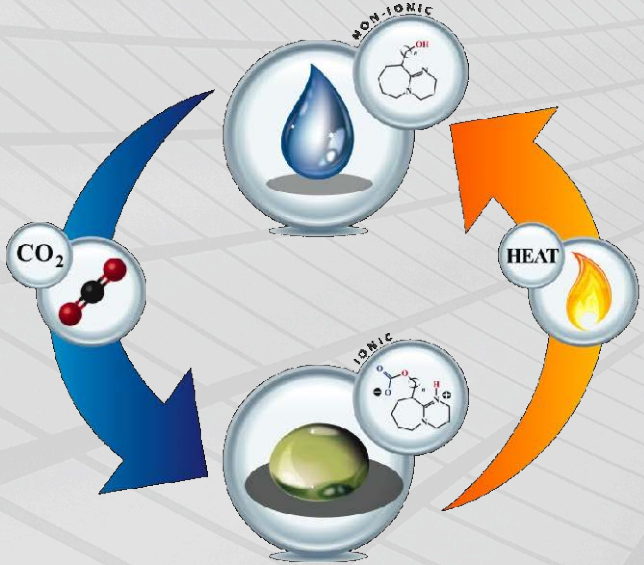

Accelerating the Development of "Transformational" Solvents for CO_2 Separations

DOE Transformation Workshop

Arlington, DC

September 23, 2014

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Overview

- Water-Lean Solvents as a Class of Transformational Solvents
- Challenges in Solvent Development: CO_2BOLs Case Study
- PNNL's Solvent Development Program
- Conclusions and Future Work

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Water-Lean Solvents as a Class of Transformational Solvents

Benefits:

- Lower heat of vaporization of water and condensation
- Lower sensible heat
- Unique thermodynamic and physical properties

Limitations:

- Full dehydration impractical
- Water tolerance (some solvents)
- Cost challenges with a custom solvent
- Viscosity can increase as a function of CO_2 loading
- Unknown compatibility with commercial processing equipment

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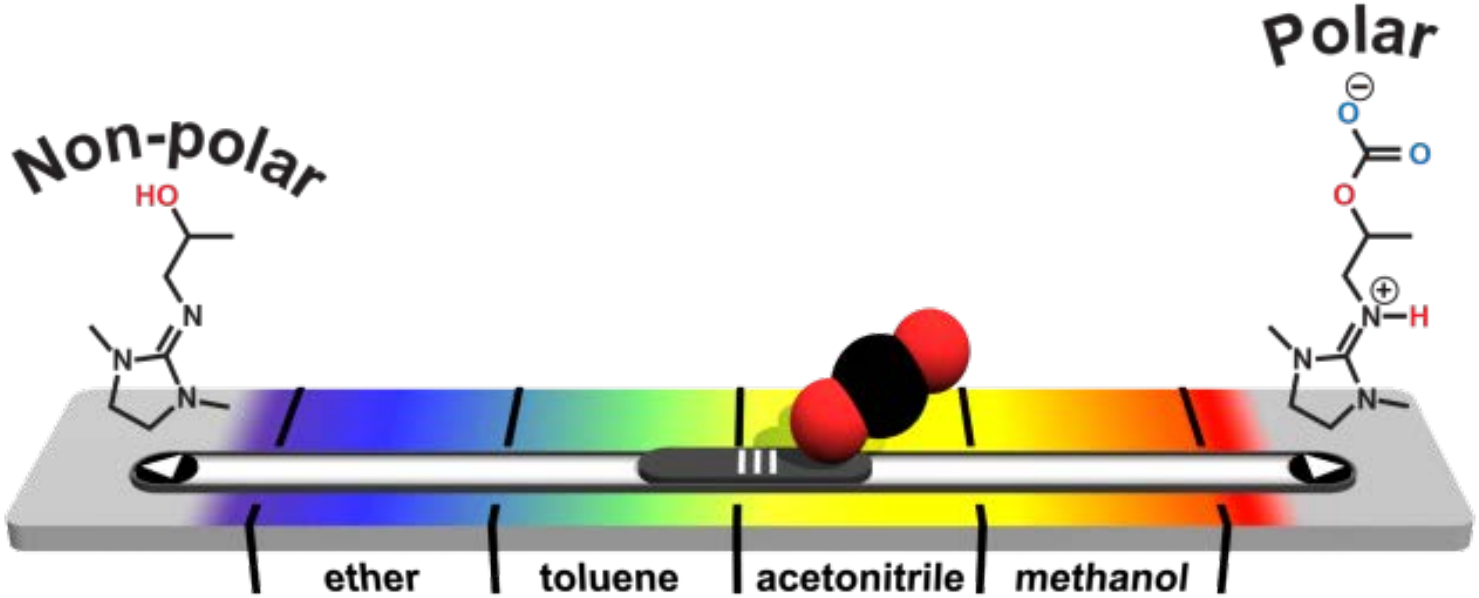
CO_2 Binding Organic Liquids (CO_2BOLs) Case Study

- Water-lean" organic switchable ionic liquid solvent system
  - 5 wt. % optimal water level in circulating solvent estimated
  - Heat of solution -80 kJ/mol
  - External polarity trigger discovered (Polarity Swing Assisted Regeneration, PSAR)



Nile Red Solvatochromatic Polarity Scale

*Nature, (**2005**), 436, 1102; Ind. & Eng. Chem. Res. (**2008**); 47, 3, 539, Energy Environ. Sci., (**2008**)*, 1, 487
Koech *et al. RSC Adv., (**2012**)*, 3, 566-572, *Energy. & Env. Sci. (**2013**)*, 6, 2233 - 2242

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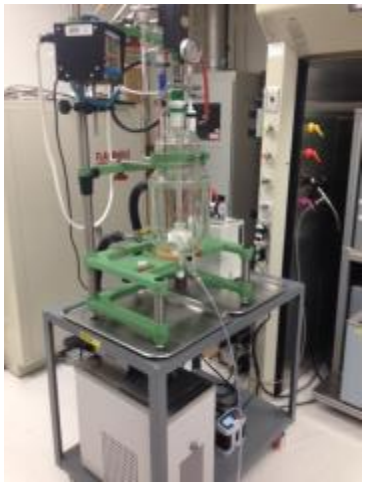
PNNL's Testing Equipment & Facilities Used for CO_2BOL Case Study

5-L Synthesis Reactor



Equilibrium PT_X Cell

Wetted Wall

Bench-Scale Portable Cart

Equilibrium Measurements

Kinetic Measurements

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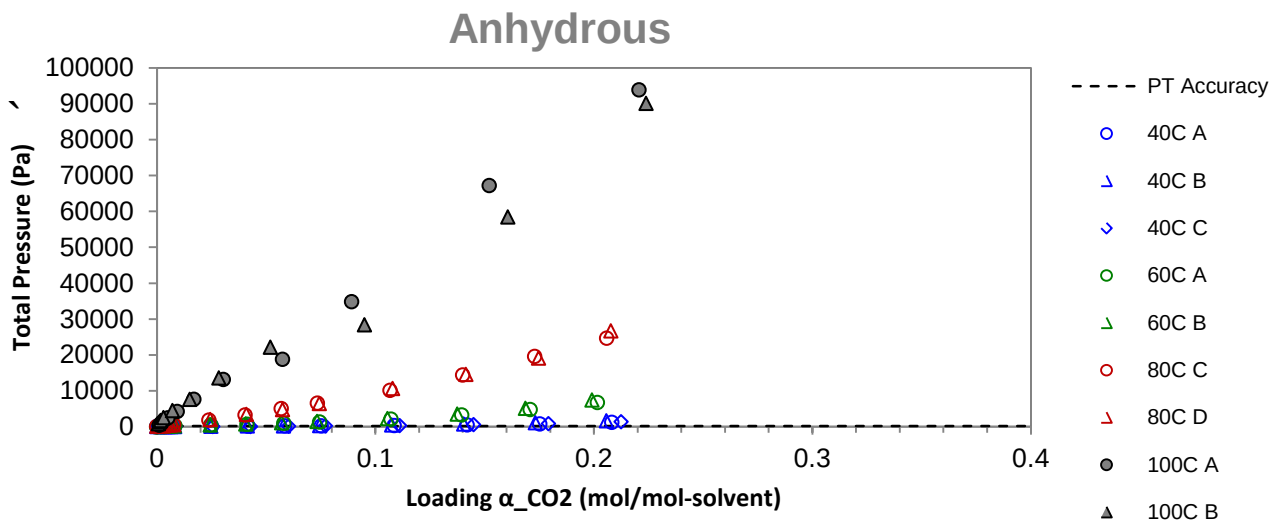
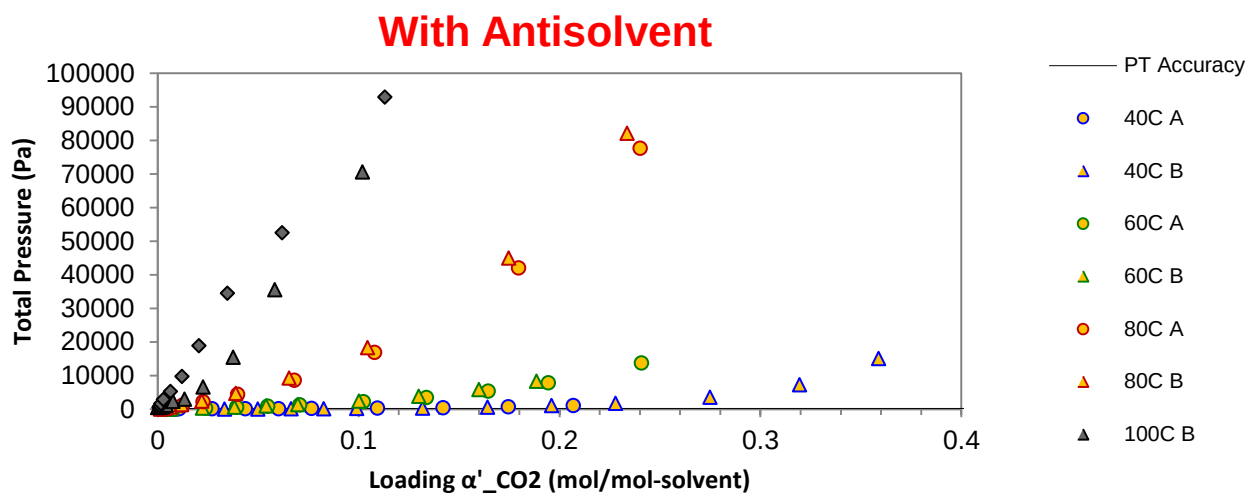
CO_2BOLs Case Study: PT_x Measurements





- Used to develop Vapor Liquid Equilibria (VLE) Curves
- Used to build thermodynamic models and set optimal absorption and stripping conditions

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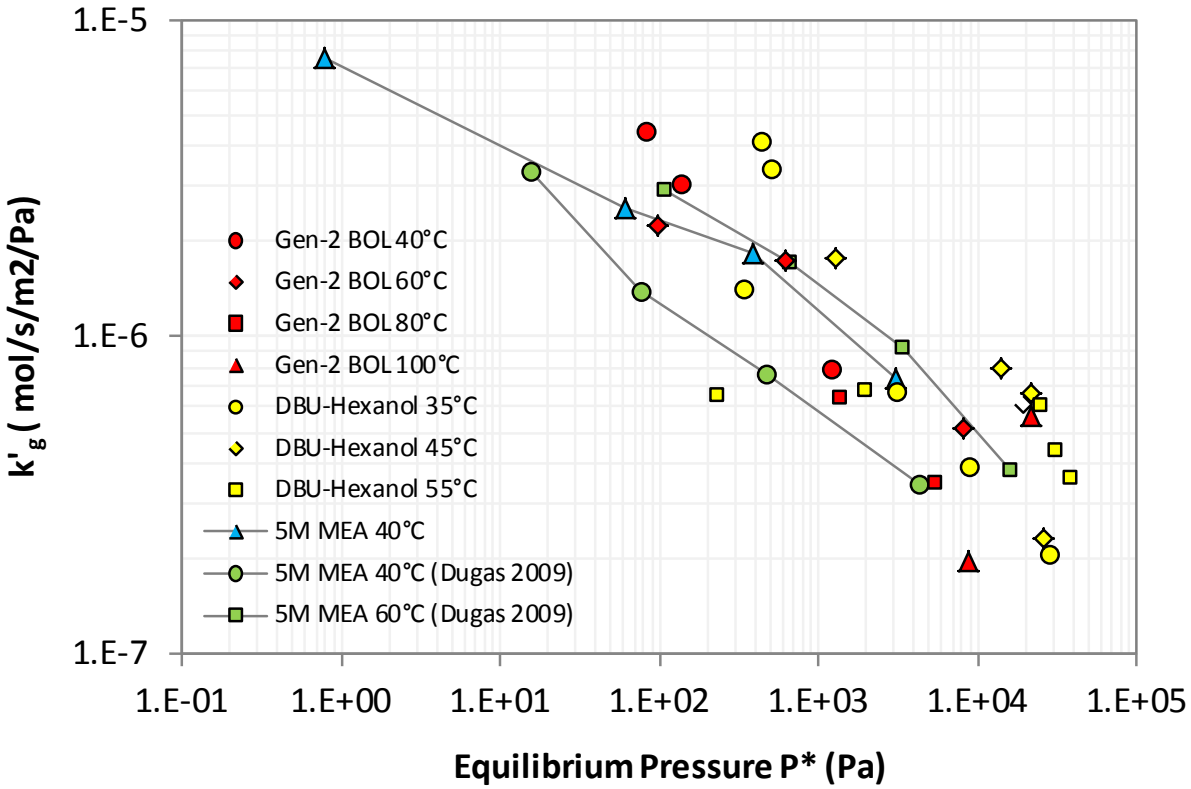
Energy. & Env. Sci. (***2013***)**,** 6, 2233 – 2242

CO_2BOLs Case Study: Liquid Film Mass Transfer



- Mass transfer of CO_2 in CO_2BOLs is comparable to MEA and Piperazine under similar driving force
- Viscosity's impact of CO_2 mass transfer is less than anticipated
  - Attributed to high CO_2 solubility in organic/ionic forms
  - Similar effect projected for other non-aqueous technologies

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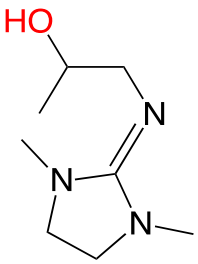
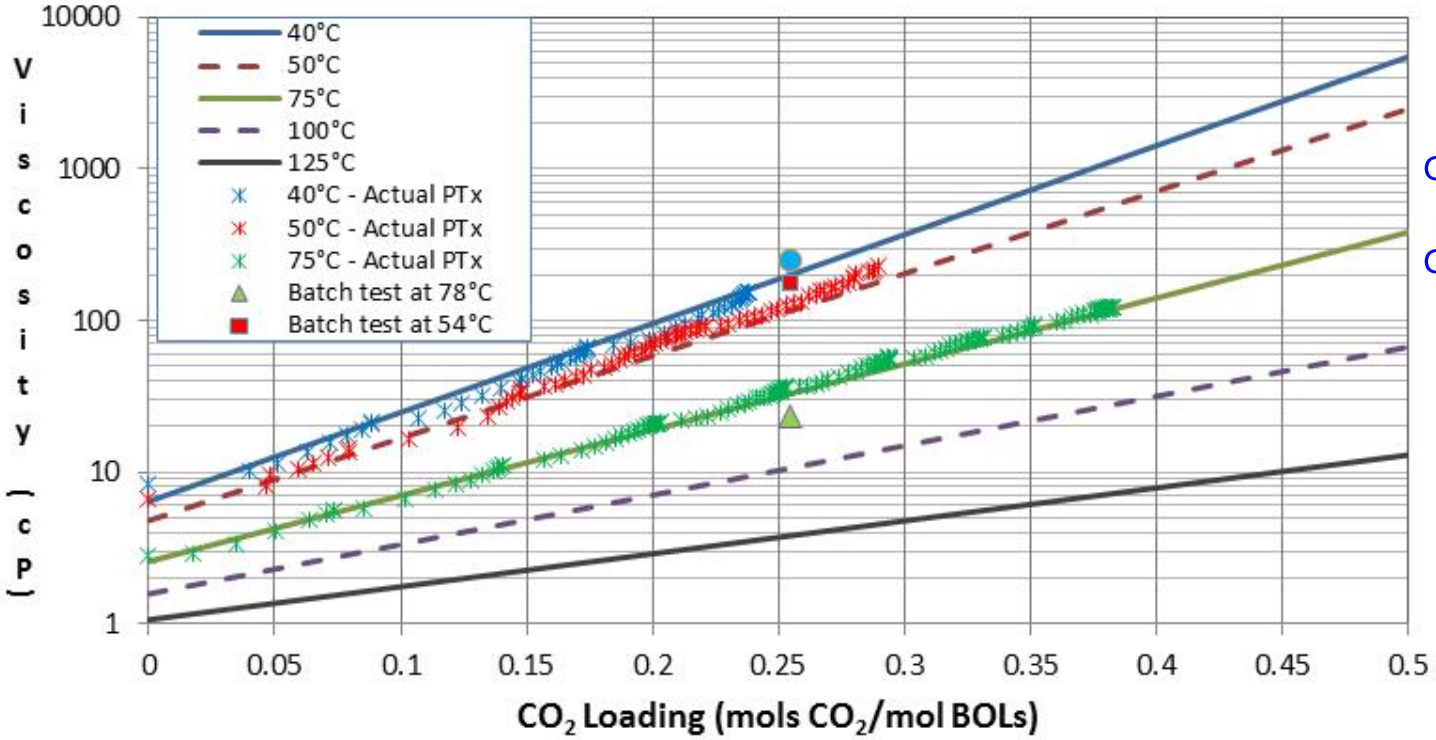
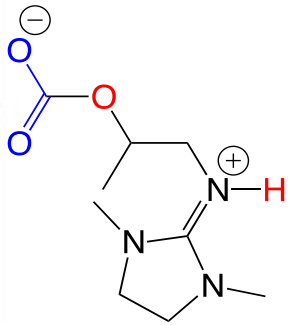
Manuscript In Preparation

CO_2BOL Case Study: Viscosity







- Significant reductions in viscosity achieved during early stages of program
- Current state: targeted 0.25 lean to 0.5 rich swing corresponds to 200-3,000cP

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Koech *et al. RSC Adv.*, (***2012***), 3, 566-572

CO_2BOL Case Study: Viscosity's Impacts on Capture Performance

OPEX

- Lower solvent lean **α** (CO_2 loading) is needed
  - Larger circulation pumps
  - Results in a higher reboiler temperature
  - Higher reboiler duty
- Potentially increased solvent circulation rate
  - Larger circulation pumps

CAPEX

- Larger cross exchanger
- Potentially larger absorber column diameter
- Higher capital infrastructure costs

Reducing rich-solvent viscosity is anticipated to remove this technical hurdle for deployment of transformational solvent systems.

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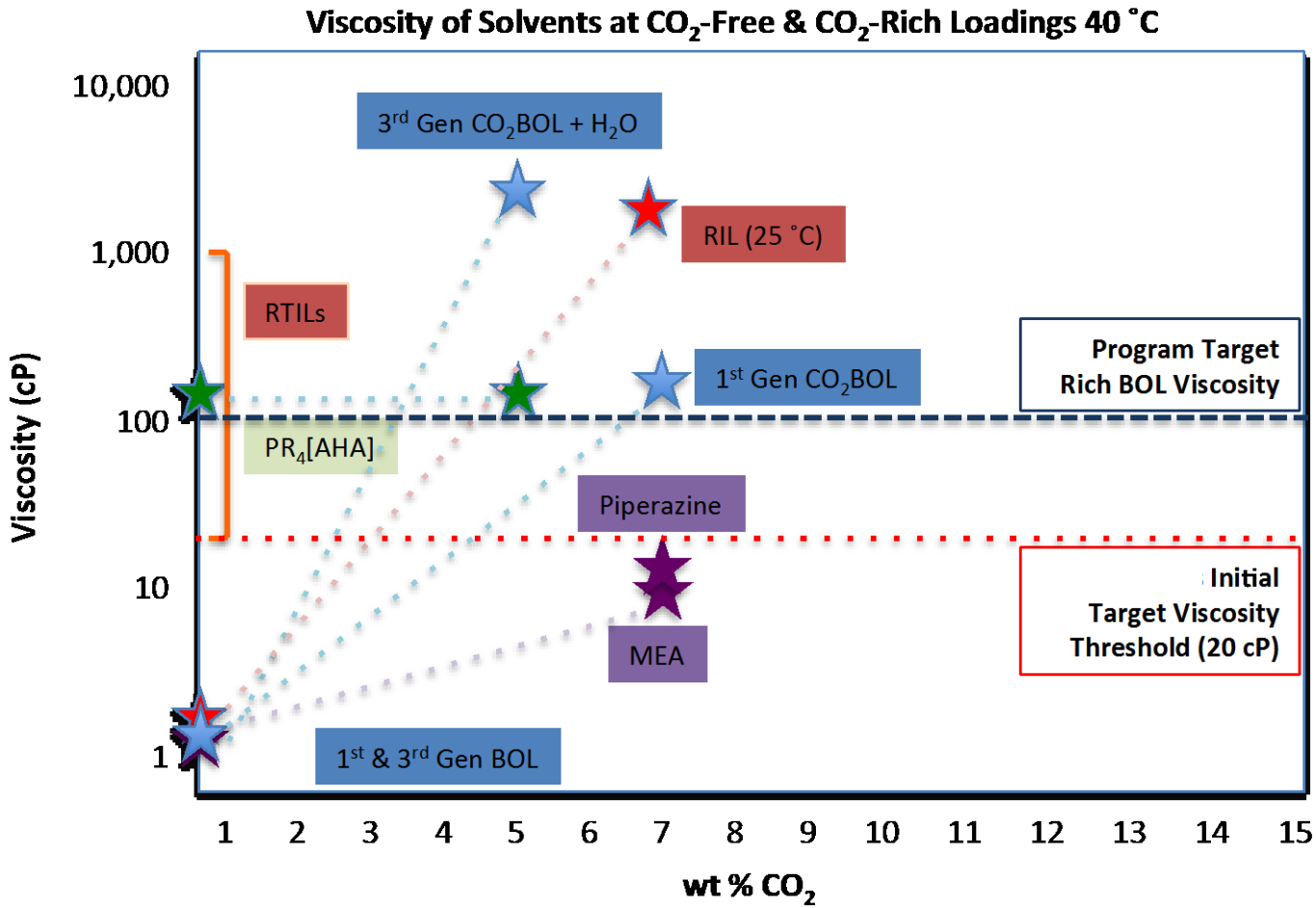
Image taken from www.ouitschem.weebly.com

Implications of Transformational Solvent Technologies to DOE's CO_2 Capture Program

- Knowledge translatable to other transformational solvent platforms
  - Thermodynamic performance validated
    - Electrolyte Aspen Plus™ models are sensitive to the Born term
  - CO_2 mass transfer for organics (at higher viscosities) is comparable to MEA and Piperazine under similar driving force
  - Viscosity impacts to CAPEX and OPEX quantified
  - Non-aqueous solvents can use existing infrastructure and hardware
    - Steady state observed at 700 cP rich solvent viscosity

- If viscosity is comparable to aqueous technologies*
  - The reboiler heat duty for organics can be as low as 57% of NETL Case 10
  - Unique physical and chemical behavior of transformational solvents such as PSAR may add an estimated 20% increase in net electric power output over NETL Case 10
  - A combined CO_2BOL/PSAR process reduce parasitic loads of NETL Case 10 by 19% at an equivalent coal feed rate

Available Viscosity Data of Water-Lean Solvent Systems



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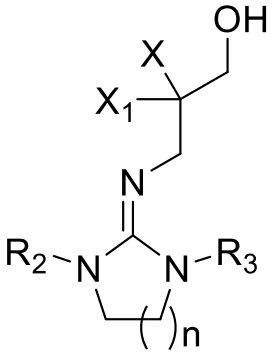
Viscosity Reduction Of Transformational Solvents Requires Fundamental Understanding With Applied Testing

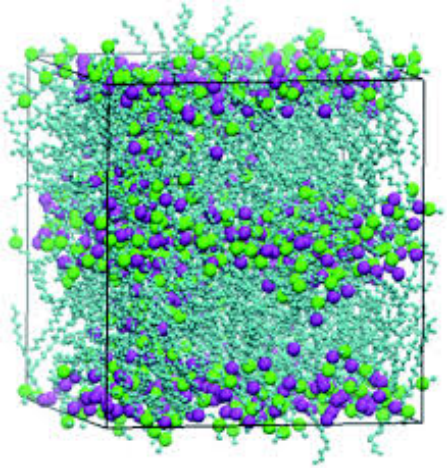
- With thousands of potential derivatives of each solvent class, it is impossible to make and test them all
- Models need to be developed to assess performance in a reasonable time
- A fundamental knowledge of solvent structure and solvent interactions is needed
- The challenge is understanding enough solvent fundamental chemistry while retaining an applied focus

PNNL's Solvent Development Program

Model Validation
Refinement of Design



Molecular Design of Molecules



Molecular Modeling & Property prediction

Synthesis & Characterization

Experimental Measurements

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Molecular Design Metrics

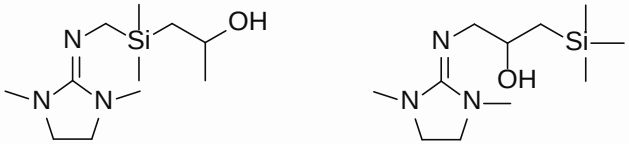
What we need (*specific for each solvent class*):

- e.g. Guanidine based CO_2BOLs
  - High basicity needed for >90% CO_2 capture
- Cyclic base core to prevent hydrolysis

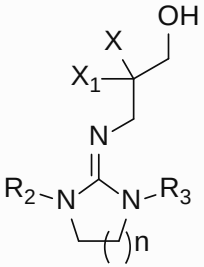
What we will study:

- Cation-anion interactions
- H-bonding orientation and strength
- Broken symmetry
- Steric crowding
- Fine tuned electronics
- Effect of hetero-atoms and charge solvation

Silane Based CO_2BOLs

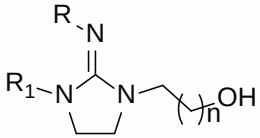


Electronic Effects



Where X and X_1 are electron withdrawing groups (EWG), F, Cl, CF_3 or electron donating groups (EDG). OMe, CH_2NMe_2
$R_2 = R_3$ = Me, CF_3, CF_3CF_2 , OMe
n = 1, 2, 3

Steric Effects



Where R = Pr, iPr, Butyl, T-Butyl
R1 = Me, Et, iPr
n = 1, 2, 3

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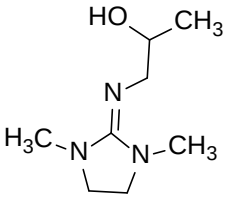
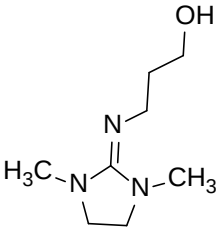
CO_2BOLs – Initial computation targets

- Model tested reference compounds to validate model
  - Evaluate inter VS intramolecular hydrogen bonding effects on viscosity
  - 3-D Steric interactions
  - Reduced intermolecular interactions
- Pure liquids and mixtures at 15%, 25%, and 50%, for all target molecules, equilibrated with simulation → moving to diffusion and viscosity calculations & analysis

Control Molecules & Complexes

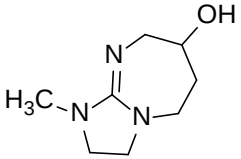


Current Best performing BOL
Viscosity ~200cP at 0.25 mol $ CO_2

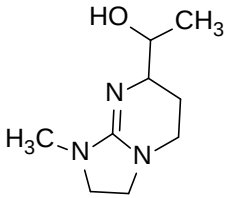


Poor performing BOL
Viscosity >>1,000 cP at 0.25 mol $ CO_2

Initial trial Molecules & Complexes



-Preserves weights and functional groups of Current BOL (2nd amine and alcohol-i.e. similar CO_2 adsorption energy)
-Restrict mobility of aliphatic side chain w. 2nd ring.
-hinder internal H-Bond.



-Preserves weights and functional groups of Current BOL (2nd amine and alcohol-i.e. similar CO_2 adsorption energy)
-Partially restrict mobility of aliphatic side chain w. 2nd ring.
-Favours internal H-Bond.
-May be a more readily synthesizable target.

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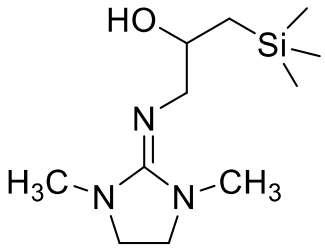
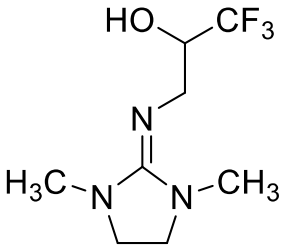
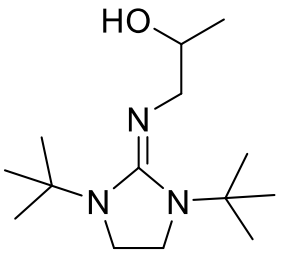
Designing New Molecular Classes of CO_2BOLs For Building Molecular Libraries



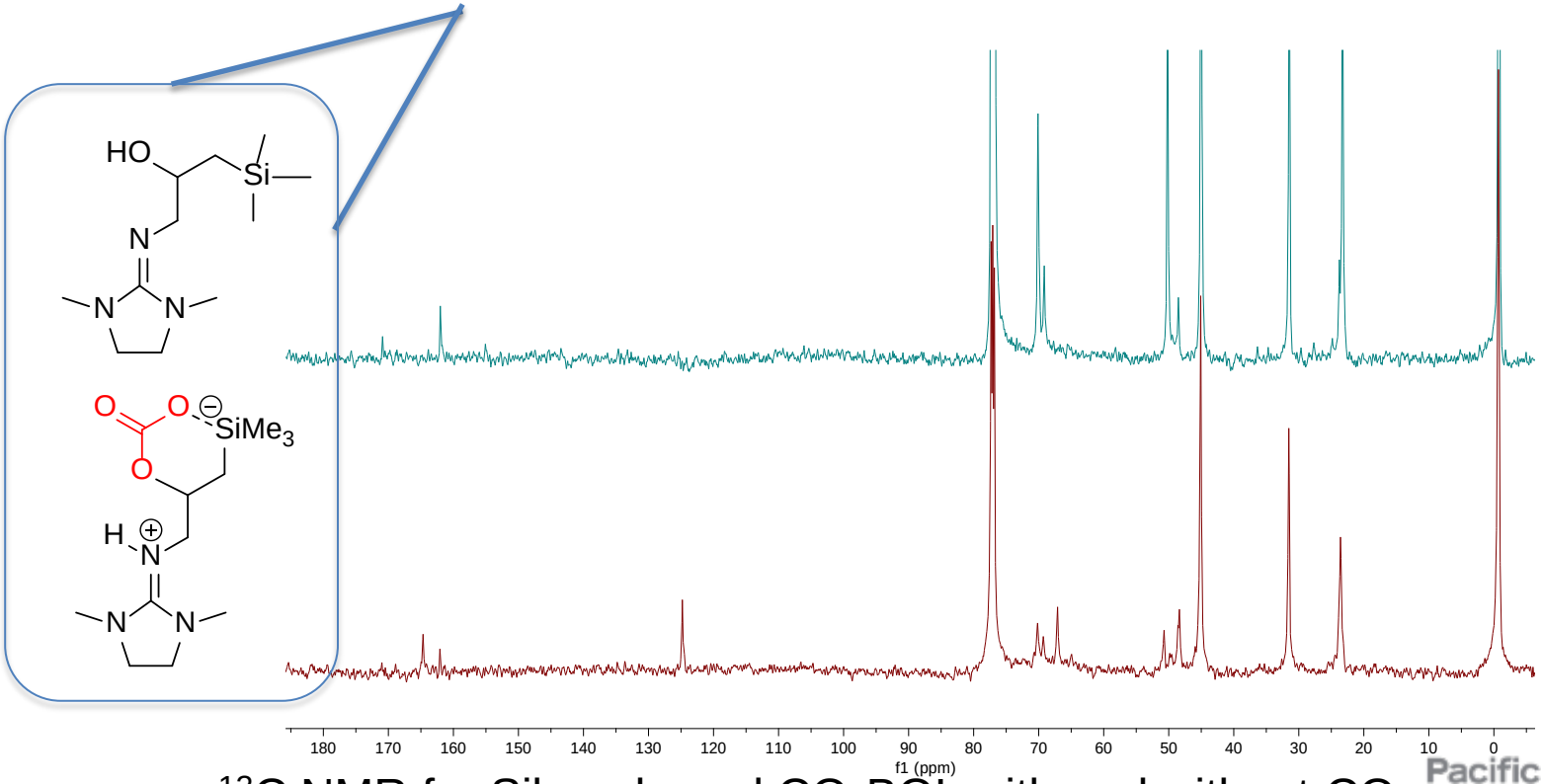
1-SiIPADM-2-BOL



1-TFIPADM-2-BOL



IPADtB-2-BOL



^{13}C NMR for Silane based CO_2BOL with and without CO_2

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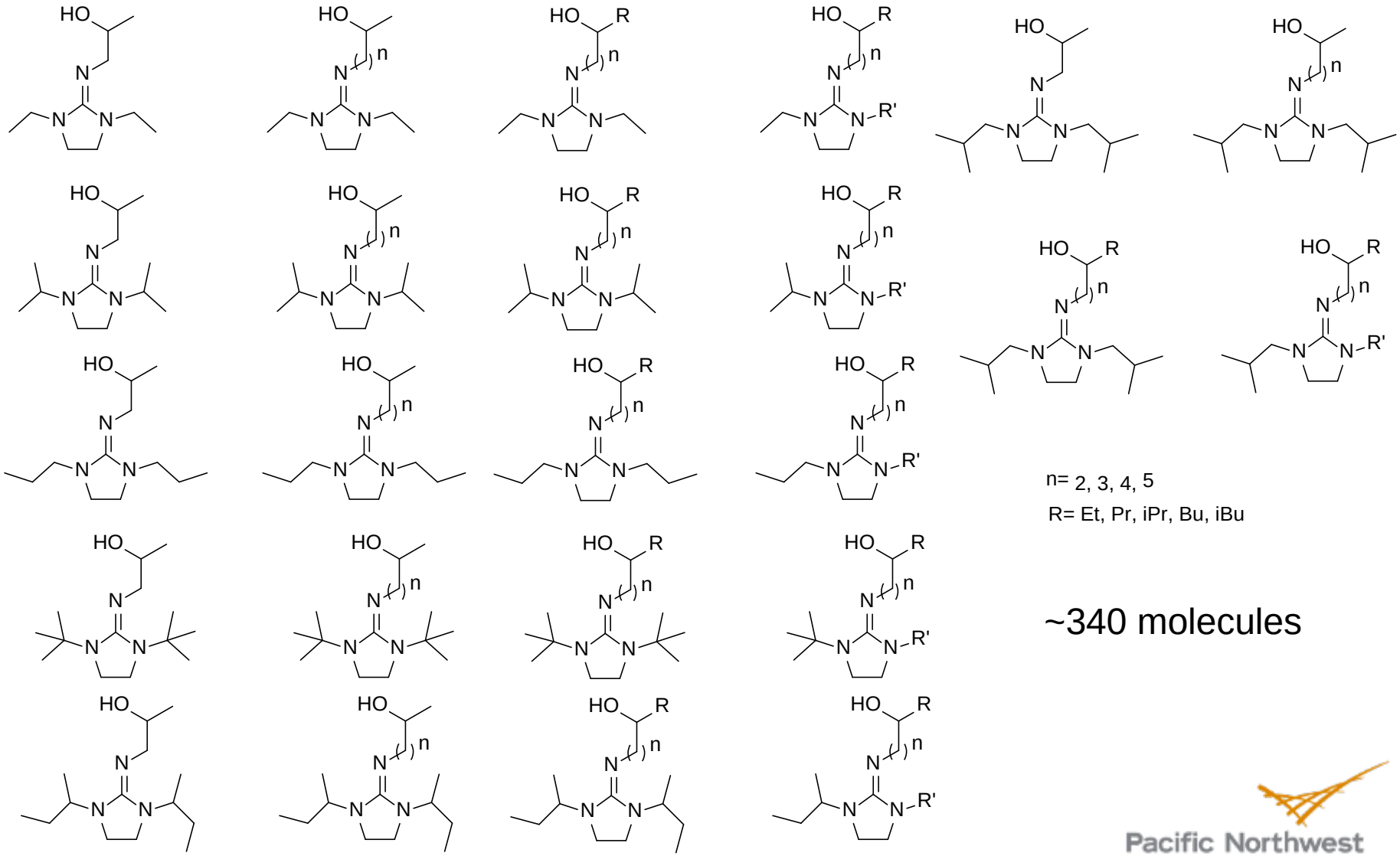
Example Library (Sterics) of CO_2BOLs For Building Molecular Modeling Tools



n= 2, 3, 4, 5

R= Et, Pr, iPr, Bu, iBu

~340 molecules

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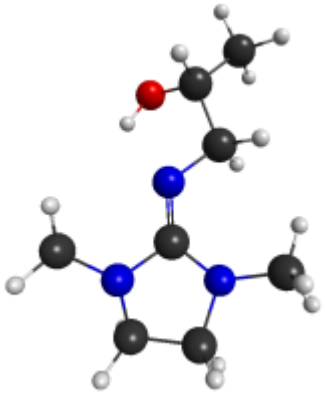
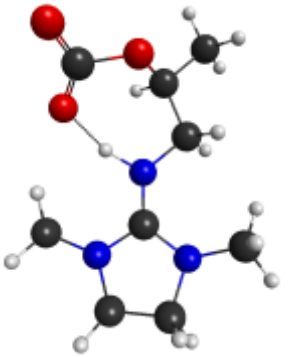
Molecular Modeling (Tools)



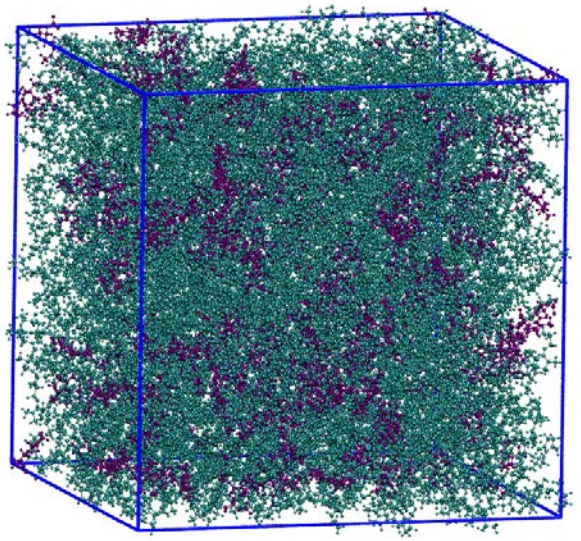
IPADM-2-BOL



CO_2-loaded IPADM-2-BOL

Ab Initio Electronic Structure for Molecular Properties:

-Accurate Description of Molecular Structure,
-Atomic charges needed for classical potentials
-Reaction energetics: H-bond strength, CO_2 adsorption energy
-Spectroscopic properties, IR/Raman, NMR, Optical
-Code/software: CP2k (***www.cp2k.org***),
NWChem (***www.nwchem-sw.org***)



Classical Molecular Dynamics (MD):

-Accurate Description of Molecular Liquid Structure,
-Potentials derived from Electronic structure
(Universal OPLS + Ab initio charges)
-Gives number and type of relevant intermolecular contacts.
-Transport properties: diffusion and viscosity*
-Code/software: GROMACS (***www.gromacs.org***)

*Viscosity can be calculated directly from long 1ms simulations or linear response on short 1-10ns.
We will evaluate reliability of latter for rapid screening of CO_2BOLs.

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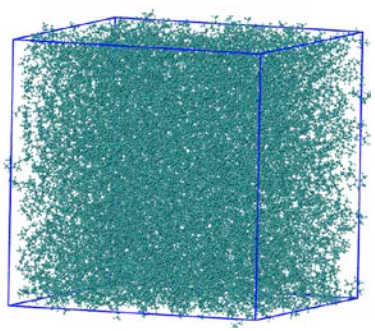
Molecular Modeling: MD results to date

1. Accurate Molecular Liquid Structure Obtained

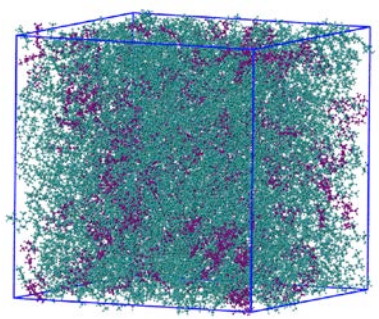
- Pure solvent and mixture with CO_2-loaded form
- MD Protocol:
  - High pressure for liquid (NPT, ~0.5 ns)
  - High temperature for mixing well (NPT, ~0.5 ns)
  - Equilibration to obtain correct density at conditions (1bar, 40 ˚C) (NPT, 5-10 ns)
  - Done until energy and volume reach steady state
- Density of koechanol: 1.012 g/cm^3 experiment, 0.964 g/cm^3 simulation, <5% error

2. Moving towards diffusion and viscosity calculations

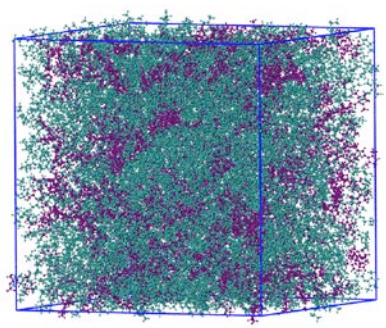
IPADM-2-BOL



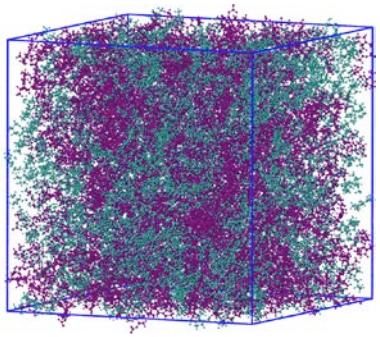
IPADM-2-BOL w/ 15% CO_2



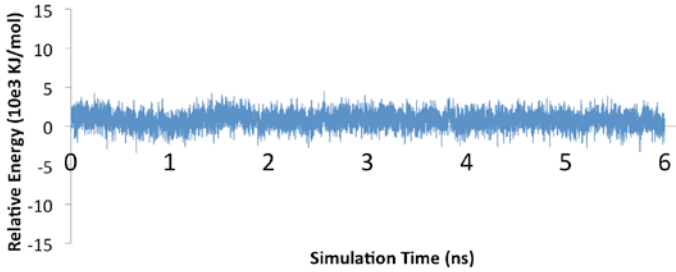
IPADM-2-BOL w/ 25% CO_2



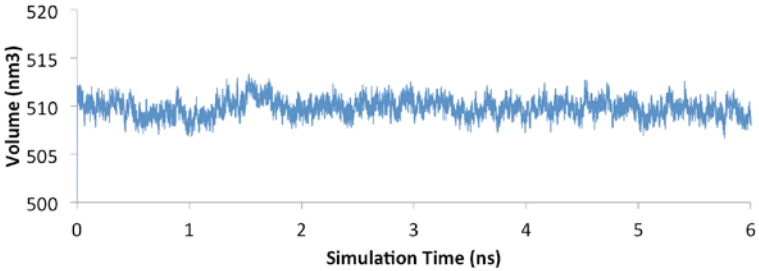
IPADM-2-BOL w/ 50% CO_2



Energy in Steady State



Volume in Steady State



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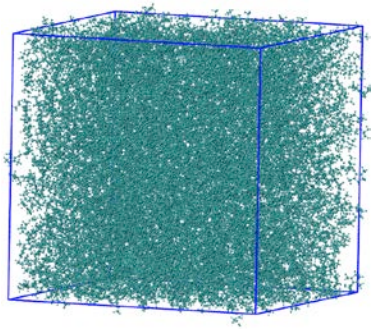
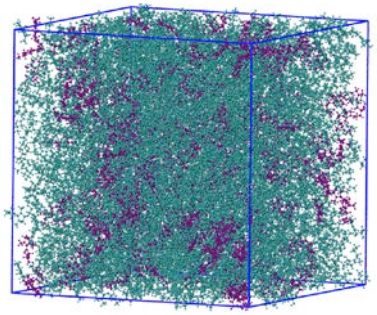
Molecular Modeling: MD results to date

System (IPADM-2-BOL)	Engineering model viscosities (cP)	Calculated viscosities from MD (cP)	Experimental values (cP)
Pure	6	15	8
15% mol CO_2 loading	47	35	36
25% mol CO_2 loading	180	150	110
50% mol CO_2 loading	~3000	>600	

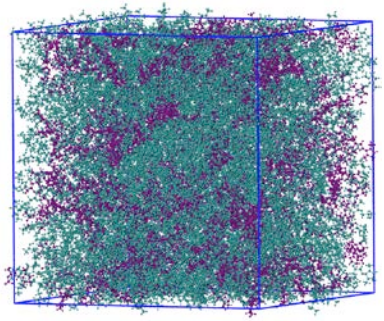
IPADM-2-BOL



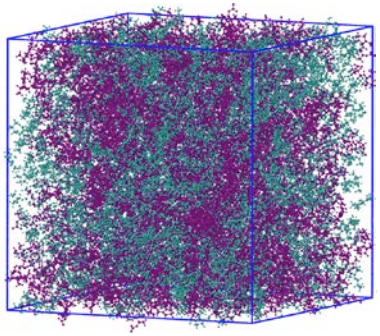
IPADM-2-BOL w/ 15% CO_2



IPADM-2-BOL w/ 25% CO_2



IPADM-2-BOL w/ 50% CO_2



Conclusions and Future Work

Combined molecular modeling, synthesis and characterization, and engineering program is advancing the field of transformational solvents.

- Develop a viscosity model that can predict key solvent physical and thermodynamic properties that control viscosity
- Collect necessary additional thermodynamic and kinetic information for a library of compounds
- Experimental validation of most advanced solvent that includes extended testing with and without water.
- Use testing data to make robust energy and LCOE predictions for a full-scale system, using Aspen Plus™ to model the system.
- Apply the viscosity model and molecular design principles to other solvents in DOE's post-combustion solvent portfolio

PNNL Program Team

Dr. Phillip Koech

Dr. Roger Rousseau
Dr. Vanda Glezakou

Dr. Feng Zheng

Solvent Design
Retrosynthetic-analysis
Synthesis & Scaleup

Computational Modeling
Physical property projections

Materials Testing
Engineering Analysis

Process Modeling
Performance Projections

Dr. Deepika Malhotra

Dr. David Cantu

Charles Freeman

Mark Bearden

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Acknowledgements

- Funding:
  - US Department of Energy Office of Fossil Energy
  - NETL PM: Andy Aurelio

- PNNL:
  - Phillip Koech
  - Roger Rousseau
  - Vanda Glezakou
  - Charlie Freeman
  - Mark Bearden
  - Feng Zheng
  - David Cantu
  - Deepika Malhotra

The Fluor Corporation
- Paul Mathias
- Kash Afshar
- Arnie Smith
- Mukund Bhakta