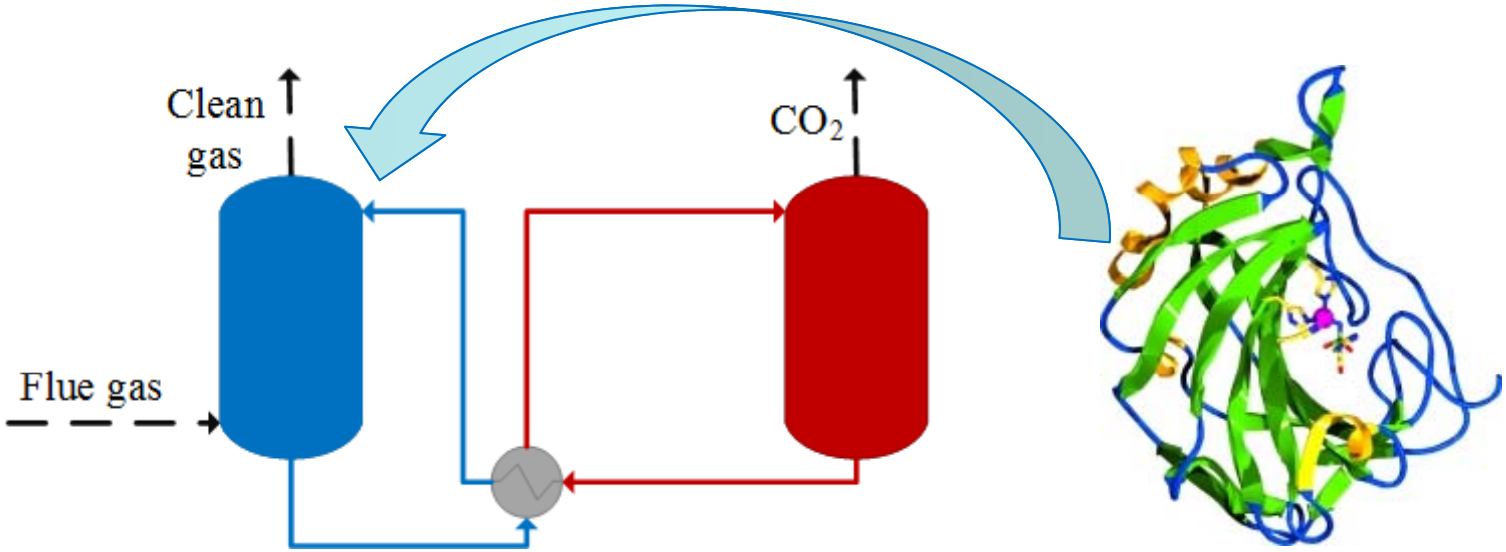
Technical University of Denmark

Kinetics of Carbonic Anhydrase in Promoted Chemical Solvents for Carbon Dioxide Absorption

Arne Gladis, Maria T Gundersen, Philip Fosbøl, John M Woodley, Nicolas von Solms



CERE
Center for Energy Resources Engineering

Post Combustion Capture Conference, Regina,08.09.2015

Overview

- **Introduction**
- **Theory and methods**
- **Experimental setup and Experiments**
- **Results and Discussion**
- **Conclusion and Outlook**

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INnovaTive Enzymes and polyionic-liquids based membRAnes as CO_2 Capture Technology

Cooperation project funded within the 7th Framework program of the European Commission, theme ENERGY.2013.5.1.2

SUPREN
Sustainable Process Engineering

KU LEUVEN

Technical University of Denmark

SINTEF

novozymes
Rethink Tomorrow

Solvionic

IK4 CIDETEC
Research Alliance

PRODINTEC
FACTORY OF FUTURE

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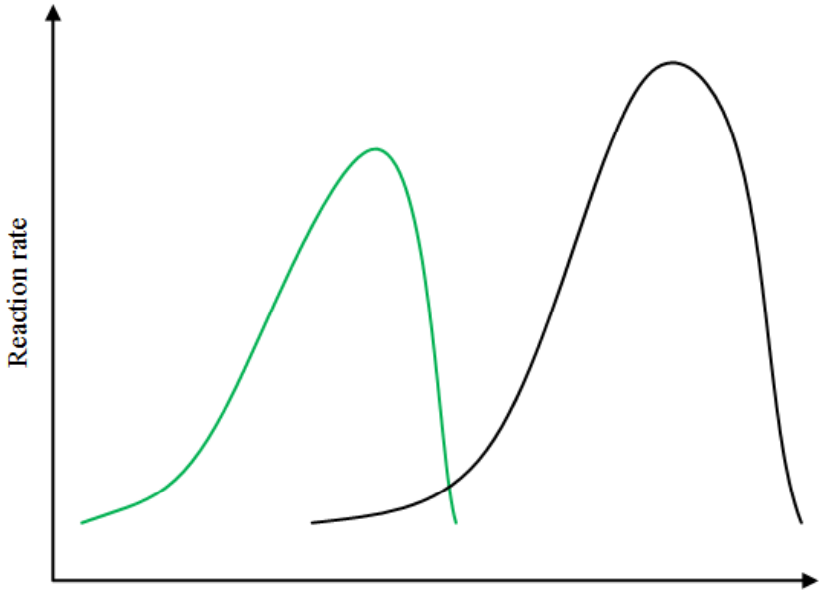
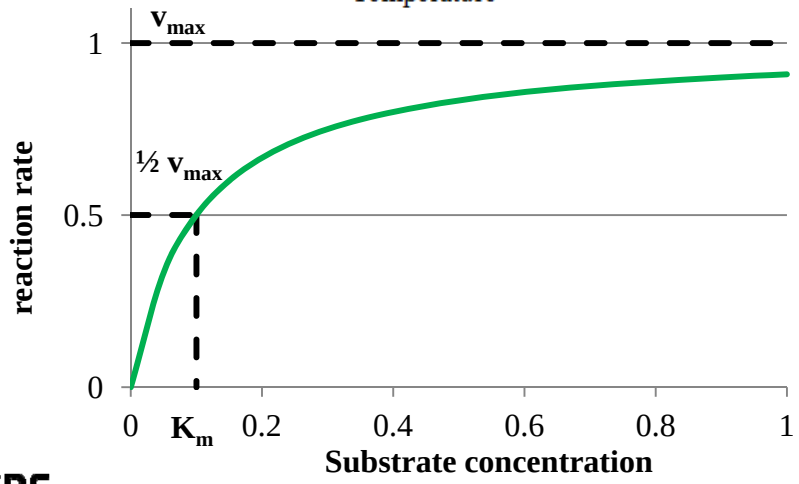
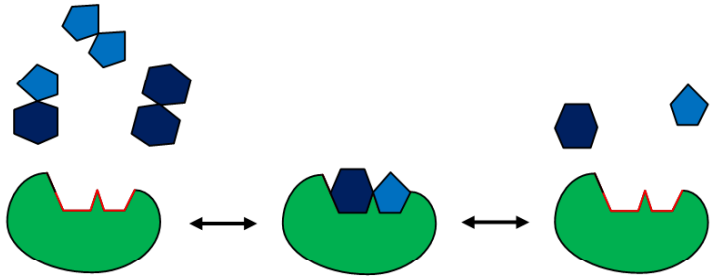
Enzymes







Michaelis Menten Kinetics

$$v = \frac{k_2[E]_0[A]}{K_m + [A]} \qquad v_{max} = k_2[E]_0$$

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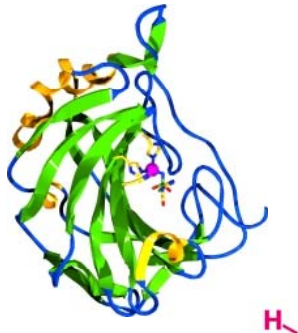
Carbonic Anhydrase

- Present in almost every living organism
- faciliates different processes like Respiration, CO_2 transport, rate enhancement of Photosynthesis
- Metalloenyzme
- One of the fastest enzymes known with up to

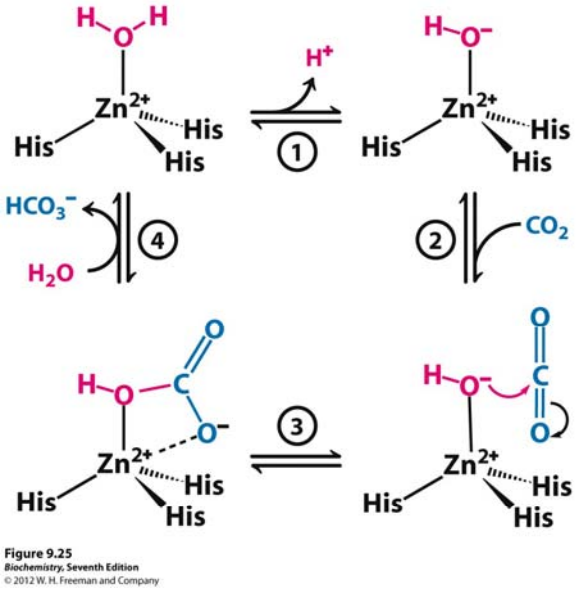
10^6 reactions per second

- Absorption rate Enhancement in CCS process



One-step mechanism:

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



Structure and reactions of chemical solvents

1.**Primary /secondary** amines

- $CO_2 + AmH \leftrightarrow AmH^+COO^-$
- $AmH^+COO^- + AmH \leftrightarrow AmCOO^- + AmH_2^+$

2.**Tertiary** amines

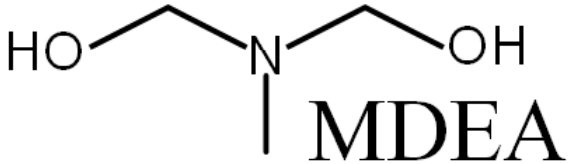
- $CO_2 + Am + H_2O \leftrightarrow AmH^+ + HCO_3^-$

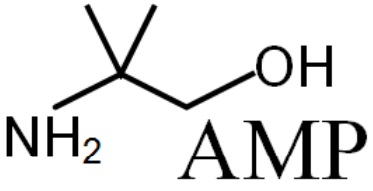
3. **Sterically hindered** amines

- $AmCOO^- + H_2O \leftrightarrow AmH + HCO_3^-$

4. Parallel reactions in **aqueous media**

- $CO_2 + H_2O \leftrightarrow H_2CO_3$
- $CO_2 + OH^- \leftrightarrow HCO_3^-$





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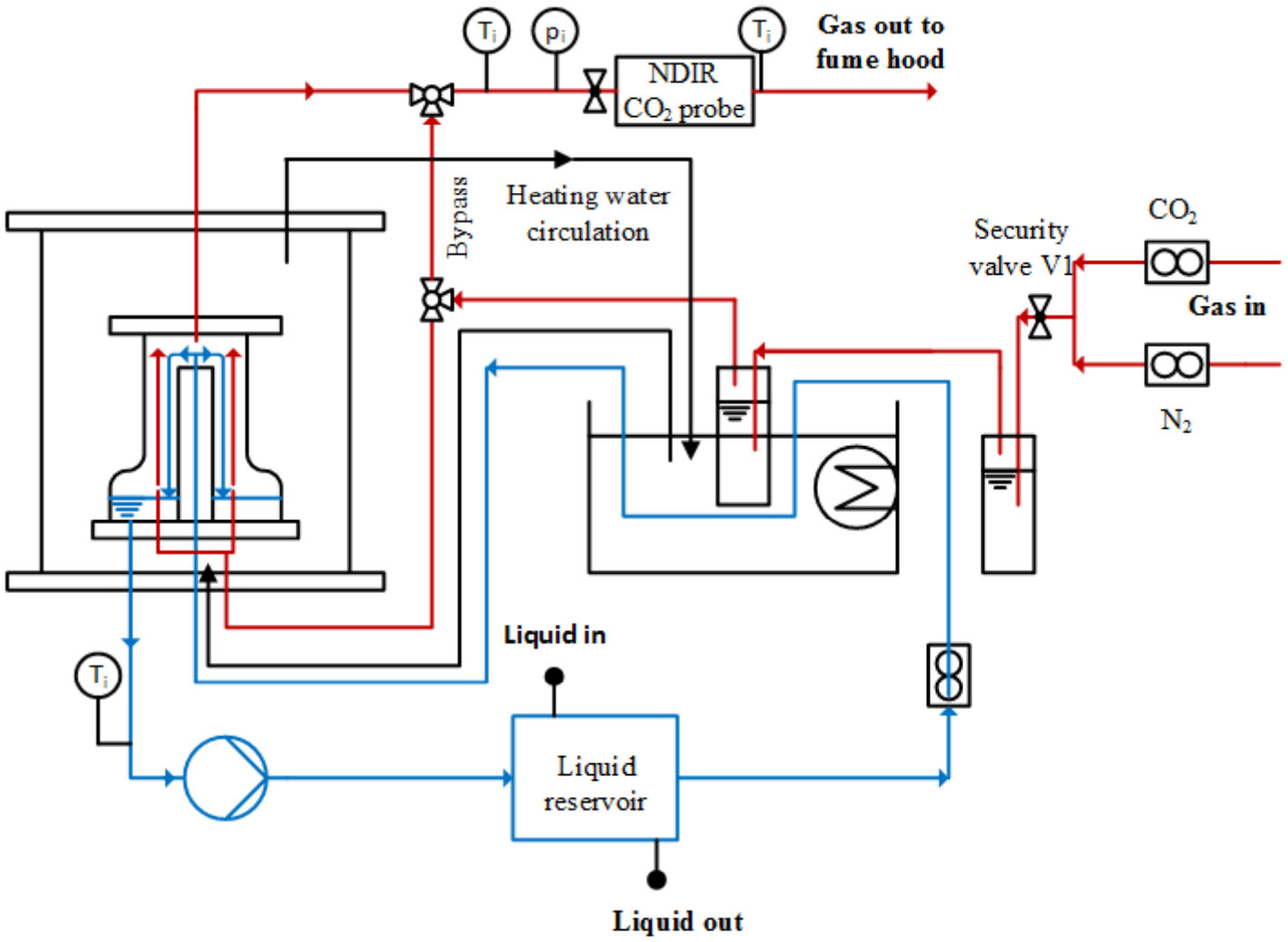
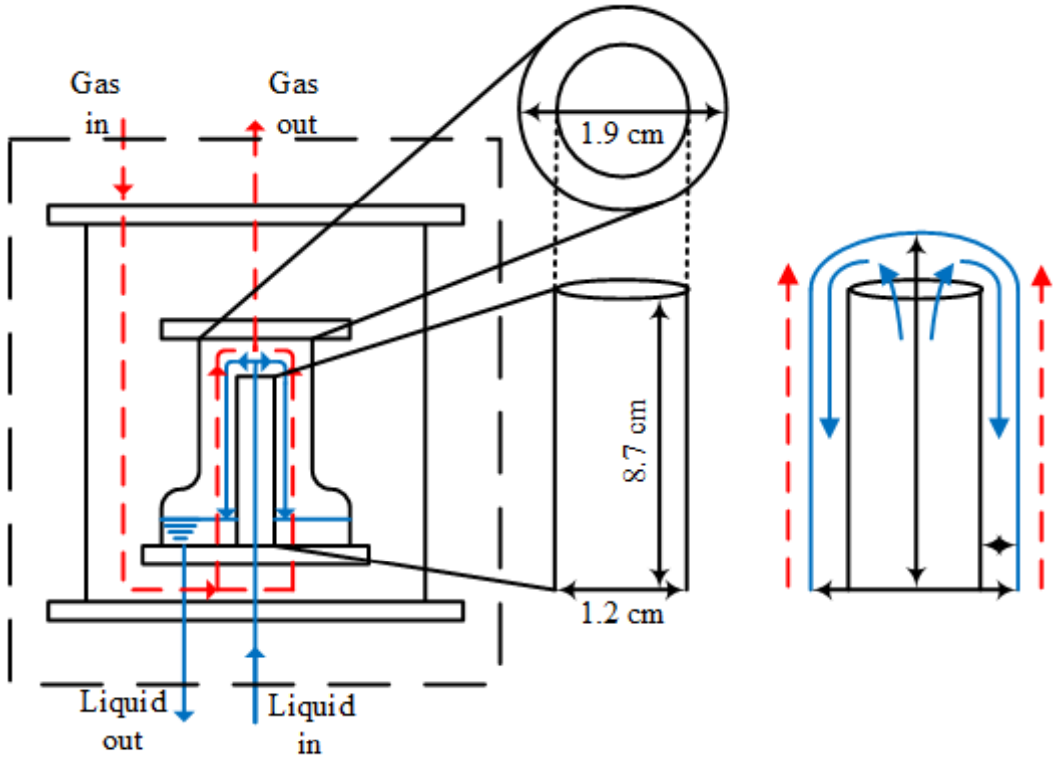
Experimental setup

Experimental setup



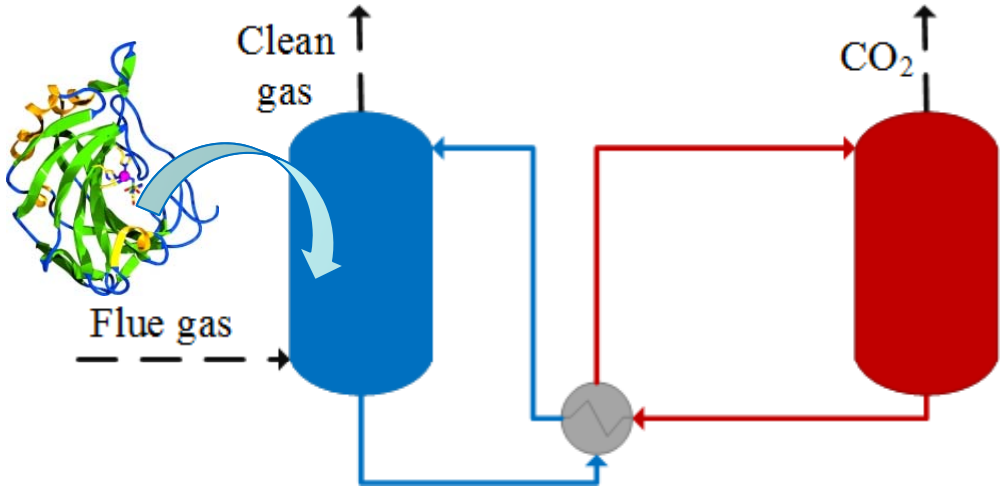
Wetted wall column



Experiments

Carbonic Anhydrase in absorber conditions

Solvent:	**30 wt% MDEA**
Temperature:	**313 K**
Enzyme conc.:	**1.5 g/l; 3 g/l**
Solvent loading:	**0-0.5**
	(mol CO_2/mol MDEA)



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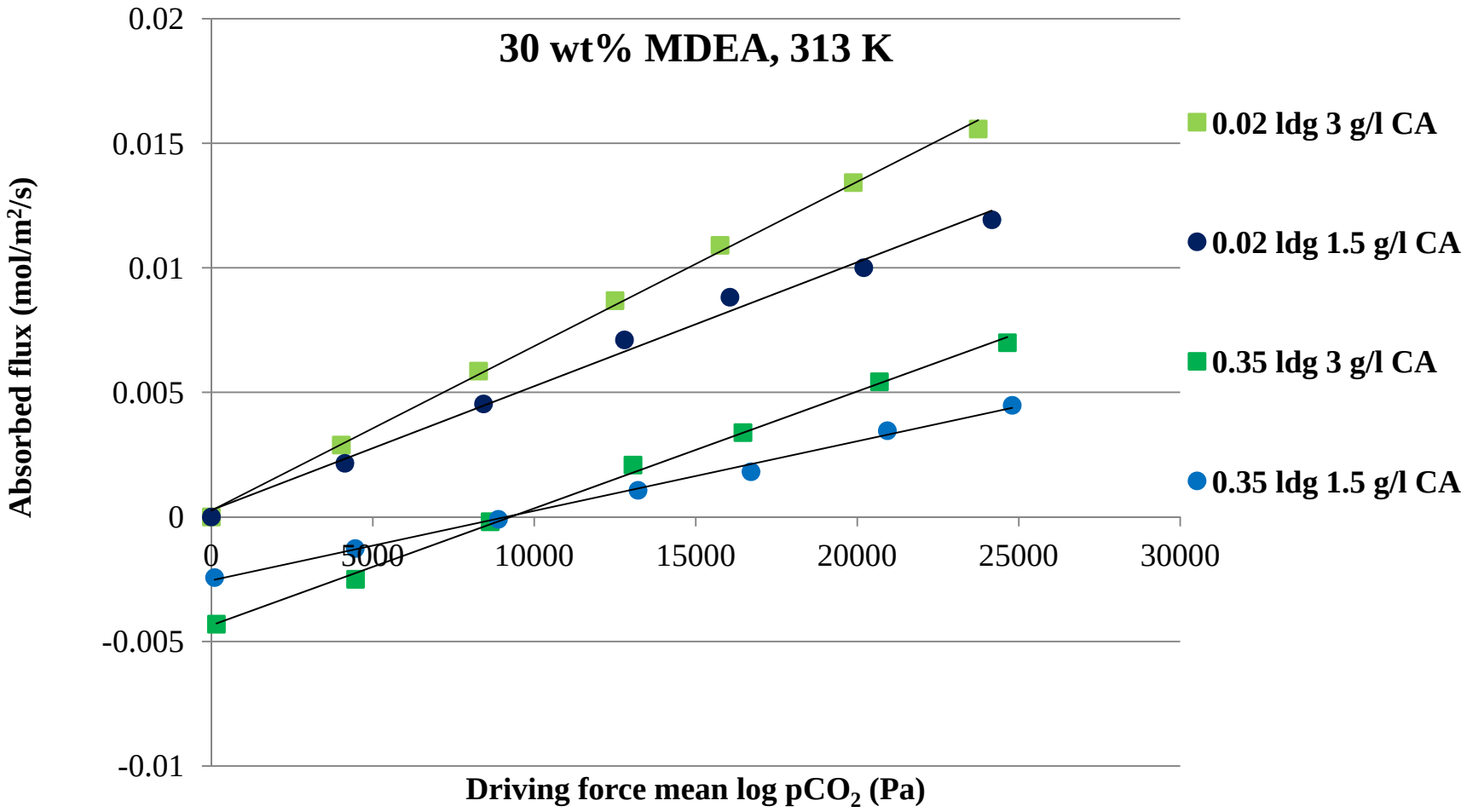
Effect of loading on CO_2 absorption



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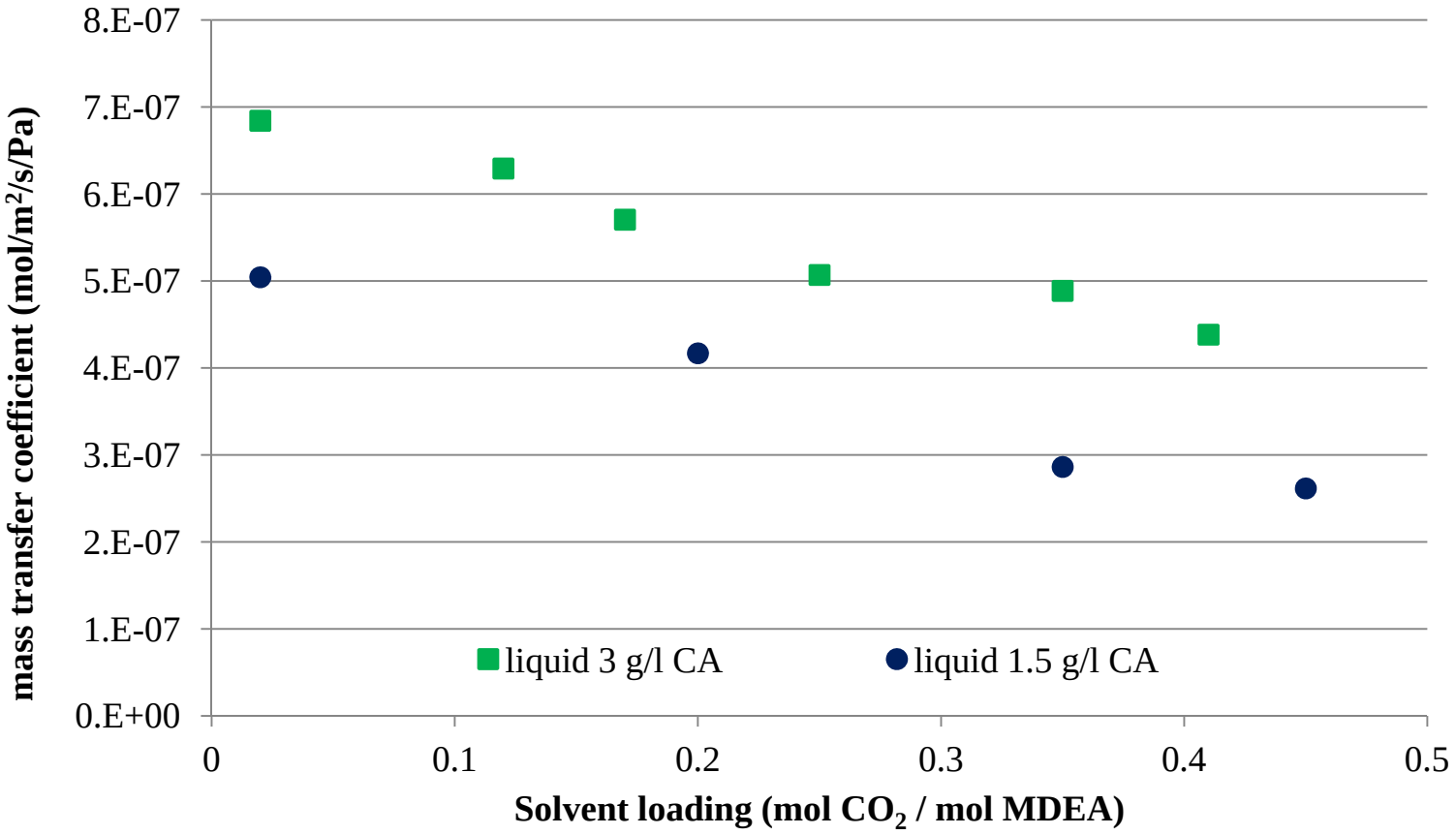
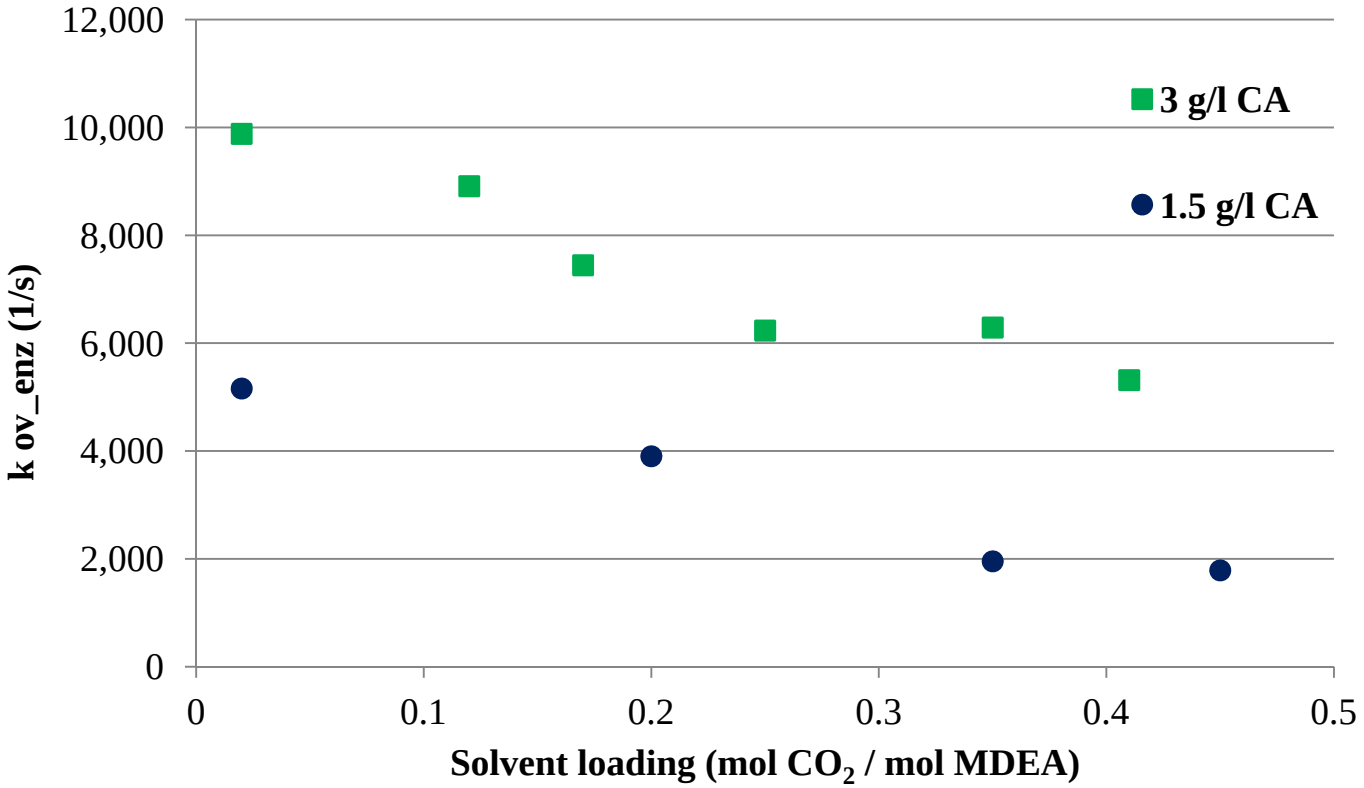


Overall enzyme reaction constant



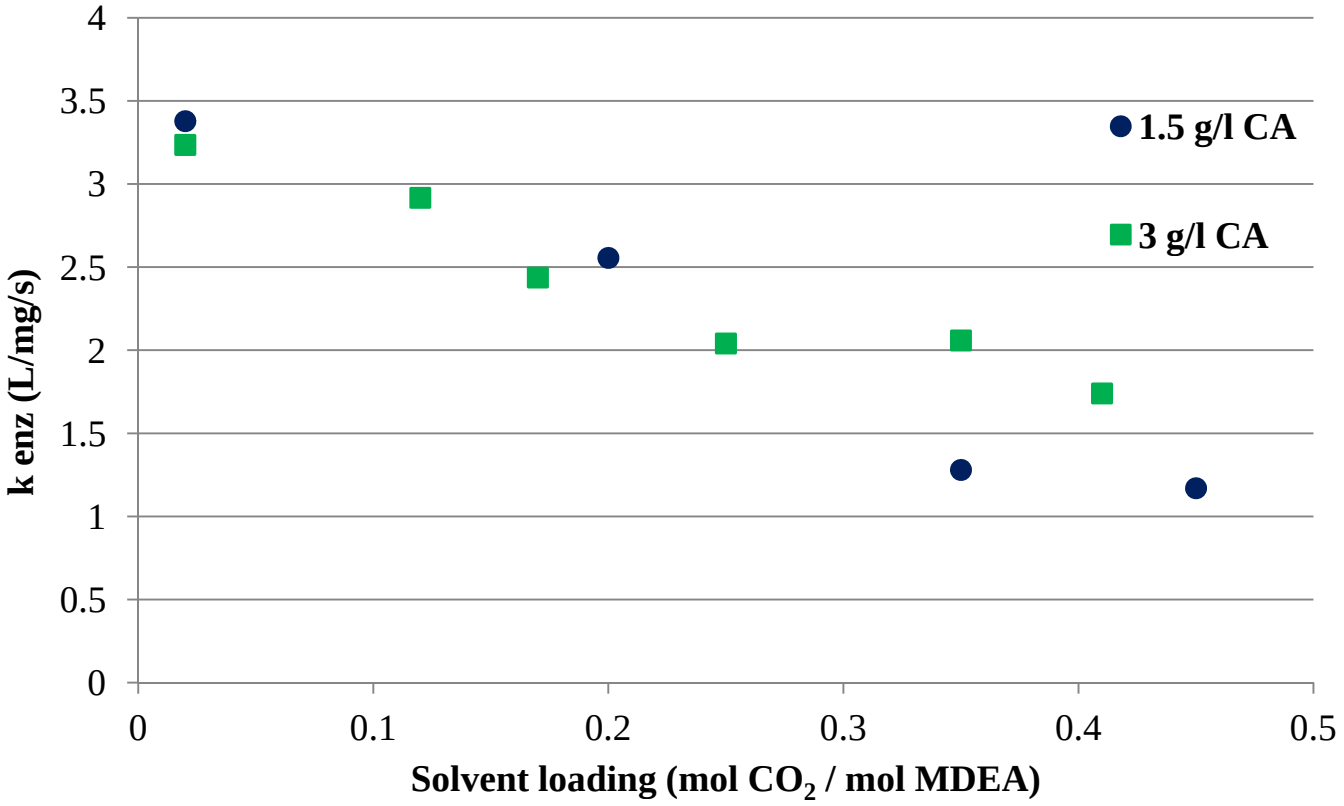
$$k_{ov\_enz} = k_{ov} - k_{ov\_MDEA}$$

$$k_{ov\_enz} = k_{enz} * C_{enz}$$

$$k_{enz} = \frac{k_{cat}}{K_m}$$

- Accounted for gas side mass transfer resistance with Sherwood Analogy
- Accounted for solvent reactions by performing absorption experiments without CA

Enzyme reaction rate constant



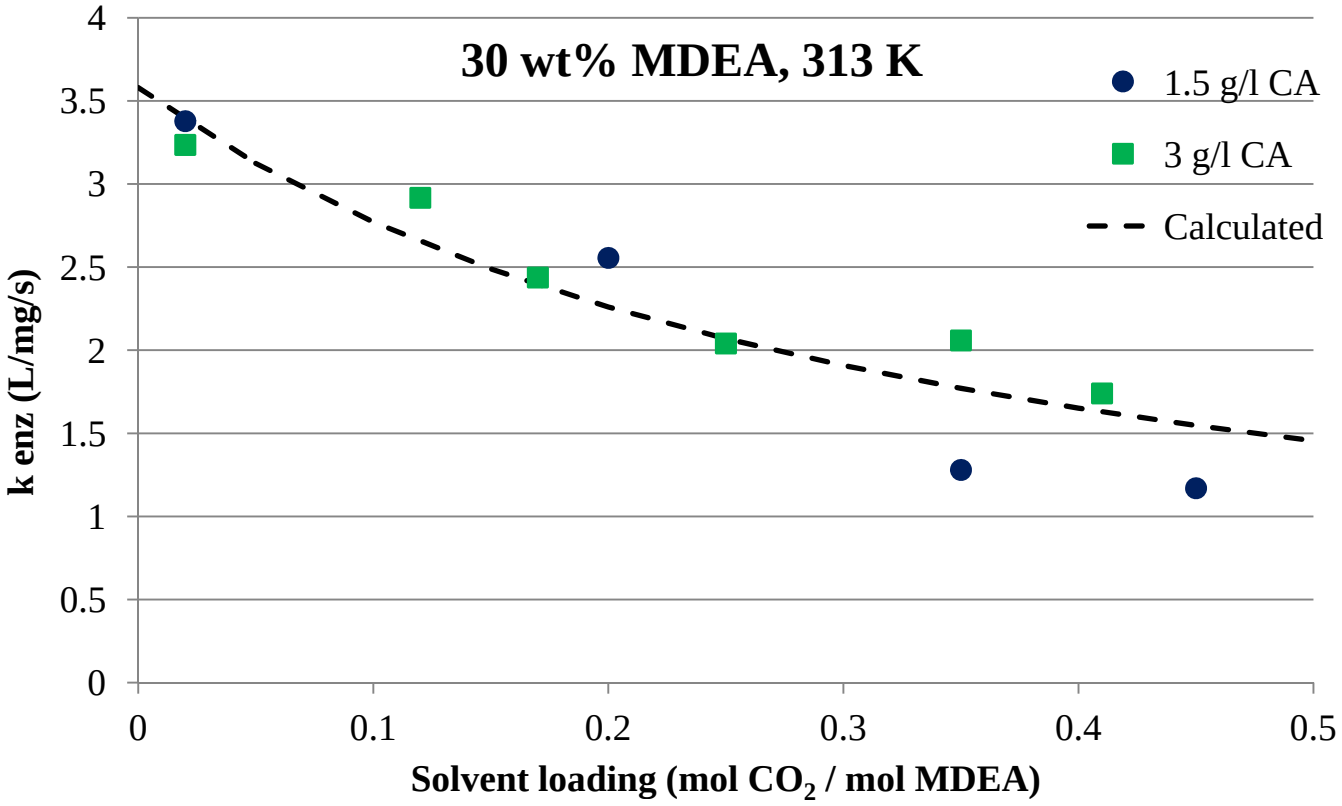
$$k_{ov\_enz} = \frac{k_{enz} * C_{enz}}{1 + \frac{C_{HCO_3^-}}{K_{IHCO_3^-}}}$$

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

- Apparent decrease in Enzyme rate constant with loading of solvent

Inhibition by HCO_3^- ? → Test with a inhibition term

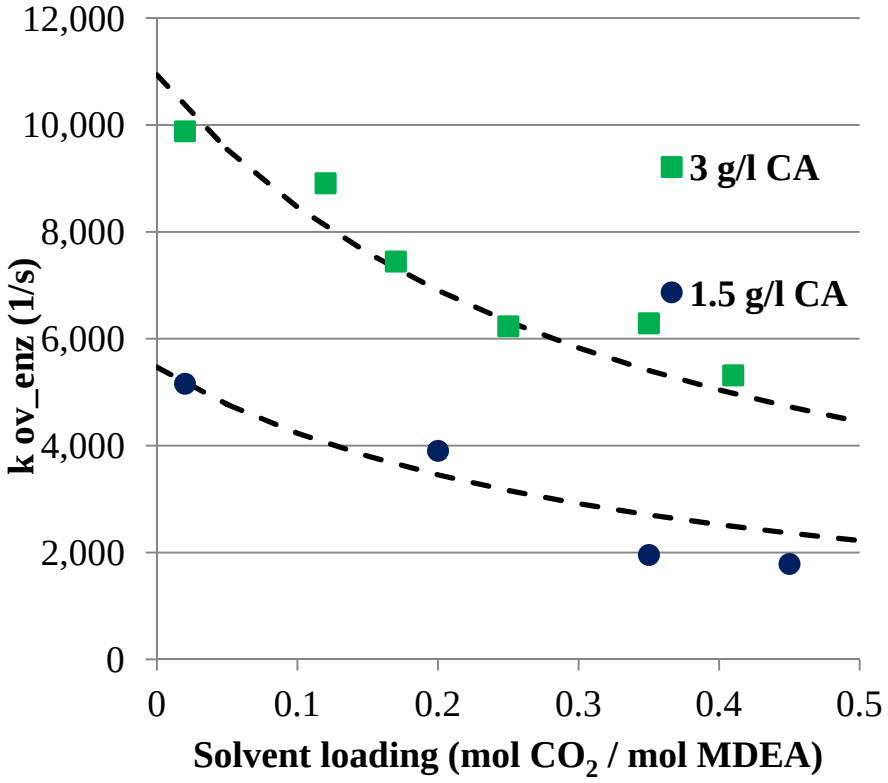
Bicarbonate inhibition

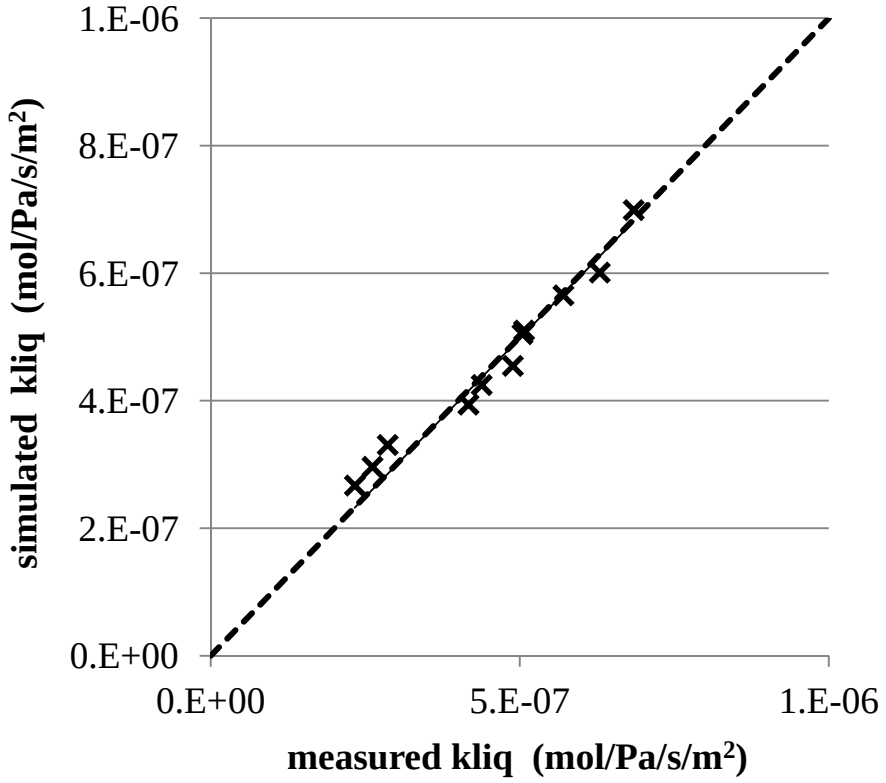


$$k_{ov\_enz} = \frac{3.58 \frac{L}{mg\ s} * C_{enz}}{1 + \frac{C_{HCO_3^-}}{877{,}5 \frac{mol}{m^3}}}$$

- Inhibition term describes the trend of decreasing reaction rate

Accuracy of kinetic model





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Conclusions

- Decrease of overall enzyme reaction rate with increased loading observed
- Decrease of reaction rate independent of enzyme concentration
- Product inhibition by HCO_3^- possible explanation of decrease in reaction rate
- Good agreement between experimental data and simple kinetic model
- enzyme reaction rate at 0.35 loading is half as high as for unloaded solvent

→ Account for that in process simulations

Future work

- Investigate enzyme performance at different temperatures
- Implement temperature dependency into kinetic model
- Compare with different solvents

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Thank you for your attention!