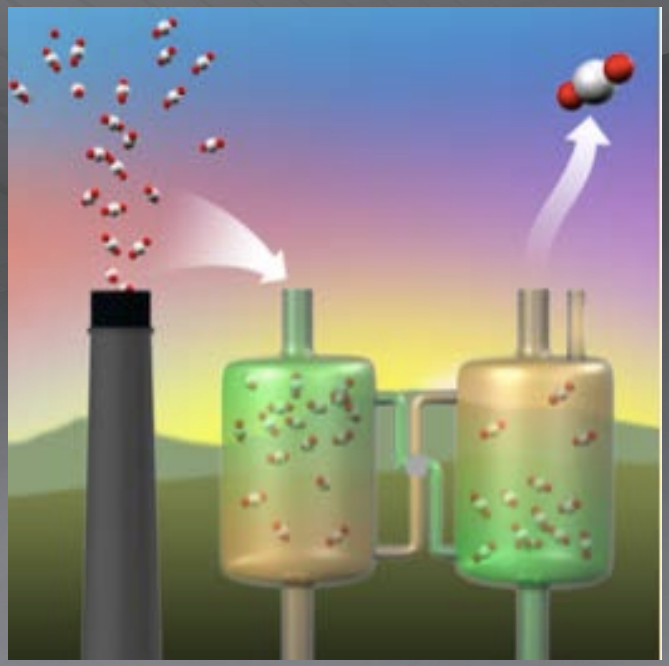

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Accelerating the development of transformational solvent systems for CO_2 separations (FWP-65872)

DAVID J. HELDEBRANT

NETL CO_2 CAPTURE TECHNOLOGY MEETING
PITTSBURGH, PA
AUGUST 24, 2017

U.S. DEPARTMENT OF
ENERGY

PNNL FY16 at a glance

Pacific Northwest
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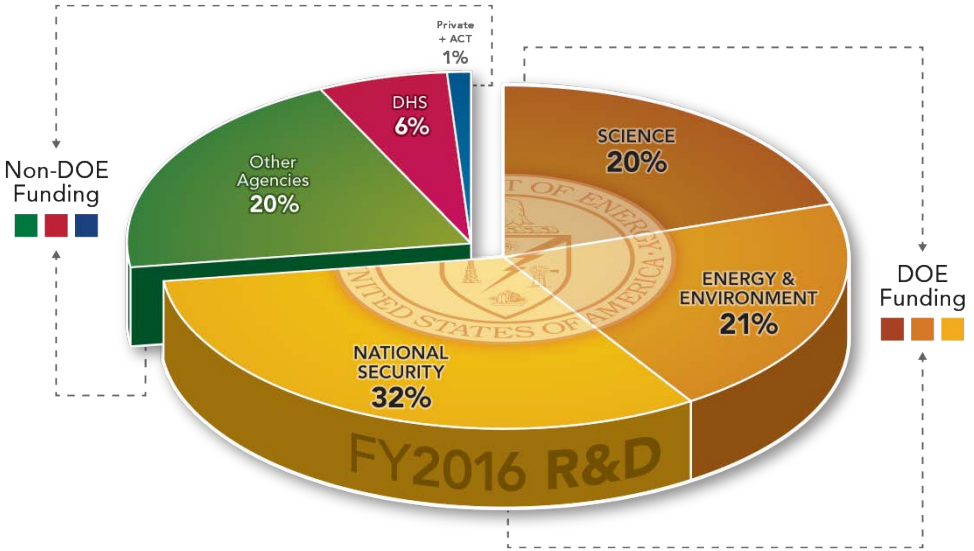
- $920.4M in R&D expenditures
- 4,400 scientists, engineers and non-technical staff
- 104 U.S. & foreign patents granted
- 2 FLC Awards, 5 R&D 100
- 1,058 peer-reviewed publications



Integrating Molecular Design, Synthesis, and Testing to DOE's Solvent Portfolio

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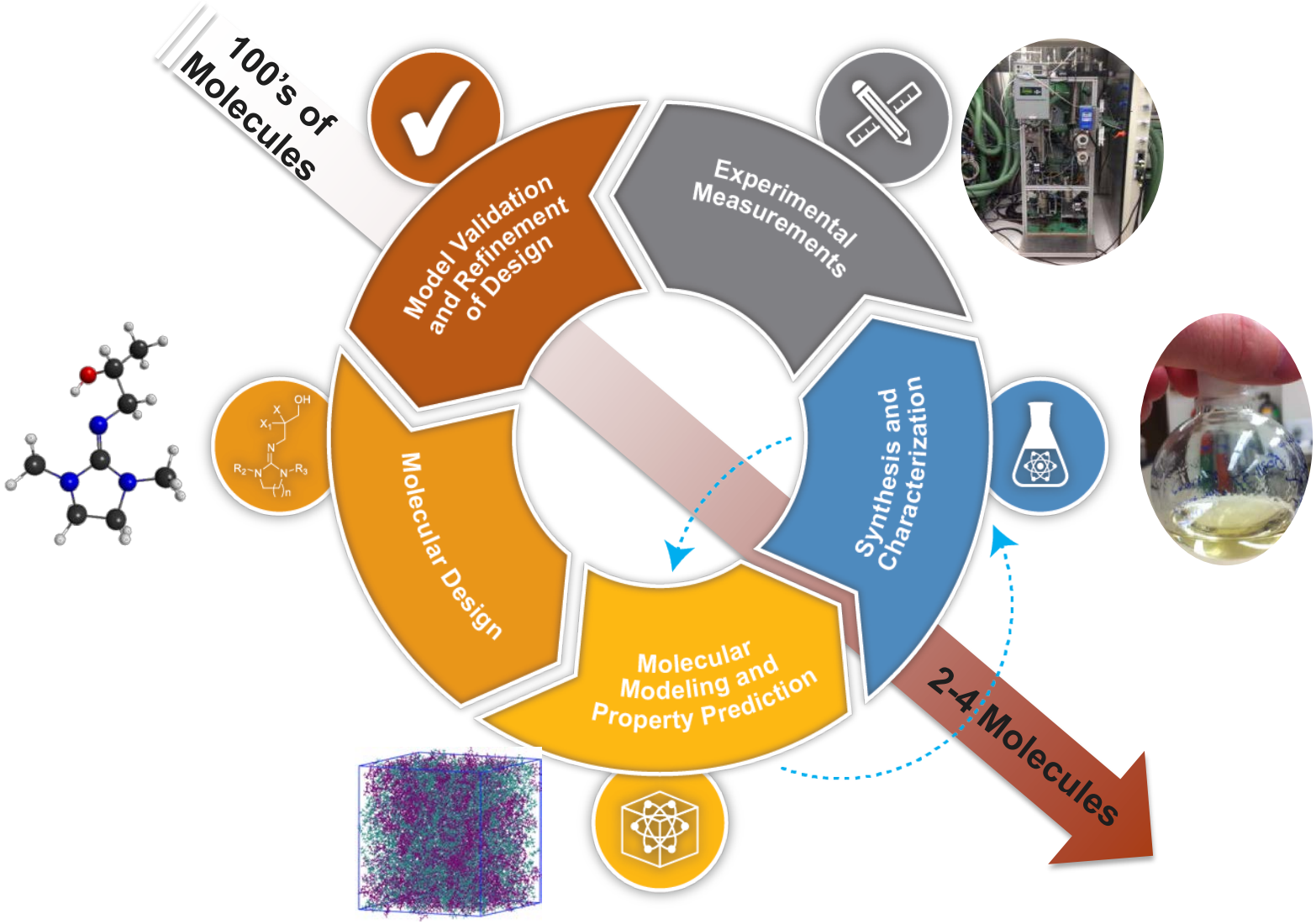
Technology-neutral program, providing molecular-level insight to enhance performance.



Chemistry of Captured CO_2

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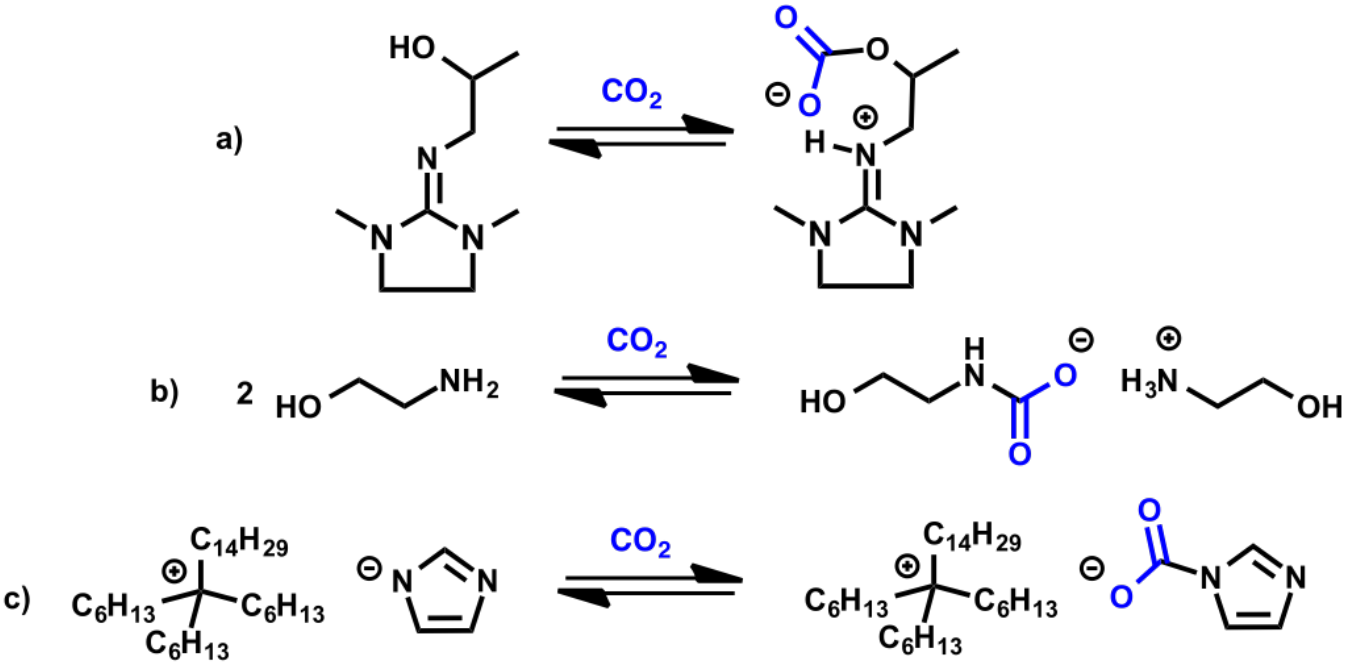
There are three binding chemistries with CO_2; all operate on similar principles.



- Alkylcarbonates (a), carbamates (b), and azoline carboxylates (c) all form salts containing electrophilic sp^2-hybridized anions
- Concentrated solvents behave similarly, *e.g.* viscosity, mass transfer

D. J. Heldebrant, P. K. Koech, V. A. Glezakou, R. Rousseau, D. Malhotra, D. C. Cantu, *Chem. Rev.*, 2017, 117 (14), 9594–9624.

Project Goals and Objectives

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Goals

- Develop tools for viscosity prediction and solvent design methodologies for reducing viscosity across all transformational solvent platforms.
- Screen hundreds of candidate molecules in order to down-select to 2-4 viable derivatives
- Develop cost-effective synthesis methodologies to bring solvent costs ~ $10/kg.

Objectives

- Develop a reduced order viscosity model that can predict key solvent physical and thermodynamic properties for all solvent chemistries.
- Collect necessary additional thermodynamic and kinetic information for a library of compounds.
- Apply tools and methodologies to two or more solvent chemistries to aid in viscosity reduction of >400 cP.
- Apply the viscosity model and molecular design principles to other solvents in DOE's post-combustion solvent portfolio

Project Schedule and Major Tasks

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Funding: $4,061,000 / 36 months

Task 1. Project Management					
1.1	General Project Management				
Task 8. Molecular Development of 3rd Solvent Class Derivatives (Cycle 1)					
8.1	Establish and Validate Computational Protocol for 3rd Solvent Class of Compounds				
8.2	Predictions of Physical and Thermodynamic Properties of up to 100 Molecules				
8.3	Synthesis of 2-4 3rd Generation Derivatives Identified From Subtask 2.2				
8.4	Laboratory Property Testing (e.g., VLE, Viscosity, Kinetics) Completed for 2-4 3rd Solvent Class Derivatives for Theory Validation (Cycle 1)				
Task 9. Molecular Development of GAP Derivatives (Cycle 2)					
9.1	Model up to 100 New GAP Derivatives or Additives and Identify 2-4 Candidate Molecules (With ≥400 cP Reduction) for Synthesis & Characterization				
9.2	Synthesize & Characterize 2-4 Promising Derivatives From Subtask 3.1				
9.3	Laboratory Property Testing (e.g., VLE, Viscosity, Kinetics) Completed for 2-4 GAP Derivatives or Additives				
Task 10. Continuous Flow Testing of Final CO_2BOL Derivative (Cycle 3)					
10.1	Synthesis of 3-4L of 1-2 Candidate CO_2BOL Solvents				
10.2	Wetted Wall Testing of CO_2BOL Solvent to Measure CO_2 Mass Transfer				
10.3	Testing Absorber and Stripper Performance on PNNL's Continuous Flow Cart With and Without PSAR Infrastructure, and With and Without Water				
10.4	Project Reboiler Heat Duty, Regen Temp, and Net Power Output for Final CO_2BOL Derivative				
Task 11. Continuous Flow Testing of Aqueous Solvents for Fluor					
11.1	Wetted Wall Testing of 6 Aqueous Solvents From Fluor to Measure CO_2 Mass -Transfer				

Aminosilicone Solvent Class

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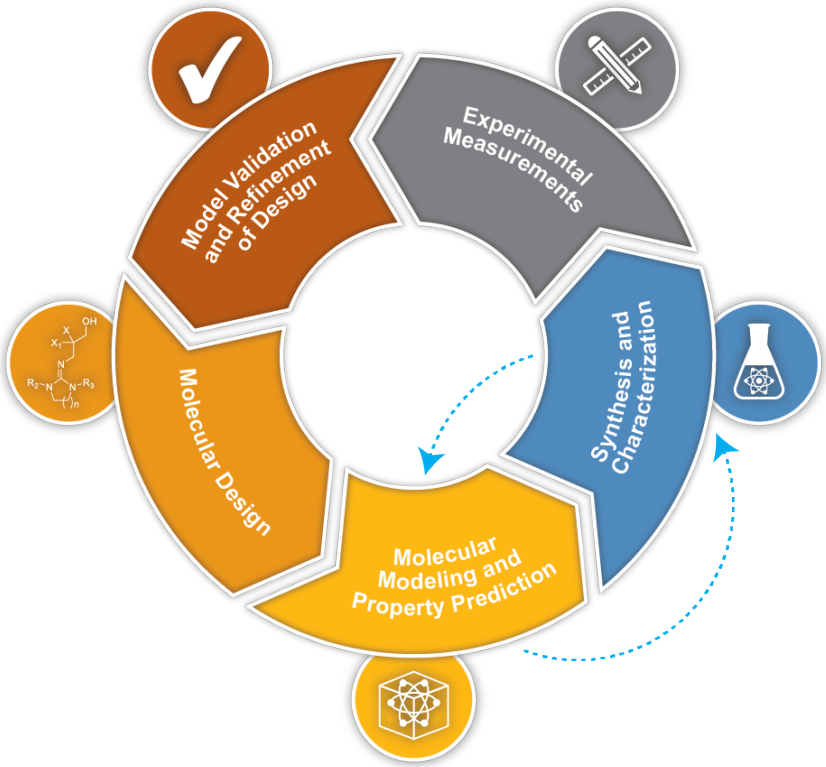
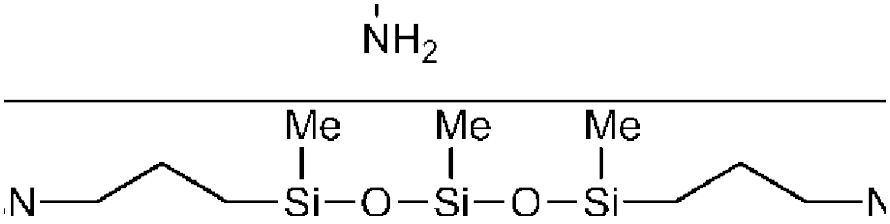
Goal: To form molecular-level insights to GAP-1 solvents.





- **Objectives:**
  - Characterize solvent structure
  - Reduce viscosity by >400 cP
  - Impact of diluents and additives
  - Mechanisms of degradation
    - Water
- **Milestones 9.1, 9.2, 9.3**

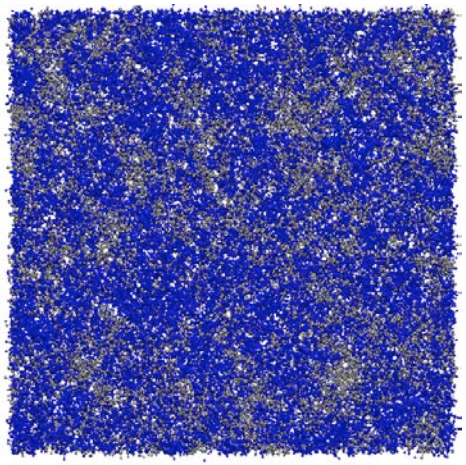
(12 months – FY17)

Aminosilicones/Triethylene Glycol Molecular Structure

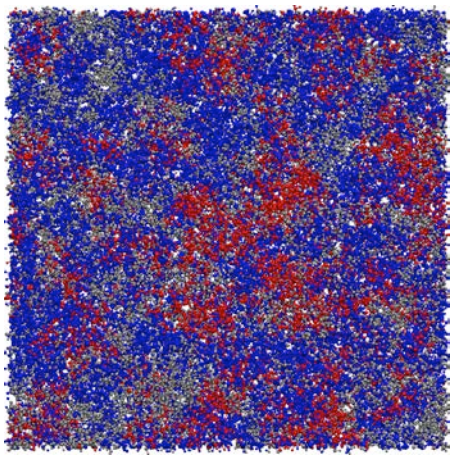
Pacific Northwest NATIONAL LABORATORY

GE Global Research

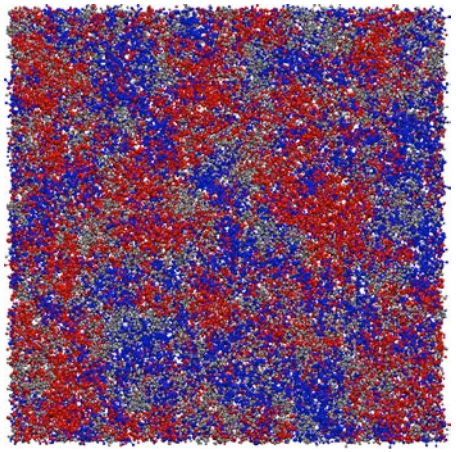
Aminosilicone Solvent Class: (Triethylene Glycol co-Solvent)[2]



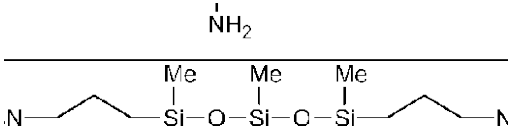
0% CO_2



25% CO_2



50% CO_2



CO_2-GAP-0: red

GAP-0: blue

TEG: silver

- TEG may not be dissolving GAP carbamates
- Co-solvent not needed

1) Cantu et al. *in preparation*

Glezakou el al. In Preparation

Aminosilicones/Triethylene Glycol Molecular Structure

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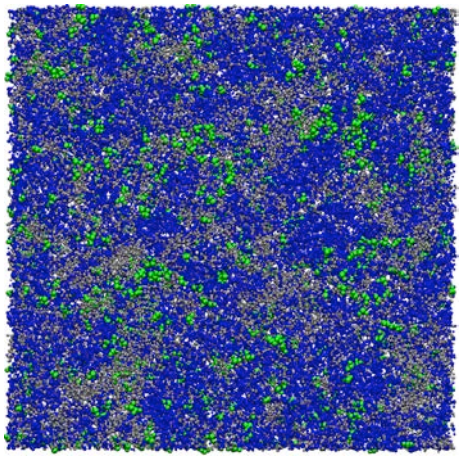
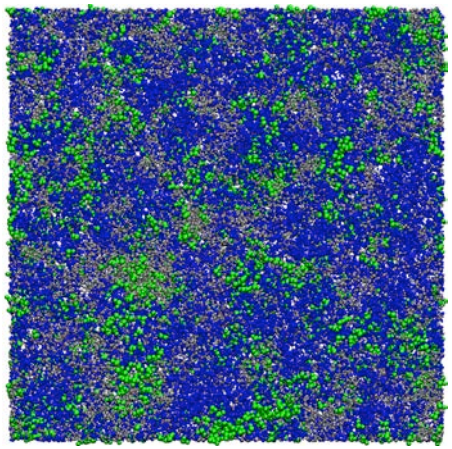
Mixtures of water and and GAP-1/TEG simulated to determine the impacts of additives such as water.

KEY:
CO_2-GAP0: **red**
GAP0: **blue**
TEG: **silver**
Water: **green**

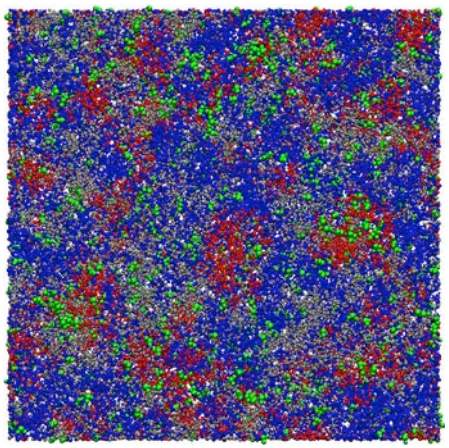
0% CO_2 loading
5%wt water



0% CO_2 loading
10%wt water



25% CO_2 loading
10%wt water



- Water acts as a diluent by solvating carbamate clusters
  - (matching experimental observations)
- Comparable solvation seen with ethylene glycol and other diluents
- Diluents do reduce viscosity at low mole fractions
  - (matching experimental observations)

Glezakou el al. In Preparation

Heterogeneous Molecular Structure May Account for Similar Performance

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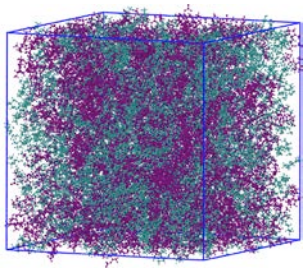
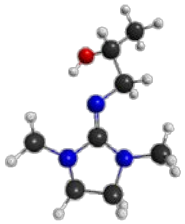
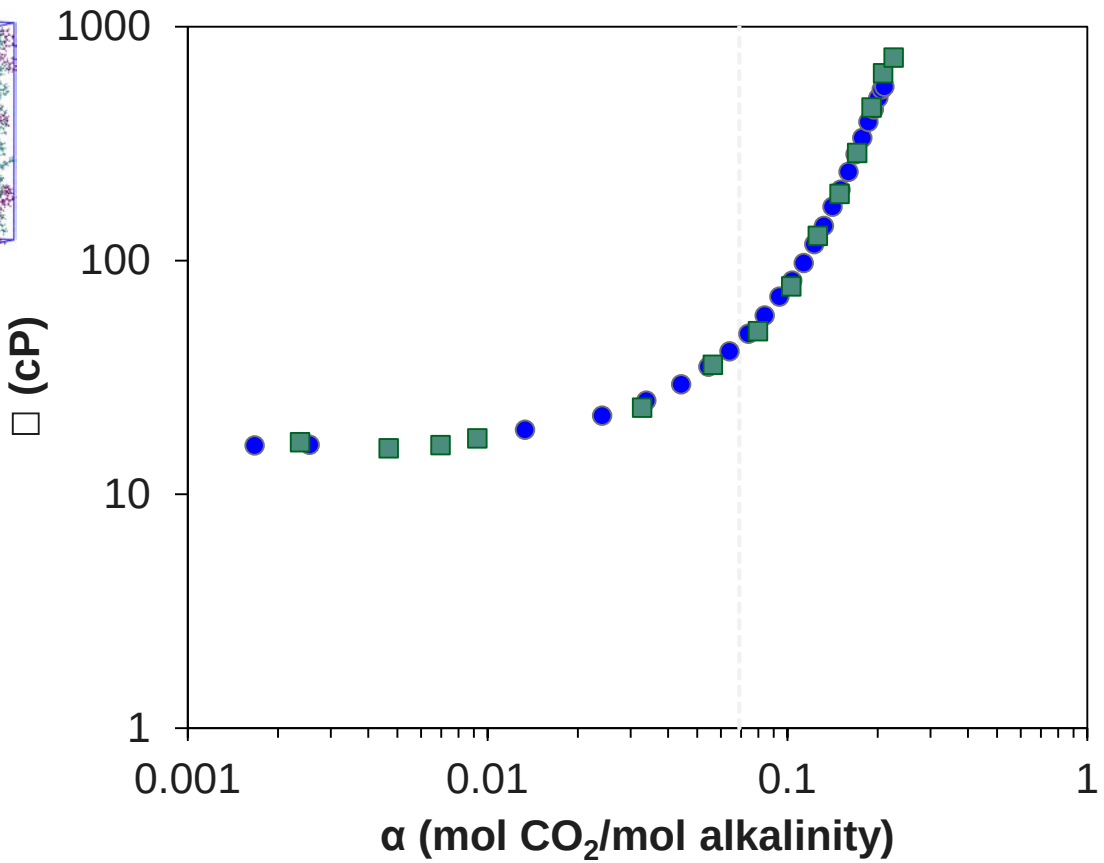
GE Global Research

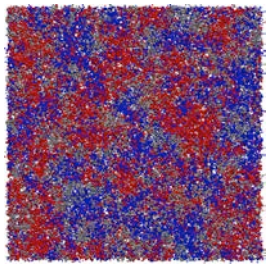
CO_2BOLs and aminosilicones show similar predicted solvent structure and viscosity profiles as a function of CO_2 loading





IPADM-2-BOL





GAP-1/TEG

1) Mathias et al *Energy Procedia,* **2015***;* Cantu *et al. J. Phys. Chem. Lett.* **2016***, 7,* 1646. 2) Glezakou *et al. Manuscript in preparation*

Heterogeneous Molecular Structure May Account for Similar Performance

Pacific Northwest NATIONAL LABORATORY
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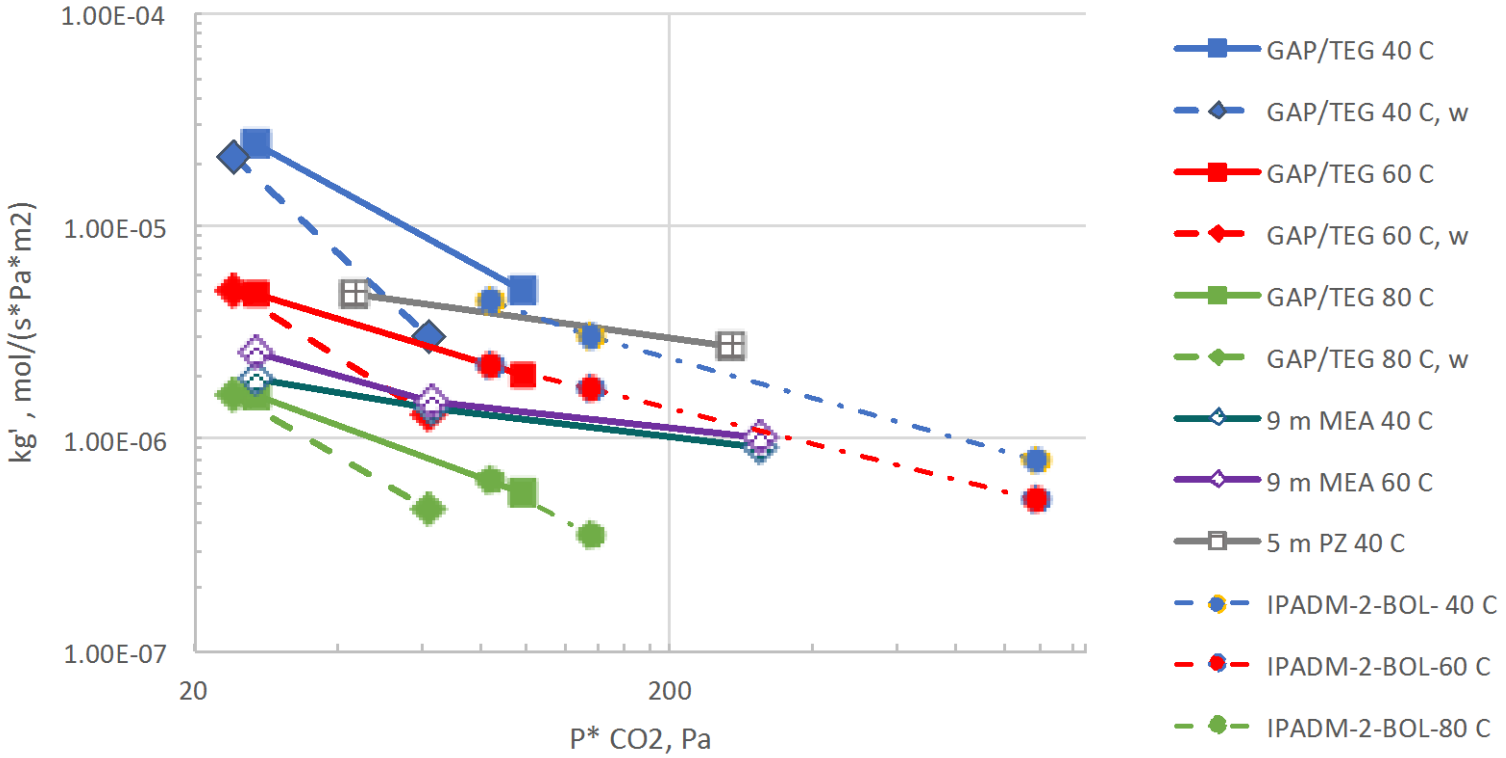
CO_2BOLs and aminosilicones show higher than expected mass transfer.



- k'_g vs. P* are comparable to MEA and piperazine under similar driving force
- Viscosity's impact of CO_2 mass transfer is less than anticipated
- IPADM-2-BOL and GAP/TEG fall on the same curve

*MEA/Piperazine data from UT Austin

Whyatt et. al. 56 (16), 4830-4836

Heterogeneous Solvent May be Good for Diffusion and Reactivity

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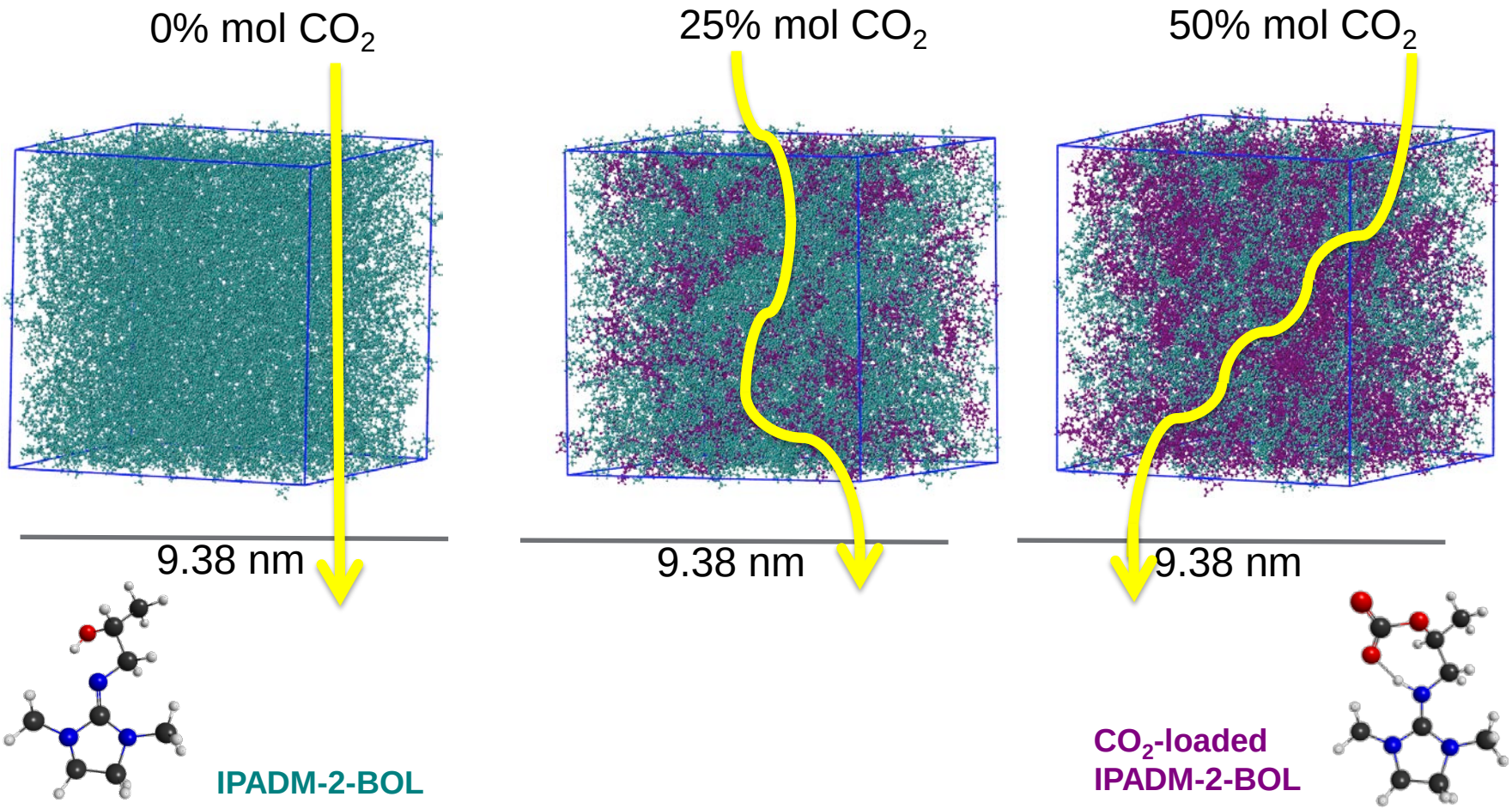


- Open solvent "pores" may provide channels for CO_2 diffusion
- High physical solubility in low CO_2 loaded regions
- Unreacted solvent always available to react with CO_2

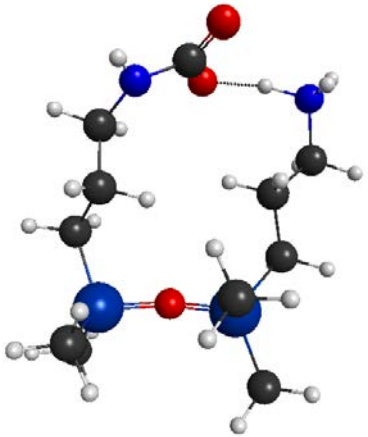
Probing the Acid/Base Equilibrium

Probing the acid/base equilibrium in aminosilicones.

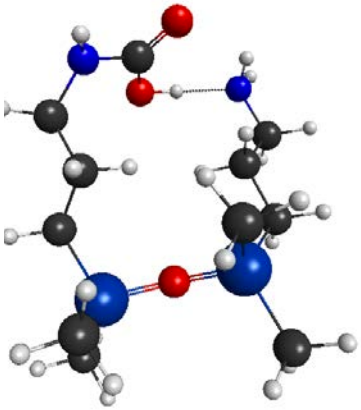
- GAP-0 and GAP-1 with implicit solvent: both isoenergetic (~0.001 kJ/mol)
  - Equilibrium likely observed in solution
- GAP-0 gas phase: Acid state is ~ 35kJ/mol lower in energy
- GAP-1 gas phase: Zwitterion is ~15 kJ/mol lower in energy

GAP-0

Zwitterion

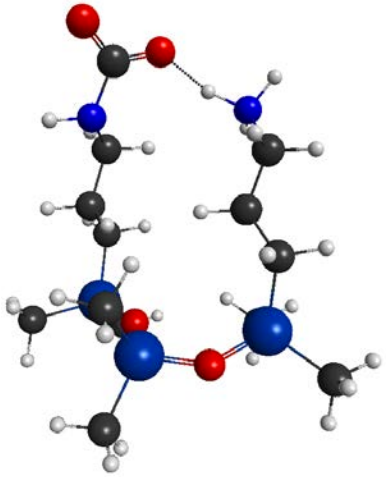


Acid

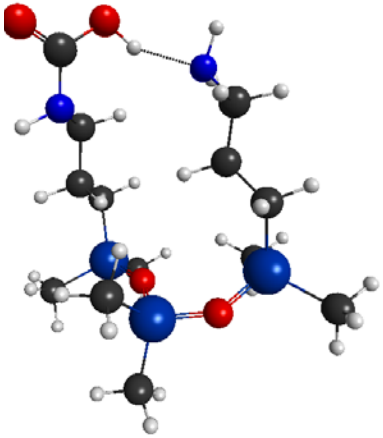


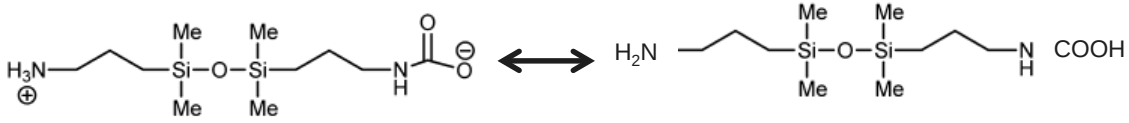
GAP-1

Zwitterion



Acid





Perry el al. Manuscript in preparation

Legacy Solvents: 3rd Generation Molecules Currently Being Modeled

Pacific Northwest NATIONAL LABORATORY
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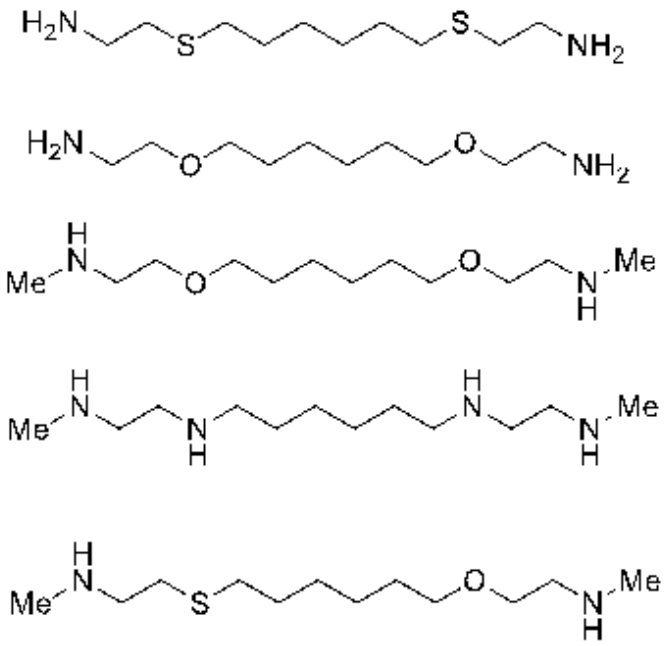
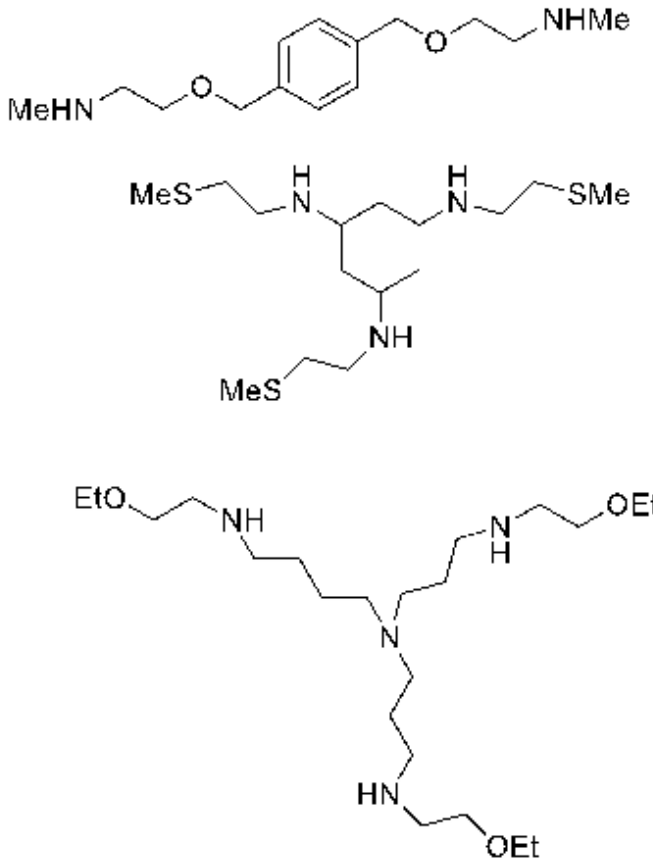
New 3rd generation derivatives designed with high P_{int} for low viscosity.





- 100% concentrated, can utilize PSAR
- Moieties promote internal H-bonding
  - Low viscosity
  - favor “acid” form
  - No hydrolysis or disproportionation
- Cheaper

Perry el al. Manuscript in preparation

Legacy 3rd Generation Solvents

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Conclusions:

- Key descriptors of viscosity identified
- Co-solvents do not reduce viscosity
- New derivatives identified
  - More durable
  - Cheaper
- 100% concentrated
  - May use PSAR

Remaining FY17 work:

- Model molecules to determine viscosity of 3rd generation
- Make and test cP/P* and k'g for a 1-2 derivatives

Amino Pyridine Solvent Class

Pacific Northwest NATIONAL LABORATORY
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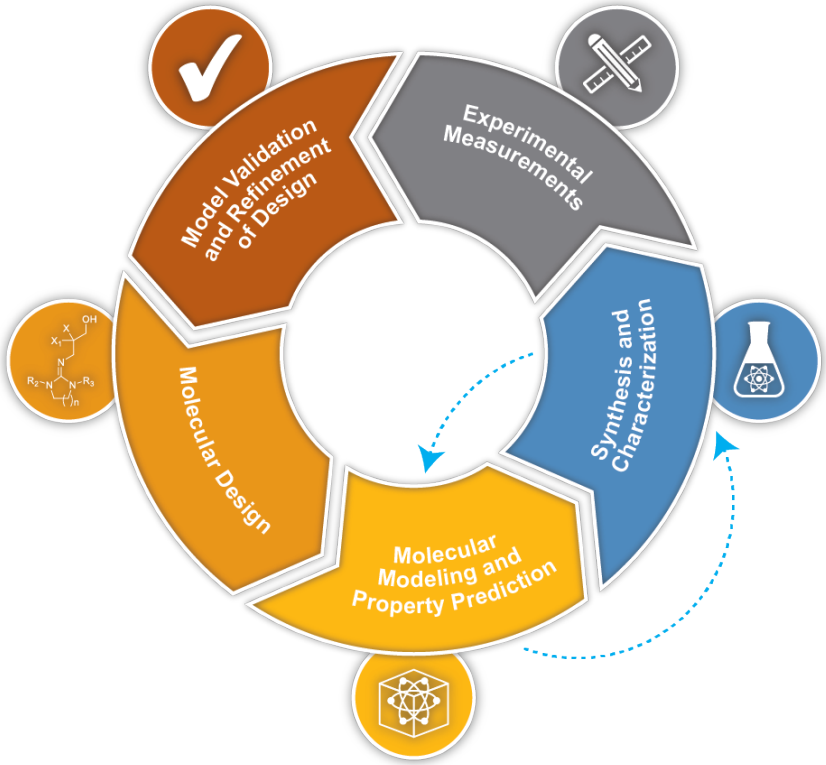
Goal: To form molecular-level insights of this newly discovered amine solvent class.



- **Objectives:**
  - Test individual compounds P* and k'g and cP
  - Reduce volatility while retaining low viscosity
- **Milestones: 8.1, 8.2**

(12 months – FY17)

New Solvent Class Derived From CO_2BOL & GAP-1 Findings

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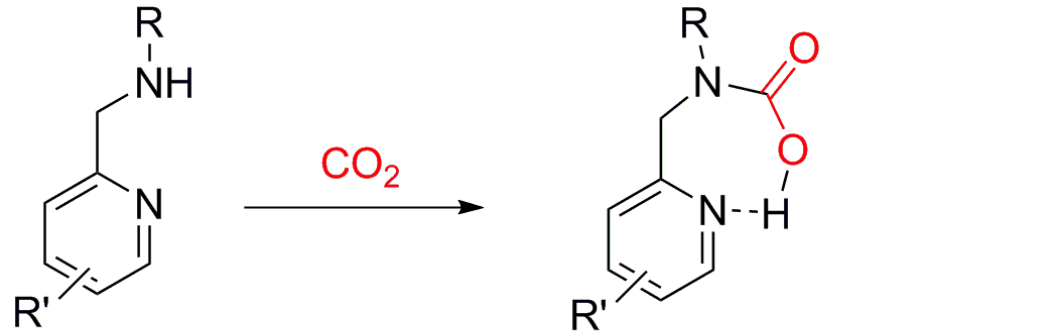
Switchable carbamate ionic liquid with similar properties as CO_2BOLs.



Pyridine-based Amine

R= H, Alkyl, Me, Et, Pr, iPr etc, EWG, CH_2CF_3, CH_2OMe etc
R' =Alkyl, OMe, NO_2, F etc

- 100% concentrated, can utilize PSAR
- Pyridine moiety can be added to GAP-1 derivatives to promote internal H-bonding
  - Low viscosity
- Unique Acid/base equilibria predicted to favor “acid” form
  - Low regeneration temperature

Koech el al. Submitted

Changing the Speciation of Amine Chemistry

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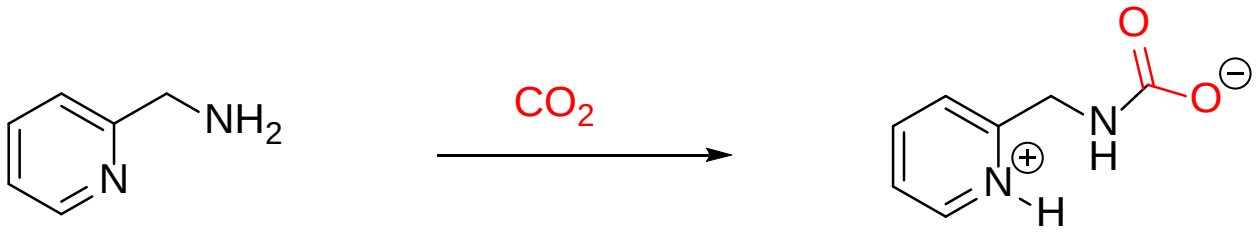
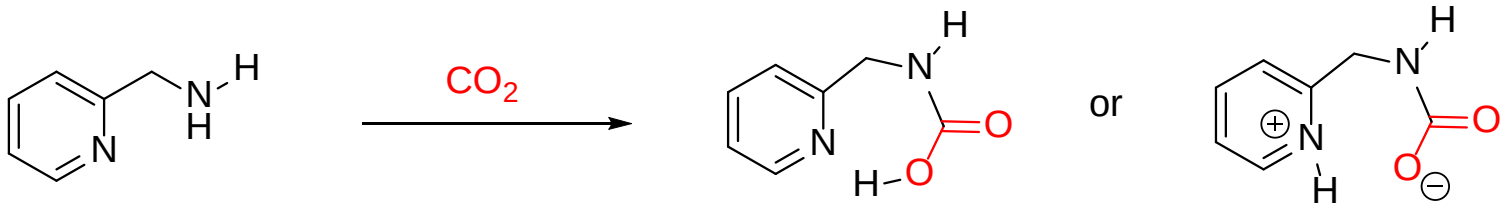
CO_2 Uptake of 2-Picolylamine Shows 1:1 Chemistry Is Achievable



Compound	CO_2 Wt%	CO_2 Mol%	Product state
neat	18	44	Solid
1:1 DMSO:	32 (15)	78.5	Liquid
Koechanol	9	44	Liquid

High P_{int} promotes a high degree of carbamic acid.



- Carbamic acid and zwitterionic carbamate salt equilibrium
- Standard 2:1 amine : binding mode

Koech el al. Submitted

CO_2 Capacity of AP Derivatives

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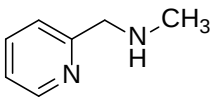
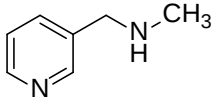
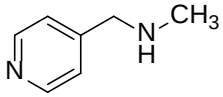
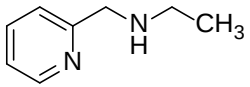
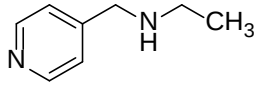
CO_2 Gravimetric Uptake of AP Derivatives at 40 ℃ Show High Capacity.

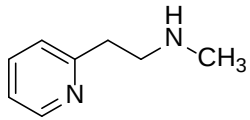

2-MAMP


3-MAMP


4-MAMP


2-EAMP


4-EAMP


2-MAEP

	CO_2 capacity at 25 °C		CO_2 capacity at 40°C	
Compound	Wt%	Mol%	Wt%	Mol%
2-MAMP	19.7	54.8	21.1	58.5
3-MAMP	19.5	54.1	20.0	54.9
4-MAMP	19.7	54.8	18.6	51.5
2-EAMP	18.2	56.5	14.0	43.3
4-EAMP	18.3	56.7	16.7	51.8
2-MAEP	17.8	55.2	19.2	59.8

- Six non-aqueous amines have high CO_2 capture capacity
- CO_2-rich solvents are liquids at room temperature
- Heat of amine reaction with CO_2 is ~75 KJ/mol

Koech el al. Submitted

Regeneration of AP Derivatives

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

CO_2 Release Profiles Show Low Regeneration Temperatures W/WO PSAR

Compound	60 °C PSAR	70 °C	80 °C	100 °C	120 °C
2-MAMP		33.8	60.5	90.3	-
3-MAMP		31.1	51.0	77.5	-
4-MAMP		35.1	51.3	93.8	-
2-EAMP	81	85	95.8	-	-
4-EAMP		71.4	85.1	98.8	-
2-MAEP		-	34.6	76.4	90.3

- Lean solvent loadings achieved at only 60 °C
- 20 ˚C temperature swing
- Increased net power, lower evaporative losses, lower thermal degradation

Koech el al. Submitted

Viscosity Profiles for AP Derivatives

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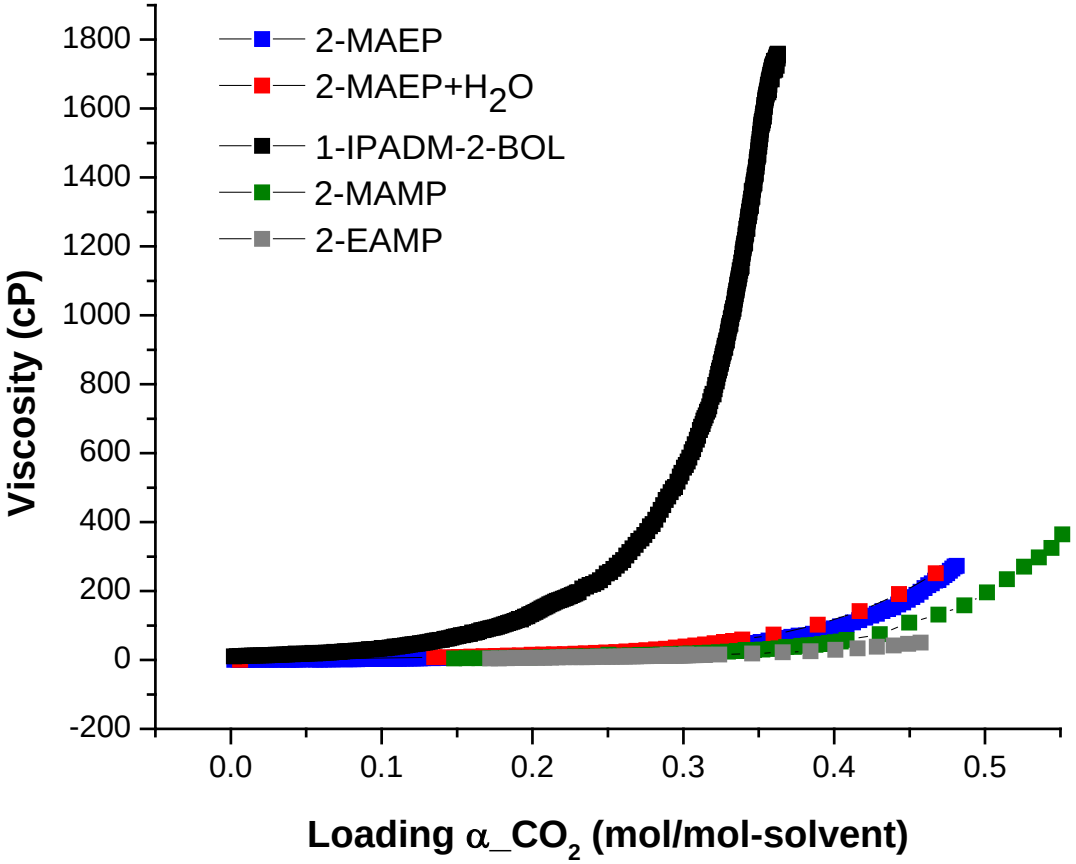
High P_{int} reduces viscosity ~90% over IPADM-2-BOL.



- 2-MAEP has 90% lower viscosity than CO_2BOL IPADM-2-BOL
- Viscosity of 2-MAEP at 40 °C almost matches that of IPADM-2-BOL at 75 °C

Koech el al. Submitted

Kinetic Profiles for AP Derivatives

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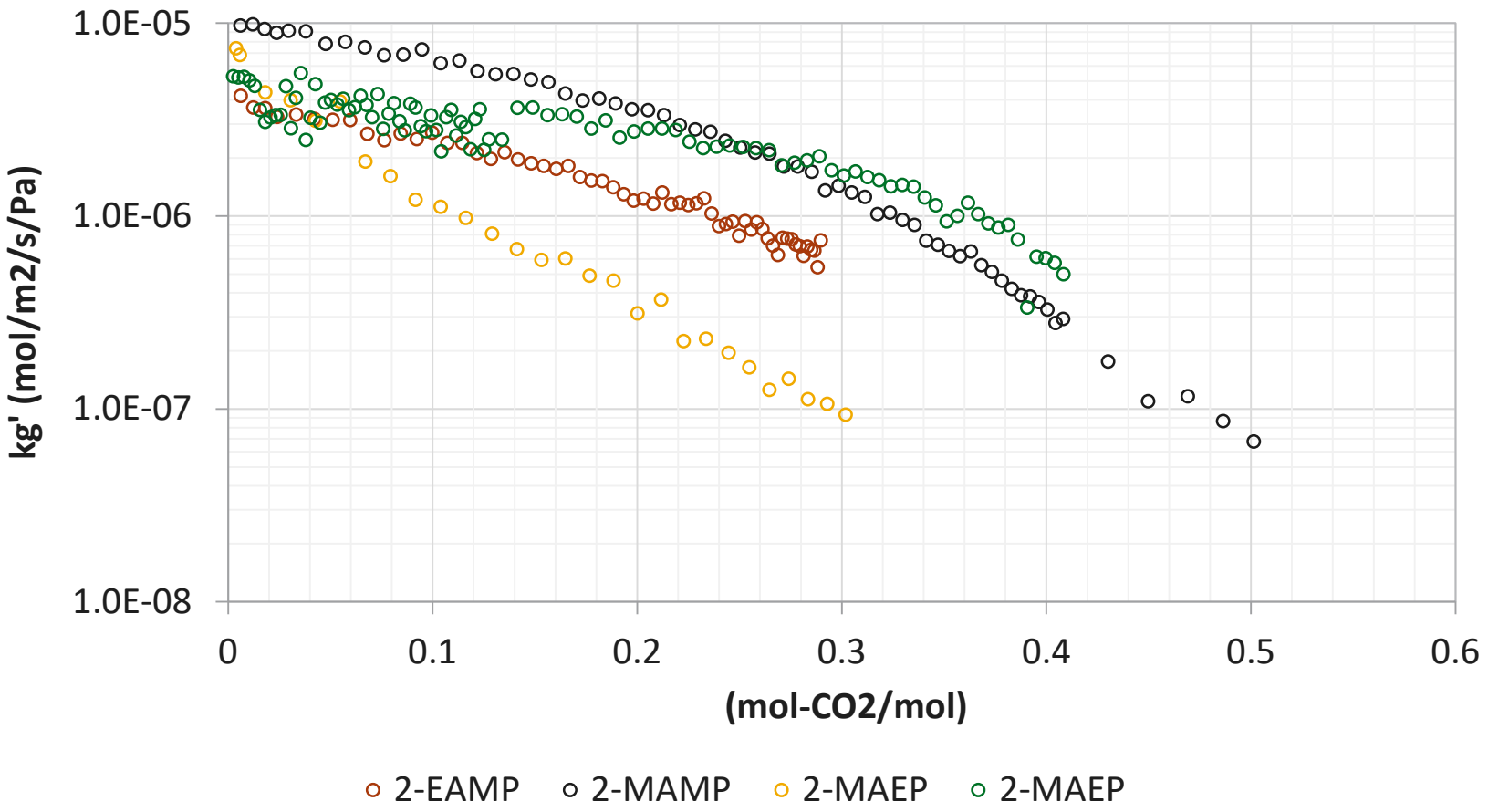
Comparable mass transfer to IPADM-2-BOL, 5M MEA, and 9 M piperazine.



Koech el al. Submitted

AP Molecular Structure

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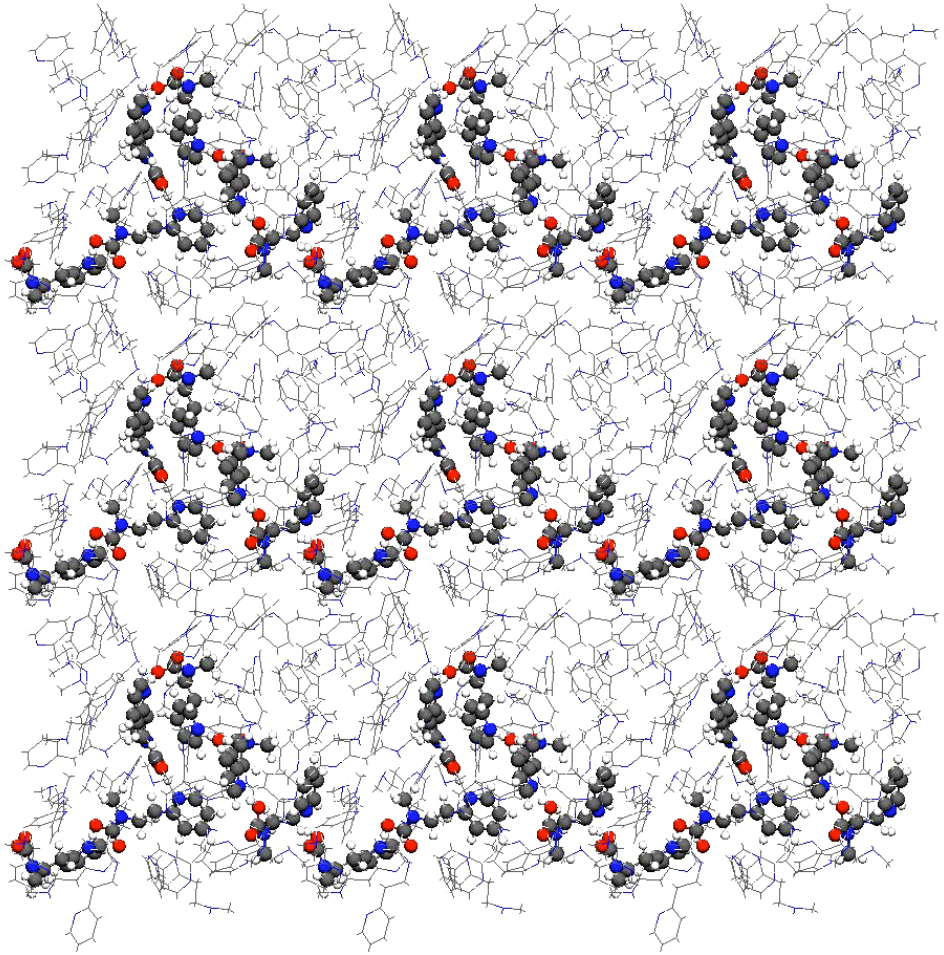
Insights into molecular structure indicate new reactivity mesoscale ordering.



- Carbamate channels show different CO_2 binding mechanisms pending location of pyridine N
- Potential CO_2 diffusion channels
- Proton shuttling observed
- Potential for cooperative binding?

Koech el al. In Preparation

2nd Generation Aminopyridines

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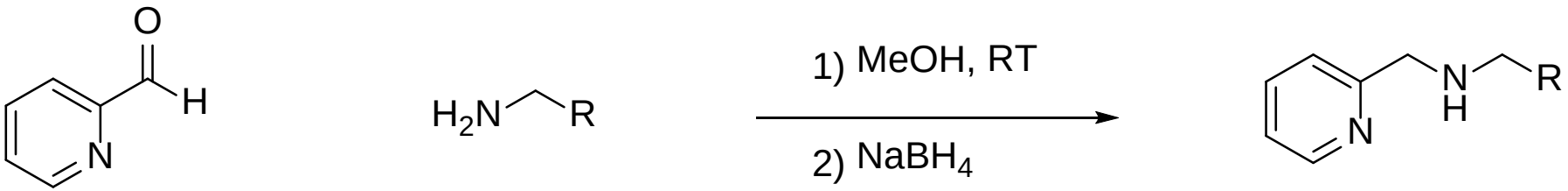
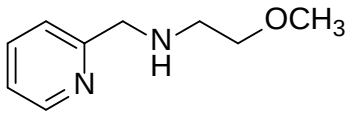
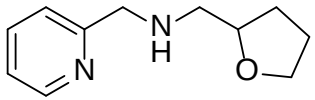
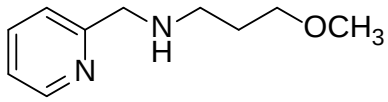
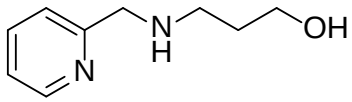
Show reduced volatility while retaining CO_2 capacity and low viscosity.



Compound	MW	BP* (°C)	Vapor Pressure* (Torr @ 25 °C)	CO_2 wt%	CO_2 mol%
	166.2	238.9 ± 20	0.0414	15.2	57.4
	192.3	304.4 ± 17	0.000935	9.4	41
	179.3	261.9 ± 20	0.0112	14.2	57.7
	204.3	315 ± 27	0.000432	7.0	32.7

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Amino Pyridine Solvent Class

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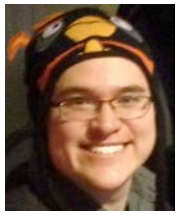
Conclusions:

- AP solvent class shows promising viscosity though high volatility
- Tunable acid/base equilibria
- Low regeneration temperature (20 ˚C swing)

Remaining FY17 work:

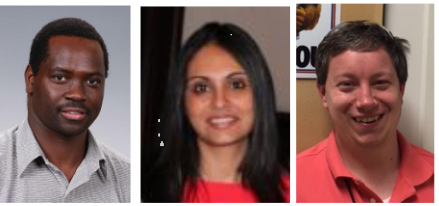
- Reduce volatility while retaining low cP
- WWC testing and PVT to confirm testing
- Explore channels in solvent with respect to mass transfer

Acknowledgements



PNNL Team

Solvent Design
Chemical Durability
Synthesis & Scaleup



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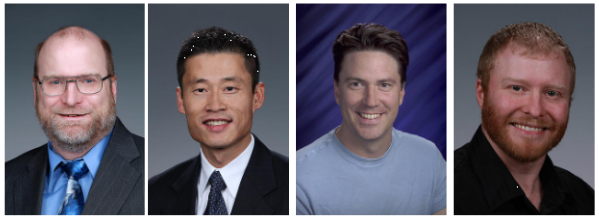
Parametric Materials Testing
& Analysis



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