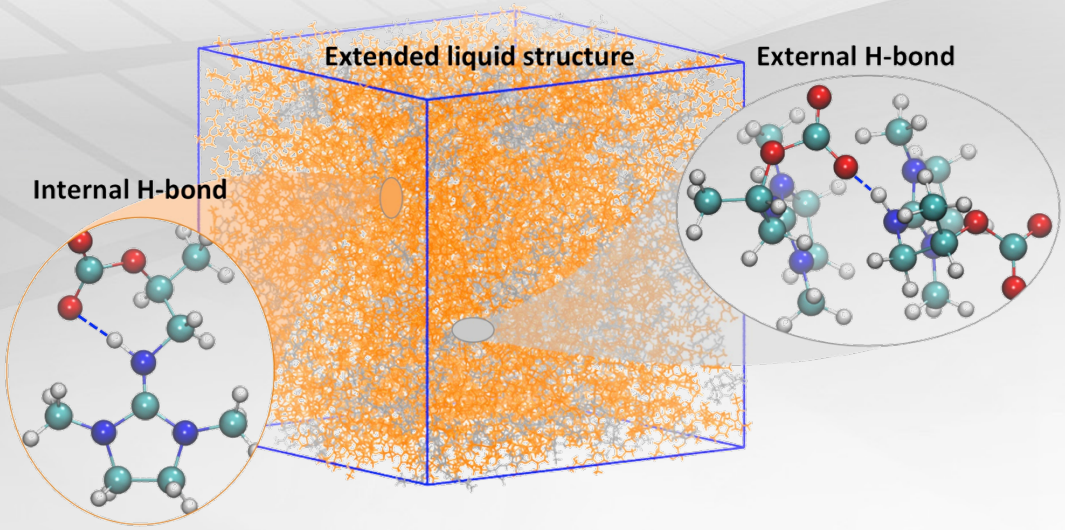

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Computational Protocols for Viscosity Reduction in CO_2 Capture Organic Solvents

VASSILIKI-ALEXANDRA GLEZAKOU

Pacific Northwest National Laboratory

CO_2 Capture Technology Meeting August 8-12 2016 - Pittsburgh

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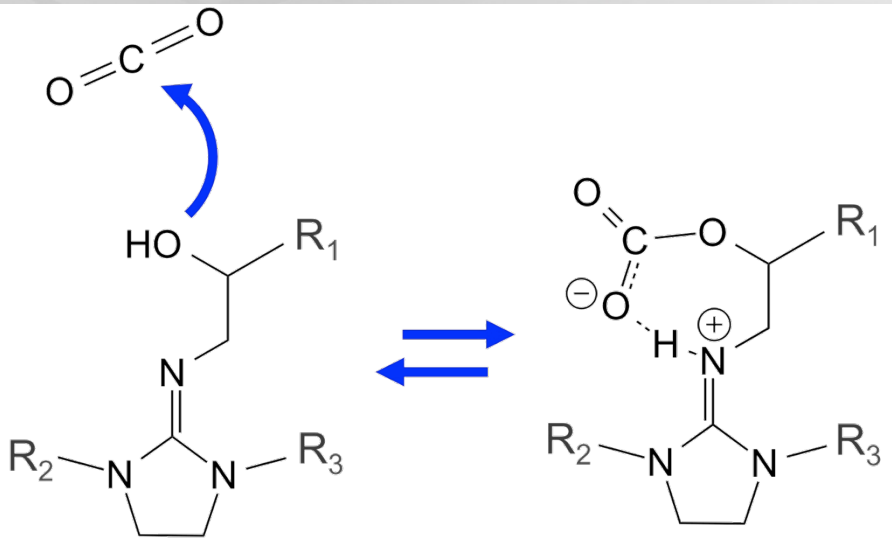
- Computational Resources NERSC, PIC, MIT

Program goals and objectives

- Enable solvent design for advancement up DOE's TRL scale to enable large-scale testing and deployment by year 2030
- Develop tools and solvent design methodologies for viscosity prediction/ reduction across all transformational solvent platforms
  - Understand the underlying molecular descriptors that control viscosity
  - Develop viscosity reduced order model that can predict key solvent physical and thermodynamic properties
  - Given a library of compounds, down-select to a small number that can reduce viscosity of current formulations by >400 cP or more
- Apply the developed viscosity model and molecular design principles to other solvents in DOE's post-combustion solvent portfolio
- Budget-permitting, conduct a bench-scale demonstration of the most advanced solvent that includes extended testing with and without water.
  - Use bench-scale testing data to make energy and LCOE predictions for a full-scale system, using Aspen Plus™ to model the system

The challenges of solvent development

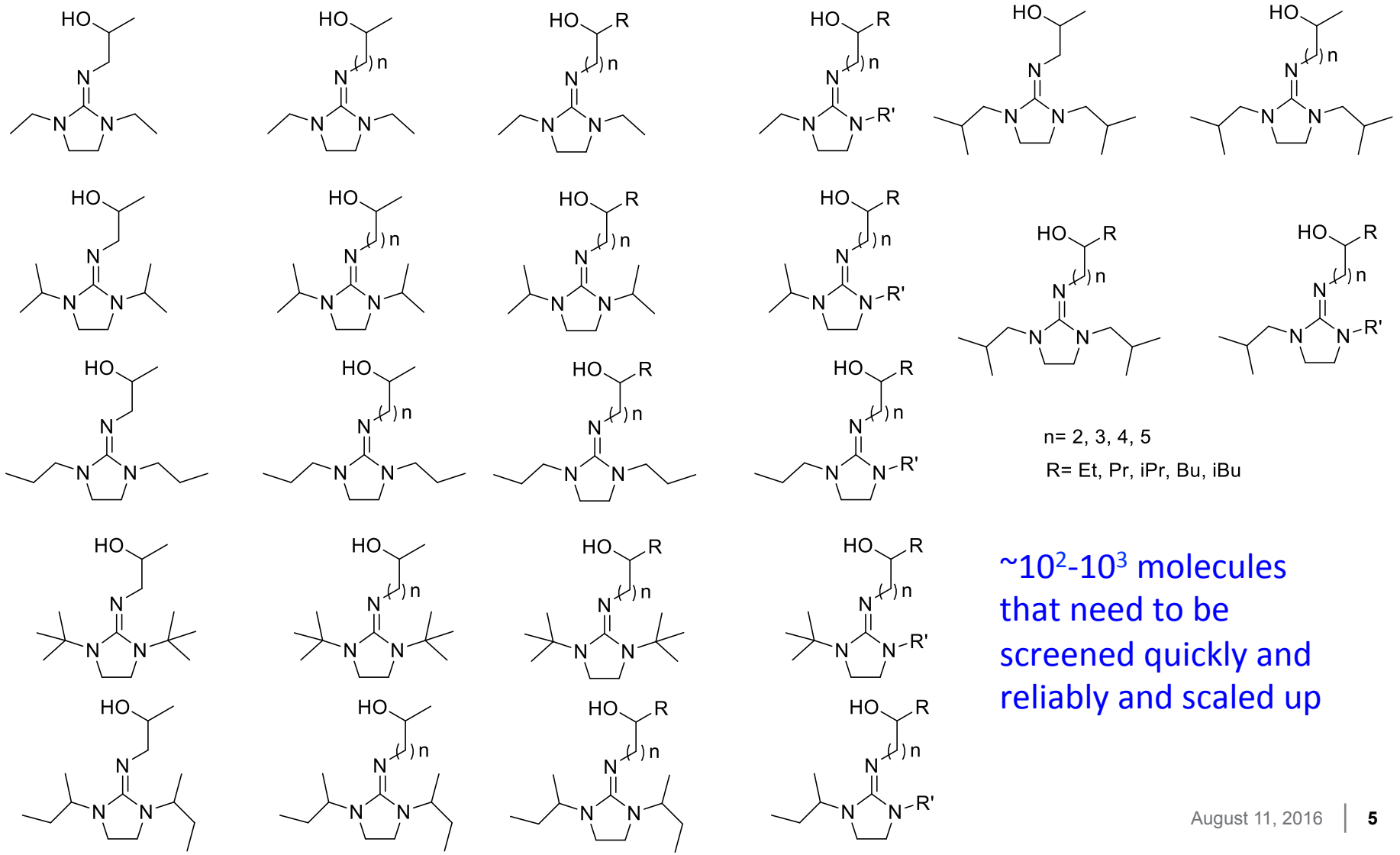


Neutral, non-viscous

Ionic liquid forms upon CO_2 capture (but does it have to?)

- The viscosity of the medium changes with CO_2 loading
- Different R groups generate a big number of compounds to be screened

Example library of CO_2BOLs – Round 1



n= 2, 3, 4, 5

R= Et, Pr, iPr, Bu, iBu

~10^2-10^3 molecules that need to be screened quickly and reliably and scaled up

Initial molecular design metrics

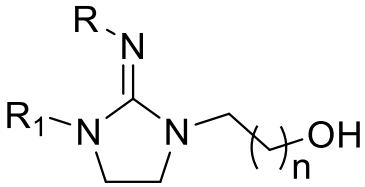
What we need (*specific for each solvent class*):

- Guanidine-based CO_2BOLs
  - High basicity needed for >90% CO_2 capture
  - Zwitterionic form has low volatility
- Cyclic base core to prevent hydrolysis

Initial design concepts:

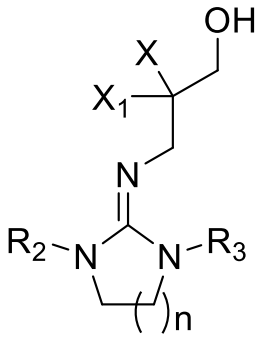
- Optimize cation-anion interactions in the Zwitterion
- Steric effects
- Fine tuned molecular electronics
- Effect of hetero-atoms

Steric Effects



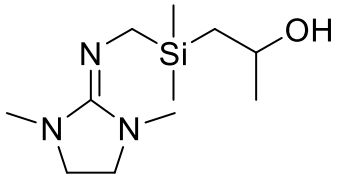
R=Pr, iPr, Butyl, tButyl
R_1=Me, Et, iPr
with n=1, 2, 3

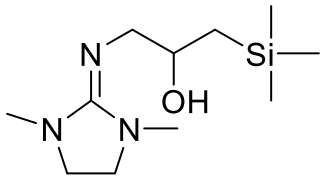
Electronic Effects



X and X_1= F, Cl, CF_3, (EWG) or OMe, CH_2NMe_2, (EDG) and R_2=R_3=Me, CF_3, $CF_3CF_2^-$, OMe with n=1, 2, 3

Silane-Based CO_2BOLs





Scientific and technology approach

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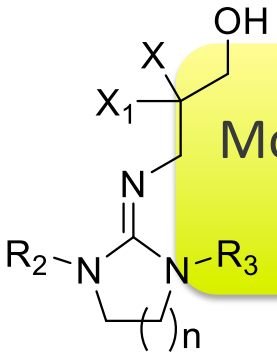
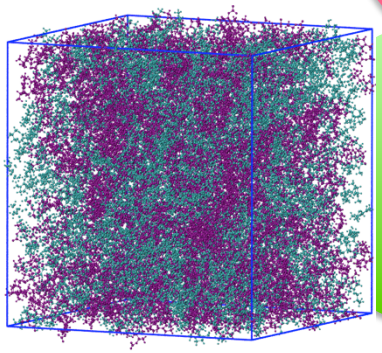
Model Validation and Refinement of Design

Molecular Library Design



Experimental Measurements



Molecular Modeling and Property Prediction

Synthesis and Characterization

Molecular modeling tools

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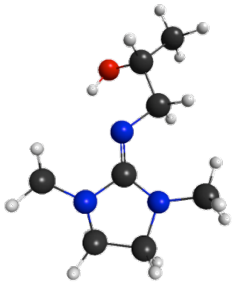
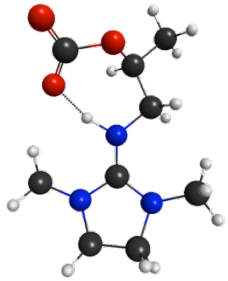
- DFT-based electronic structure for molecular properties (~10^{2}-10^{3} atoms)
  - Accurate description of molecular properties
    - Atomic charges needed for classical potential
    - Reaction energetics: H-bonding, CO_2 absoption energy
- *Ab initio* Molecular Dynamics and accelerated free energy sampling methods (metadynamics, Blue moon,) ~10^{3} atoms
  - Reactivity including temperature effects and dynamic behavior, free energy estimates
- Classical Molecular Dynamics (MD) (~10^{4}-10^{5} atoms)
  - Accurate description of molecular liquid structure, with potentials derived from electronic structure (Universal OPLS with *ab initio* charges)
  - Obtain number and type of relevant intermolecular contacts
  - Transport properties: diffusion and viscosity
- Codes, Software:
  - CP2K (www.cp2k.org), NWChem (www.nwchem.org), Gaussian09 (http://www.gaussian.com/g_prod/g09.htm)
  - Viscosity can be directly computed from long simulations (1μs), Software: GROMACS (www.gromacs.org)
- Desired outcome is a reduced model
  - Shift through many candidates in short time (few days)



IPADM-2-BOL

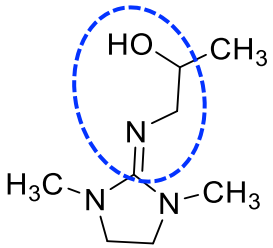


CO_2-loaded IPADM-2-BOL

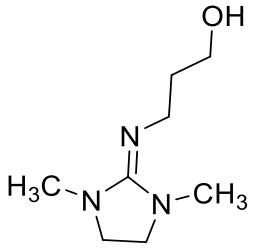
CO_2BOLs – Initial computation targets

- Initial and new computational targets
  - 3-D steric interactions
  - Reduced intermolecular interactions
- Simulate pure liquids and mixtures at 15%, 25%, and 50%, determine viscosity from analysis of trajectories
- Evaluate inter- *vs* intra-molecular hydrogen bonding effects on viscosity

Control Molecules & Complexes

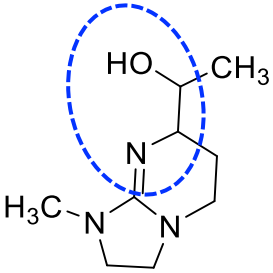


Initial best-performing BOL
Viscosity ~ 200cP at 0.25 mol %CO_2

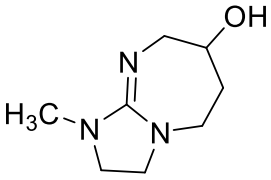


Poor performing BOL
Viscosity >>1,000 cP at 0.25 mol %CO_2

Initial trial Molecules & Complexes



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



-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.
-Hinders internal H-Bond.

Validation of molecular model[1]

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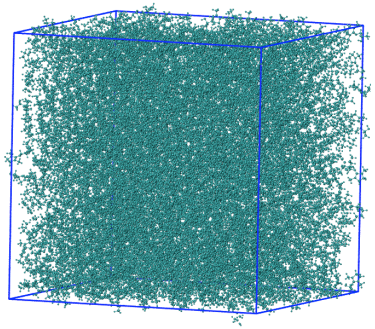
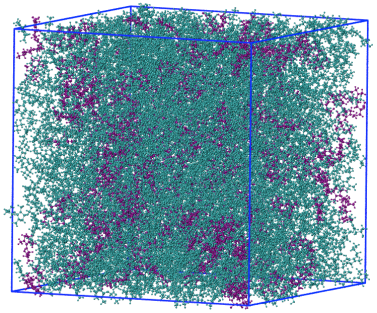
System (IPADM-2-BOL)	Experimental values (cP)	Calculated viscosities from MD (cP)
Pure (0% CO_2)	8	15
15% mol CO_2 loading	36	35
25% mol CO_2 loading	110	150
50% mol CO_2 loading	~3000[2]	>1000

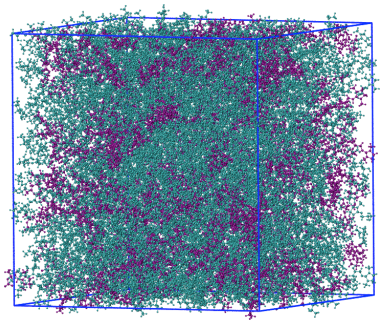
IPADM-2-BOL (0% CO_2)



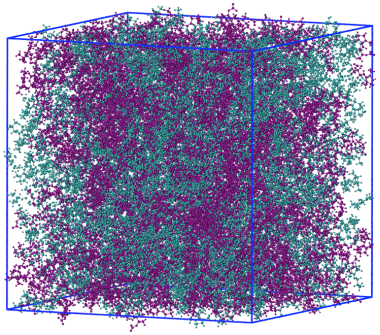
IPADM-2-BOL (15% CO_2)



IPADM-2-BOL (25% CO_2)



IPADM-2-BOL (50% CO_2)



[1]DJH et al. 2014, Energy Procedia 63, 8144-8152, in press. [2]ASPEN Plus projection

Molecular level interactions: Hydrogen bond

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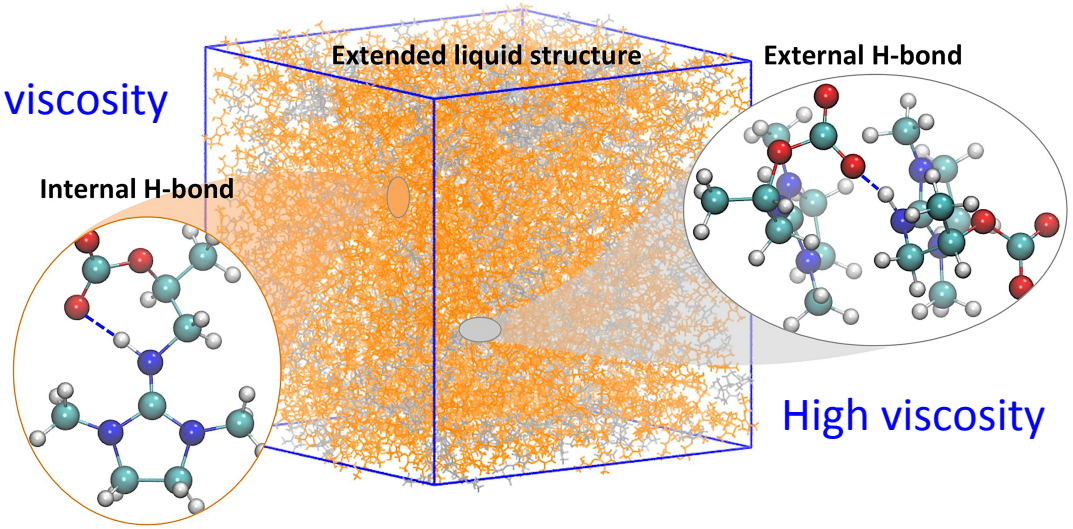
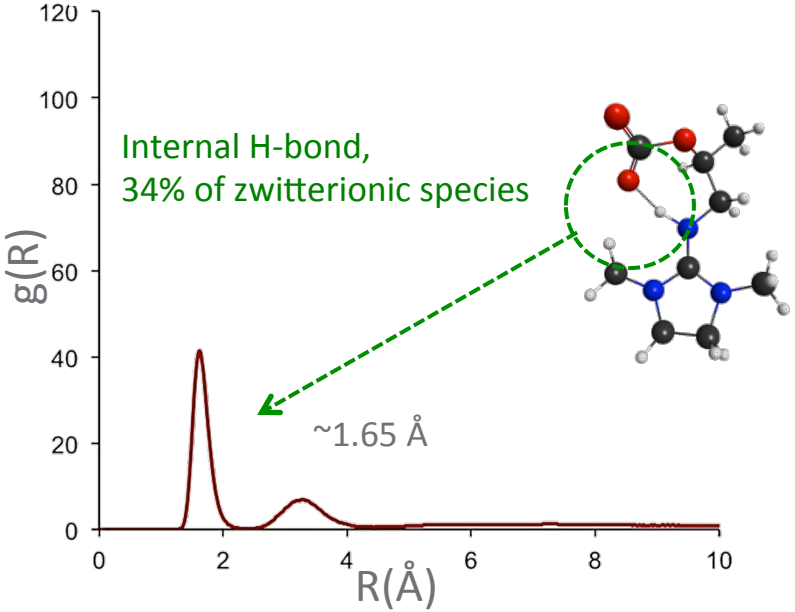
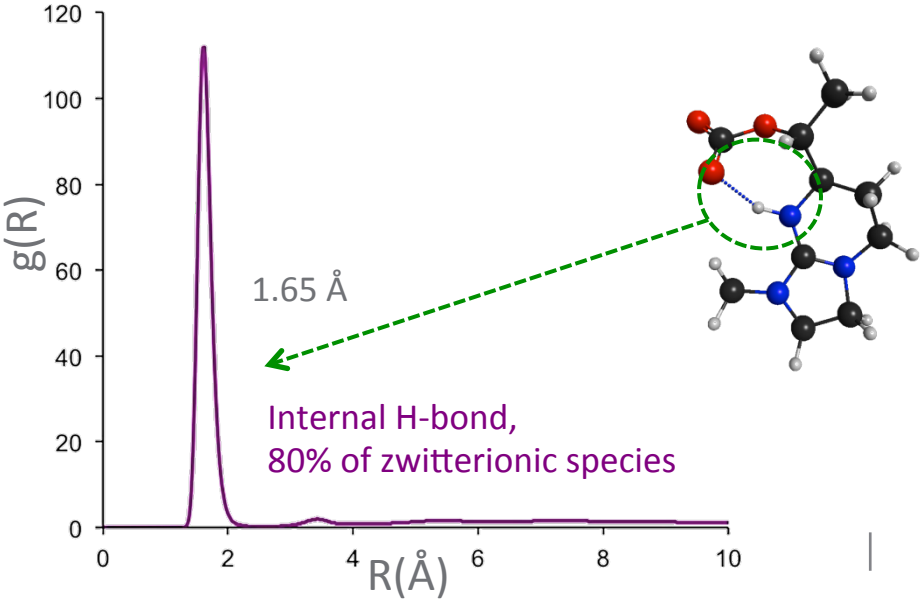


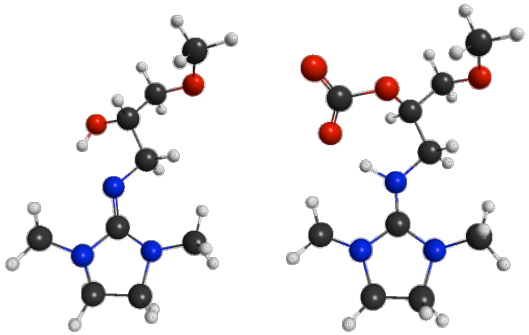
Advanced molecular design:
Locking in the internal H-bond (~80%)
Lower projected cP at all CO_2 loadings
At 50%: KOL >1500 cP
VOL ~800 cP



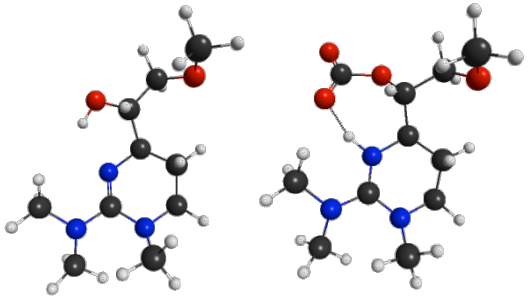


Molecular modifications that have deliberate effect on viscosity

- Ether groups close to the CO_2 binding site increase the % of zwitterionic molecules with internal hydrogen bonds in Koechanol.
- MD predicts a 30% reduction in the viscosity of ether Koechanol compared to Koechanol, both at 25% mol CO_2 loading.
  - Koechanol (34% internal H-bond and 10% stacking) **150 cP**

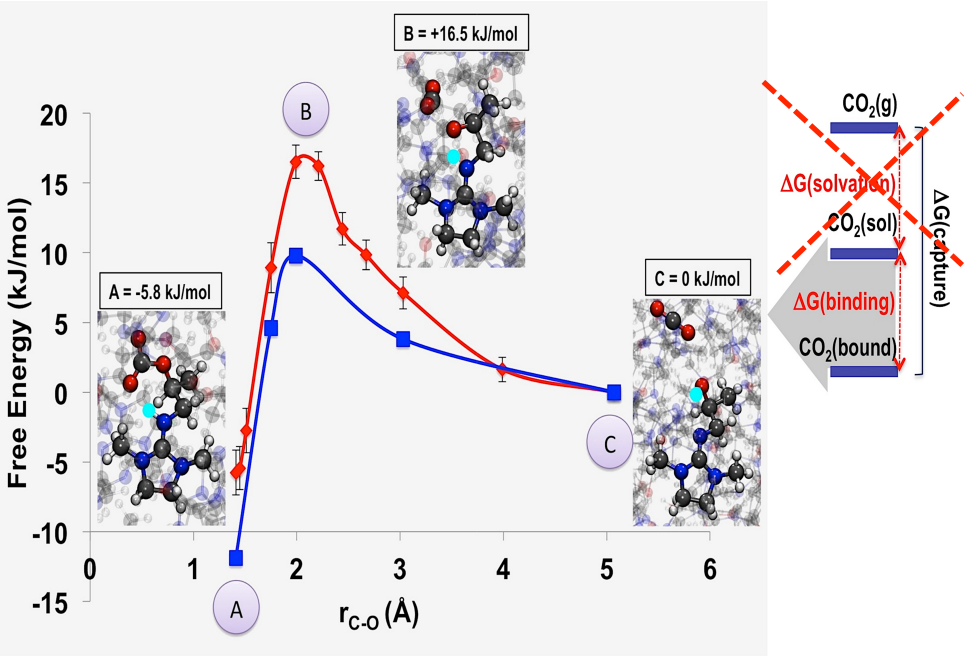


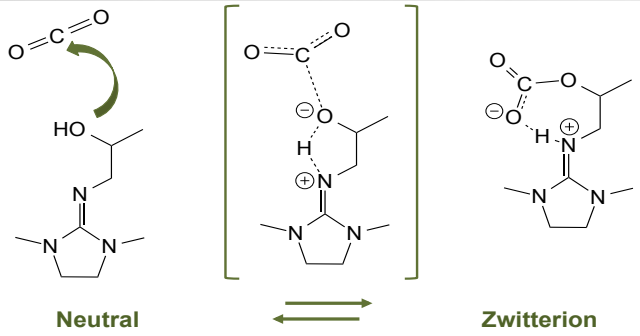
Ether Koechanol
(52% internal H-bond)
(9% stacking)
100 cP (MD)
exp. observation, lower than Koechanol

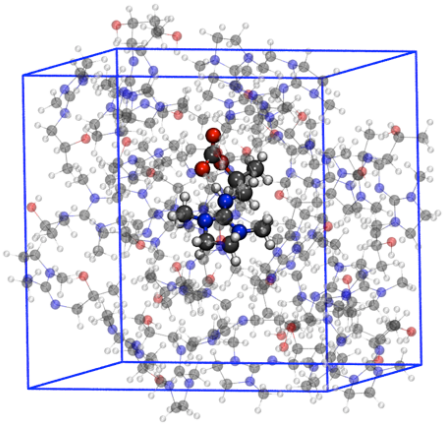


Ether open Vandanol
(61% internal H-bond)
(20% stacking)
120 cP

Towards a reduced model: thermodynamics of CO_2 binding



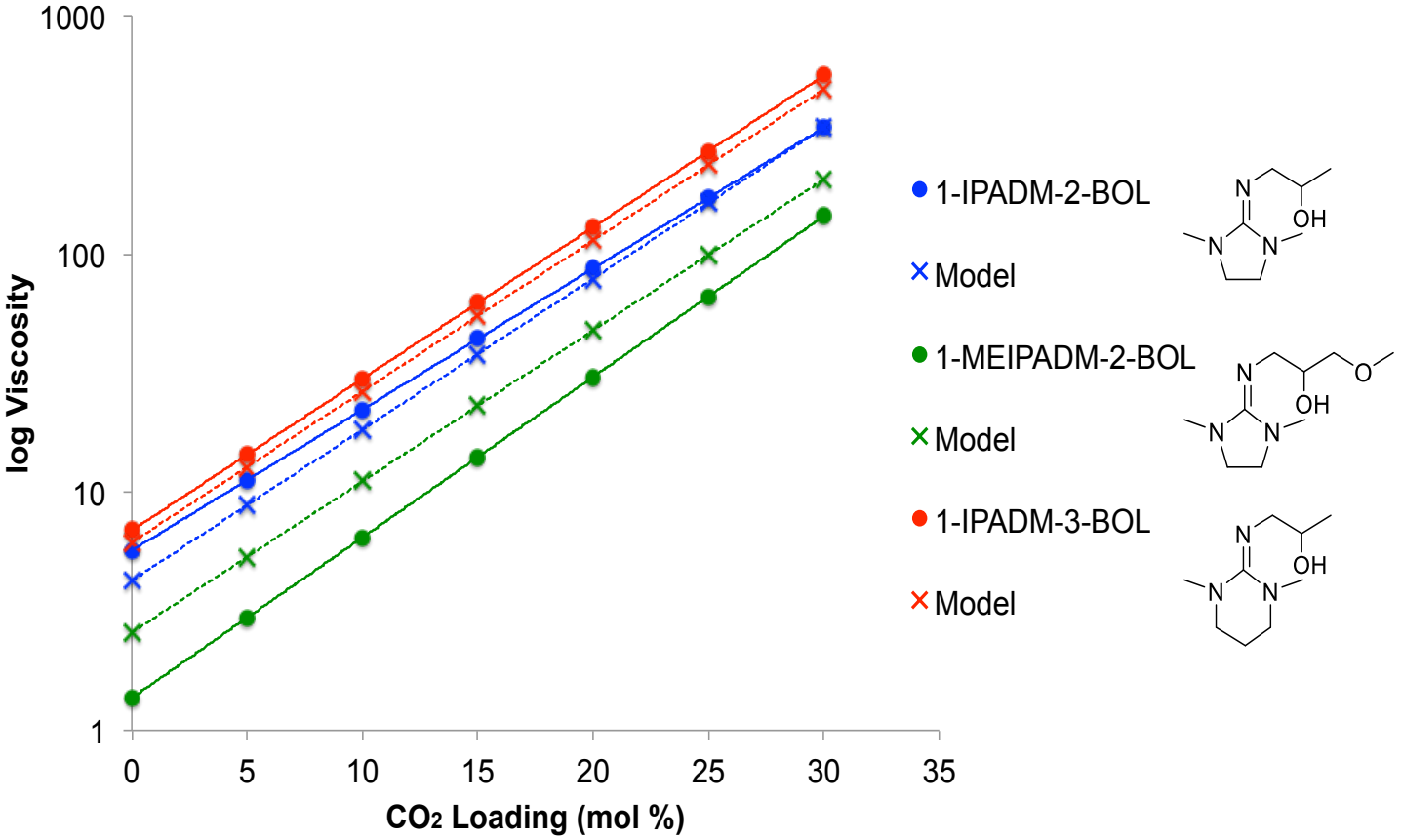




- CO_2 binding free energy, optimally ca -15 to -20 kJ/mol
- Red line is binding free energy from blue moon dynamics, blue line is ΔE from AIMD
- Confirmation of the equilibrium from NMR data

1. *D. C. Cantu et al. J. Phys. Chem. Lett., 2016, 7 (9), pp 1646–1652*
2. *Mathias PM et al. (2015) ChemSusChem , 8, 3617-3625.*

Viscosity dependency on loading



- Exponential dependency on loading.
  - Dependence confirmed by MD and experiment

Reduced Model: Explicit H-Bonding

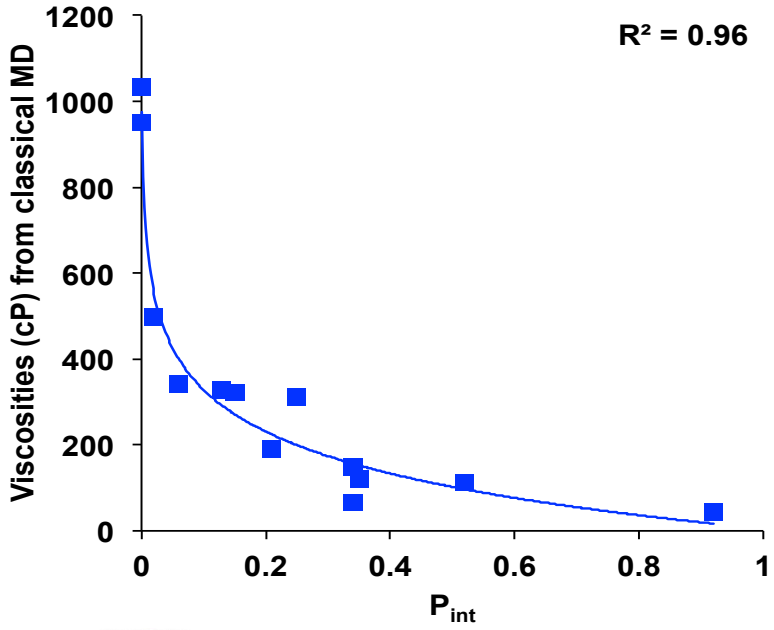
$$\eta = c_1 \ln\left(\frac{P_{int}}{1 - P_{int}}\right) \exp\left(c_2 L\right)$$

From MD or DFT

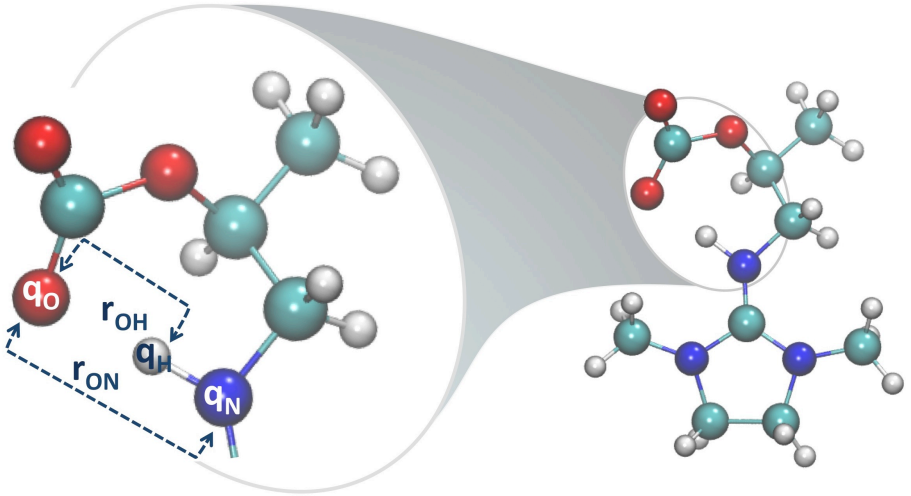
$$P_{int} = aX + b$$

From DFT
(ESP charges)

$$X = \frac{q_N q_O}{r_{NO}} + \frac{q_O q_H}{r_{OH}} + \frac{q_N q_H}{r_{NH}}$$

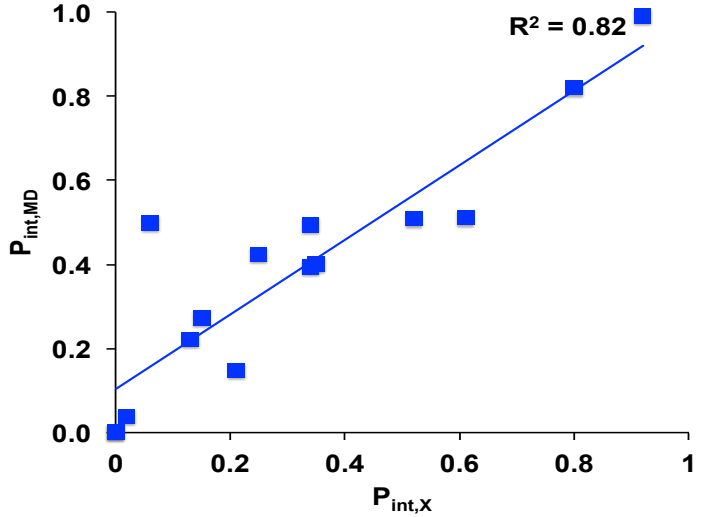


- If $\mathbf{r_{O\text{-}H}} > 2.0$ Å, then $\mathbf{P_{int}} = 0.001$
- If $\mathbf{r_{O\text{-}H}} < 2.0$ Å, then
- Difference between electrostatic repulsion (NO) and attraction (OH)

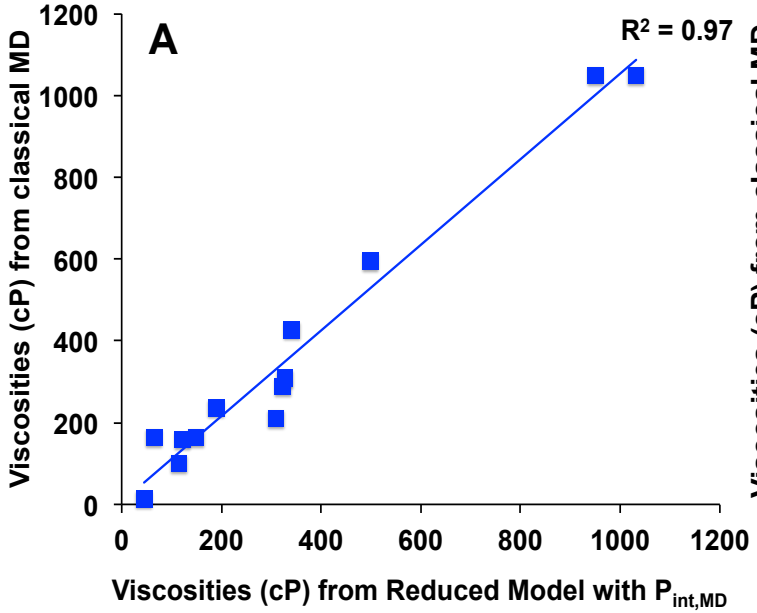


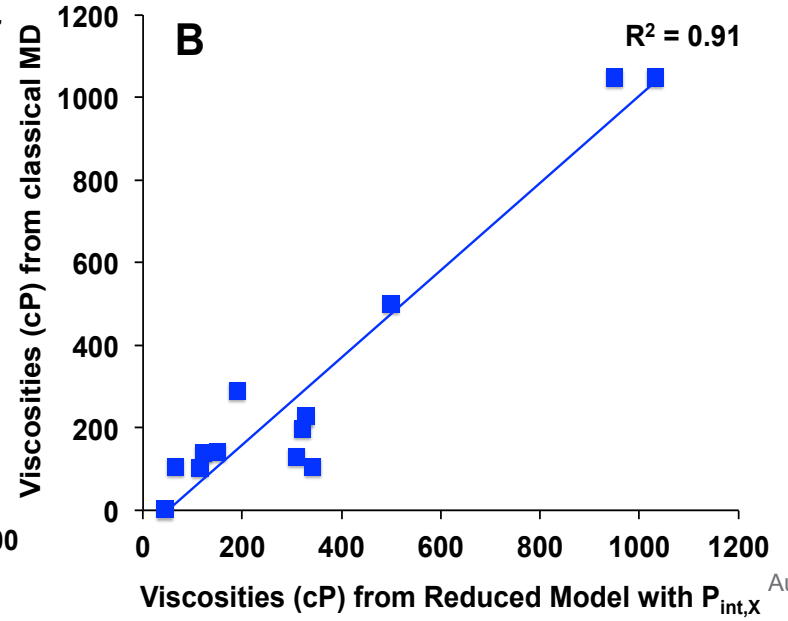
D. C. Cantu et al. submitted

Structure/Viscosity Correlations



- The reduced model recovers ~80% of the H-bonding determined by MD
- Over 90% of correlation between viscosity and H-bonding by either MD (A), or RM (B)



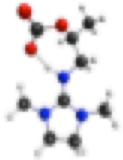


200 compounds screened computationally!

- First cycle: 200 compounds screened by molecular simulation and reduced models
  - Predicted viscosities
  - CO_2 binding energy
- Approximately 25 compounds by full MD of liquid state
- Down-selected to 5 best candidates for further investigation
  - Full MD to validate/tune reduced model
  - Synthetic targets

Molecules for computational screening

1. Based on the Koechanol scaffold:



Compound	R1	R2	R3	R4	R5
KOL	CH_3	CH_3	CH_3	H	H

Blanks = CH_3 in R1-R3, H in R4-5, for clarity

Ether-only Variants					
AKL		CH_2OCH_3	CH_2OCH_3		
BKL				CH_2OCH_3	CH_2OCH_3
CKL	CH_2OCH_3				
EKL		CH_2-O-CH_3			
IKL				CH_2OCH_3	
JKL	CH_2OCH_3			CH_2OCH_3	CH_2OCH_3
LKL				OCH_3	OCH_3
MKL	OCH_3				
OKL				OCH_3	
PKL	OCH_3			OCH_3	OCH_3
Fluoro-only Variants					
DKL		CH_2CF_3	CH_2CF_3		
FKL		CH_2CF_3			
GKL	CH_2CF_3				
QKL				CH_2CF_3	CH_2CF_3
RKL				CH_2CF_3	
SKL	CH_2CF_3			CH_2CF_3	CH_2CF_3
UKL		CF_3	CF_3		
VKL		CF_3			

Another 100 compounds screened in cycle-2

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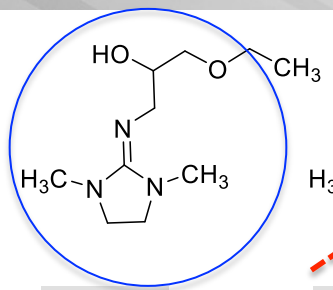

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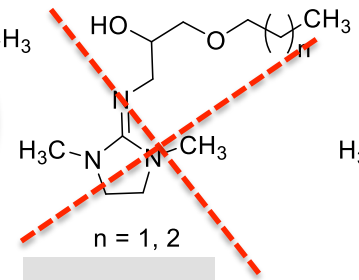

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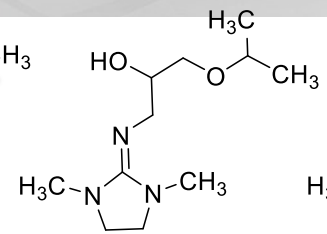

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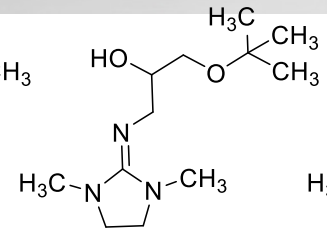

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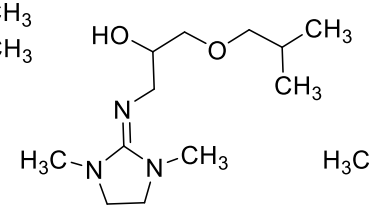

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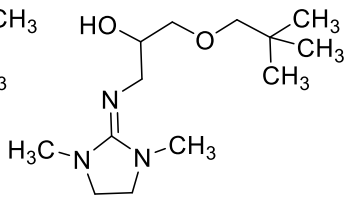

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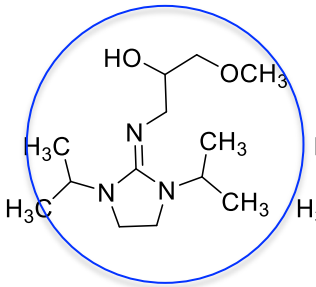

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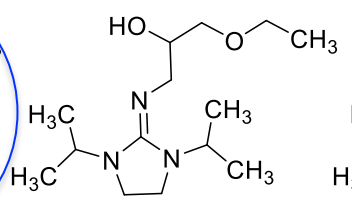

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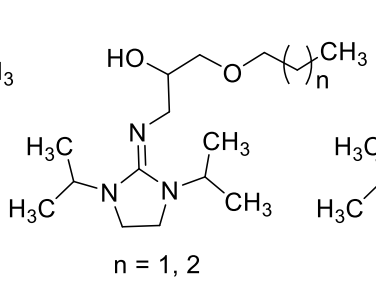
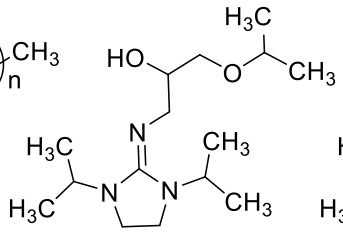


n/a, 14



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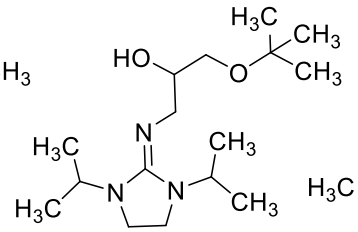

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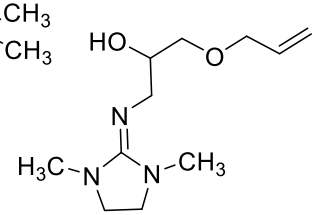

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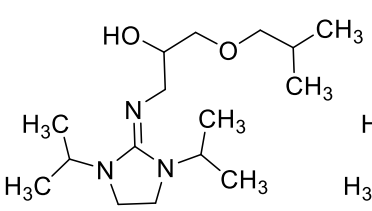

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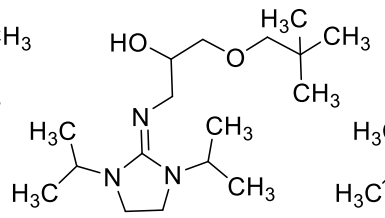

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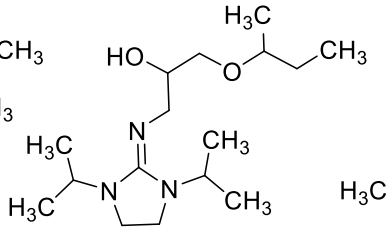

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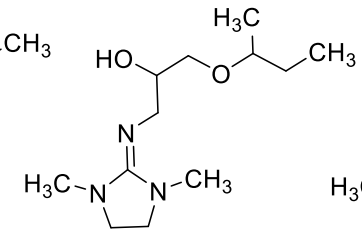

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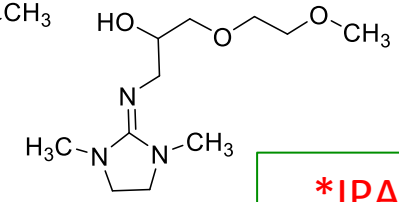
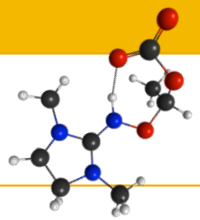
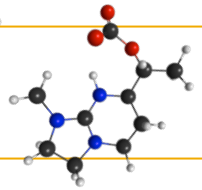
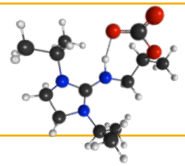
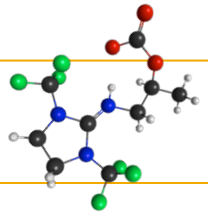
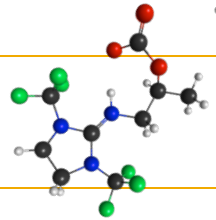


198

*IPADM-2-BOL = 150 cP

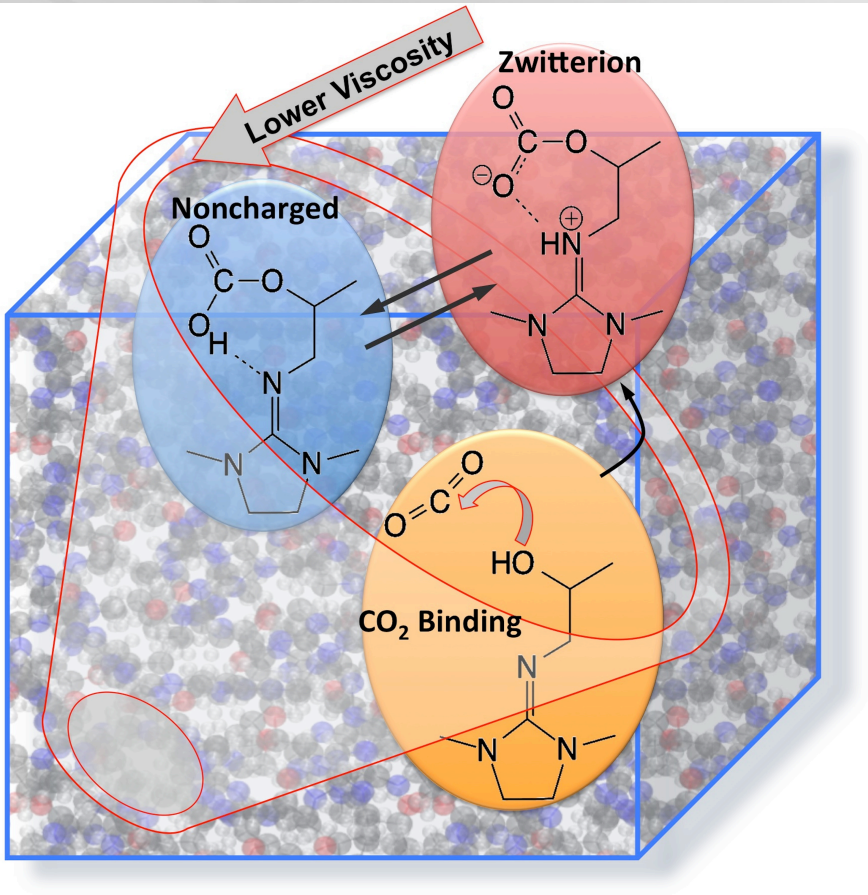
Best five candidates not exp. verified yet.

Compound	Pint Model Predicted	ΔΔE (kJ/mol) (CO_2 BE)	η (cP) (25%) Reduced
1 	92%	-1.2	12
2 	90%	-2.0	15
3 	85%	-5.3	23
4 	83%	-7.3	27
5 	76%	-9.1	40

Viscosity of original IPADM-2-BOL at 25% ~150 cP

ΔΔE computed relative to IPADM-2-BOL

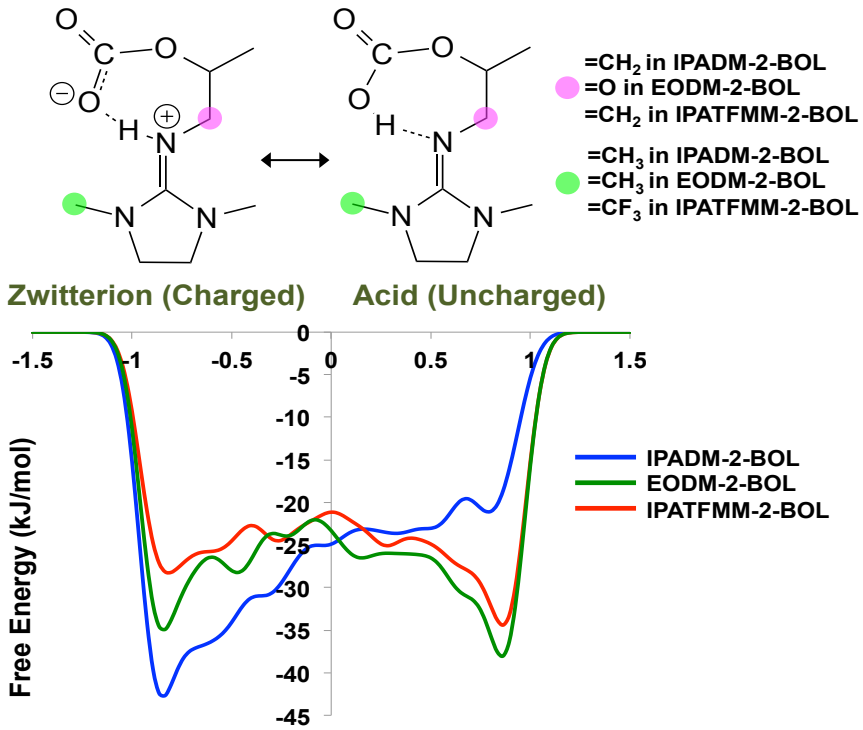
Novel insight from MD: Neutral capture



- Dynamic equilibrium between Zwitterion and its acid equivalent

D. C. Cantu et al. J. Phys. Chem. Lett., 2016, 7 (9), pp 1646–1652

Theoretical suggestion: Non-ionic CO_2 capture solvent systems

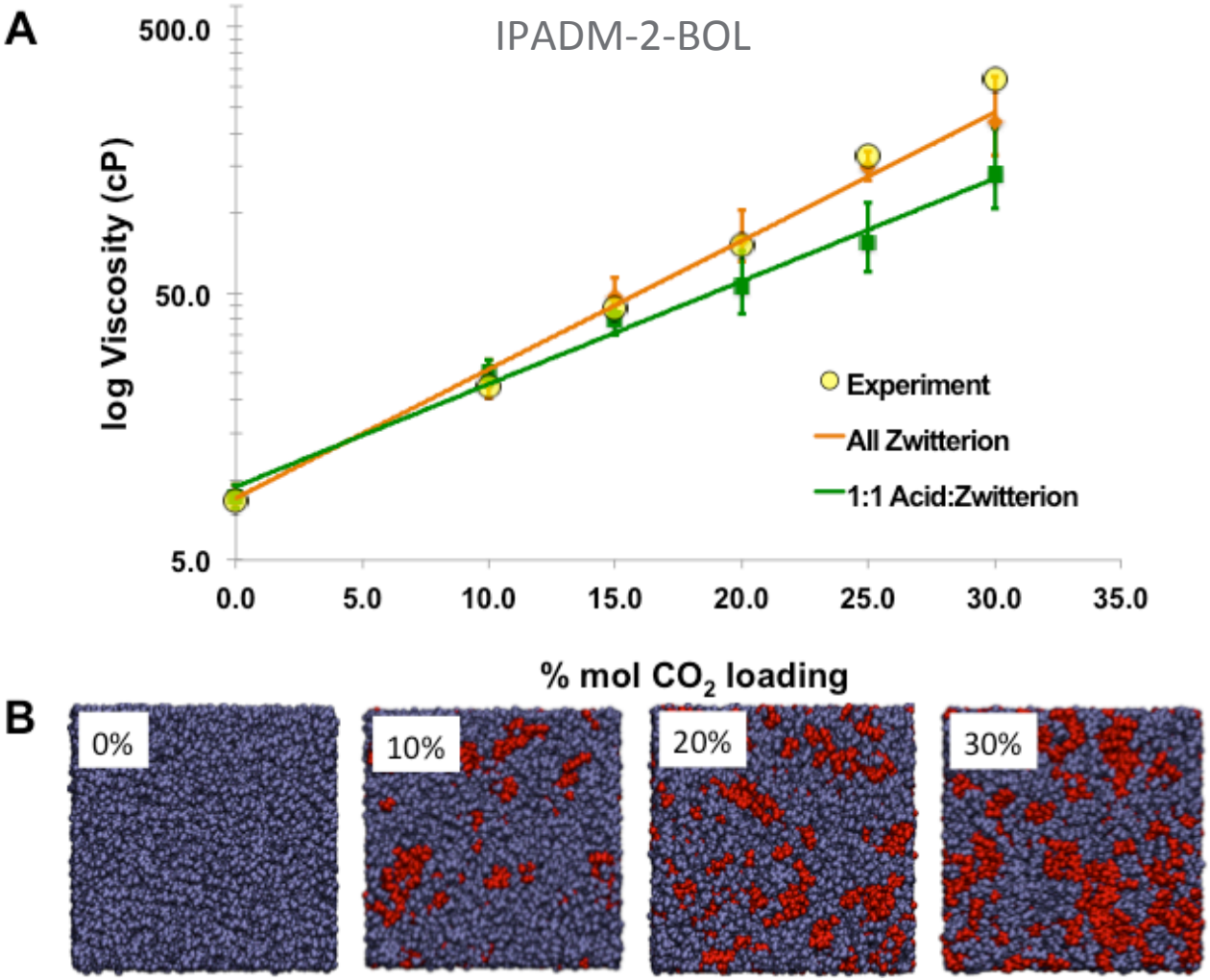


- We determined the acid-base equilibrium of several model CO_2BOL systems.
  - We found that we can modify the electronic structure of the molecule to shift the equilibrium towards a neutral CO_2 binding species.
  - Preliminary data of viscosities from classical MD simulations indicate significant improvement

25% mol CO_2 loading	IPATFMM-2-BOL Viscosity (cP)	EODM-2-BOL Viscosity (cP)
All zwitterion	328.5 *+415.4 -117.7*	45.5 *+8.0 -5.9*
1:1 acid:zwitterion	214.2 *+45.0 – 31.7*	17.9 +1.9 -1.6
All acid	137.9 *+21.3 -16.3*	14.2 +0.7 -0.6

D. C. Cantu et al. J. Phys. Chem. Lett., 2016, 7 (9), pp 1646–1652

Neutral capture is more impactful at higher loadings



The same principles apply to different solvents: Class 2 GE solvents

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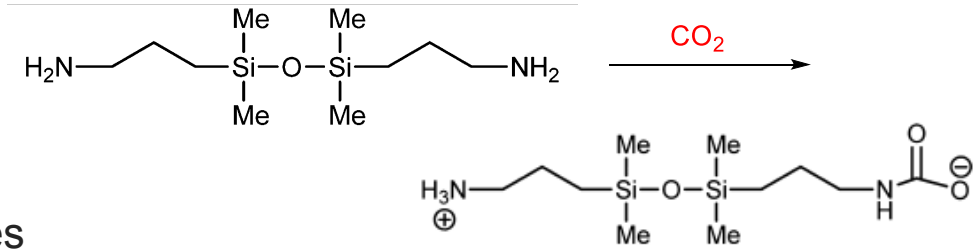
- Model validation
- GAP class of solvents
- CO_2 loadings (mol %): 0, 25, 50
- **Densities** at 40, 80 and 120 °C
- Heterogeneous solvent: different phases



Zwitterion

System	Density at 40 C	Density at 80 C	Density at 120 C
GAP-0/TEG 0% CO2	975.5 kg/m^3	932.7 kg/m^3	884.6 kg/m^3 exp: 844.2 (5% error)
GAP-0/TEG 25% CO2	992.5 kg/m^3	952.3 kg/m^3	906.6 kg/m^3
GAP-0/TEG 50% CO2	1008.7 kg/m^3	970.6 kg/m^3	927.4 kg/m^3
GAP-1/TEG 0% CO2	969.0 kg/m^3 exp: 1000.1 (4% error)	917.9 kg/m^3 exp: 982.7 (7% error)	869.5 kg/m^3 exp: 859.8 (1% error)
GAP-1/TEG 25% CO2	983.7 kg/m^3	939.2 kg/m^3	892.7 kg/m^3
GAP-1/TEG 50% CO2	1003.6 kg/m^3	960.8 kg/m^3	915.8 kg/m^3

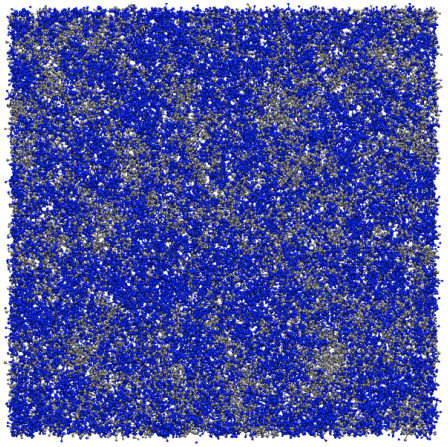
GAP solvent structure

- CO_2 loadings (mol %): 0, 25, 50
- **Preliminary viscosities** at 40 °C
- Also starting temperature dependence runs

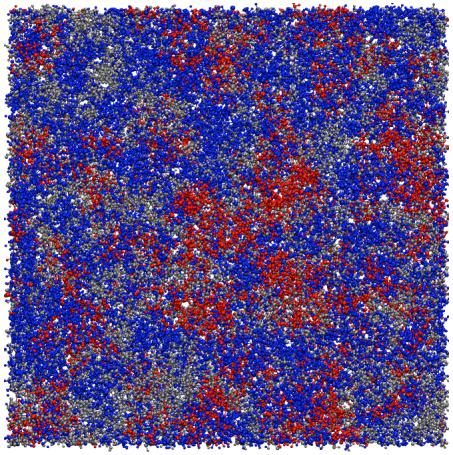
System at 40 C	0% mol CO2	25% mol CO2	50% mol CO2
GAP-0/TEG	26 +5/-4 cP	65 +14/-10 cP	154 +35/-24 cP
GAP-1/TEG	9 +1/-1 cP (exp: ~19 cP)	51 +23/-11 cP (exp: ~ 90 cP)	*

*: in progress

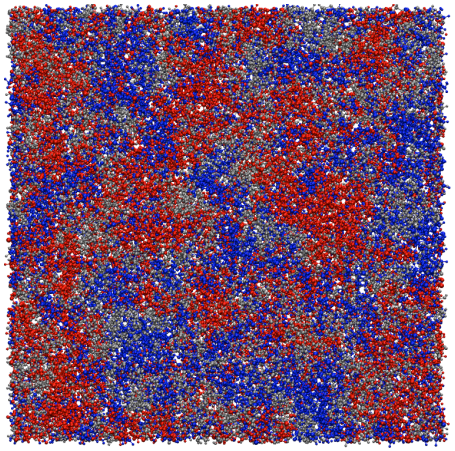
- Heterogeneous solvent structure



GAP-0/TEG 0% CO_2



GAP-0/TEG 25% CO_2



GAP-0/TEG 50% CO_2

CO_2-GAP-0: red
GAP0: blue
TEG: silver

As in Ionic Liquids, H-bonds between RNH_2^+---^-OOCN are present in the extended liquid structure

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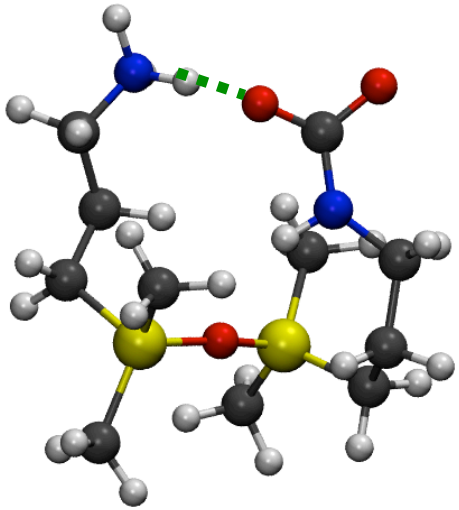
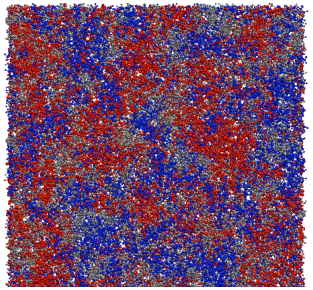
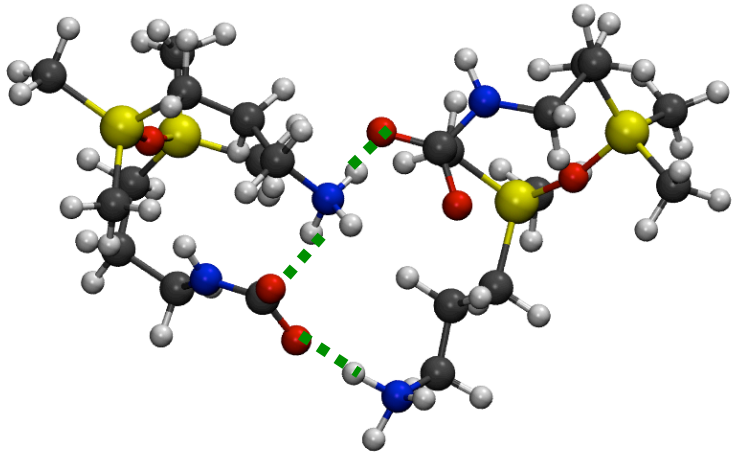
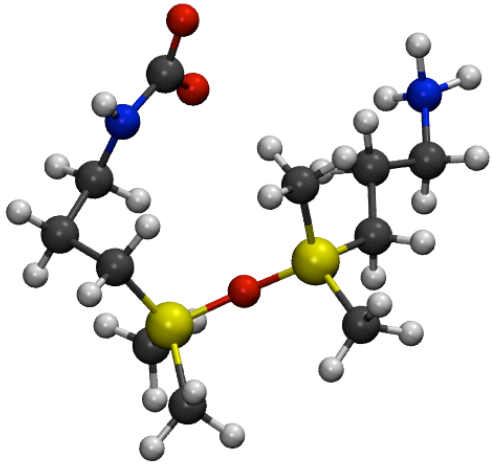
- GAP-0 in TEG (40% wt)
- CO_2 loadings (mol %): 0, 25, 50
- Because CO_2-loaded molecules cluster, they form strong H bonds (RNH_2^+ to $NCOO^-$) within the molecule, and with other molecules



"Closed" conformation
H-bond within molecule





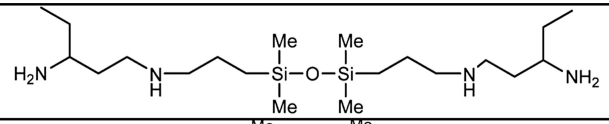
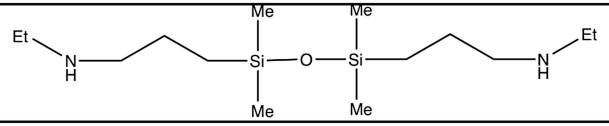
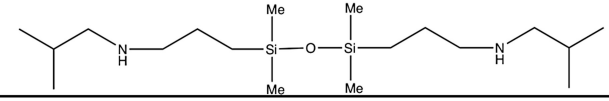


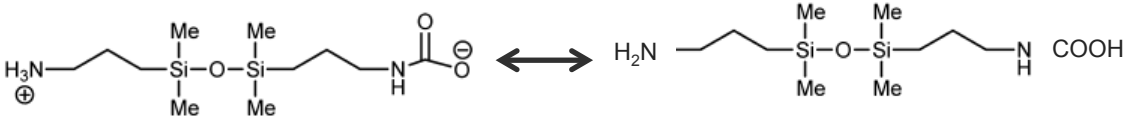
"Open" conformation
No H-bond within molecule

H-bonds present between one "closed" CO_2-GAP-0 and one "open" CO_2-GAP-0

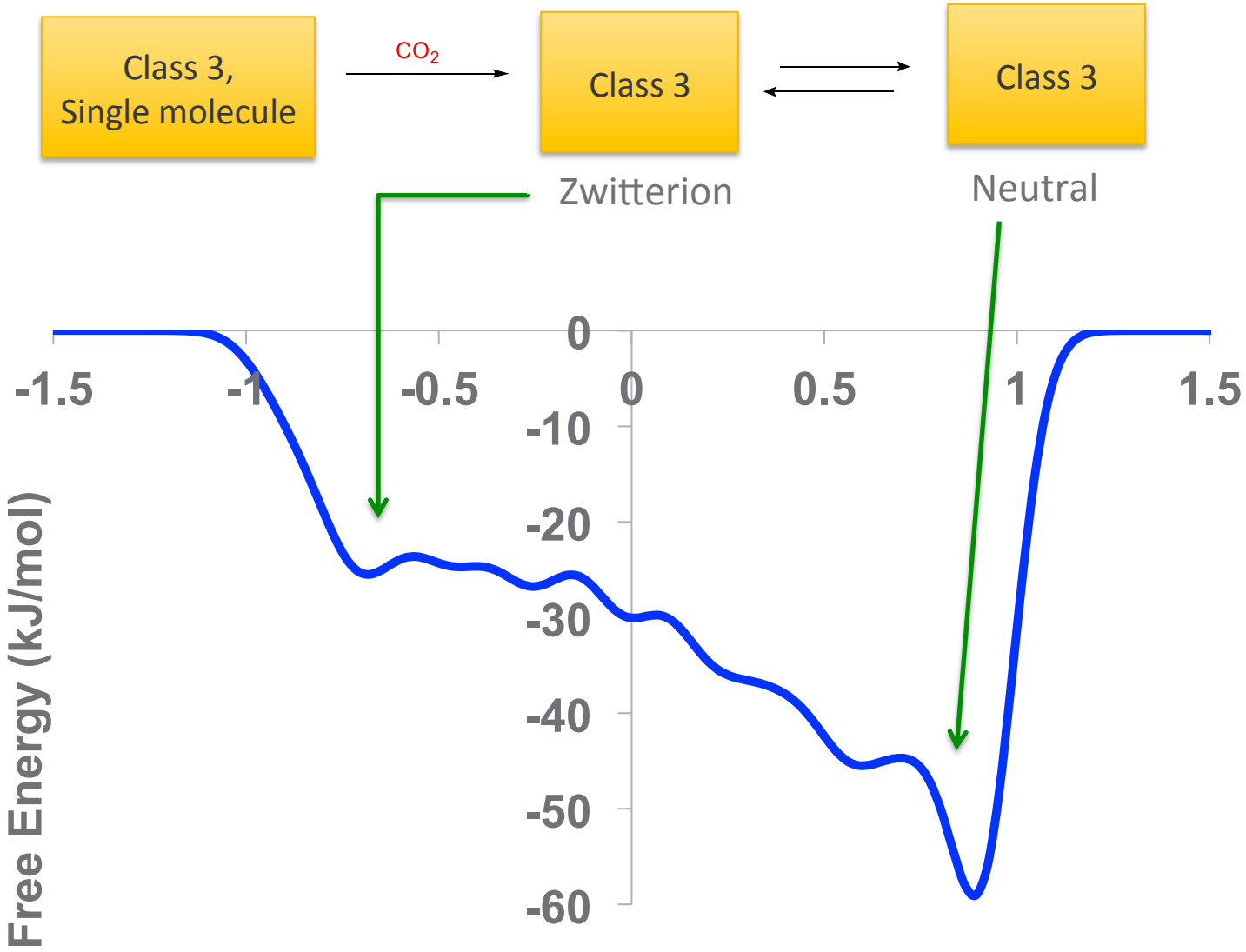
Screen 50 compounds for acid/base equilibrium

- Screen 50 compounds for CO_2-binding energy and acid/base equilibrium
- Known and new compounds
- Acid/base properties of 14 compounds still running or being double checked
  - Preliminary data presented here

Compound	Structure	Acid/Base Eq ΔE(A-Z) in kJ/mol Keq=[A]/[Z] at 40 °C	CO_2 Binding Within 25 kJ/mol of the CO_2 binding energy of GAP-0 or GAP-1
GAP-Dytek		-4.6 ~5/1	Yes
GAP-Et		+41.5 all zwitterionic	Yes
GAP-Ib		-8.2 ~23/1	Yes



Design principles for neutral capture apply in new solvent class (PNNL, patent pending)



Equilibrium strongly shifted towards the neutral

Three different classes of compounds, a common behavior

Aminopyridines

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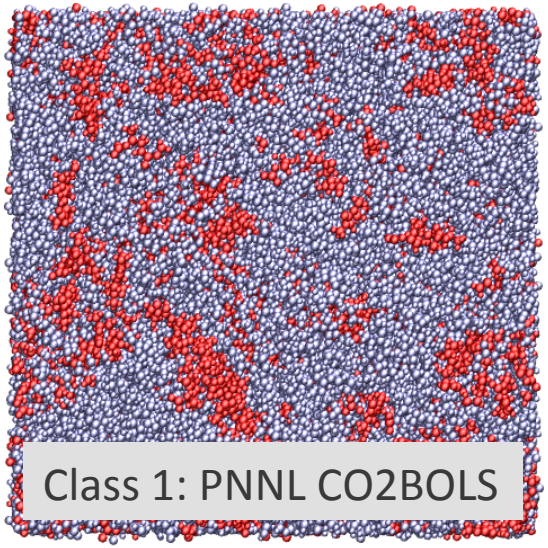
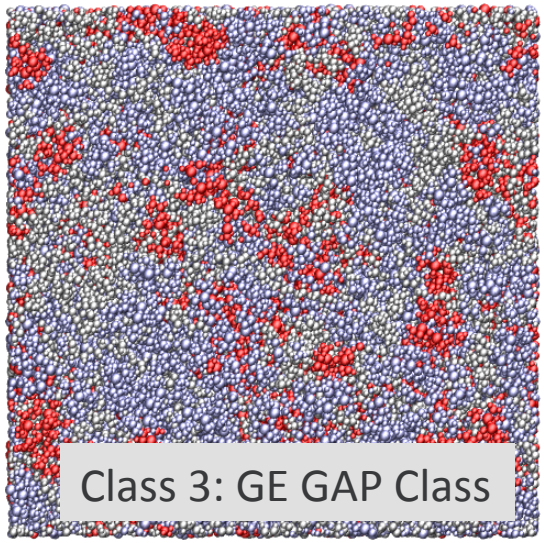
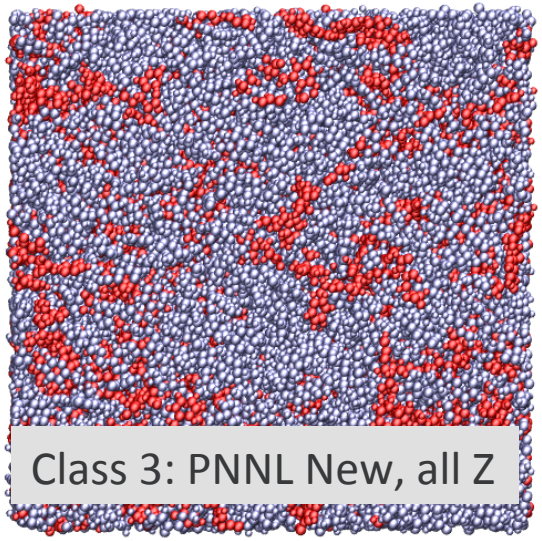


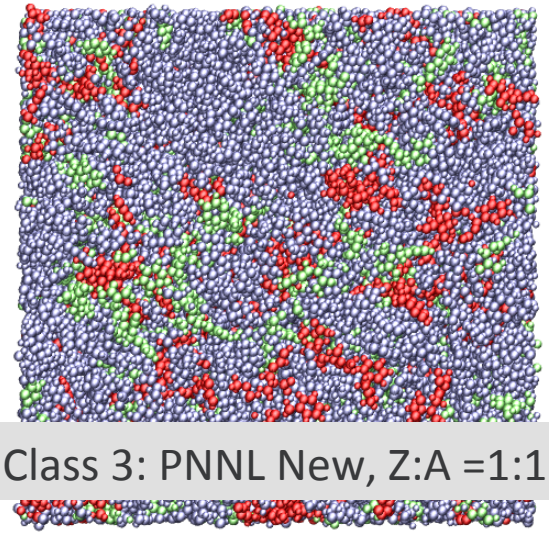
Class 1: PNNL CO2BOLS



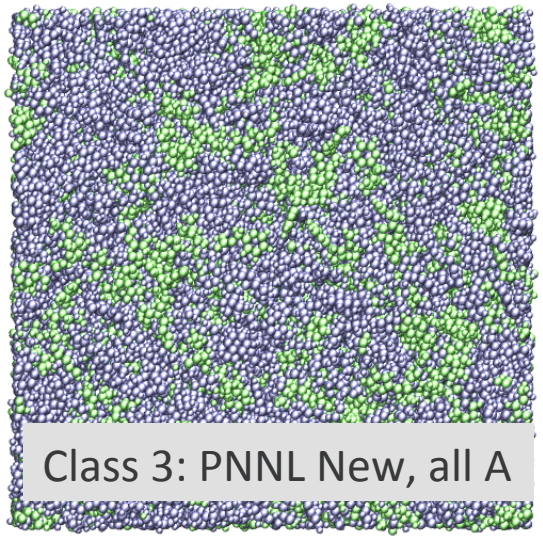
Class 3: GE GAP Class



Class 3: PNNL New, all Z

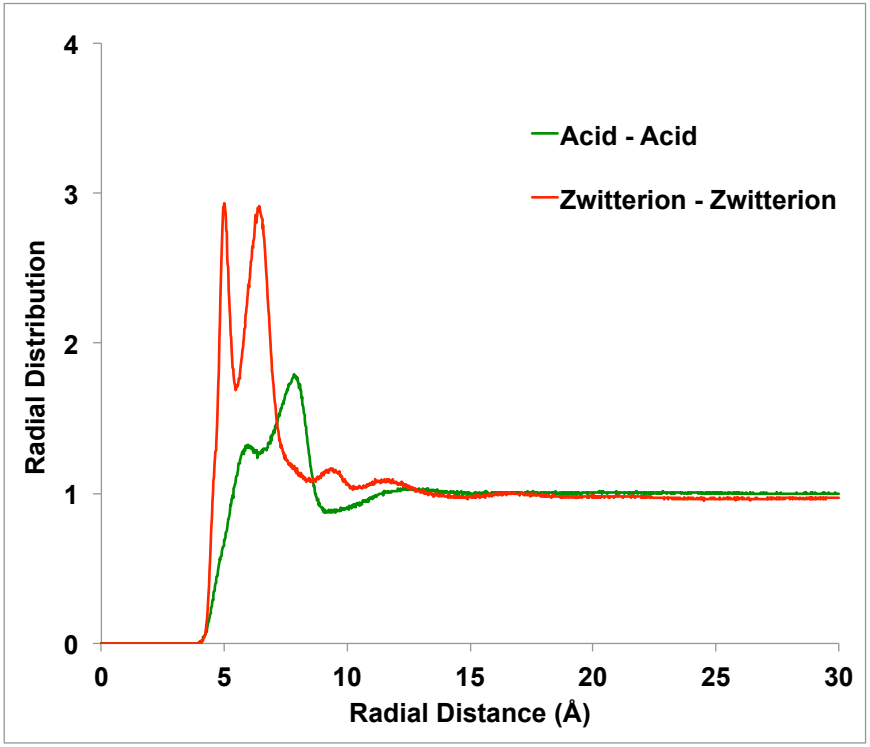


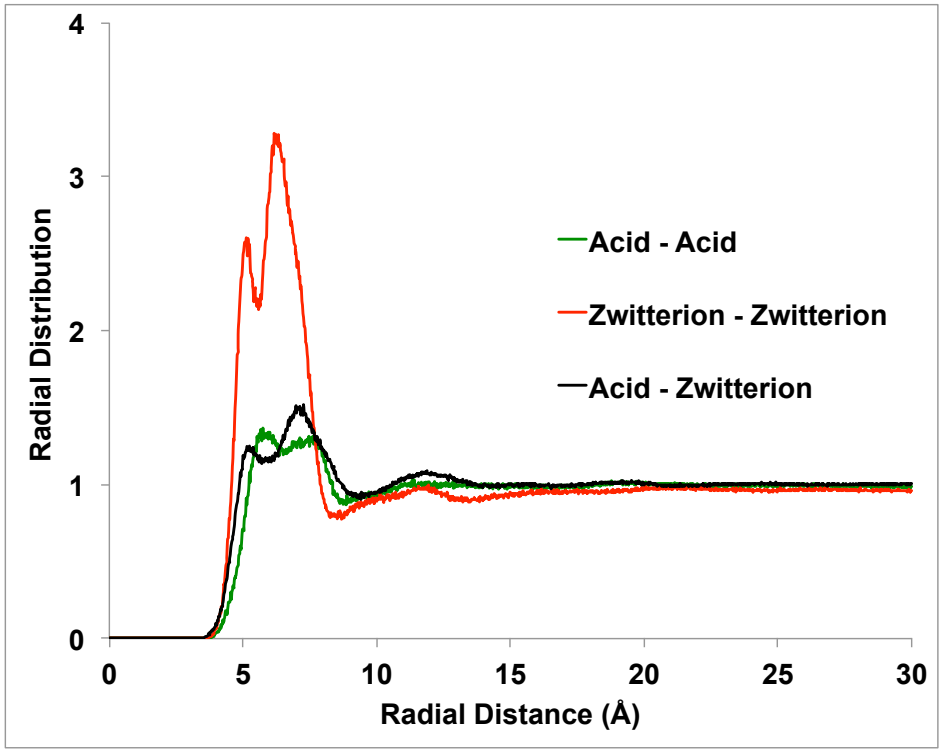
Class 3: PNNL New, Z:A =1:1

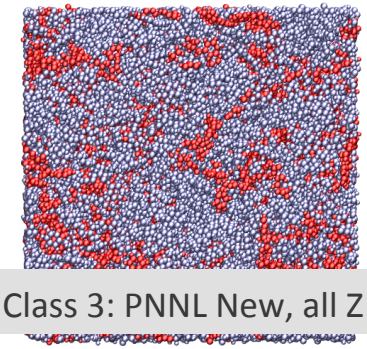


Class 3: PNNL New, all A

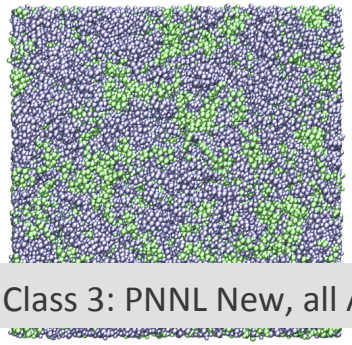
Class 3: PNNL new system



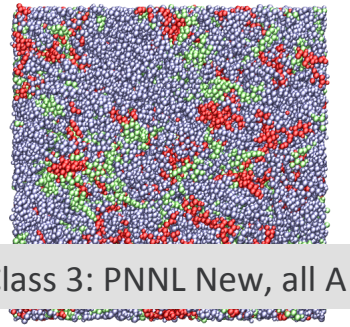




Class 3: PNNL New, all Z

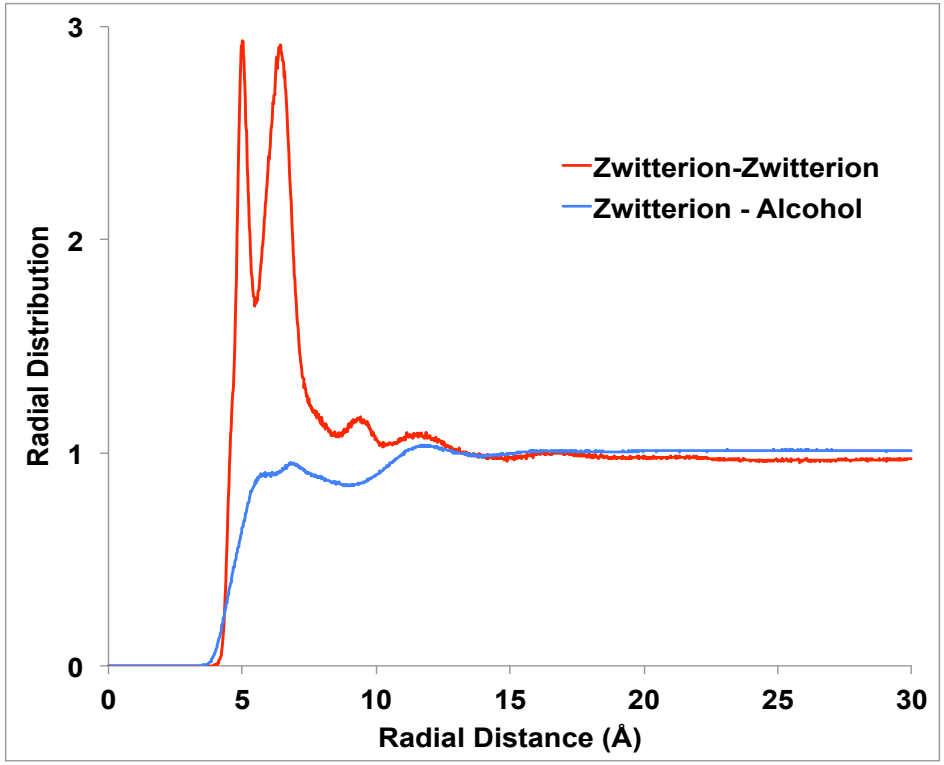


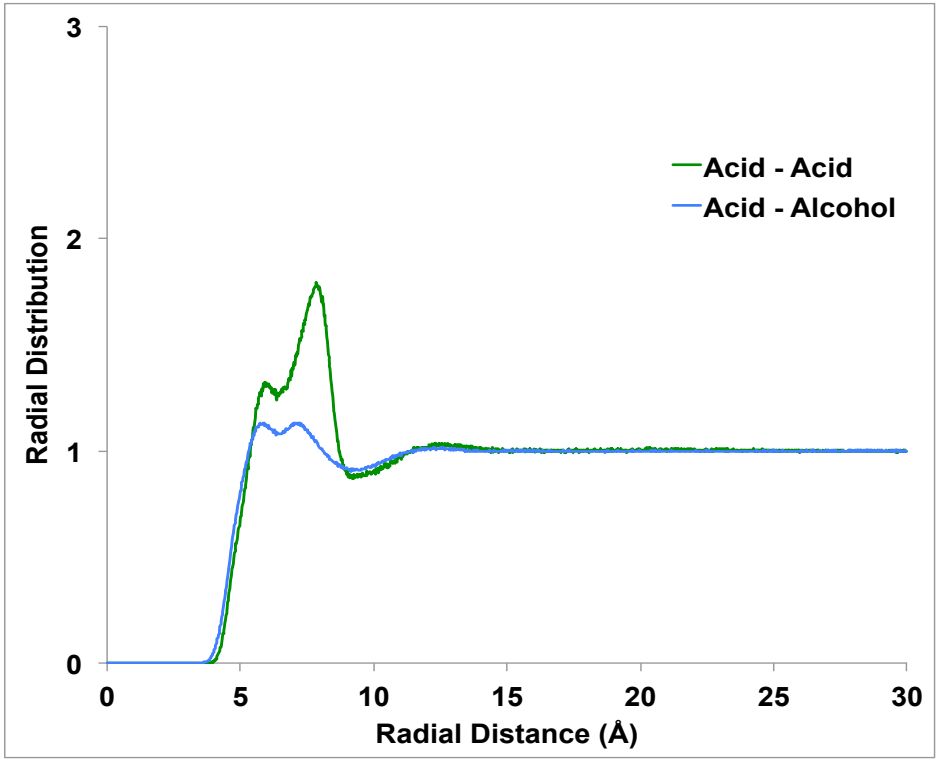
Class 3: PNNL New, all A

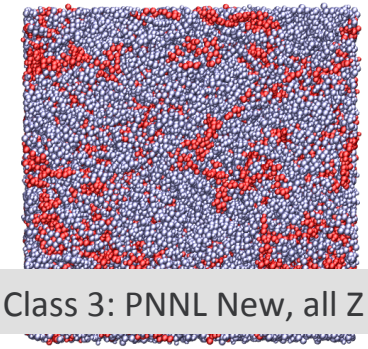


Class 3: PNNL New, all A

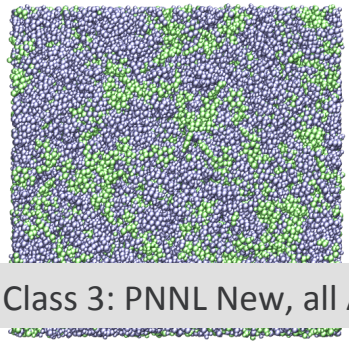
Class 3: PNNL new system







Class 3: PNNL New, all Z



Class 3: PNNL New, all A

Summary

- Molecular simulations were used to identify the critical structure property factors that affect viscosity in three different classes of CO_2 capture solvents:
  - Class 1, PNNL CO2BOLs
  - Class 2, GE GAP solvents
  - Class 3 PNNL new single component solvents
- A reduced order model was constructed that can be used for quick and reliable screening
  - Can be adjusted to fit other classes
- Novel insights pointing at neutral capture have the potential of drastic viscosity reductions in all classes of solvents

THANK YOU FOR YOUR ATTENTION!