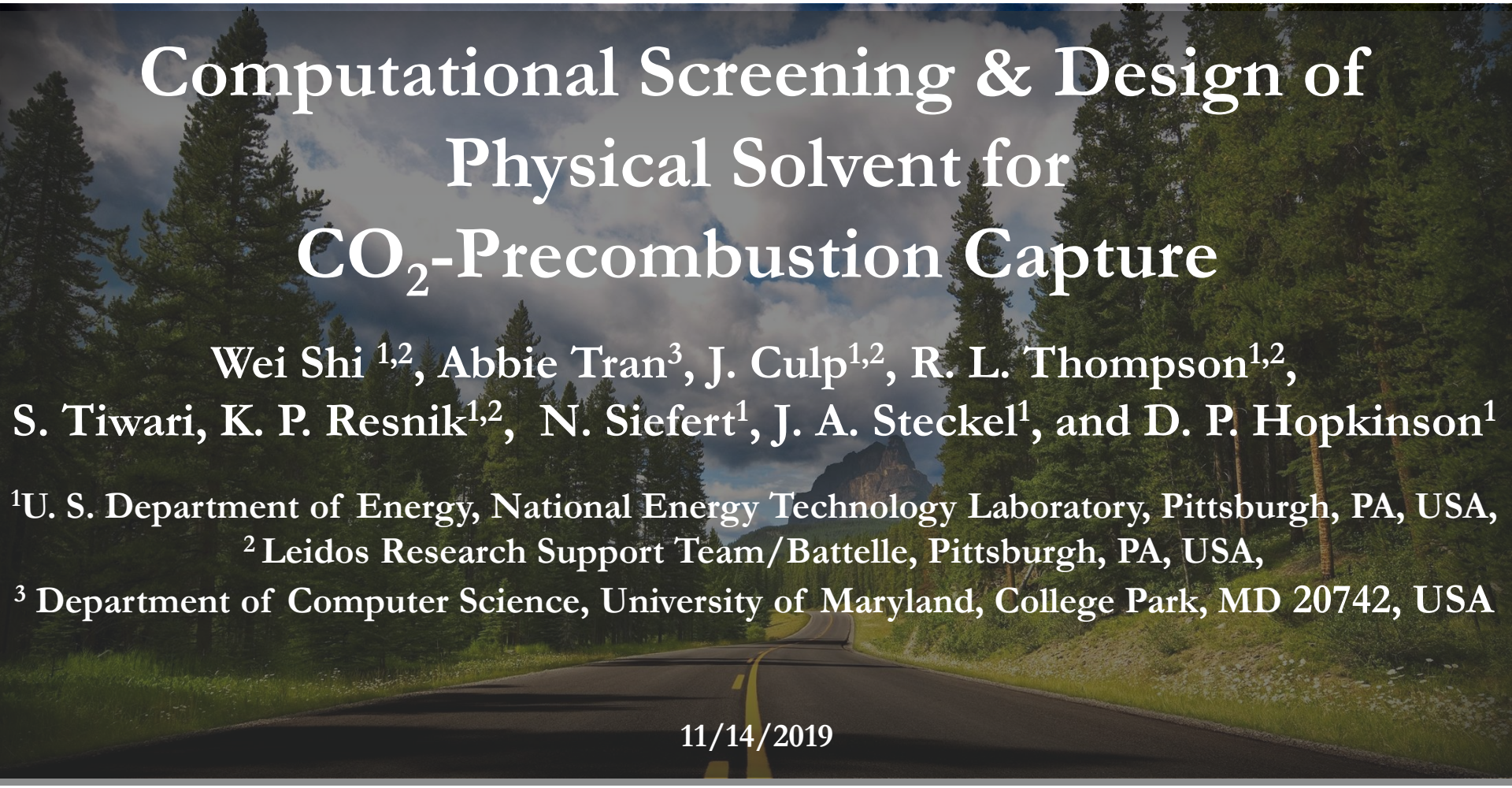


Computational Screening & Design of Physical Solvent for CO_2-Precombustion Capture

Wei Shi [1,2], Abbie Tran[3], J. Culp[1,2], R. L. Thompson[1,2], S. Tiwari, K. P. Resnik[1,2], N. Siefert[1], J. A. Steckel[1], and D. P. Hopkinson[1]

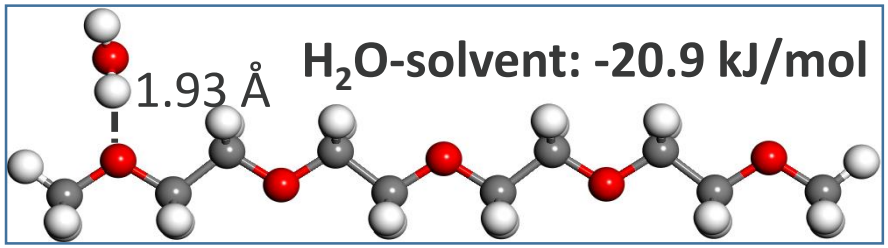
[1]U. S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA, USA,
[2] Leidos Research Support Team/Battelle, Pittsburgh, PA, USA,
[3] Department of Computer Science, University of Maryland, College Park, MD 20742, USA

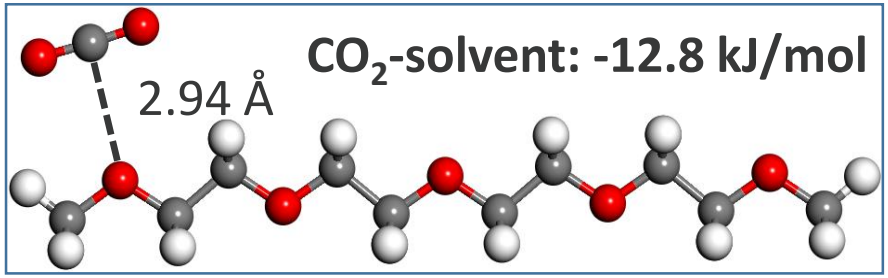
11/14/2019

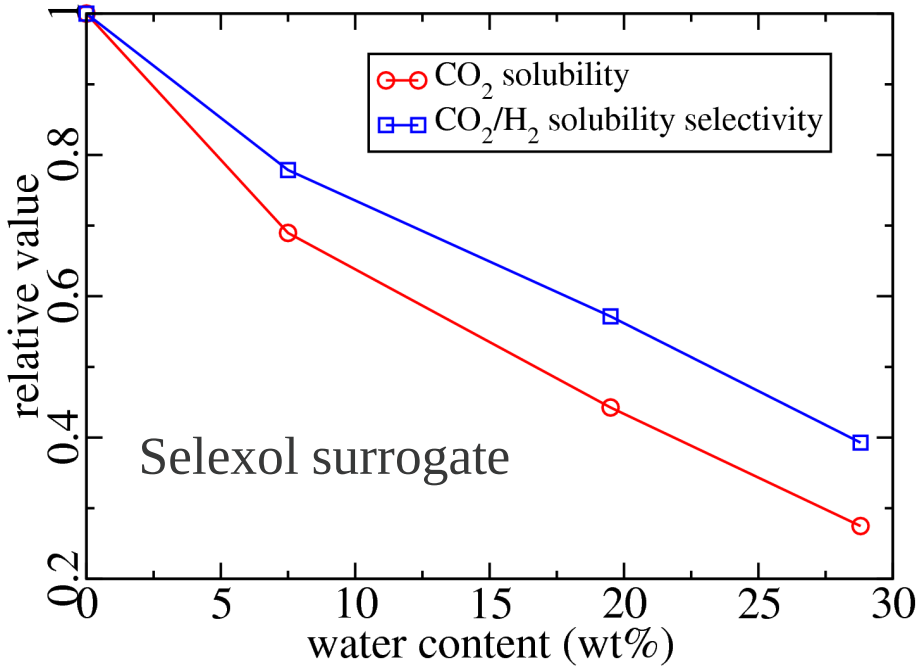
Objective:

- **Objective: Search & design hydrophobic physical solvents (large/medium sized-molecule) from computational screening for CO_2 pre-combustion capture (loading above 2 mol/MPa.L @ 298 K) to be absorbed ~25 °C and desorbed ~80 °C**
- **Important property requirements**
  - High CO_2 loading
    - CO_2 absorption isotherms to be linear or concave up between 0-30 bar
  - High CO_2/H_2 selectivity
  - High hydrophobicity
  - Low vapor pressure & low viscosity
  - Melting point below ~30 °C
  - Low foaming
  - Preferentially only contains C, H, O, N atoms
  - Cheap, non-environmental, safety, & health issues

Two Reasons to Care About Hydrophobicity

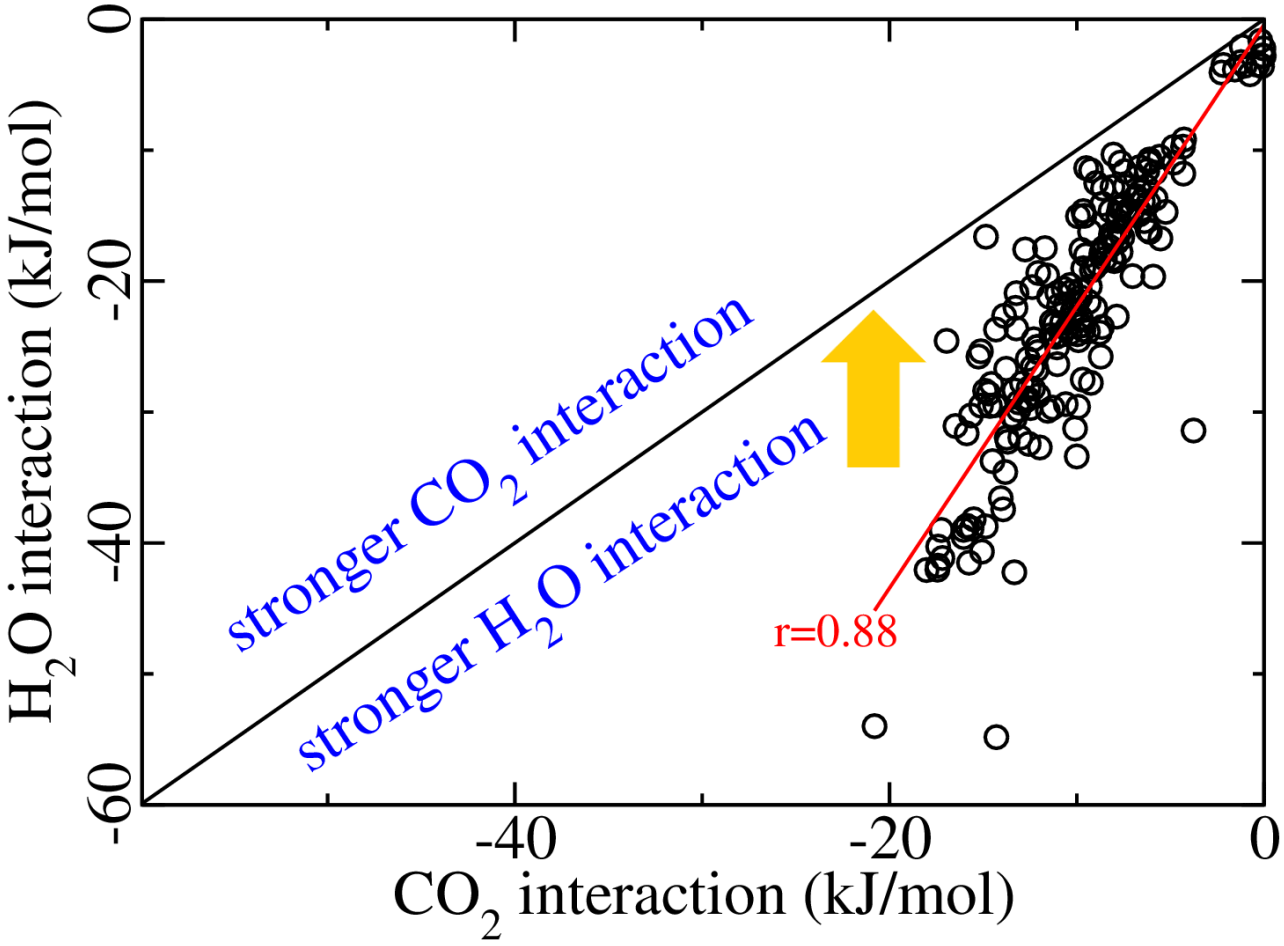






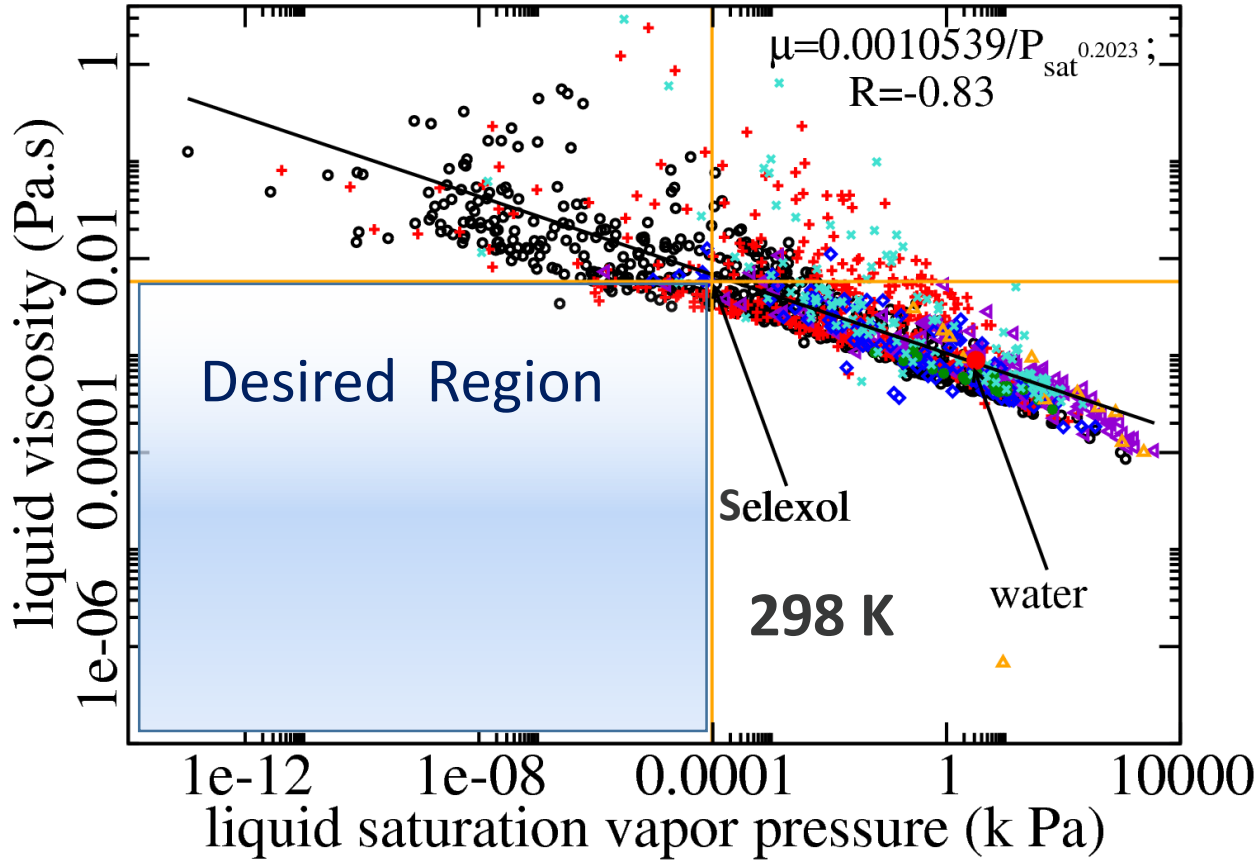
- **H_2O competes for CO_2 interaction with solvent.**
  - —Presence of water significantly & unfavorably decreases both CO_2 loading and CO_2/H_2 selectivity.
- **Potential equipment corrosion problems for hydrophilic solvents**

H_2O-functional Group Interaction Correlates with CO_2-functional Group Interaction



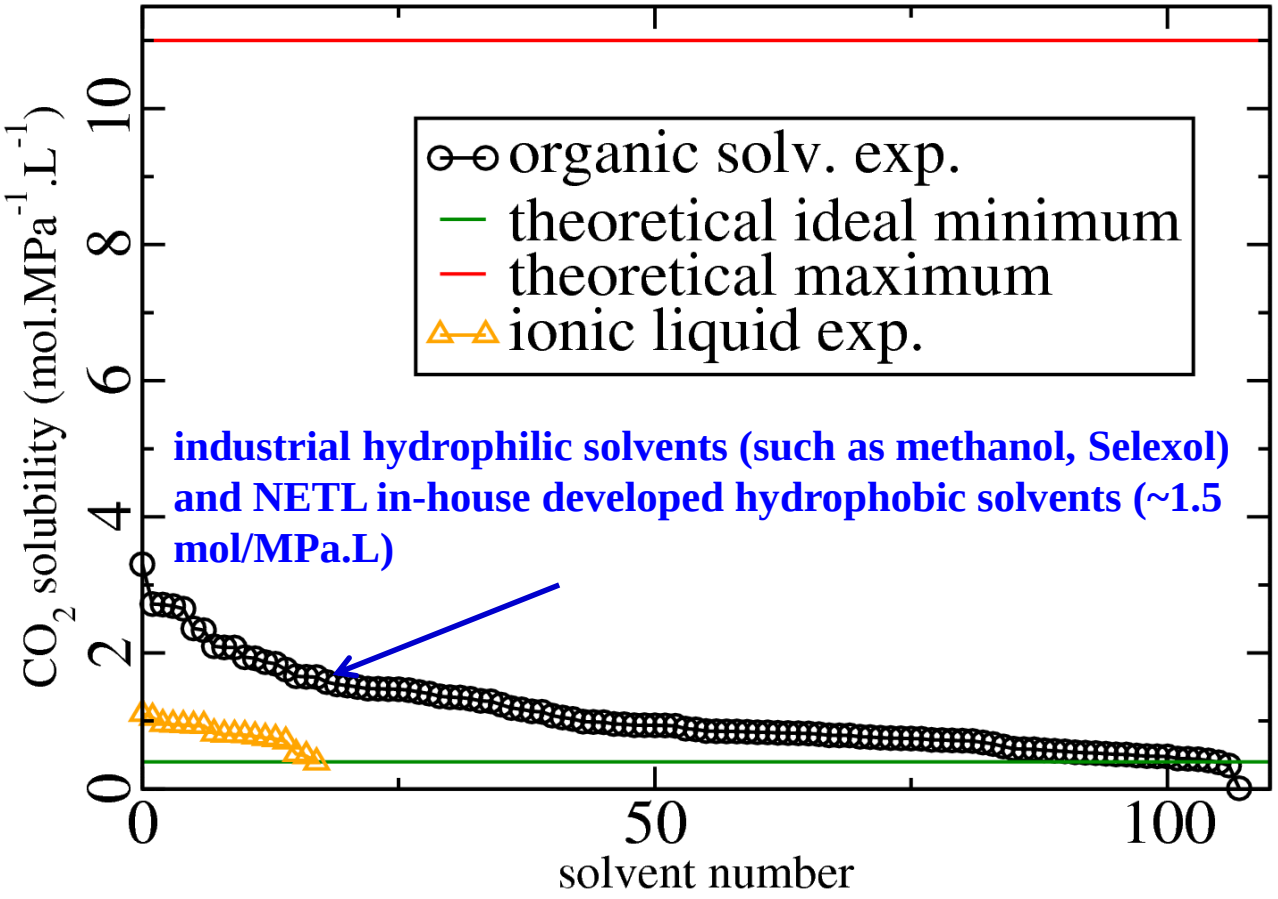
- Minimizing water absorption by adding $–CH_2$-functional groups could decrease CO_2 absorption

Compromise Between Solvent Viscosity and Vapor Pressure



- 53 solvents exhibit both smaller vapor pressure and smaller viscosity than Selexol

Why 2 mol/MPa.L as the Objective?



- 10 solvents could exhibit high CO_2 loading above 2.0 mol/MPa.L, but they have low molecular weight (less than 100 g/mol) and they are volatile.

A Must: Integrated Computational Method

NIST database for pure compounds (~23,000)

- Melting (T_m), boiling (T_b) temperatures, viscosity (μ), saturation vapor pressure (P^{sat}), surface tension (σ), density (molar volume)

Open literature to complement properties missing in NIST Database

- flash point, safety, health, environment
- Price

In-house computational database: quantum mechanics for gas – chemical function group interactions

- CO_2, CH_4, H_2, H_2O, H_2S, COS, SO_2, O_2, N_2, etc.

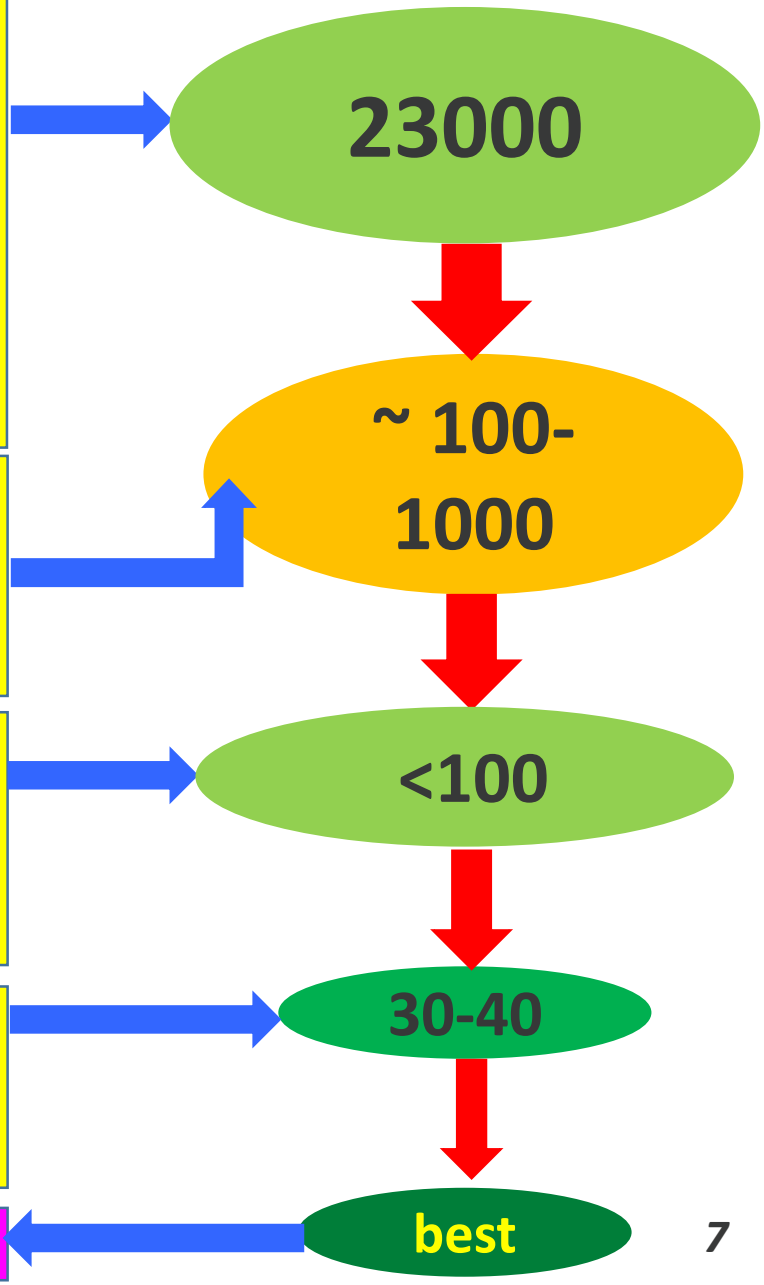
In-house machine learning and Monte Carlo molecular simulation

- Chief criteria: CO_2 solubility, CO_2/H_2 solubility selectivity, heat of absorption, H_2O solubility

In-house simulation: Molecular Dynamics

- Surface tension, heat capacity, viscosity, CO_2 diffusivity, density, vapor pressure, therm. conduct.

Experimental testing & TEA analysis



Best Screened Solvent: CASSH-1

Solvent	Selexol	CASSH-1
Viscosity (cP)	5.8	5.1
Density (g/cm^3)	1.030	0.960
Molecular weight (g/mol)	280	260
Vapor pressure (mmHg)	7.3×10^{-4}	1/100 of Selexol
Freezing point (°C)	-28	0
Normal boiling point (°C)	275	300
Hydrophobicity	very hydrophilic	very hydrophobic
Foaming	no	no
Safety, health, environment	no	no
CO_2 loading (mol/MPa.L)	1.25 ± 0.01	1.463 ± 0.007
CO_2/H_2 loading selectivity	75.8 ± 0.8	66.4 ± 0.4

- **Bench-scale (60 L) exp. confirmed CASSH-1 has higher CO_2 loading and higher CO_2/H_2 loading selectivity in simulated fuel gas mixture [1]**

[1] N. Siefert, et al. 2019 NETL Carbon Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting, Aug 26-30, Pittsburgh, PA

Learnings from Computed CO_2 Loadings in 35 CASSH-1 Similar Solvents

- Dimerization/trimerization of functional group could significantly decrease CO_2 loading (1.3-1.7 times) due to significantly decreased solvent free volume fraction (1.4-1.6 times)
- Replacing terminal $-CH_3$ by –CN and $-CF_3$ doesn't improve CO_2 loading
- Decreasing number of $-CH_2-$ could increase CO_2 loading (<20%)
  - –increasing the functional group concentration and
  - –increasing the solvent free volume fraction
- C(=O)NC(=O) group increases both CO_2 loading and CO_2/H_2 selectivity

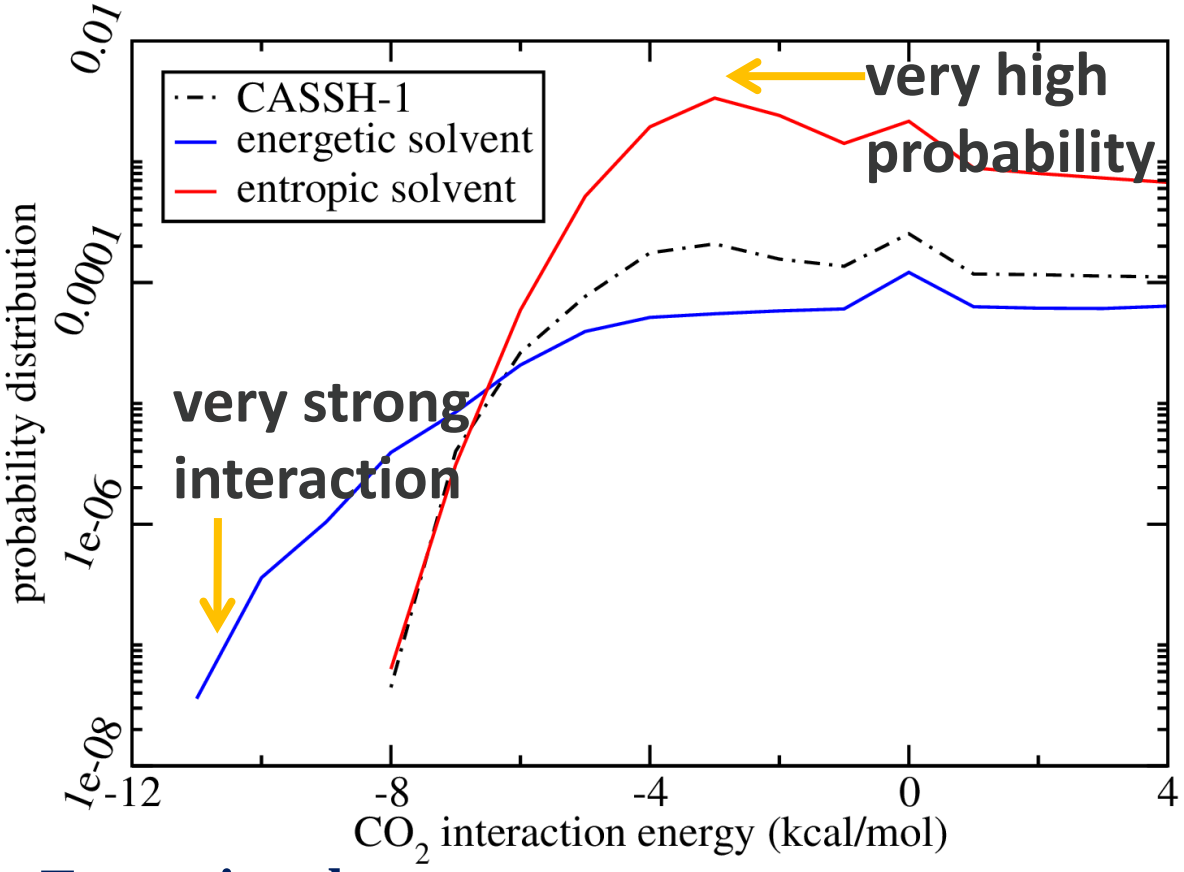
energetic solvent

CO_2: 10.1 (4) mol/MPa.L;
CO_2/H_2: 459 (18); fv = 0.06943 (5)

Commercially available from PubChem

CO_2: 1.61 (8) mol/MPa.L;
CO_2/H_2: 162 (8); fv = 0.0552 (1)

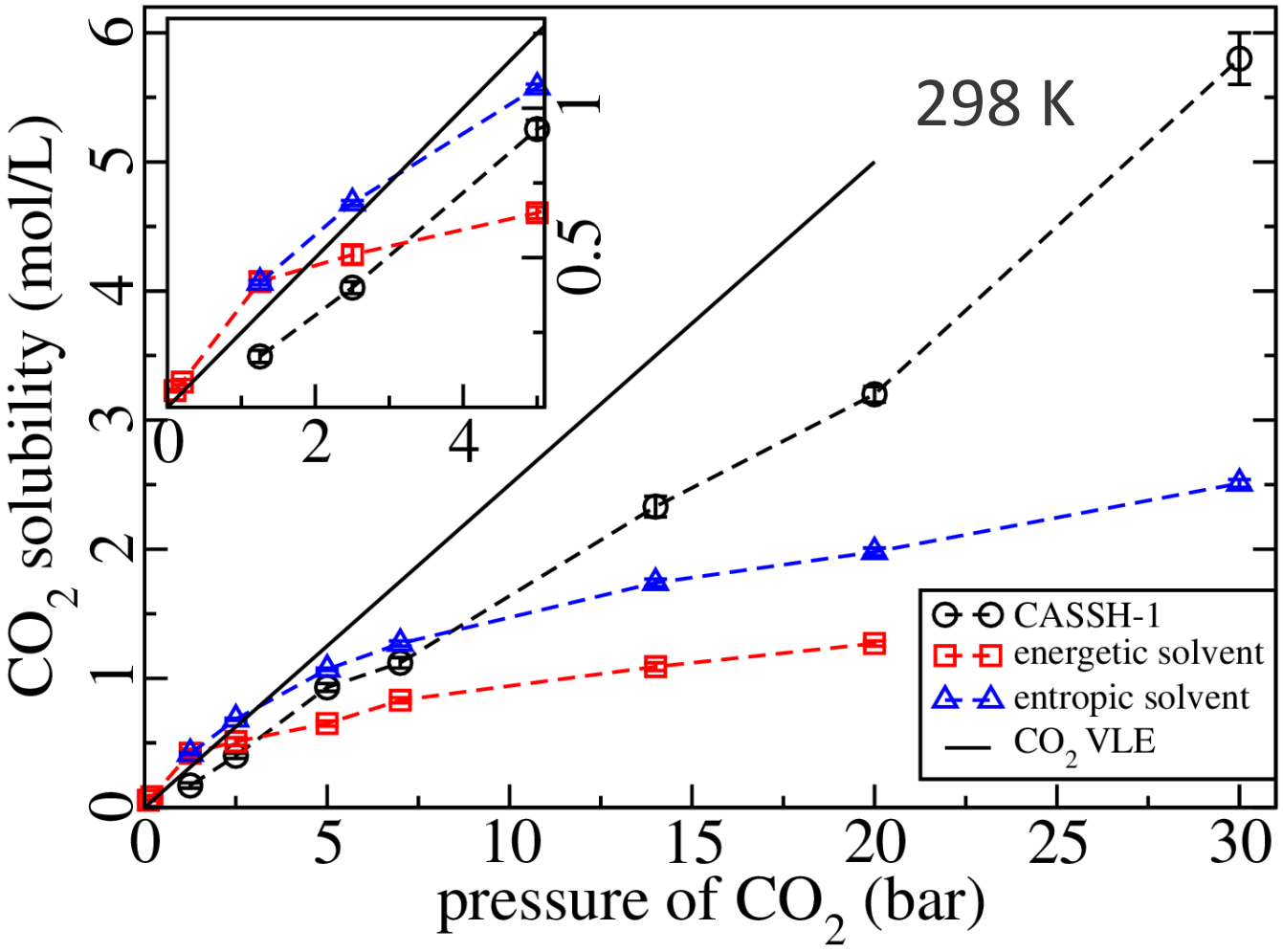
New Concepts: Energetic & Entropic Solvents



- **Energetic solvents**
  - Exhibit very strong interactions with CO_2
  - But probability for strong interaction is very low
  - High CO_2 loading and high CO_2/H_2 solubility selectivity only at low pressures

- **Entropic solvents**
  - Very high probability of favorable interactions with CO_2 & why?
  - But lack of very strong interactions
  - High CO_2 loading and high CO_2/H_2 selectivity at low & intermediate pressures

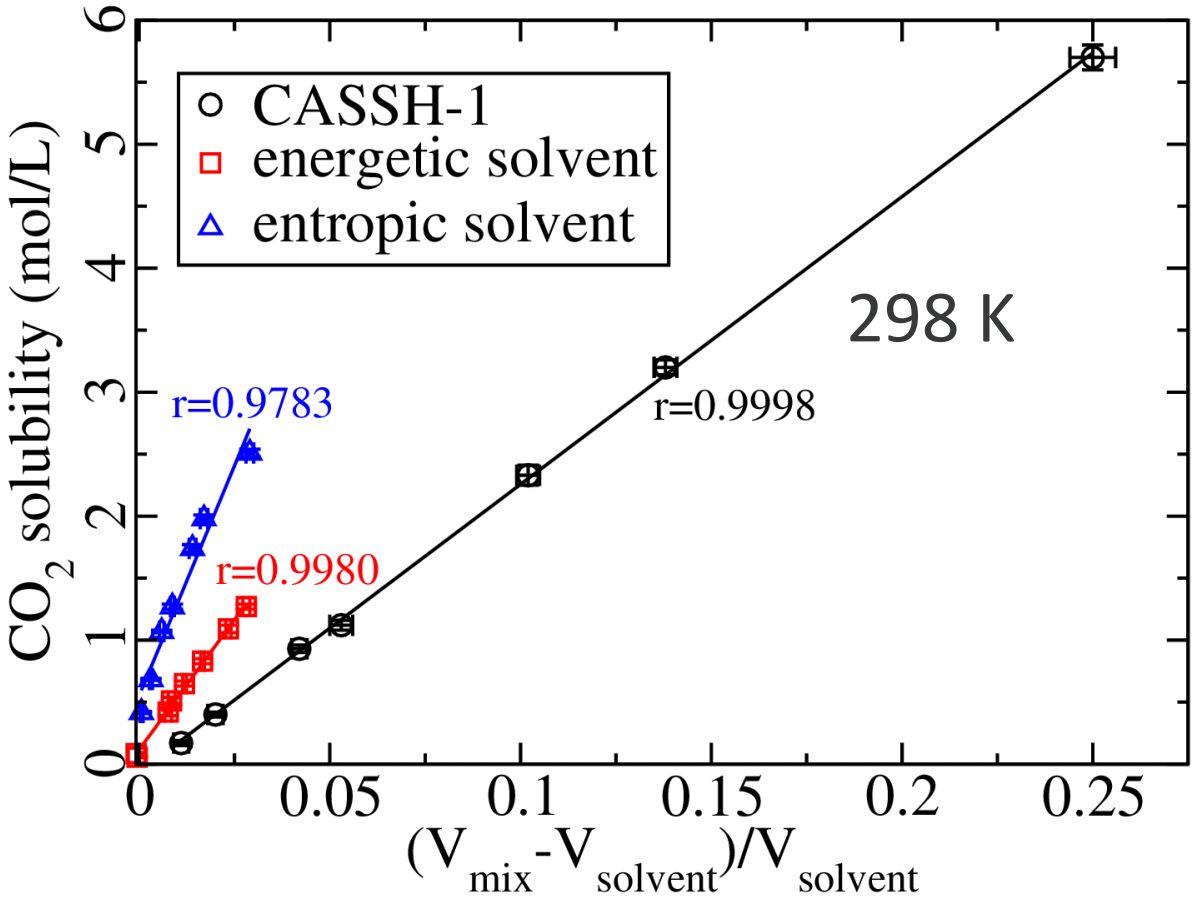
CO_2 Full Absorption Isotherms in CASSH-1, Energetic & Entropic Solvents



- CASSH-1 exhibits linear/concave up absorption isotherm between 0-30 bar
- Entropic and energetic solvents only exhibit high CO_2 loadings below (1.25-2.5) bar

- Blend of CASSH-1 with entropic solvents?

CO_2 Solubility and Volume Expansion Exhibit Almost Perfect Positive Linear Correlation



solvent	Mol. W. (g/mol)
CASSH-1	260
Energetic	370
Entropic	700

- At the same CO_2 loading, the volume expansion decreases in the same order as the molecular weight

Conclusions

- CASSH-1 solvent was identified from the computational screening of the NIST database, and it has been experimentally confirmed to perform better than Selexol at bench-scale (60 L) using a real gas mixture.
- Simply adding more functional groups significantly decreases CO_2 solubility due to decreased solvent free volume fraction.
- Decreasing-CH_2- groups typically increases CO_2 loading.
- Two new concept solvents, energetic and entropic solvents, show CO_2 loadings higher than 2.5 mol/MPa.L below 2.5 bar.
- Enough solvent volume expansion upon CO_2 absorption is necessary to obtain linear CO_2 loading up to 30 bar.

Acknowledgements

- **NETL Internal Collaborators**
  - **Solvent project**: Robert Thompson, Jeffrey Culp, Hong Lei
  - **SBEUC Support team**
  - **Computation materials engineering team**: Surya Tiwari, Samir Budhathoki, Jan Steckel, Dan Sorescu, Steven Richardson
  - **CO_2 Capture team**
- **NETL external contacts**
  - Rafiqul Gani @ Technical University of Denmark, retired
  - Kevin Joback @ molecularknowledge.com
  - Edward Maginn @ University of Notre Dame
  - Karl Johnson and Badie Morsi @ University of Pittsburgh
  - Dr. Paul Thiessen @ NIH for PubChem database

This work was performed in support of the US Department of Energy's Fossil Energy Carbon Capture Research Program. The Research was executed through the NETL Research and Innovation Center's Transformational Carbon Capture Field Work Proposal. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003..

This work was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract with Leidos Research Support Team (LRST). Neither the United States Government nor any agency thereof, nor any of their employees, nor LRST, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.