Technical University of Denmark

On the mass transfer of CO_2 in enzyme enhanced solvents - comparison with conventional solvent systems

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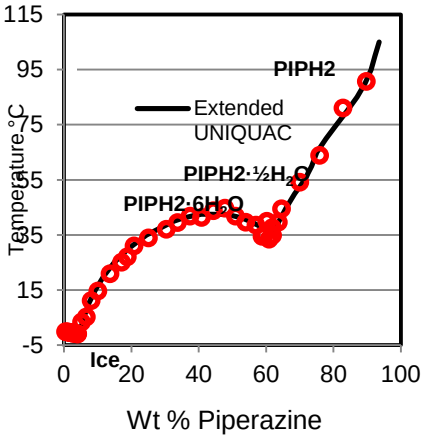


Modelling

- Energy consumption
- Heat of reaction
- Thermodynamics
- Kinetics

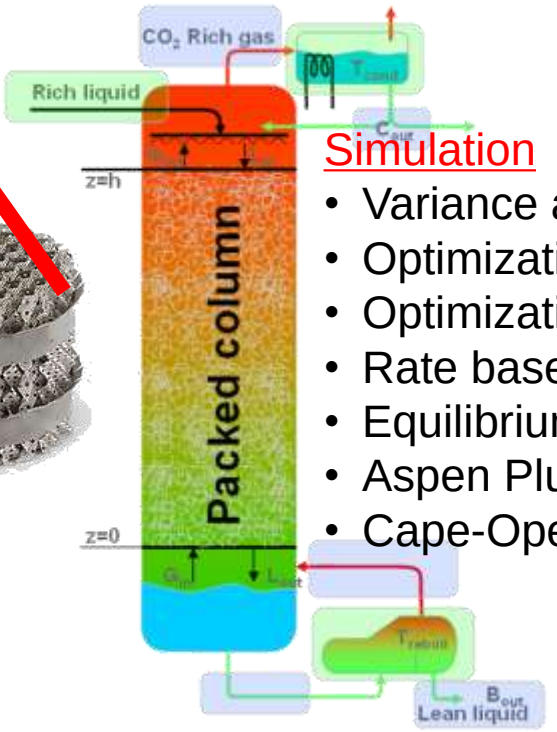
Pilot tests

- Real life tests
- Solvent study
- Packing testing
- Energy requirements
- Mass transfer

DTU CO_2 Research

Experimental

- Physical Properties
- Equilibrium
- Kinetics



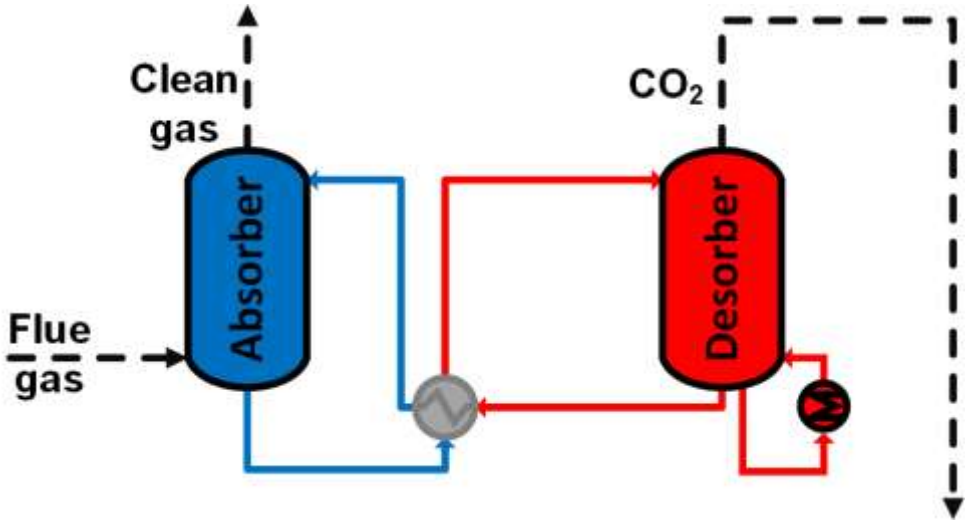
Simulation

- Variance analysis
- Optimization of energy use
- Optimization of packing
- Rate based approach
- Equilibrium approach
- Aspen Plus
- Cape-Open

Overview

- **Benchmarking overall mass transfer**
  - **Energy consumption**
- **Benchmarking solvent capacity**

Ideal solvent for postcombustion CCS



Low capital costs

→ High mass transfer rates

Low operational costs

→ High solvent capacity
→ Low energy demand for regeneration

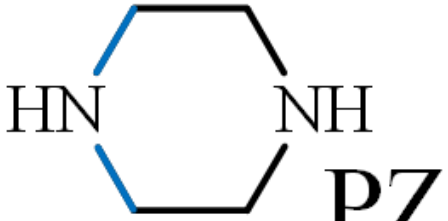
Solvents

Alkanolamines are the most prominent group of solvents for CO_2 capture

Primary

MEA

Secondary



PZ

Tertiary

MDEA

Carbonate salt

K_2CO_3

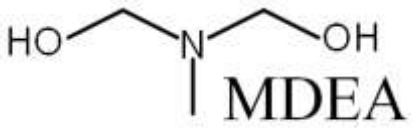
Solvents in CCS

Absorption rate of CO_2

K_2CO_3

Carbonate salt

$\Delta H_R \approx 15 - 27 \frac{kJ}{mol}$

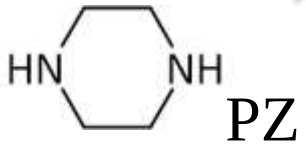


Tertiary amine

$\Delta H_R \approx 50 - 65 \frac{kJ}{mol}$

Primary amine

$\Delta H_R \approx 80 - 85 \frac{kJ}{mol}$



Secondary amine

$\Delta H_R \approx 75 - 85 \frac{kJ}{mol}$

Carbonate salt solutions and tertiary amines are not even considered as potential solvents because of slow absorption kinetics

Solvents in CCS

Absorption rate of CO_2

K_2CO_3

Carbonate salt

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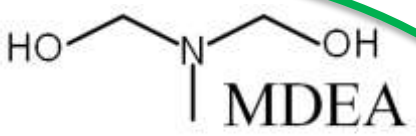

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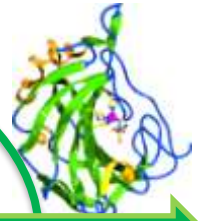

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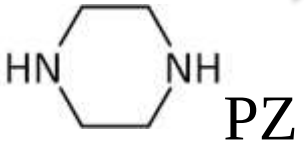


Secondary amine

$\Delta H_R \approx 75 - 85 \frac{kJ}{mol}$

The enzyme carbonic anhydrase (CA) can catalyze the reaction of bicarbonate forming solvents and speed up the absorption rates

$$CO_2 + H_2O \overset{CA}{\leftrightarrow} H^+ + HCO_3^-$$

WWC Experiments

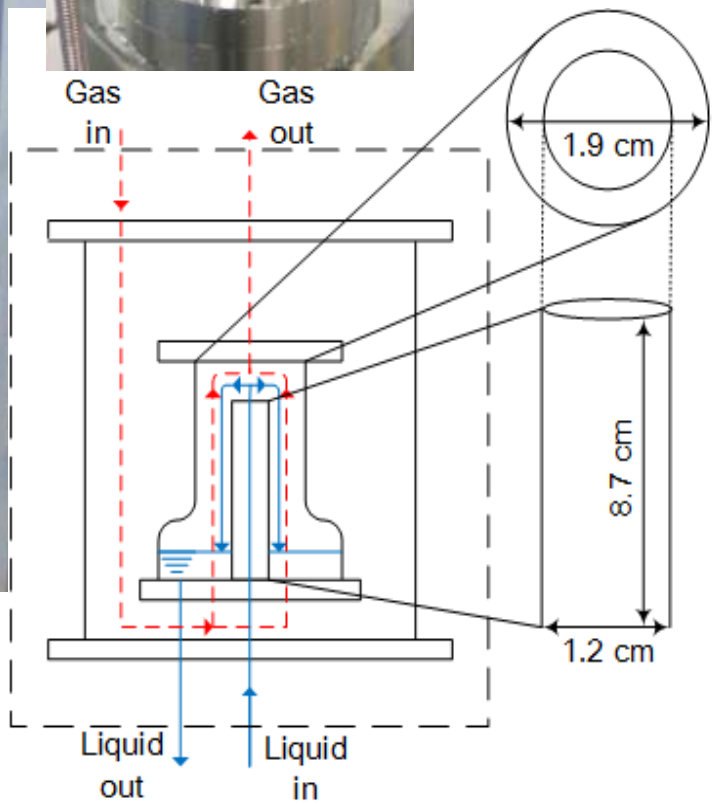
Comparison of absorption behavior of conventional solvents and enzyme ehanced solvents on a wetted wall column

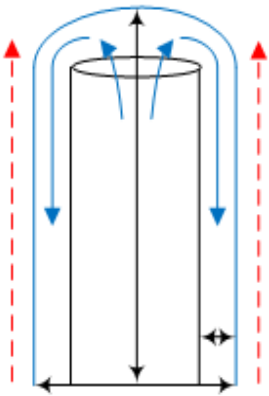
Solvent	Solvent type
30 wt% MDEA + 8.5 g/L CA	Enzyme enhanced solvent
30 wt% MDEA + 5 wt% PZ	Chemically promoted solvent
30 wt% MEA	Primary amine

Determine effect of:

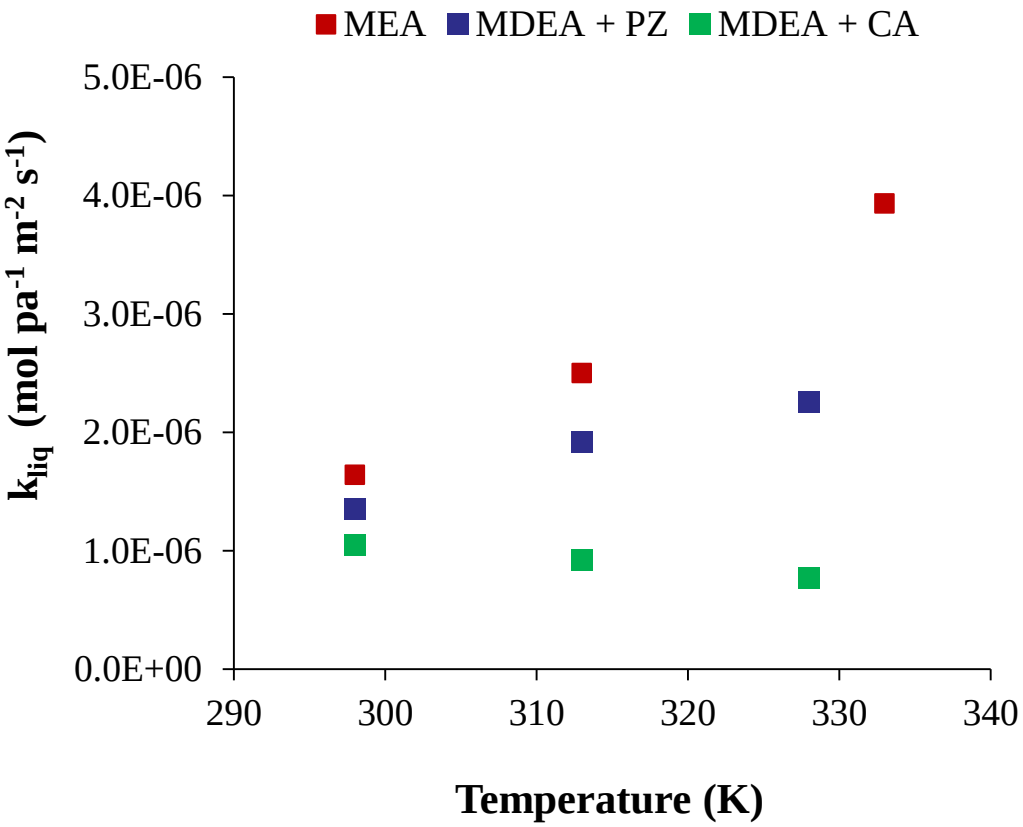
- Temperature (298- 333 K)
- Solvent loading

WWC – measurements





Effect of temperature on CO_2 mass transfer



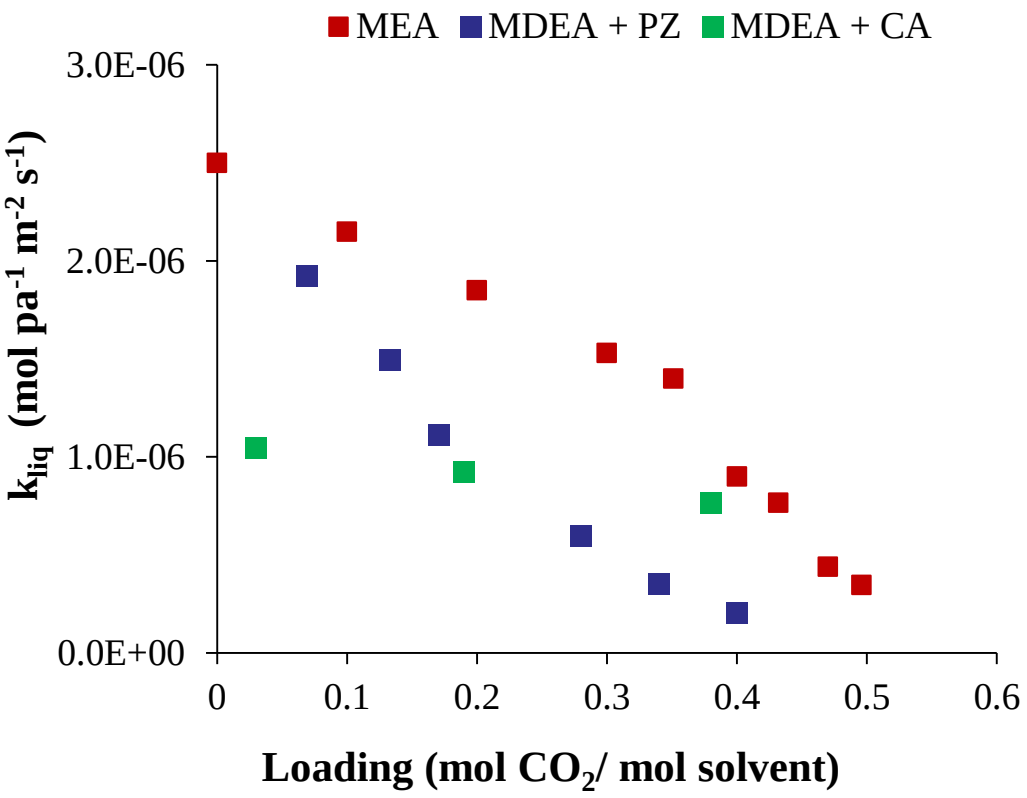
30 wt% MEA, unloaded

30 wt% MDEA 5 wt% PZ, unloaded

30 wt% MDEA + 8.5 g/L CA, unloaded

- Opposing trends for conventional and enzyme enhanced solvents
- Reaction kinetics increase for conventional solvents
- Enzyme kinetics are not increasing with temperature

Effect of solvent loading on CO_2 mass transfer



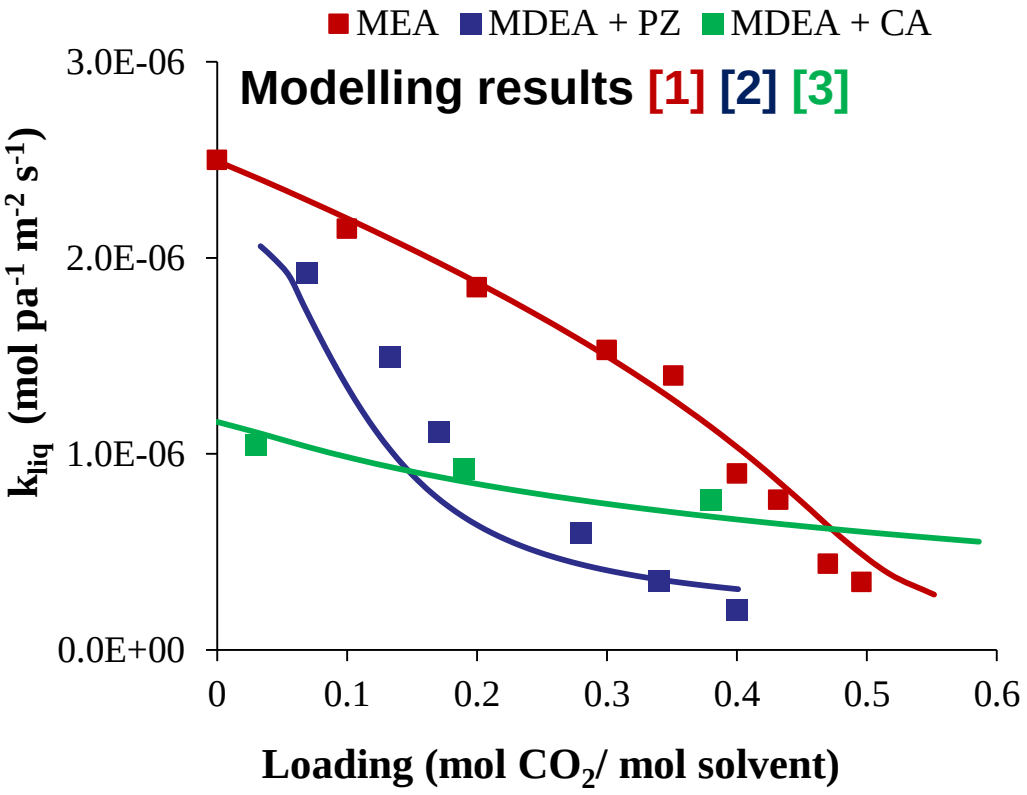
30 wt% MEA,

30 wt% MDEA 5 wt% PZ,

30 wt% MDEA + 8.5 g/L CA

- Rapid decline in mass transfer upon loading for conventional solvents
- Just slight deline in mass transfer for enzyme enhanced solvents

Effect of solvent loading on CO_2 mass transfer



Reaction Rates:

Conventional solvents:

$$k_{ov}^{Am} = k_{Am} \cdot C_{Am}$$

→**Dependent on active amine concentration**

Enzyme enhanced solvents:

$$k_{ov}^{CA} = \frac{C_{CA} \cdot k_{CA} \cdot C_{H_2O}^2}{K_{MS}\left(1 + \frac{C_{HCO_3}}{K_{MP}}\right) + C_{CO_2}}$$

→**Independent on active amine concentration**

Different reaction mechanism can explain the different mass transfer of conventional and enzyme enhanced solvents.

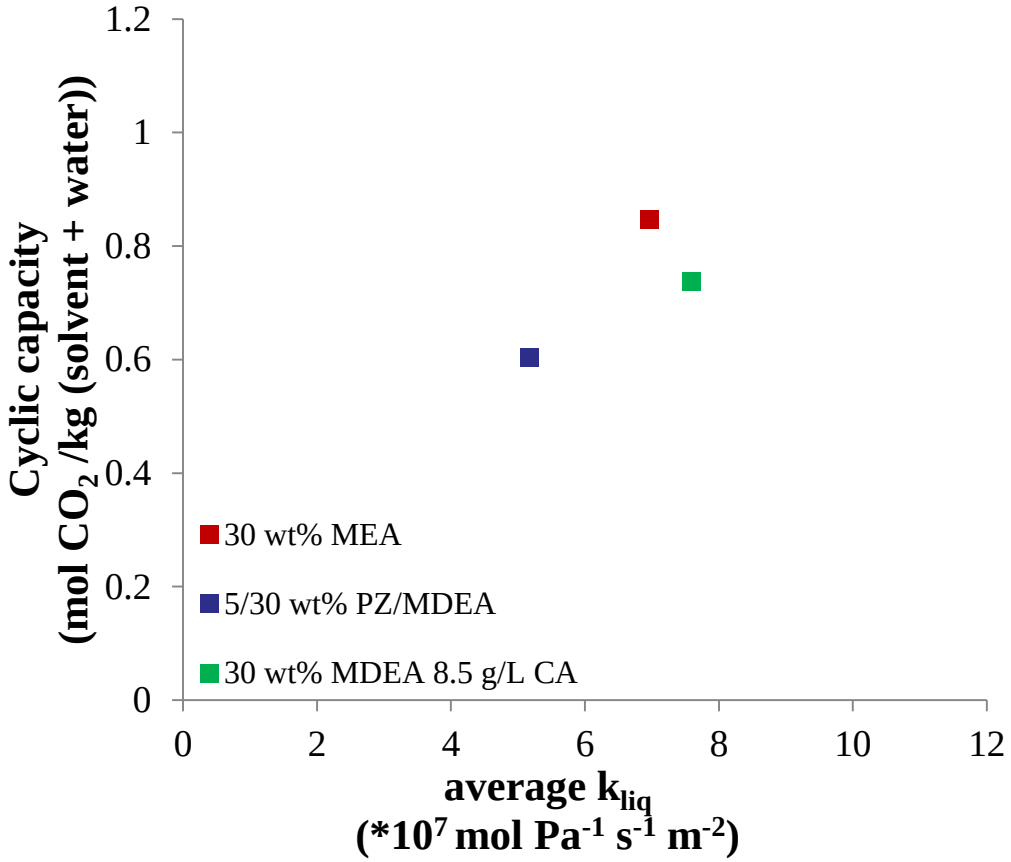
[1] G. F. Versteeg, L. A. J. . van Dijck, and W. P. M. van Swaaij, "On the Kinetics between CO2 and Alkanolamines both in aqueous and non-aqueous solutions. An overview," *Chem. Eng. Commun.*, vol. 144, pp. 113–158, 1996.
[2] J. Gaspar and P. L. Fosbøl, "Practical Enhancement Factor Model based on GM for Multiple Parallel Reactions: Piperazine (PZ) CO2 Capture," *Chem. Eng. Sci.*, 2016.
[3] A. Gladis, M. T. Gundersen, R. Nerup, P. L. Fosbøl, J. M. Woodley, N. von Solms, R. Neerup, P. L. Fosbøl, J. M. Woodley, and N. Von Solms, "CO2 mass transfer model for carbonic anhydrase enhanced MDEA solutions," *Chem. Eng. J.*, vol. 335, no. October 2017, pp. 197–208, 2018.

Benchmark of experiments

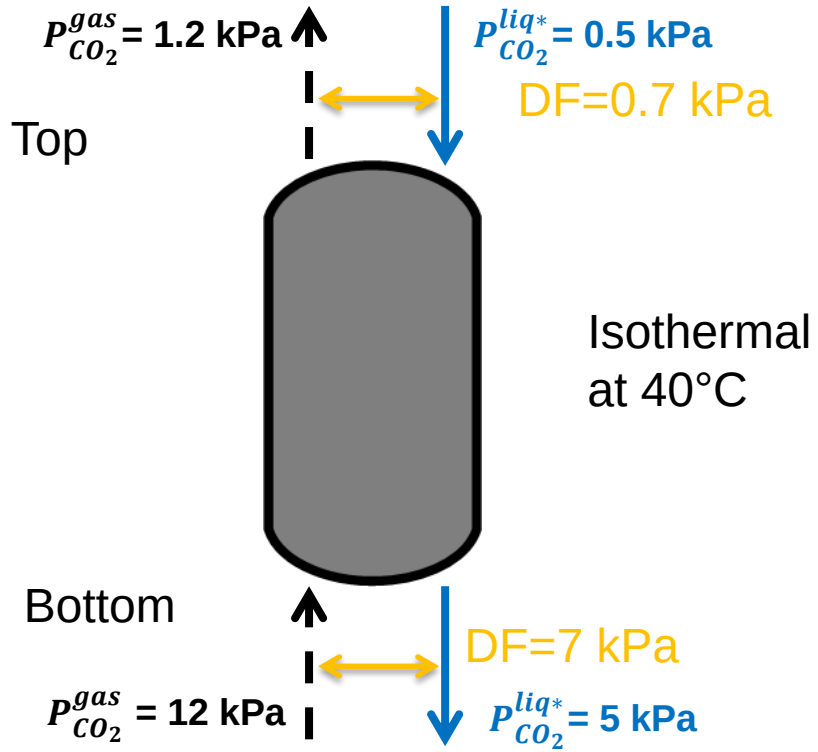
Comparison of the average liquid side mass transfer coefficient as well as the cyclic capacity of the different solvents

Benchmark of experiments

Comparison of the average liquid side mass transfer coefficient as well as the cyclic capacity of the different solvents



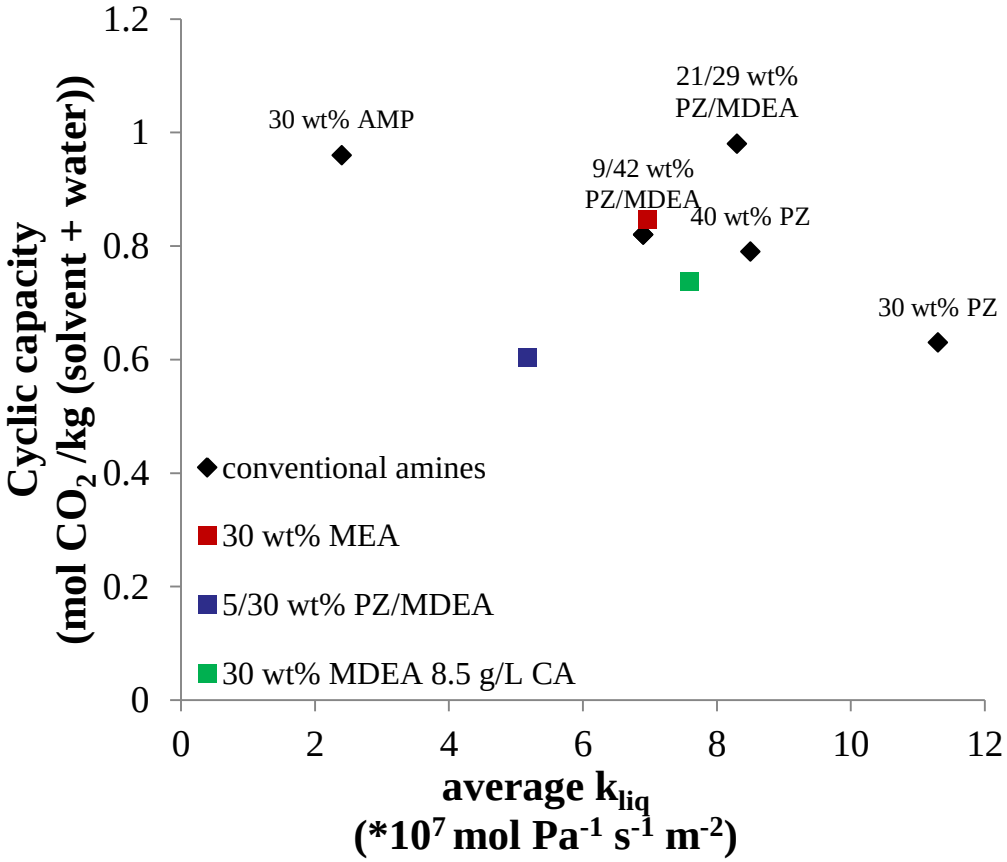
Definition of average k_{liq} by Li and Rochelle [4].



[4] L. Li, H. Li, O. Namjoshi, Y. Du, and G. T. Rochelle, "Absorption rates and CO 2 solubility in new piperazine blends," *Energy Procedia*, vol. 37, pp. 370–385, 2013.

Benchmark of experiments

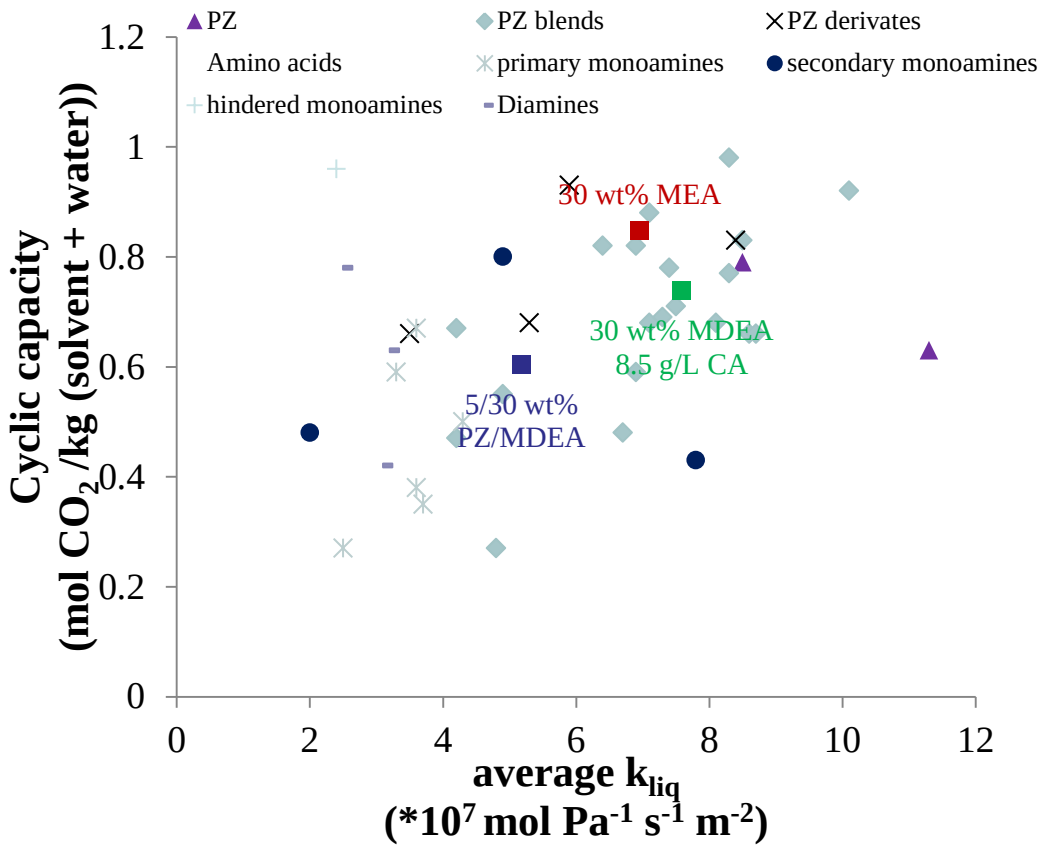
Comparison of the average liquid side mass transfer coefficient as well as the cyclic capacity of the different solvents



- Enzyme enhanced MDEA has highest average k_{liq} in own experiments
- Just solvents with high PZ concentration (>21%) have a higher mass transfer
- MDEA+CA solvents have a comparable cyclic capacity at 298 K

Benchmark of experiments

Comparison with literature values [5]



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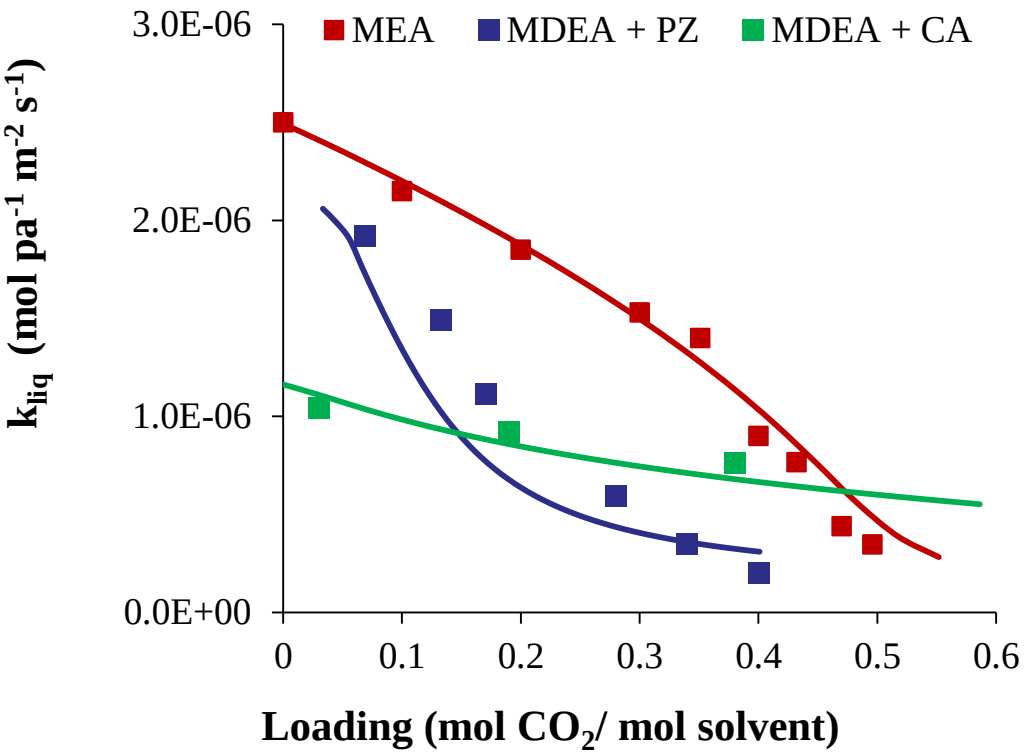
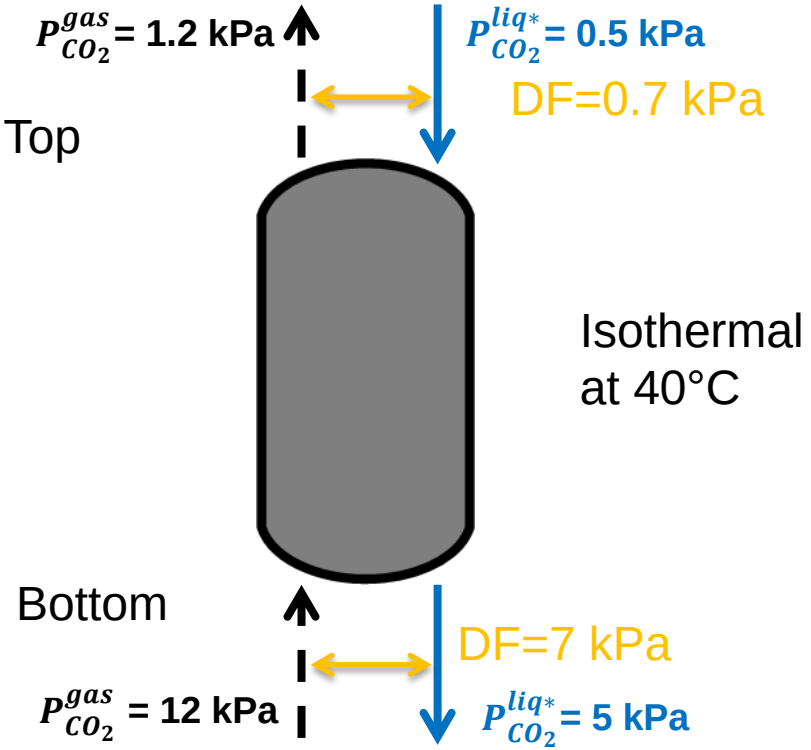
[5]: G. T. Rochelle, "Conventional amine scrubbing for CO 2 capture," in *Absorption-Based Postcombustion Capture of Carbon Dioxide*, 2016.

Benchmark of experiments





Enzyme enhance solvents show a good performance compared to conventional solvents, because of the high mass transfer at higher solvent loadings (higher driving forces in the bottom of absorber)

Conclusion

- Reaction mechanism of enzymes different than amines
- Enzyme enhanced solvent have potential to utilize lower absorption temperature to maximize cyclic capacity
- Enzyme enhanced solvents show comparable mass transfer as well as cyclic capacity compared to conventional solvents

Need of precise process modelling for comparison and benchmark of total systems
(See also our Poster: Process Model Validation of enzyme enhanced CO_2 capture)

Thank you for your attention