosity not a Barrier to Transport
Path Forward: Economics and Design

- Existing MEA Design As Initial Template
- Optimal Solvent Candidate
- Measured Thermodynamics and Rate Data
- Optimize Processing Conditions
- Determine Economic Viability Of Process
Process Flow Diagram for Typical Solvent CO₂ Scrubbing System
Energy Requirements

• Energy Removed
  ✓ Heat of Adsorption of CO$_2$
  ✓ Cooling of Exit Stream

• Energy Added
  ✓ Head of Desorption of CO$_2$
  ✓ Makeup for Losses in Heat Transfer
ASPEN Flow Sheet for Process

- Industry Standard Design Software
- Permits Process Alternatives, Optimization
- Calculates Flows, Rates, Energy, Economics
Structure/Property Relationships

• Empirical Examples: Hammett Equation, Kamlet-Taft
• Goal: Effect of Structure on Properties
• Change Structure
  ✓ Substituent Groups
  ✓ Chain Length
• Assay Effect on Properties
  ✓ Equilibrium Constants
  ✓ Heat of Reaction
  ✓ Transport – i.e. Viscosity
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
Additional Benefits of Project

• Education
  ✓ Postdoctoral Students, PhDs, BS Students
  ✓ Chemical Engineering and Chemistry
  ✓ Technical Skills Related to Energy Issues
  ✓ Critical Thinking About Energy Issues

• Other Potential Applications
  ✓ CO$_2$ Capture from Combustion
    ➢ Other Fossil Fuels
    ➢ Biofuels
  ✓ CO$_2$ Capture from Fermentation