Ionic Liquids for Post-Combustion CO_2 Capture

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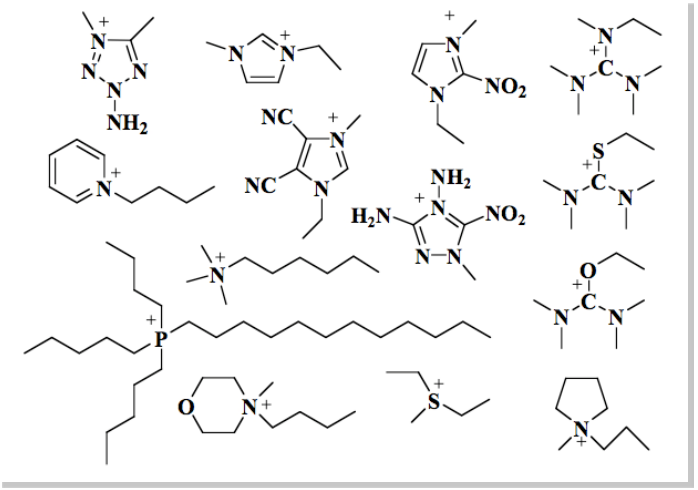
Outline

- Background
- Physical solubility of gases in ILs
- Chemical complexation of ILs with CO_2
  - Doubling capacity
  - Eliminating viscosity increase
  - Tuning reaction enthalpy
  - Details on reaction chemistry
- Phase change ionic liquids
- Conclusions

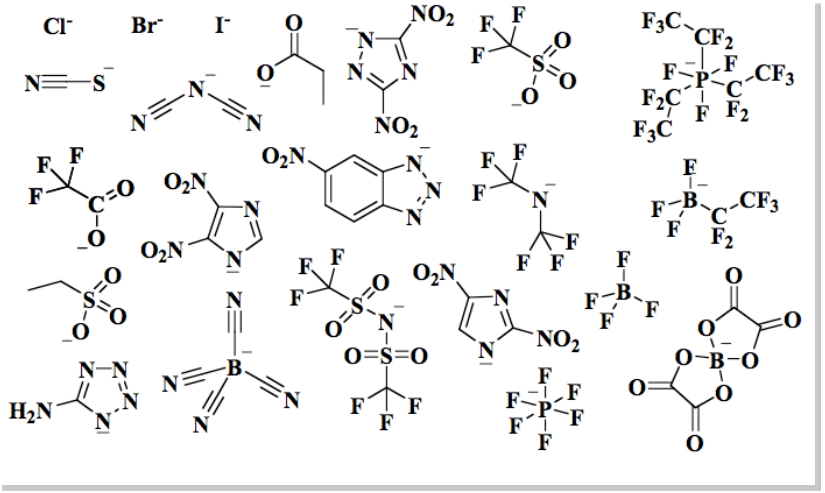
Ionic Liquids

- Pure salts that are liquid around ambient temperature
  - Not simple salts like alkali salts
- Many favorable properties
  - **Nonvolatile**
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity

Examples of cations



Examples of anions



Ionic Liquids

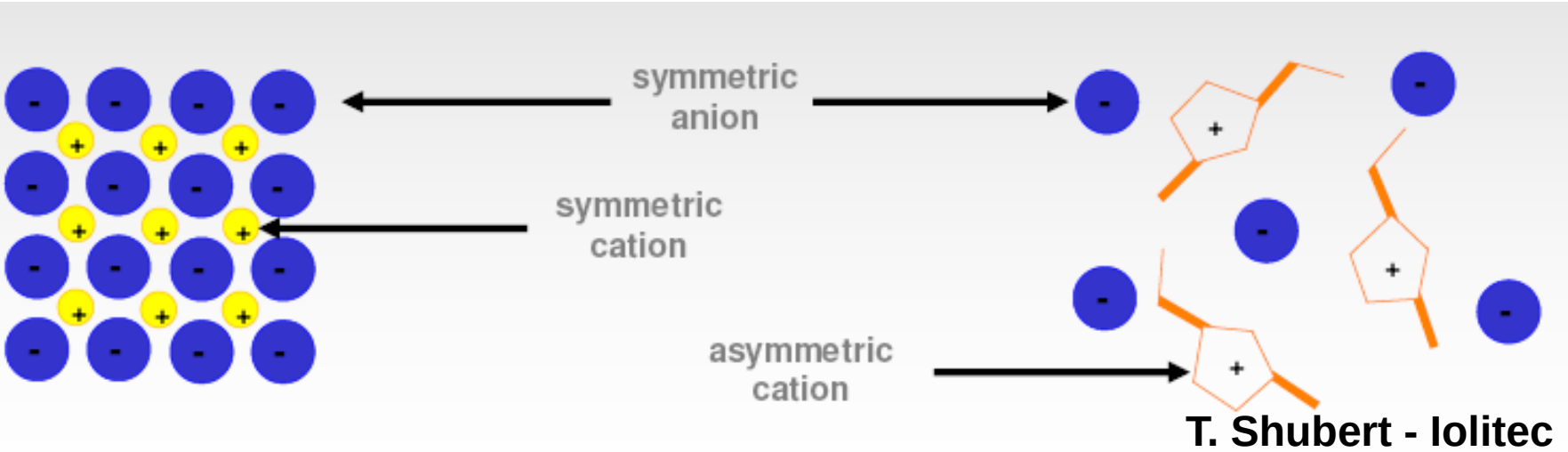


Table salt
NaCl
T_m = 1474 °F
(801 °C)

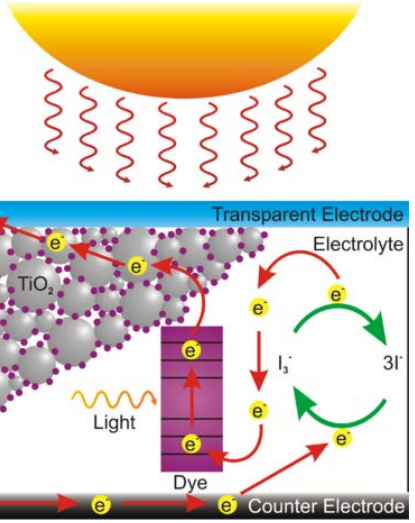
Ionic Liquid
T_m << room temperature

My Research Group

- Design, synthesis and purification of new ILs
- Thermophysical properties
  - Melting points, decomposition temperatures, viscosities, densities, ionic conductivities
  - Excess enthalpies
- Phase behavior
  - Gas solubilities, VLE, LLE, SLE
- Electrochemical properties
  - Electrochemical windows, electrochemical reduction of CO_2, electroplating
- Reactivity (with CO_2)
- Macroscopic thermodynamic modeling

Energy Applications of Ionic Liquids

- Separations
  - Gas separations (CO_2 capture)
  - Breaking azeotropes
  - Organics from fermentation broths
- Cooling and Heating
  - Absorption cooling
  - Co-fluid vapor-compression refrigeration and heat pumps
- Electrolytes
  - Batteries
  - Fuel cells
  - Supercapacitors
  - Dye sensitized solar cells
- Biomass Processing
- Heat Transfer Fluids



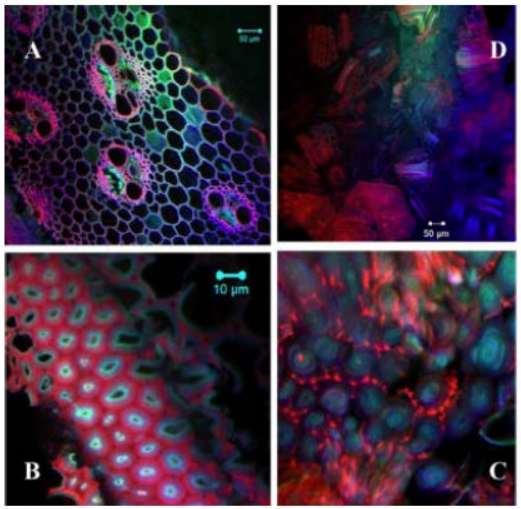


Figure 4. In situ dynamic study of switchgrass dissolution in ethyl methyl imidazolium acetate. Confocal fluorescence images of switchgrass stem section before pretreatment (**a**), and after 20 (**b**) and 50 (**c**) min of pretreatment. Complete breakdown of organized plant cell wall structure (**d**) is observed after 2 h.

jbei
Joint BioEnergy Institute

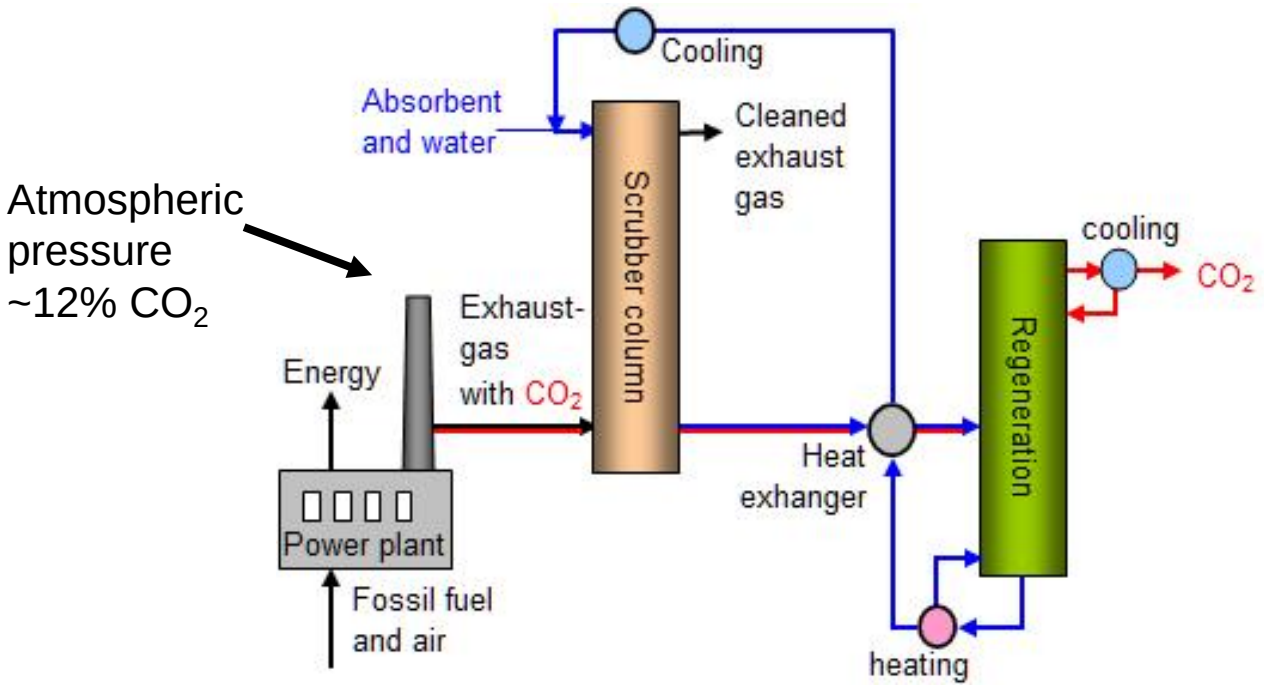
Important CO_2 Separations

- CO_2 from natural gas
- CO_2 from air
- Pre-combustion gases
- Post-combustion flue gas

CO_2 Capture

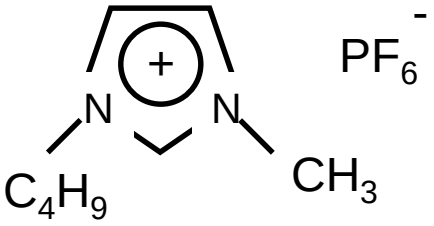
- 85% of primary energy from burning of fossil fuels
- > 50% of electricity generation from coal (more from NG)
- Point sources like power plant good targets for CO_2 capture
- Need lower energy processes for removal of CO_2 from post-combustion flue gas
- Commercial options - dilute aqueous amine solutions
  - Primarily, monoethanolamine (MEA)
  - High parasitic energy load (~28%)
  - Corrosive, side reactions
  - Degrades at low temperatures
- Alternative – ionic liquids

Post-Combustion Flue Gas

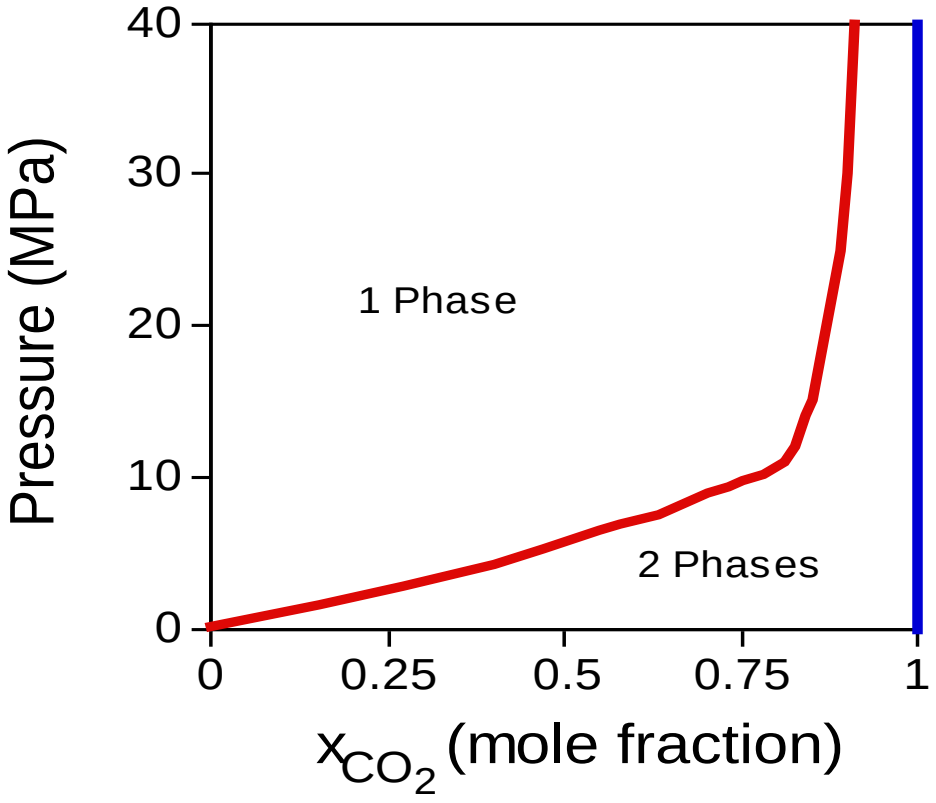


http://www.bellona.org/factsheets/1191913555.13

First Gas Solubility in IL



[bmim][PF_6]



- no detectable IL in CO_2 phase at 40C and 13.8 MPa
- significant solubility of CO_2 in IL
- 1.3-7.2 mole % IL mixtures immiscible at 40 MPa

Blanchard , Hancu, Beckman and Brennecke., Nature, May 6, 1999

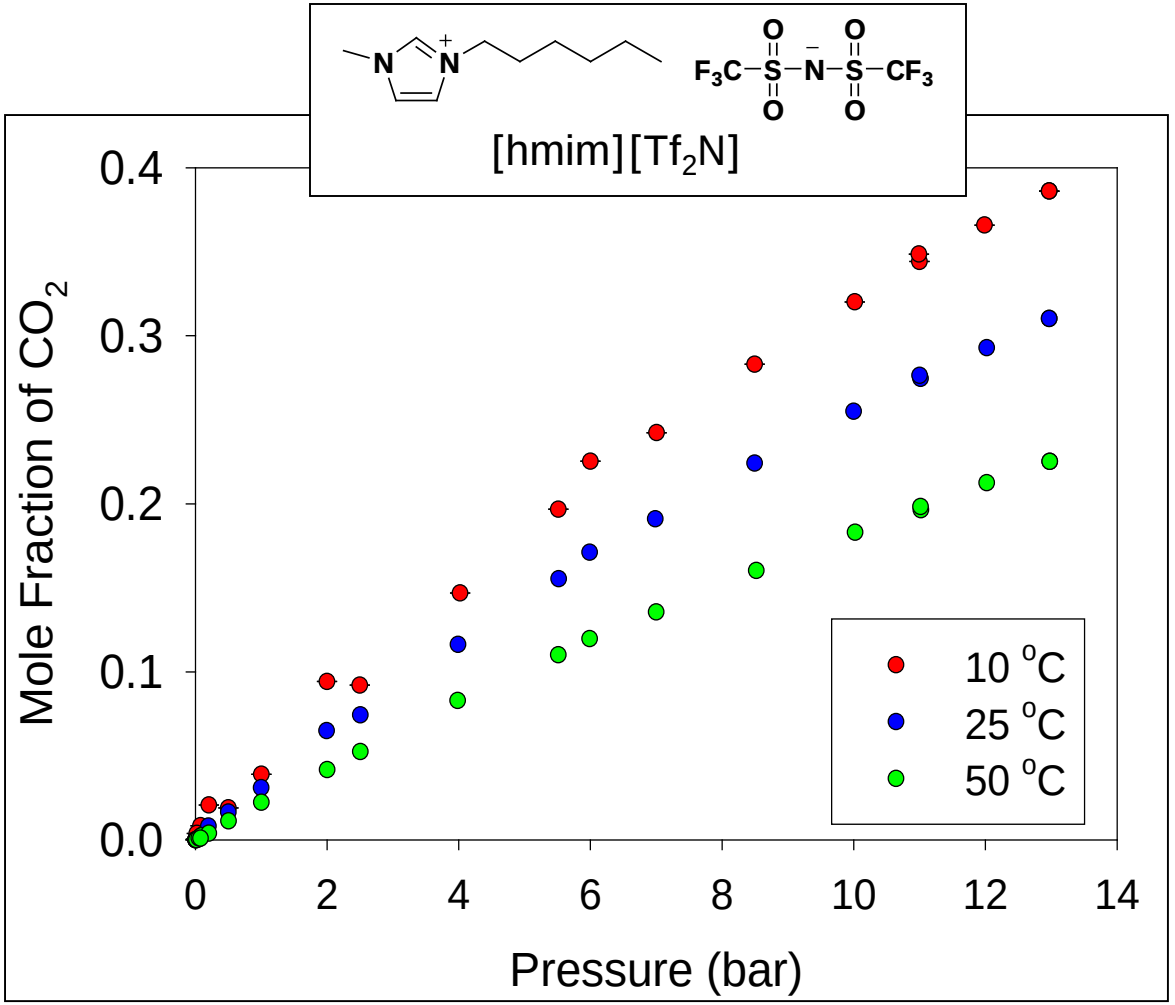
Physical Dissolution of CO_2

- Gas solubility

solubility ↑ pressure ↑

solubility ↓ temperature ↑

- Important for reusability of ILs
  - Absorb at low T
  - Remove at high T
- Trend seen for CO_2 solubility in all ILs measured

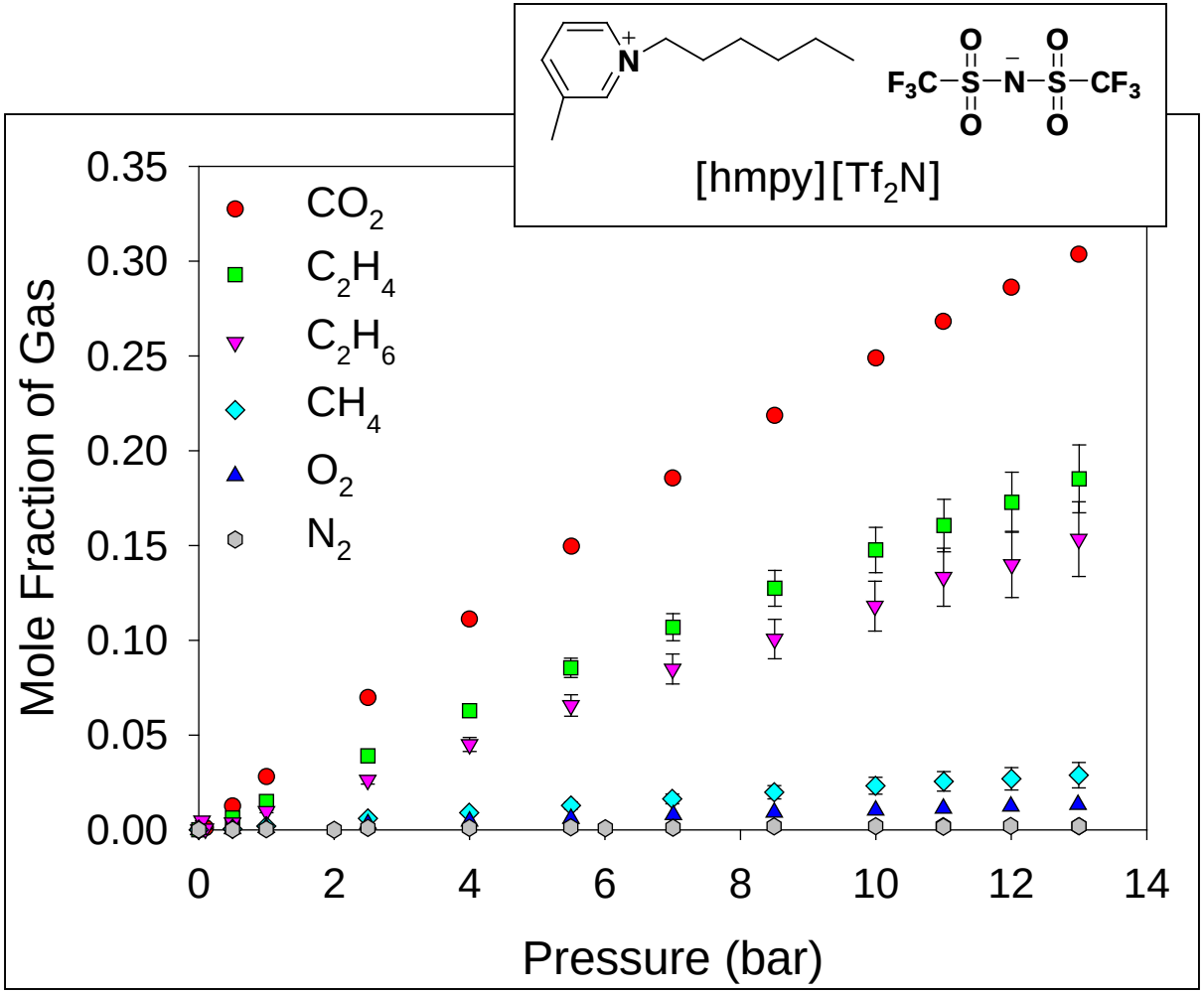


Muldoon, et al., JPC B, 2007, 111, 9001-9009

Mark Muldoon

Physical Dissolution of Gases in ILs

- Selectivity of CO_2 over N_2, O_2, etc. is good even for physical dissolution of CO_2 in ILs



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

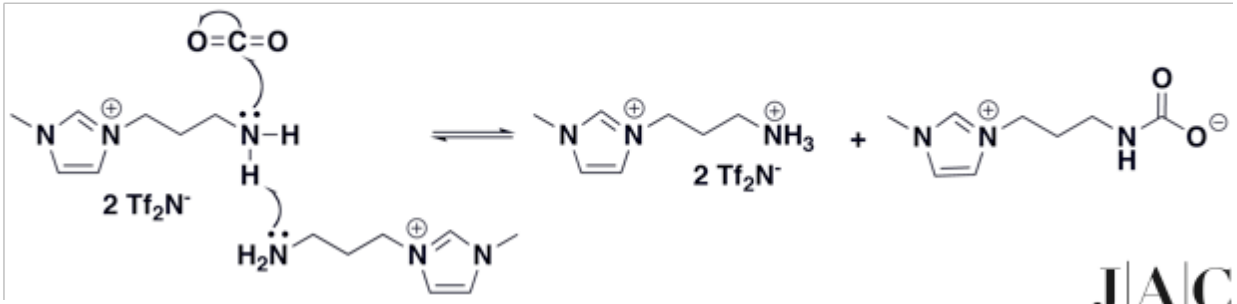
Jessica (Anderson) Kuczenski

Need Chemical Complexation with CO_2
Low partial pressures for post-combustion

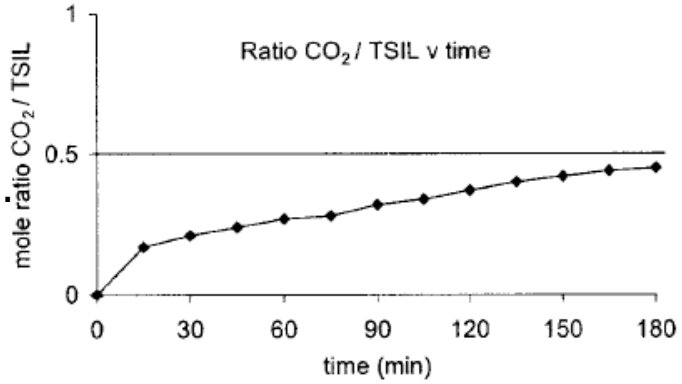
- **Physical solubility**
  - **Low heat of absorption**
  - **~ -12 kJ/mol by T dependence of isotherms and direct calorimetric measurements**
  - **Low regeneration energy**
  - **Large IL circulation rates**
  - **Desorption at low P increases compression costs**
  - **Would need ~10x increase in 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



1 atm CO_2
Room temp.



J|A|C|S
COMMUNICATIONS
Published on Web 01/19/2002

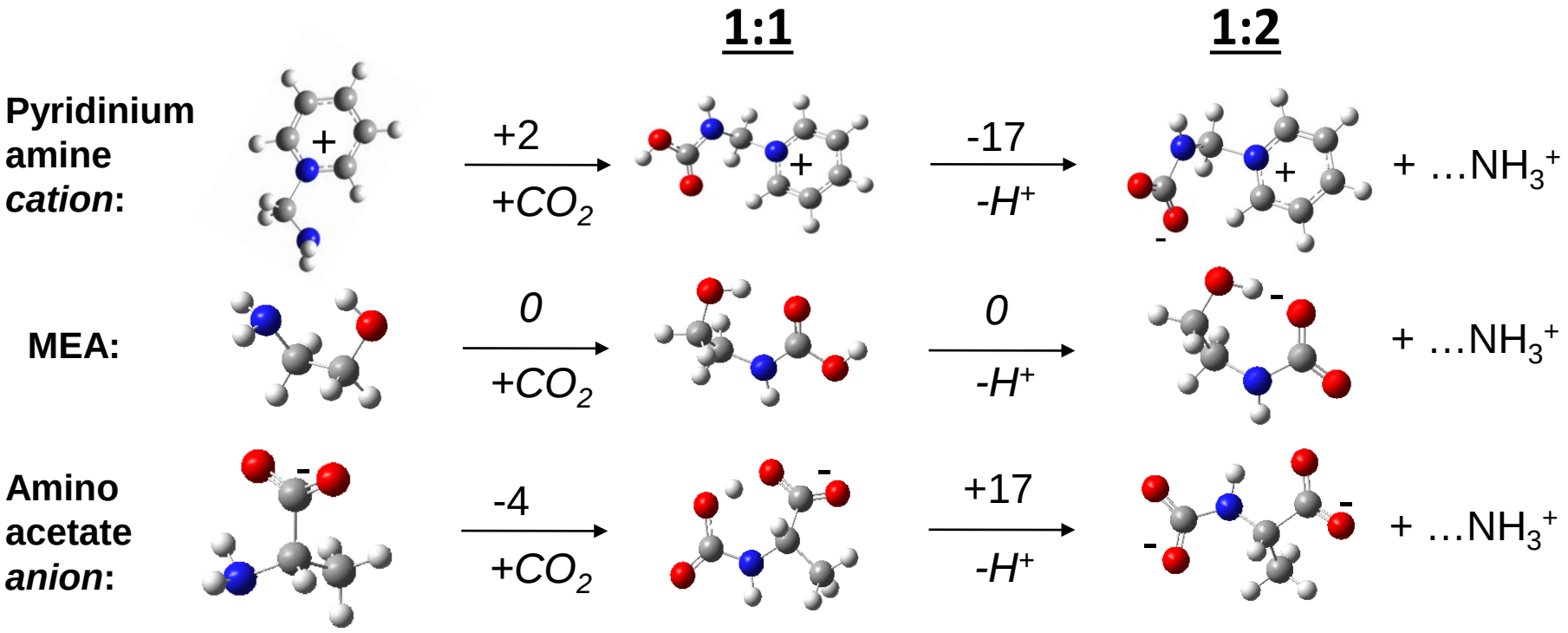
CO_2 Capture by a Task-Specific Ionic Liquid

Eleanor D. Bates, Rebecca D. Mayton, Ioanna Ntai, and James H. Davis, Jr.*
Department of Chemistry, University of South Alabama, Mobile, Alabama 36688

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

Can We Get Higher Capacity Than 1:2?

Reaction energies in kcal/mol relative to MEA

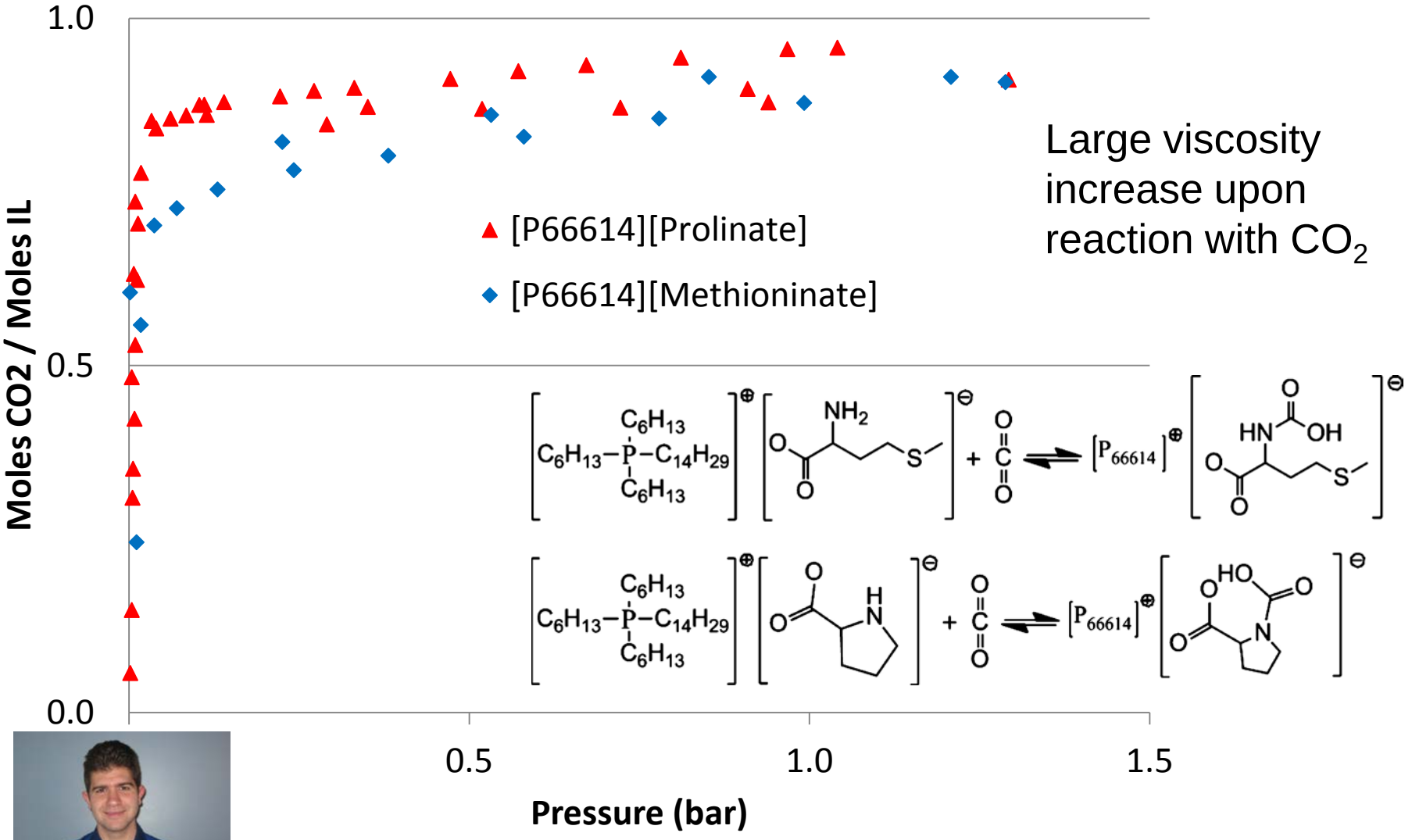


- Local cation tethering favors 1:2 binding
- Local anion tethering disfavors 1:2 binding
- Tethering ion and tethering point as important as functional groups in controlling CO_2 reactions

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

1:1 Uptake with Amine on Anion

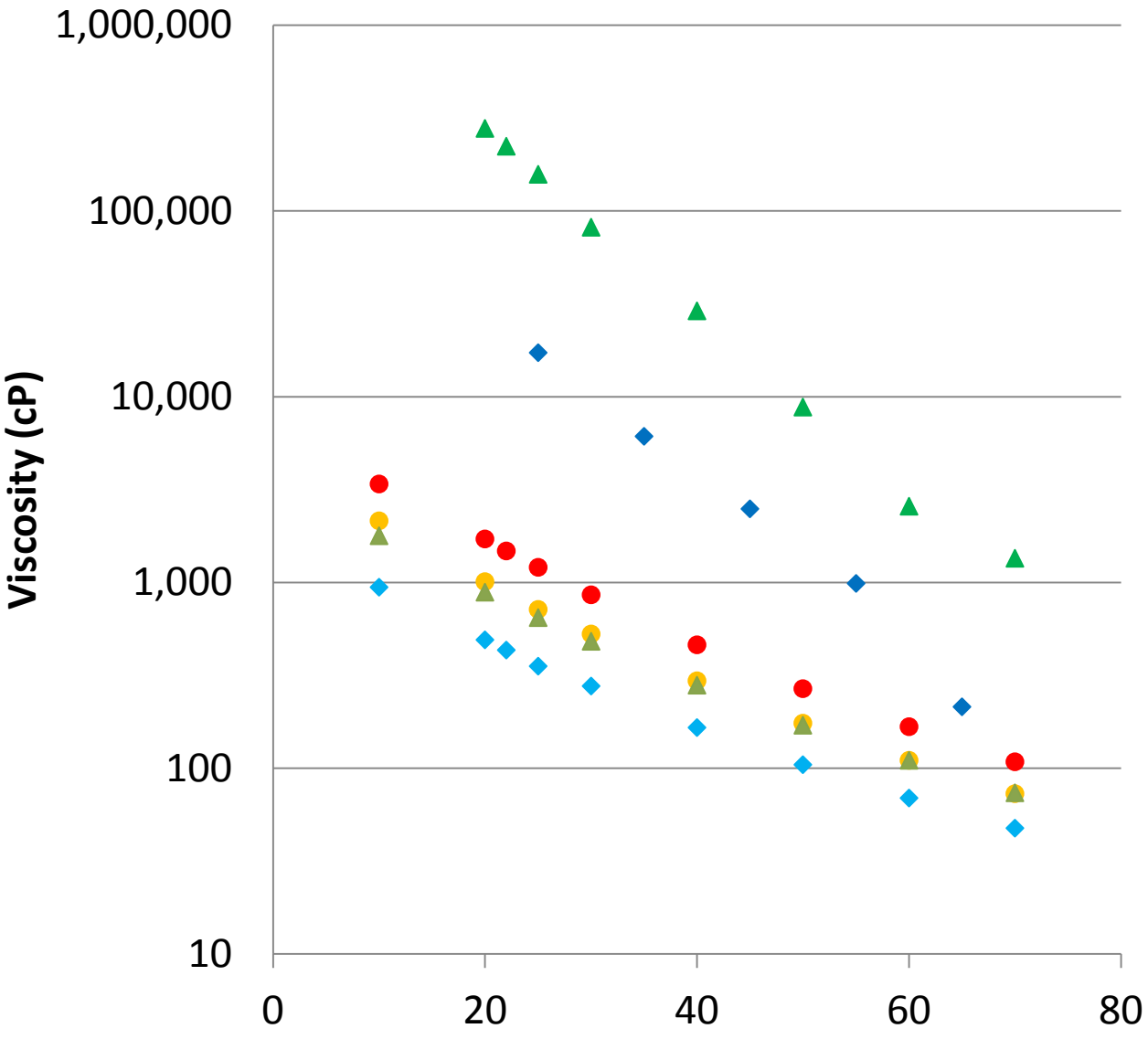
Forms carbamic acid, not carbamate



Brett Goodrich

Goodrich et al., JPC B, **2011,** 115, 9140

Effect of CO_2 on Viscosity



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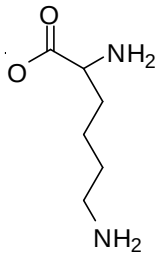
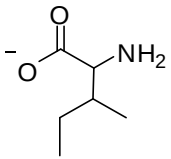
Goodrich et al., JPC B, **2011,** 115, 9140

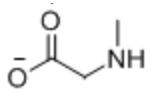
Effect of CO_2 on Viscosities



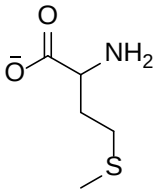
Lysinate



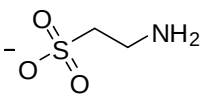
Isoleucinate



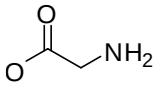
Sarcosinate



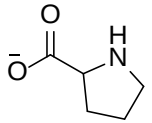
Methioninate



Taurinate

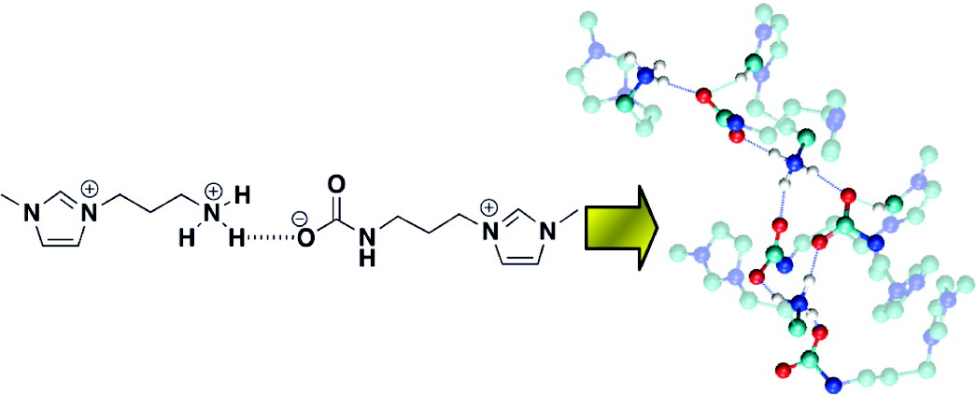


Glycinate



Prolinate

Decreasing CO_2 Saturated Viscosity

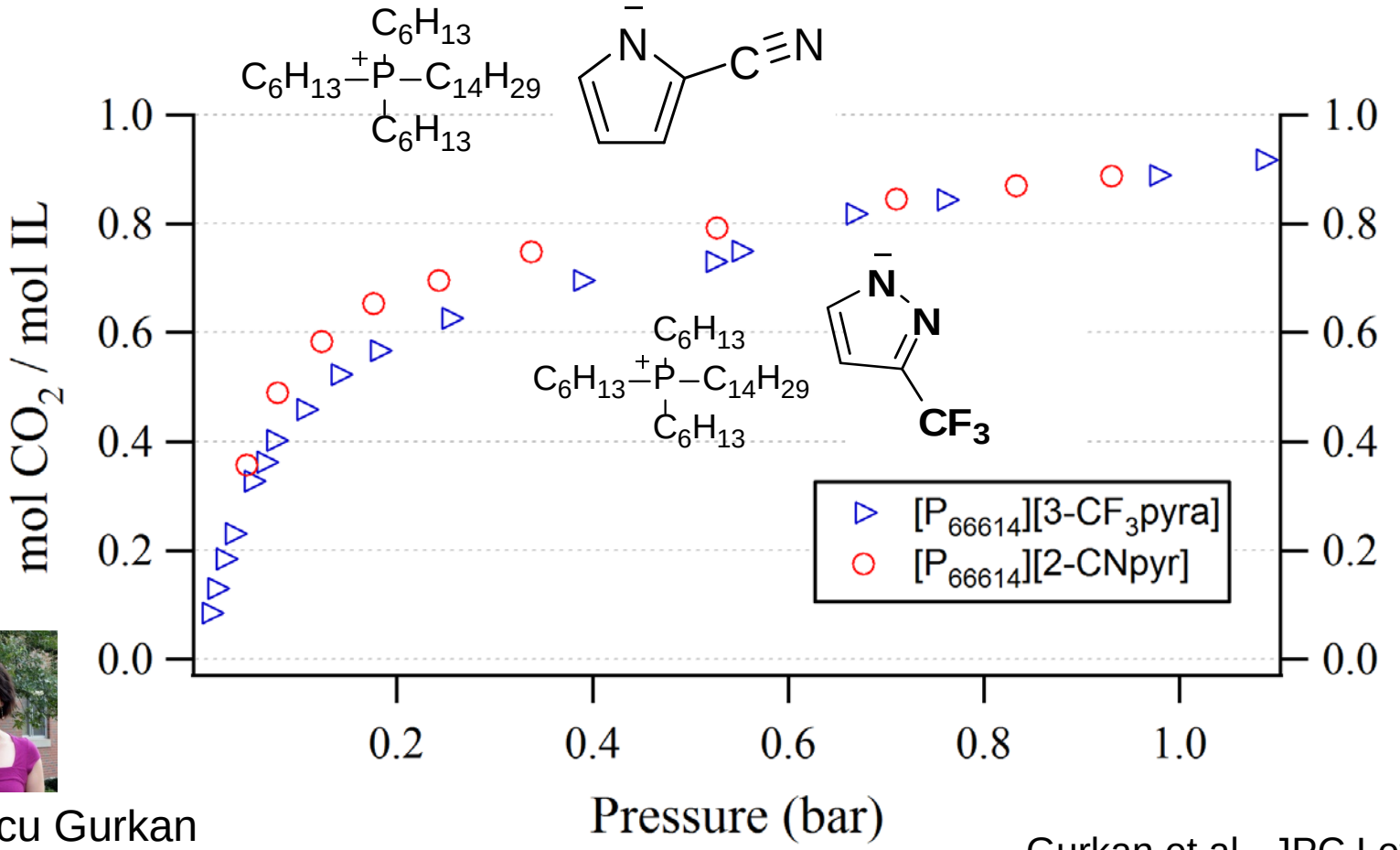


- Viscosity Increases with CO_2 because of the formation of a hydrogen bonding network
- Prolinate, due to its ringed structure, has the least amount of free hydrogens able to participate in hydrogen bonding.

Gutowski, K. E.; Maginn, E. J., *J. Am. Chem. Soc.* **2008**, *130*(44), 14690-14704

AHA – aprotic heterocyclic anions

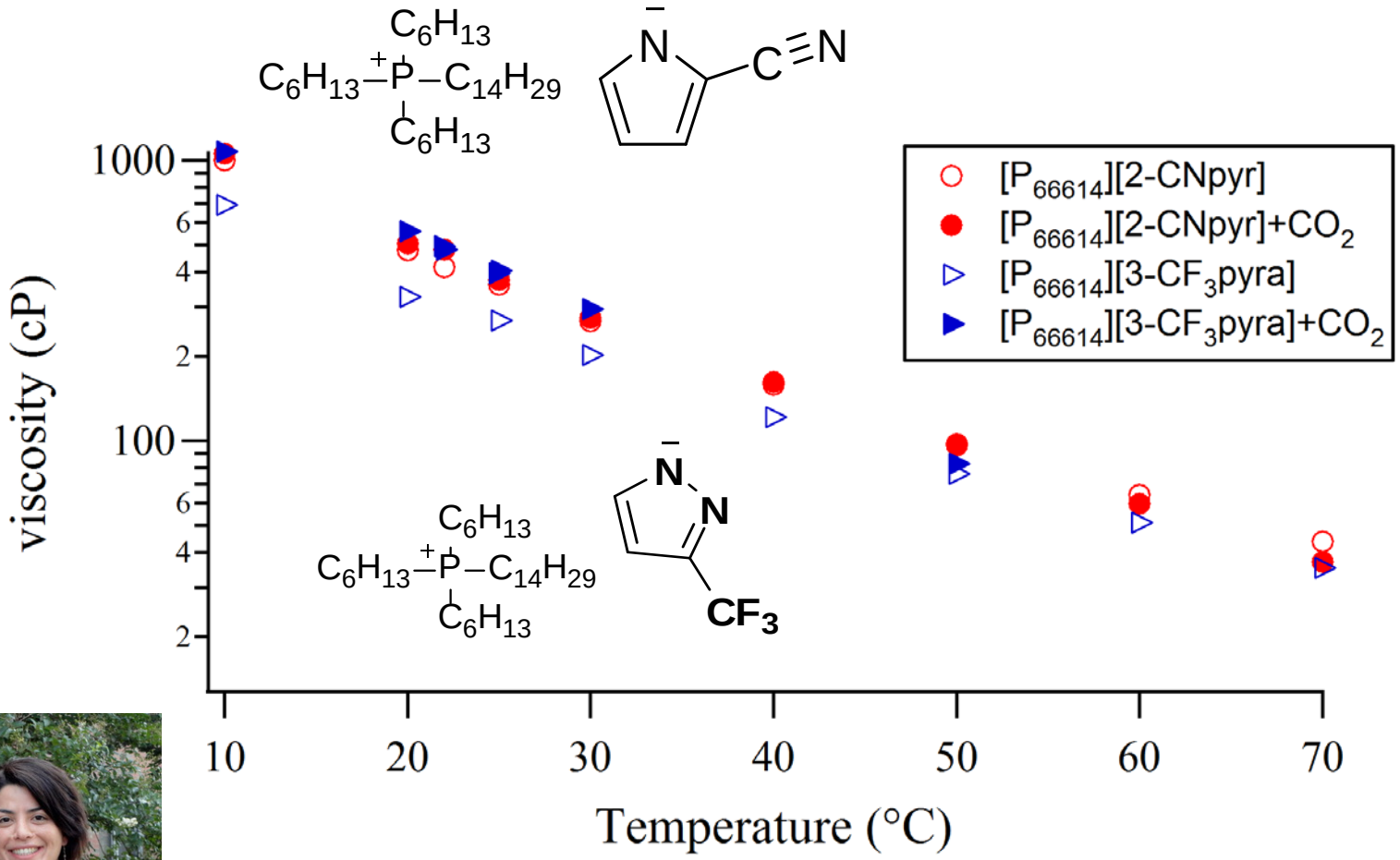
- Retain amine in ring structure
- Further reduce free hydrogens to reduce hydrogen bonding



Burcu Gurkan

Gurkan et al., JPC Lett, 2010

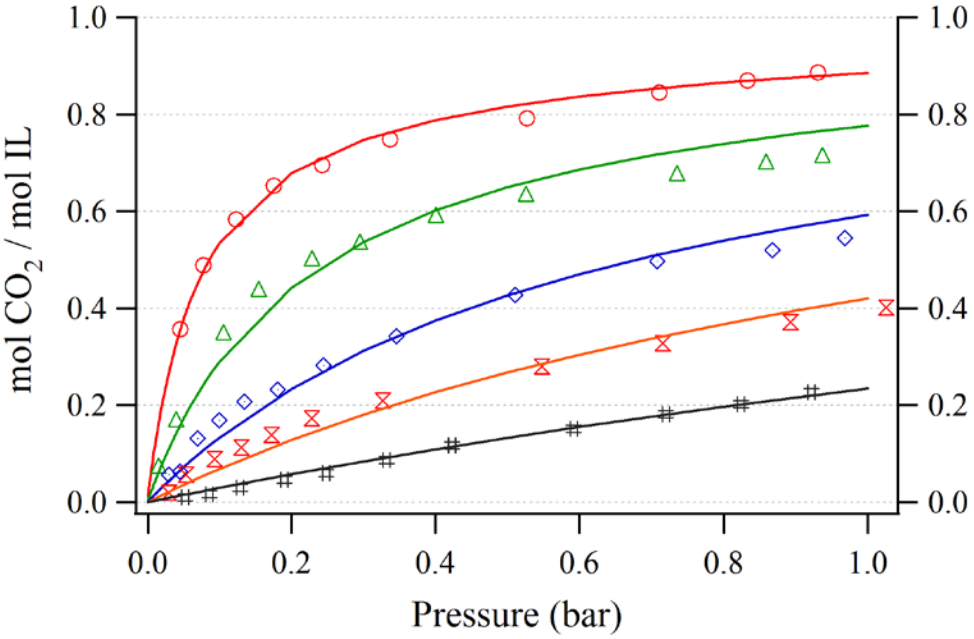
Eliminate Viscosity Increase by Using AHA – aprotic heterocyclic anions

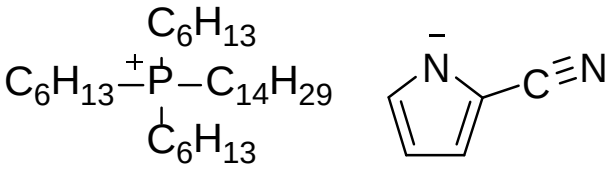


Burcu Gurkan

Gurkan et al., JPC Lett, 2010

AHA CO_2 Uptake as Function of T





ΔH_{phys} = -10 kJ/mole CO_2

ΔH_{chem} = -43 kJ/mole CO_2

$$CO_{2(g)} \rightleftharpoons CO_{2(phys)}$$

$$CO_{2(g)} + IL \rightleftharpoons IL\text{-}CO_2$$

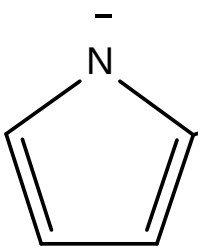
$$z = \frac{P_{CO2}/H}{1 - P_{CO2}/H} + \frac{k_1 P_{CO2} C_3}{1 + k_1 P_{CO2}}$$

Gurkan et al., JPC Lett, 2010

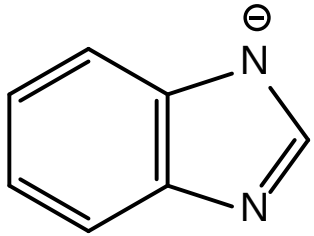
Different Aprotic Heterocyclic Anions

Adjust ΔH_{chem} with electron withdrawing groups

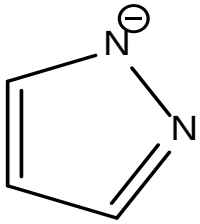
pyrrolides



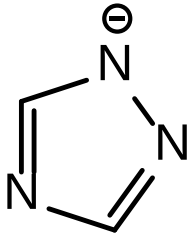
imidazolides



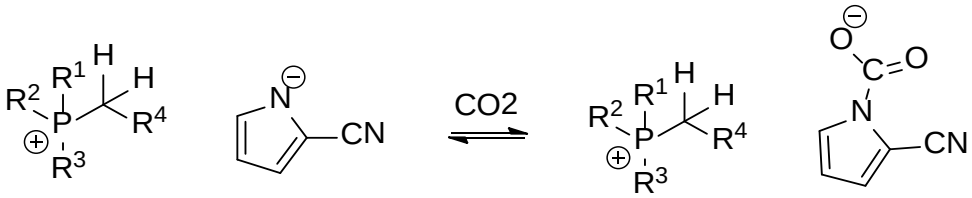
pyrazolides

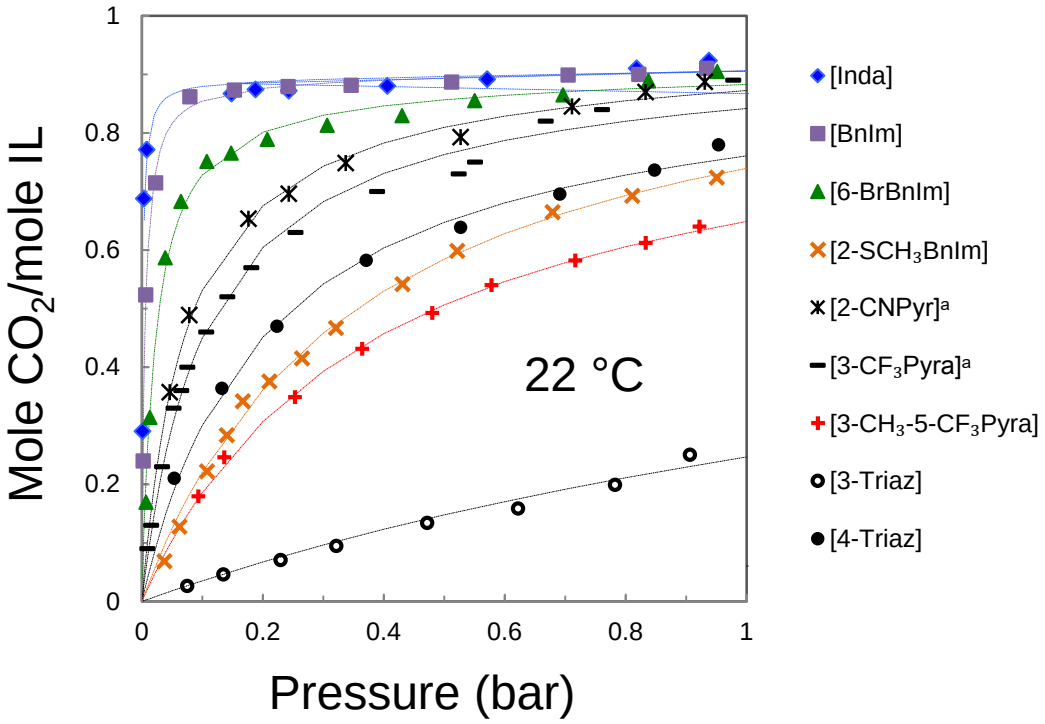


triazolides

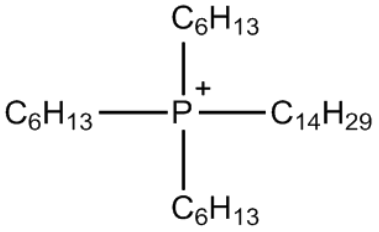


Tuning Reaction Enthalpy of AHA ILs





ΔH_{rxn} (kJ/mol)
-54
-52
-48
-41
-45
-44
-41
-37
-42

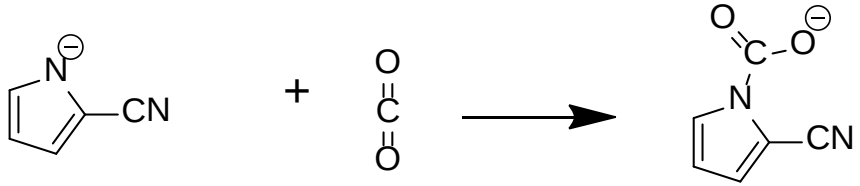


Seo et al., JPC B, 2014, 118, 5740

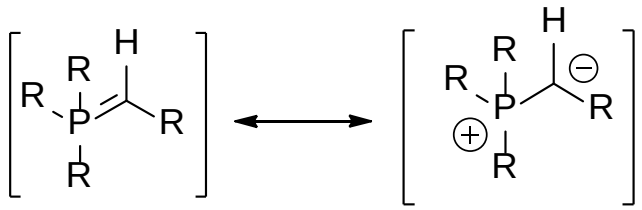
Sam Seo

Phosphonium Ylide Formation

- At room temperature carbamate salt is formed and cation is inert:



- Increasing reaction temperature leads to formation of a phosphonium ylide in the presence of CO_2 due to apparent acidity of the proton on the α-carbon [a]

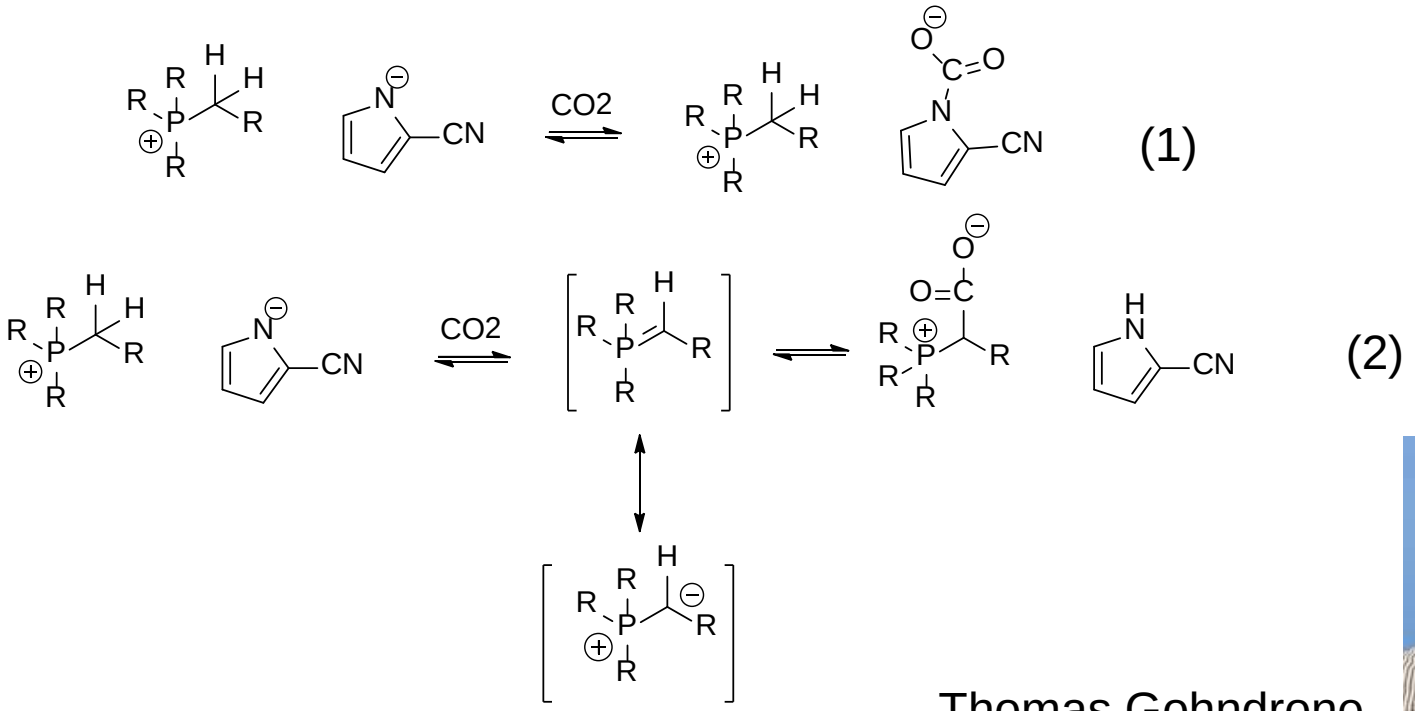


- At 60°C all AHA ionic liquids studied react CO_2 with cation
  - 2-CNpyr at 60°C showed significant reaction with cation even though at the temperatures of the rate experiments it was not prevalent.
  - Similar mechanism to formation of carbene in imidazolium ILs [b,c]

[a] *Ramnial, T. et. al. The Journal of Organic Chemistry 2008*
[b] *Gurau G. et. al. Angew. Chem. Int. 2011*
[c] *Besnard M. et al. Chemm. Commun. 2012*

CO_2 Reacts with Cation and Anion

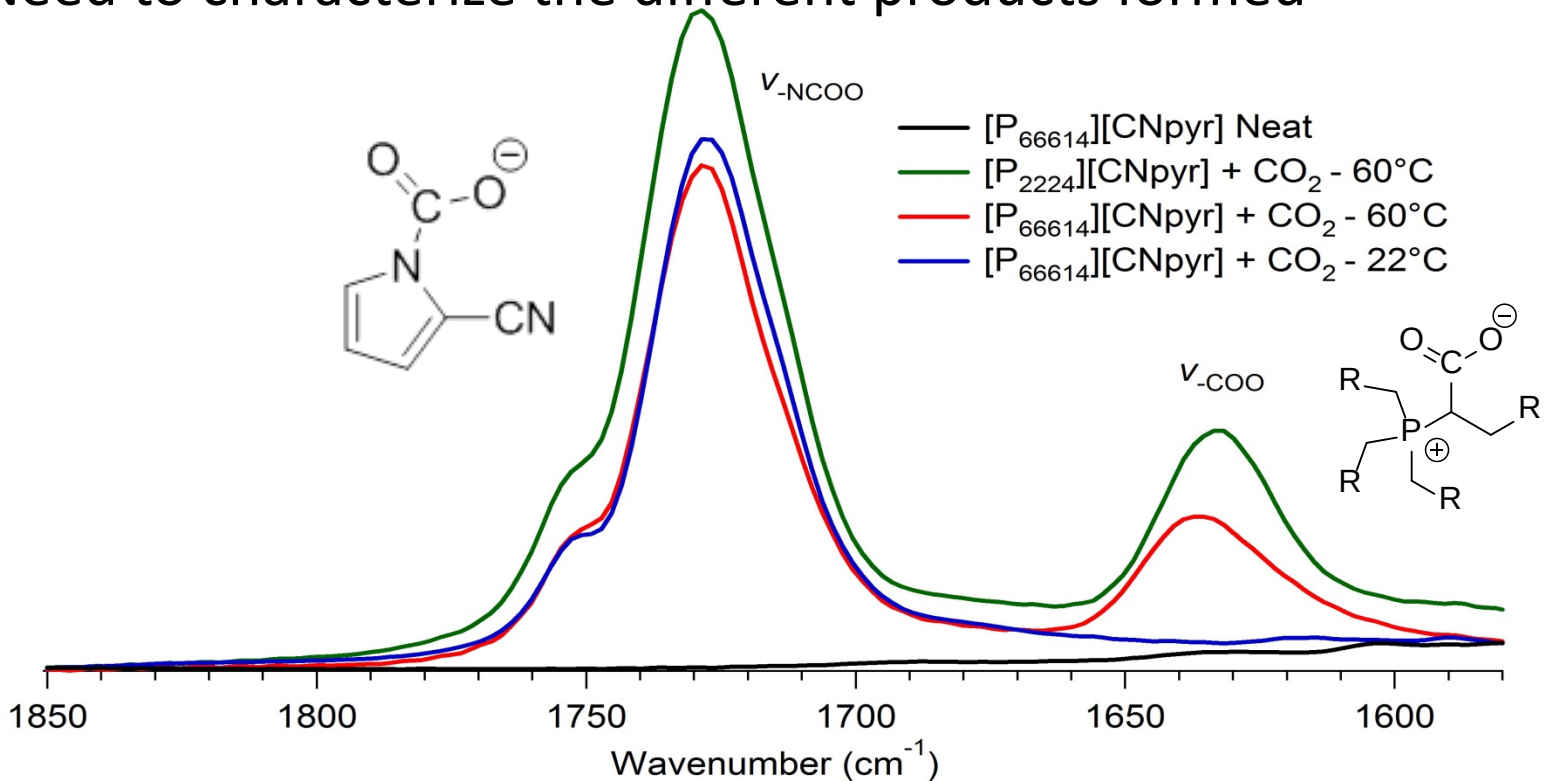
- 2 reactions are taking place in parallel at higher temperatures
  - At low temperatures reaction 2 is kinetically limited
- Both reactions are reversible



Thomas Gohndrone

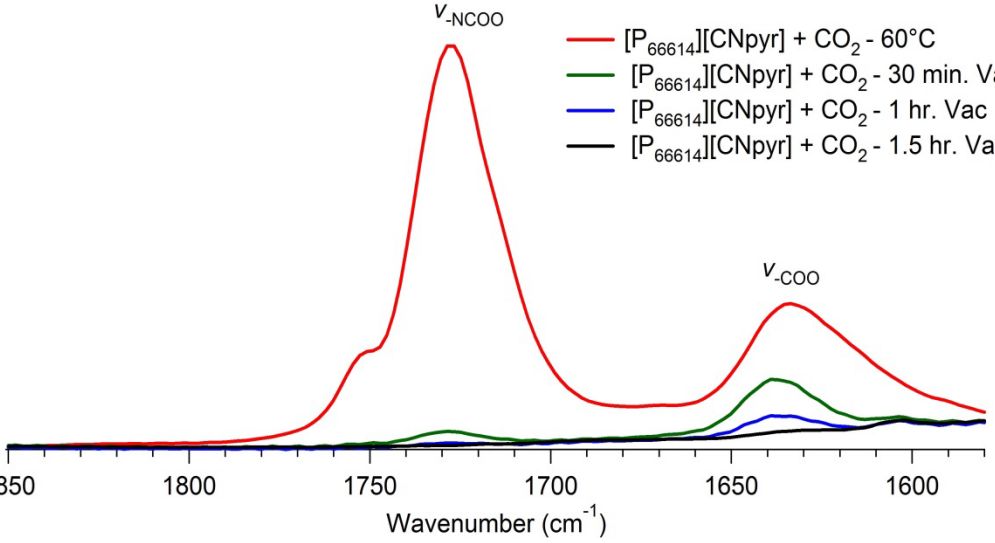
In-Situ ATR FTIR for P_{xxxx} 2-CNpyr

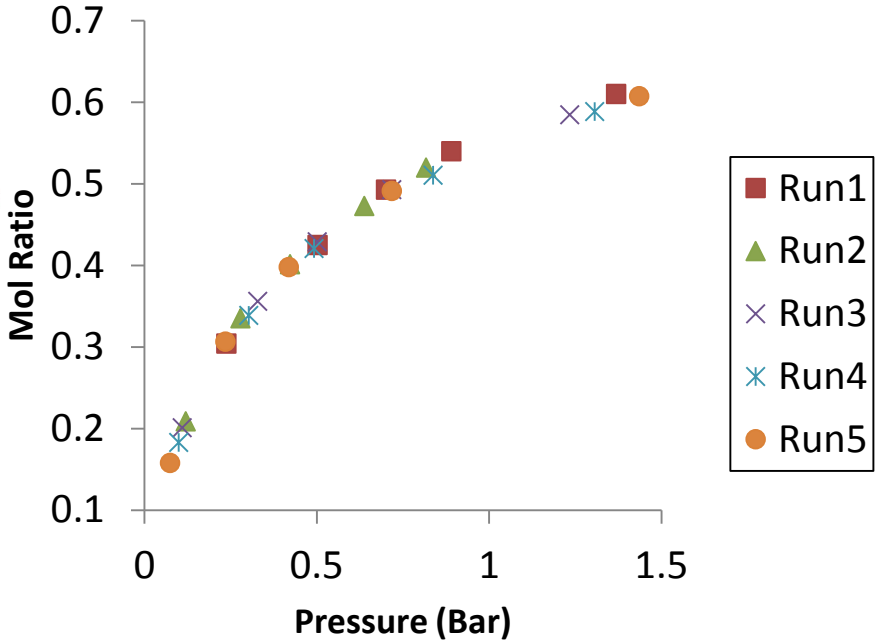
- IR spectrum different when reaction occurs at 22°C and 60°C
  - 2 different carboxylic group stretching peaks after reaction at 60°C
  - Seen with different size cations as well
- Need to characterize the different products formed



Reversibility – $[P_{66614}][2\text{-CNpyr}]$

- The anion-CO_2 is desorbed faster than the cation- CO_2 during the stripping process
  - Desorb under vacuum at 60°C
  - Process is fully reversible

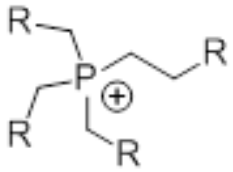




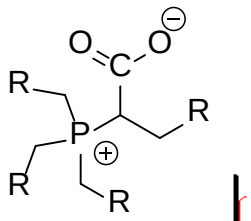
^{31}P NMR for $[P_{66614}][2\text{-CNpyr}]$

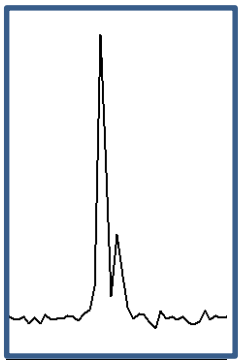
- IL reacted with CO_2 at 22°C
  - Same as neat IL

All samples have ~1-1.5% of methylated impurity at 39 ppm

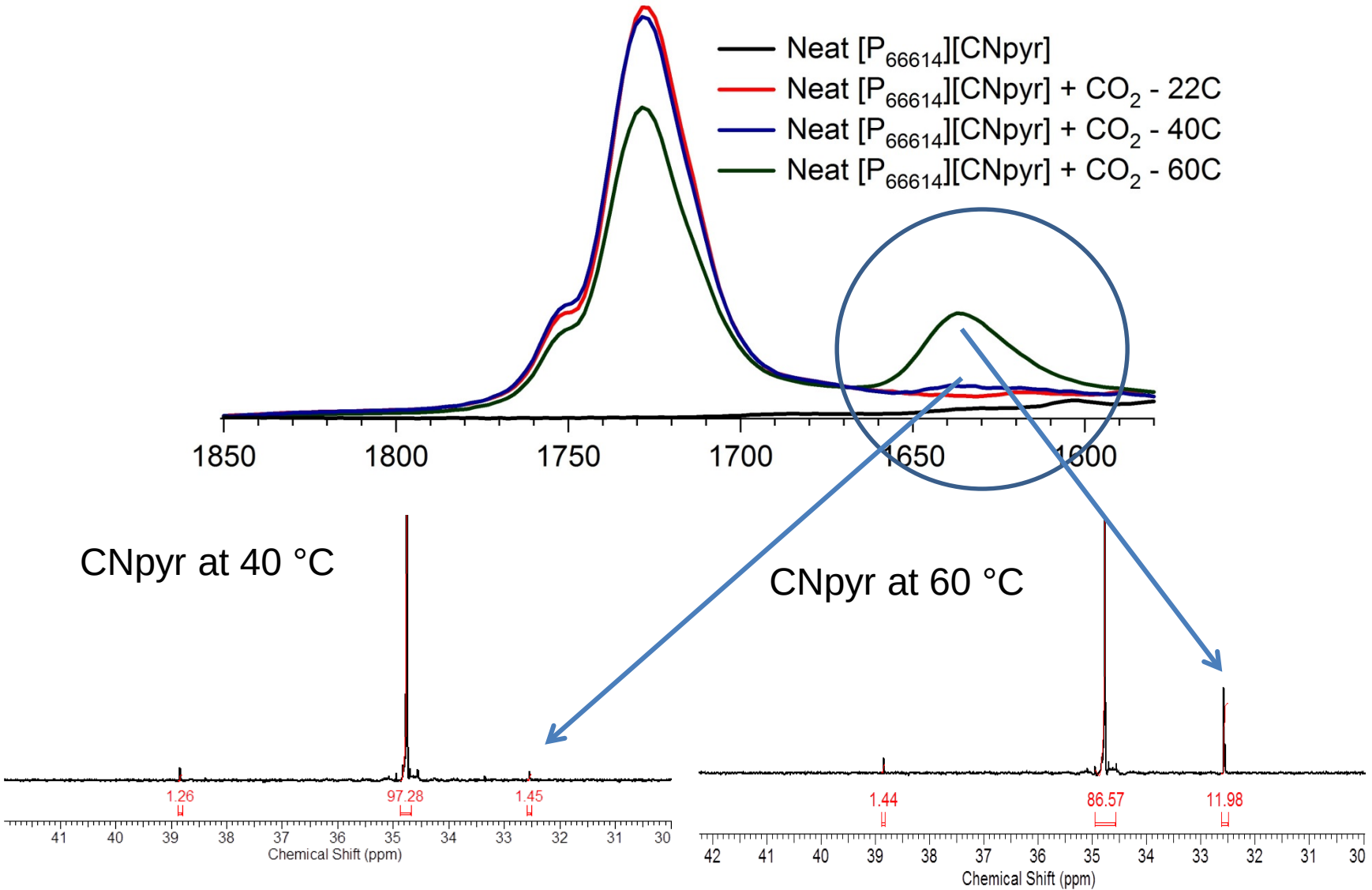


- IL reacted with CO_2 at 60°C
- Additional peak at 32.5 ppm shows evidence of P-C coupling
- After vacuum/desorption peak at 32.5 ppm is no longer present



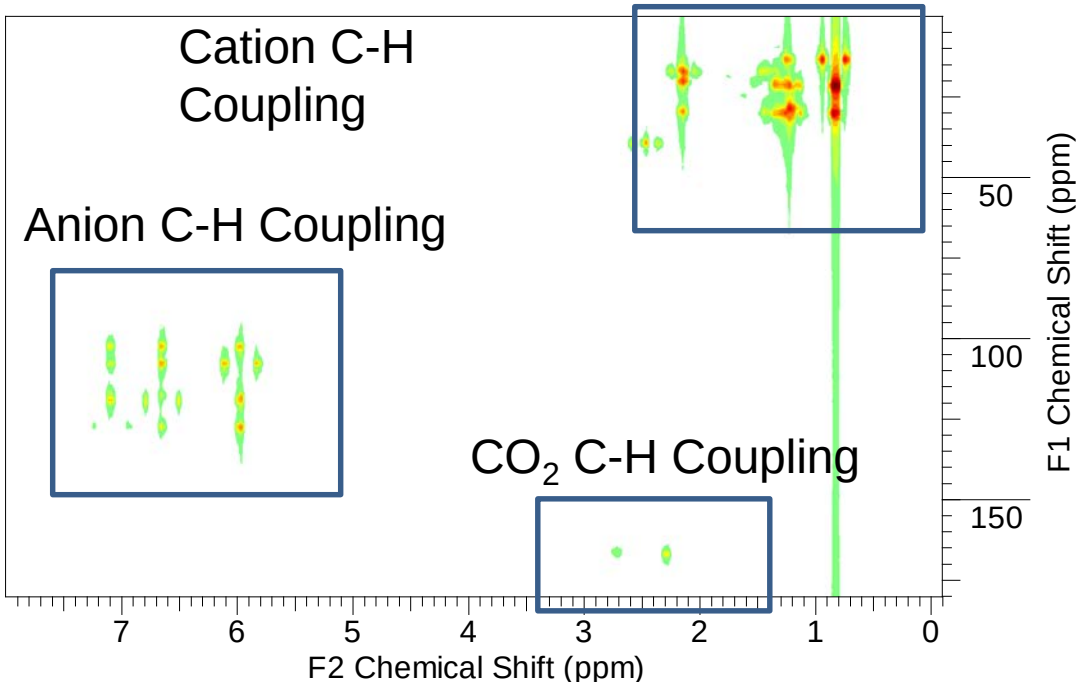


NMR and FTIR Consistent

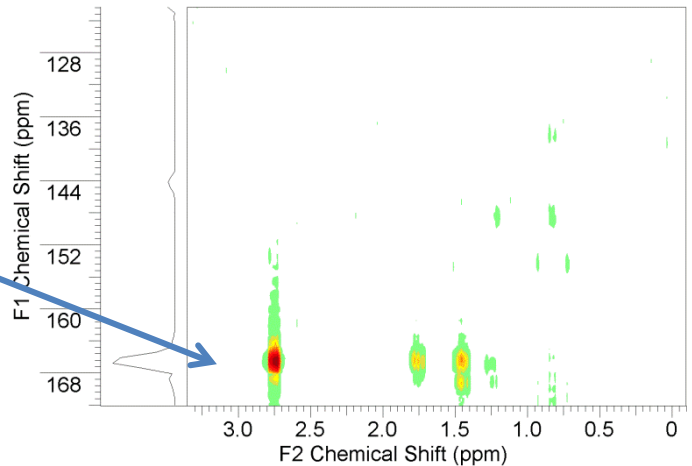


HMBC 2-D NMR

- Heteronuclear Multiple Bond Correlation shows 2-3 bond C-H coupling
  - New ^{1}H Peak at 2.77 (phosphonium H region)
  - New ^{13}C peak at 166 ppm
  - They are coupled
- Evidence that CO_2 is in fact bound to the cation

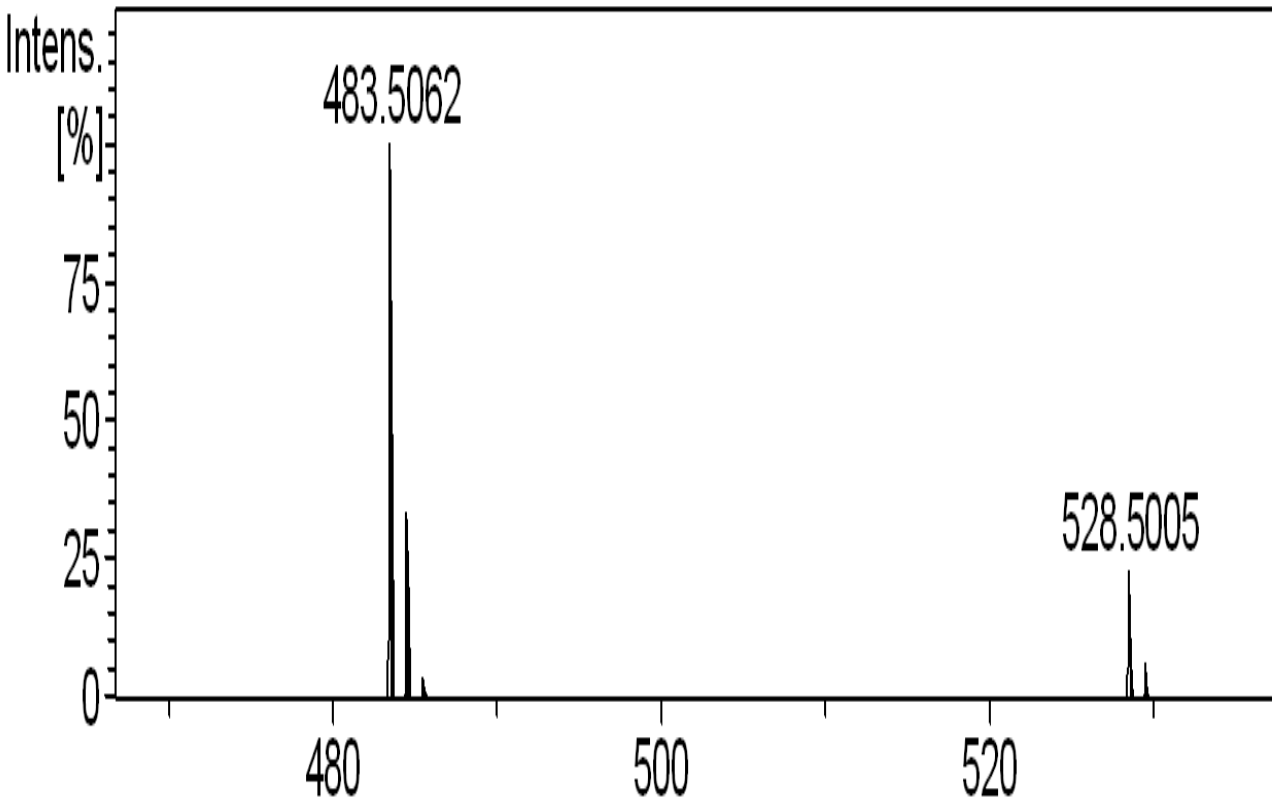


- Labeling CO_2 with ^{13}C increases the intensity of CO_2 C-H coupling



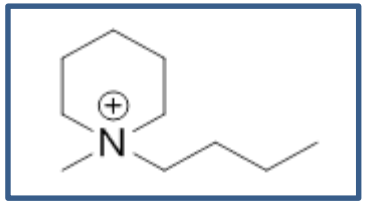
ESI Mass Spectroscopy – Positive Mode

- Positive mode electron mass spec of Phosphonium IL-CO_2 complex.
  - P_{66614} Molecular Weight = 483.5
  - P_{66614} + ^{13}C labeled CO_2 = 528.5

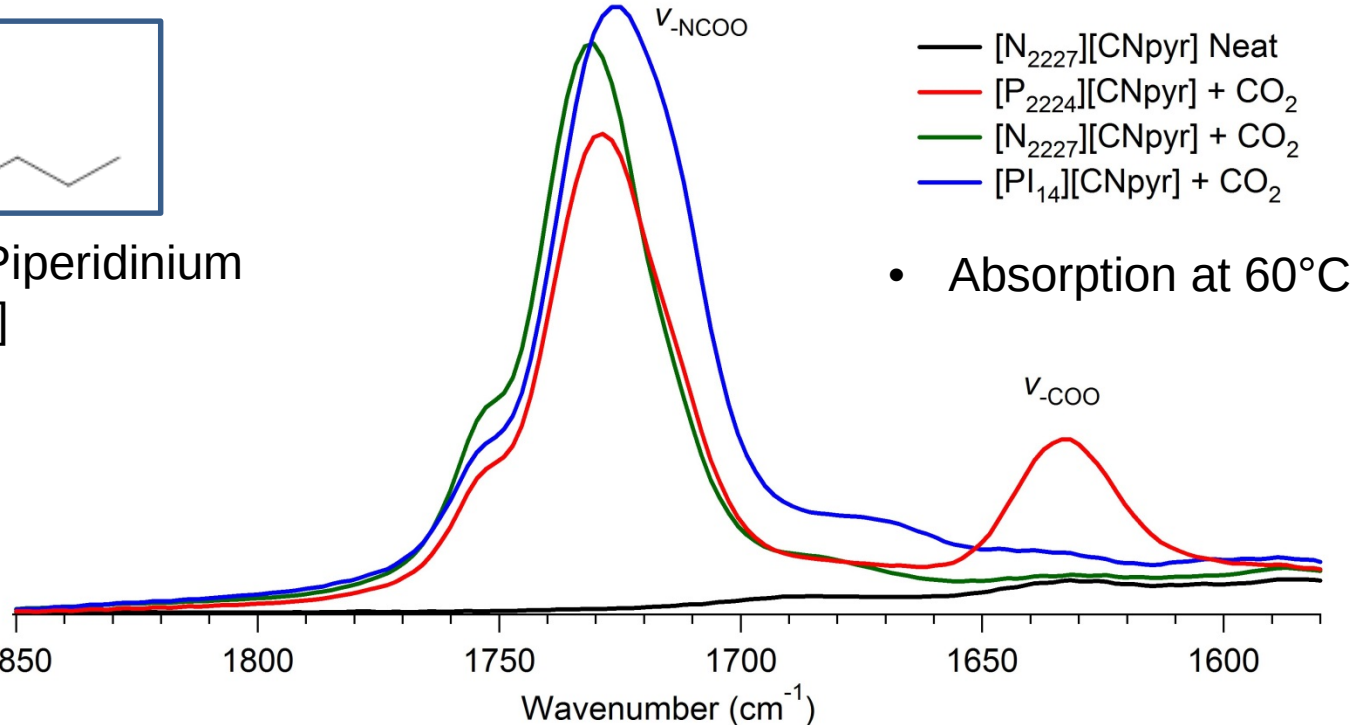


Eliminating Ylide Formation

- Replacing the phosphonium cation with ammonium eliminates ylide formation
  - Phosphonium ylide is more stable than ammonium
  - No change in CO_2 uptake due to the reaction with cation



Butyl-Methyl-Piperidinium
$[PI_{14}]$

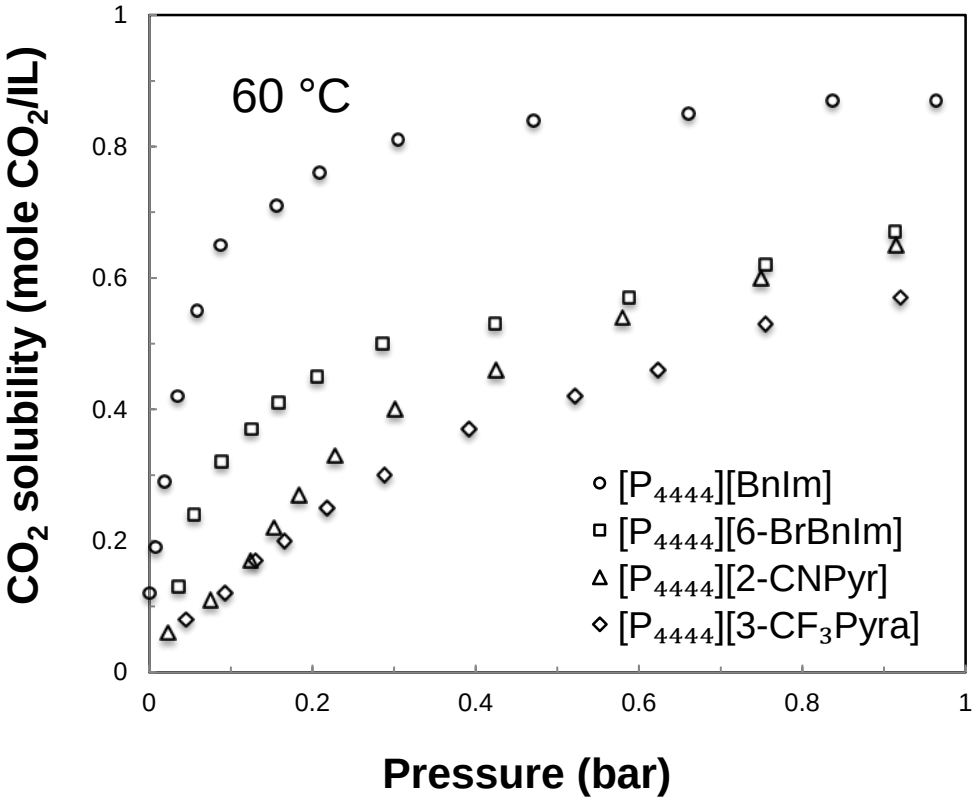


- Absorption at 60°C

Discovery of Phase Change Ionic Liquids

All T_m > 45 °C

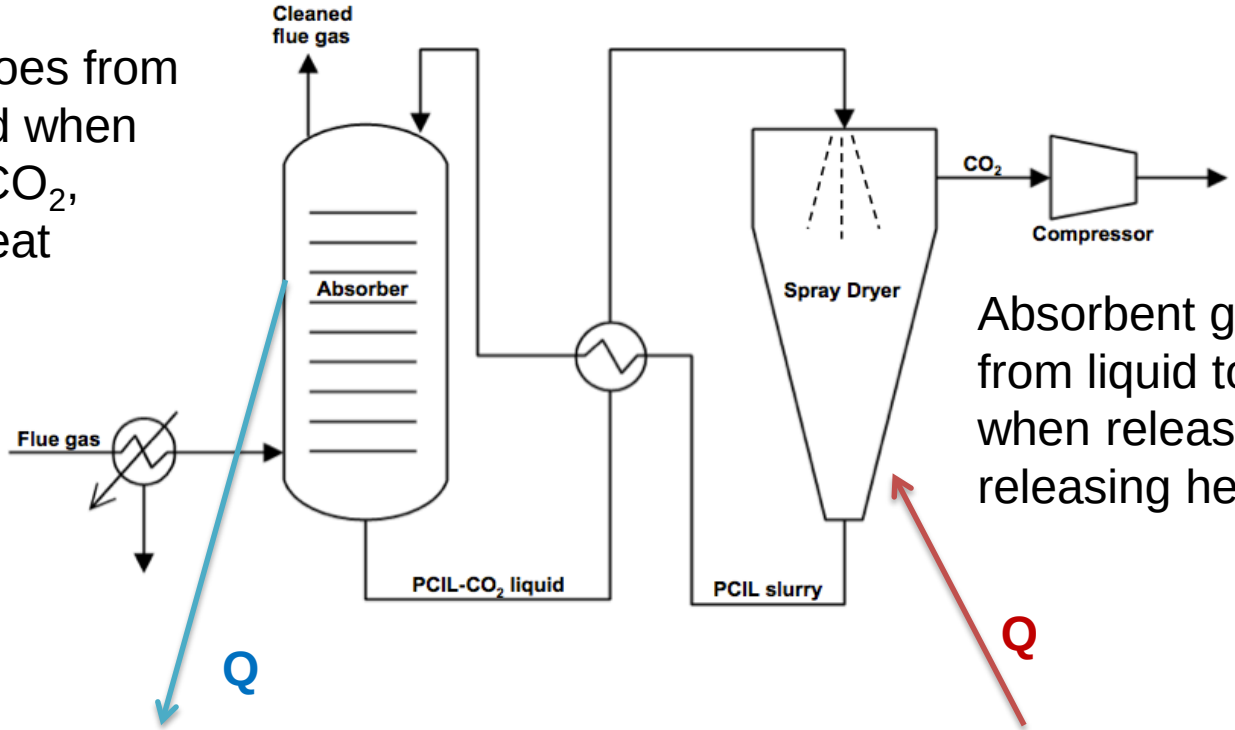
Remained liquid at 22 °C with 1 bar CO_2 pressure



$T_{m,\ complex} < T_{m,\ unreacted}$

CO_2 Capture with Phase Change Material

Absorbent goes from solid to liquid when reacts with CO_2, absorbing heat

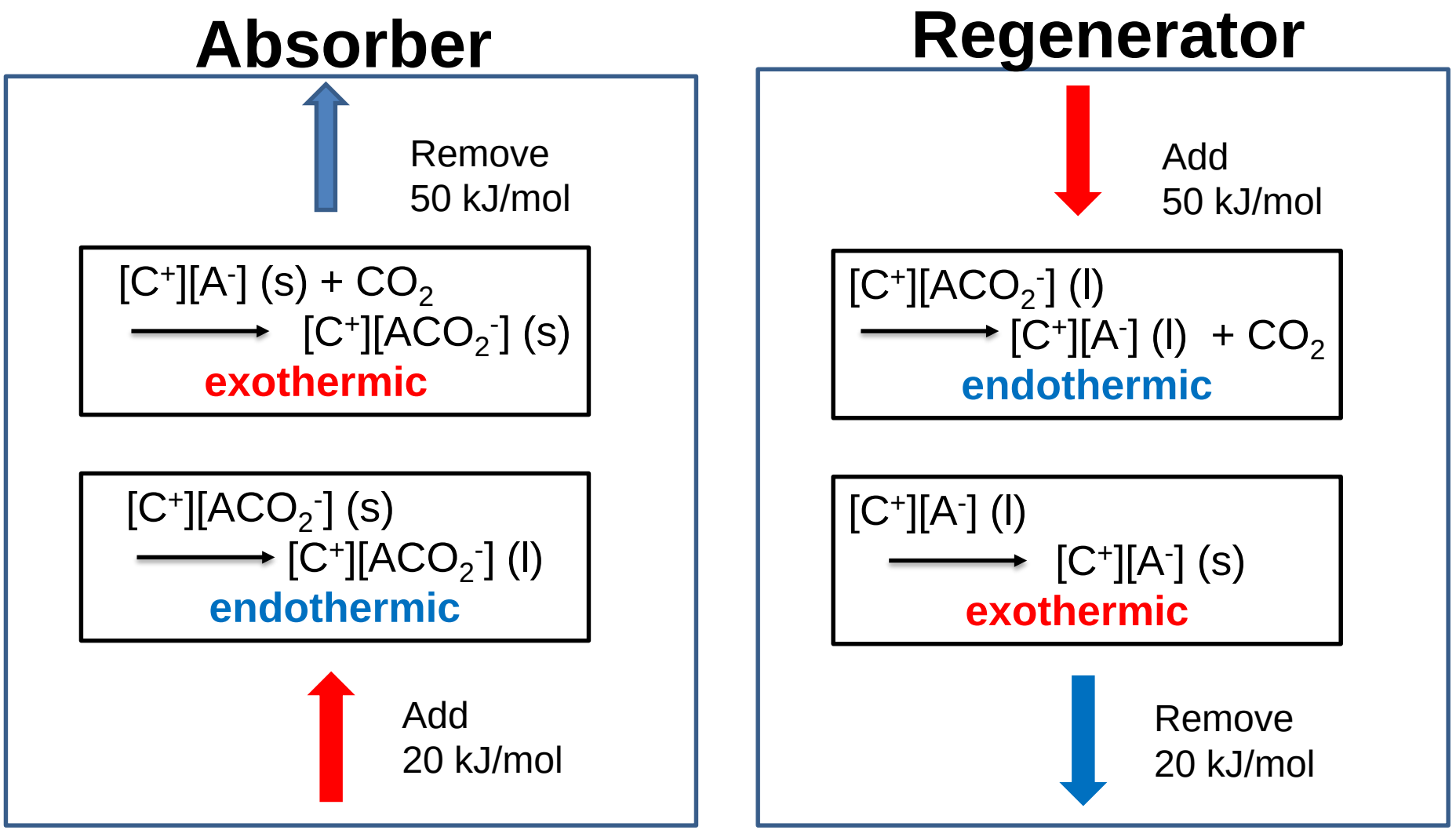


Absorbent goes from liquid to solid when releases CO_2, releasing heat

'Melting' of absorbent reduces cooling duty

Heat duty in stripper reduced by the heat of fusion of the phase change material

CO_2 Capture with Phase Change Material

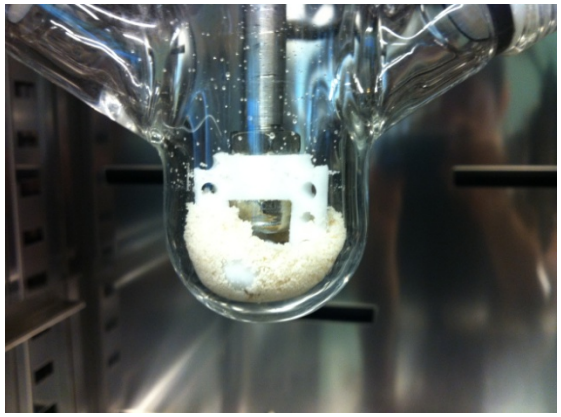


Q_{net} = Remove 30 kJ/mol

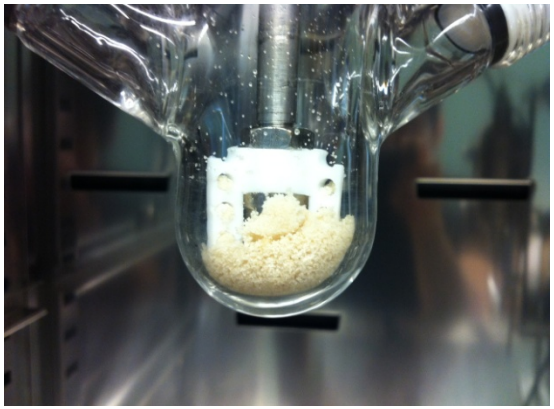
Q_{net} = Add 30 kJ/mol

Phase Change Ionic Material

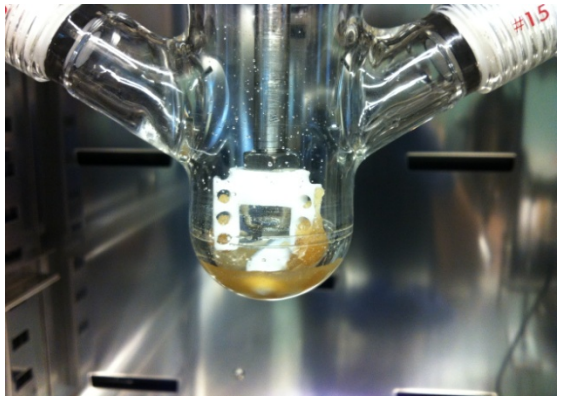
70 °C



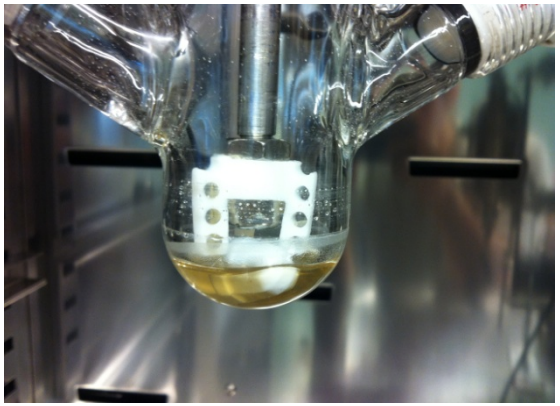
Pure material; T_m=166 °C; no CO_2



60 mbar CO_2

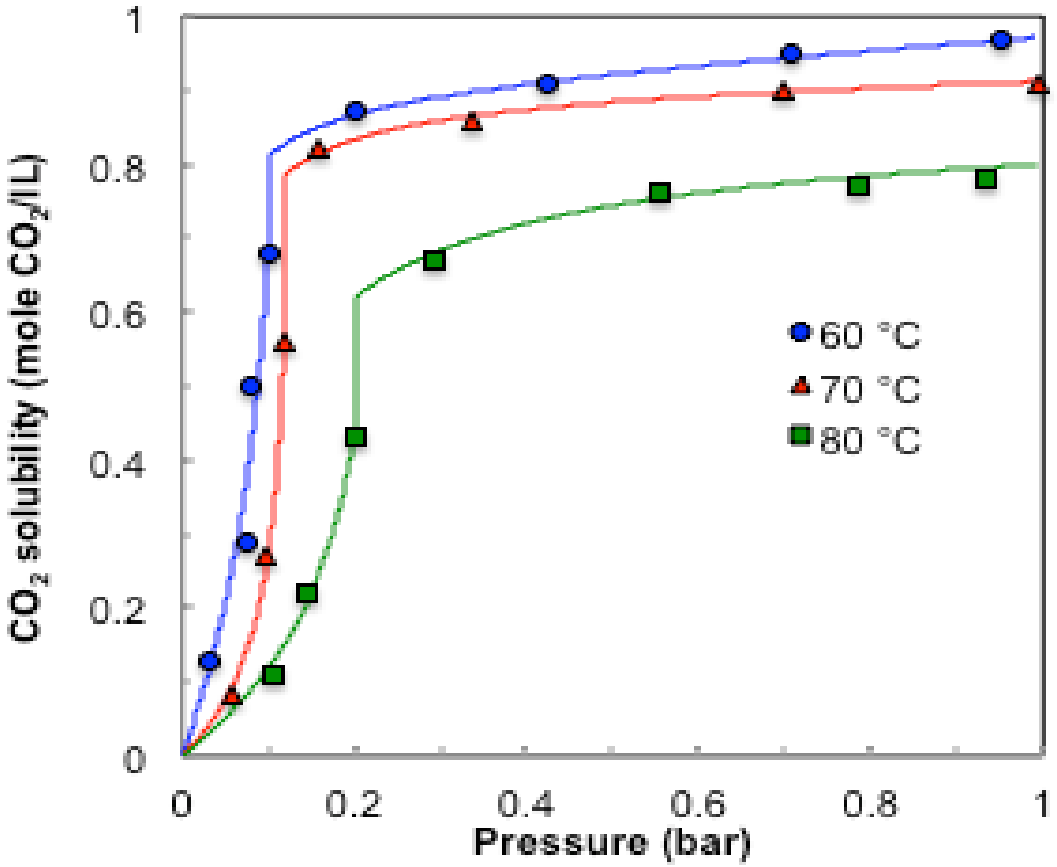


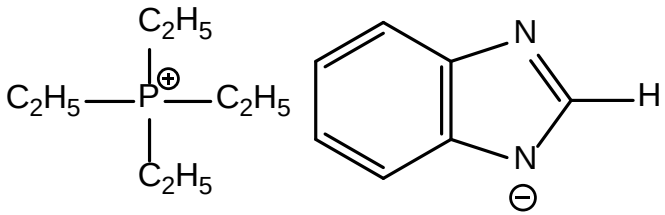
100 mbar CO_2



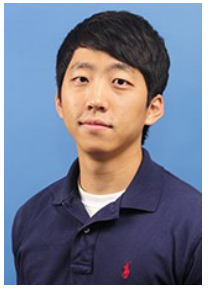
150 mbar CO_2

CO_2 Uptake Curves



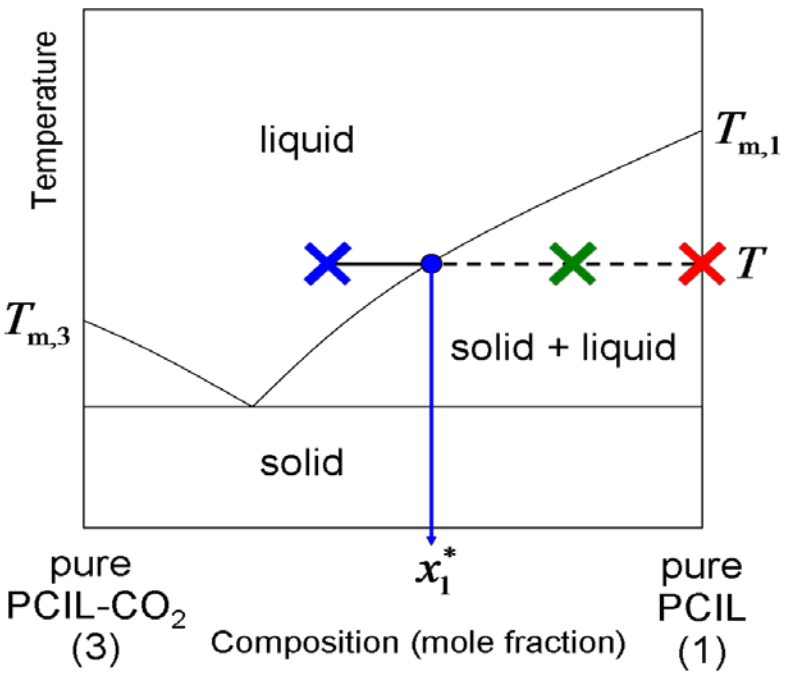


T_m = 166 °C
Δh_{fus} = -19.9 kJ/mole
Δh_{chem} = -52 kJ/mole

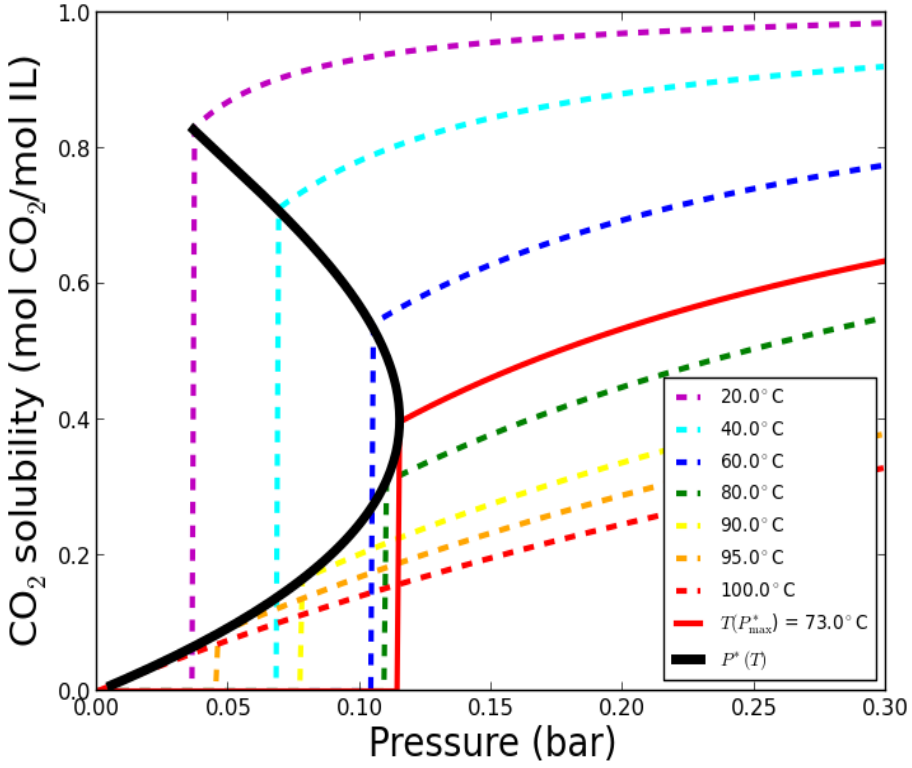


Seo et al., Energy & Fuels, 2014, 28, 5968-5977

Thermodynamic Model



Eutectic Model of PCIL System



Typical PCIL isotherms for idealized model, for the parameter values ΔH_{fus} = −20 kJ mol^{-1}, $T_{m,1}$ = 100 °C, ΔH_{rxn} = −50 kJ mol^{-1}, ΔS_{rxn} = −130 J mol^{-1} K^{-1}, ΔH_{phys} = −13 kJ mol^{-1}, ΔS_{phys} = −73 J mol^{-1} K^{-1}.

3 component, 3 phase, 1 rxt = 1 DOF
Fixed T, SVLE at one P*

Seo et al., Energy & Fuels, 2014, 28, 5968-5977

Process Modeling

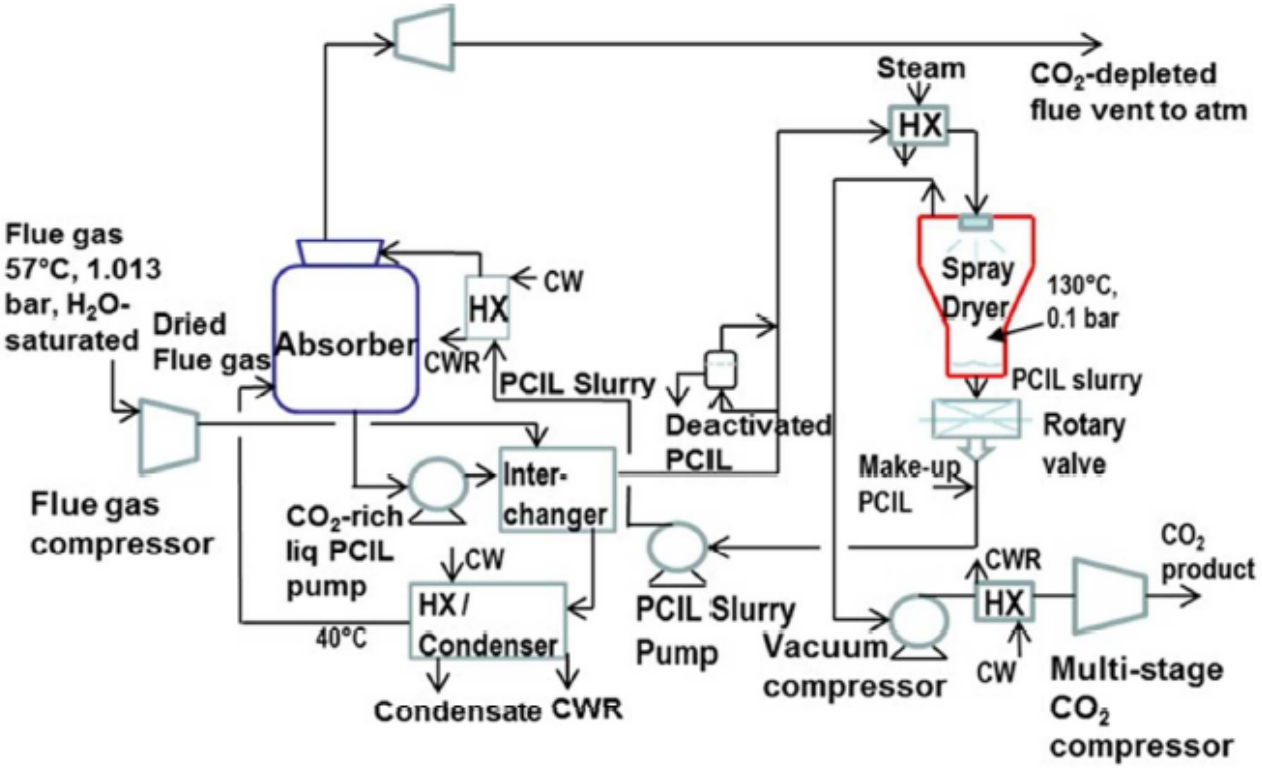


Figure 5. Process flow diagram for CO_2 capture in full-scale plant

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Eisinger and Keller, Energy & Fuels, 2014, 28, 7070-7078

Laboratory Demonstration

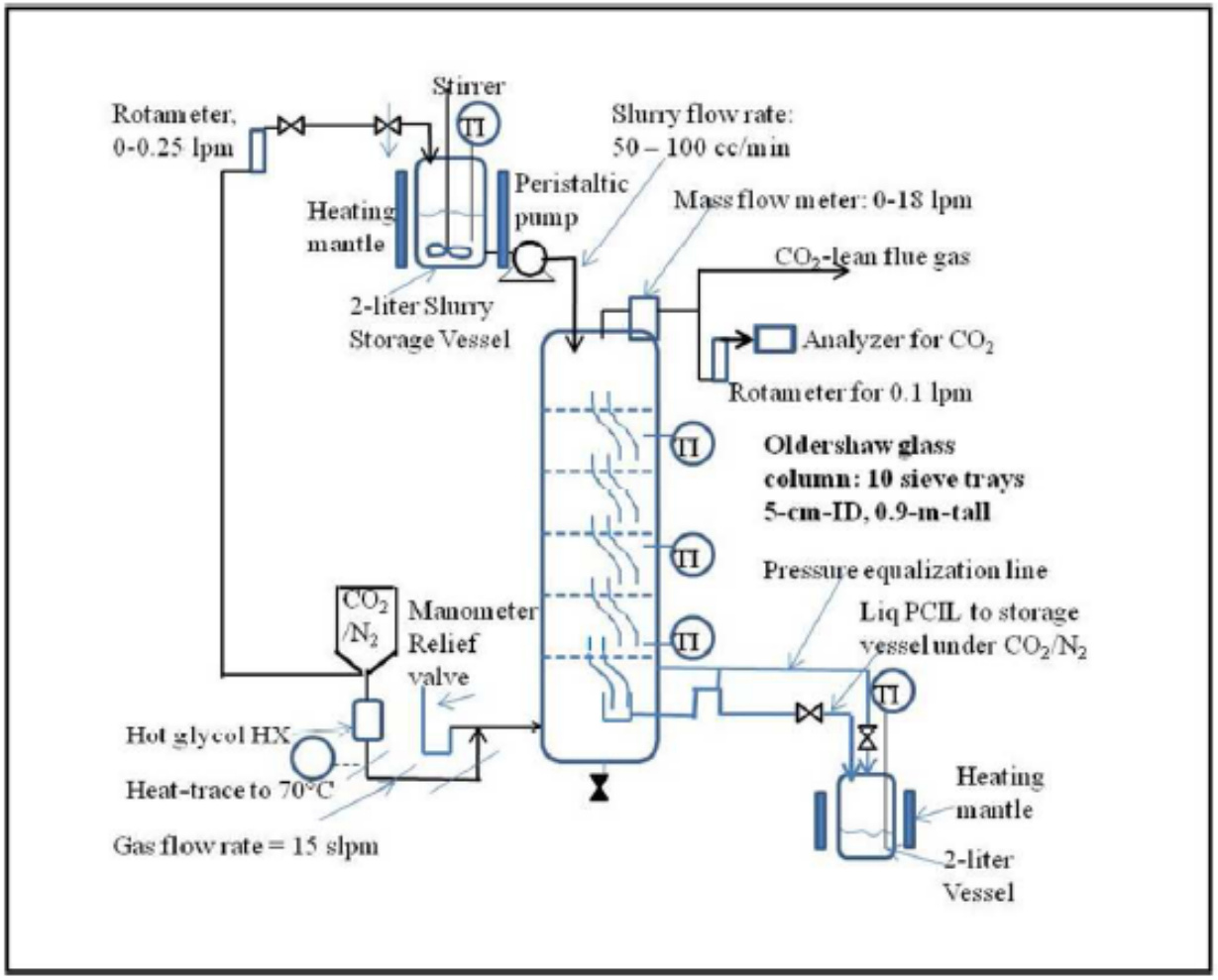

Figure 7. Absorber for CO_2 capture

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Eisinger and Keller, Energy & Fuels, 2014, 28, 7070-7078

Laboratory Demonstration

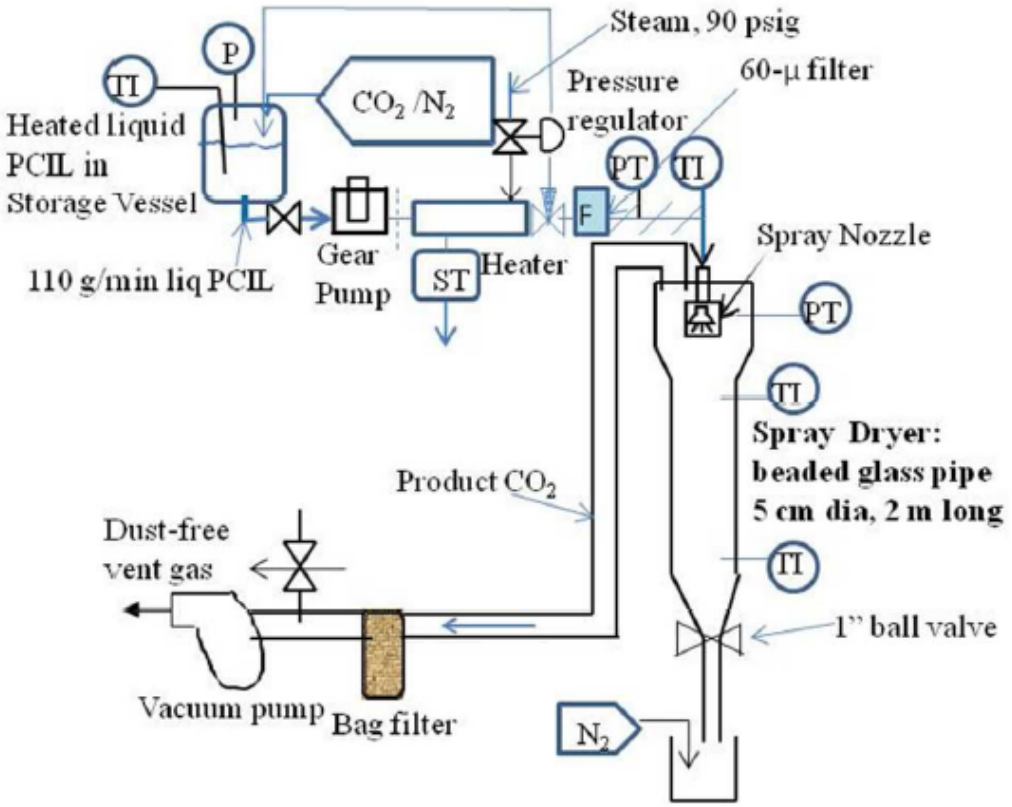

Figure 8. Spray dryer for regeneration of the liquid complex

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Eisinger and Keller, Energy & Fuels, 2014, 28, 7070-7078

Process Modeling

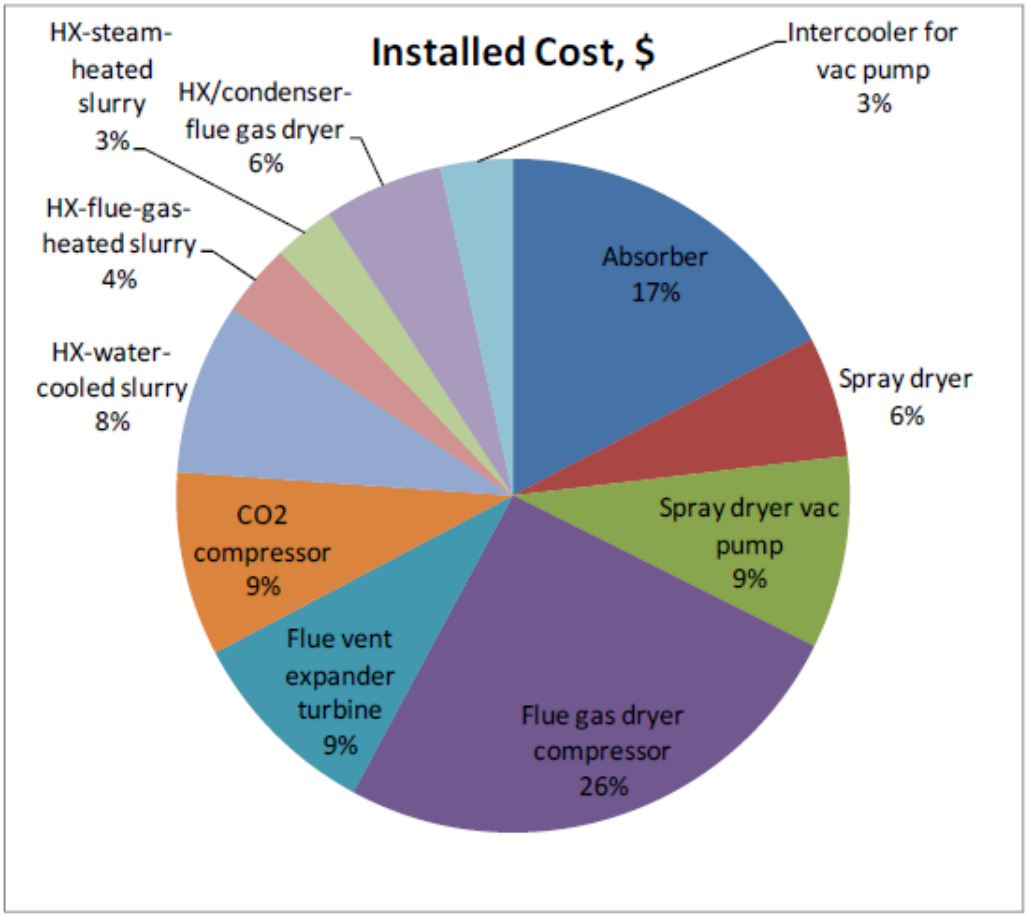

Figure 13. Contribution of major equipment to capital cost

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Phase Change Ionic Material for CO_2 Capture

- Only some materials have $T_m^{complex} <<< T_m^{IL}$
- Best system operability if T_m^{IL} and ΔH_{fus} large in magnitude
- Can DRAMATICALLY reduce energy load for CO_2 capture process
  - Partly due to phase change (ΔH_{fus})
  - Partly due to sharp increase in capacity at "phase change pressure"

- 23% parasitic power
- 4.1¢ /kWh increase in COE
- \$48/ton CO_2 avoided

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Conclusions

- Ionic liquids are tunable solvents with potential for many energy related applications, including CO_2 capture
- Can make AHA ILs with 1:1 uptake and no viscosity increase upon reaction with CO_2
- Can tune ΔH_{rxt} with electron donating/withdrawing groups
- Can tune CO_2 capacity with ΔS_{rxt}
- Can take advantage of materials (PCILs) where $\mathbf{T_{m,\ complex} < T_{m,\ unreacted}}$
- Phase Change Ionic Liquids just 23% parasitic energy and 4.1¢ /kWhr increase in COE

Acknowledgments

- Bill Schneider, Ed Maginn, and Mark Stadtherr and their research groups