Screening of Physical Solvents for Pre-Combustion Capture Using a Combined Approach of Data Mining and Molecular Simulation

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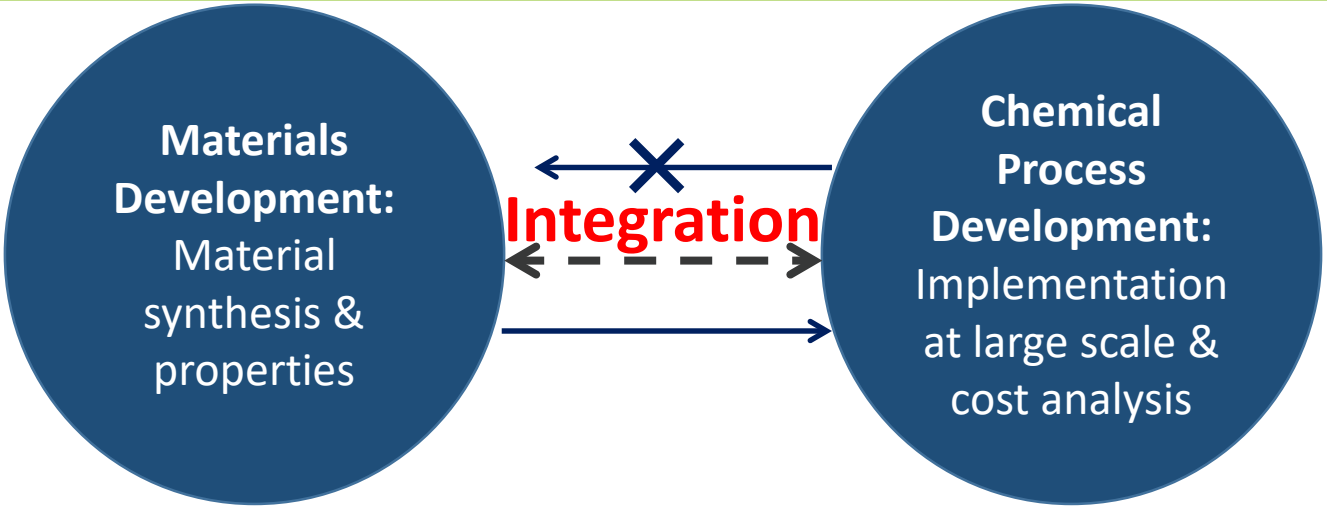
Objectives

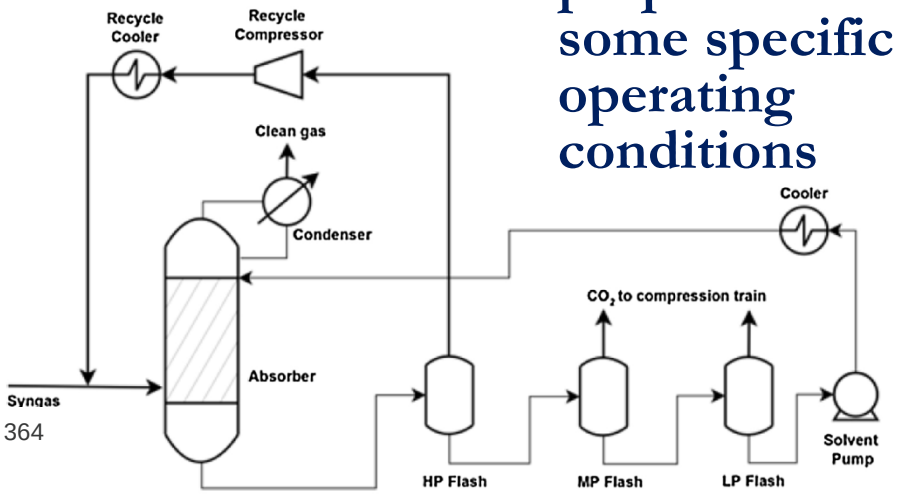
- **Identify promising physical solvents for CO_2 pre-combustion capture from commercially available organic compounds.**
  - **Database search:**
    - ✓NIST database software: melting point, normal boiling point
    - ✓Open literature: safety, environment, biology properties and price
  - **Simulation:**
    - ✓In-house computational database development
    - ✓CO_2 solubility, CO_2/H_2 solubility selectivity
  - **Experiment and simulation:** in case of missing important pure compound properties
- **The best identified compounds are purchased and tested at NETL and further modified for improvements.**

Decouple the Integration of Materials and Process Development



- **Challenge: solvent and process are coupled.** Different solvents may lead to optimal performance at different operating conditions, such as T & P

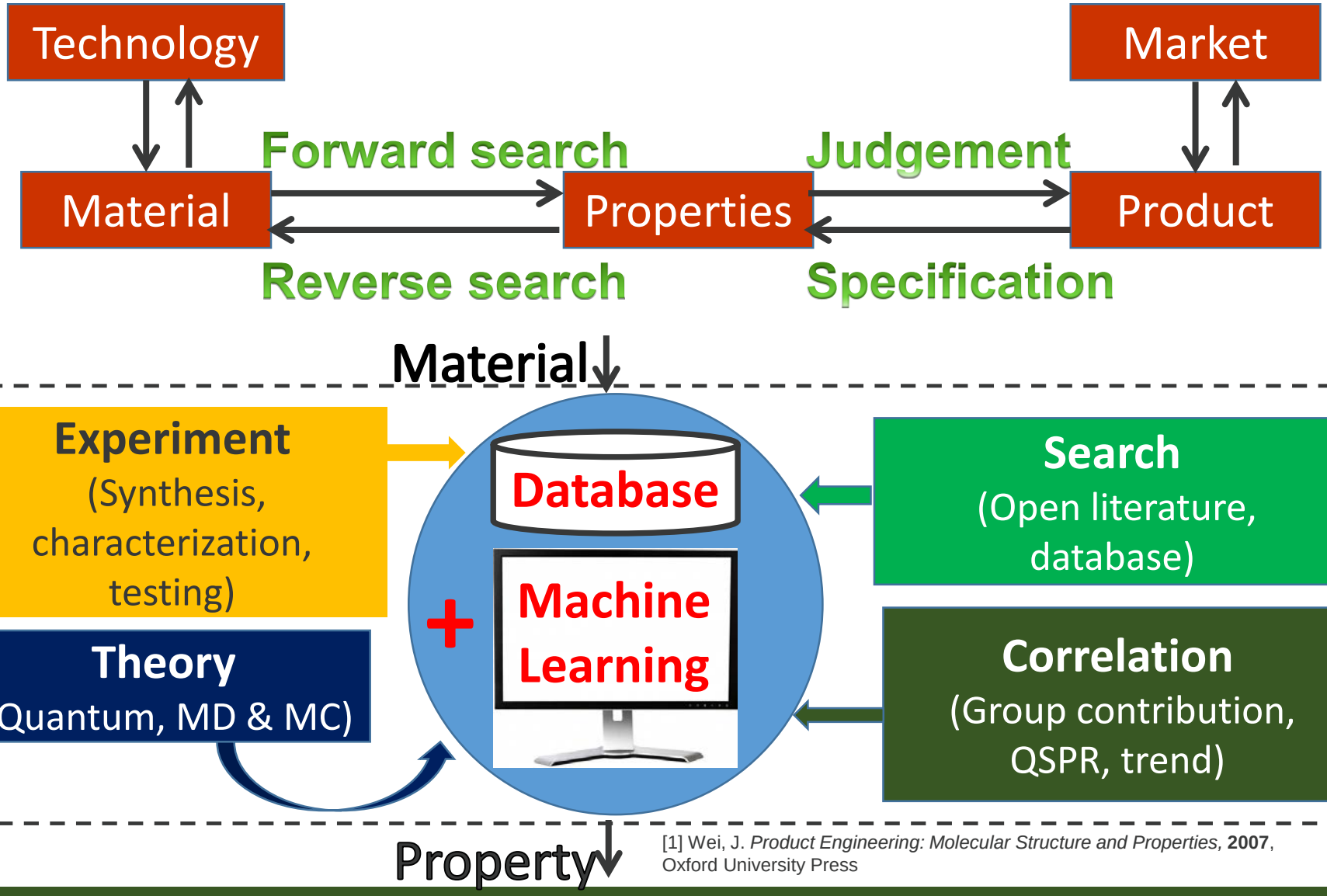
- **Strategy:** decouple the integration through sub-optimization by first screening solvents, which has "the best performance properties" under some specific operating conditions



Process flow diagram for precombustion CO_2 capture using a physical solvent.

[1] Siefert, N. et al., *International Journal of Greenhouse Gas Control* **2016**, 364
[2] Burr, B. et al. *Hydrocarbon Processing* **2009**, 43
[3] Bucklin, R. et al. *Energy Progress*, **1984**, 137
[3] Burger, J. et al. *AIChE J.* **2015**, 3249

Forward & Reverse Search Review



[1] Wei, J. *Product Engineering: Molecular Structure and Properties*, **2007**, Oxford University Press

Integrated Computational Method Development

NIST database for pure compounds (~23,000)
- Melting (T_m), boiling (T_b) temperatures, viscosity, surface tension, density (molar volume)

Open literature
- Physical properties, such as flash point
- Safety, health, environment
- Price

~ 600 compounds
T_m < 30°C &
T_b > 260°C

In-house computational database: quantum mechanics for gas – chemical function group interactions
- CO_2, CH_4, H_2, H_2O, H_2S, SO_2, O_2, N_2, etc.

in-house comp. database

In-house molecular simulation: Monte Carlo
- Chief criteria: CO_2 solubility, CO_2/H_2 solubility selectivity, heat of absorption
- H_2O solubility (hydrophobicity/hydrophilicity)

<100

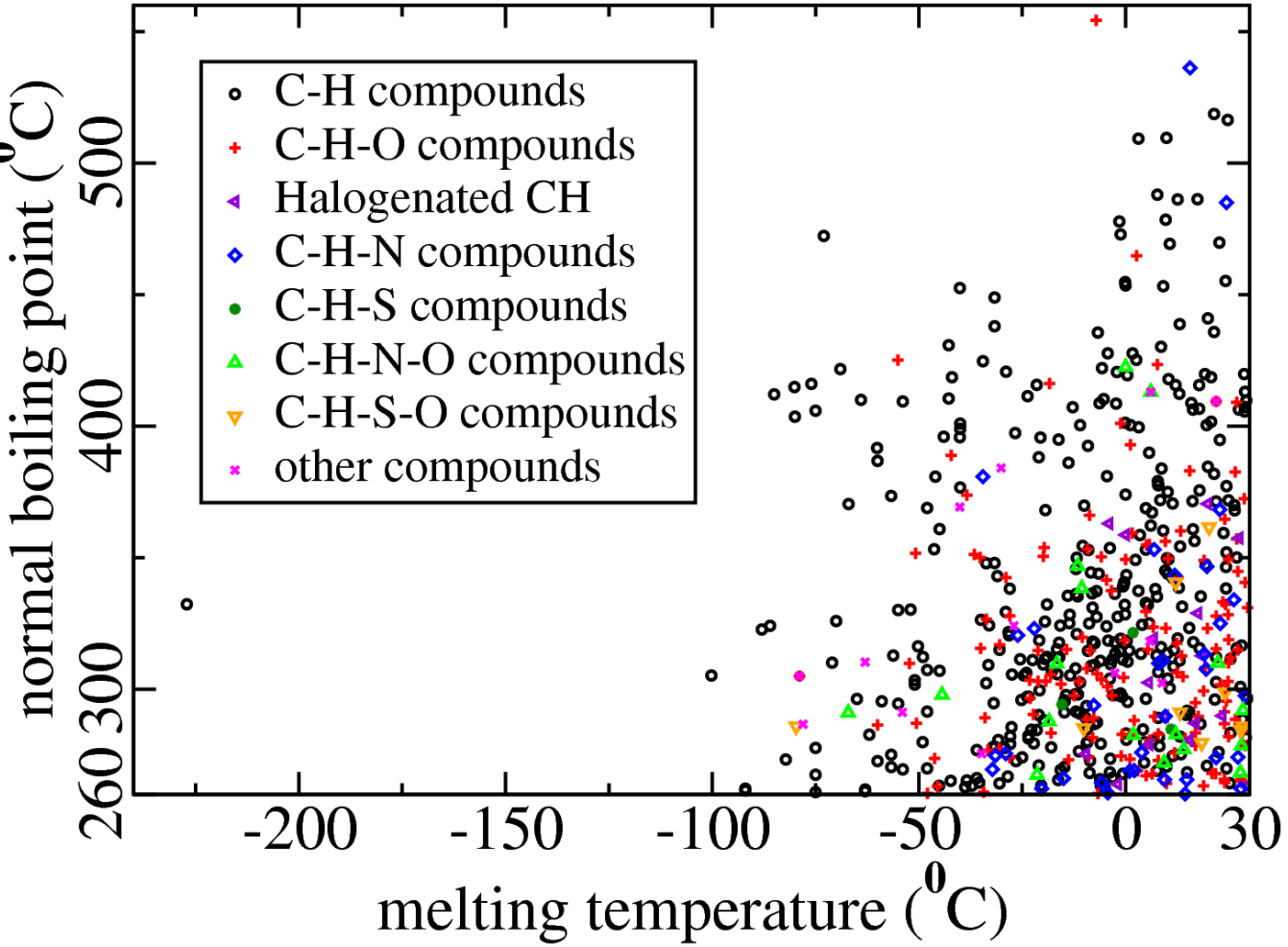
In-house simulation: Molecular Dynamics
- Surface tension, heat capacity, viscosity, CO_2 diffusivity, density, vapor pressure, therm. conduct.

10s

Experiment: New chemical synthesis and testing

best

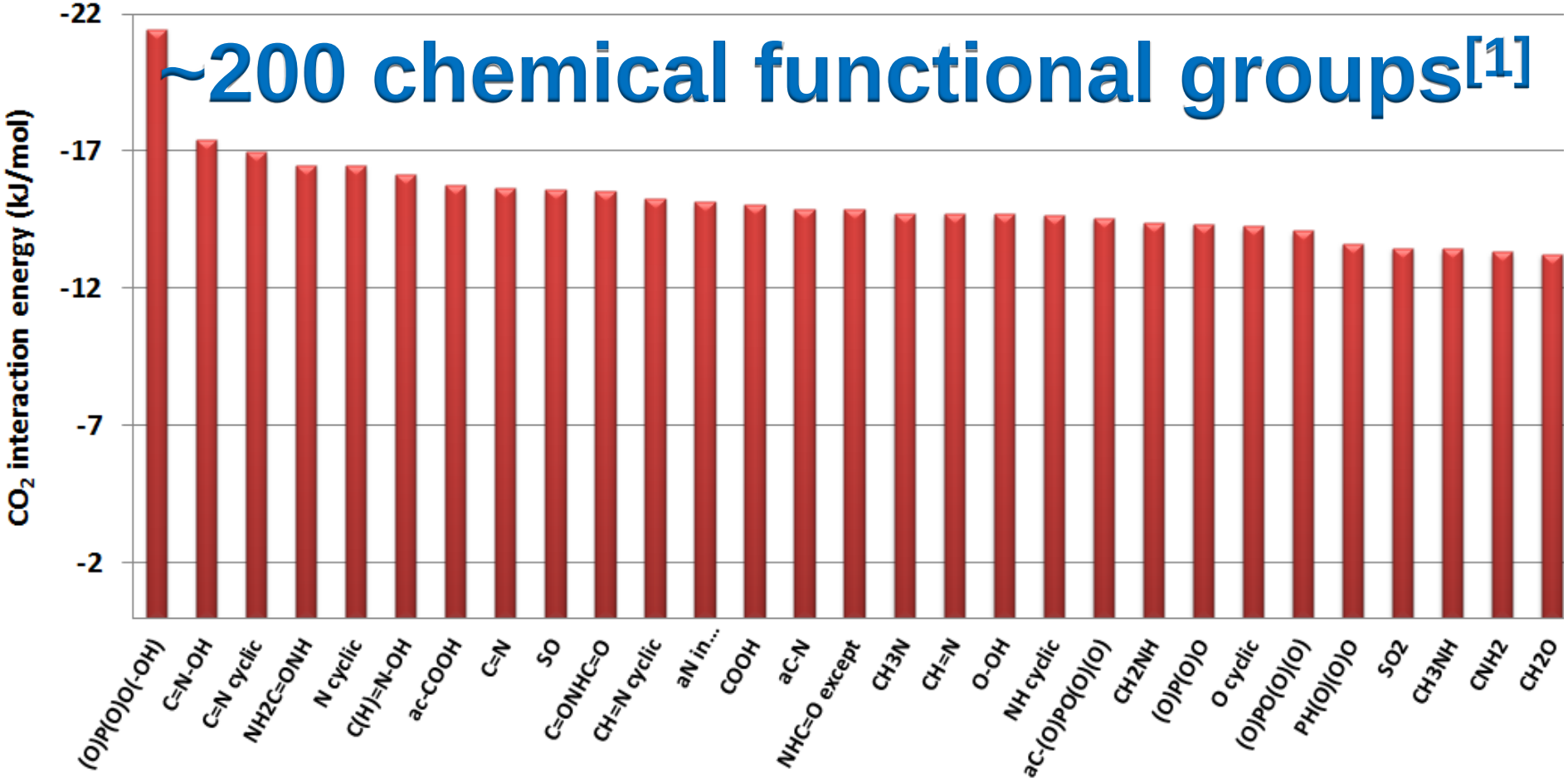
Significantly Narrow Down Solvent Search: (23,000→600) from the NIST Software



- The NIST database software contains 22,731 pure compounds.
  - 8155 exp. data sets for melting point
  - 9981 exp. data sets for normal boiling point
- The software provides reverse search tools.

- **~600 compounds were found in NIST database: T_m < 30°C & T_b > 260°C**

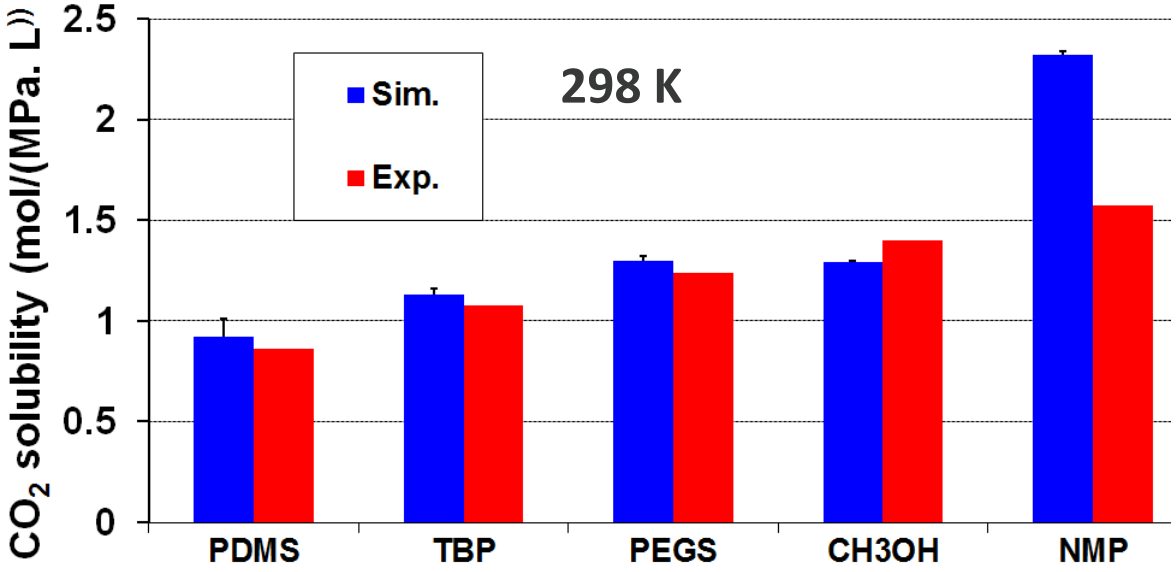
In-house Computation Database: Chemical Functional Groups Interacting with CO_2



- PHO_4, C=N, etc. interact most strongly with CO_2 (> 15 kJ/mol)
- -O- ether group interacts strongly with CO_2 (~ 10-12 kJ/mol)
- -CH, $-CH_2$, $-CH_3$ interact most weakly with CO_2 (< 1 kJ/mol)

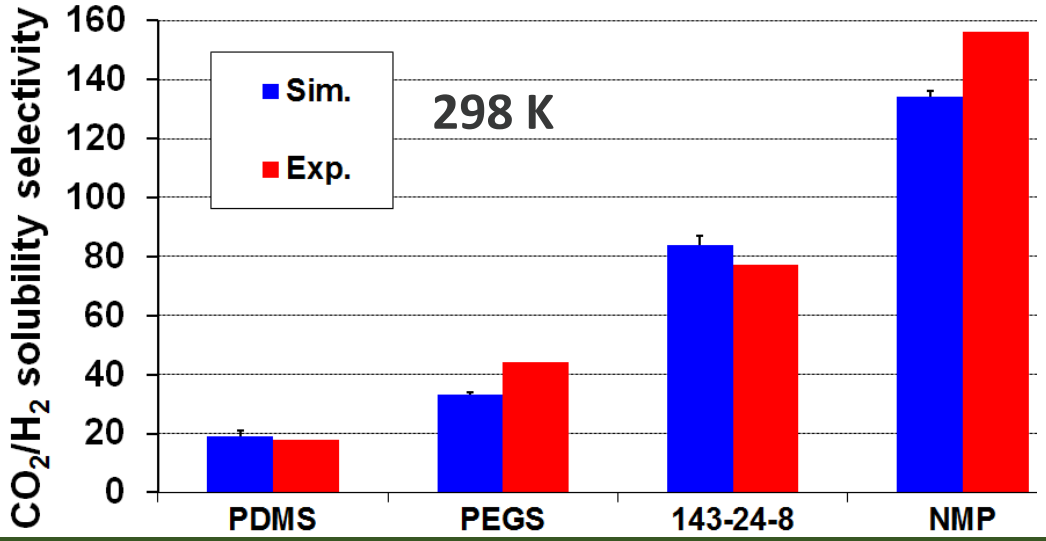
[1] Marrero, J.; Gani, R. *Fluid Phase Equilib.* **2001**, 183

Experimental Validation of Simulation: CO_2 Solubility and CO_2/H_2 Solubility Selectivity



- Simulated CO_2 solubility values agree with the experimental data in most cases
  - Consistent trends

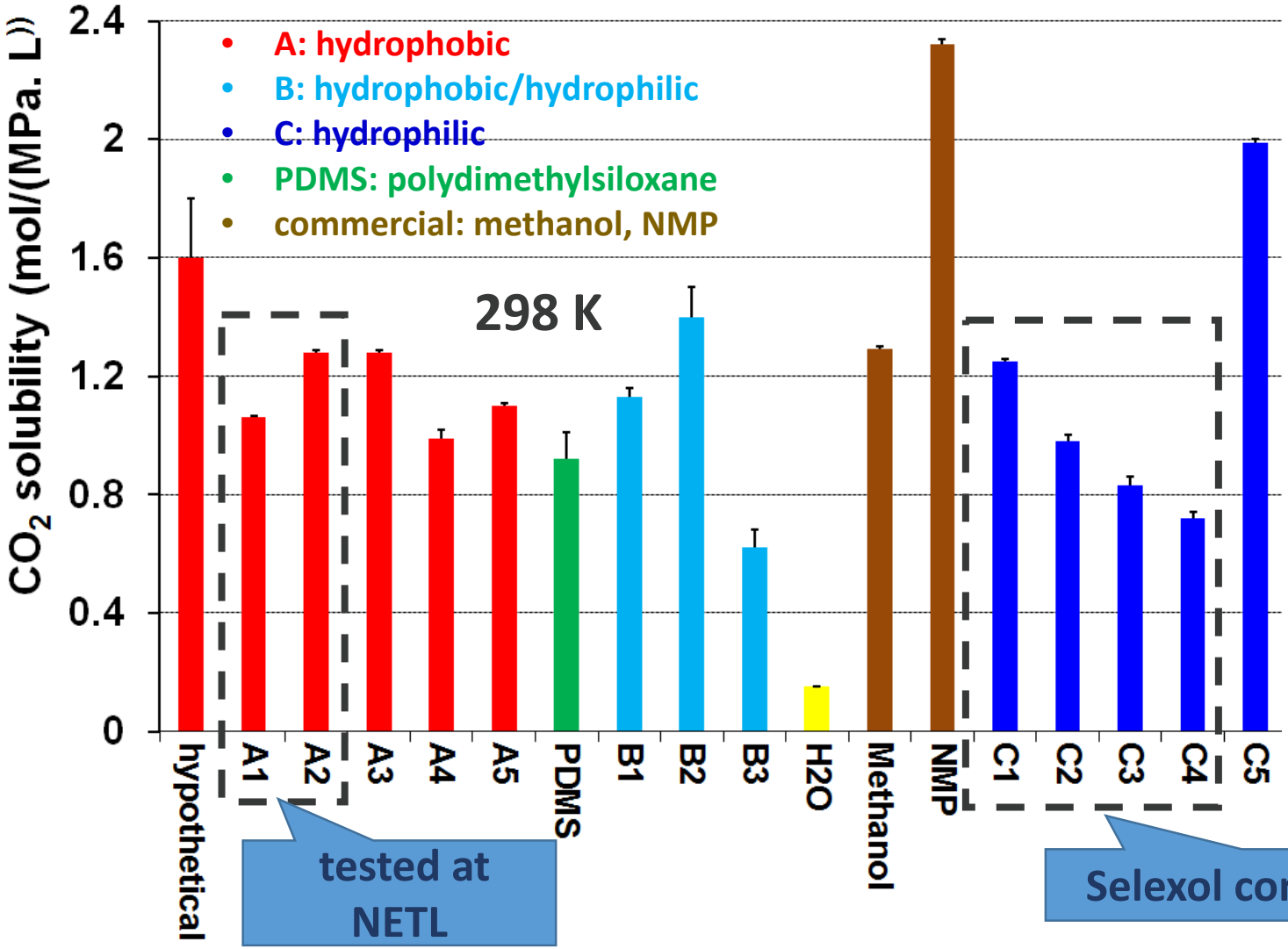
PDMS: polydimethylsiloxane
TBP: Tributyl phosphate
PEGS: NETL PEG-Siloxane-1
NMP: N-Methyl-2-pyrrolidone
CAS 143-24-8: Selexol surrogate



- Simulated CO_2/H_2 solubility values are also close to the experimental data
  - Same trends

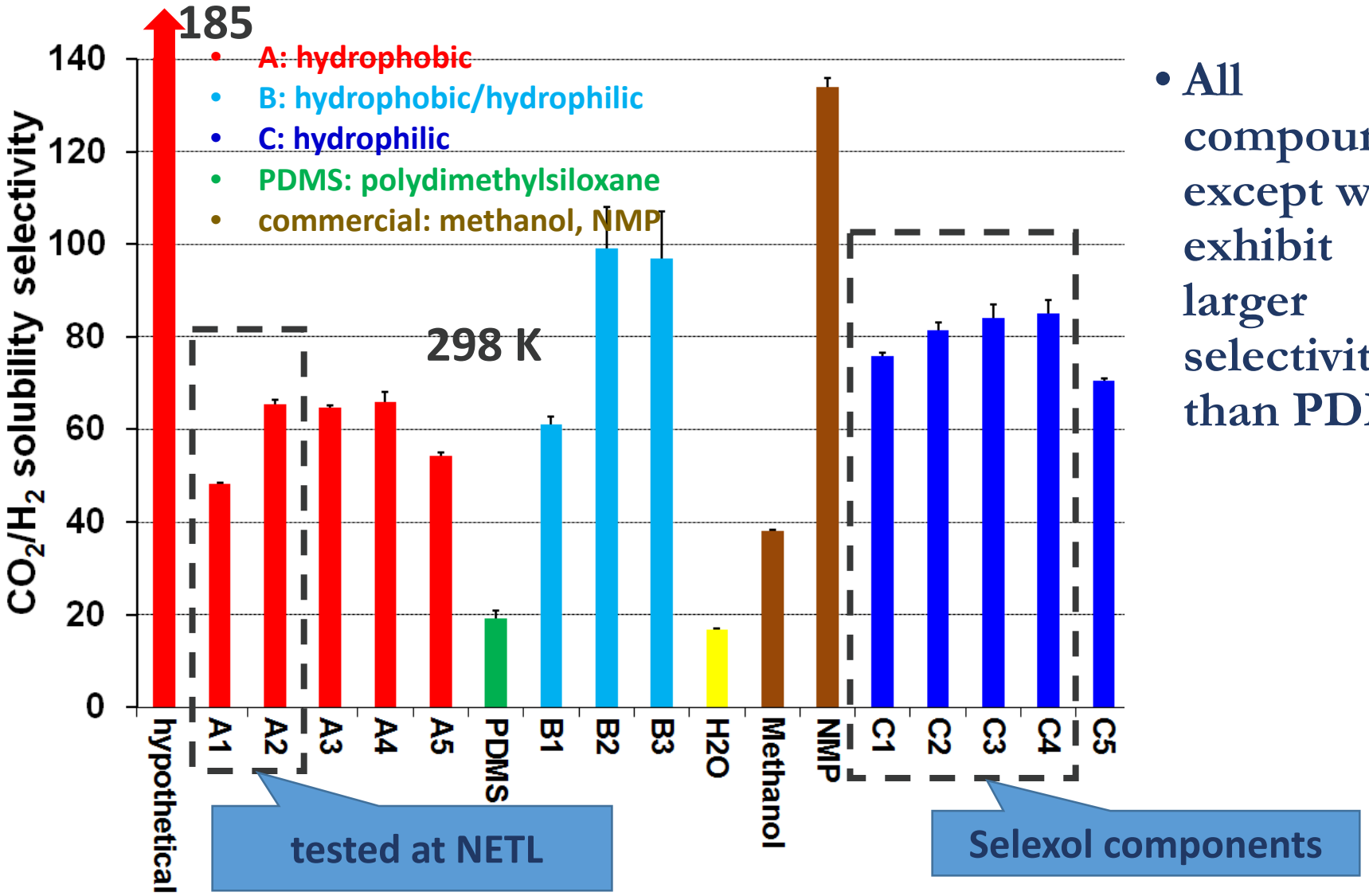
[1] Shi, W. et al., *J. Phys. Chem. C* **2015**, 19253
[2] Shi, W. et al., *J. Phys. Chem. C* **2016**, 20158
[3] Burr, B. et al. *Hydrocarbon Processing* **2009**, 43

Some Solvents with High CO_2 Solubility at Ambient Condition Are Identified



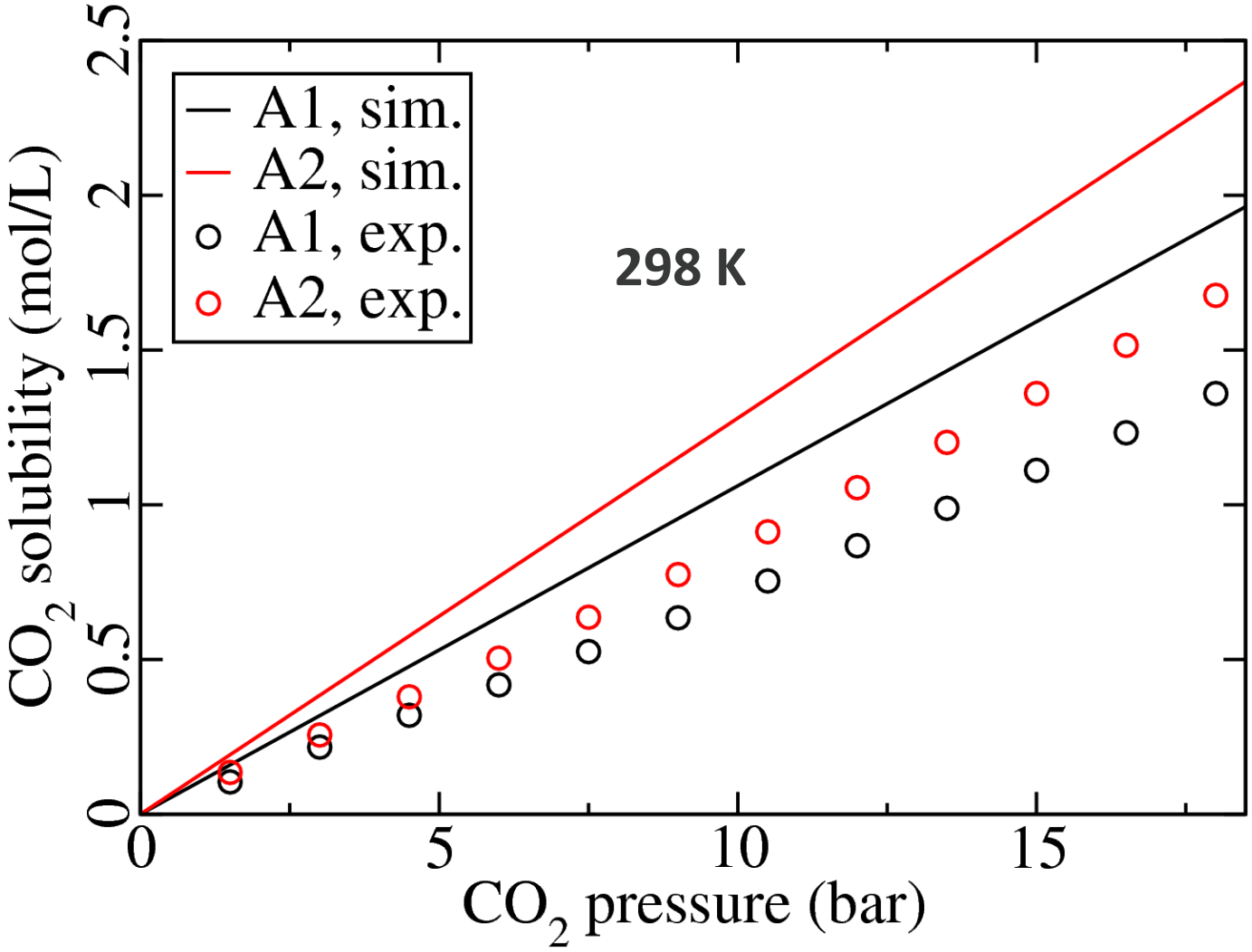
- The following compounds exhibit larger CO_2 loading than PDMS
  - —A1-A5 & Hypothetical
  - —B1-B2
  - —Commercial
  - —C1-C2,C5

Some Solvents with High CO_2/H_2 Solubility Selectivity Are Identified



- All compounds except water exhibit larger selectivity than PDMS

A2 & A1 Identified from Simulation; Experimentally Tested at NETL



A1: Commercial

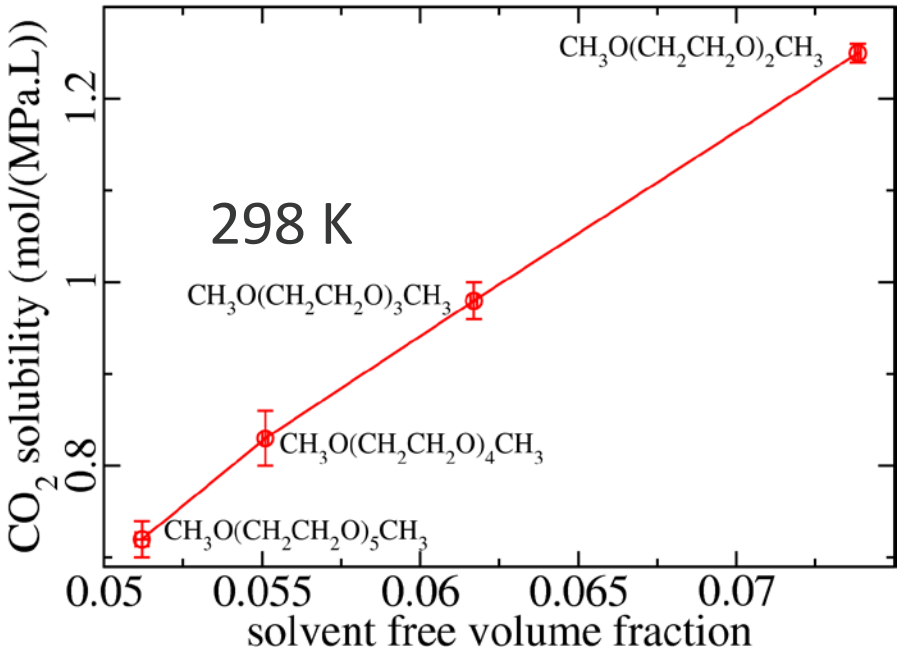
A2: Modified at NETL

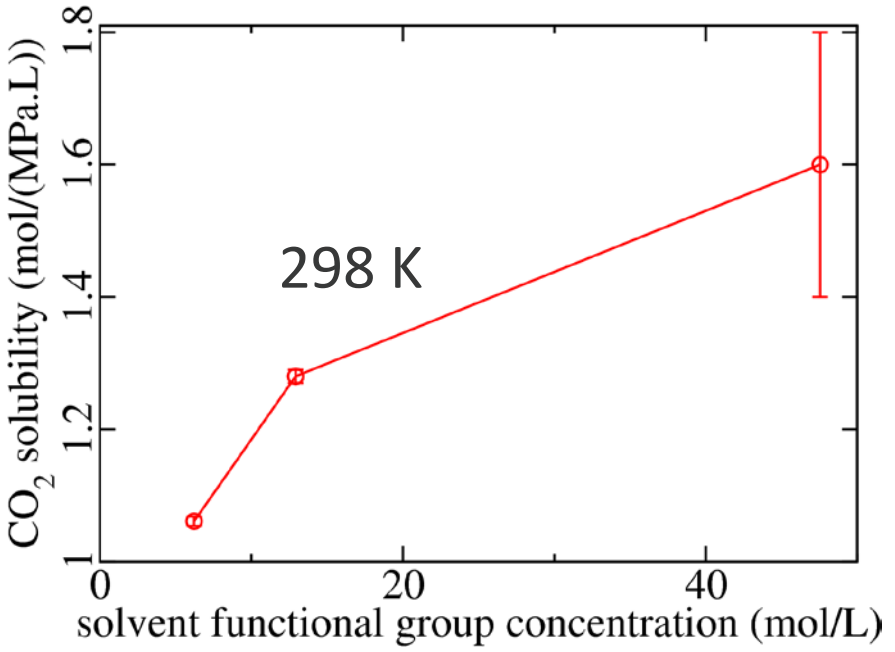
- Both sim. and exp. show that A2 exhibits larger CO_2 loading than A1

Other Favorable Properties: Solvent A1

- **Open literature data**
  - —Reasonably cheap
  - —No environment, health, and safety issues
  - —$T_{melting} < 10°C$, $T_{boiling} > 275°C$, $T_{flash} \sim 125°C$
- **Simulated and exp. data obtained at NETL**
  - —Reasonably high CO_2 loading (1.06 mol/(MPa. L))
  - —Sufficient high surface tension: little to no foaming
  - —Reasonably low viscosity
- **Simulated data waiting for experimental confirmation**
  - —High CO_2/H_2 solubility selectivity (~50 at 25°C)
  - —Much more hydrophobic than NETL PEG-Siloxane-1
  - —Low CO_2 heats of absorption (~ -10 kJ/mol)
  - —Low heat capacity
  - —High CO_2 diffusivity in the solvent

Three Factors to Determine CO_2 Solubility



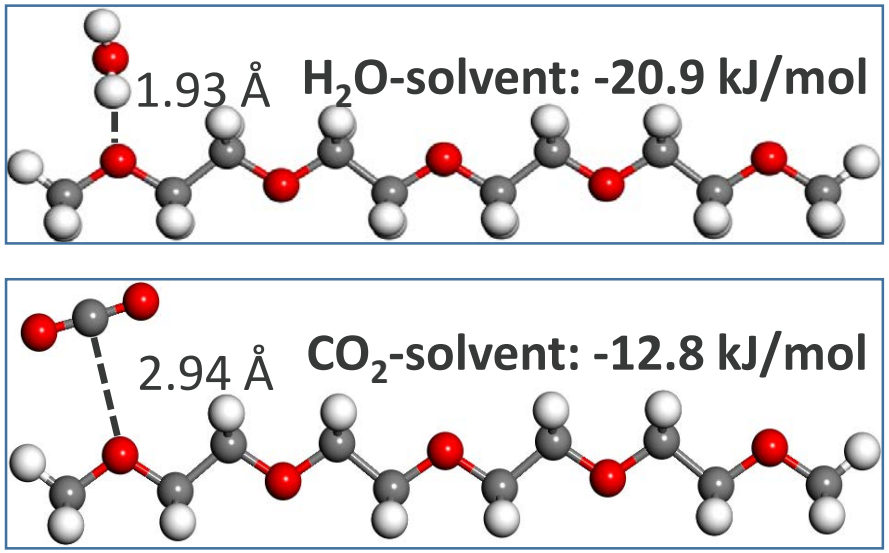


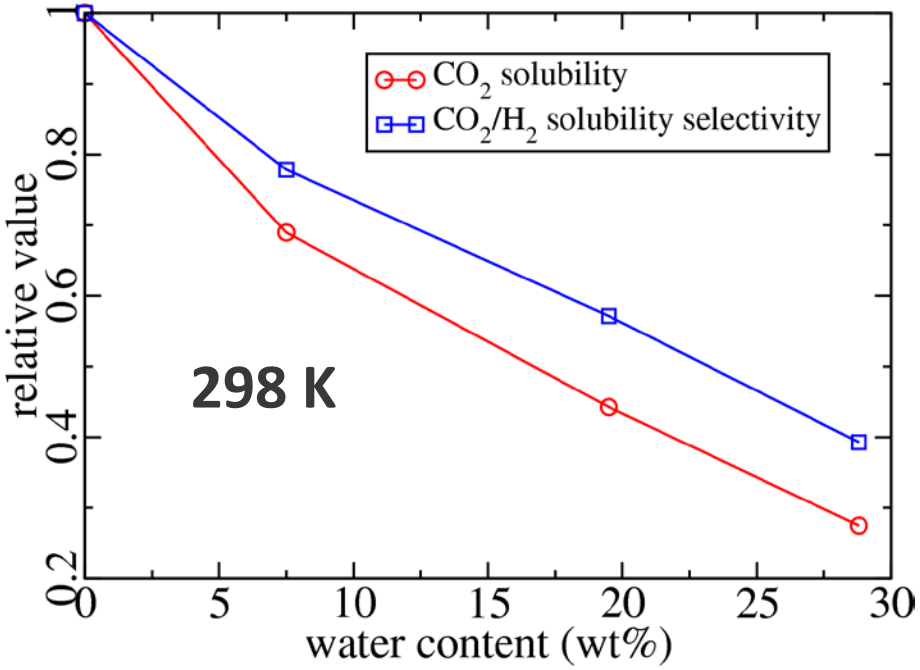
- **CO_2 solubility increases with:**
  - —Free volume fraction
  - —Function group concentration
  - —CO_2-solvent interaction

- **Why Selexol $(CH_2CH_2O)_n$?**
  - —Pros: large functional concentration & strong CO_2-solvent interaction
  - —Cons: small free volume fraction
  - —$(CH_2O)n$ scores better than $(CH_2CH_2O)n$ for all three factors

- **Relevant machine learning codes have been developed to predict CO_2 loading from free volume fraction, group concentration, and CO_2 interaction.**

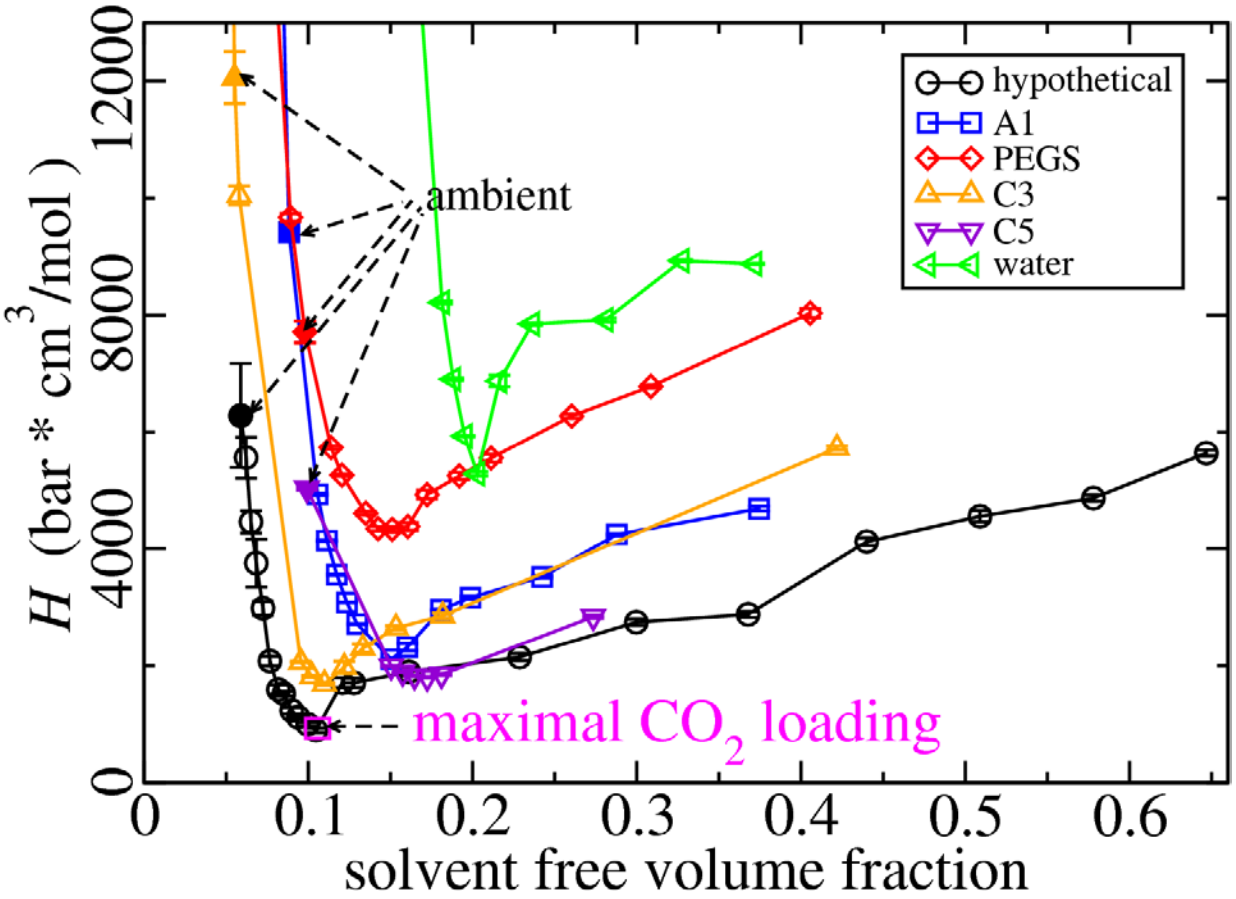
Water Decreases CO_2 Solubility and CO_2/H_2 Selectivity in Hydrophilic Solvent





- **Adding 7.5 wt.% water in hydrophilic Selexol surrogate will decrease-**
  - —CO_2 solubility (dry solvent based) by 1.45 times, partly due to water interaction with the –O- group
  - —CO_2/H_2 selectivity by 1.28

Largest CO_2 Physical Solubility in any Organic Compound at 298 K

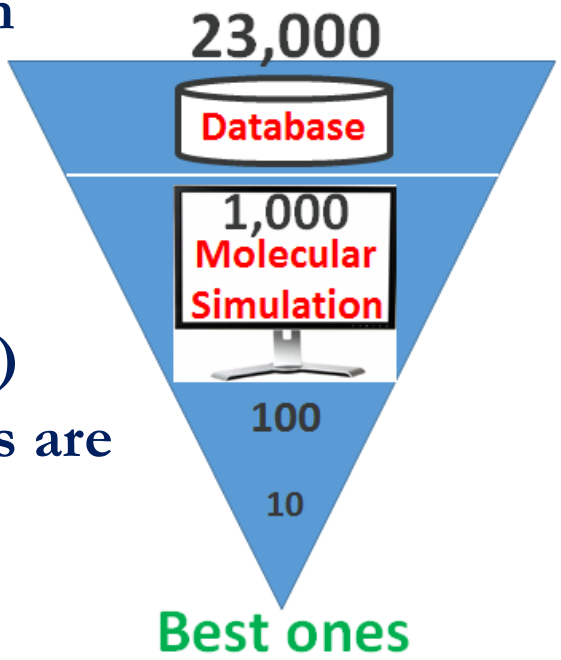


- When the solvent density is decreased by ~10% compared to ambient condition, it exhibits the largest CO_2 loading.

- The largest possible CO_2 loading at 298 K in any organic compound is 11 mol CO_2/(MPa. L); minimum CO_2 loading is 0.40 mol CO_2/(MPa. L); largest CO_2/H_2 solubility selectivity is ~300

Conclusions

- Developed an integrated computational approach
- Built an in-house computational database



- 23,000 compounds from NIST were screened.
- About 20 promising solvents were identified; two of them (1 commercial, 1 modified at NETL) were tested and the experimental CO_2 solubilities are consistent with simulations.
- The CO_2 loading limits in any organic physical compound at 298 K were obtained.
  - —Maximum: 11 mol/(MPa. L)
  - —Minimum: 0.40 mol/(MPa. L)
  - —Maximum CO_2/H_2 solubility selectivity: 300
  - —Allows comparison with any other organic material
  - —Useful in process modeling to estimate the minimum operating and capital cost

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  - —Computational materials group
  - —HPCEE super computer cluster
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