Enzyme enhanced CO_2 absorption

Effect of pKa on enzyme kinetics

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Carbonic anhydrase (CA)

- Is a group of zinc-metallo enzymes
- Is found in almost all living organisms
- Has a pKa value of approx. 7.1
- Catalysis CO_2 hydration at high pH
- Catalysis HCO_3^- dehydration at low pH
- Molecular weight ca 30 000 g/mol

- CA II is most fast of all CA variants
- CA II is found in our red blood cells
- CA II facilitates respiration

Kinetics

- during CO_2 absorption into aqueous tertiary amine solutions:

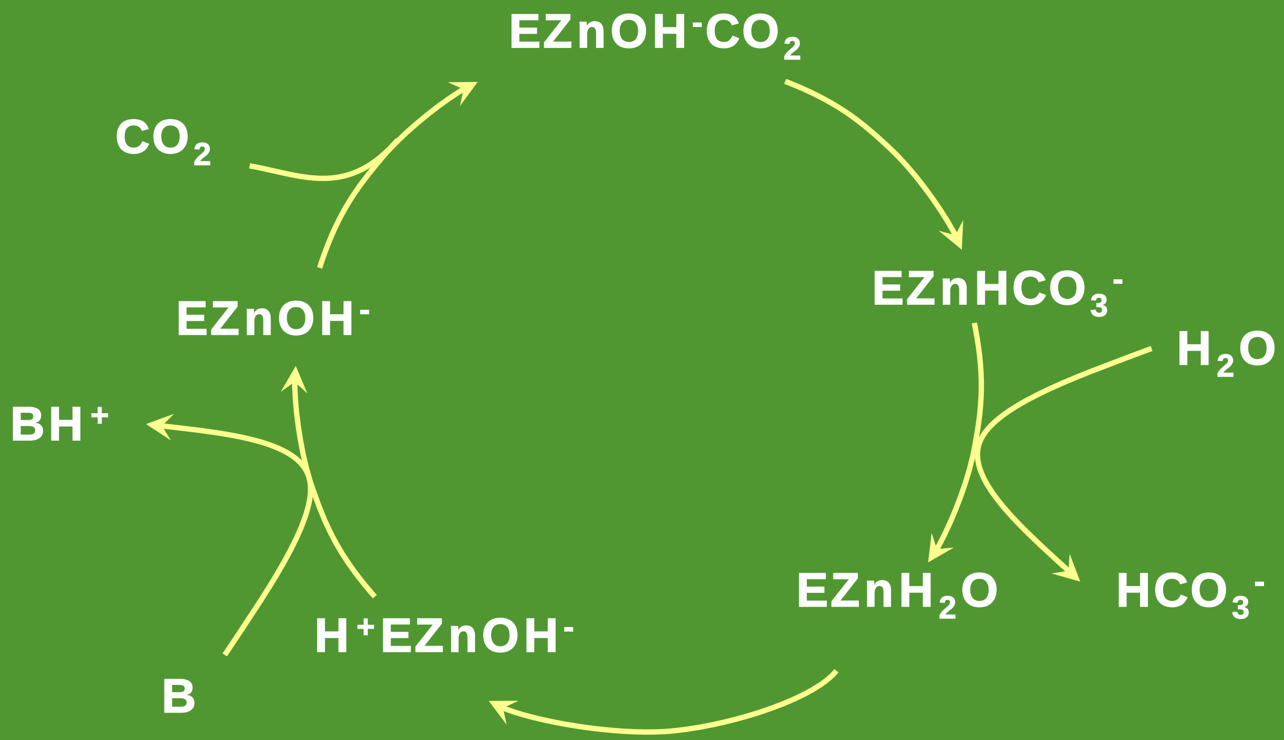
- R1: $CO_2 + R_3N + H_2O \xrightarrow{k_{Am}} HCO_3^- + R_3NH^+$
  - $R_{CO2} = k_{Am} \cdot c_{Am} \cdot c_{CO2} = k_{Am}' \cdot c_{CO2}$

- R2: $CO_2 + OH^- \xrightarrow{k_{OH}} HCO_3^-$
  - $R_{CO2} = k_{OH} \cdot c_{OH} \cdot c_{CO2} = k_{OH}' \cdot c_{CO2}$

- R3: $CO_2 + 2\ H_2O \xrightarrow{k_{H2O}} HCO_3^- + H_3O+$
  - $R_{CO2} = k_{H2O} \cdot c_{CO2}$

- $k_{OV} = k_{Am}' + k_{OH}' + k_{H2O}$

Mechanism of CO_2 hydration with CA



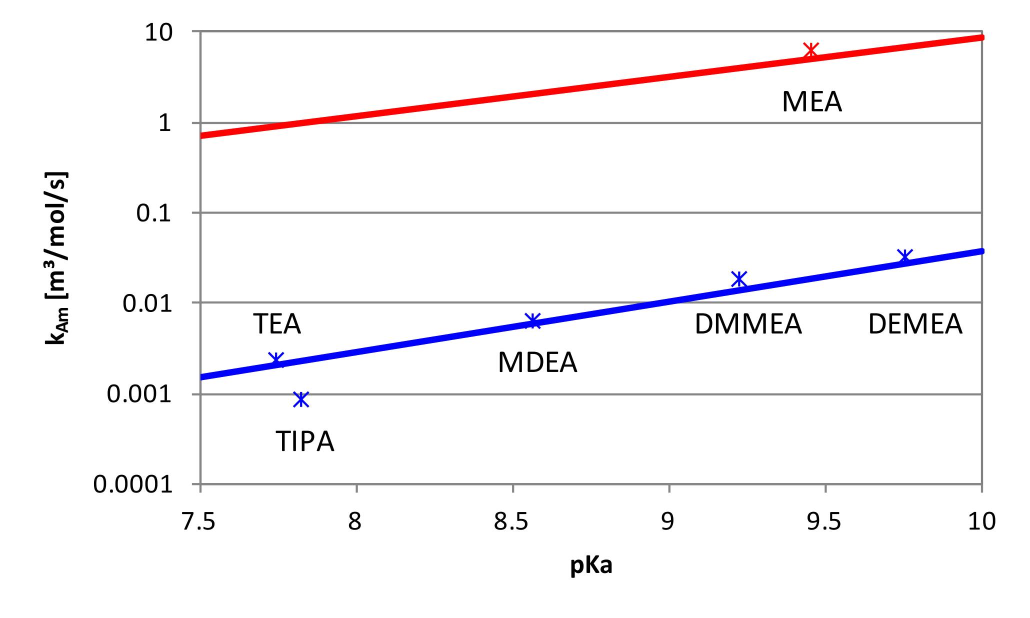
k_{Am} and pKa

- **Versteeg et al (1996):**
  - Primary & secondary amines:

$$\ln(k_{Am}) = 1.0 \cdot pKa + 16.26 - \frac{7188}{T}$$

  - Tertiary amines:

$$\ln(k_{Am}) = 1.3 \cdot pKa + 11.48 - \frac{8270}{T}$$



Mass transfer

- **Absorption rate**

$$J = k_L \cdot E \cdot \left(mC_G - C_L \right)$$

- **Enhancement factor**
  - Total reaction rate

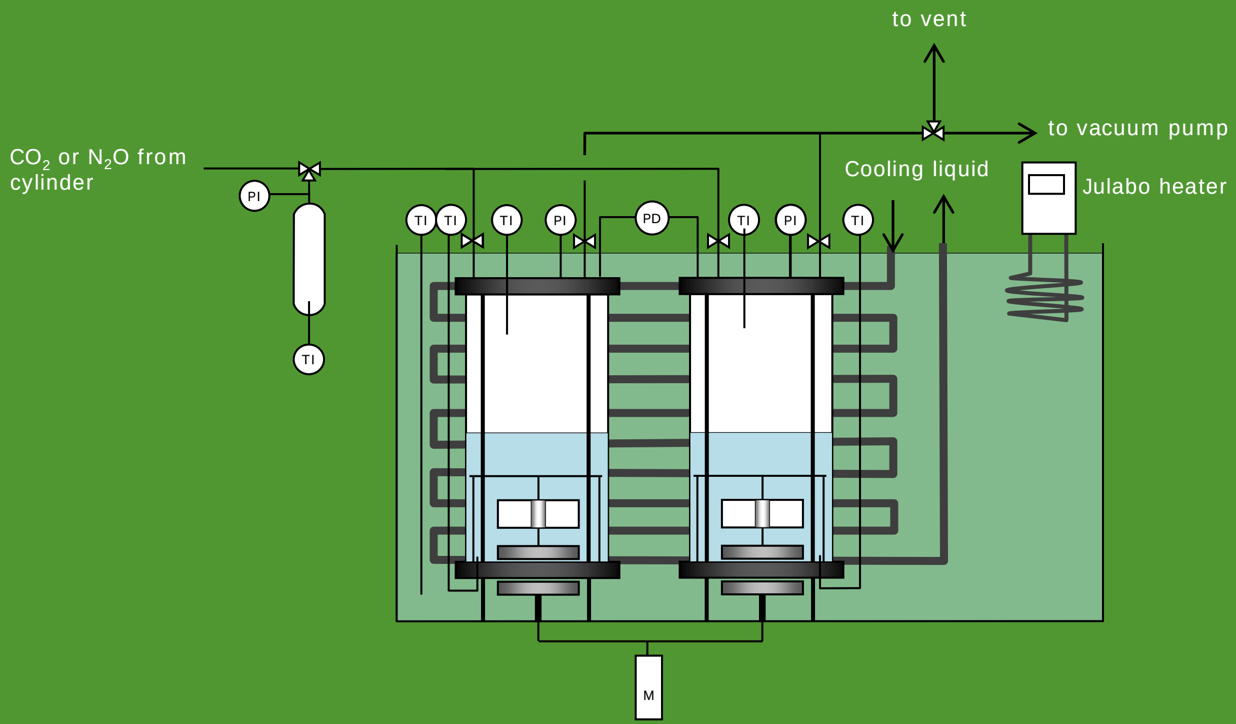
$$R_{CO2} = k_{OV} \cdot C_{CO2}$$

  - At certain (pseudo-first-order) conditions

$$E = Ha = \frac{\sqrt{k_{OV} D_{CO2}}}{k_L} \quad \Rightarrow \quad J = \sqrt{k_{OV} D_{CO2}} \cdot \frac{mP_{CO2}}{RT}$$

Set-up

- **Stirred Cell Contactor**



Features :

- Pressure readout
- Temperature readout
- Temperature control

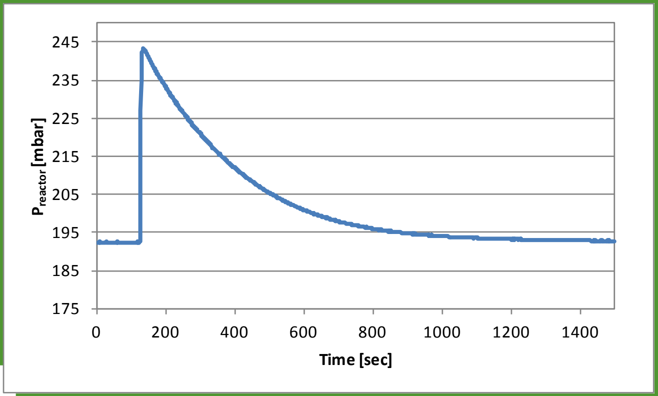
- Liquid phase stirring
- Flat gas-liquid interface

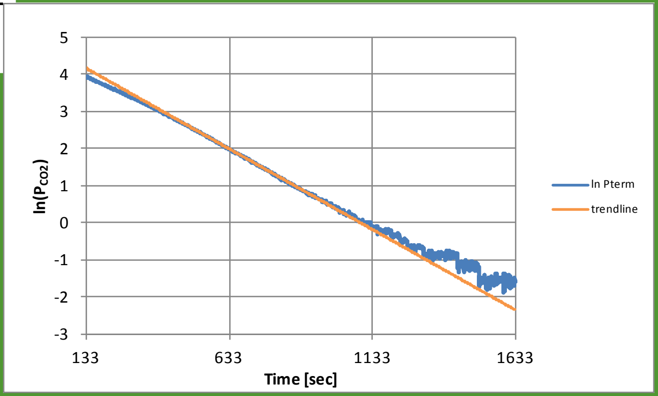
- Vacuum connection
- CO_2 / N_2O connection

Procedure

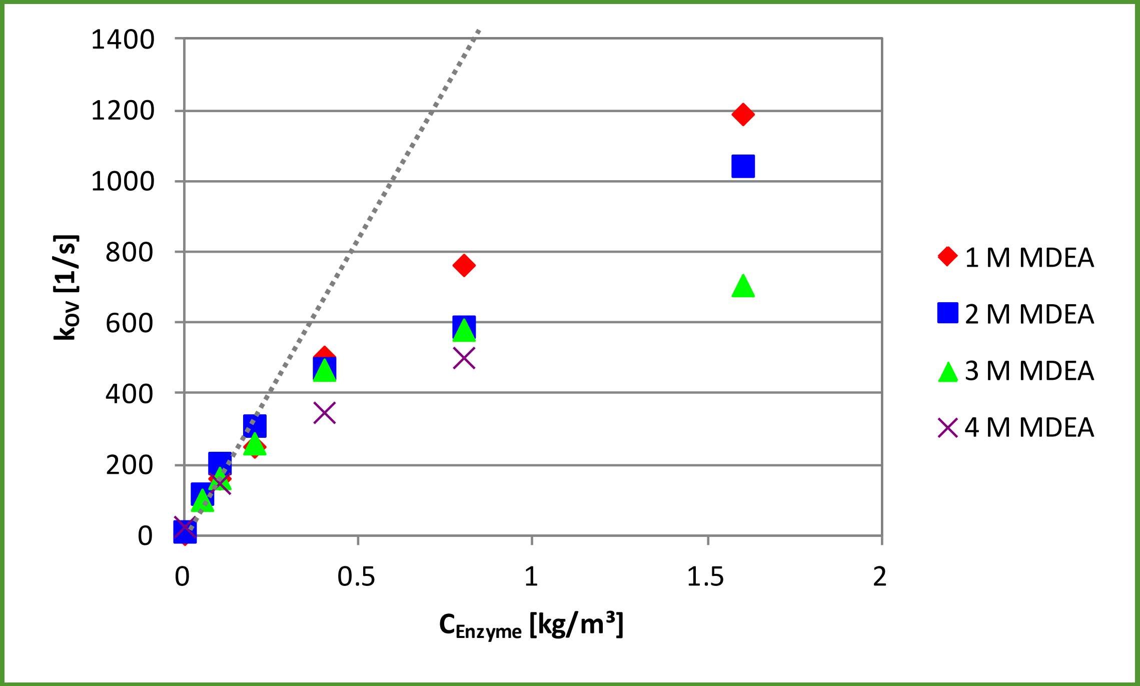
- **Stirred Cell Contactor**
  - **Flux Equation:** $$J = \sqrt{k_{OV} D_{CO2}} \cdot \frac{m_{CO2} P_{CO2}}{RT}$$
  - **Gas phase MB:** $$\frac{d}{dt} \frac{P_{CO2} V_G}{RT} = -J_{CO2} A$$

⇨ **Overall Equation:** $$\frac{d \ln P_{CO2}}{dt} = -\sqrt{k_{OV} D_{CO2}} \frac{m_{CO2}}{V_G} A$$





Absorption rate experiments

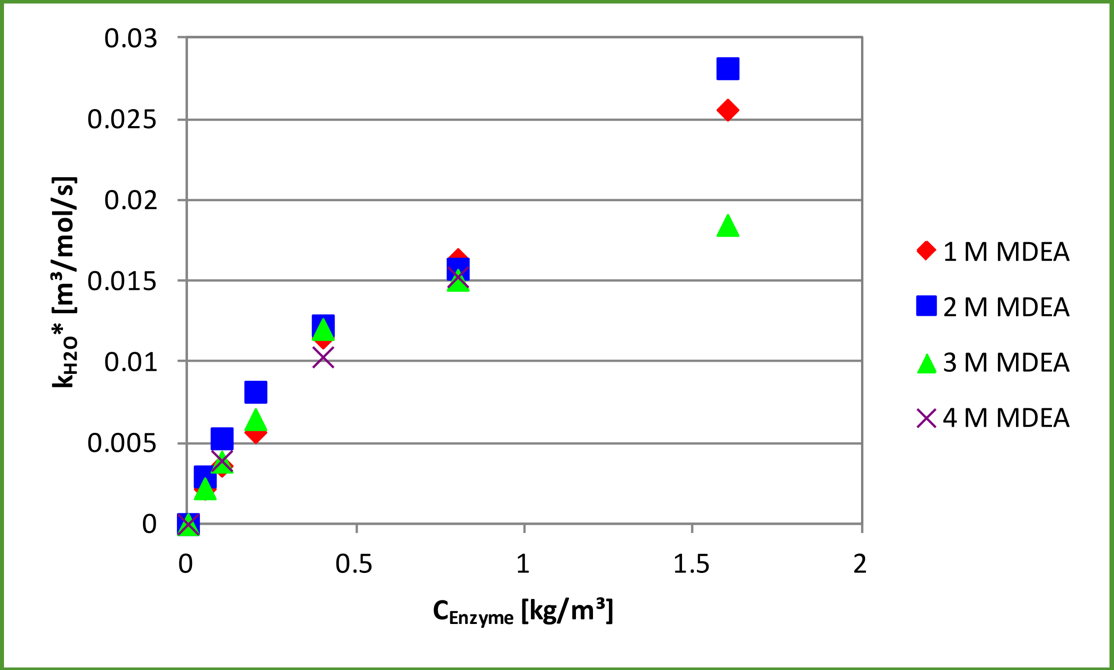


- Overall reaction rate increases with increasing enzyme concentration
  - At low enzyme concentration reaction rate linear dependent on enzyme concentration
  - At higher enzyme concentration rate increase levels off

Absorption rate experiments

- k_{H2O}* is calculated as:

$$k^{*}_{H2O} = \frac{k_{OV,with\ CA} - k_{OV,without\ CA}}{C_{H2O}}$$



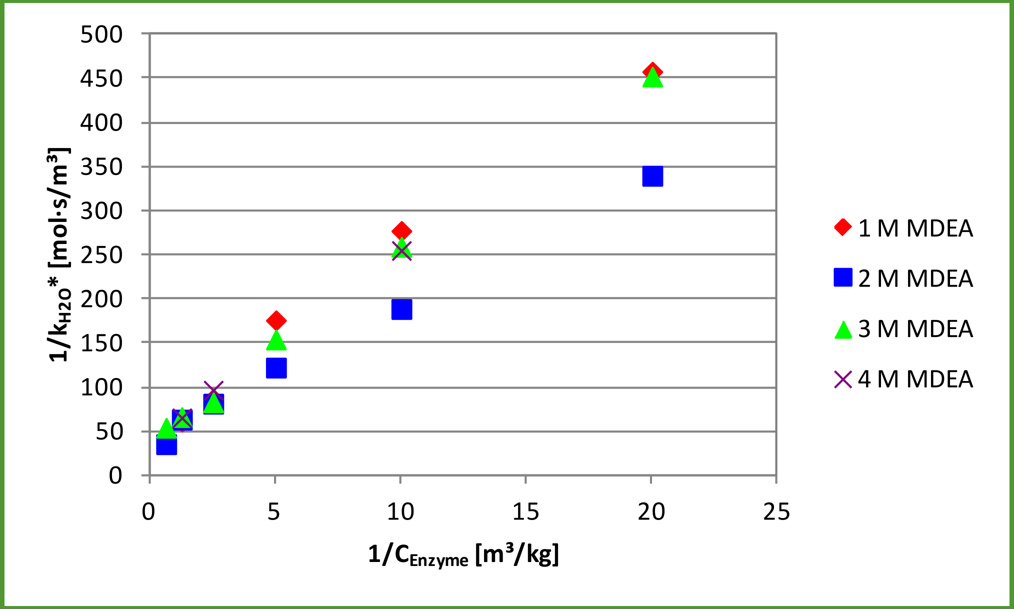
- Catalyzed reaction is independent of MDEA concentration
- Catalyzed reaction is first order in water

⇨ Reaction 3 is enhanced by enzyme

PROCEDE

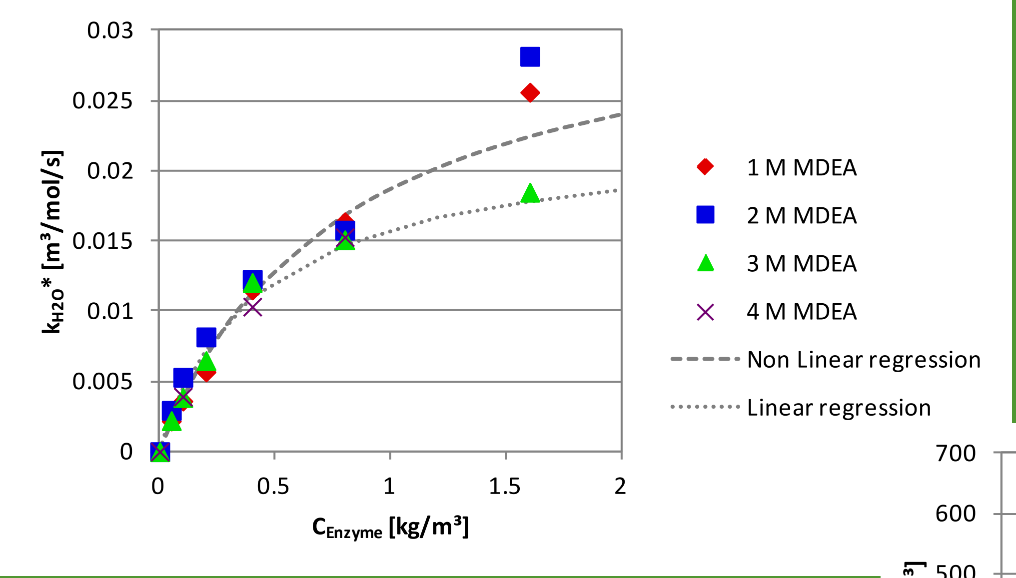
Absorption rate experiments

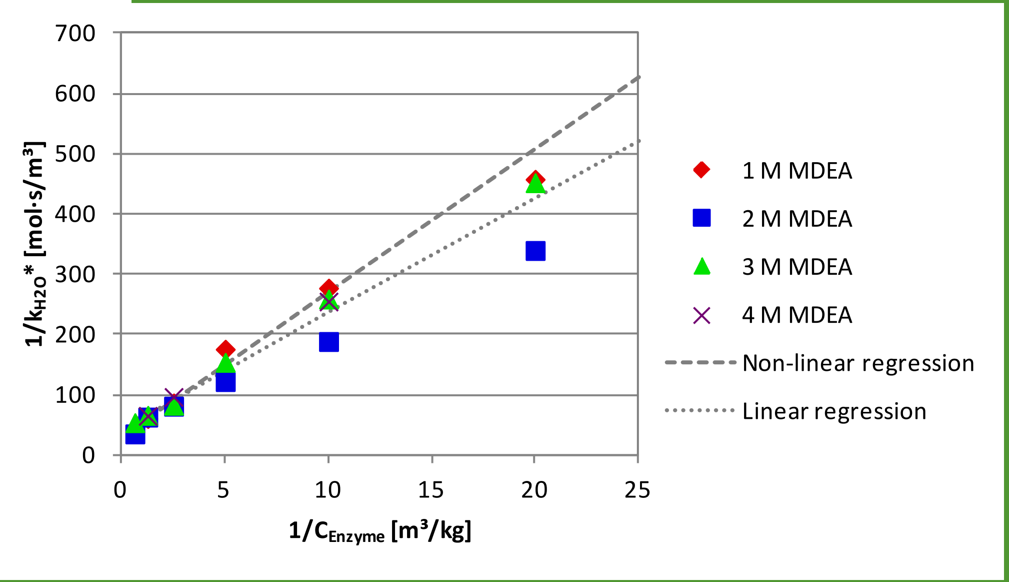
- Enzymatic rate constant, $k_{H2O}{}^*$: $$k^*_{H_2O} = \frac{k^*_3 C_{Enzyme}}{1 + k^*_4 C_{Enzyme}}$$
- Or linearised: $$\frac{1}{k^*_{H_2O}} = \frac{1}{k^*_3} \cdot \frac{1}{C_{Enzyme}} + \frac{k^*_4}{k^*_3}$$



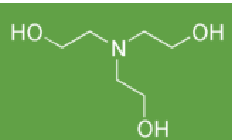
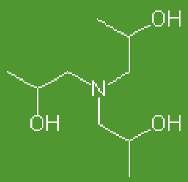
PROCEDE

Absorption rate experiments

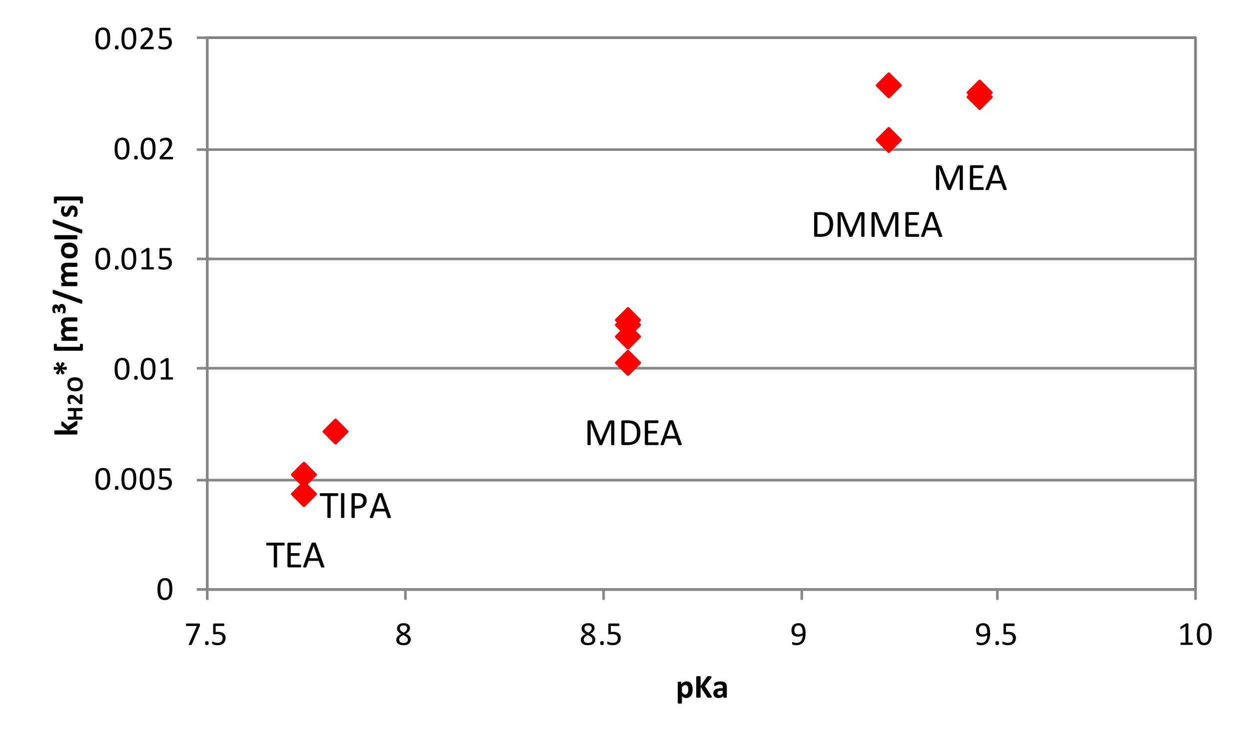




pKa effect

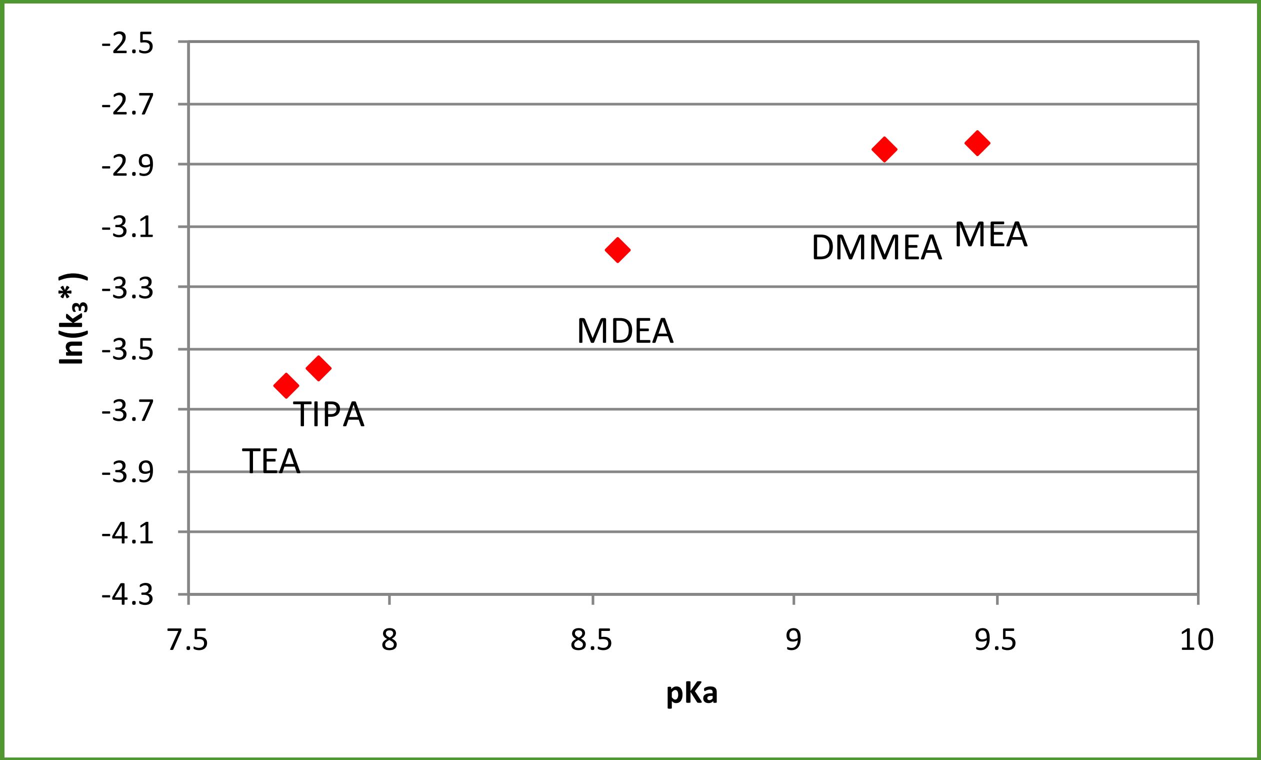
Amine	Structure	MW [g/mol]	C_{H2O} @ 1 M Am [kmol/m³]	pKa
TEA		149.19	48.3	7.74
TIPA		191.27	45.5	7.82
MDEA		119.16	49.3	8.56
DMMEA		89.14	50.1	9.22
MEA		61.08	52.1	9.45

pKa effect



pKa value of amine has large influence on k_{H2O}*

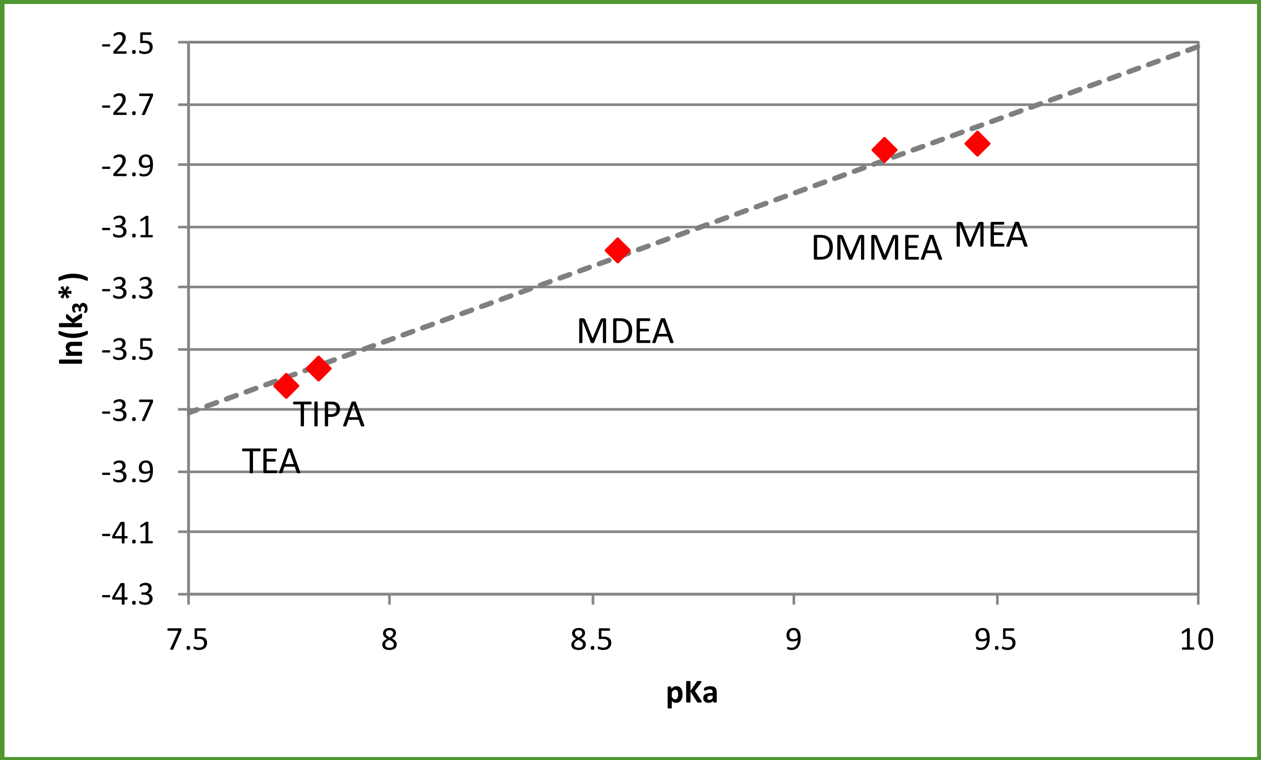
pKa effect



-2.5
-2.7
-2.9
-3.1
-3.3
-3.5
-3.7
-3.9
-4.1
-4.3
ln(k3*)
DMMEA
MEA
MDEA
TIPA
TEA
7.5
8
8.5
9
9.5
10
pKa

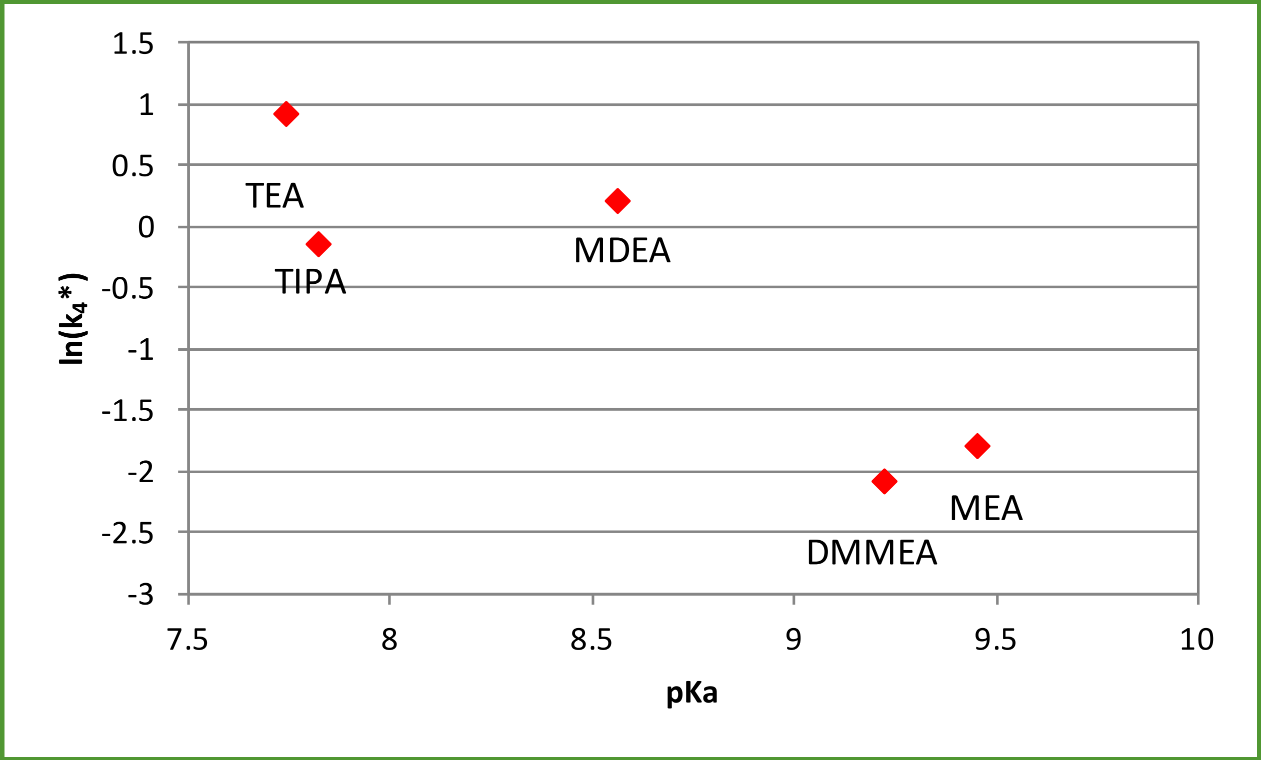

PROCEDE

pKa effect



$$k_3^* = 6.7 \cdot 10^{-4} \exp(0.48 \cdot pKa) \quad [m^6 kg^{-1} mol^{-1} s^{-1}]$$

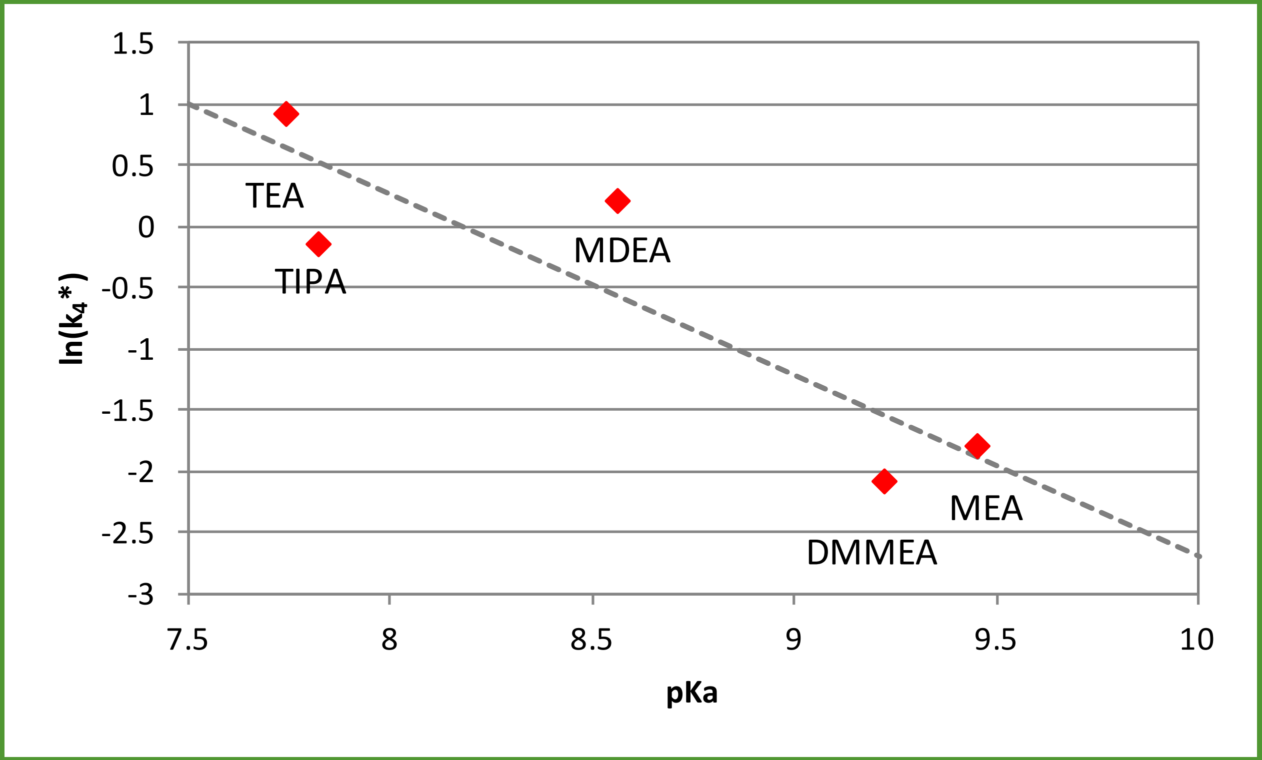
pKa effect



ln(k4*)
pKa
TEA
TIPA
MDEA
DMMEA
MEA
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
7.5
8
8.5
9
9.5
10

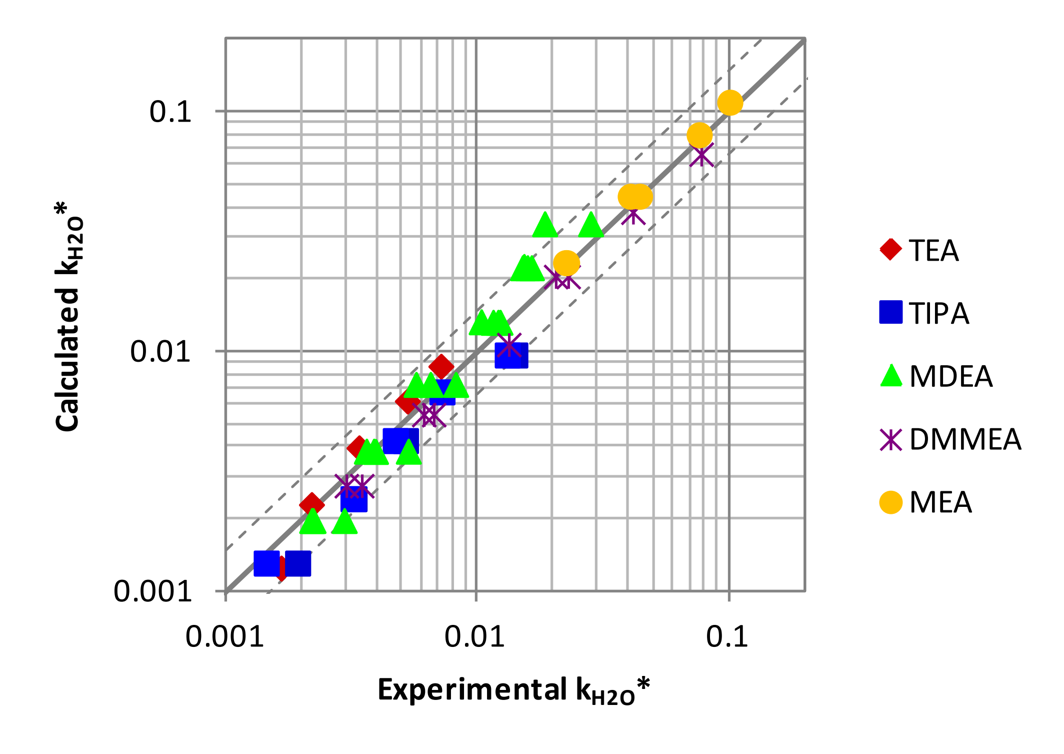
PROCEDE

pKa effect



$$k_4^* = 1.8 \cdot 10^5 \exp(-1.5 \cdot pKa) \quad [m^3 kg^{-1}]$$

pKa effect



$$k^{*}_{H2O} = \frac{6.7 \cdot 10^{-4} \exp(0.48 \cdot pKa) \cdot C_{Enzyme}}{1 + 1.8 \cdot 10^{5} \exp(-1.5 \cdot pKa) \cdot C_{Enzyme}}$$

Summarising

- **Carbonic Anhydrase enhances CO_2 absorption**
- **Catalysed CO_2 absorption is:**
  - Independent of amine concentration
  - First order in water
- **=> CA catalyses the CO_2 hydration reaction**
- **Enzymatic reaction rate constant:**

$$k_{H2O}^{*} = \frac{k_3^{*} C_{Enzyme}}{1 + k_4^{*} C_{Enzyme}}$$

- **pKa of amine has large influence on k_{H2O}***
  - The more basic the amine the faster the CO_2 hydration
  - The more basic the amine the faster the enzyme regeneration