DOE Project NT0005287

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 21-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 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
    - ➢ Develop Scalable Process for Synthesis
- **Bottom Line:** Superior Process for Post-Combustion CO_2 Capture from Coal-Fired Power Plants

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	79	417	85	434	85	1251	263
Equipment	92	71		118				150
Supplies	30		76		75		228	
Services	21		38		38		114	
Travel	9		9		9		27	
TOTAL	524	150	540	203	556	85	1620	413
Share %		28.6		37.5		15.2		27

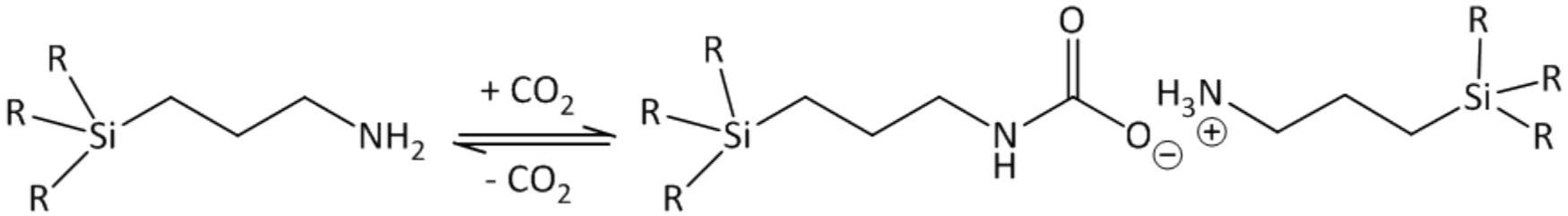
Overall Project Performance Dates

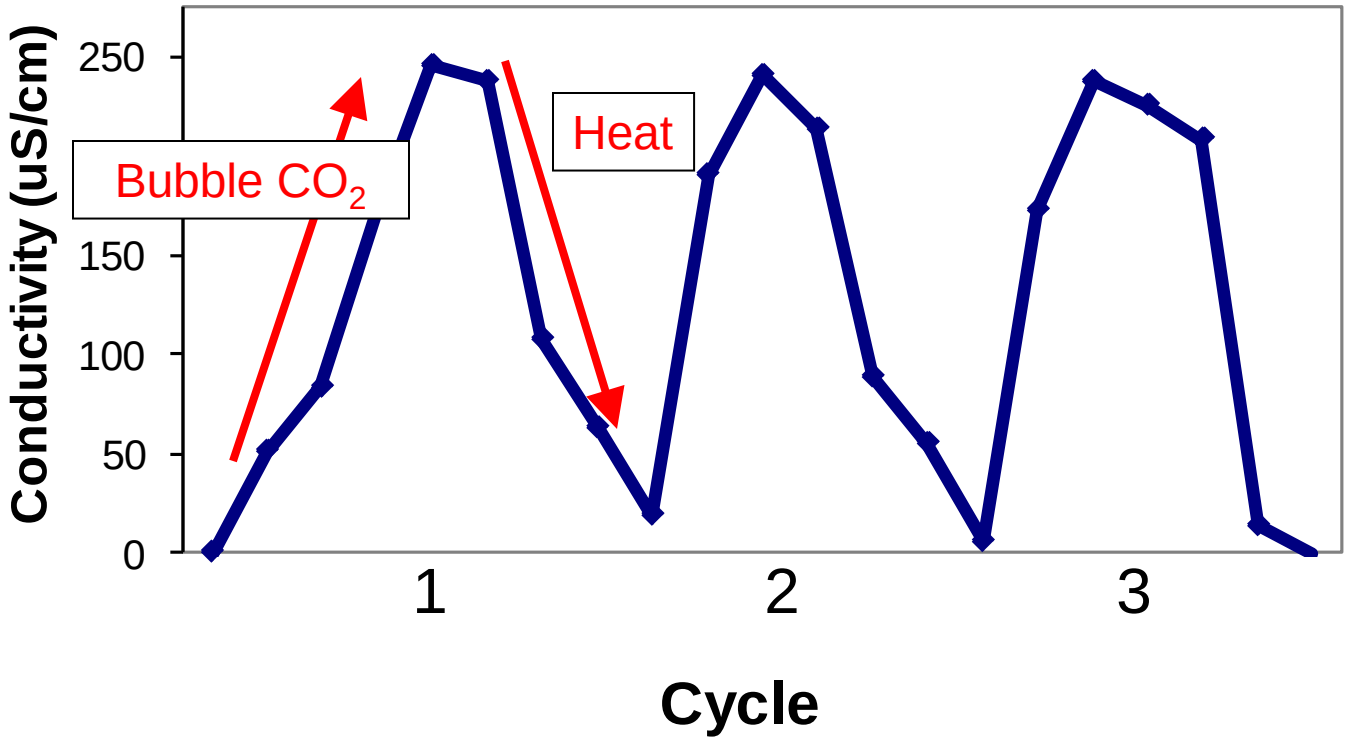
First Year				Second Year				Third Year			
Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
PROJECT MANAGEMENT, PLANNING, AND REPORTING											
1-COMPONENT SILYL AMINE-BASED ILS											
1-COMPONENT SILYL GUANIIDINE-BASED ILS											
				THERMODYNAMICS AND RATES OF IL FORMATION							
							OPTIMIZE CO2 CAPTURE SOLVENT STRUCTURE				
							PROCESS DESIGN AND ECONOMIC ANALYSIS				

Project Participants

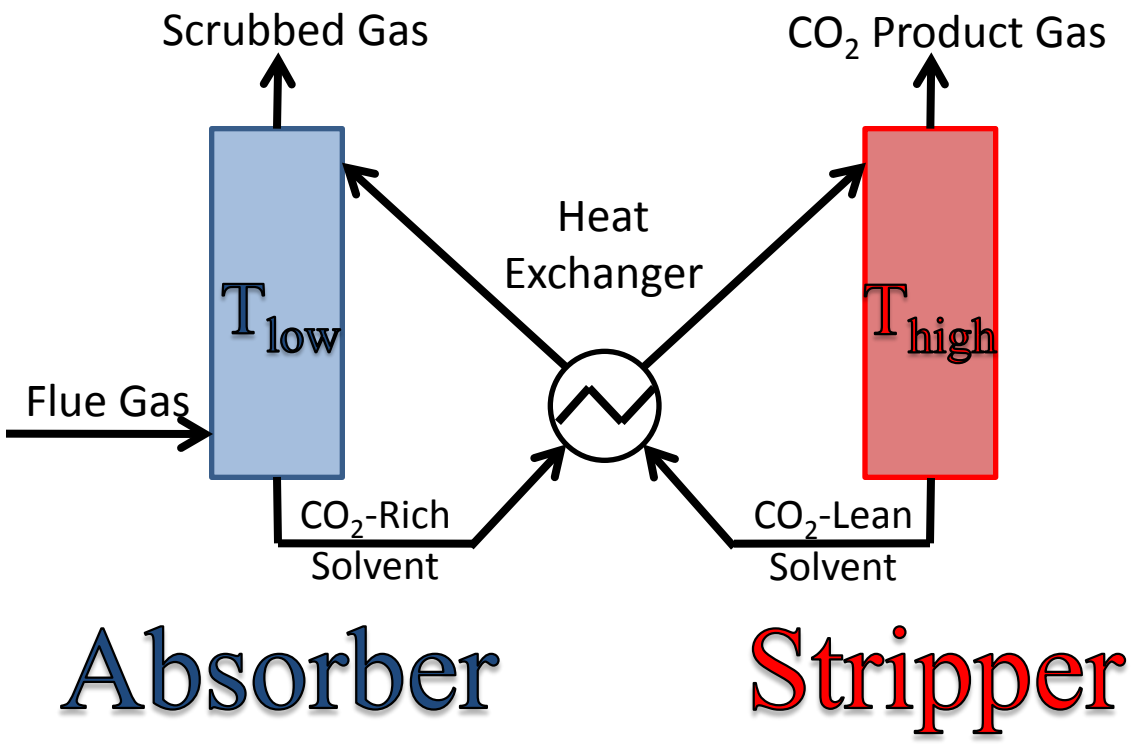
- Chemical Engineers and Chemists Supported on this Grant
  - ✓Faculty – Charles Eckert, Charles Liotta
  - ✓Postdocs – Elizabeth Biddinger, Manish Talreja, Manjusha Verma
  - ✓PhD Students – Olga Dzenis, Ryan Hart, Gregory Marus, Amy Rohan
  - ✓Undergraduate – Melissa Burlager
- Other Contributors
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

Scientific Background: Sustainable Reversible Ionic Liquids (RevILs)





Advantages of RevILs for CO_2 Capture



Heat Energy

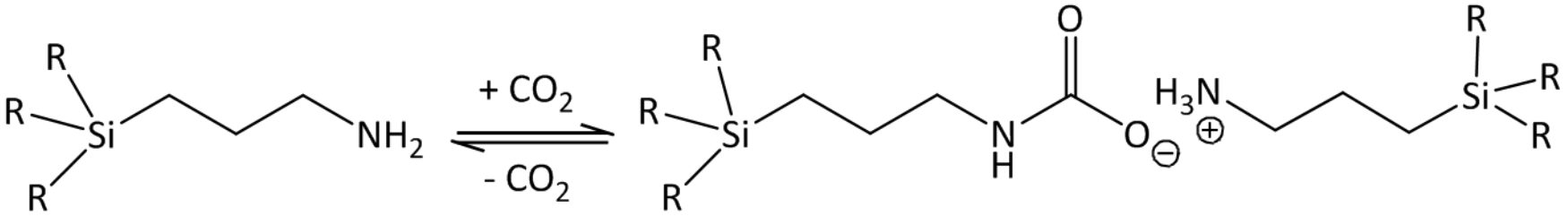
$Q = mC_p\Delta T +$ Regeneration

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 ⇌ (+ CO_2 / - CO_2) Ionic Liquid

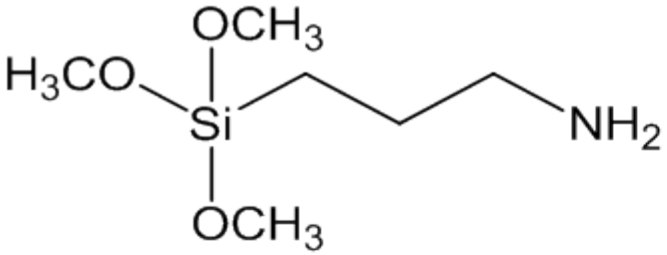
Added Capacity By **Physical Absorption**

Ionic Liquid ⇌ (+ CO_2 / - CO_2) CO_2 Swollen Ionic Liquid

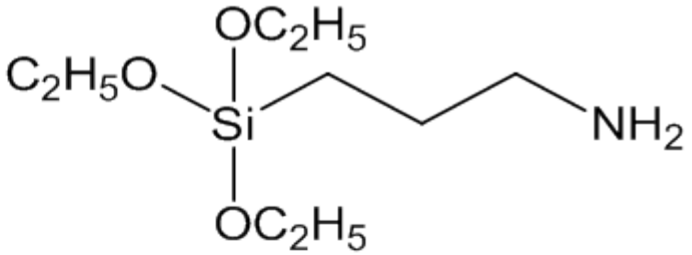
Technical and Economic Challenges

- 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

Progress and Current Status
First and Second Generation RevILs



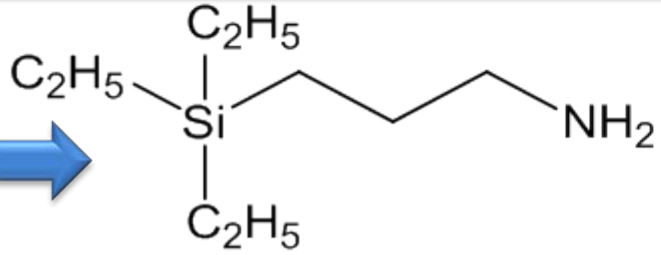
(3-aminopropyl)trimethoxysilane **(TMSA)**



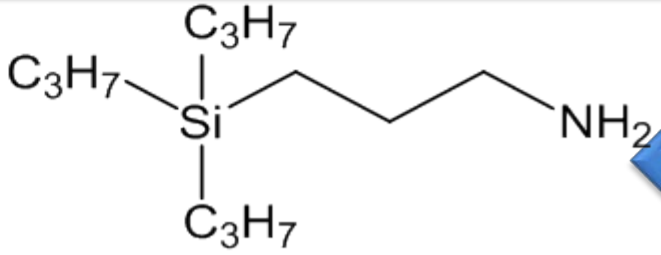
(3-aminopropyl)triethoxysilane **(TESA)**

Si-O-C is unstable in the presence of water

Alkyl substituted compounds were synthesized to improve stability



(3-aminopropyl)triethylsilane **(TEtSA)**



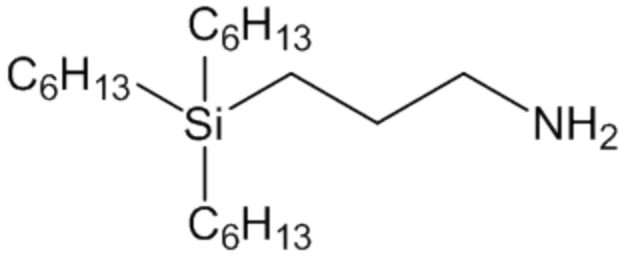
(3-aminopropyl)tripropylsilane **(TPSA)**

Third Generation Silyl-Amine Reversible Ionic Liquids

- Much Easier Synthesis than Guanidines
- Superior Capacity to Guanidines
- Structure is Easily Modified

Ionic Liquid	Swelling	Physical Absorption Capacity (mol/kg amine)
TEtSA	16%	12.3
TPSA	31%	17.9

* Capacities measured at 900 psi and 35 C.
(Published in Fuel, 2009)

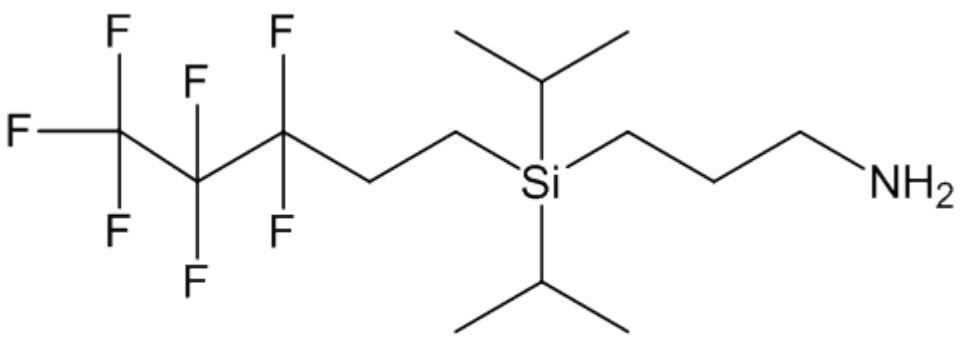


(3-aminopropyl)trihexylsilane **(THSA)**

Structure Property Relationships

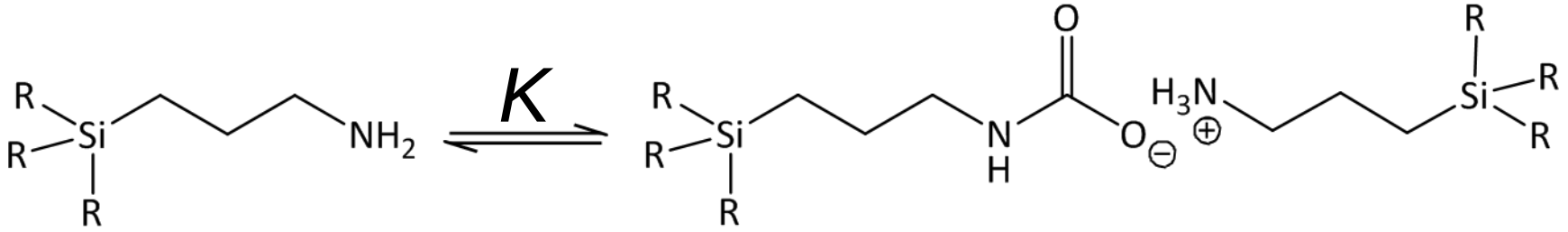
- Test Compounds
  - ✓Not for Field Application
  - ✓Rather to Show Effects of Stucture
- Effect of Electron Distribution
- Void Volume for Physisorption

Strong electron withdrawing group



(3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane **(FSA)**

Developing an Optimal Solvent Thru Structure Property/Relationships



Equilibrium Constant

$$K = \frac{a_{IonicLiquid}}{a_{Precursor}\, a_{CO2}}$$

Solution Nonideality

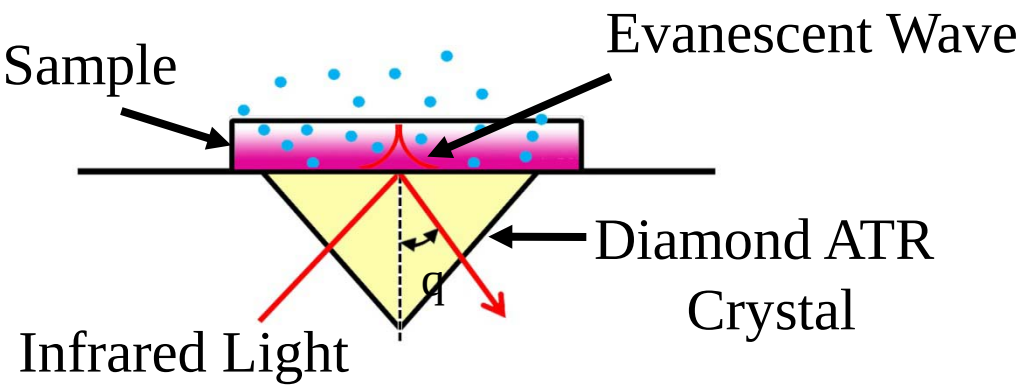
van 't Hoff Plot

Thermodynamic Properties

$$K = \exp\left[\frac{-\Delta G^{abs}}{RT}\right] \qquad \frac{d(\Delta G^{abs}/RT)}{dT} = -\frac{\Delta H^{abs}}{RT^2}$$

Novel Spectroscopic Technique for Measuring CO_2 Absorption

- How it works:



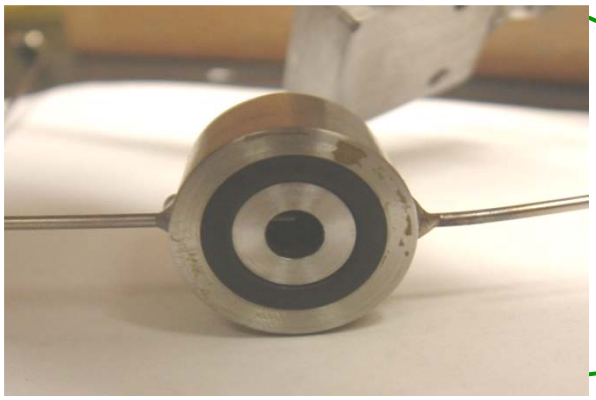
- Application of Beer-Lambert Law:

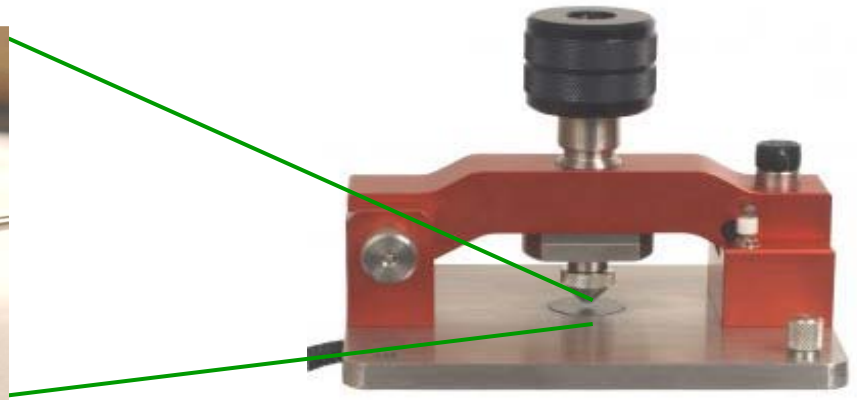
$$A = \varepsilon \cdot b \cdot c$$

A = absorbance [A.U.]
ε = molar absorptivity [L mol^{-1} cm^{-1}]
b = path length [cm]
c = concentration [mol L^{-1}]

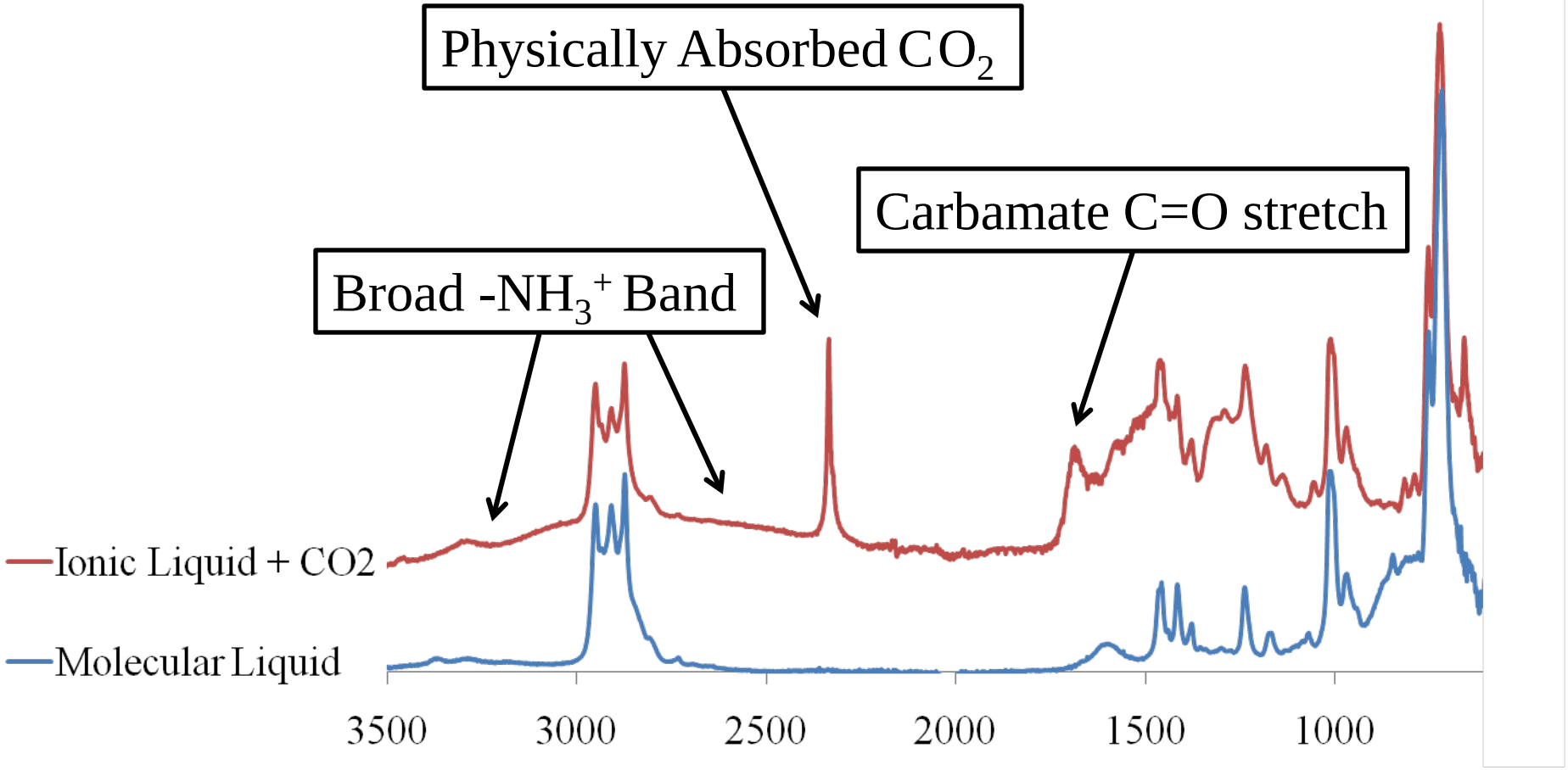
Custom Design Sample Cell for ATR

- Design Collaboration with *Prof. Sergei Kazarian*
  - ✓Ease of Assembly, Operation, and Maintenance
  - ✓Low Volume, High Pressure
  - ✓Custom Built to Our Specifications
  - ✓Rapid and Accurate Measurements
  - ✓Measures both Chemical and Physical Absorption





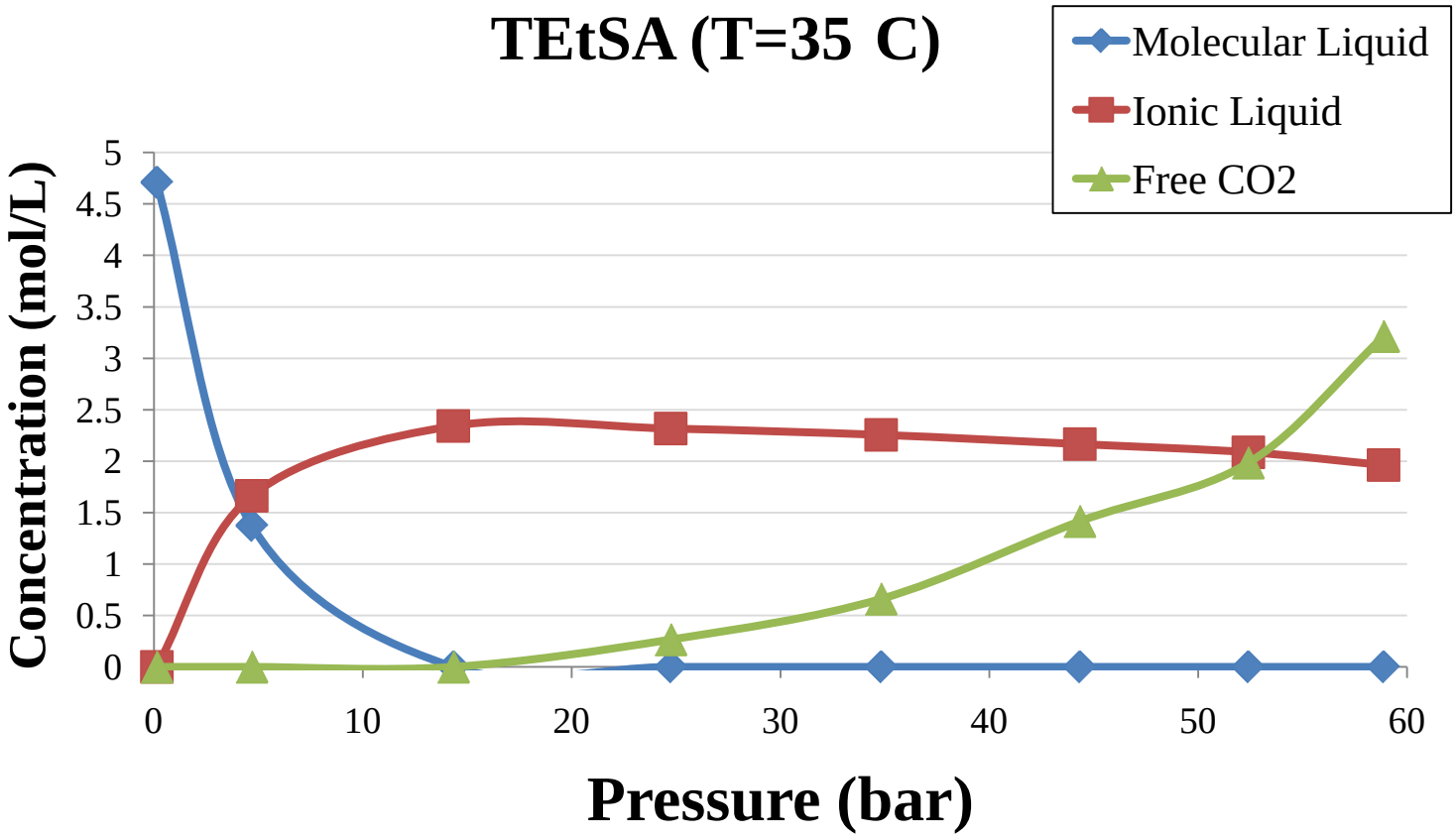
Infrared Spectra of TEtSA Ionic Liquid - Formation and Physical Absorption -



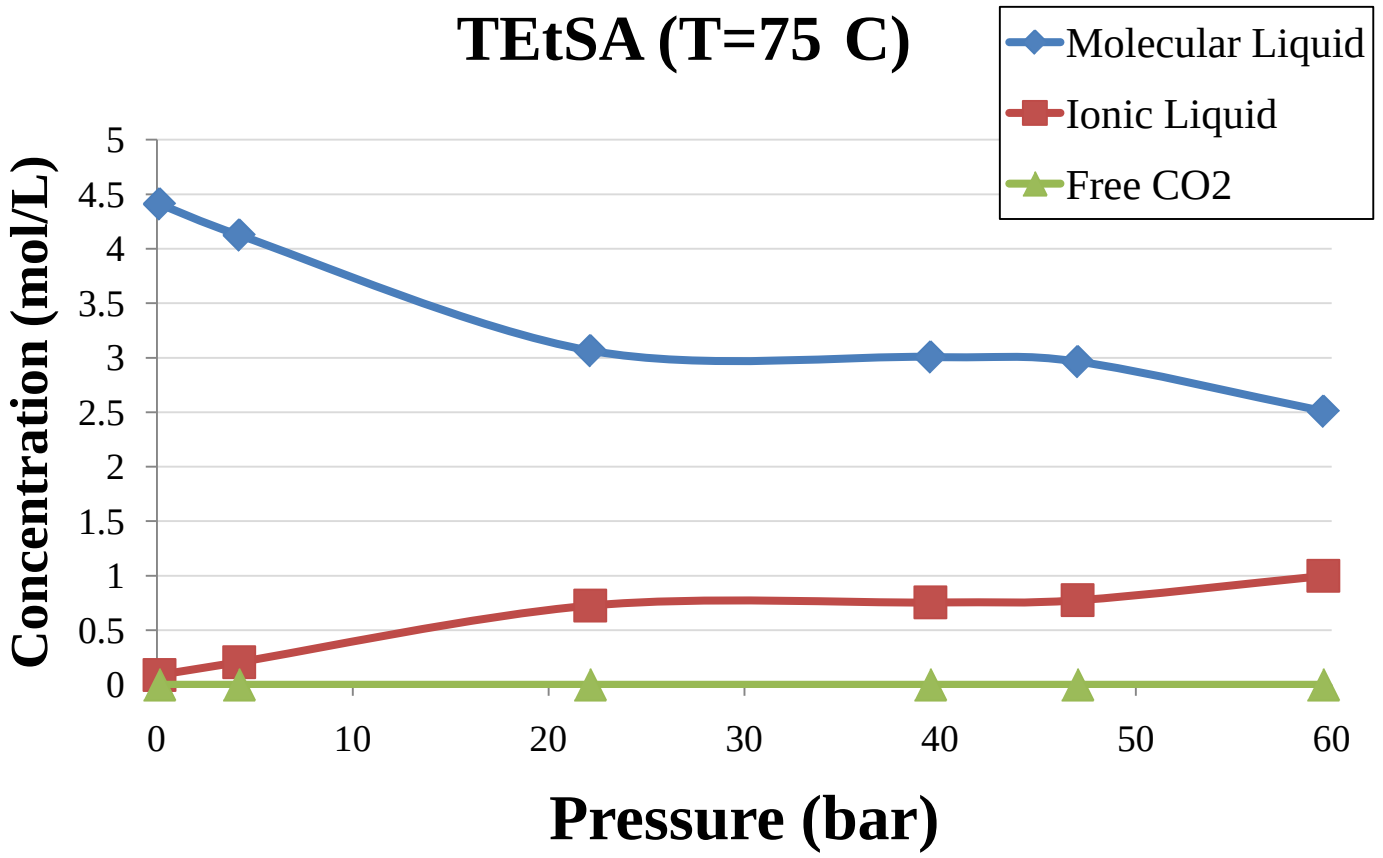
Project Methodology

- 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

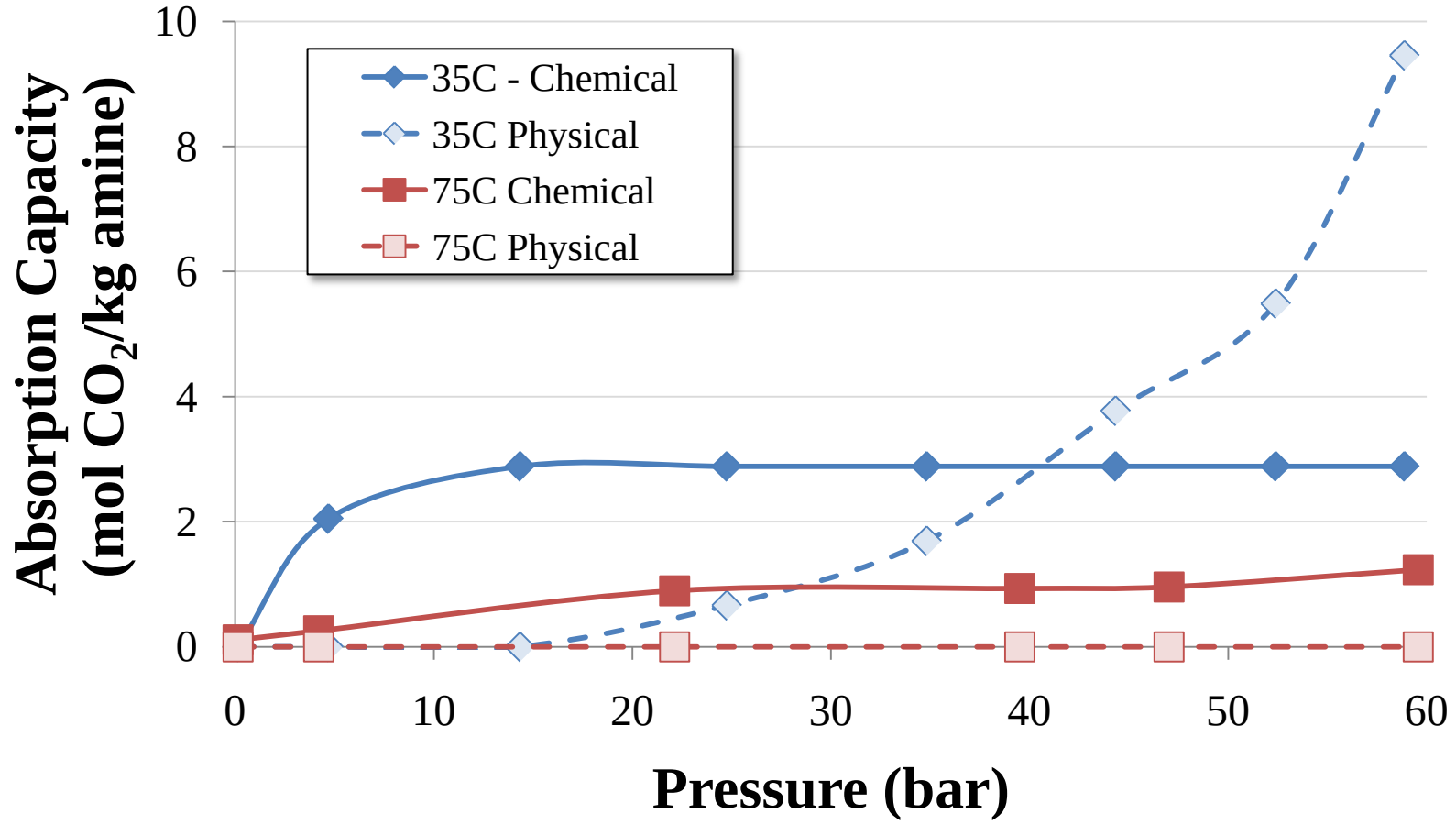
Ionic Liquid Formation Favored at Low Temperatures



At 75°C, Much Different Equilibrium



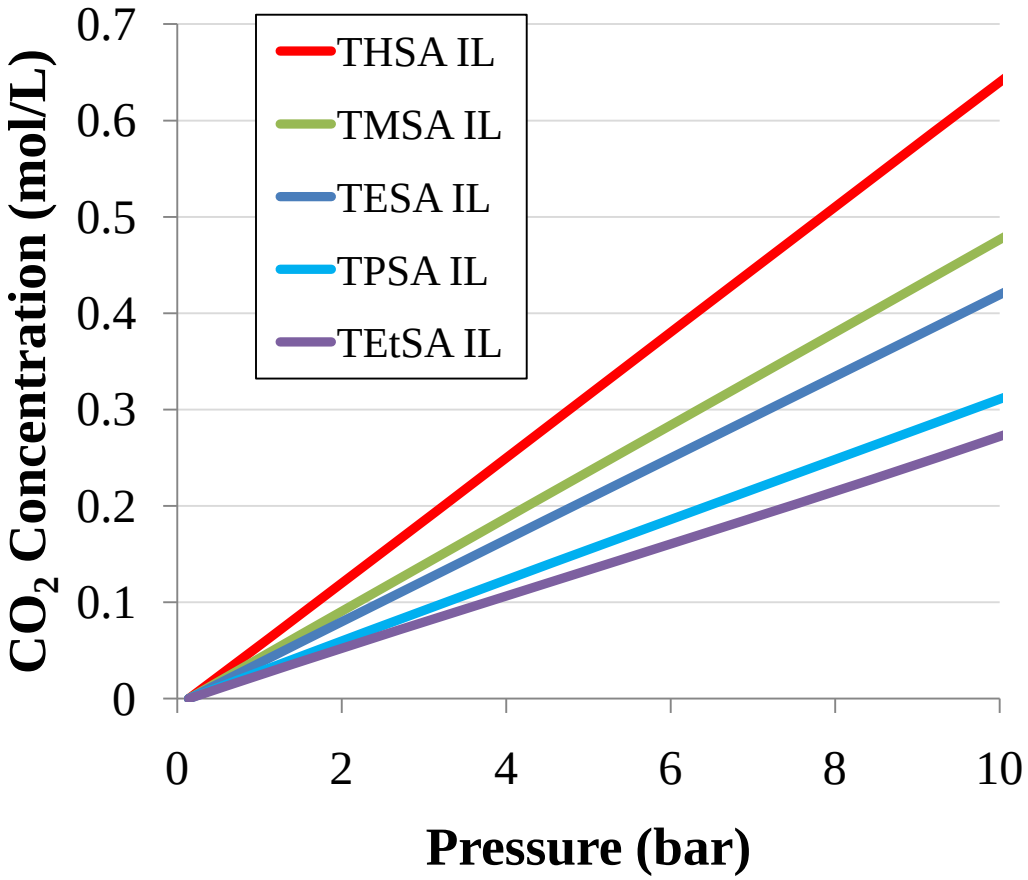
ATR FT-IR Reveals Capacities and Equilibrium



* Physical Absorption Detection Limit = 0.5 mol/L

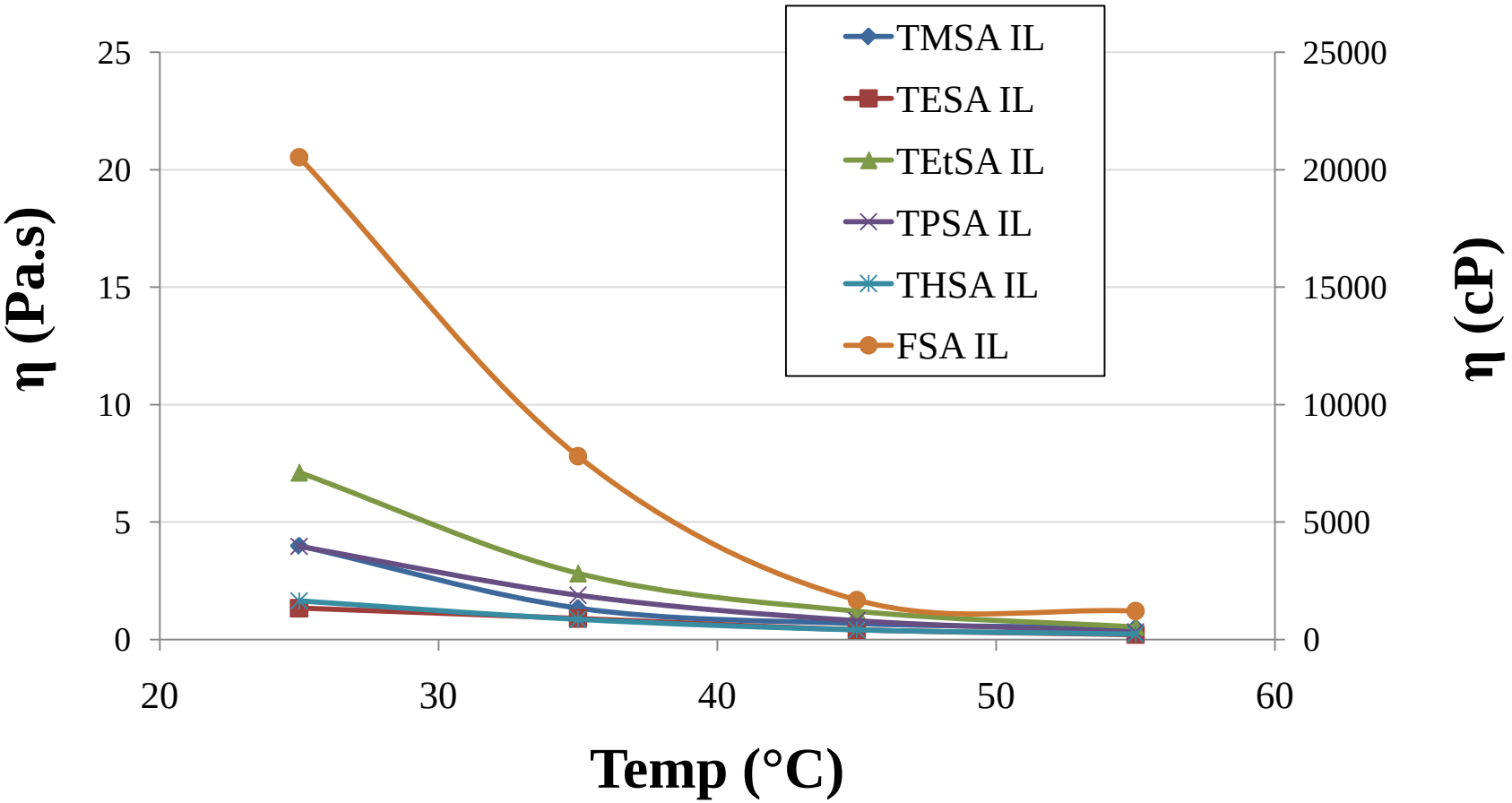
Enhancement of Physical Absorption in Ionic Liquids (T=35°C)

Double the capacity for alkyl amines!



Compound	Void Volume (L/mol)	Henry's Law Constant (L·bar/mol)
TMSA	0.357	20.8
TESA	0.466	23.8
TEtSA	0.423	37.0
TPSA	0.520	32.3
THSA	0.822	15.6

Project Challenge: Viscosity of Ionic Liquids



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 CO_2 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

Support From DOE Has Generated...

- 3 Publications
- Presentations:
  - ✓ 8 Invited (1 Student Authored)
  - ✓ 8 Conferences (5 Student Authored)
- 1 Invention Disclosure
- 7 Collaborations:
  - ✓ 4 Academic
  - ✓ 3 Industrial
- 2 Students Graduated
  - ✓ Vittoria Blasucci, PhD ChBE (Exxon)
  - ✓ Hillary Huttenhower, PhD Chem (Pratt and Whitney)
- To Graduate this Term
  - ✓ Ryan Hart, PhD ChBE
  - ✓ Ali Fadhel, PhD ChBE
  - ✓ Melissa Burlager, BS 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
  - ✓Develop and Test for 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