Molecular Simulations for Improved Process Modeling of an Acid Gas Removal Unit

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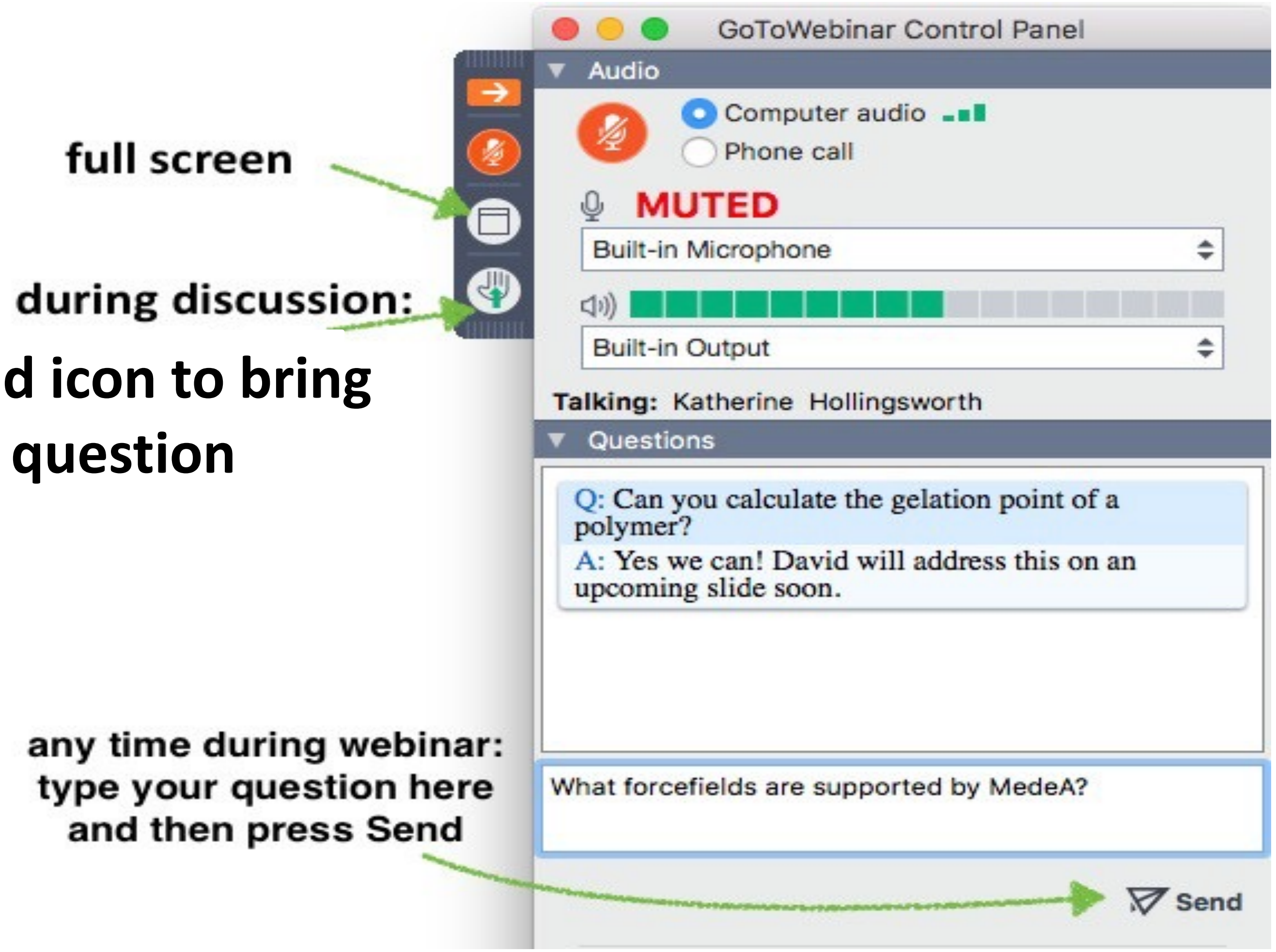

full screen

during discussion:

any time during webinar:
type your question here
and then press Send

● Computer audio
○ Phone call

MUTED

Built-in Microphone

Built-in Output

Talking: Katherine Hollingsworth

Q: Can you calculate the gelation point of a polymer?

A: Yes we can! David will address this on an upcoming slide soon.

What forcefields are supported by MedeA?

Webinar Speakers

Katherine Hollingsworth
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Xavier Rozanska
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CCUS Project Supported and Funded by TotalEnergies

- Lead Scientist and Corresponding author at TotalEnergies SE:

Frédérick de Meyer – frederick.de-meyer@totalenergies.com

- Total Exploration Production Development and Support to Operations Liquefied Natural Gas – Acid Gas Entity, CCUS R&D Program, 92078 Paris, France
- Centre de Thermodynamique des Procédés (CTP), 77300 Fontainebleau, France

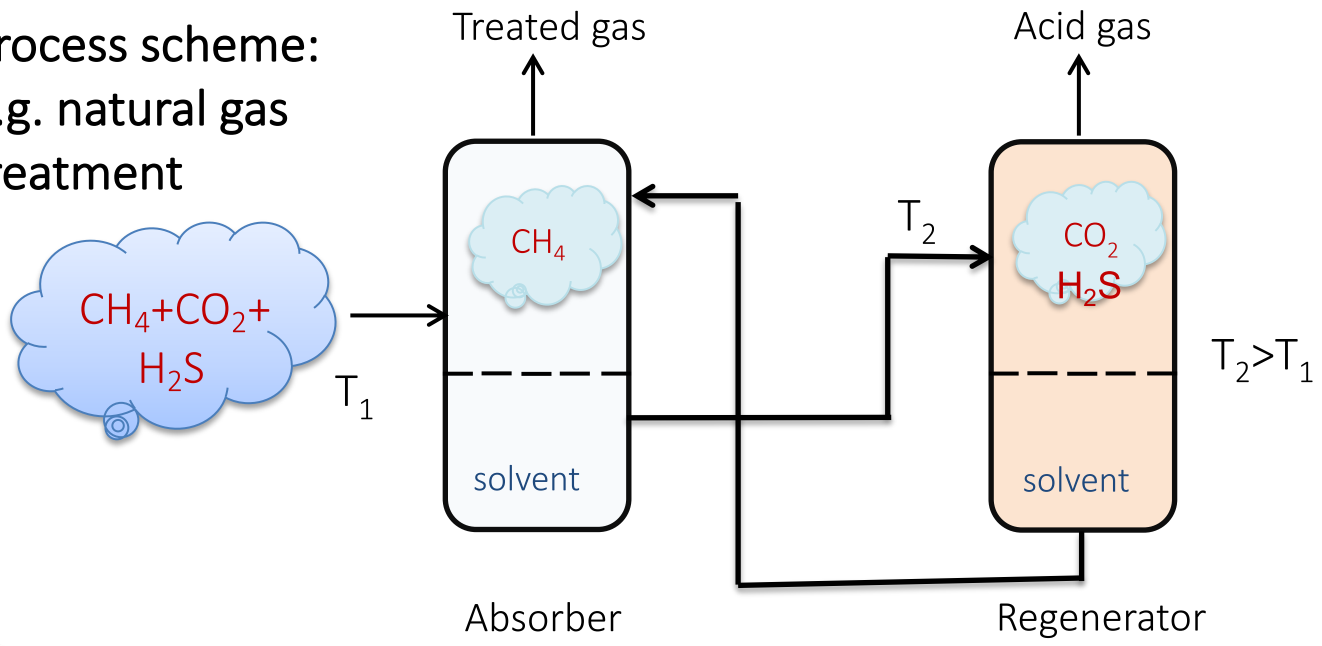
Oral contribution in ESAT (2021)

Manuscript (in preparation)

CO_2 capture

- Net-zero emission targets, consistent with the Paris Agreement
- Carbon capture technologies: absorption (most mature technology), adsorption, cryogenic.
- Need for better solvents: lower energy consumption, lower amine degradation, faster kinetics, higher absorption capacity, etc.

Process scheme: e.g. natural gas treatment


Treated gas

Acid gas

$CH_4+CO_2+H_2S$

T_1

CH_4

T_2

CO_2 H_2S

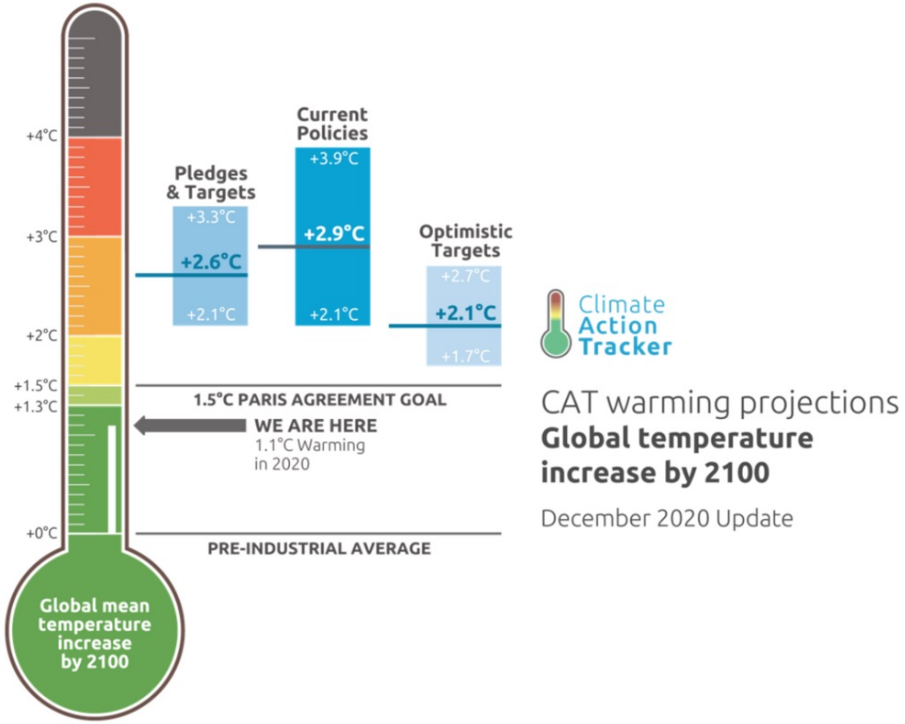
$T_2>T_1$

solvent

solvent

Absorber

Regenerator



CAT warming projections
Global temperature increase by 2100
December 2020 Update

Similar scheme for flue gas treatment

Finding optimum solvents for acid gas removal processes

- Need for large arrays of data related to acid gas absorption but also other physico-chemical properties of the solvents

- Challenges of experiments:
  - Cost
  - Reproducibility
  - Safety (e.g. H_2S)
  - Difficulty to perform under desired conditions (e.g. low acid gas partial pressures)
  - Difficulty to measure certain quantities (e.g. physical absorption properties in presence of reactions)
  - Underlying mechanisms – theoretical aspects
  - Large array of solvents / co-solvents
  - Availability of solvents / co-solvents

- How can simulations and molecular modeling help?

Property Calculation

Property	Property Symbol	Method used	Additional information
Vapor Liquid Equilibrium (VLE) • Density • Saturation Pressure • Vaporization Enthalpy	$\rho(T)$ $P_{sat}(T)$ $\Delta H_{vap}(T)$	MM (Monte Carlo)	FF: AUA+, TIP4P, EPM2, KL
Henry Solubility Constant	$k_H(P,T)$	MM (Monte Carlo)	FF: AUA+, TIP4P, EPM2, KL
Solubility		MM (Monte Carlo)	FF: AUA+, TIP4P, EPM2, KL
Viscosity	$\eta(P,T)$	MM (molecular dynamics)	FF: PCFF+
Diffusivity	$D(P,T)$	MM (molecular dynamics)	FF: PCFF+
Thermal Conductivity	$\lambda(P,T)$	MM (molecular dynamics)	FF: PCFF+
Surface Tension	$\gamma(P,T)$	MM (molecular dynamics)	FF: PCFF+
Reaction Thermochemistry	$\Delta E_r(0\ K)$, $\Delta H_r(T)$, $\Delta G_r(T)$	QM (energy minimization)	Ab initio DFT
Reaction Kinetics	$\Delta G^{\#}(T)$, $k(T)$, $r(T)$	QM & MM (molecular dynamics)	Ab initio DFT / FF: PCFF+

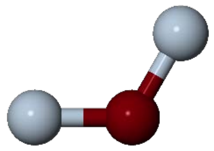
MM: molecular mechanics, QM: quantum mechanics, FF: ForceField

Solvents & Gas species studied

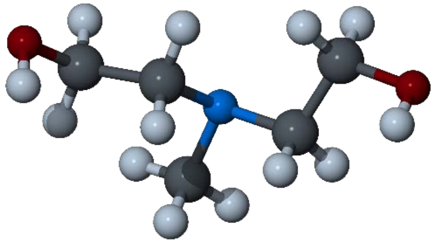
Solvents:

1. H_2O
2. MDEA (methyl diethanolamine)
3. Aqueous MDEA solution (30% wt)

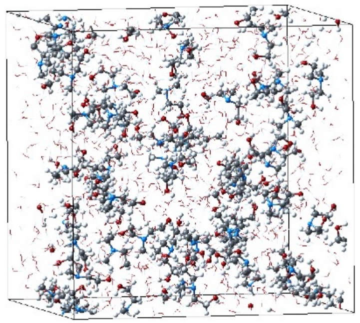
H_2O



MDEA



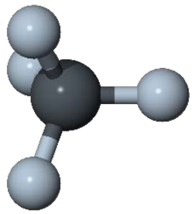
MDEA & H_2O



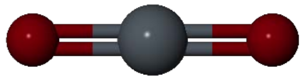
Gases:

1. Methane - CH_4
2. Carbon dioxide - CO_2
3. Hydrogen Sulfide - H_2S

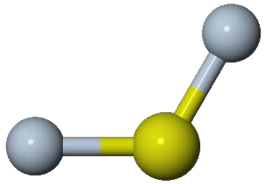
CH_4



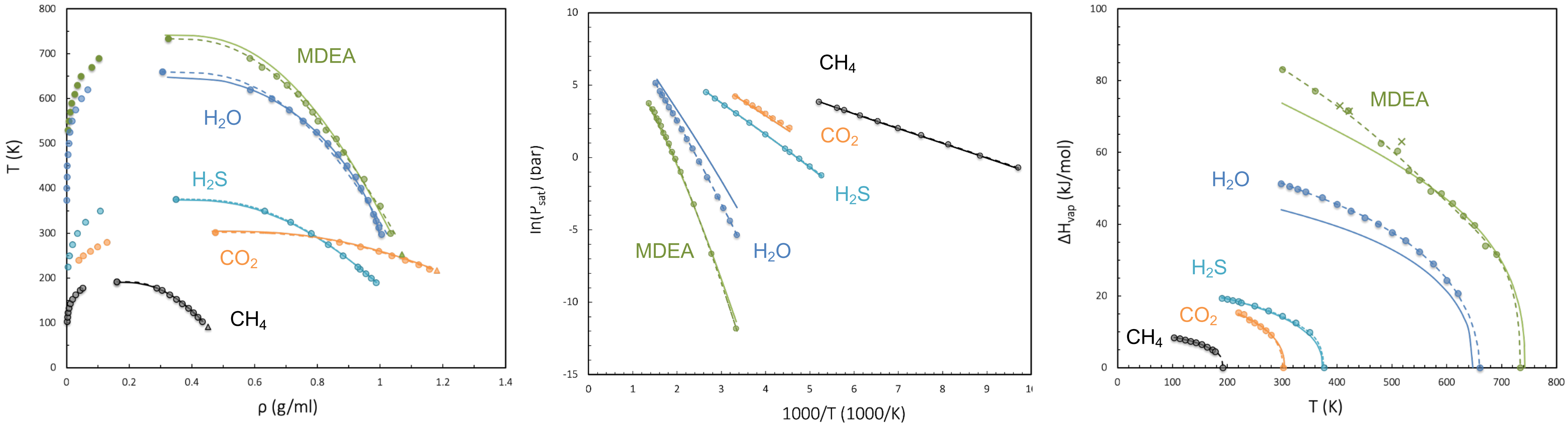
CO_2



H_2S



Vapor Liquid Equilibrium (VLE)



Monte Carlo simulations in the Gibbs Ensemble (*MedeA GIBBS*)

Full lines	(——):	fit to experimental data from NIST and DIPPR
Dashed lines	(------):	fit to simulation results
Circles	(●):	raw simulation results
x symbols	(×):	raw experimental data

- NIST: NIST Chemistry WebBook, SRD 69 https://webbook.nist.gov/chemistry/fluid/
- DIPPR: Wilding et al., Dippr project 801, FPE 150-151, p. 413 (1998)

Henry Solubility

- $K_{H,i} = \frac{f_i}{x_i}$

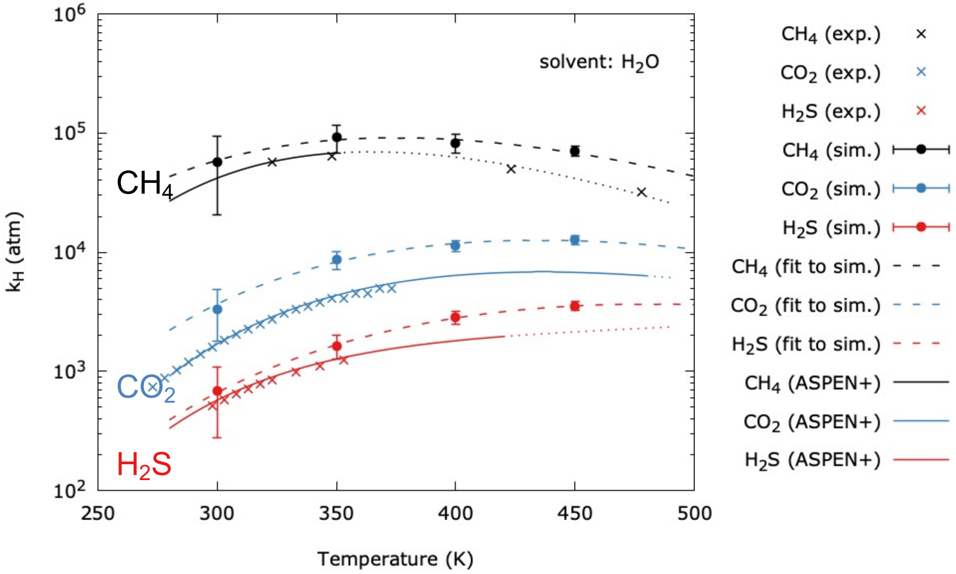
  where f_i is fugacity of the gas species i, computed for a concentration x_i in the solvent

- The **Henry Solubility Constant** refers to solubility only due to physical absorption
- The **Apparent Henry Solubility Constant** refers to apparent solubility due to both physical and chemical absorption

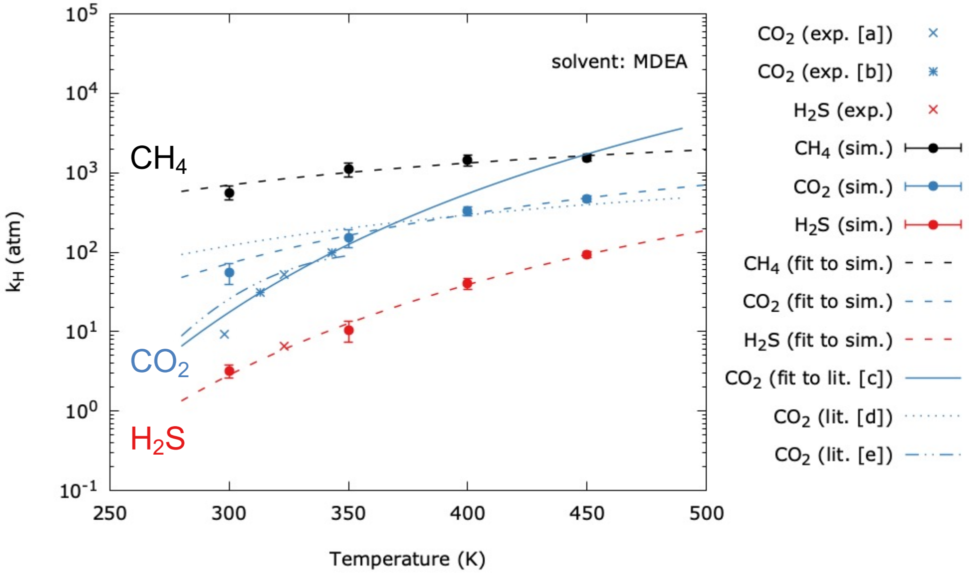
- **Simulations** provide: **Henry Solubility constants**
- **Experiments** (shown in the figures) provide: **Apparent Henry Solubility constants** – except if otherwise stated

Henry Solubility Constant

- Simulations accurately predict Henry solubility constants ranking and temperature dependence
- Semi-quantitative agreement is achieved (order of magnitude) for all three solutes in water



Monte Carlo simulations in the Gibbs Ensemble (*MedeA GIBBS*)



Monte Carlo simulations in the Gibbs Ensemble (*MedeA GIBBS*)

Left plot:

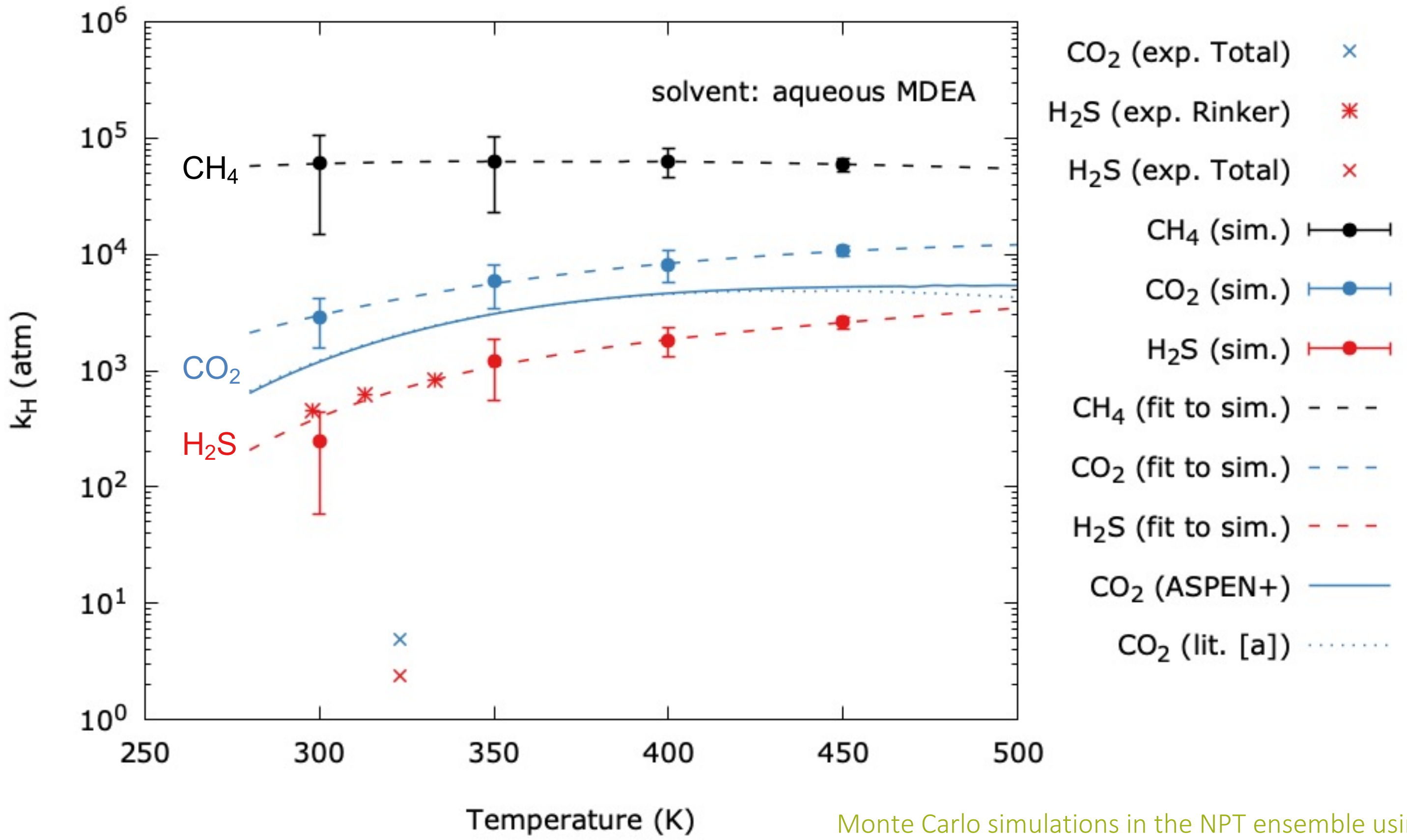
- Exp. data for CO_2/H_2S/ CH_4 from:
  - Gillespie *et al.*, Gas Processors Association. (1982)
  - Carroll *et al.*, J. Phys. Chem. Ref. Data 20, p. 1201 (1991); Crovetto *et al.*, J. Phys. Chem. Ref. Data 20, p. 575 (1991); *Prini et al.*, J. Phys. Chem. Ref. Data 18, p. 1231 (1989)
  - Iliuta *et al.*, J. Chem. Eng. Data 52, p. 2 (2007); Sander, Atmos. Chem. Phys. 15, p. 4399 (2015)
- CO_2 / CH_4 / H_2S (ASPEN+): ASPEN+

Right plot:

- Exp. data for CO_2 [a] / H_2S from: TotalEnergies, Internal data (2019)
- Exp. data for CO2 [b]: Skylogianni *et al.* (2020)
- CO_2 (lit [c]): Skylogianni *et al.* (2020)
- CO_2 (lit [d]): Zhang & Chen (2011)
- CO_2 (lit [e]): TotalEnergies, Internal data (2019)

Henry Solubility Constant

- Aqueous solution of MDEA: 30% wt
- Simulations results for H_2S are in agreement with experiments reporting measuring only physisorption of H_2S in MDEA, using a protonated MDEA solution
- Simulation results for CO_2 overpredict the Henry constant (underestimate the solubility) of CO_2 in MEDEA but accurately predict the temperature dependence of the Henry constant

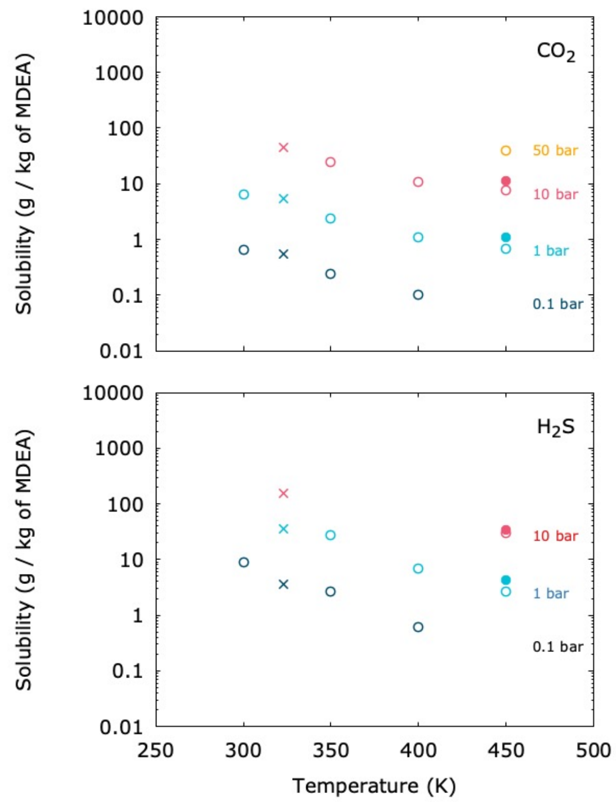


Monte Carlo simulations in the NPT ensemble using Widom test insertions (*MedeA GIBBS*)

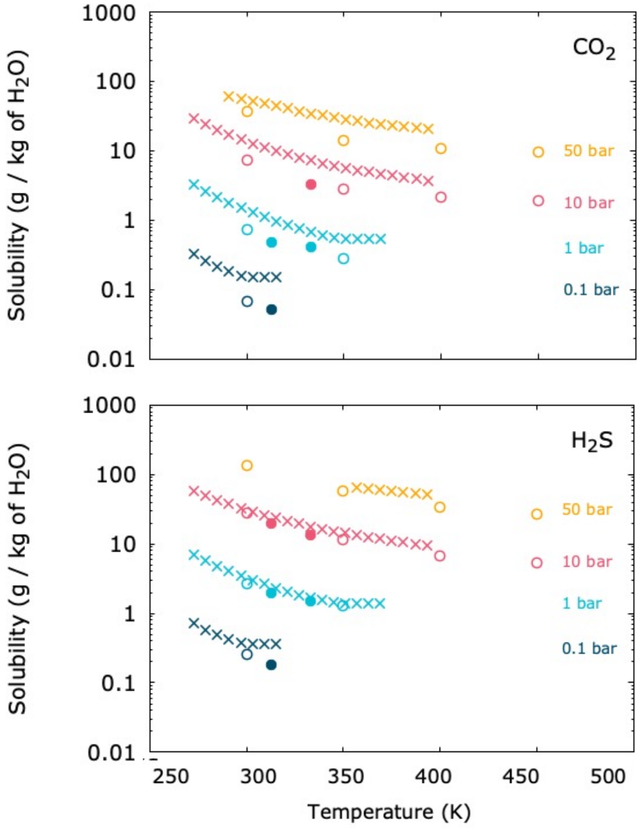
- Exp. TOTAL: TotalEnergies (2019) – unpublished work
- Exp. Sandal: Rinker *et al.*, The Canadian J. of Chem. Eng. 78 (2000)
- CO_2 (ASPEN+): ASPEN+
- CO_2 (lit): Zhang *et al.*, Ind. & Eng. Chem. Res. 50, p. 163 (2011)

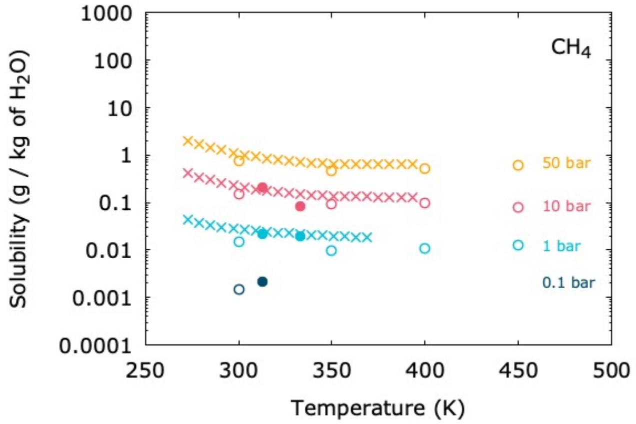
Solubility

Solvent: MDEA



Solvent: H_2O





Monte Carlo simulations in the isochoric isothermal Gibbs ensemble and the NPT ensemble using Widom test insertions (*MedeA GIBBS*)

- x symbols correspond to experimental data from Total Energies (2019)
- circles correspond to simulation results
  - Filled circles: direct output of GEMC simulations
  - Open circles: determined using the calculated Henry Solubility Constants (from NPT simulations)

Diffusivity

Self-Diffusion Coefficient

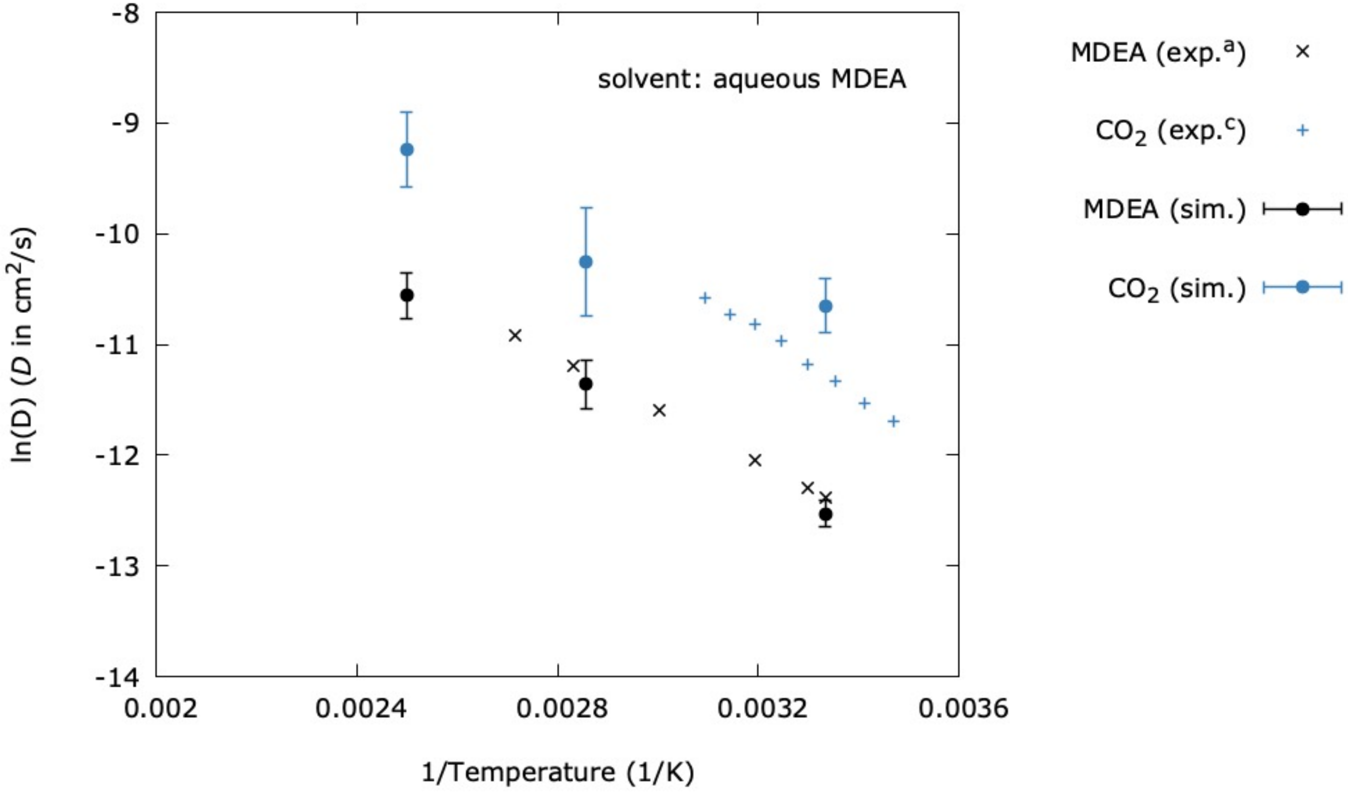
- Run NVE simulations and calculate the Mean Squared Displacement of the molecules

$$MSD = \left\langle \left(r(t) - r(t_0) \right)^2 \right\rangle$$

r(t) and *r(t_0)* are the position vectors of the gas molecule i at times t and *t_0*, respectively; Brackets <> denote the ensemble average over time origins, providing the mean square displacement (MSD)

- Calculate the self-diffusion coefficient of the molecules through their MSD

$$D = \frac{1}{6} \cdot \frac{\left\langle \left(r(t) - r(t_0) \right)^2 \right\rangle}{t}$$



Equilibrium molecular dynamics simulations in the NVE ensemble (*MedeA LAMMPS*)

- Exp. MDEA (a): Snijder et al., *Journal of Chemical & Engineering Data*. 38, p. 475-480 (1993)
- Exp. CO_2 (c): Al-Ghawas et al., *Journal of Chemical & Engineering Data* 34, p. 385-391 (1989)

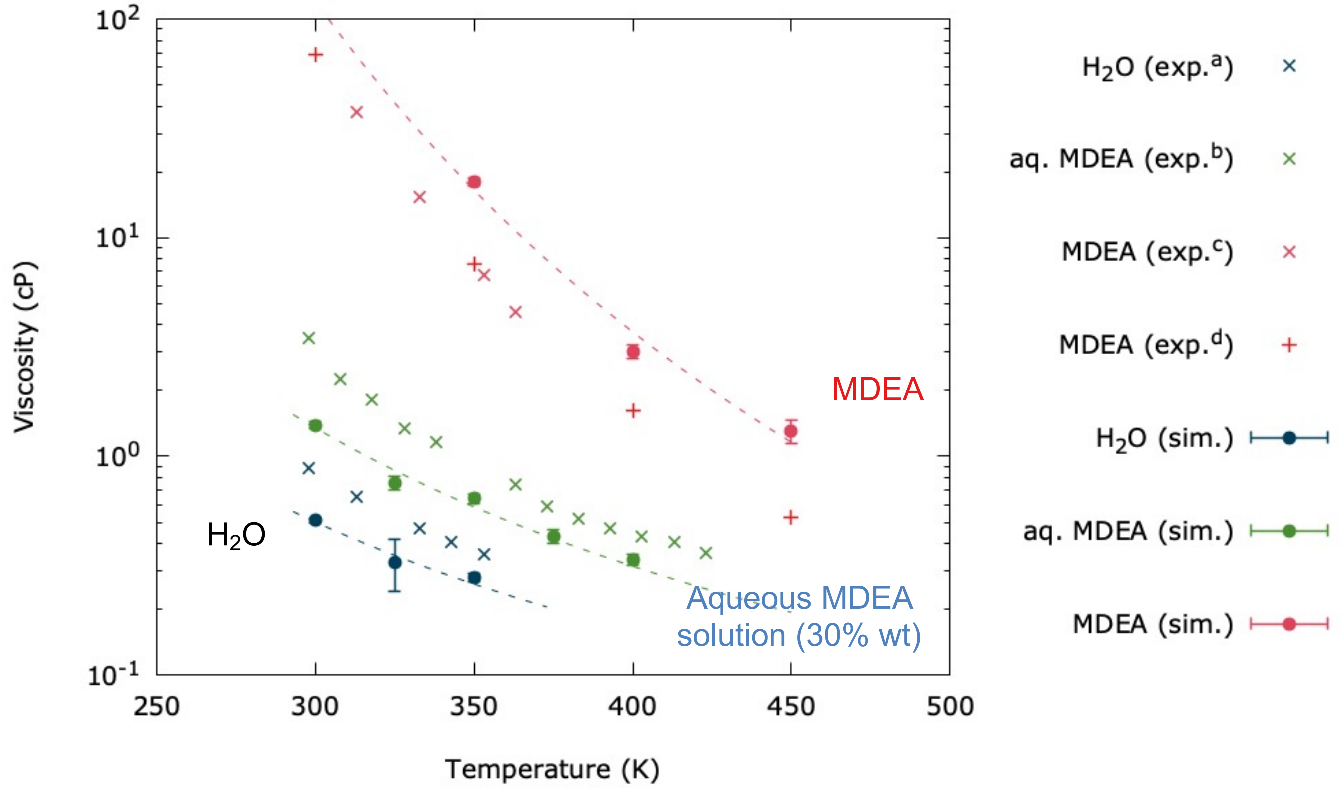
Viscosity

- The Green-Kubo method is used for the calculation of viscosity during equilibrium molecular dynamics (EMD) simulations

$$\eta = \frac{V}{kT}\int_0^\infty \langle P_{ij}(0)P_{ij}(t)\rangle dt$$

where V is the volume of the cell, k the Boltzmann's constant, T is the temperature, P_{ij}, i, j = x, y, z are components of the shear stress tensor

- Calculated viscosities of MDEA and the aqueous solution of MDEA (30% wt) predict the temperature dependence of the viscosity



Equilibrium molecular dynamics simulations in the NVE ensemble (*MedeA LAMMPS*)

- Exp. H_2O (a): Teng et al., J. Chem. Eng. Data 39, p. 290 (1994)
- Exp. aqueous MDEA solution (30% wt) (b): Arachchige et al., Ann. Trans. Of the Nordic Rheol. Soc. 22 (2014)
- Exp. MDEA (c): Yusoff et al., J. Ind. & Eng. Chem. 20, p. 3349 (2014)
- Exp. MDEA (d): Wilding et al., Dippr project 801, FPE 150-151, p. 413 (1998)

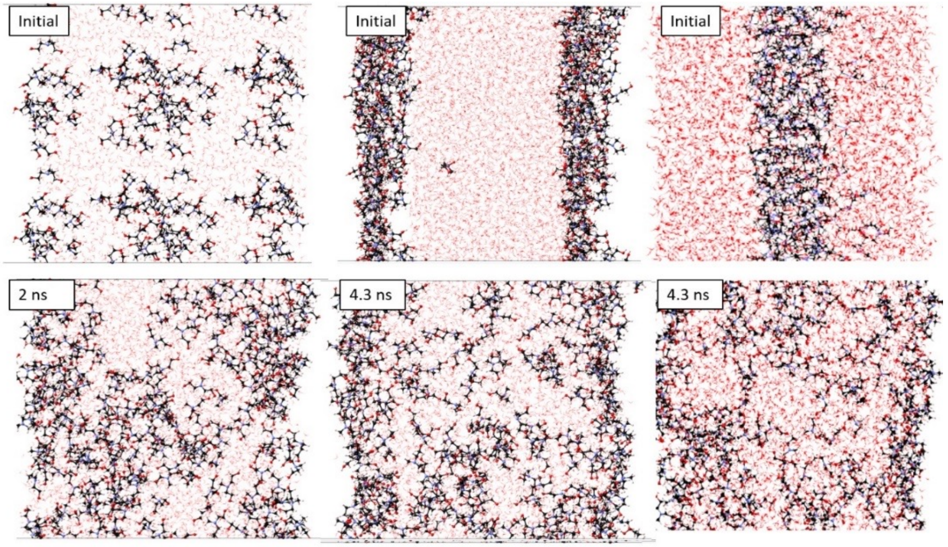
Surface Tension

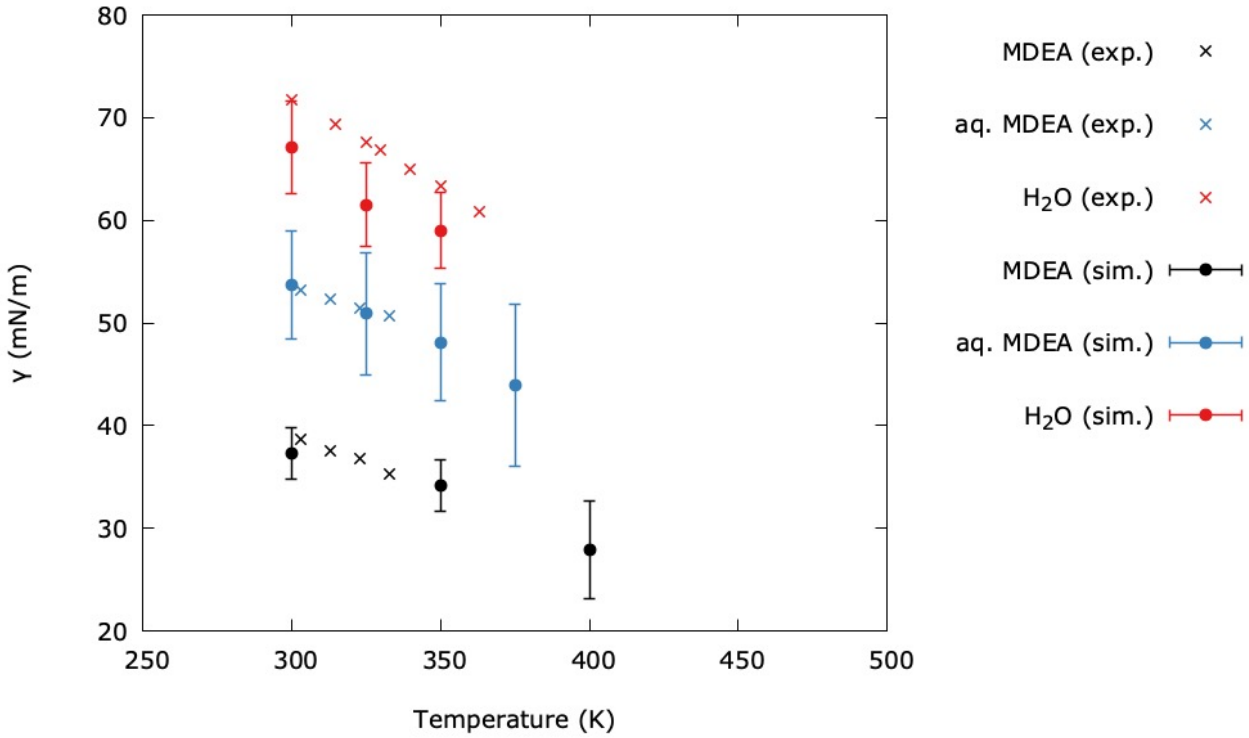
- Calculation of surface tension during MD simulations in the NVT ensemble

$$\gamma = 0.5L\left\{\langle\sigma_z\rangle - \frac{1}{2}\left[\langle\sigma_x\rangle + \langle\sigma_y\rangle\right]\right\}$$

where L is the cell length in the direction normal to the interface and brackets <> denote the time average

- Qualitatively and quantitatively, the results agree well with experimental data for MDEA, H_2O and the aqueous solution of MDEA (30% wt)





Equilibrium molecular dynamics simulations in the NVT ensemble (*MedeA LAMMPS*)

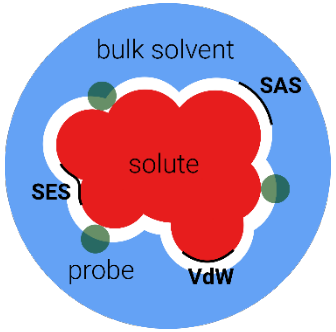
- Exp. MDEA: Wilding et al., Dippr project 801, FPE 150-151, p. 413 (1998)
- Exp. aqueous MDEA solution (30% wt): Muhammad et al., J. Chem. & Eng. Data 53, p. 2226 (2008)
- Exp. H_2O: Vargaftik, Volkov, & Voljak, 1983

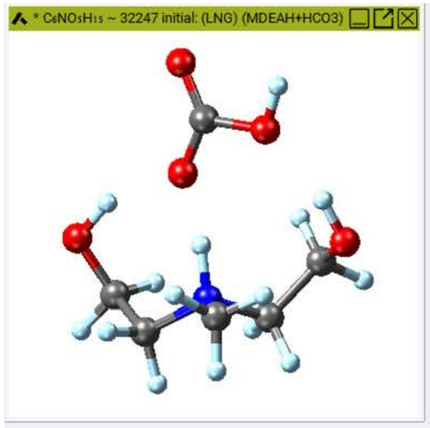
Understanding Experimental Reaction Thermochemistry and Kinetics with Simulations

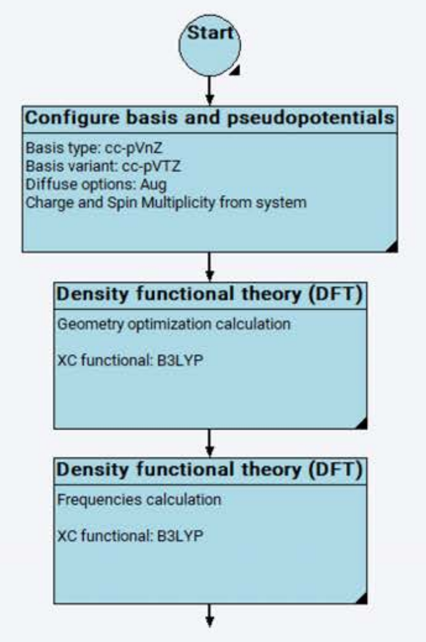
- The DFT simulations predict the enthalpies of chemisorption of H_2S and CO_2 in aqueous MDEA solutions in quantitative agreement with experiments

Reaction	Solvent	Computed $\Delta H^*(298K)$ (kJ mol^{-1})	Experimental ΔH (kJ mol^{-1})
$H_2S_{(s)}+MDEA_{(s)} \rightarrow MDEAH{\cdot}SH_{(s)}$	Aqueous MDEA	-49	-41
$CO_{2(s)}+H_2O{\cdot}MDEA_{(s)} \rightarrow MDEAH{\cdot}HCO_{3(s)}$	Aqueous MDEA	-59	-59

Source experimental data: Carey *et al. Gas Separation & Purification* **1991**, *5*, 95-109.







Configure basis and pseudopotentials

Basis type: cc-pVnZ
Basis variant: cc-pVTZ
Diffuse options: Aug
Charge and Spin Multiplicity from system

Density functional theory (DFT)

Geometry optimization calculation

XC functional: B3LYP

Density functional theory (DFT)

Frequencies calculation

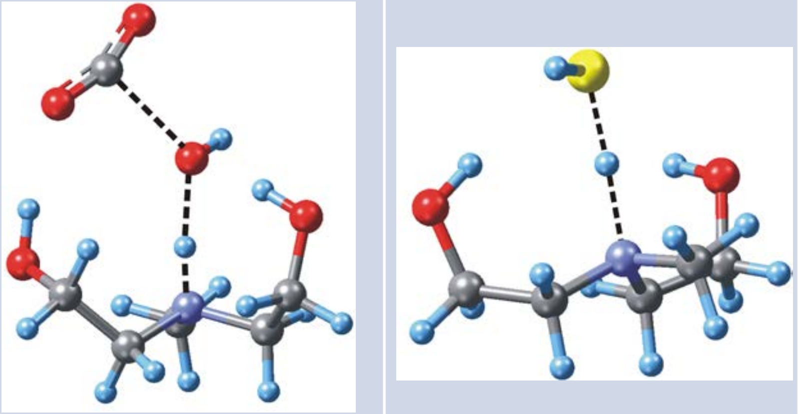
XC functional: B3LYP

Understanding Experimental Reaction Thermochemistry and Kinetics with Simulations

- The DFT simulations predict the faster rates of chemisorption of H_2S than CO_2 in aqueous MDEA solutions in qualitative agreement with experiments

Reaction mechanism	Solvent	$\Delta H^{\#}$(298K) (kJ mol^{-1})	$\Delta G^{\#}$(298K) (kJ mol^{-1})	$\log_{10}(k(298K))$ (s^{-1})
$H_2S_{(s)}$+$MDEA_{(s)}$ → $MDEAH{\cdot}SH_{(s)}$	MDEA 30%w/water	5.8	13.0	10.5
$CO_{2(s)}$+$H_2O{\cdot}MDEA_{(s)}$ → $MDEAH{\cdot}HCO_{3(s)}$	MDEA 30%w/water	28.7	50.7	3.9

Transition states of the chemisorption reactions



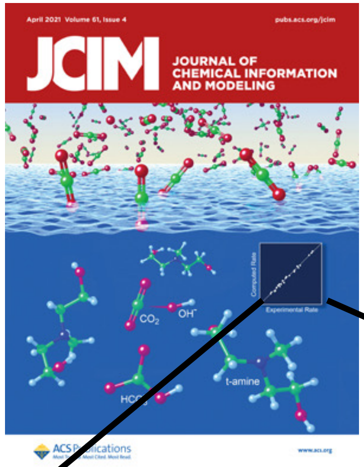
CO_2+H_2O+MDEA

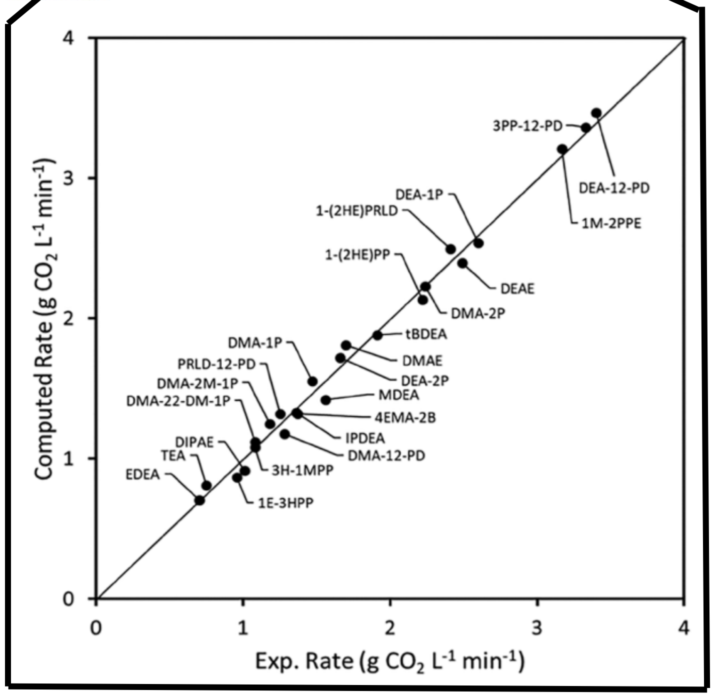
H_2S+MDEA

Understanding Experimental Reaction Thermochemistry and Kinetics with Simulations

- From qualitive to quantitative agreement between the computed and experimental rates of absorption of CO_2
  - We extended the kinetics analysis including the CO_2 chemisorption rates of 24 additional aqueous amines in a screening procedural study
  - the CO_2 kinetics is explained by two contributions:
    - The concentration of $OH^{(-)}$ (governed by the pK_a of the amine)
    - The activation energy of the reaction: $CO_{2(s)}+OH^{(-)}_{(s)} \rightarrow HCO_3^{(-)}_{(s)}$

- More information:
  - *J. Chem. Inf. Model*. 2021, 61, 1814
  - www.materialsdesign.com/webinars/ - *Development of New Solvents for CO_2 Capture Using Molecular Simulations*





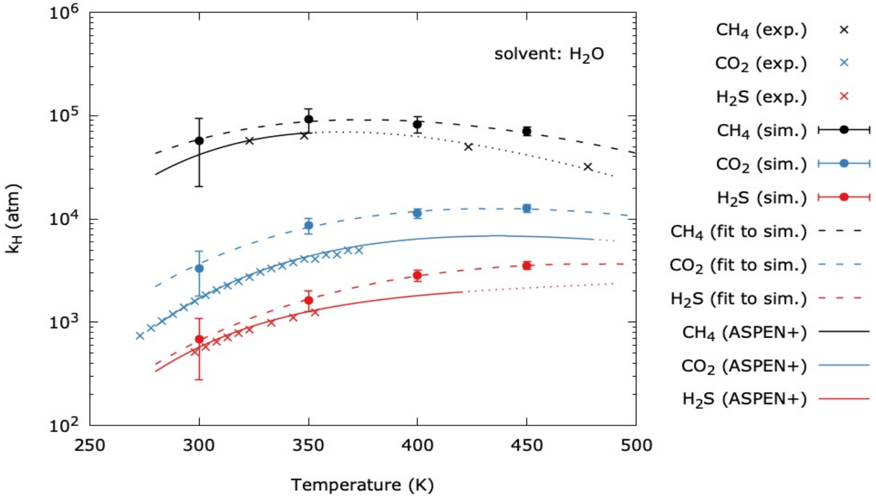
Credits – Software & People

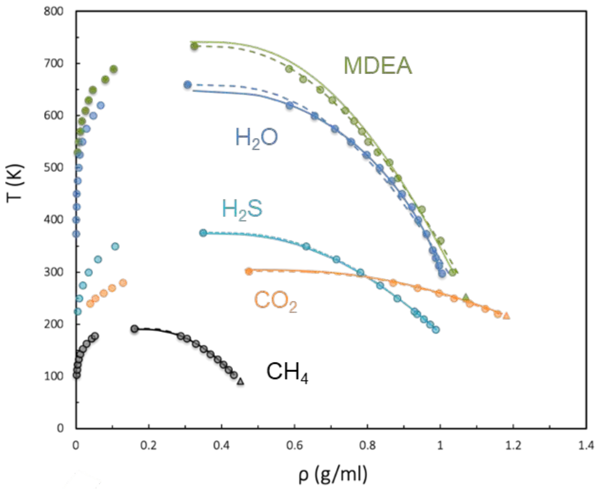
- **MedeA**: building/computing/post-processing of results performed within *MedeA 2.26*; *MedeA* is a registered trademark of Materials Design, Inc., San Diego, USA - www.materialsdesign.com
- **GIBBS**: The calculations have been performed with *MedeA GIBBS*, using: Gibbs 9.6, IFP Energies Nouvelles, Rueil-Malmaison & Laboratoire de Chimie-Physique, Université Paris Sud, CNRS, France.
- **LAMMPS**: The calculations have been performed with *MedeA LAMMPS*, using: LAMMPS 29-Oct-2020. LAMMPS stands for Large-scale Atomic/Molecular Massively Parallel Simulator. S. Plimpton, *Fast Parallel Algorithms for Short-Range Molecular Dynamics*, J Comp Phys, 117, 1-19 (1995) - www.lammps.sandia.gov
- **GAUSSIAN**: The calculations have been performed with *MedeA Gaussian* , using: Gaussian 16 - https://gaussian.com/citation/

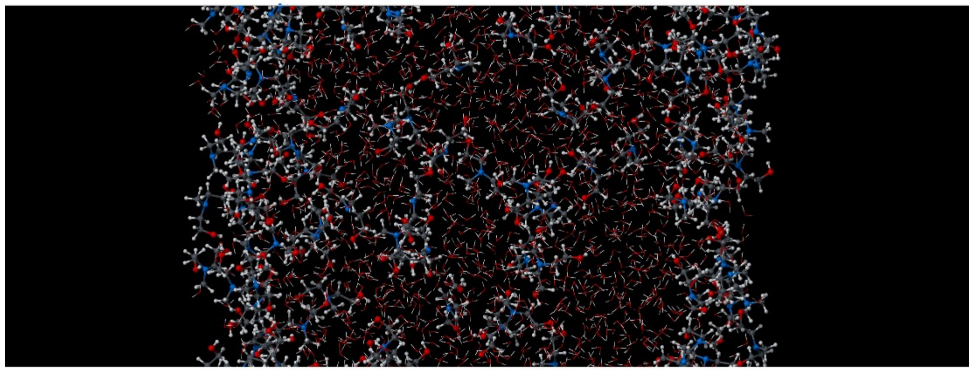
- **PEOPLE:** Thank you: Erich Wimmer, Benoit Minisini, Alexander Mavromaras, etc.

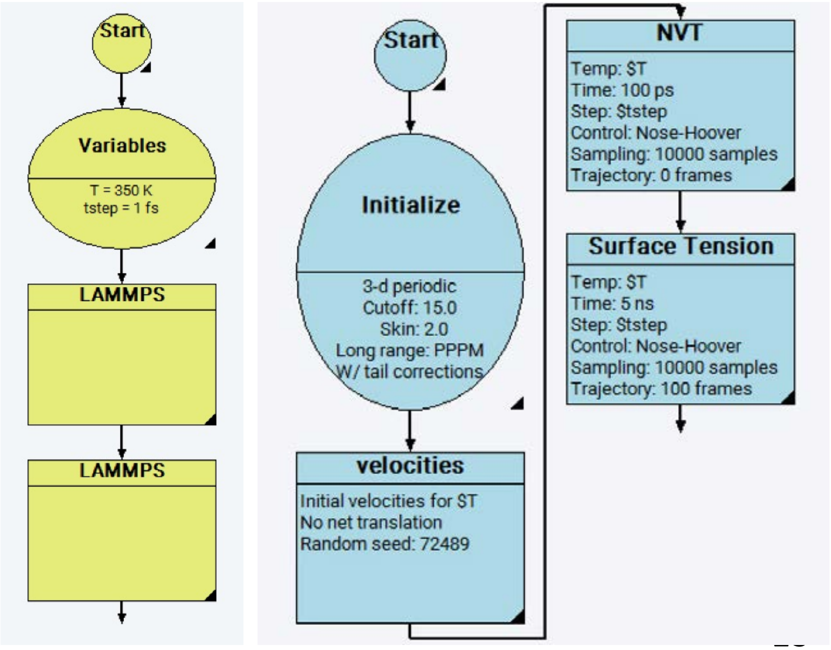
Conclusions – Perspectives

- Establishment of calculation protocols (molecular simulations) for each property studied
  - VLE - pure compounds (density, saturation pressure, vaporization enthalpy)
  - Solubility – mixtures
  - Transport properties (viscosity, diffusivity)
  - Surface tension









Start

Variables
T = 350 K
tstep = 1 fs

LAMMPS

LAMMPS

Start

Initialize
3-d periodic
Cutoff: 15.0
Skin: 2.0
Long range: PPPM
W/ tail corrections

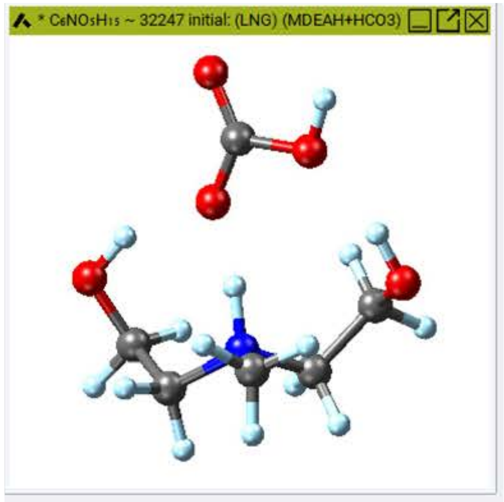
velocities
Initial velocities for $T
No net translation
Random seed: 72489

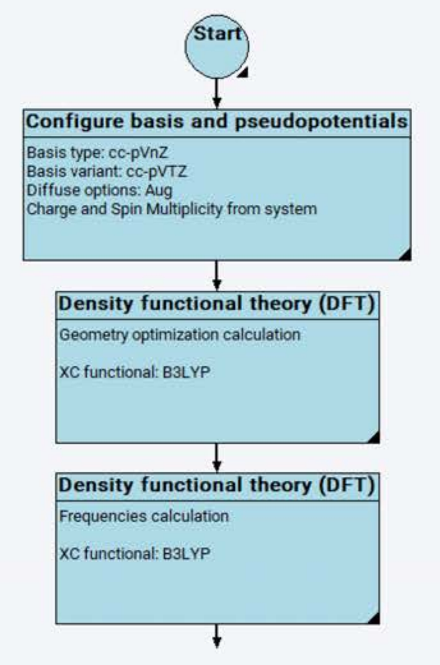
NVT
Temp: $T
Time: 100 ps
Step: $tstep
Control: Nose-Hoover
Sampling: 10000 samples
Trajectory: 0 frames

Surface Tension
Temp: $T
Time: 5 ns
Step: $tstep
Control: Nose-Hoover
Sampling: 10000 samples
Trajectory: 100 frames

Conclusions – Perspectives

- Identification and analysis of reaction mechanisms
  - Reaction thermochemistry: $\Delta E_r(0\ \mathrm{K})$, $\Delta H_r(T)$, $\Delta G_r(T)$
  - Reaction kinetics: $\Delta G^{\#}(T)$, $k(T)$, $r(T)$





Basis type: cc-pVnZ
Basis variant: cc-pVTZ
Diffuse options: Aug
Charge and Spin Multiplicity from system

Geometry optimization calculation

XC functional: B3LYP

Frequencies calculation

XC functional: B3LYP

- Description and discussion of strengths and limitations of the employed techniques
- Application of the developed computation protocols on large sets of existing and hypothetical solvents can provide engineers access to consistent data sets that can
  - Be used directly as input in process modeling, and
  - Help identify possible candidates for experiments

Molecular Simulations for Improved Process Modeling of an Acid Gas Removal Unit

MedeA modules used in today’s webinar

https://www.materialsdesign.com/compute-engines

https://www.materialsdesign.com/analysis-tools

- MedeA Environment
- MedeA LAMMPS
- MedeA Gaussian
- MedeA GIBBS

Publications

https://www.materialsdesign.com/Publications

Application Notes

https://www.materialsdesign.com/application-notes

Webinar: Live and Recorded

https://www.materialsdesign.com/webinars

- Development of New Solvents for CO_2 Capture Using Molecular Simulations
- Harness the Power of LAMMPS Molecular Dynamics Code with MedeA
- Classical Forcefields for Modeling Materials on Atomic Scale
- Fluid Properties from Molecular Simulation Applications in Chemical Engineering and the Oil & Gas Industry

For questions or comments contact:

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khollingsworth@materialsdesign.com

UGM 2021

The Materials Design annual user event will be online again for 2021.

Plenary Speakers and panels to be announced soon.

https://ugm.materialsdesign.com/

Question and Answer Session

Dr. Marianna Yiannourakou

Materials Design

Dr. Xavier Rozanska

Materials Design

Questions about Materials Design Webinars

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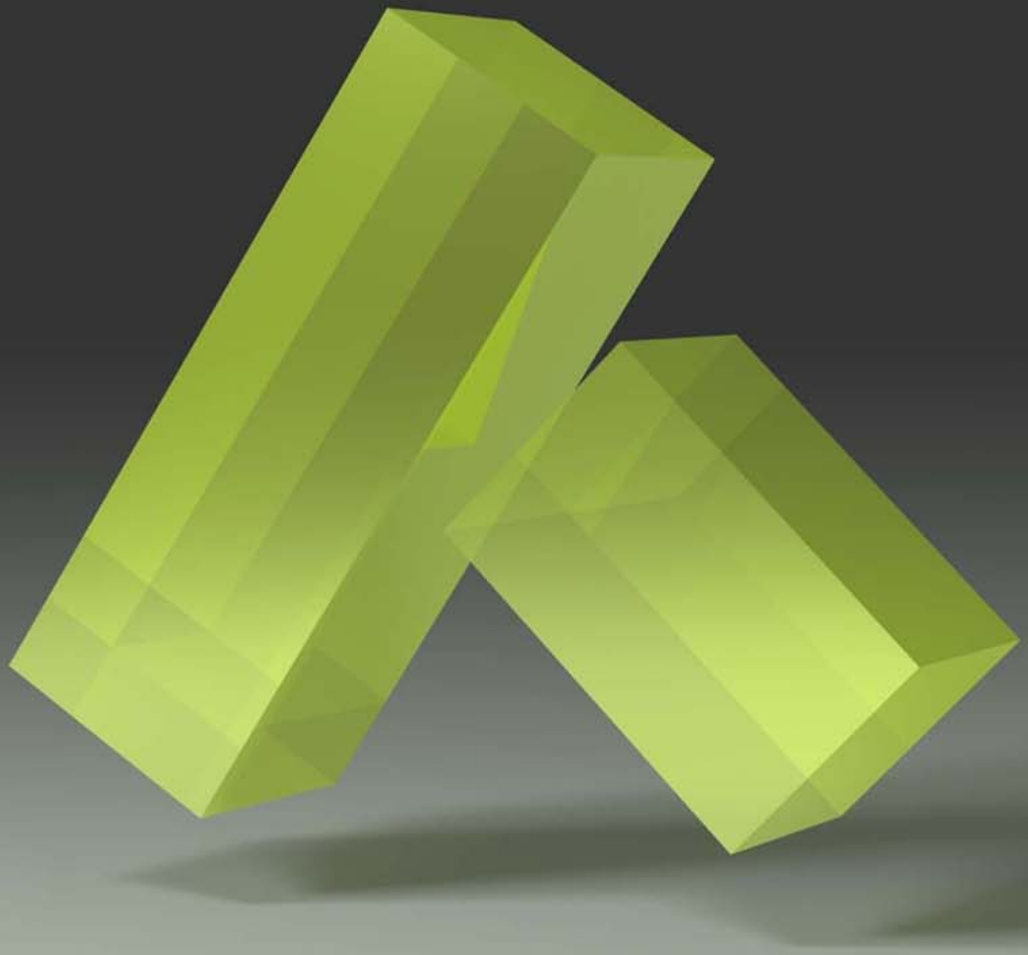

MedeA

Innovation by Simulation