Ionic Liquids: Breakthrough Absorption Technology for Post-combustion CO_2 Capture

Project NT43091

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August 23, 2011

Outline

- Project status
- Background
- Research breakthroughs
  - Increasing capacity with chemical complexation
  - Eliminating viscosity increases
  - Tuning reaction enthalpies
- Reaction kinetics
- Laboratory scale unit
- Commercialization study
- Conclusions

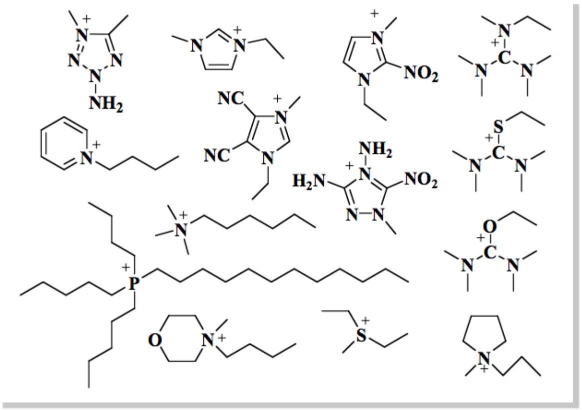
Project Status

- Project funding:
  - DOE Share: $2,741,784
  - Non-DOE share: $1,411,264
- Performance dates:
  - March 1, 2007- February 29, 2012
- Project participants:
  - University of Notre Dame (lead)
  - Babcock and Wilcox
  - DTE Energy
  - EMD Chemicals / Merck
  - Koei Chemical
  - Trimeric Inc.
  - MATRIC
- Project objectives:
  - Develop ionic liquid solvents that can be used as a cost effective post-combustion CO_2 capture solvent

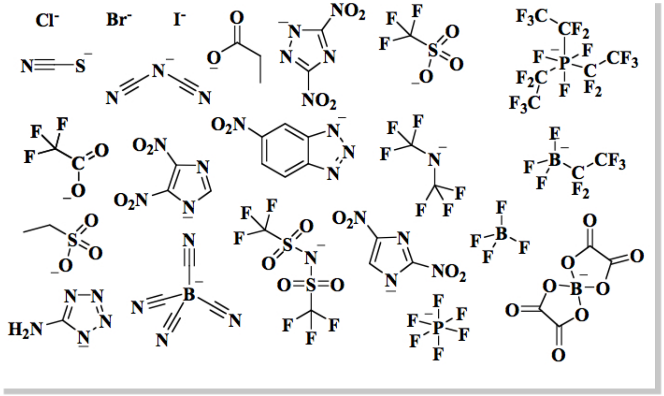
Ionic Liquids and Their Potential as CO_2 Sorbents

- Pure salts that are liquid around ambient temperature
  - Not simple salts like alkali halides
- Many favorable properties
  - Nonvolatile
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity
  - High intrinsic CO_2 solubility and selectivity

Examples of cations

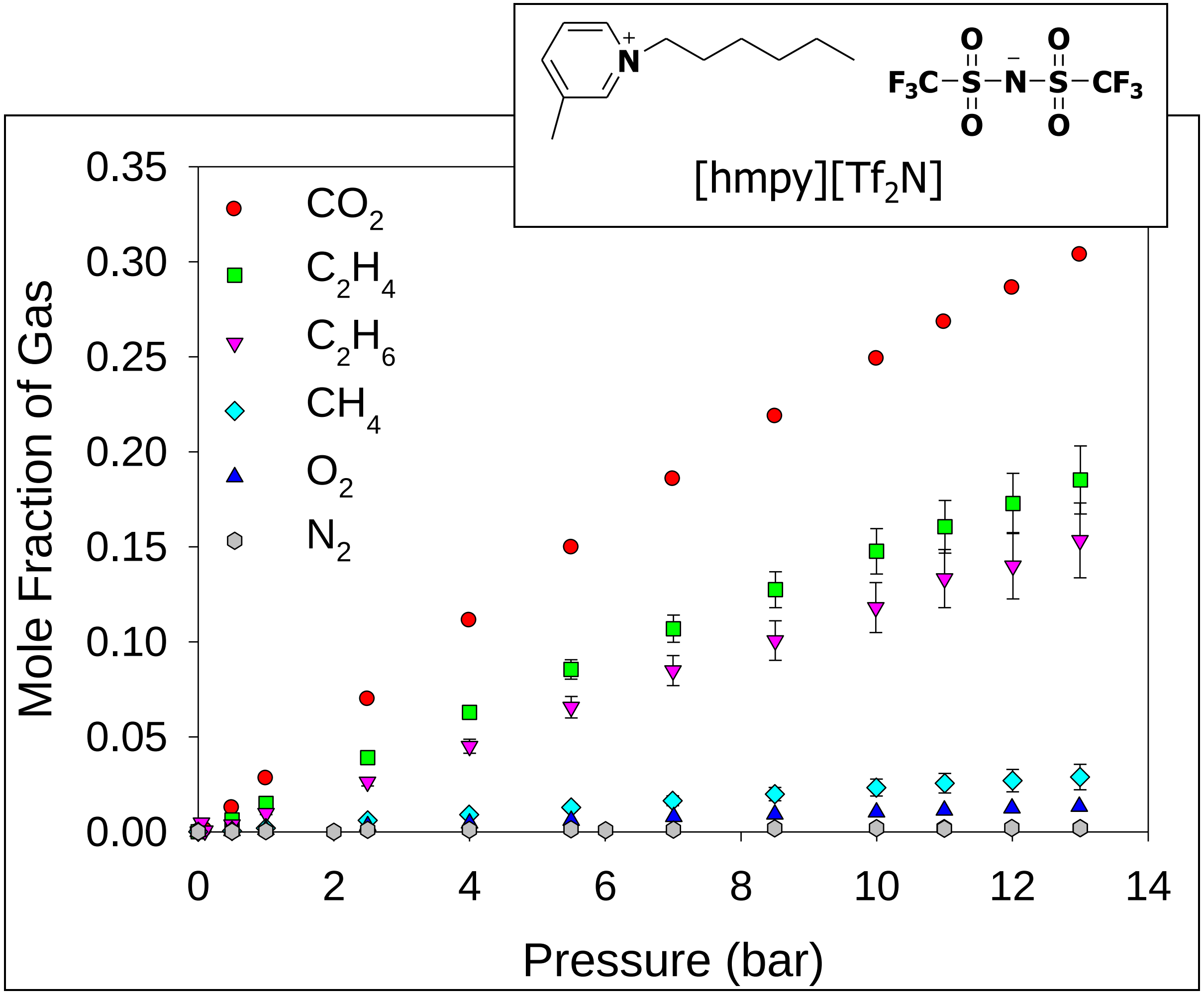


Examples of anions



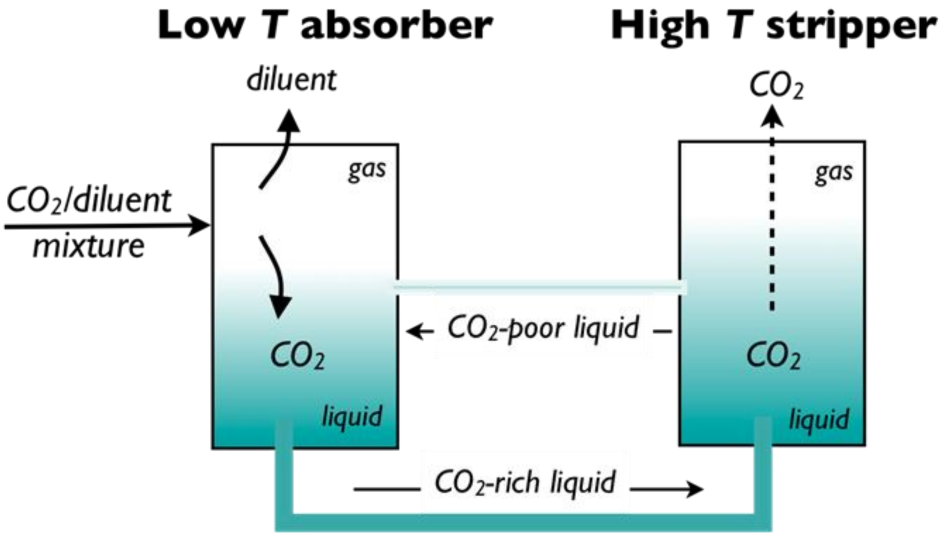
Pure Gas Solubility – Other Gases

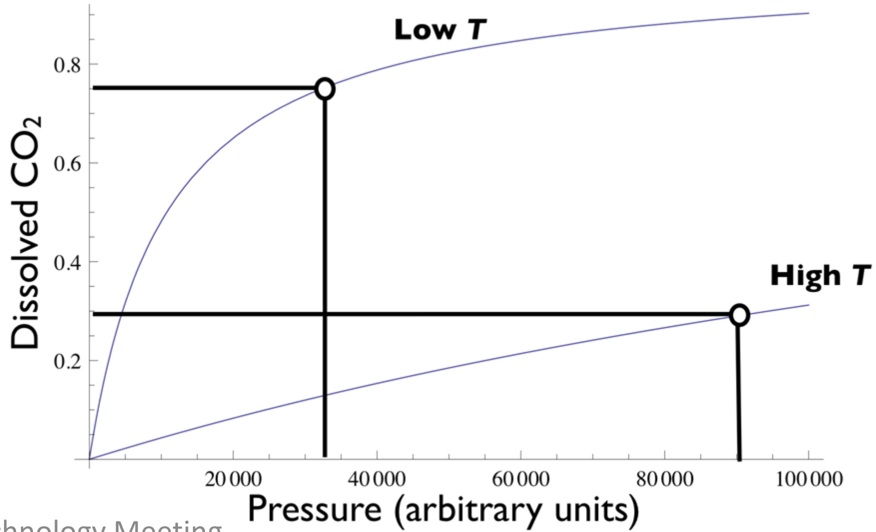
- Gas solubility measured in [hmpy][Tf_2N]
  - Similar trends are seen with other ILs
- CO_2 has the highest solubility of the gases measured
- Good selectivity!



Anderson, et al., ACR, 40, 2007, 1208-1216

Process Configuration





ILs vs. Aqueous Amines

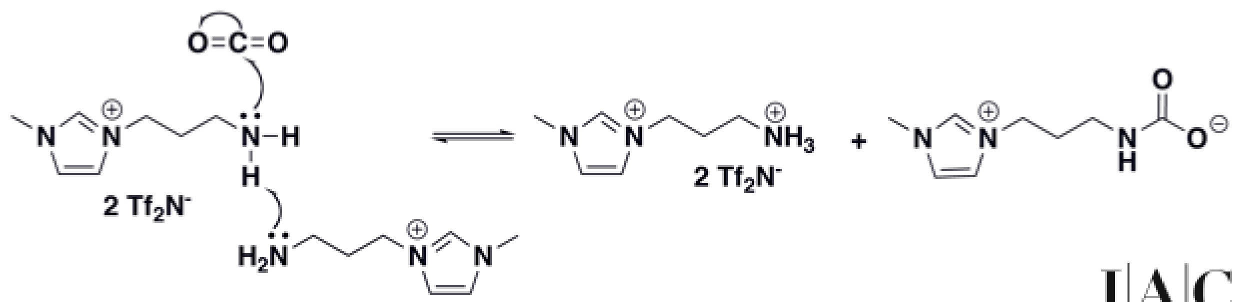
- **Benefits**
  - **Better oxidative stability**
  - **Better thermal stability**
  - **No added water so reduce energy needed in regenerator for evaporation of water**
- **Challenges**
  - **Capacity**
  - **Viscosity**
  - **Enthalpy**
  - **Water stability**
  - **Cost**

Increasing Capacity

- **Physical solubility**
  - **Low heat of absorption**
  - **~12 kJ/mol by T dependence of isotherms and direct calorimetric measurements**
  - **Low regeneration energy**
  - **Large IL circulation rates**
  - **Desorption at low P increases compression costs**
  - **Would need ~10x increase in solubility to beat aqueous MEA**
- **Chemical complexation**
  - **Strong enough to increase capacity and decrease IL circulation rates**
  - **Weak enough to keep regeneration energies (and temperatures) down**

Build on Amine Chemistry

TSIL CO_2 reaction mechanism



J|A|C|S COMMUNICATIONS

Published on Web 01/19/2002

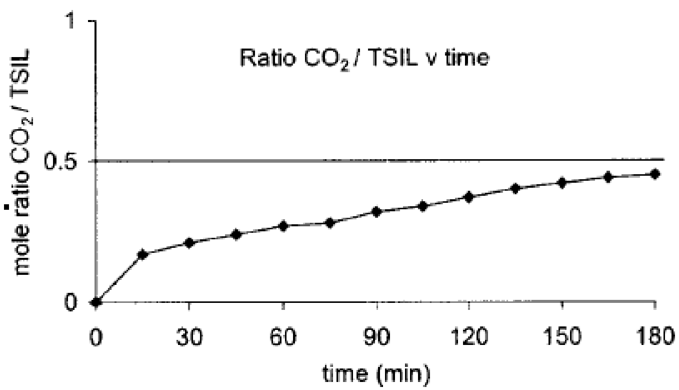
CO_2 Capture by a Task-Specific Ionic Liquid

Eleanor D. Bates, Rebecca D. Mayton, Ioanna Ntai, and James H. Davis, Jr.*

Department of Chemistry, University of South Alabama, Mobile, Alabama 36688

926 VOL. 124, NO. 6, 2002 ■ **J. AM. CHEM. SOC.**

1 atm CO_2
Room temp.

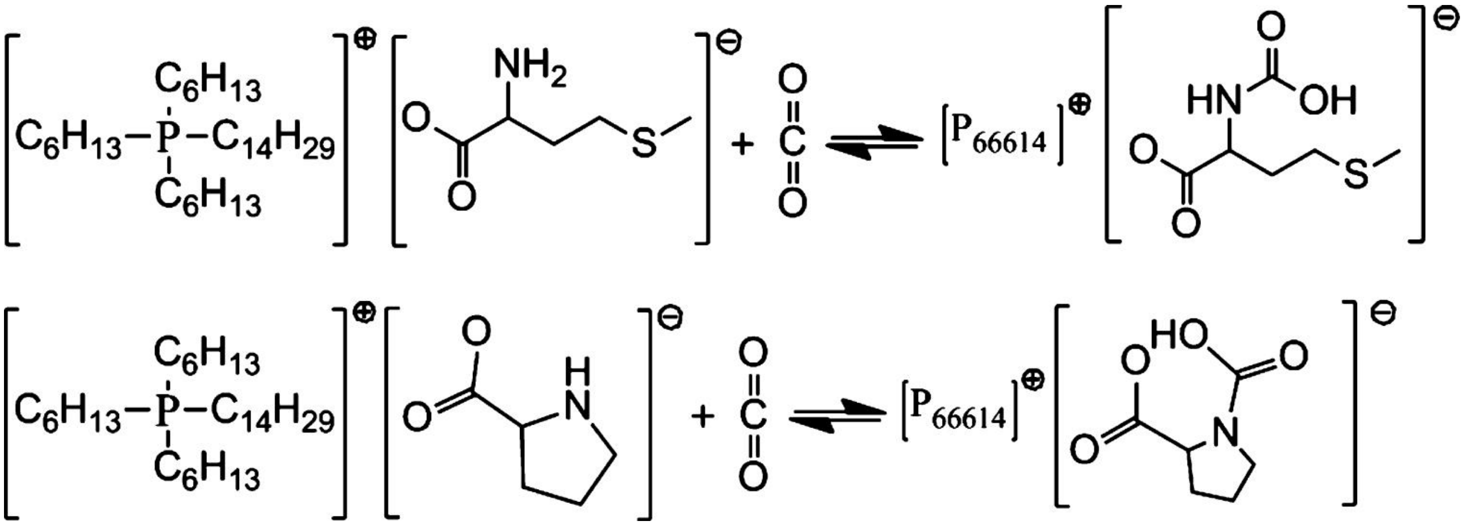


- Results in 1:2 CO_2 to IL molar uptake
- Huge increase in viscosity

Can We Get Higher Capacity Than 1:2?

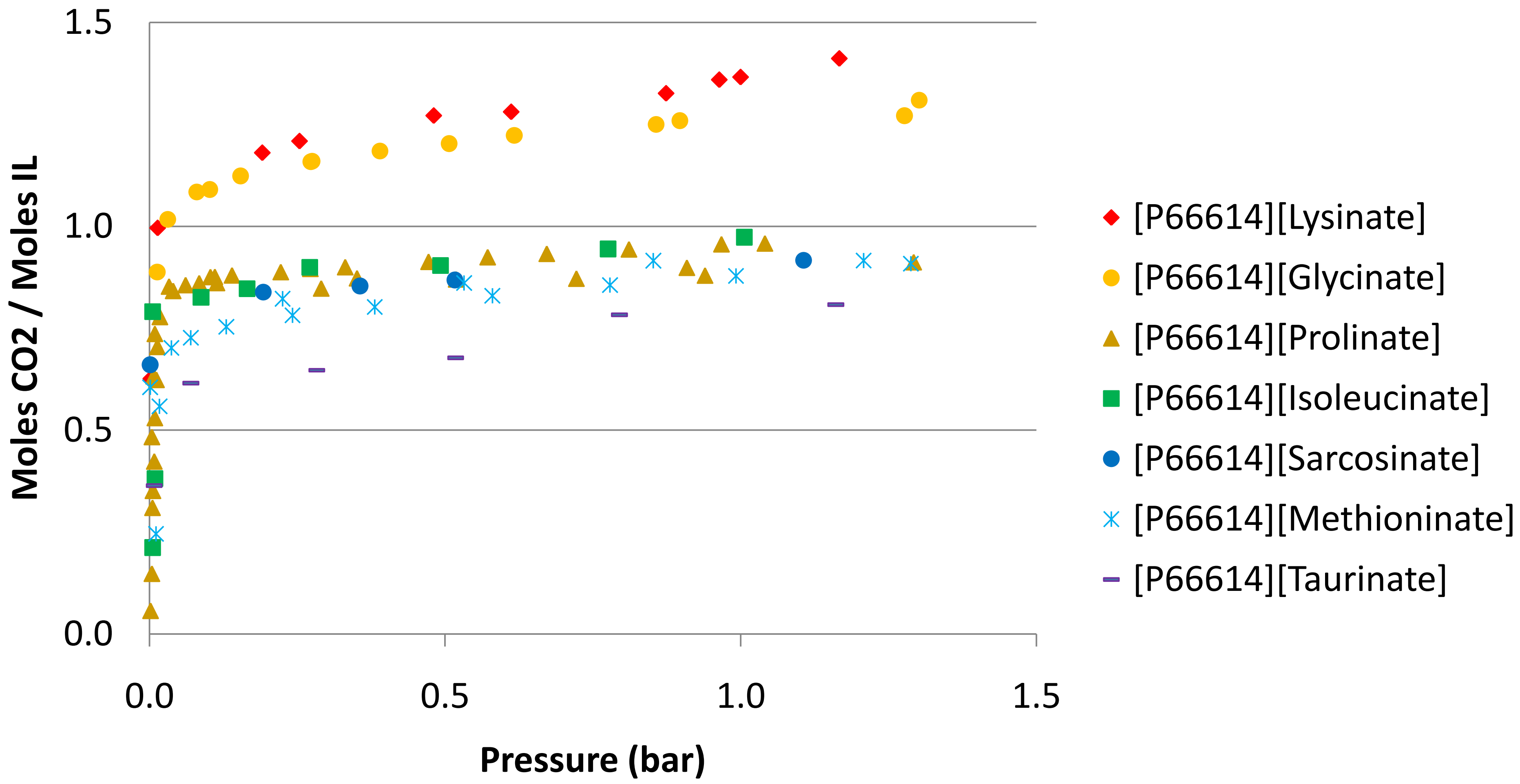
- Theory (DFT calculations) showed:
  - Local cation tethering favors 1:2 binding
  - Local anion tethering favors 1:1 binding
  - PUT AMINE ON THE ANION

Mindrup and Schneider, *ACS Symp. Series* **2010**



Gurkan et al., J. Am. Chem. Soc., 2010

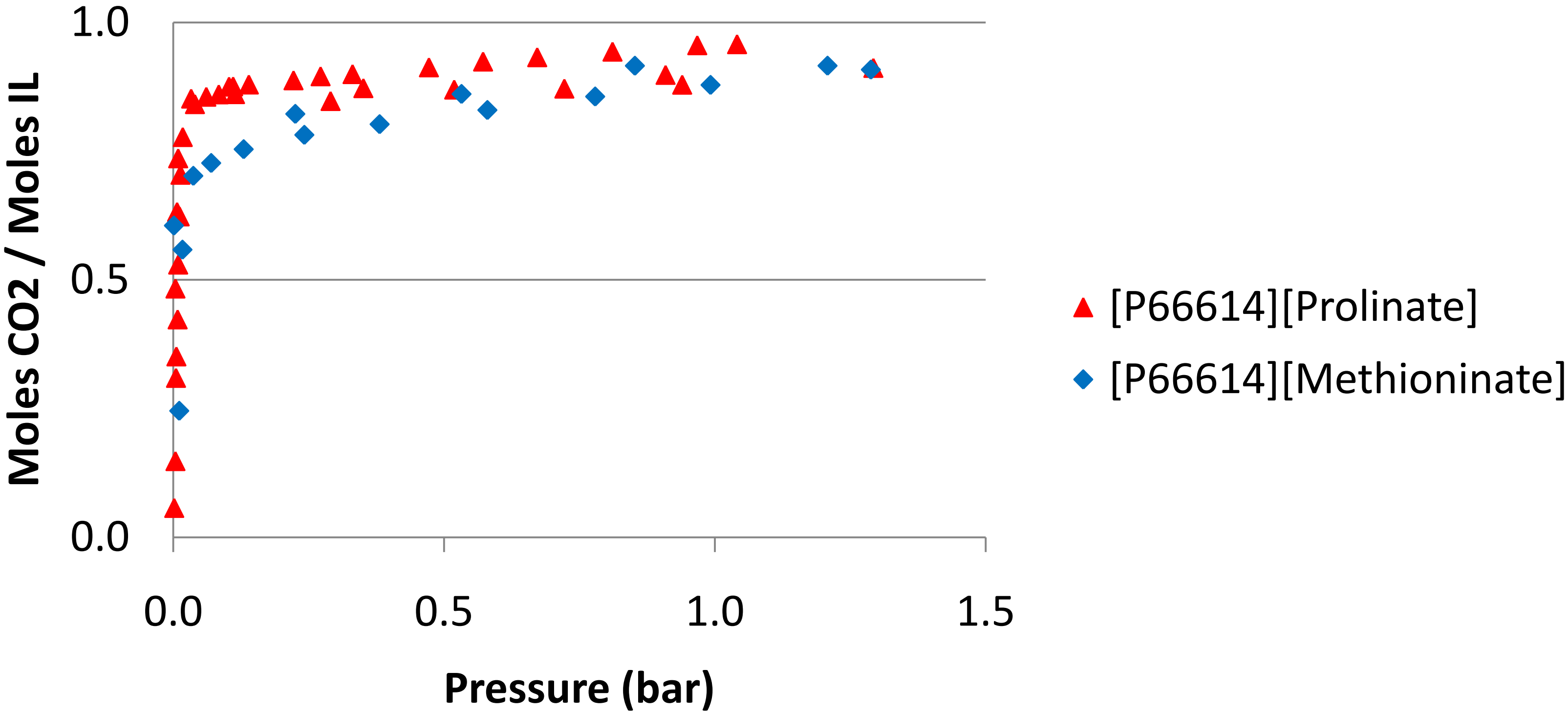
CO_2 Uptake for Amino Acid ILs



- All 7 amino acids absorbed significantly more than 0.5 moles CO_2/IL
- Lysinate & Glycinate absorbed more than 1 mole CO_2/IL

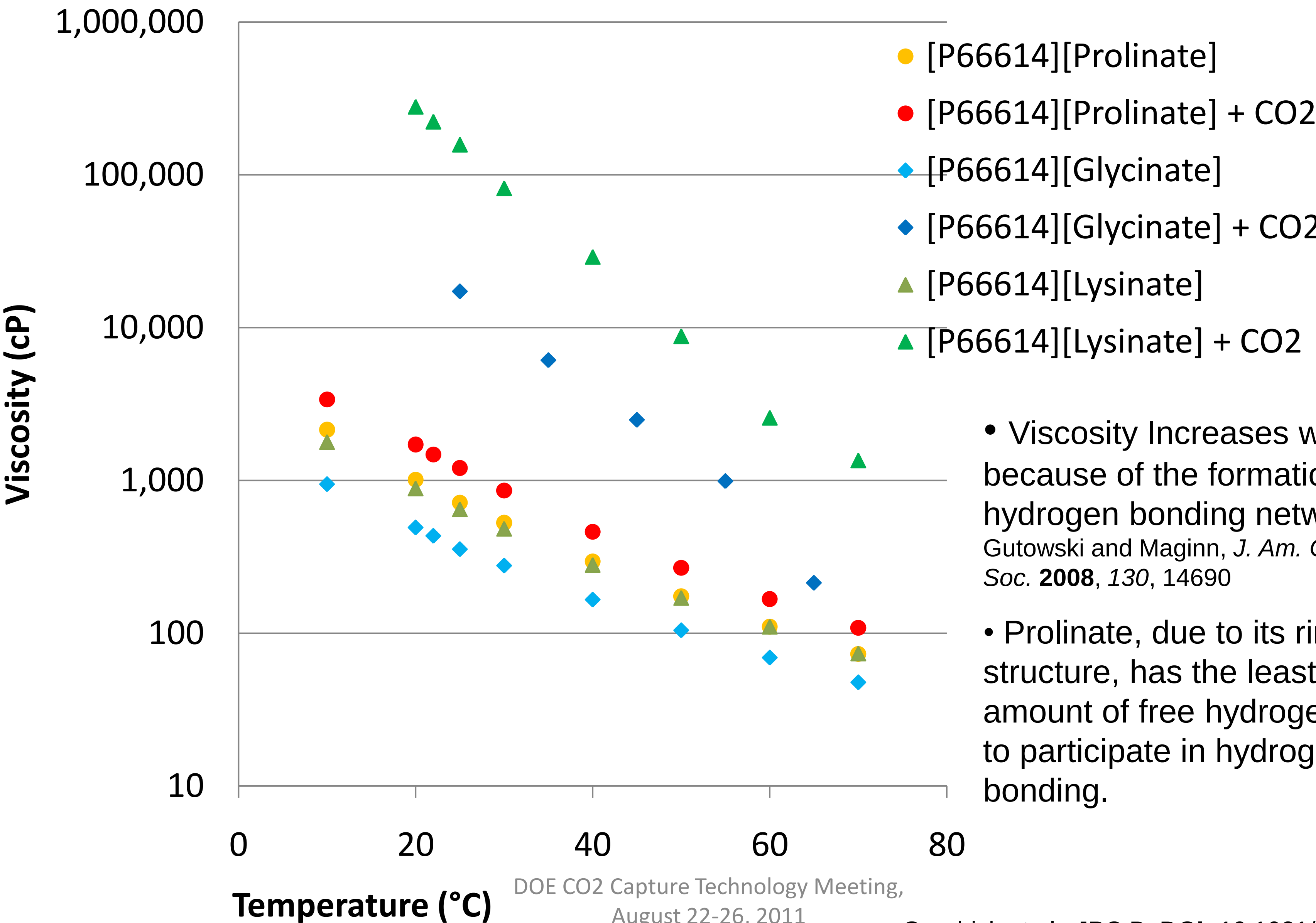
Goodrich et al., JPC B, **DOI:** 10.1021/jp2015534

Comparison of Measured ΔH with CO_2 Absorption Isotherms



Ionic Liquid	ΔH, kJ/mol_{CO_2}
$[P_{66614}]$[Prolinate]	-80
$[P_{66614}]$[Methioninate]	-64

Effect of CO_2 on Viscosity

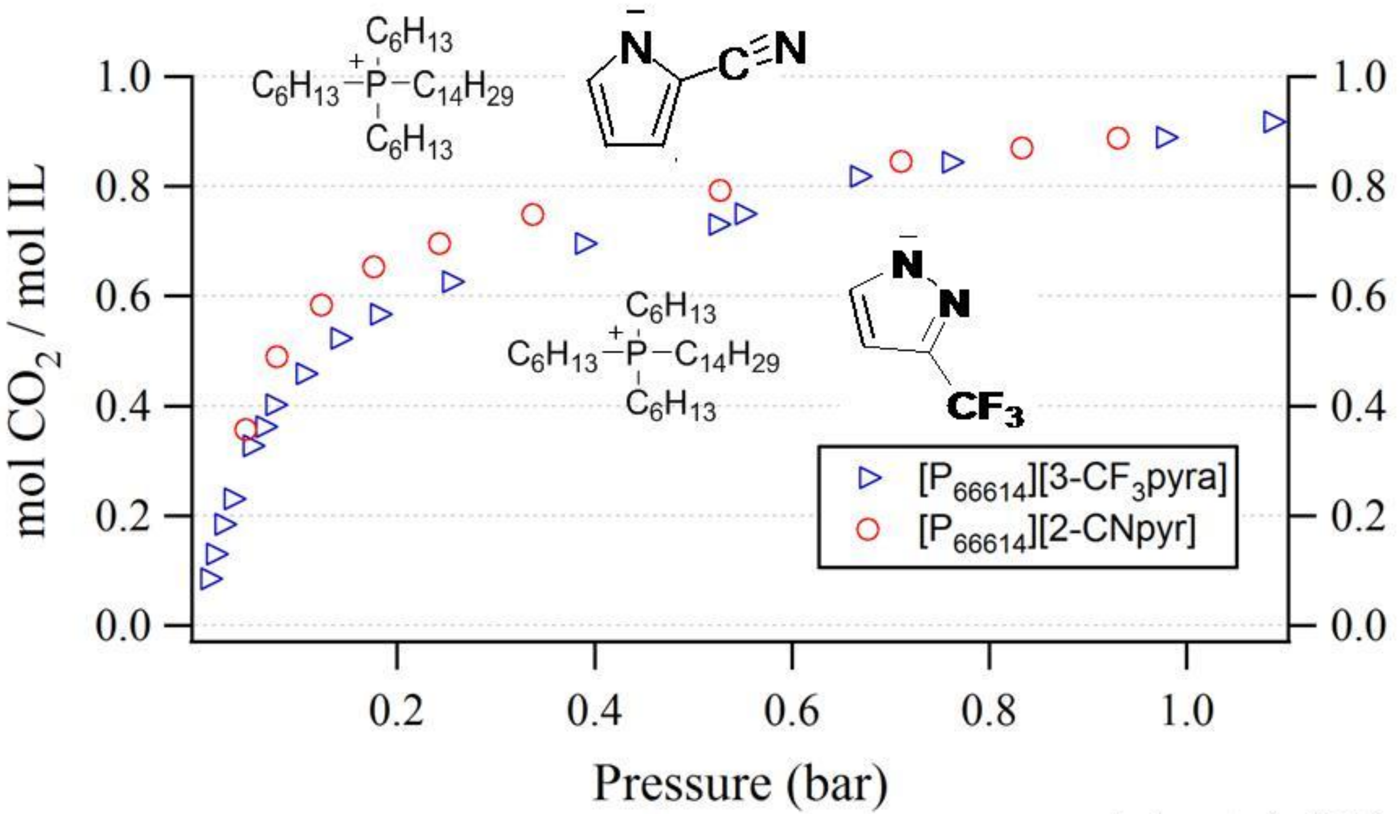


- Viscosity Increases with CO_2 because of the formation of a hydrogen bonding network
  Gutowski and Maginn, *J. Am. Chem. Soc.* **2008**, *130*, 14690
- Prolinate, due to its ringed structure, has the least amount of free hydrogens able to participate in hydrogen bonding.

Goodrich et al., JPC B, **DOI:** 10.1021/jp2015534

AHA – aprotic heterocyclic anions

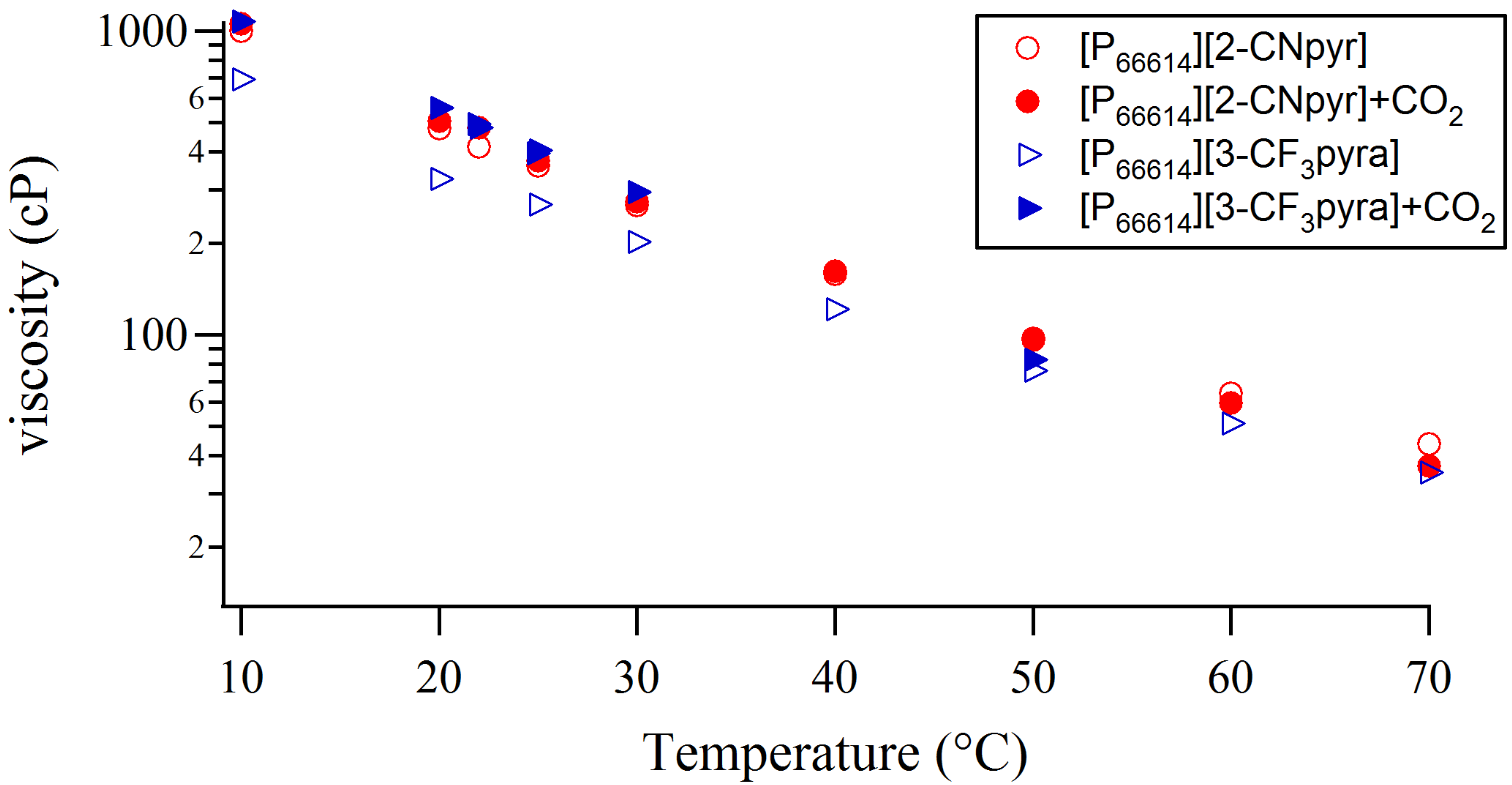
- Retain amine in ring structure
- Further reduce free hydrogens



Gurkan et al., JPC Lett, 2010

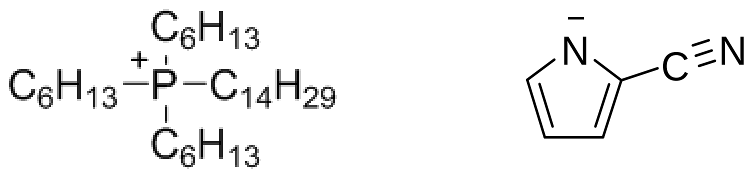
AHA Viscosities

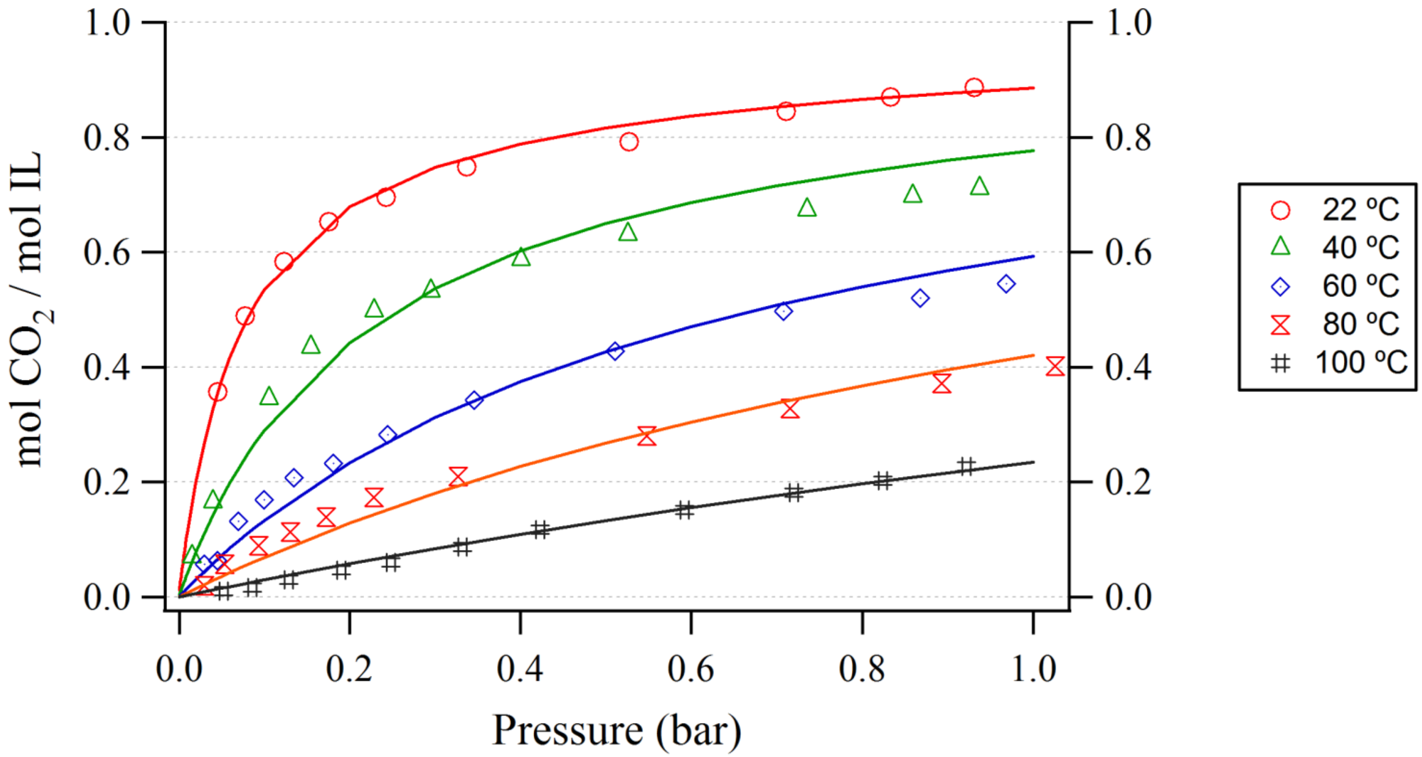
Very small viscosity increase when saturated with CO_2 at 1 bar and 22 C



Gurkan et al., JPC Lett, 2010

AHA CO_2 Uptake as Function of T

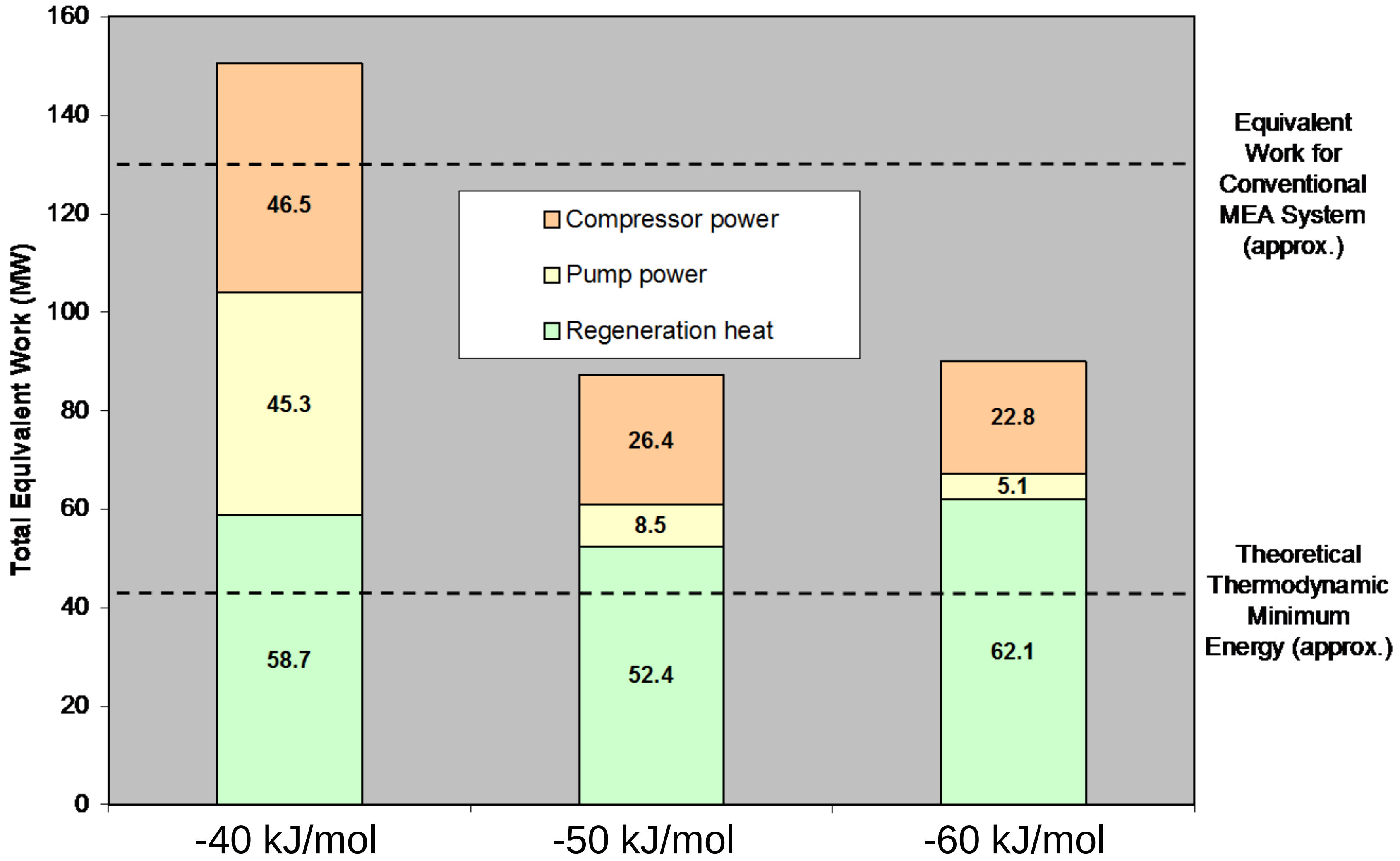




- Fit isotherms and get ΔH_{rxt} = -43 kJ/mol

Gurkan et al., JPC Lett, 2010

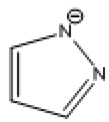
Total Equivalent Work



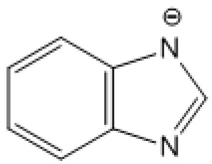
Trimeric

Different Aprotic Heterocyclic Anions

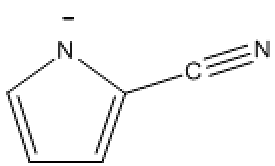
pyrazolides

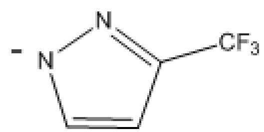


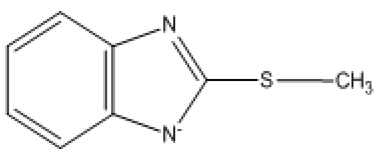
imidazolides



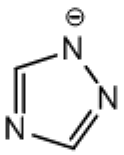
pyrrolides

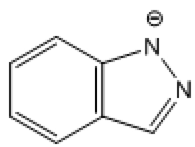


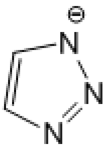


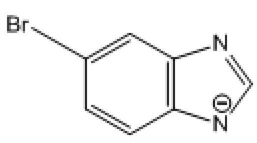


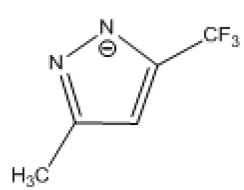
triazolides







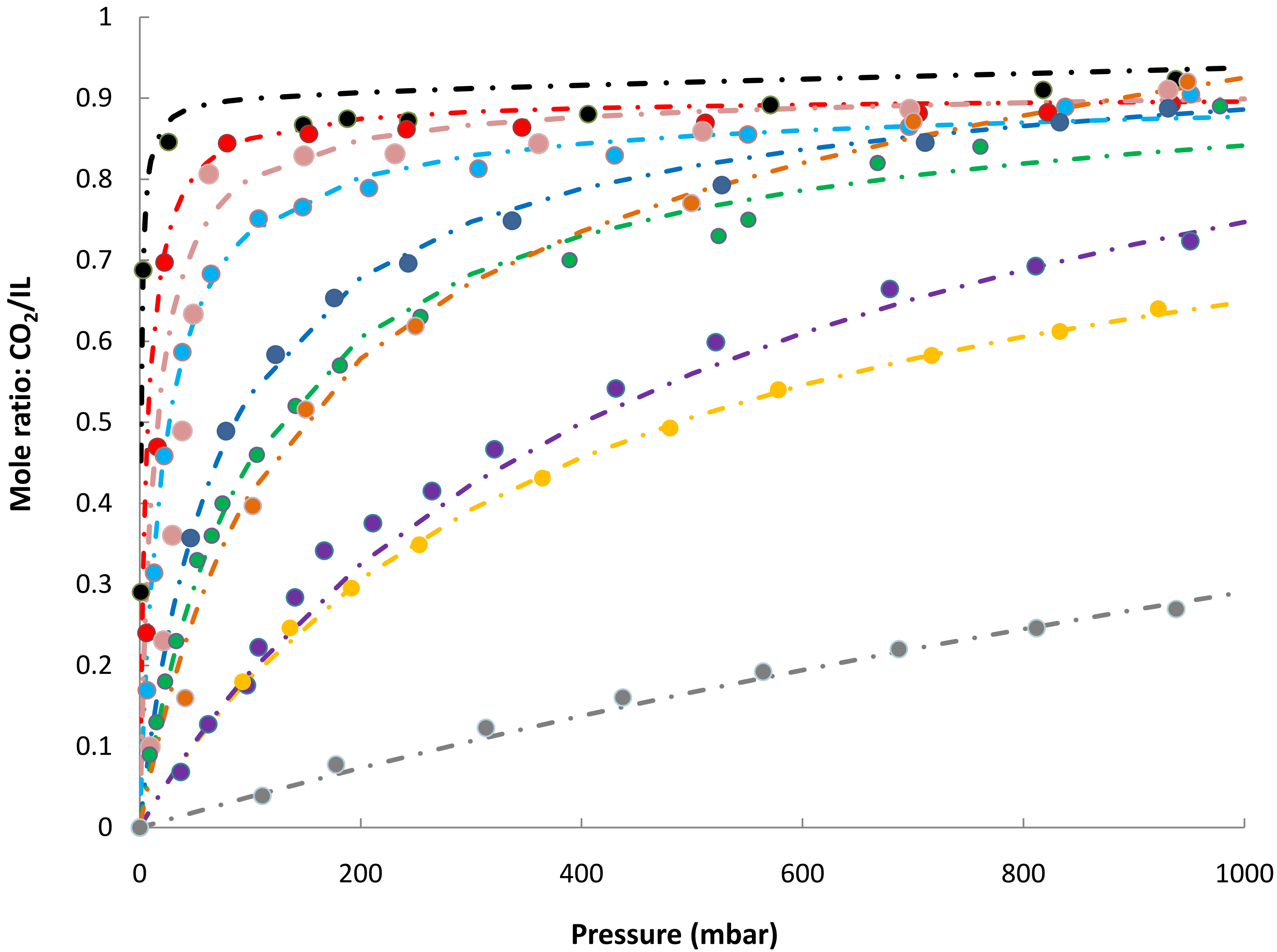




$-80°C < T_g < -65°C$

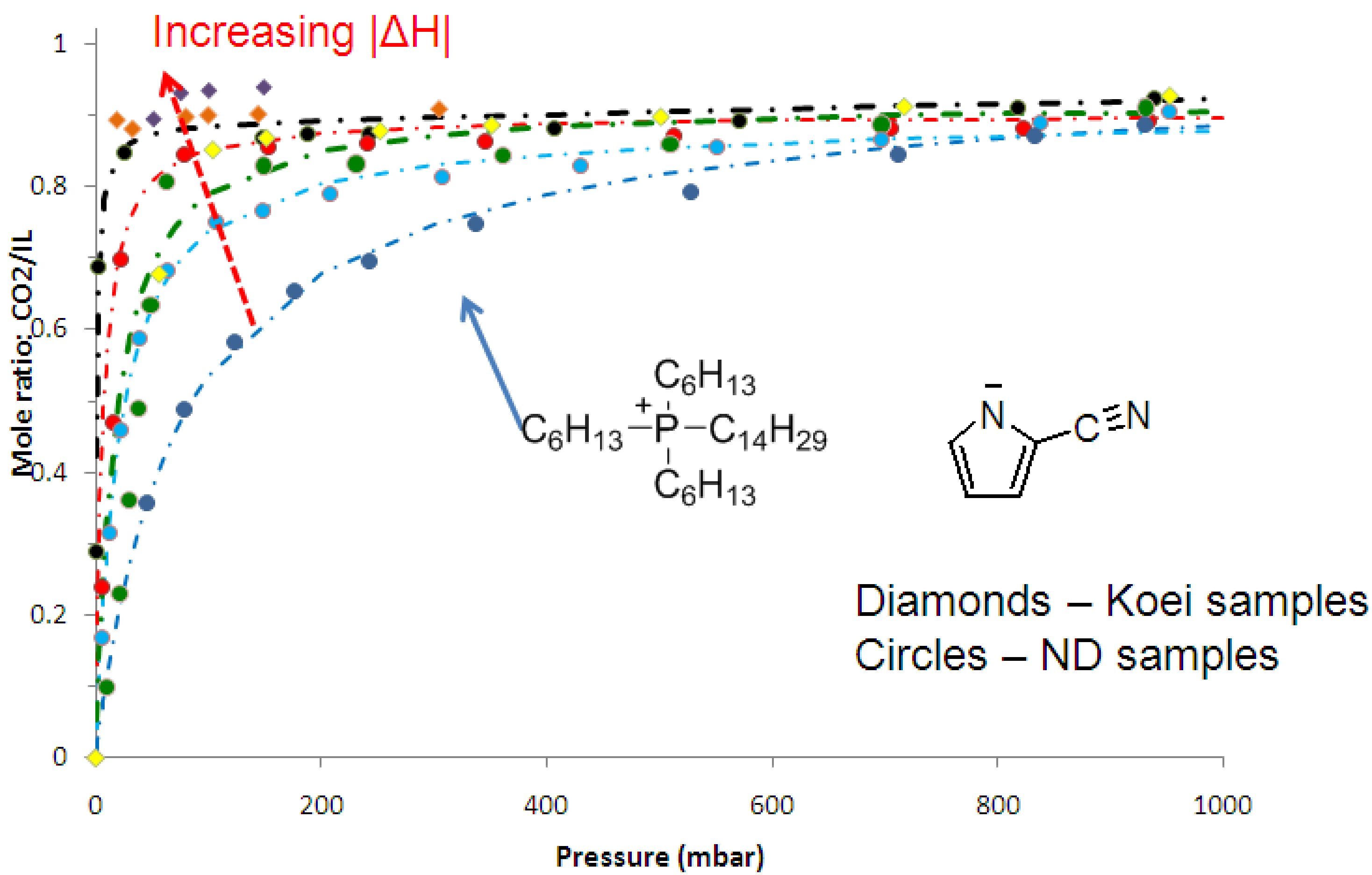
$260°C < T_{decomp} < 330°C$

AHA CO_2 Uptake

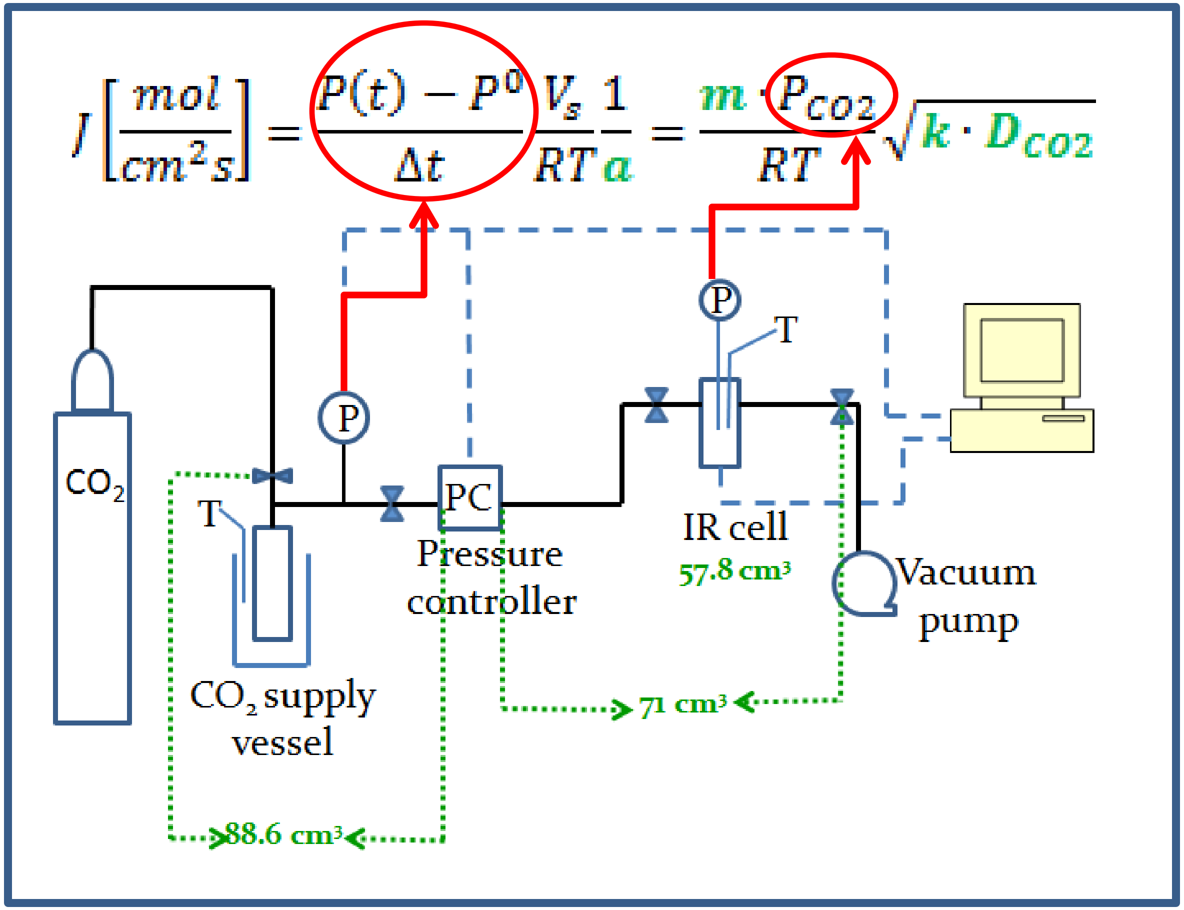


Can tune reaction enthalpy both up and down

AHA CO_2 Uptake



Reaction Rates



-Dilute in tetraglyme to eliminate mass transfer resistances

- Measure reaction rates from pressure drop as a function of time

- Verify reaction products with IR spectroscopy

- 0.05 to 0.15 M

- 22ºC to 60ºC

Reaction Rates

- Measured rates for $[P_{66614}][Pro]$, $[P_{66614}][CNpyr]$, and $[P_{66614}][CF_3pyra]$
- All rates faster than MEA
- All activation energies less than MEA

0.5 and 1M MEA at 22 C, k_R = ***5,400*** *l/mol.s*

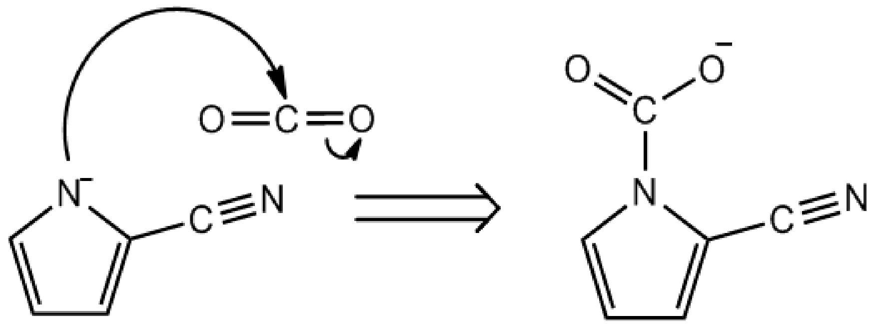
Hikita et al., **13** (1977) *Chem. Eng. J. and the Biochem. Eng. J.*

E_a = *41.8 kJ/mol* for MEA

Blauwhoff et al. *Chemical Engineering Science* **39**, 207 (1984)

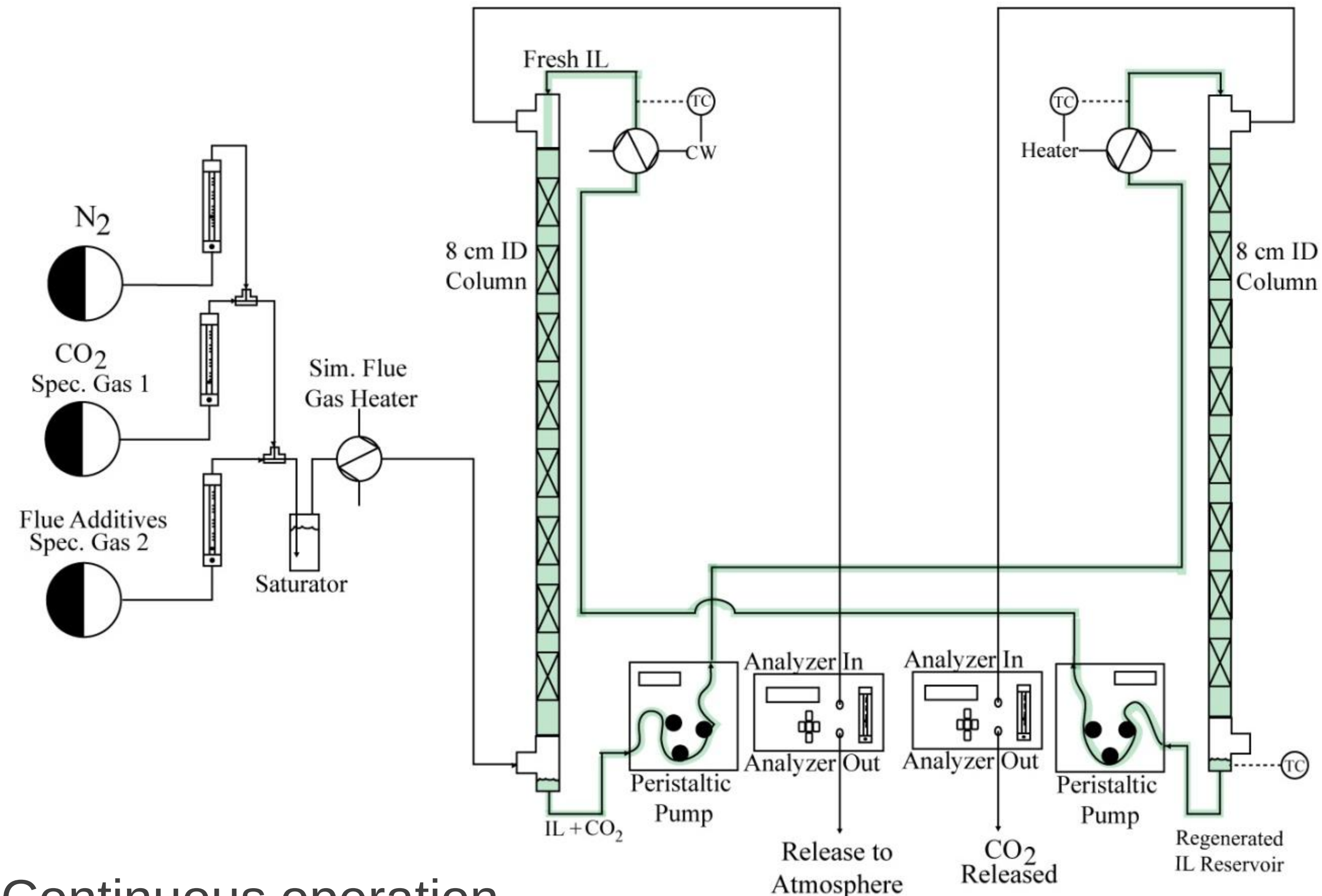
Reaction Rates – Activation Energies

AHA ILs



Do not expect reaction rates to be a limiting factor in CO_2 capture by anion-functionalized ILs

Lab-scale Absorption Experiments



- Continuous operation
- Can run columns separately
- 2 liter liquid samples

Absorber/Desorber for CO_2 Removal

- We have run continuous steady-state operation of absorber and regenerator
- Verified with MEA
- Running with $[P_{66614}][Pro]$
- Will run with AHA IL
- Measuring HTUs

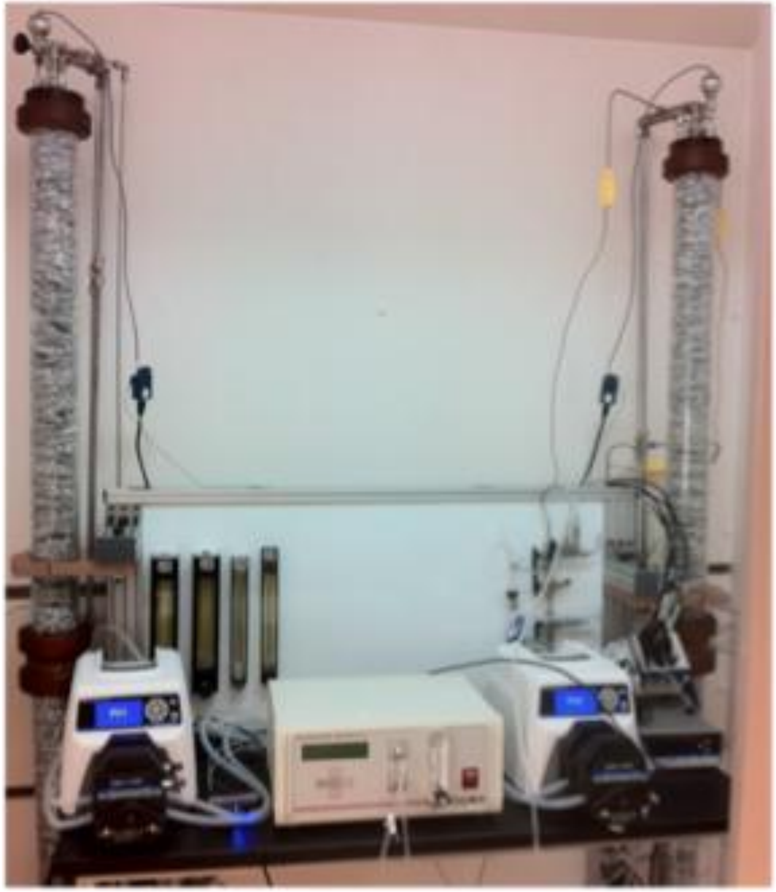
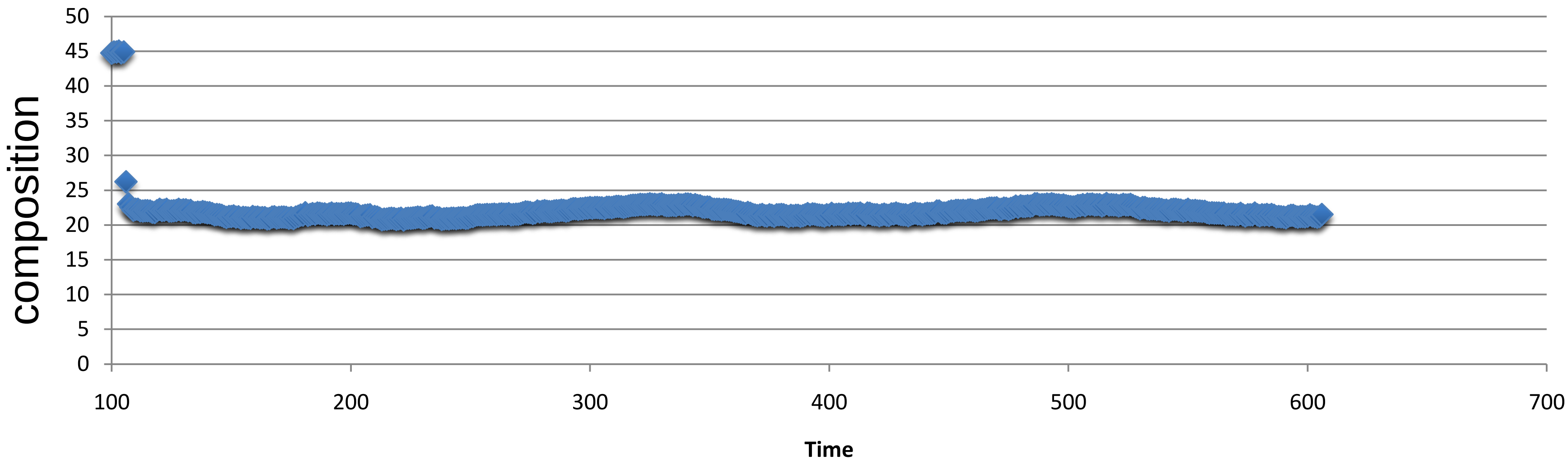
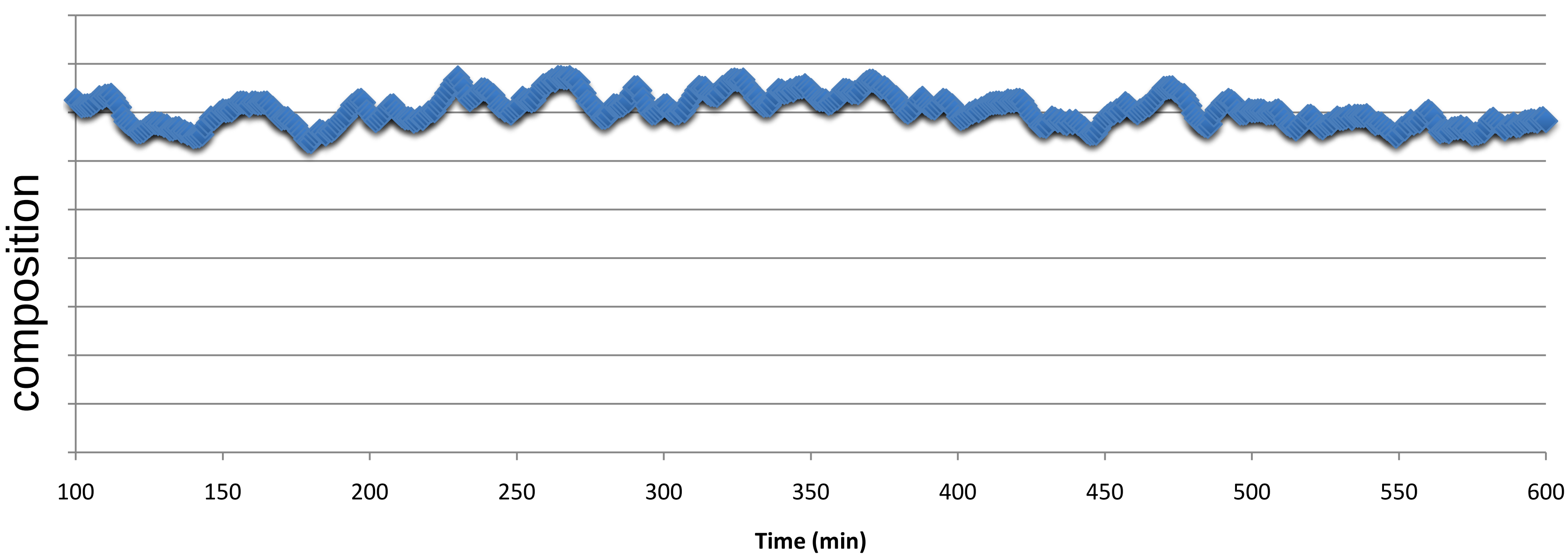


Figure 1: Image of the lab-scale unit constructed for Task 18.

Steady State Absorber Run 3



Steady State CO2 Desorber Run 3



Commercialization Study

- Market size for CO_2 capture processes such as the IL-based one is potentially huge.
  - Total 627 coal-fired plants in US in 2006
  - 51% are >100 MW and > 28% efficiency (94% of total CO_2 emissions)
- Tax of \$45 - \$60/ton of emitted CO_2 would be required to promote significant adoption of CCS (Geisbrecht and Dipietro, 2009)
  - ~100 GW of existing plants (32% of the plant capacity) would be retrofitted in this range, leading to CO_2 emissions reduction in power sector of 70 – 85%.
  - Tax of less than \$30/ton, no plants would be retrofitted.
  - More affordable and scalable process lowers the price point for adoption, and increases penetration

Geisbrecht, R. and Dipietro, P., "Evaluating Options for U.S. Coal Fired Power Plants in the Face of Uncertainties and Greenhouse Gas Caps: the Economics of Refurbishing, Retrofitting, and Repowering," Energy Procedia 1, p. 4347 (2009))

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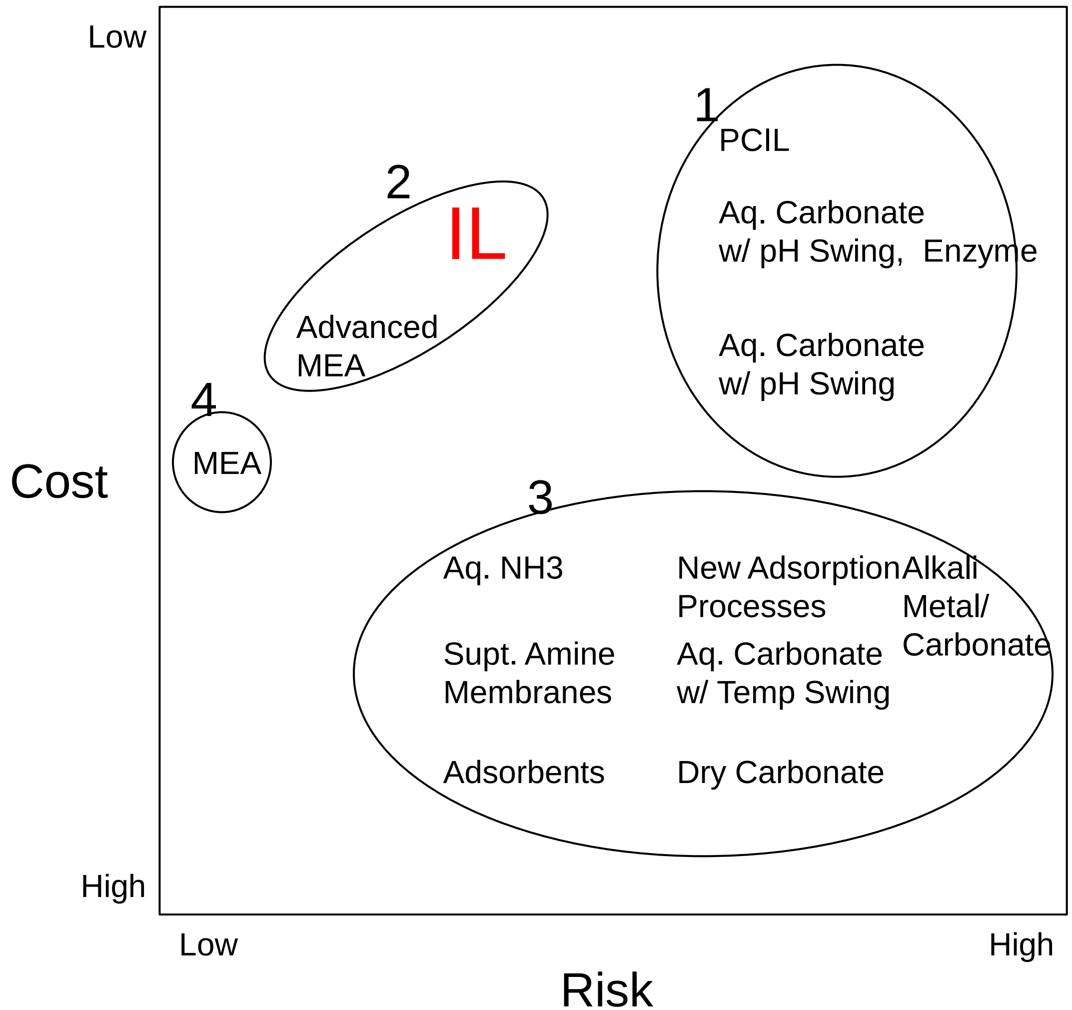
Benefit vs. Risk Evaluation

1 - Potential for low cost but very high risk

2 - Potential for lower cost at moderate risk

3 - Currently cost estimates and risk are high

4 - Low risk but high cost



Commercialization of CO_2 Capture with ILs

- Risk vs. Cost
  - Risk profile indicates multiple solutions should be pursued
  - Development and deployment cost is large, suggesting down-selects should be made early
  - Focus on processes with potential to be substantially less expensive than MEA, even if risky
  - IL process and lower-energy variations of the MEA process should continue to be pursued as retrofit options
- Scale-up of the IL-based CO_2 capture process to the point of full-scale demonstration is doable in ten years or less.
  - Multi-step sequential scale-up, not including full-scale demonstration, is an estimated $60 million.
  - Construction and 1 ½ years of operation of the full-scale demonstration separation process will cost roughly $600 million.

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Conclusions

- Ionic liquids have potential for variety of CO_2 capture applications
- One mole CO_2 per mole ionic liquid achievable with anion tethered amine-functionalized ionic liquids
- AHA ILs eliminate increase in viscosity upon reaction with CO_2
- Demonstrated ability to 'tune' reaction enthalpy of ILs with CO_2 without increases in viscosity
- Reaction rates faster than MEA
- Currently running laboratory scale unit
- Commercialization study indicate potential for low cost with moderate risk

SEI Sustainable Energy Initiative

Acknowledgments

NETL Project 43091

Coworkers:

Elaine Mindrup, Mandelle Danser, Thomas Sentfle, Tom Rosch, Hao Wu, Jindal Shah, Marcos Perez-Blanco, Matthew LeMay, Burcu Gurkan, Juan de la Fuente, Erica Price, Devan Kestel, Samuel Seo, Marjorie Massel, Levi Wilson, Michael Glaser, David Zadigan, Brett Goodrich, Lindsay Ficke, Dan Pohlman, Aruni DeSilva, Mauricio Quiroz-Guzman