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

NETL Project 43091

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Project Overview

- Funding and cost share
  - Total project: $3,550,718
  - Federal portion: $2,447,138 (69%)
  - Cost share: $1,103,580 (31%)
- Project performance dates: Mar 1, 2007-June 30, 2010
- Project participants
  - Notre Dame (molecule design, thermodynamics, property measurement, synthesis, project management)
  - Babcock and Wilcox (corrosion, design of lab scale unit)
  - DTE (consultation, feasibility of process designs)
  - Air Products (thermodynamics, process design, molecule design)
  - EMD / Merck (synthesis, molecule design)
  - Trimeric (process design and system analysis)

Overall Project Objectives

- Design new molecules based on ionic liquids that will enable post-combustion CO_2 capture that meets DOE goals
  - 90% CO_2 capture from flue gas
  - Less than a 35% increase in the cost of electricity
- Key aspect: exploit ionic liquid properties
  - Compound diversity
  - Negligible volatility
  - Wide liquidus range, thermal stability

Background – What Are Ionic Liquids?

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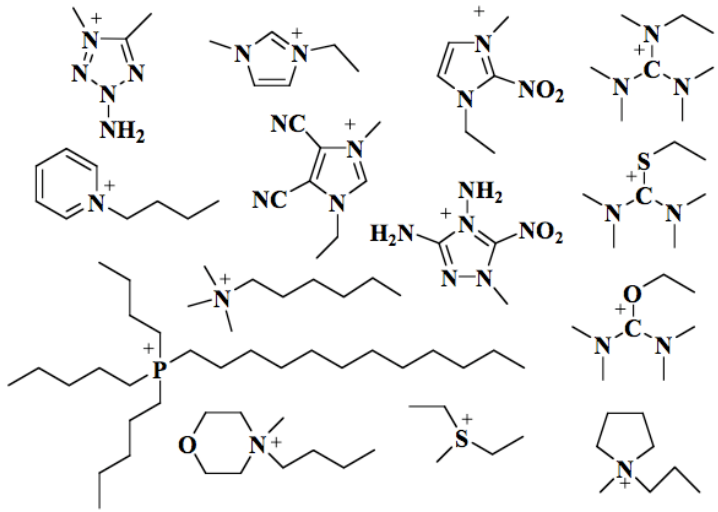
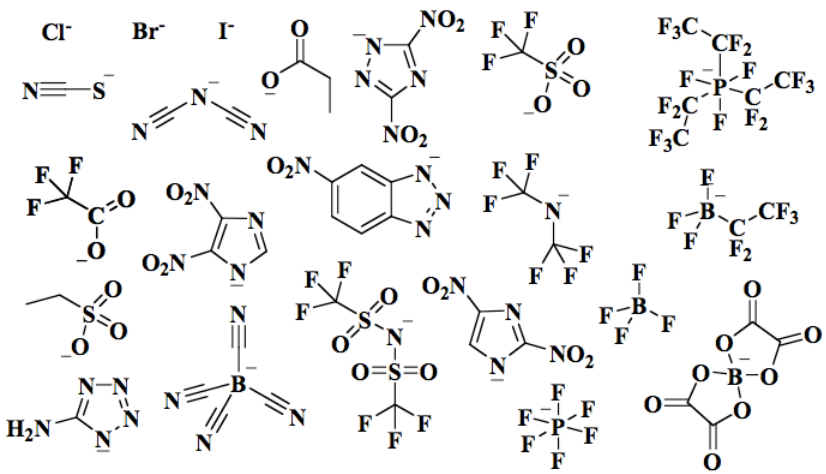
- Salts that are liquid at ambient temperatures
- Huge diversity of potential compounds
  - Mix and match cations and anions





Why investigate ionic liquids?

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- IL properties favorable for CO_2 capture
  - Negligible volatility
    - Unique process configurations?
  - High intrinsic physical solubility for CO_2
    - Can add chemical functionality
  - Opportunity to "tune" properties
    - Computational methods enable molecule "design"
    - "Molecularomics"
- Possible to achieve better performance than aqueous amines

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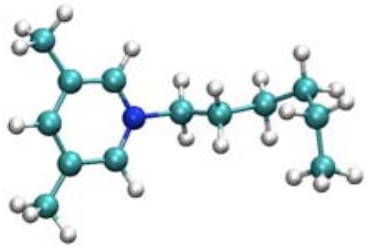
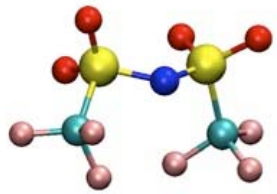
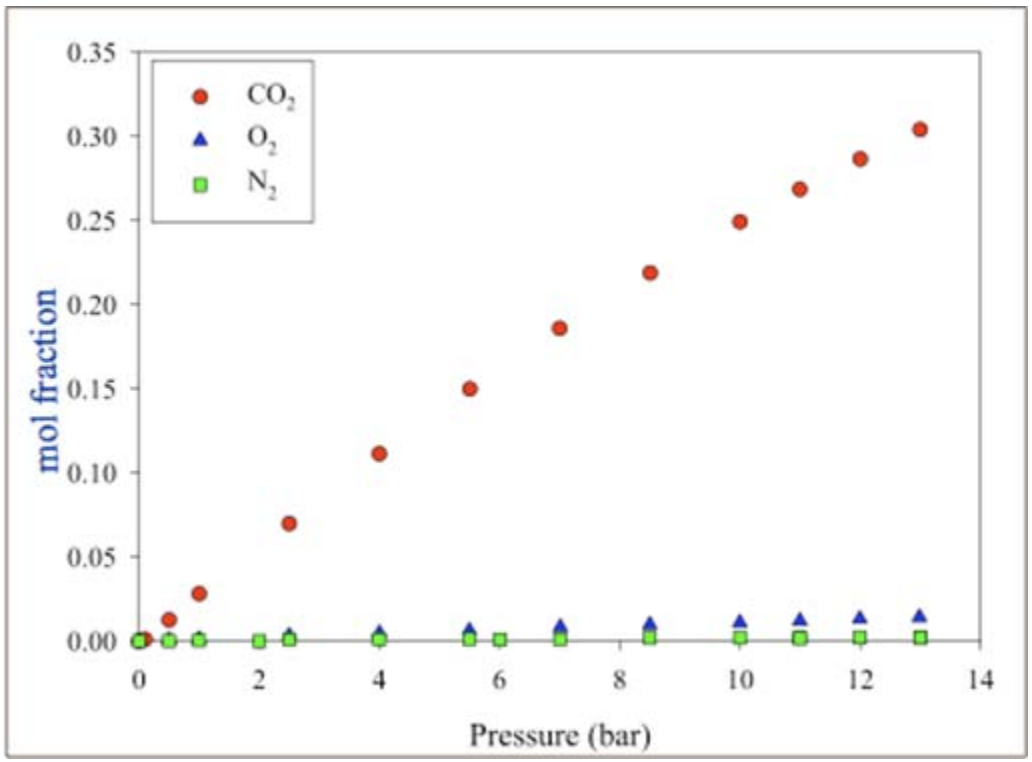
Previous results





1-n-hexyl-3,5-dimethylpyridinum bis(trifluoromethane-sulfonyl)amide

Experimental solubility measurements



- Very high physical solubility for CO_2
- Low solubility of O_2, N_2

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Predict properties with computation

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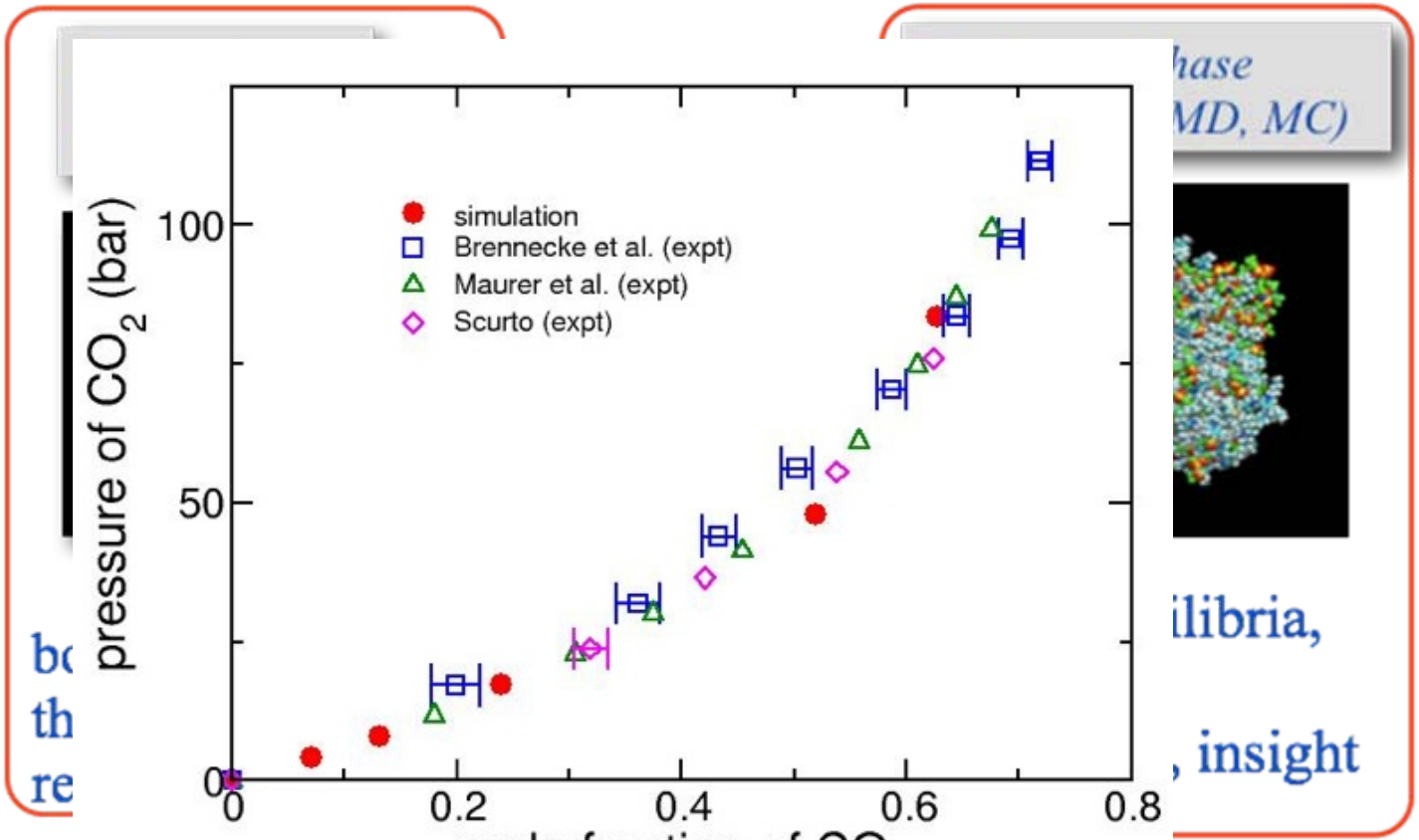

Base Case Process

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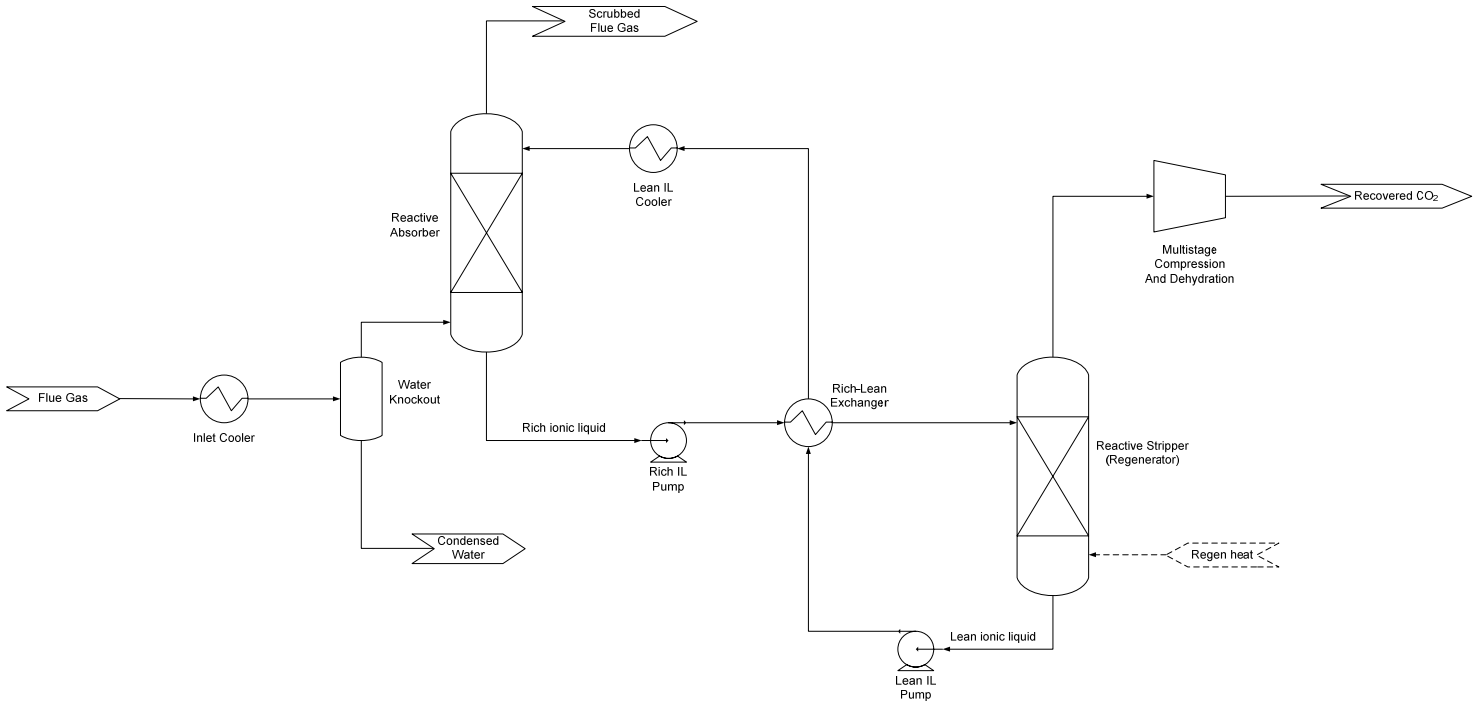

- Conventional absorber / stripper configuration
  - "Drop in" replacement for MEA
- Other processes possible

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Findings from previous work

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- Physical solubility: low enthalpy of absorption
  - ~ 12 kJ/mol
  - Very low regeneration energy and temperature, but…
  - CO_2 capacity too low => high circulation rates
  - Desorption at too low pressure => high compression costs
- Increase capacity by adding chemical functionality
  - Increases enthalpy of absorption / desorption and capacity
  - Increases regeneration temperature and energy, but reduces circulation rates

Fundamental questions

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- What functional groups should be used?
  - Mechanism
  - Capacity
  - Enthalpy
- Other questions
  - Stability
  - Cost
  - Water solubility
  - Corrosion

Known chemical functionality

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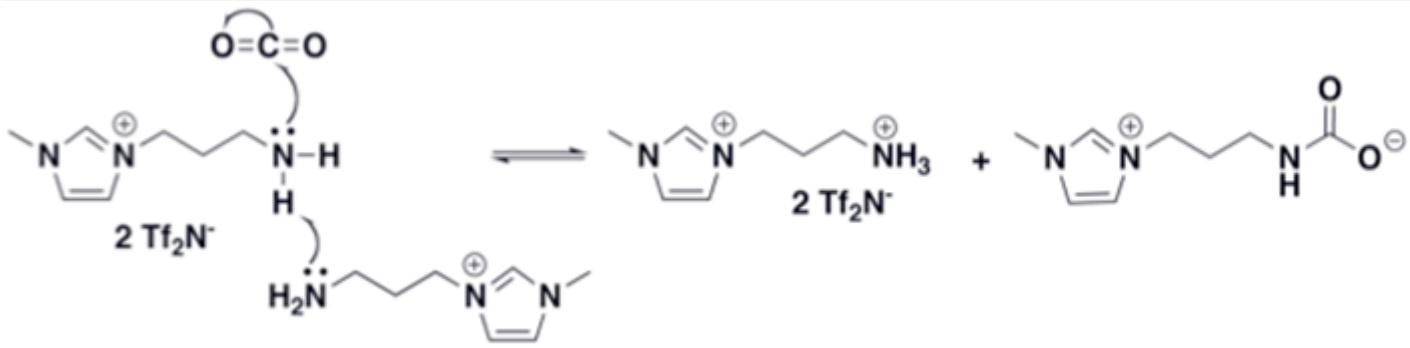

- Tether amine on cation ("task specific" IL)
  - Same basic mechanism as amine
  - 2:1 mechanism

Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., *J. Am. Chem.*, **2002**, *124*, 926.

Problems with conventional TSILs

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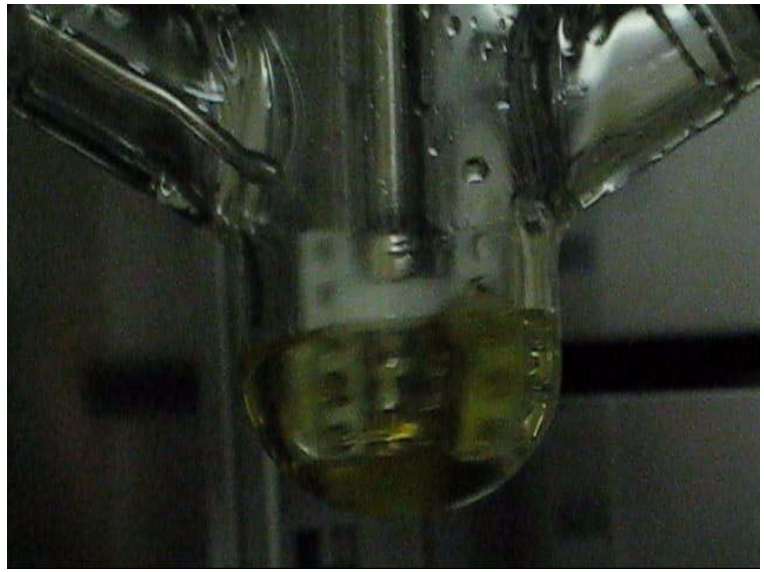
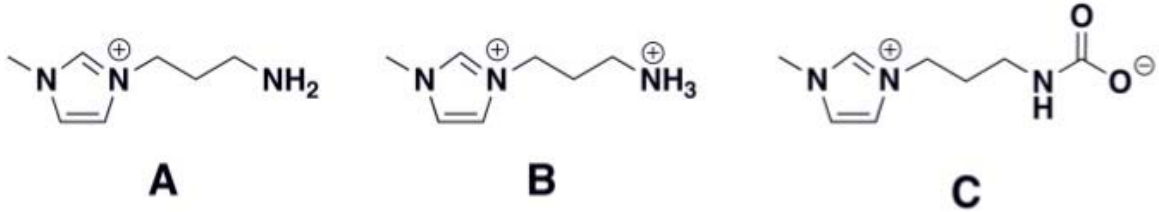
No CO_2



17 mbar CO_2

- Liquid becomes quite viscous upon contact with CO_2
- 2:1 mechanism is inefficient; 1:1 mechanism possible?

Why does TSIL become viscous?



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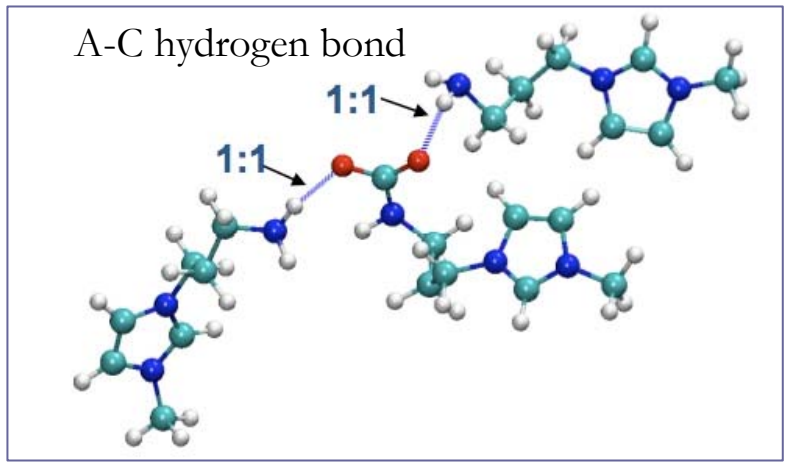

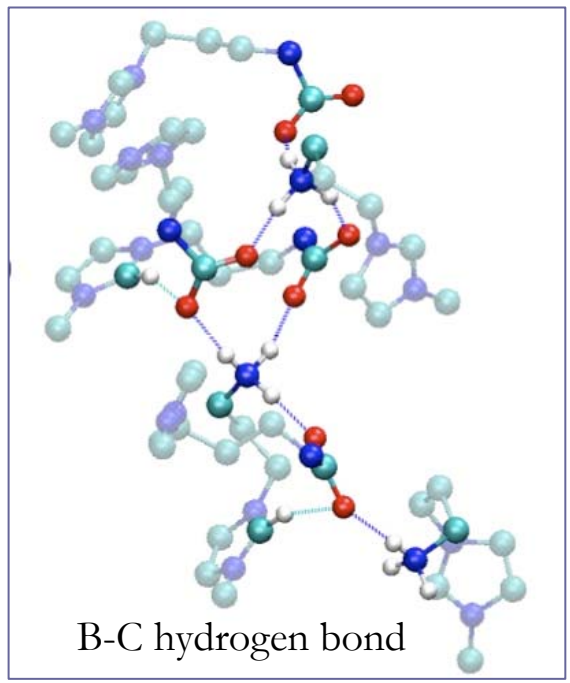

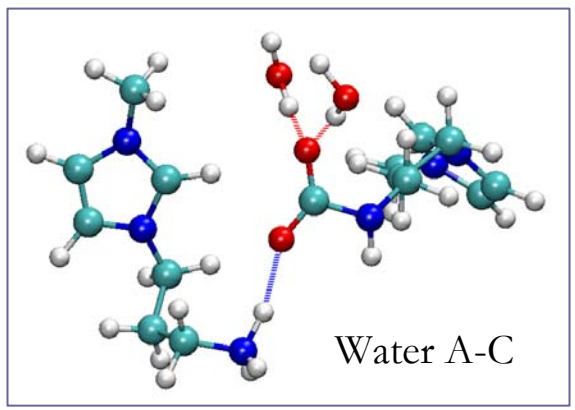

Can you design functional groups for 1:1 binding?

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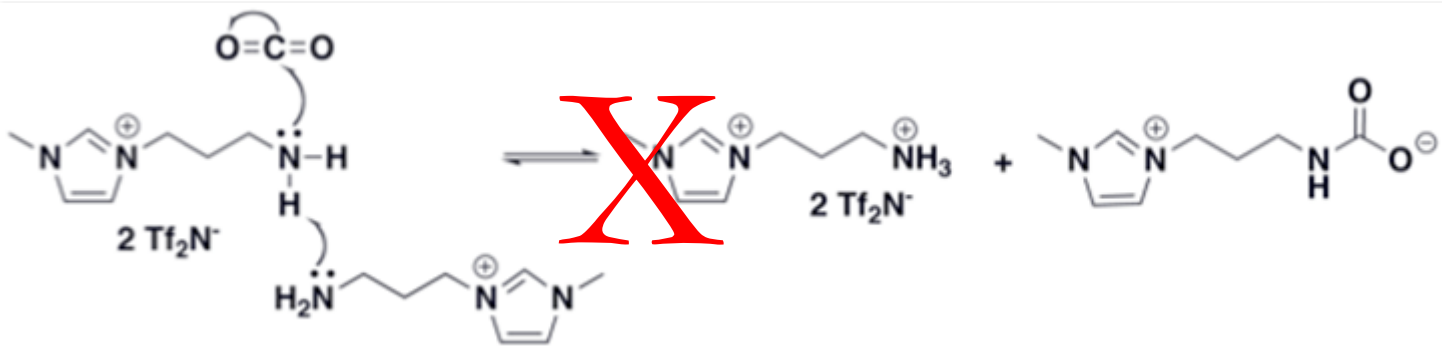
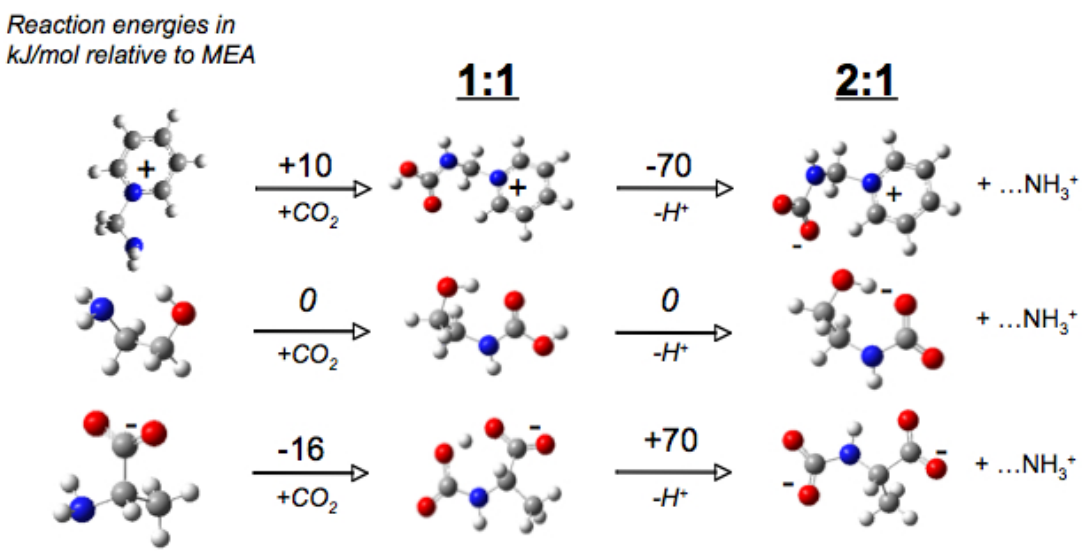


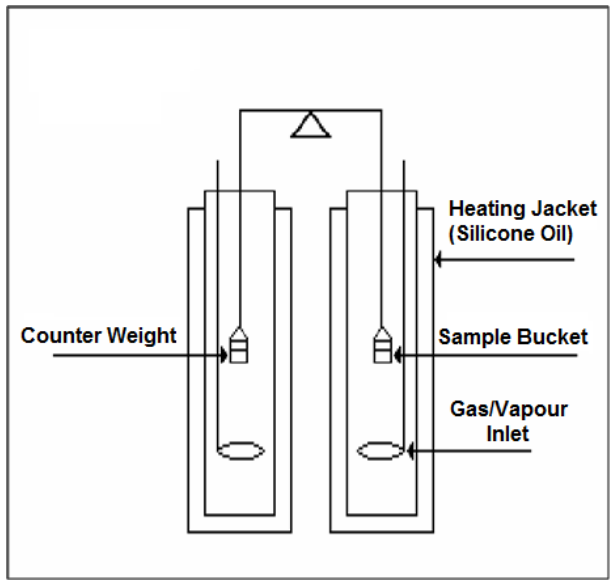


Objectives of current project

- Optimize thermodynamic and transport properties of IL solvent for use in CO_2 capture
  - Tight integration of process modeling and design with molecule design
- Goals
  - Achieve 1:1 complexing
  - Discover optimal enthalpy, capacity, process conditions
  - Design molecule to reduce viscosity of complex
- Tools
  - Computational molecule discovery
  - Accurate thermodynamic property measurements
  - Synthesis
  - Process modeling / analysis

Experimental Capabilities

- Gas absorption – gravimetric balances



- Low pressure (5 mbar – 20 bar)
- Temperatures: 20-150 °C
- 75 mg samples

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Gas Absorption - IGA

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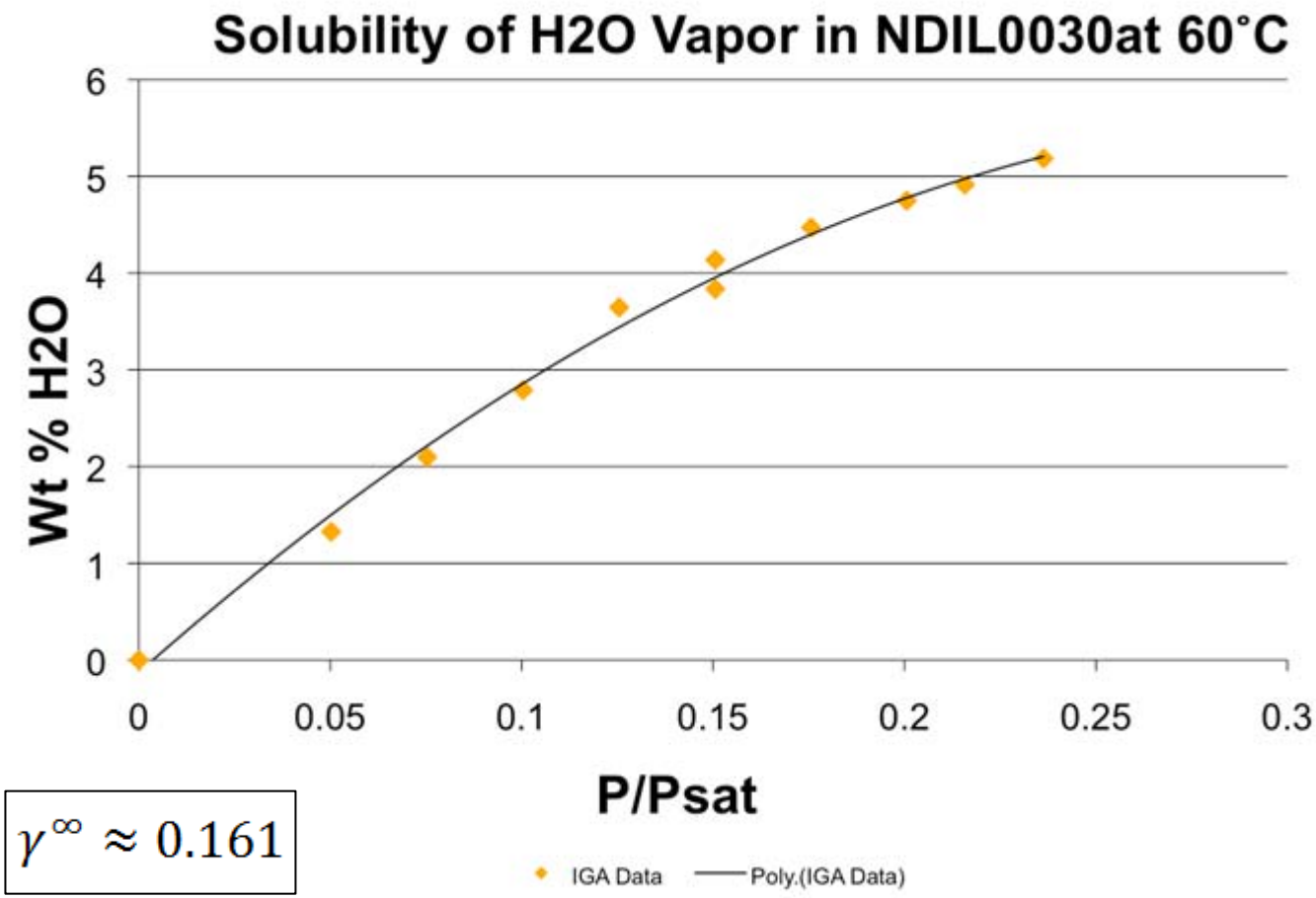

$$\gamma^{\infty} \approx 0.161$$

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Magnetic suspension balance

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Magnetic Suspension Control Unit

Magnetic Suspension Balance

Magnetic Suspension Coupling

- Resolution 10 μg
- Temperature range 20-250 °C (Heater 450 °C)
- Pressure range UHV-150 bar
- Measuring load 0-25 g
- Reproducibility ±0.002 mg

Typical result, N_2 absorption

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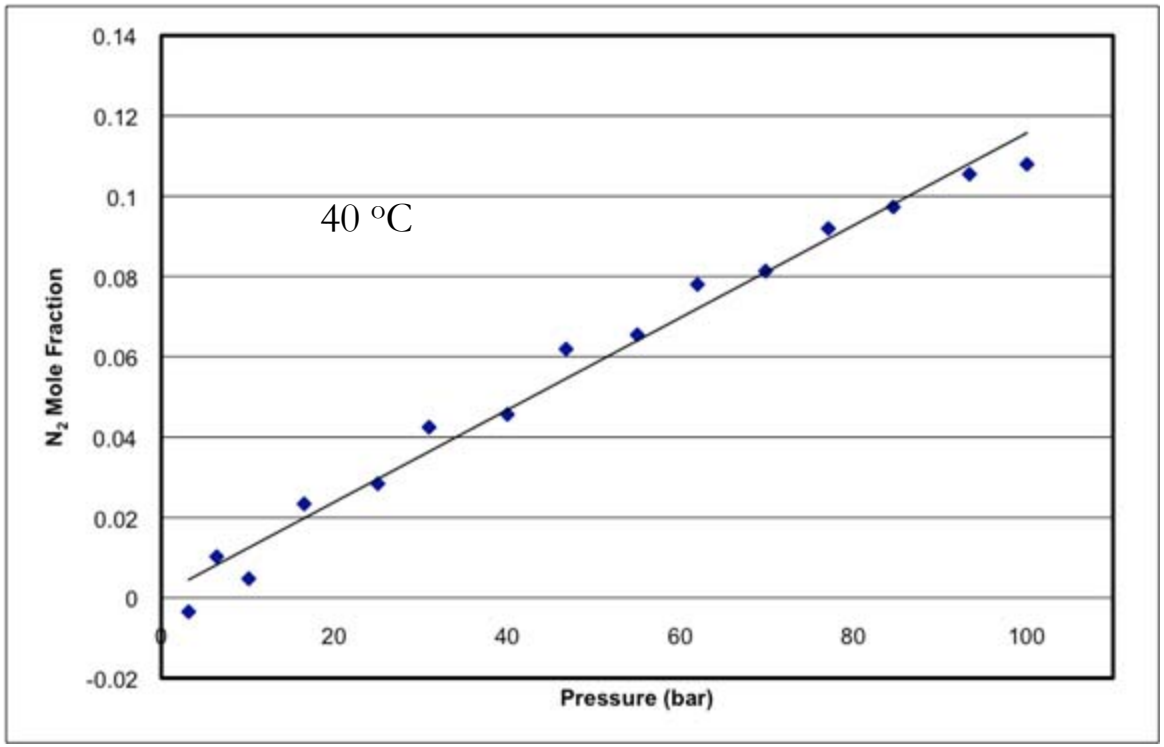

- High P used to estimate Henry's constant of low solubility gases
- Also can use with SO_2

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Volumetric apparatus

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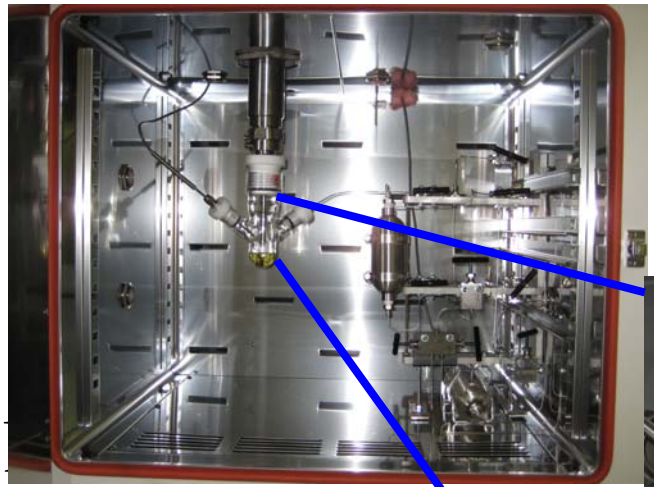

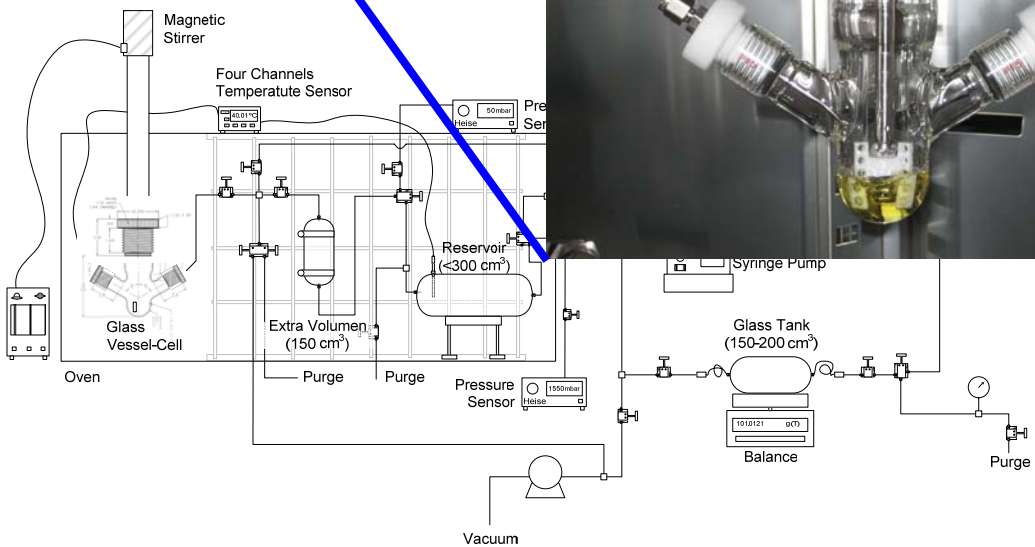

Typical CO_2 isotherm, 1:1 Mechansim

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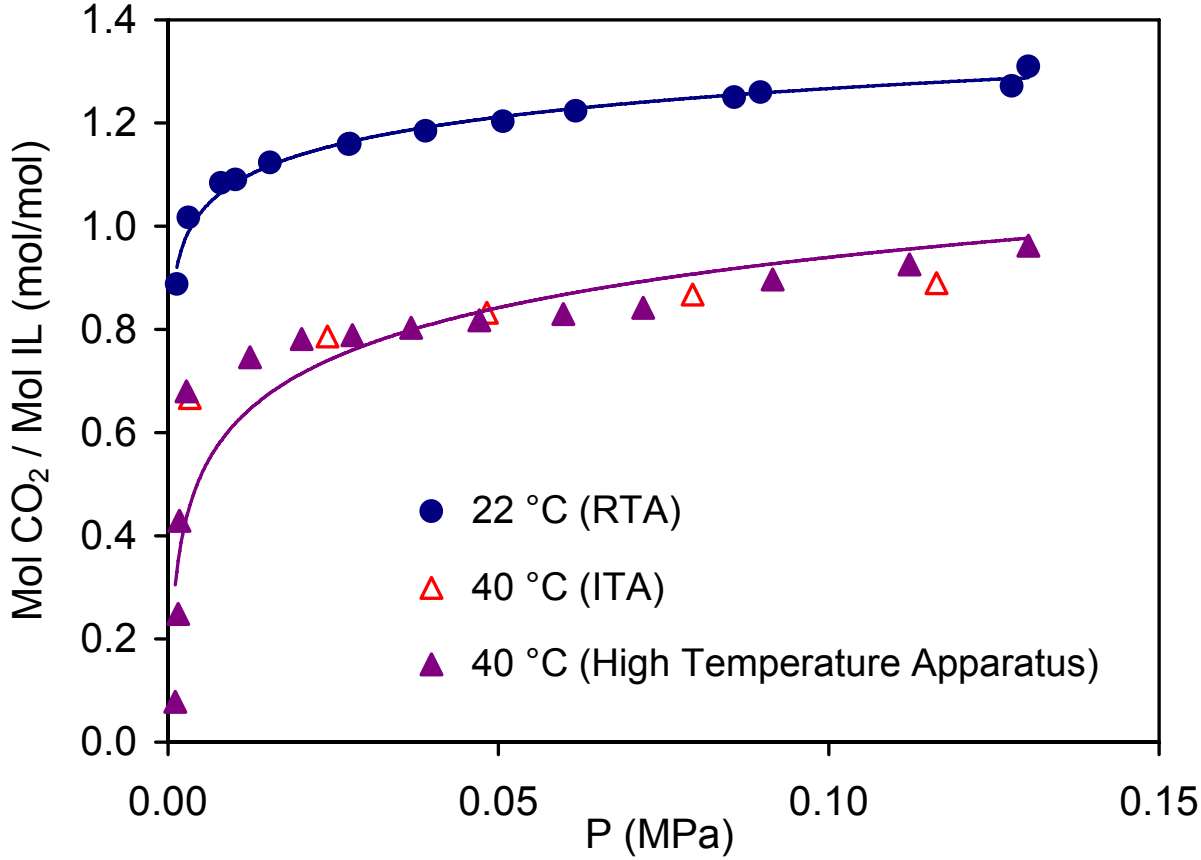

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Liquid density measurement

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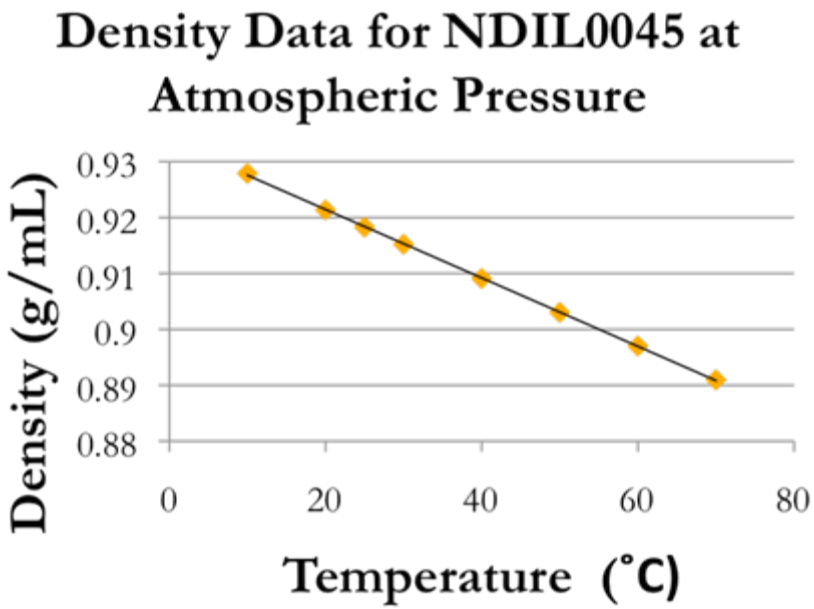

- Anton Par 4500 Densitomiter
  - Vibrating tube
  - 10-90 °C
  - 10^{-5} g/ml reproducibility

Calorimeter

- MicroDSCIII Calorimeter
  - Direct measurement of enthalpy of complexation / absorption

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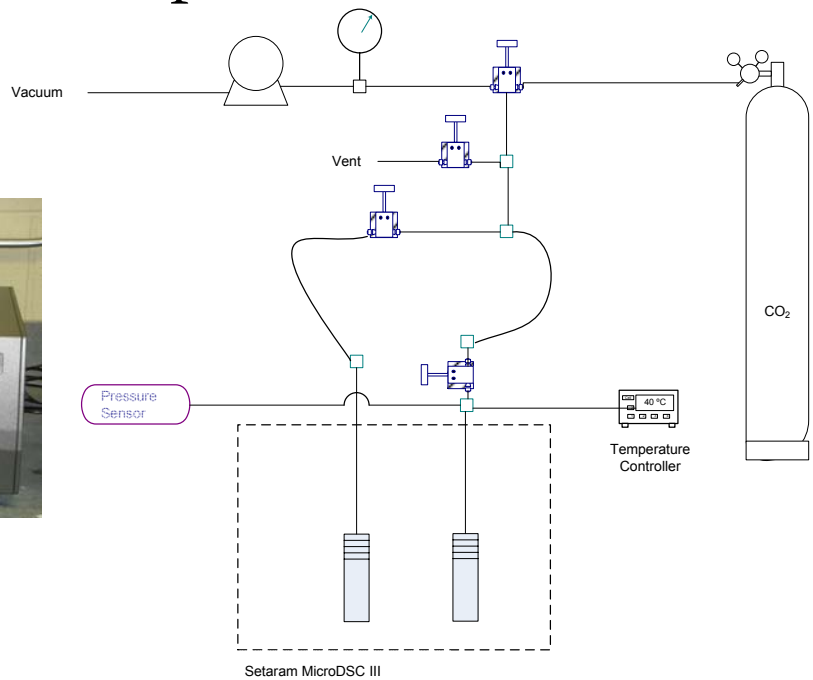

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Brookfield rheometer

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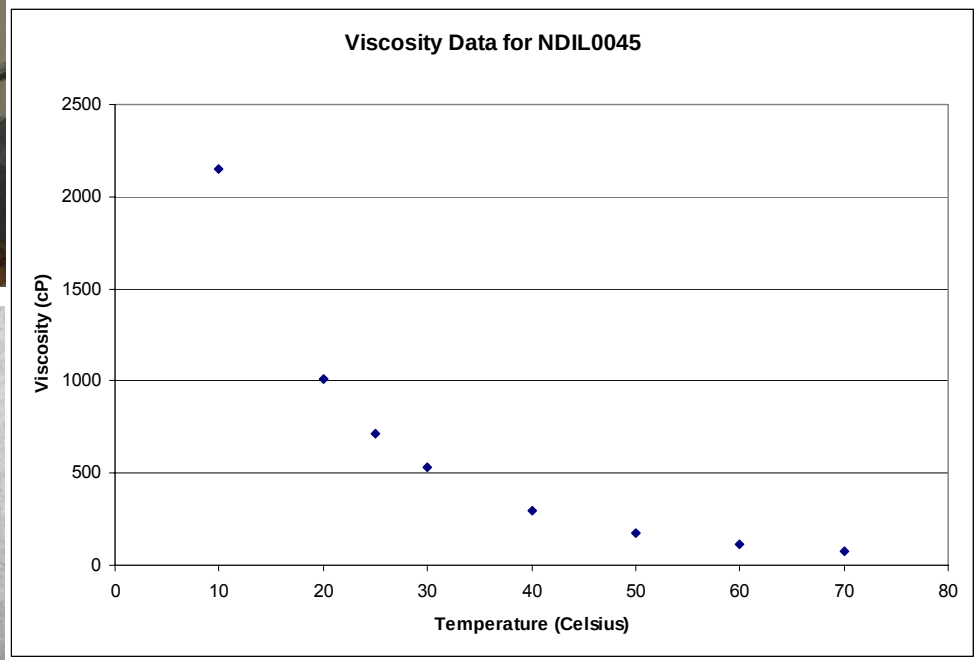

- 10-70 °C
- Equipped to work with gas flow over sample

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In situ IR

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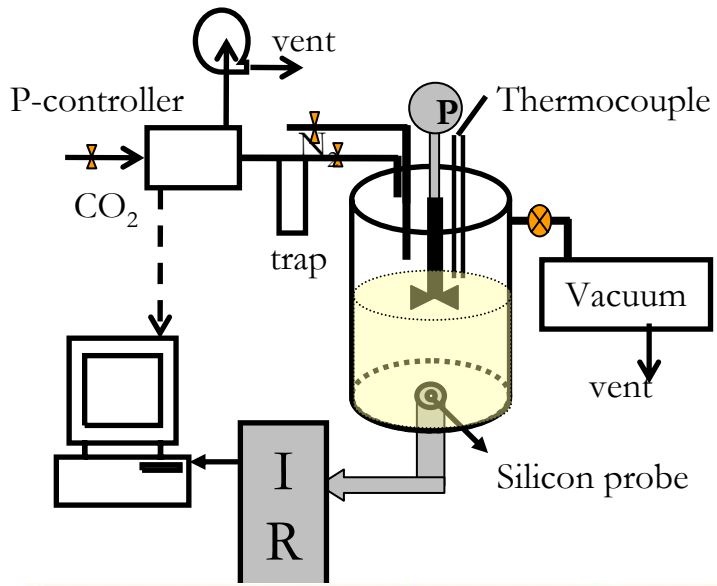

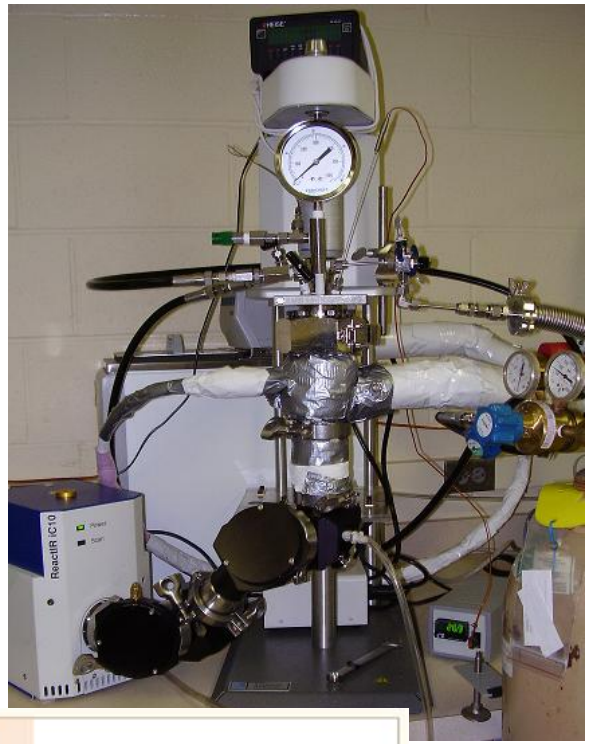

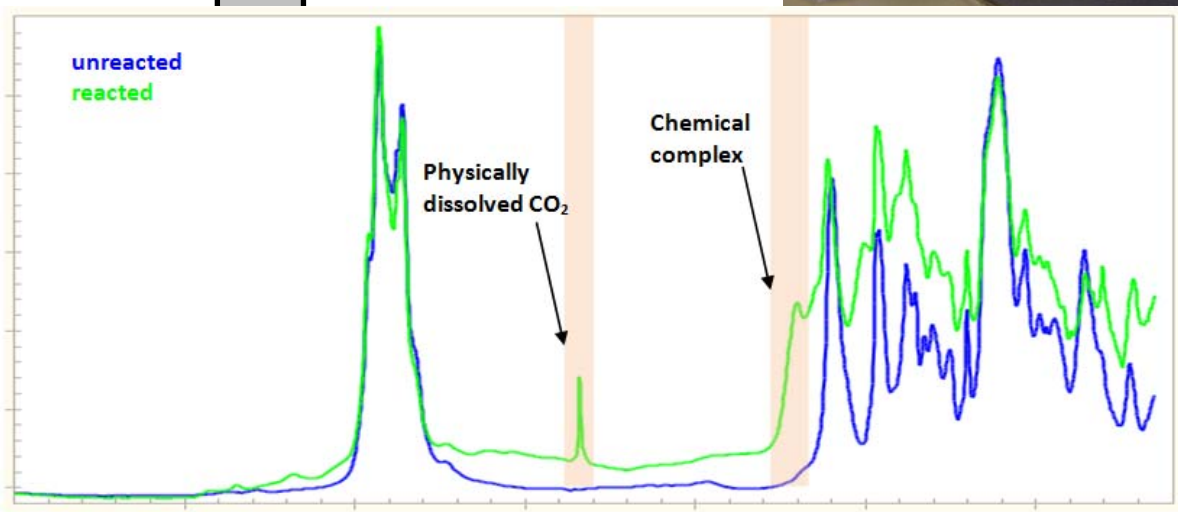

Computational capability

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- First principles modeling to enable reaction enthalpies, equilibria to be computed
- Classical condensed phase Monte Carlo and molecular dynamics for physical properties (viscosity, density, water solubility, heat capacity)

Computational results

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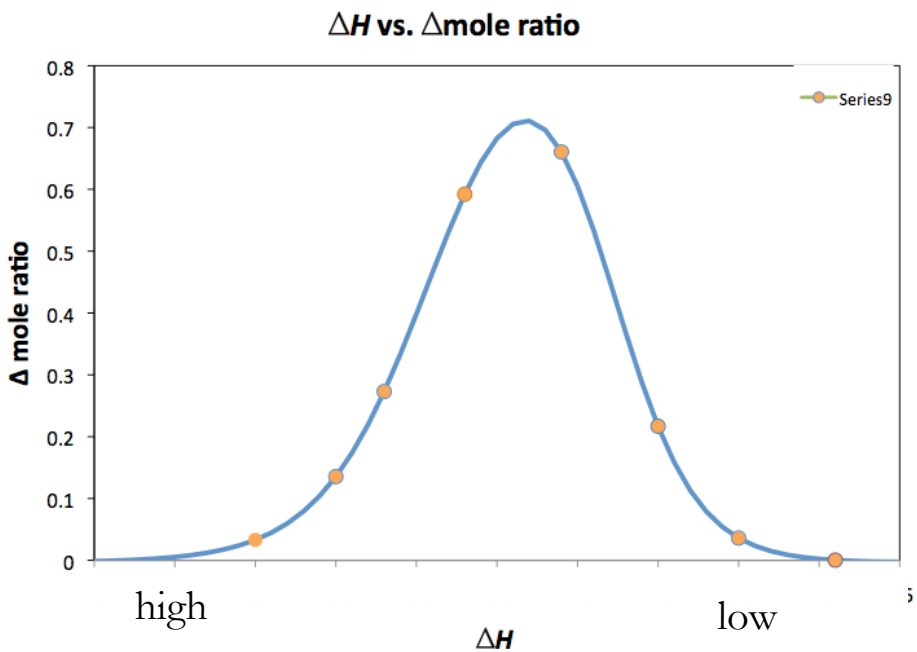

- Relationship between reaction enthalpy and capacity
- Identified target compounds spanning relevant range of enthalpies

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Computational results

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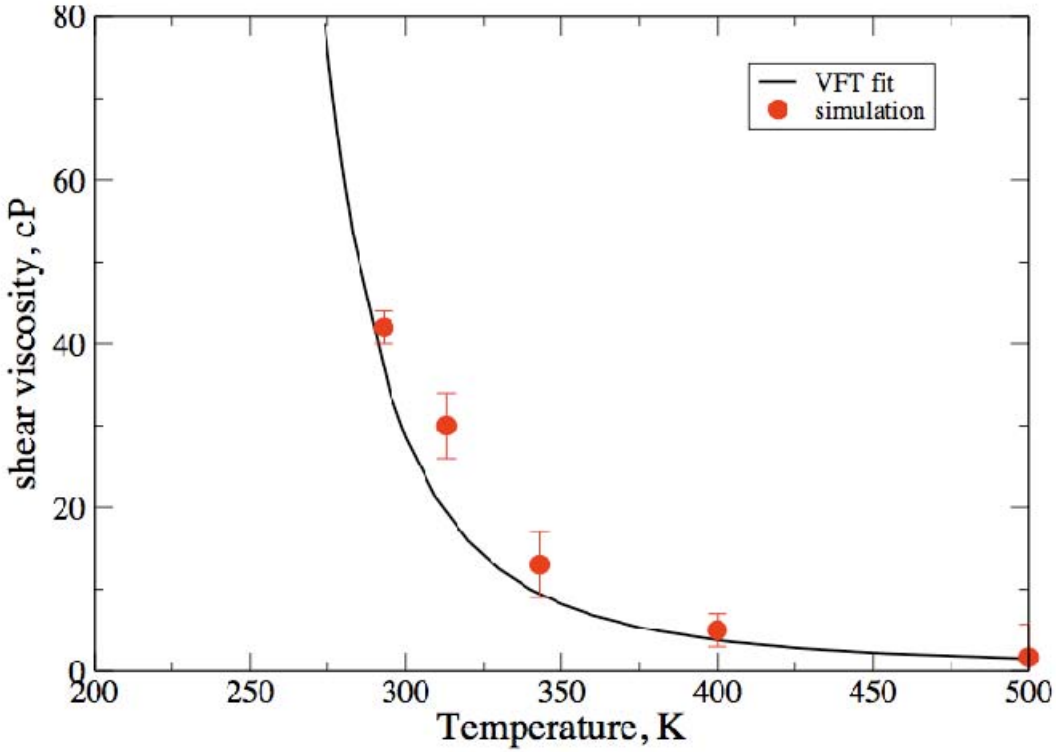

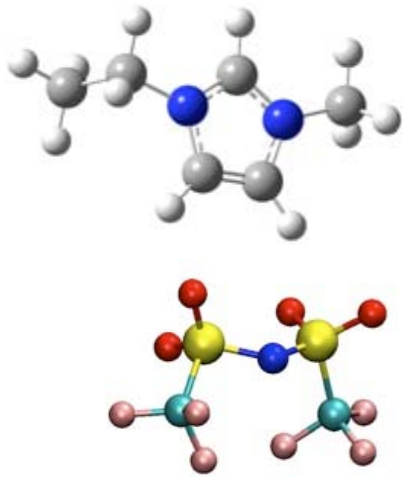

- Quantitative prediction of properties like viscosity
  - Often easier to compute at extreme conditions than measure
  - Fill in gaps for process modeling

Trimeric sensitivity analysis

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- Process simulation was used to evaluate the sensitivity of a representative 500 MW coal plant CO_2 capture process to ionic liquid properties
- Results of the sensitivity analysis will be used to guide the development of next-generation ionic liquids
- Sensitivity variables
  - Stoichiometry: ND proposed both 1:1 and 2:1 (IL:CO_2) stoichiometries; preliminary modeling to date assumed 1:1.
  - Enthalpy of reaction: ND proposed a range of (low-high) based on molecular modeling.
  - Loading (K_{eq}): Sensitivity includes a range of CO_2 loadings that result from the above enthalpies of reaction.
  - Water miscibility: Both partially- and fully-miscible systems are included. Activities coefficients modeled with NRTL using experimental data

Preliminary results: much lower parasitic energy than MEA

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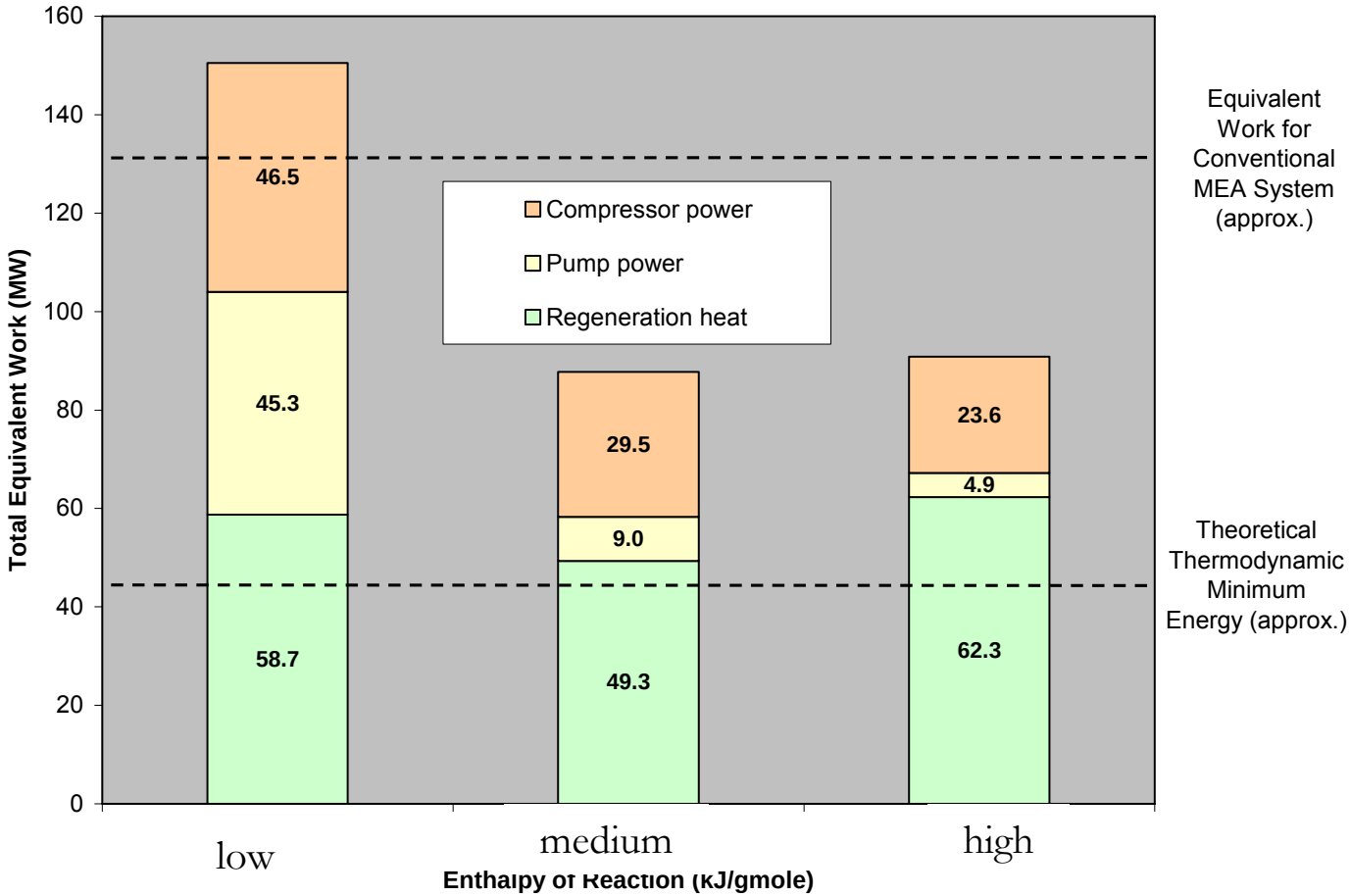

Future work – this project

- Synthesize new compounds identified from modeling
  - EMD and ND currently working on
- Confirm predicted thermodynamics experimentally
  - Enthalpies, capacities, water solubility
- Test for other key properties
  - Thermal stability
  - Corrosivity
  - Viscosity
- Evaluate process configurations
  - Capital cost
- Refine process models and costs
- Design and construct lab-scale test unit
- Synthesize ca. 40 l samples and run in test unit

Future work – next project

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- Further refine compounds
  - More detailed experimentation, process modeling
  - Cost, stability, material compatibility, additives
- More realistic flue gas testing
- Utilize lab-scale data for more detailed process model
- Explore novel process configurations
- Plan for slip stream / pilot tests
  - B&W facility
  - DTE plant

Acknowledgements

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- Collaborators
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  - Babcock and Wilcox (George Farthing, Lisa Rimpf)
  - DTE (Bill Rogers)
  - Merck / EMD (Will Pitner, Brendan Luu)
  - Trimeric (Kevin Fisher, Duane Myers, Katherine Searcy)

Notre Dame Team

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Current members

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