DOE Project NT0005287

Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture

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Chemical Engineering and Chemistry 22-Year Collaboration at Georgia Tech

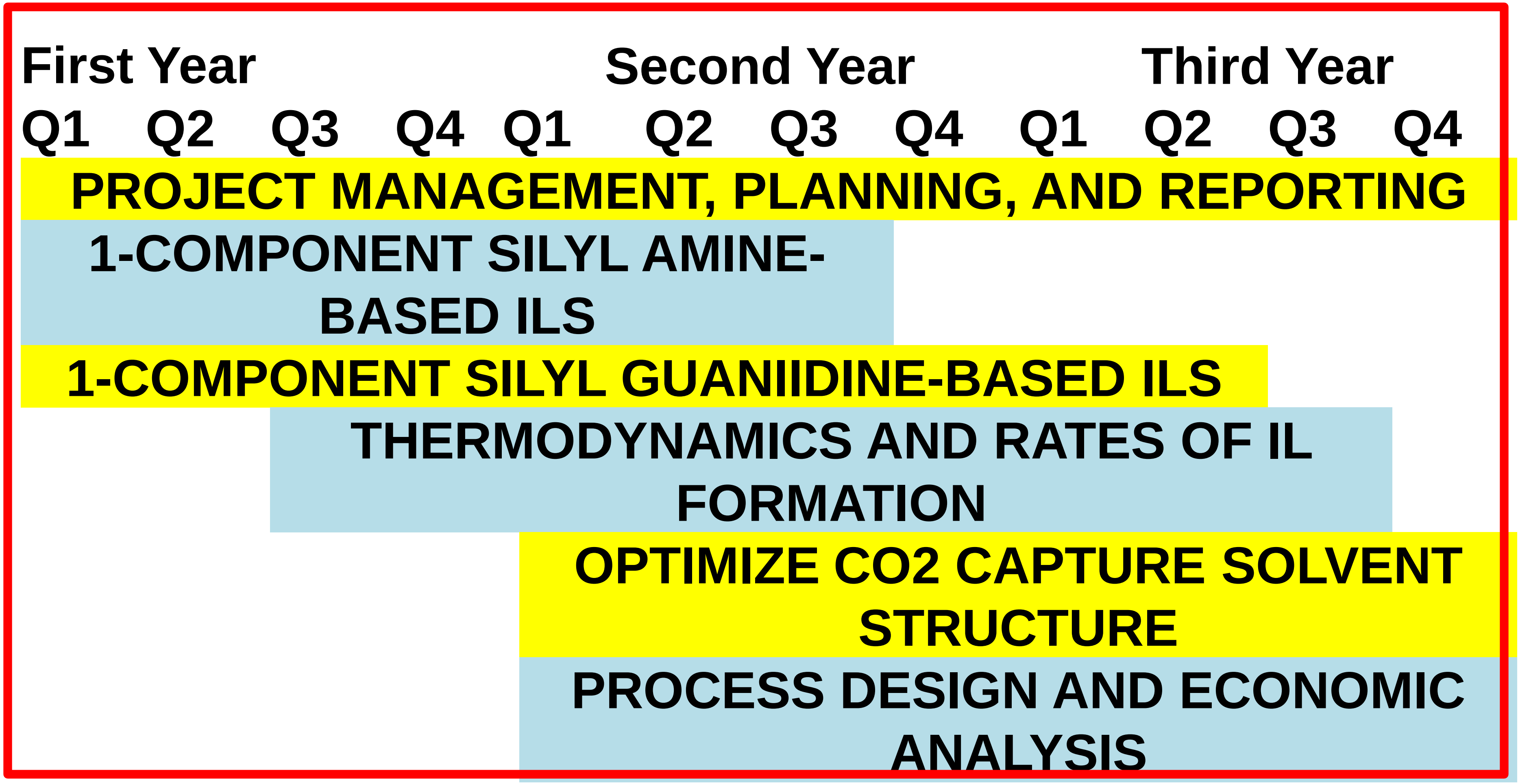
- Jointly Directed Students and Postdoctorals
  - ✓Chemical Engineers
  - ✓Chemists
  - ✓> 50 PhDs Completed
- >50 Joint Research Grants
- >250 Publications and Presentations
- **2004 Presidential Green Chemistry Challenge Award**

Funding – $ in Thousands

By Budget Period, DOE and Cost Share

Expenditure	BP1 DOE	BP1 Share	BP2 DOE	BP2 Share	BP3 DOE	BP3 Share	Total DOE	Total Share
Personnel	372	92	417	101	434	87	1251	263
Equipment	92	62		120				150
Supplies	30		76		75		228	
Services	21		38		38		114	
Travel	9		9		9		27	
TOTAL	524	154	540	221	556	87	1620	462
Share %		23		29		14		22

Overall Project Performance Dates



Project Participants

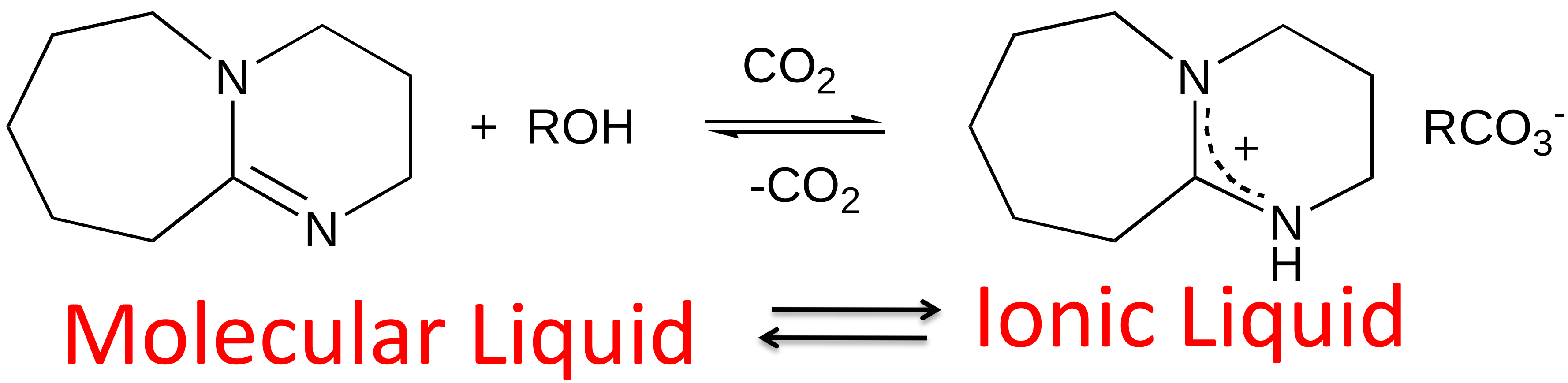
- Chemical Engineers and Chemists Supported on this Grant
  - ✓Faculty – Charles Eckert, Charles Liotta
  - ✓Postdocs – Elizabeth Biddinger, Manish Talreja, Manjusha Verma
  - ✓PhD Students – Olga Dzenis, Ryan Hart, Gregory Marus, Amy Rohan, Emily Nixon
  - ✓Undergraduate – Melissa Burlager
- Other Contributors
  - ✓Research Scientist – Pamela Pollet
  - ✓PhD Students – Kyle Flack, Jackson Switzer
  - ✓Undergraduates – Sean Faltermeier, Paul Nielson

Project Goal: CO_2 from Coal-Fired Power Plants

- Long-Term Goal
  - ✓ Capture 90% of CO_2 with less than 30% cost increase by 2020
- This Project
  - ✓ **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, Scalable Process for Synthesis
- **Bottom Line:** Superior Process for Post-Combustion CO_2 Capture from Coal-Fired Power Plants

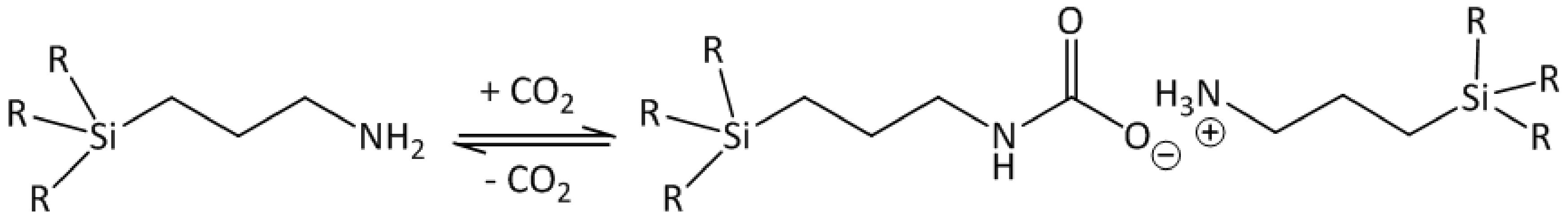
Scientific Background: First Reversible Ionic Liquid (RevIL) – Amidine Absorbs and Releases CO_2

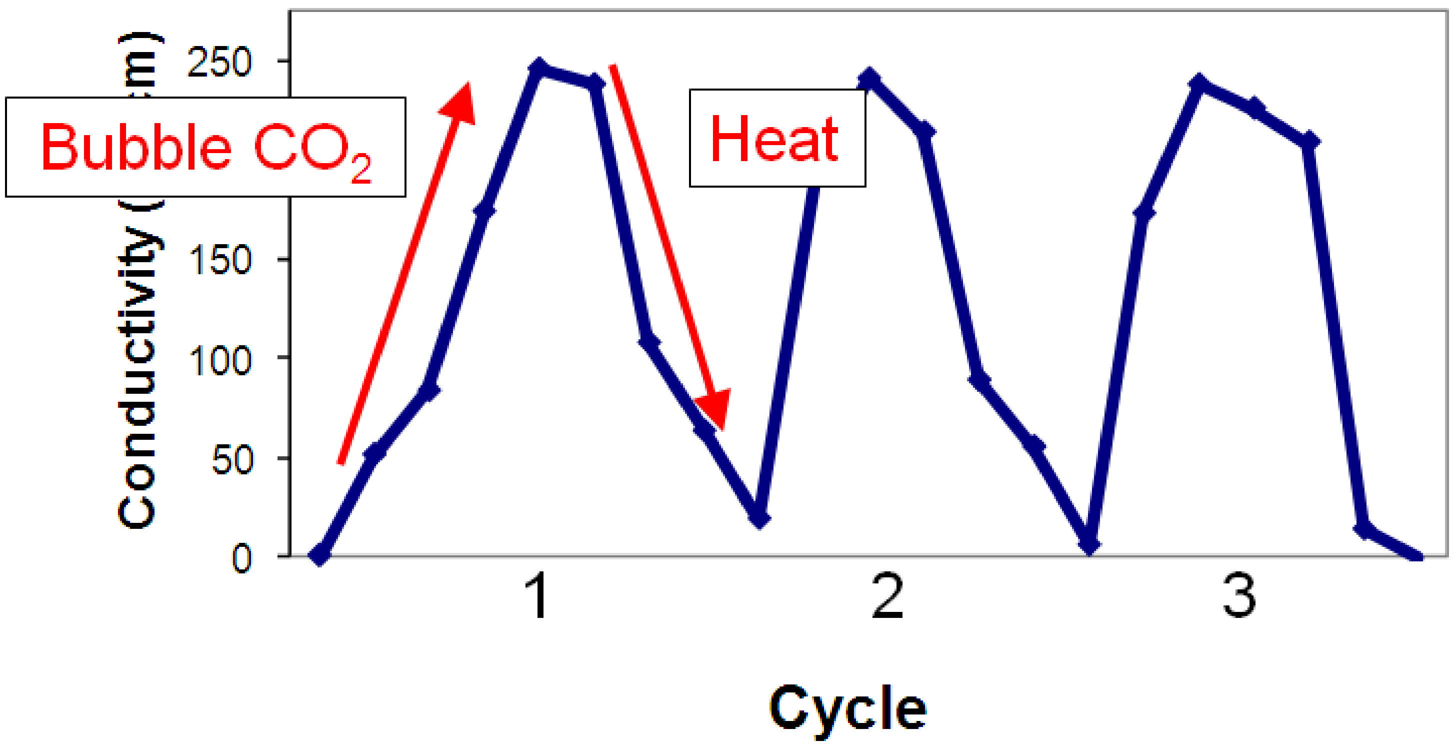
- DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene)
  - ✓ Absorbs CO_2 with Alcohol at Ambient T
  - ✓ Releases CO_2 with Inert Gas Sparge or at Higher T
  - ✓ All Done at Ambient Pressure – No High Pressure
  - ✓ Many Other Examples



Jessop, Heldebrant, Li, Eckert, Liotta, *Nature* **2005**, *436*, 1102.

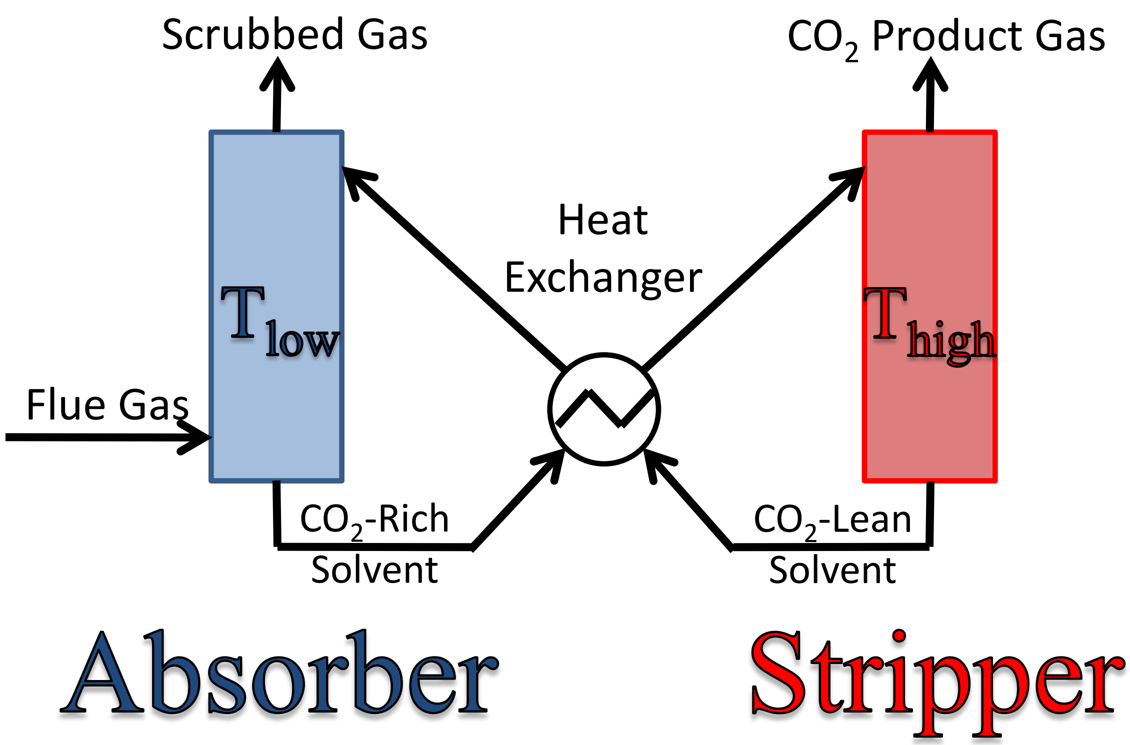
Silyl Amines: Superior Performance





Advantages of RevILs for CO_2 Capture

Typical Conditions: P = Ambient, T_{low} = 40-50 C. T_{high} = 70-100 C



Heat Energy

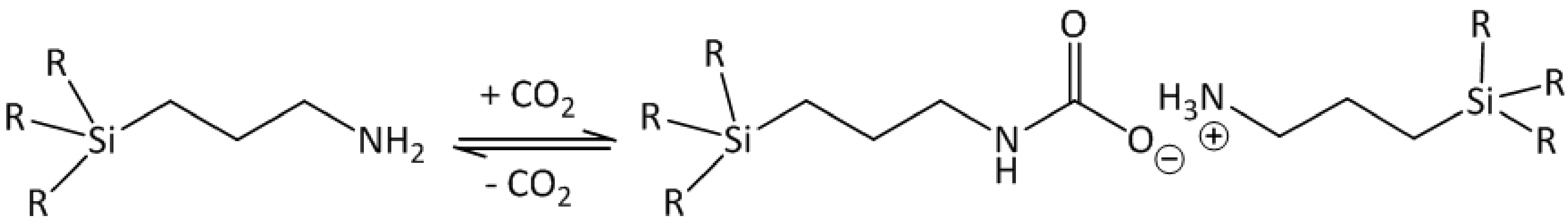
$Q = mCp\Delta T + \Delta H_{rxn}$ (regen.)

Cost Savings

1. Minimize solvent and energy needs
2. Optimize ΔT and ΔH_{rxn}
3. Optimize both physisorption and chemisorption

Utilizing a Dual Capture Mechanism

Highly Selective **Chemical Absorption**



Molecular Liquid $\underset{-CO_2}{\overset{+CO_2}{\rightleftharpoons}}$ Ionic Liquid

Added Capacity By **Physical Absorption**

Ionic Liquid $\underset{-CO_2}{\overset{+CO_2}{\rightleftharpoons}}$ CO_2 Swollen Ionic Liquid

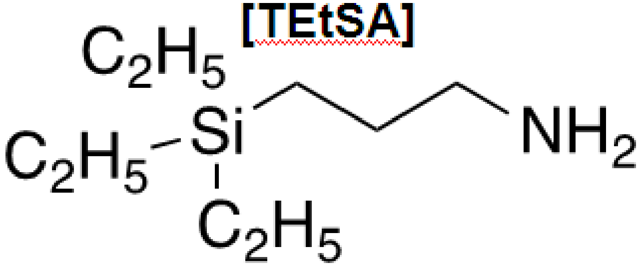
Technical and Economic Challenges

- Optimize Solvent Structure
  - ✓Capacity – Maximize Both Capacities
  - ✓Uptake/Release – Optimize ΔT and ΔH_{rxn}
- Minimize Solvent Cost/Losses
  - ✓Scaleup for Effective Manufacture
- Eliminate Transport Limitations
  - ✓Both Mass and Heat
  - ✓Control Viscosity

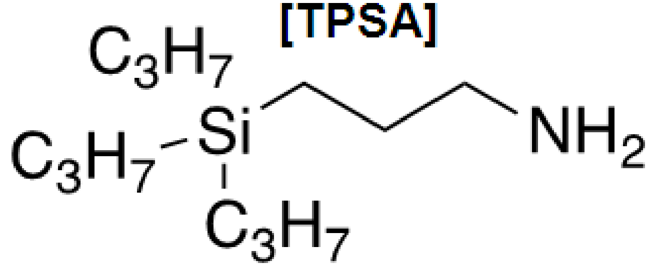
Typical Silyl Amines Studied

- Effects of Silylation
  - ✓Easier Synthesis. Structure is Easily Modified
  - ✓Superior Capacity and Lower Viscosity

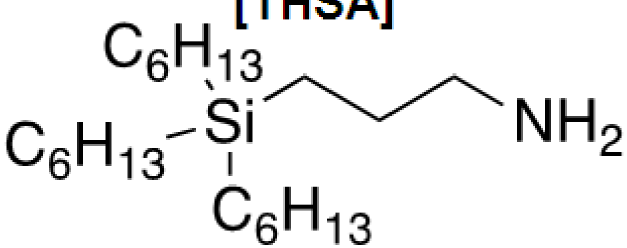
(3-aminopropyl)triethylsilane [TEtSA]



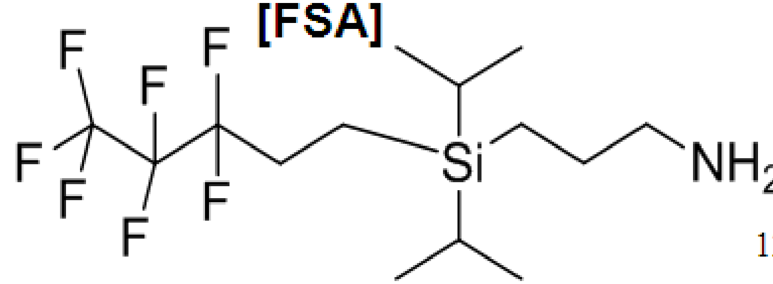
(3-aminopropyl)tripropylsilane [TPSA]



(3-aminopropyl)trihexylsilane [THSA]



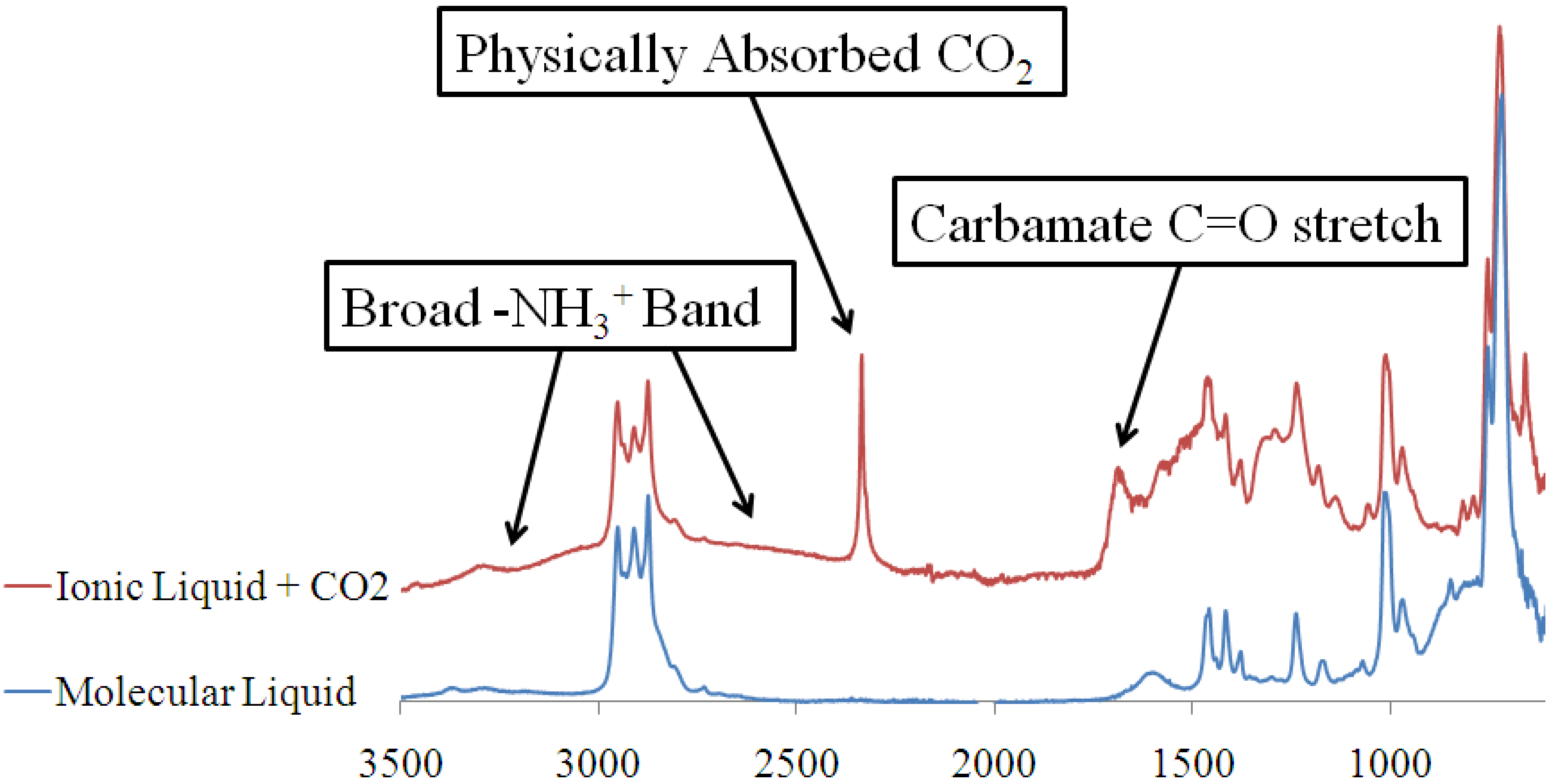
(3-aminopropyl)diisopropyl(perfluoropentyl)silane [FSA]



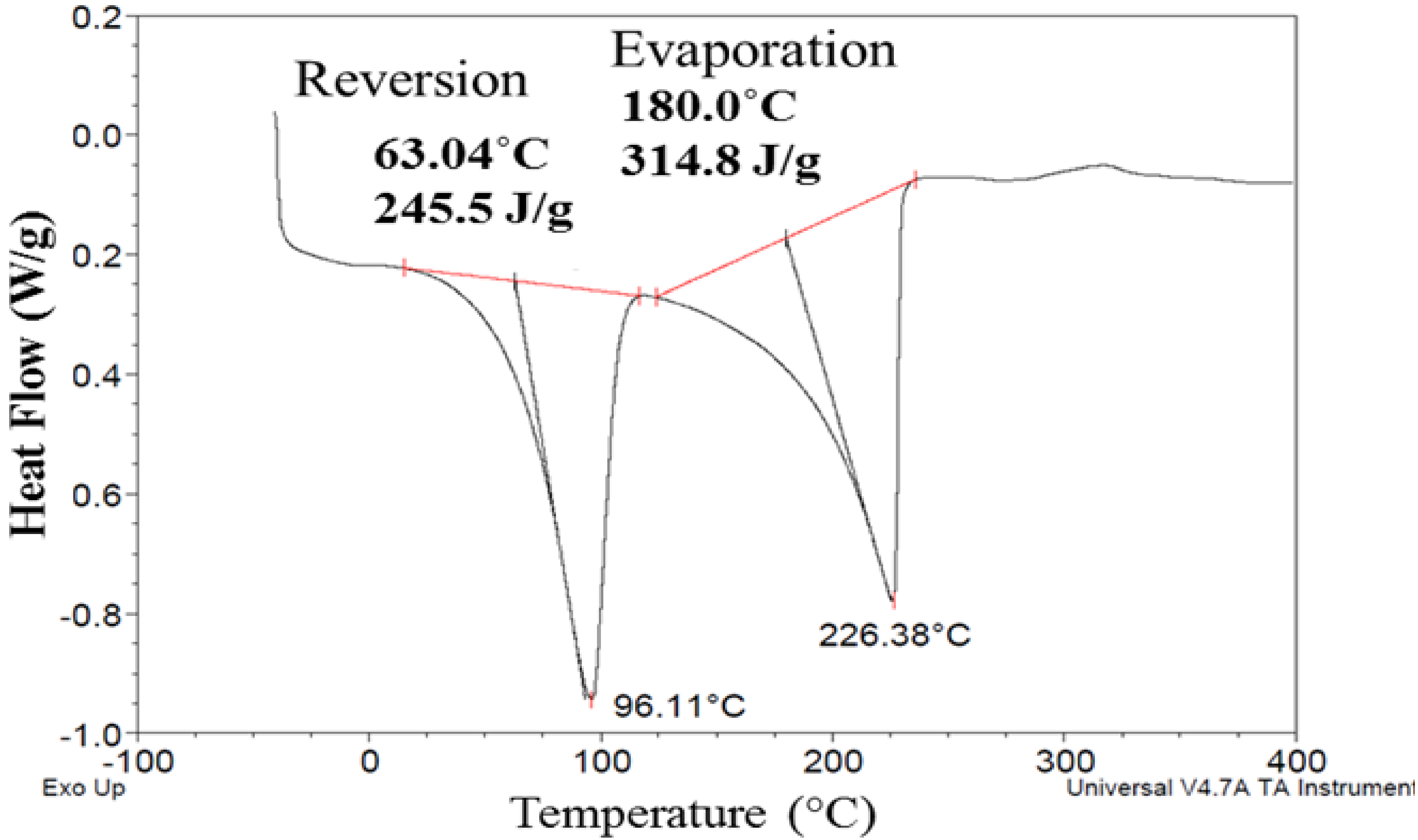
Properties Measured

- Thermodynamics
  - ✓Equilibrium Constant for Chemisorption
  - ✓Henry's Law Constant for Physisorption
  - ✓Enthalpy Effects
  - ✓Capacity
- Rates
  - ✓Chemical Kinetics
  - ✓Transport Properties

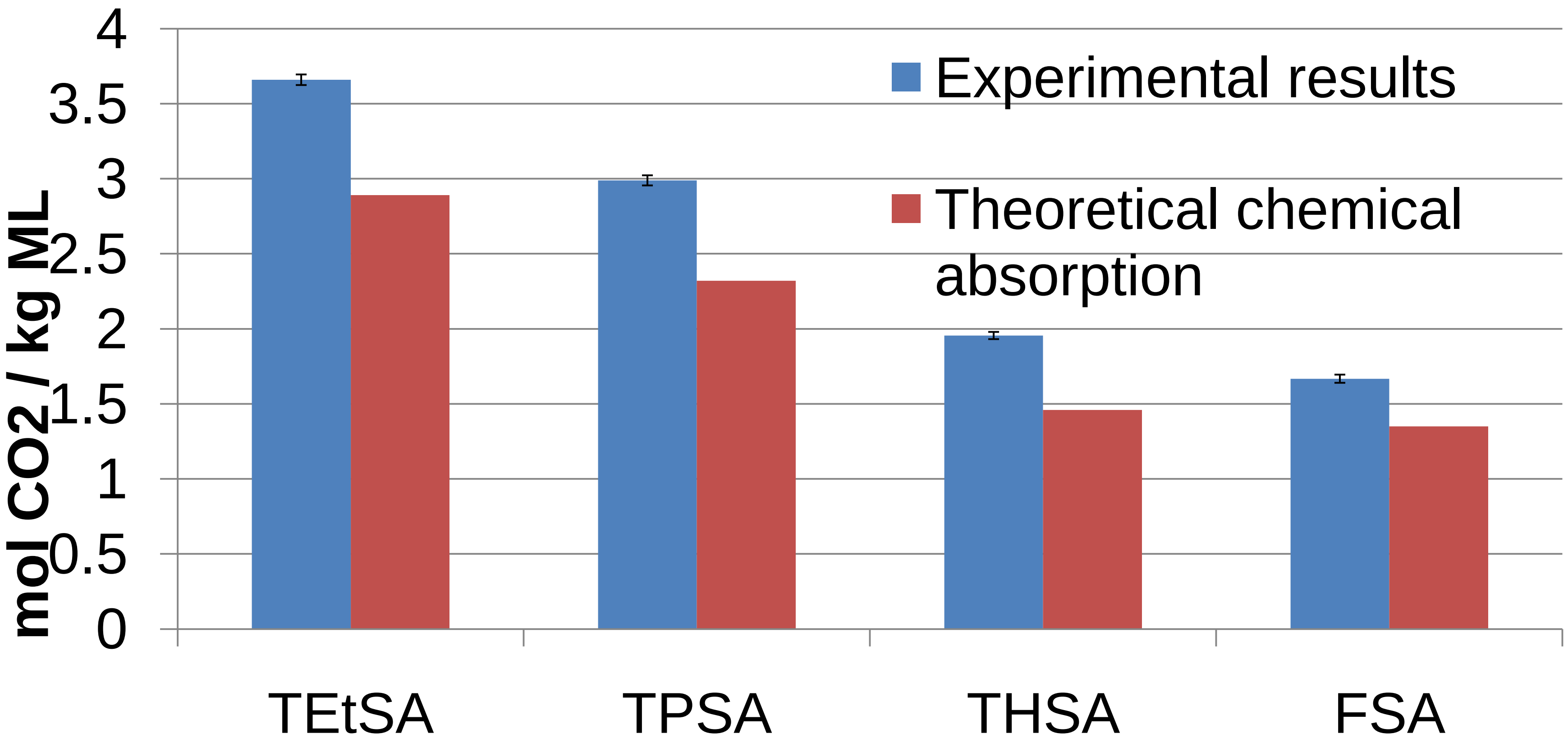
Infrared Spectra of TEtSA Ionic Liquid - Formation and Physical Absorption -



Differential Scanning Calorimetry -- TPSA



Capacity Comparison, Experimental vs Theoretical for Chemisorption Only

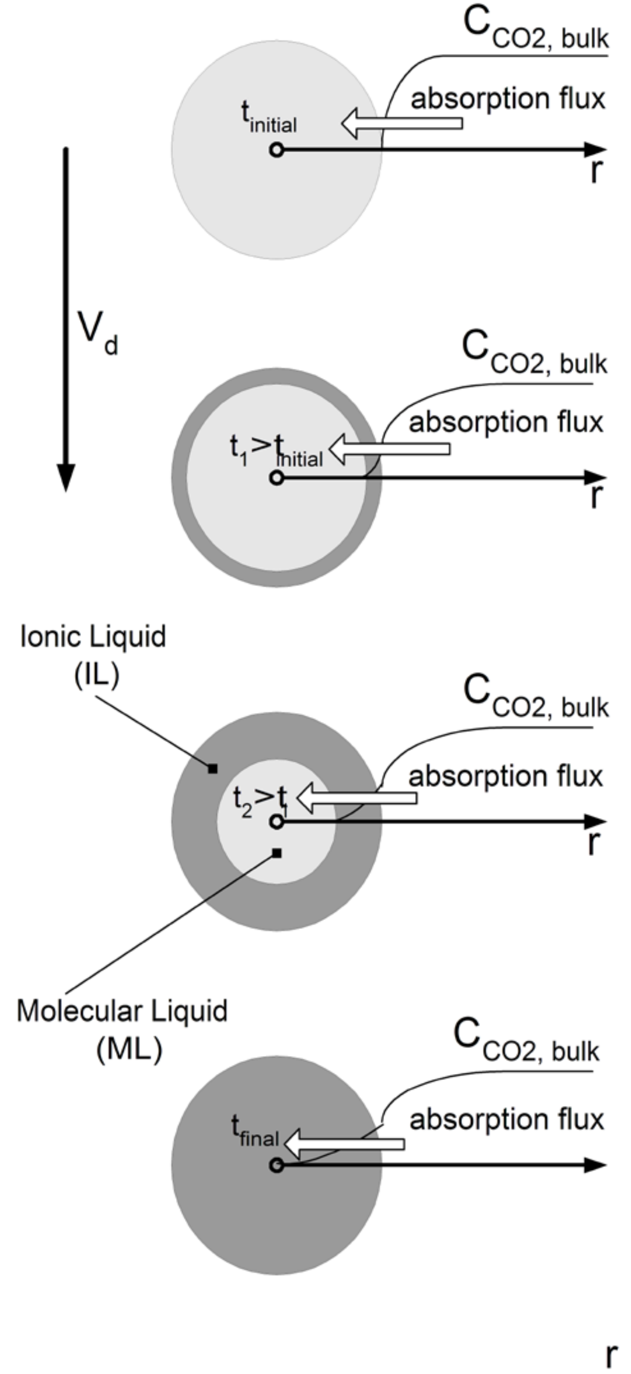


Project Methodology

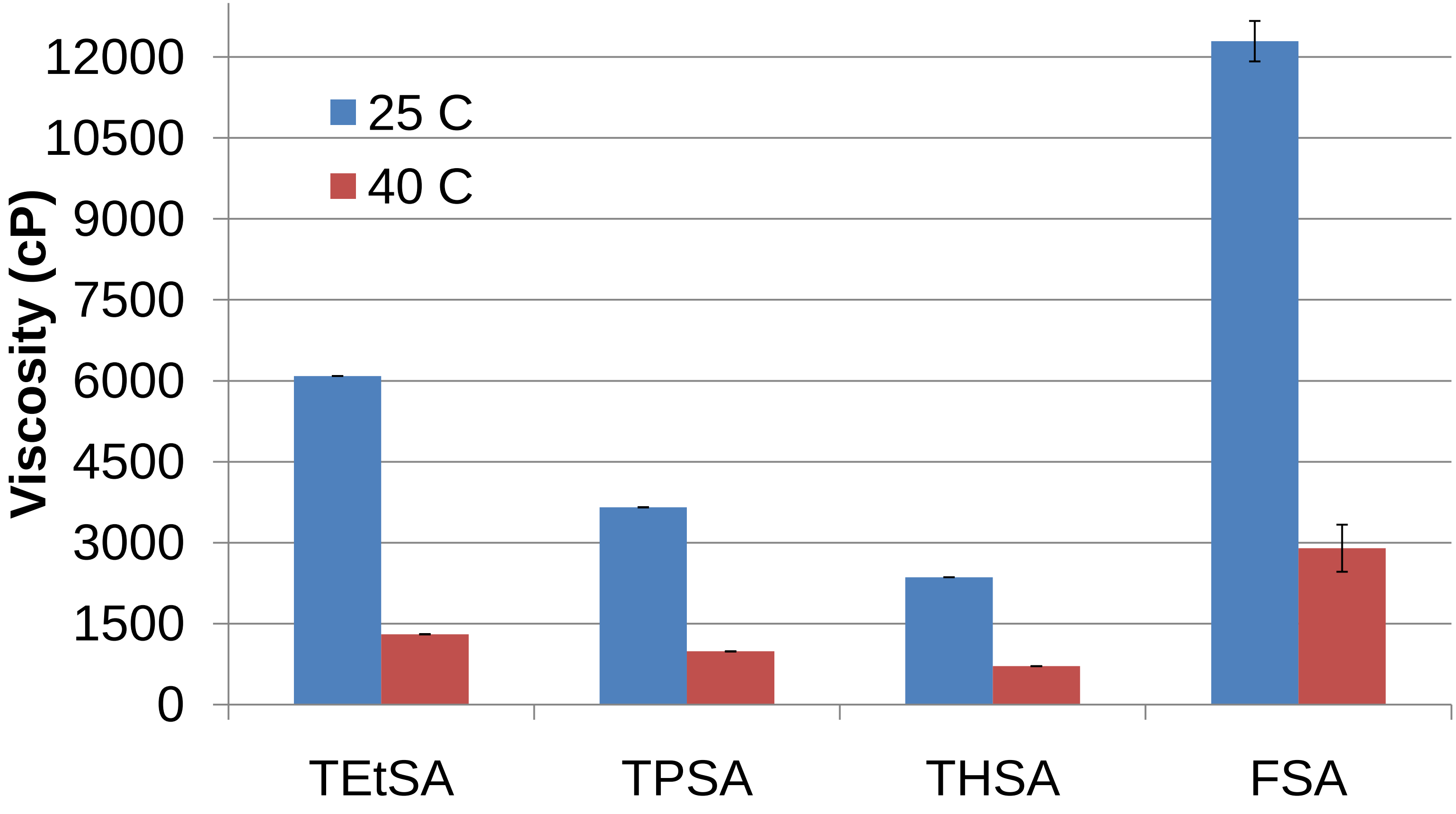
- Synthesis and Characterization of Novel Compounds
  - ✓1-Comp. Silyl Guanidine-Based ILs
  - ✓1-Comp. Silyl Amine-Based ILs
- Thermodynamics of IL Formation with CO_2
- Rates of Uptake/Release
- Optimize Solvent Structure for CO_2 Capture
- Process Design & Economic Analysis

Project Challenge: Transport to Falling Droplets in a Scrubber

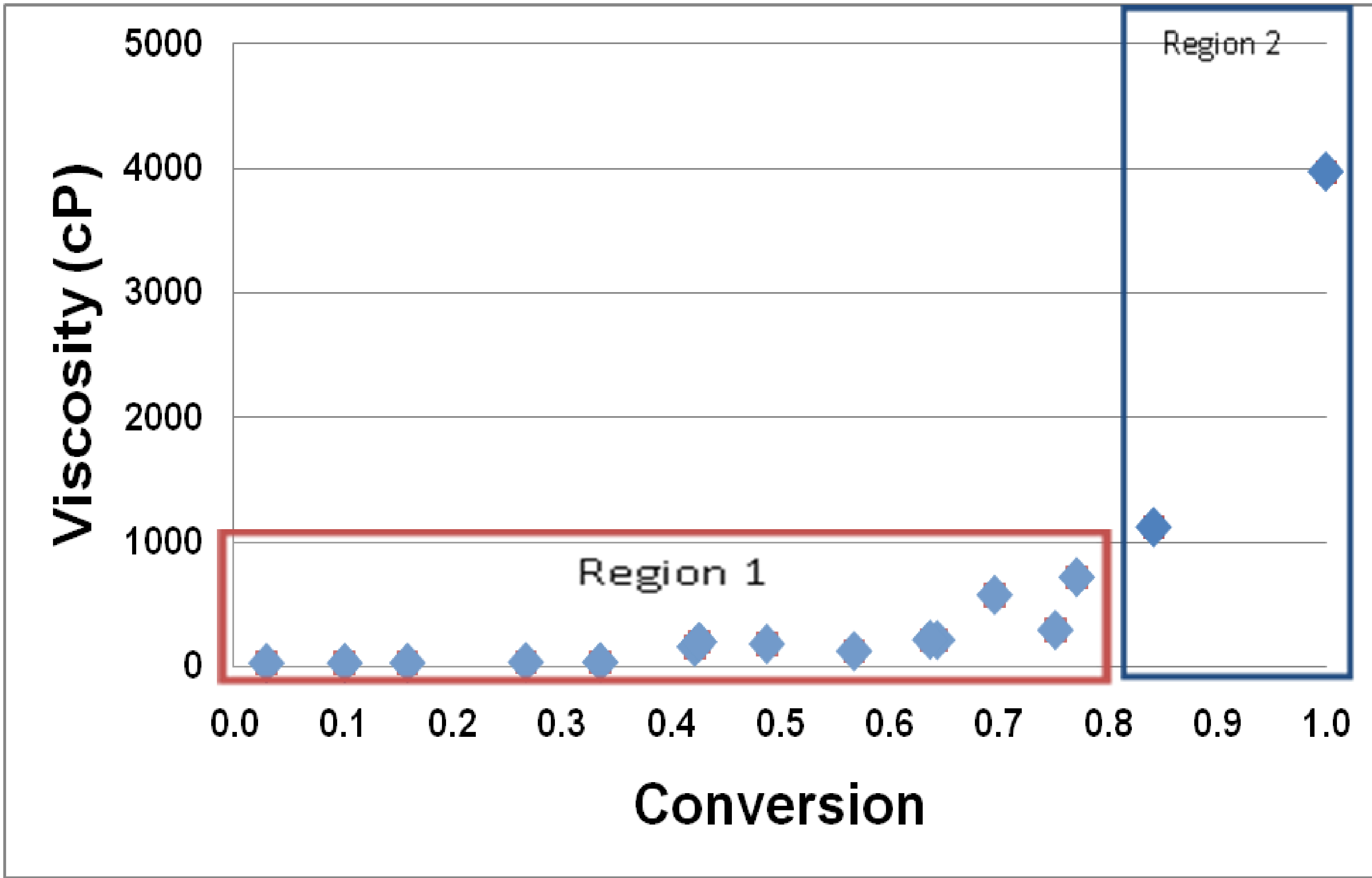
- Mass Transfer of CO_2 to the Falling Droplet
- Heat Transfer from the Falling Droplet
- Effect of Water
- Balance of Viscosity and Capacity



Project Challenge: Viscosity of Ionic Liquids

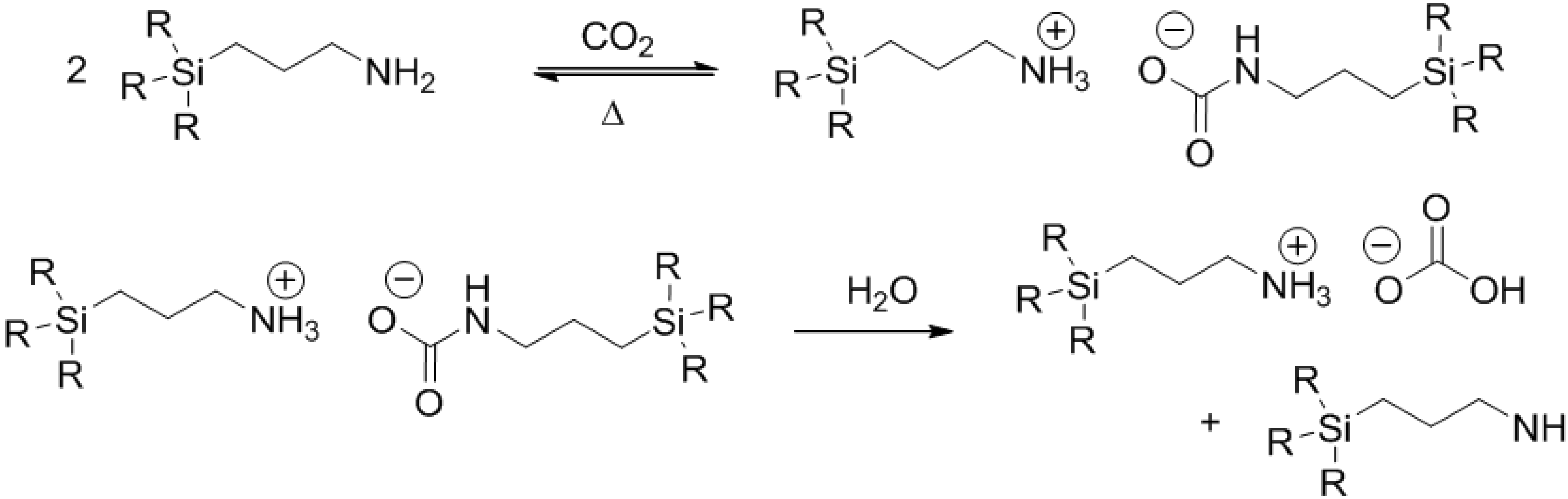


Viscosity vs. Extent of Reaction

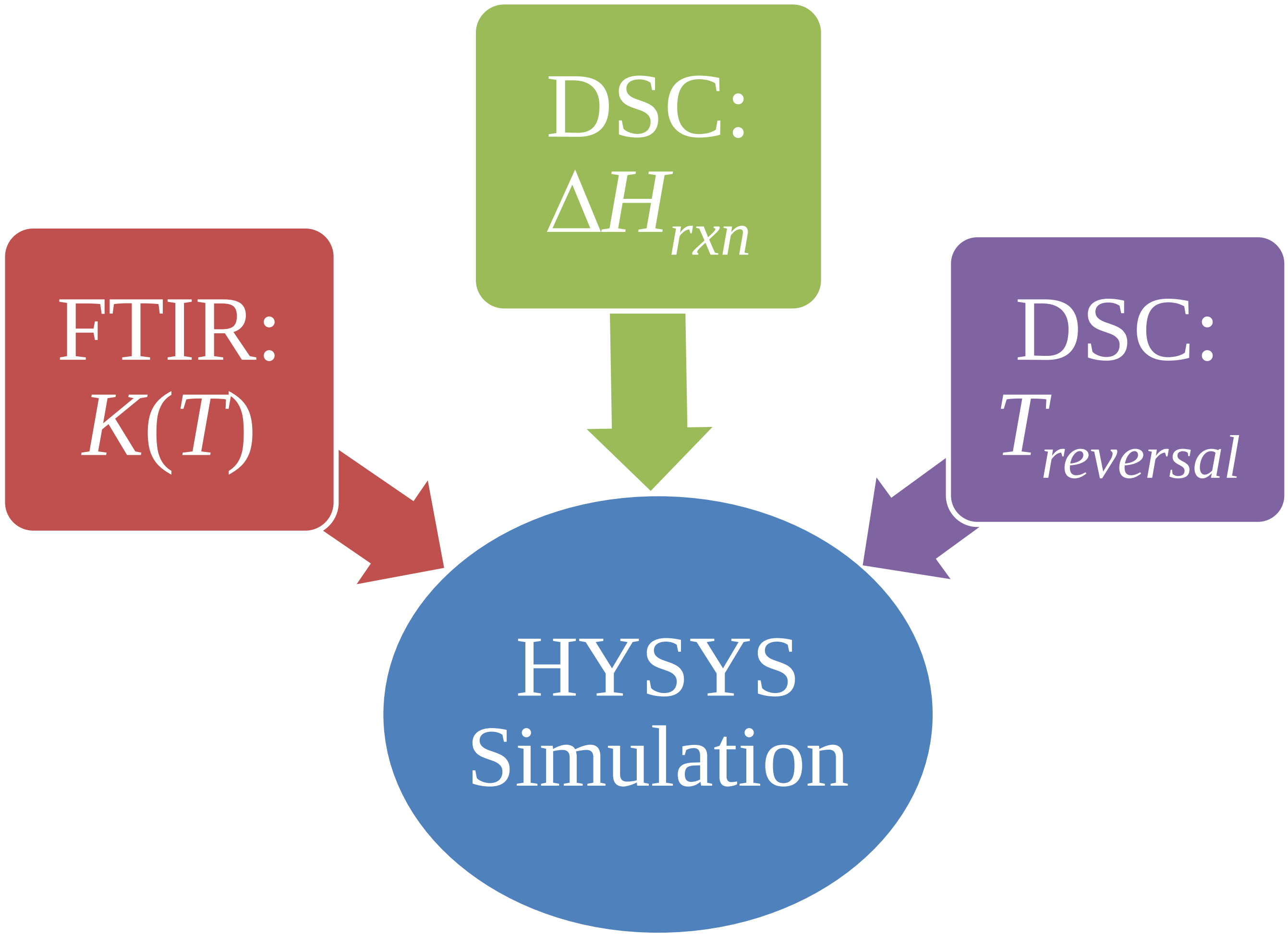


Potential Management of Viscosity

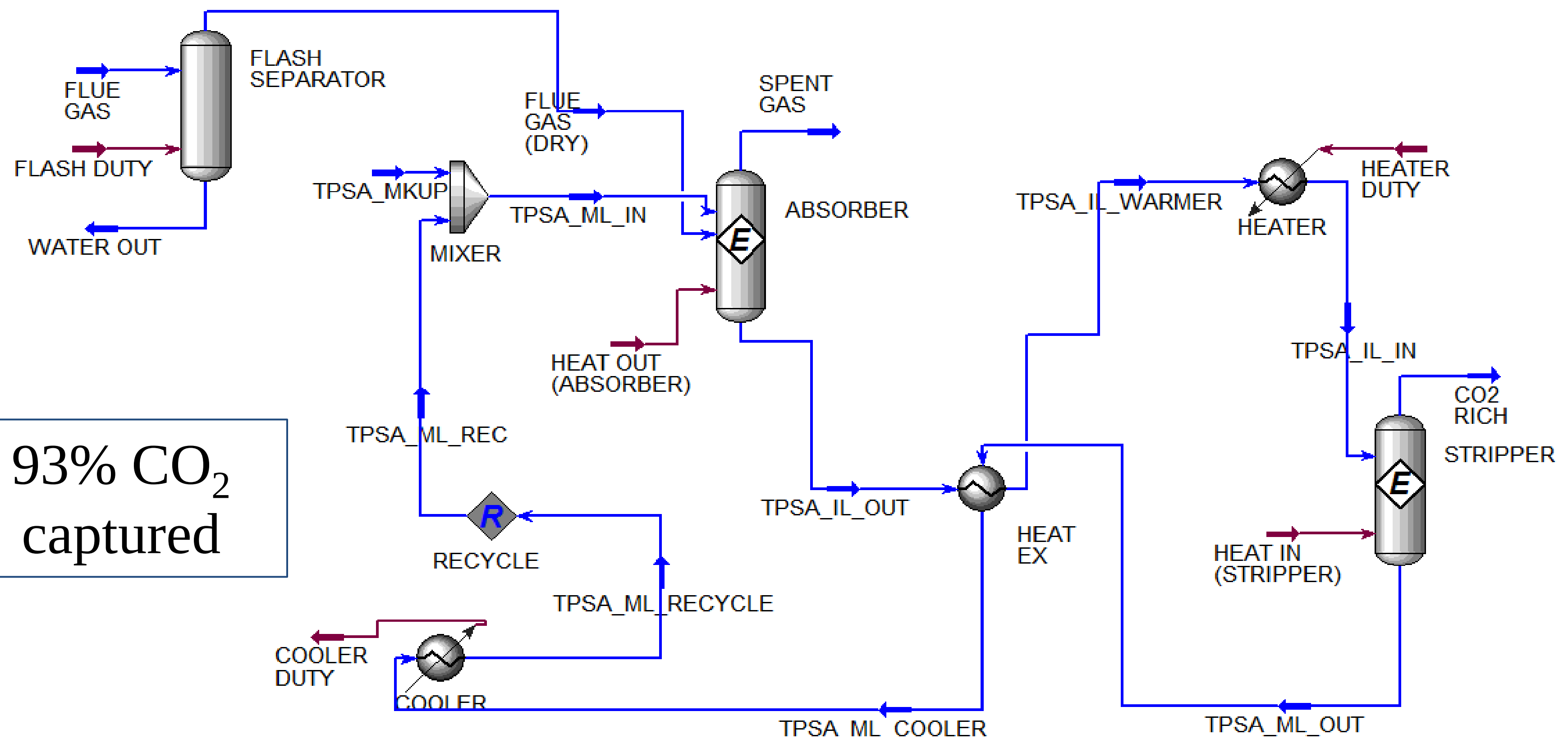
- Reaction Slightly Less than Complete
- Add Water
  - ✓Always Present, 10-15%
- Water Also Increases Capacity
  - ✓Forms Bicarbonate in Presence of Amine



Integrating Experimental Data into Process Design



HYSYS Simulation



93% CO_2 captured

- Preliminary Estimate for TPSA: 1.5 MJ/kg CO_2
- Literature Value for 30% Aq. MEA: 3.5 MJ/kg CO_2

Support From DOE Has Generated...

- 5 Articles Published, 2 More Submitted
- 8 Invited Presentations
- 13 Conference Presentations, 3 More Upcoming
- 2 Invention Disclosures
- 7 Collaborations:
  - ✓ 4 Academic
  - ✓ 3 Industrial

- 5 Students Graduated
  - ✓ Vittoria Blasucci, PhD ChBE (Exxon)
  - ✓ Hillary Huttenhower, PhD Chem (Pratt and Whitney)
  - ✓ Ryan Hart, PhD ChBE (Exponent)
  - ✓ Ali Fadhel, PhD ChBE (GE)
  - ✓ Melissa Burlager, BS ChBE (Grad School)
- To Graduate this Term
  - ✓ Greg Marus, PhD ChBE

Project Objectives and Timing: Milestones

Milestone Title	**Finish**	**Verification Method**
A Complete Project Management Plan	9/30/08	PMP approved by DOE COR
B 1-Comp. Silyl Amine-Based ILs	06/30/10	Successful Synthesis and Characterization
C 1-Comp. Silyl Guanidine-Based ILs	02/28/11	Successful Synthesis and Characterization
D Thermo & Rates of IL Formation	6/30/11	Successful Measurements
E Optimize CO_2 Capture Solvent Structure	10/31/11	Optimal Solvent Identified
F Process Design and Economic Analysis	10/31/11	Design and Scaleup Completed
G Write Final Report	12/31/11	Final Report Submitted

Future Testing & Development

- This Project
  - ✓Complete Determination of Optimum RevIL
  - ✓Design and Economic Analysis
- Next Project
  - ✓IL Scaleup for Economic Manufacture
  - ✓Address Rates, Transport Issues
- Scale-Up Potential
  - ✓Already Working with Industrial Partner ConocoPhillips