Nitrosamine Formation in Amine Scrubbing

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Outline

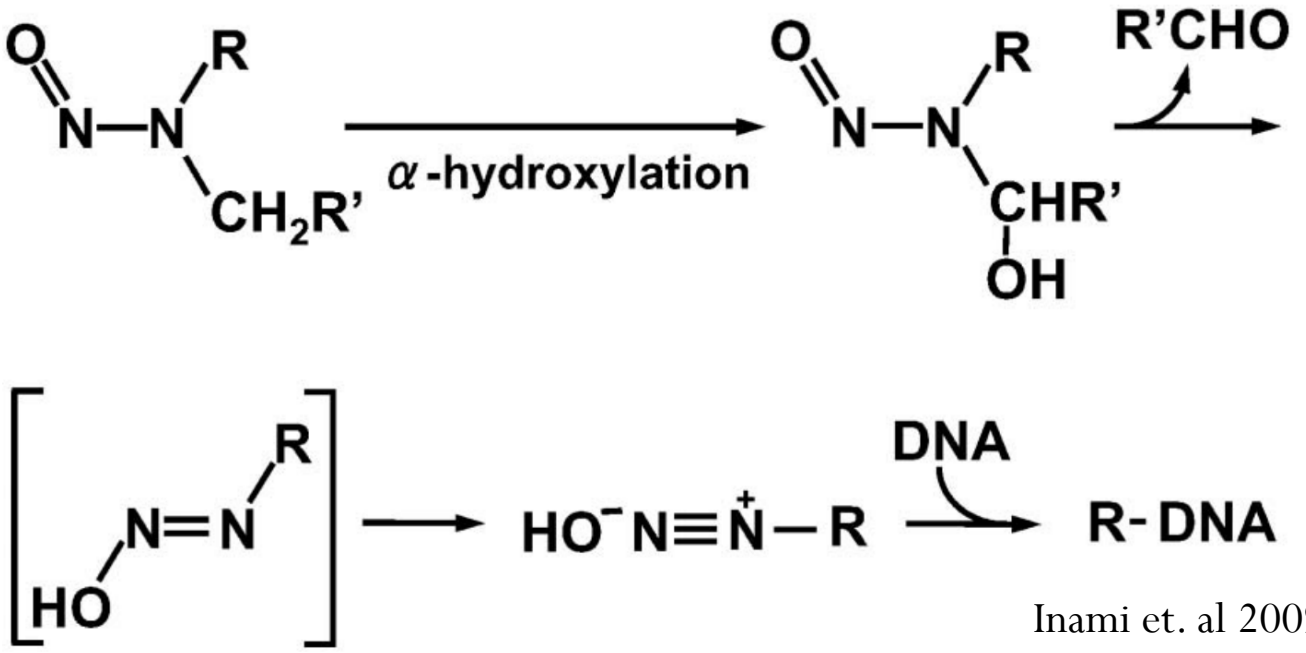
- Motivation
  - Carcinogenicity
  - Nitrosamine Cycle
- Current Work
  - NO_2 absorption
  - Nitrosation from nitrite
- Nitrosamine accumulation

Motivation

Maximize environmental benefit of amine scrubbing

Nitrosamine Carcinogenicity

- React in target organs to form diazonium-carbocation intermediates
- Leads to DNA alkylation and tumor growth
- Over 80% are carcinogenic



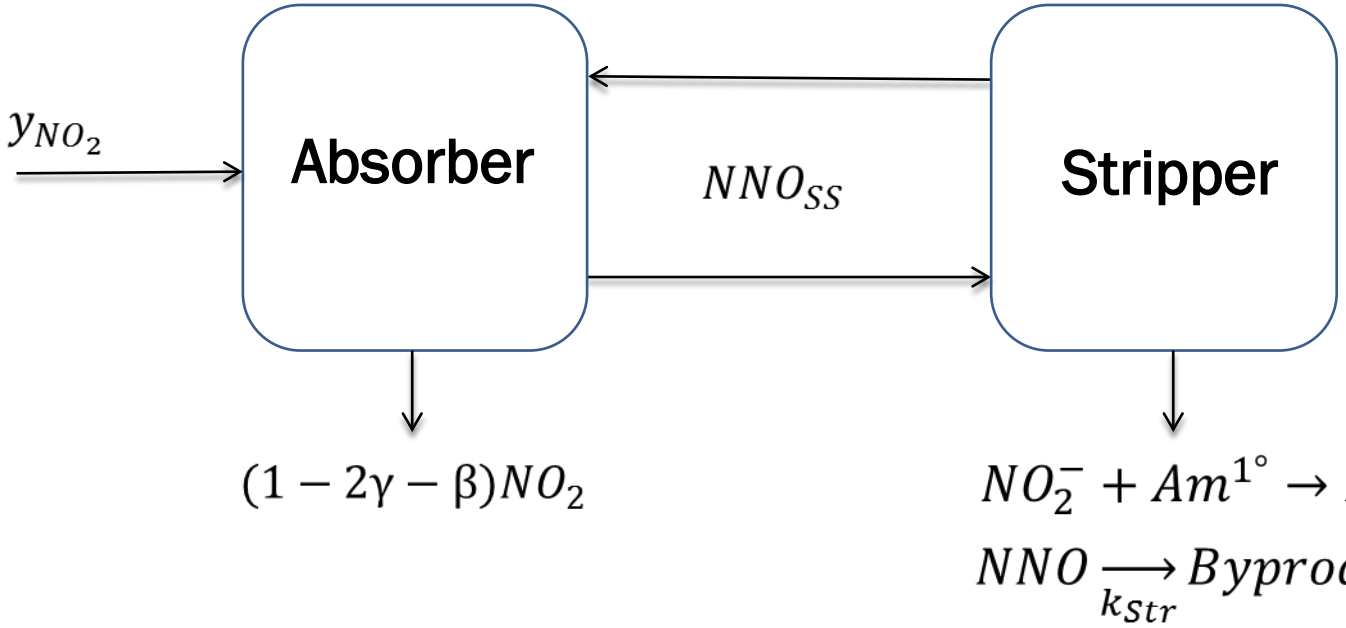
Inami et. al 2009

Nitrosamine Cycle

$$\beta NO_2 + Am \rightarrow NO_2^- + Am\cdot$$

$$\gamma 2NO_2 + Am \rightarrow AmNO + NO_3^-$$

$$\delta NO_2^- + Am^{2^\circ} \rightarrow AmNO$$



$$NNO_{SS} = \frac{y_{NO_2}\frac{G}{L}\left(\delta\beta + \frac{1}{2}\gamma\right)}{k_{Str}\tau_{Str}}$$

Nitrosamine Formation

NO_2 absorption

Nitrosation from nitrite

NO_2 Absorption Chemistry

- **Hydrolysis**

$$2NO_2 \leftrightarrow N_2O_4$$

$$N_2O_4 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O$$

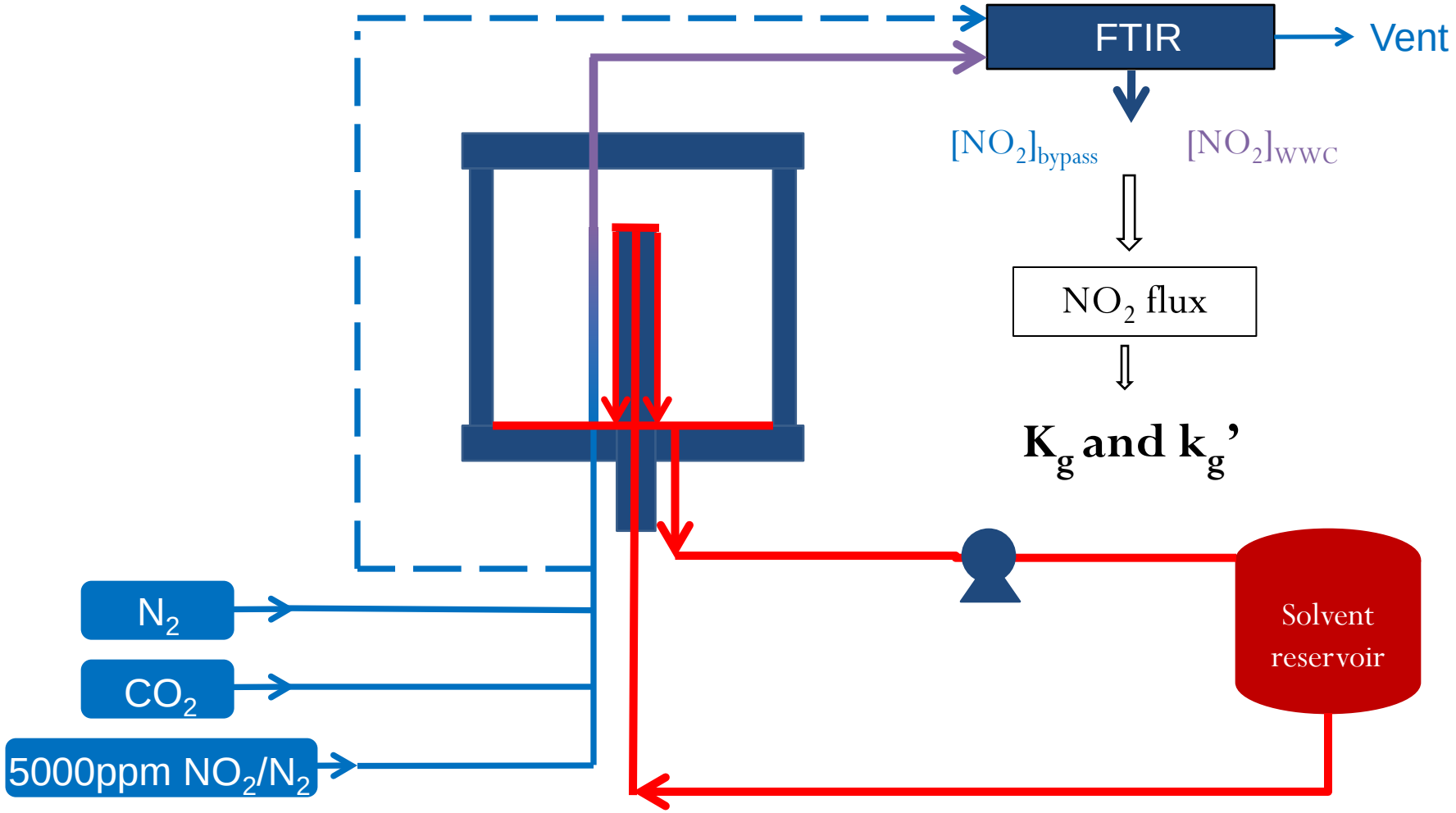
Gas Phase Nitrosation

$$N_2O_4 + Am + OH^- \rightarrow AmNO + NO_3^- + H_2O$$

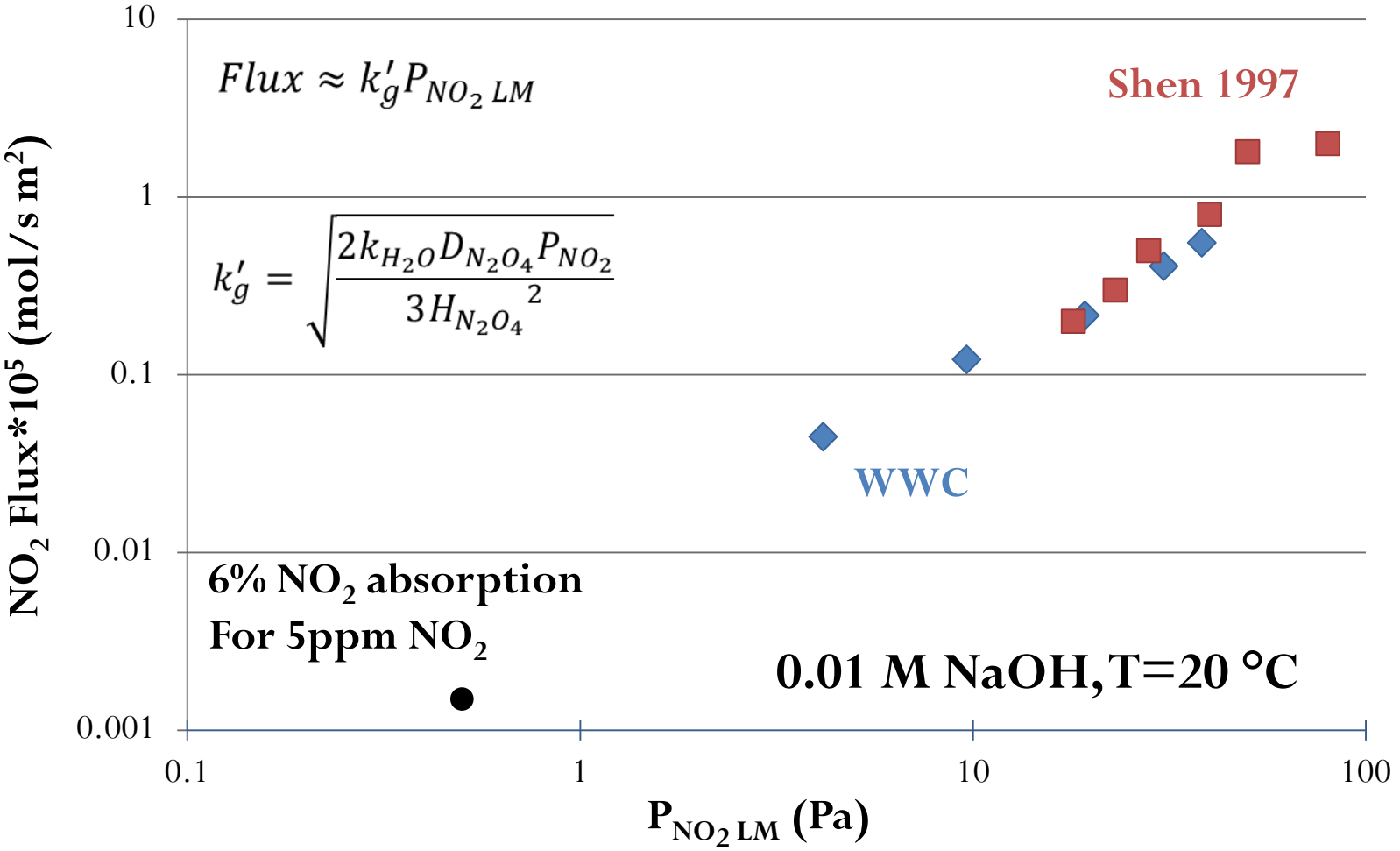
Absorption as nitrite

$$NO_2 + Am + OH^- \rightarrow NO_2^- + Am\cdot + H_2O$$

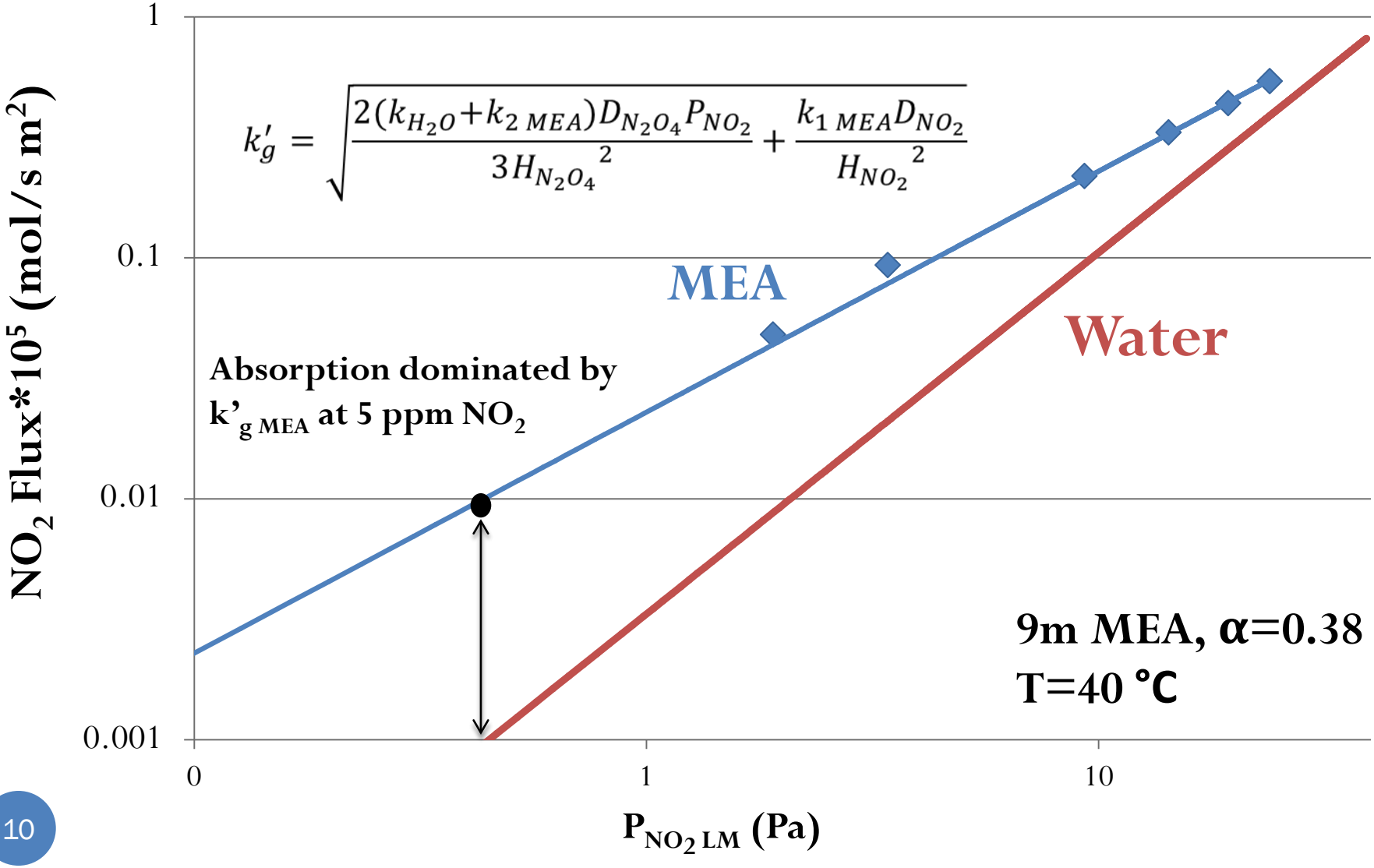
The Wetted Wall Column



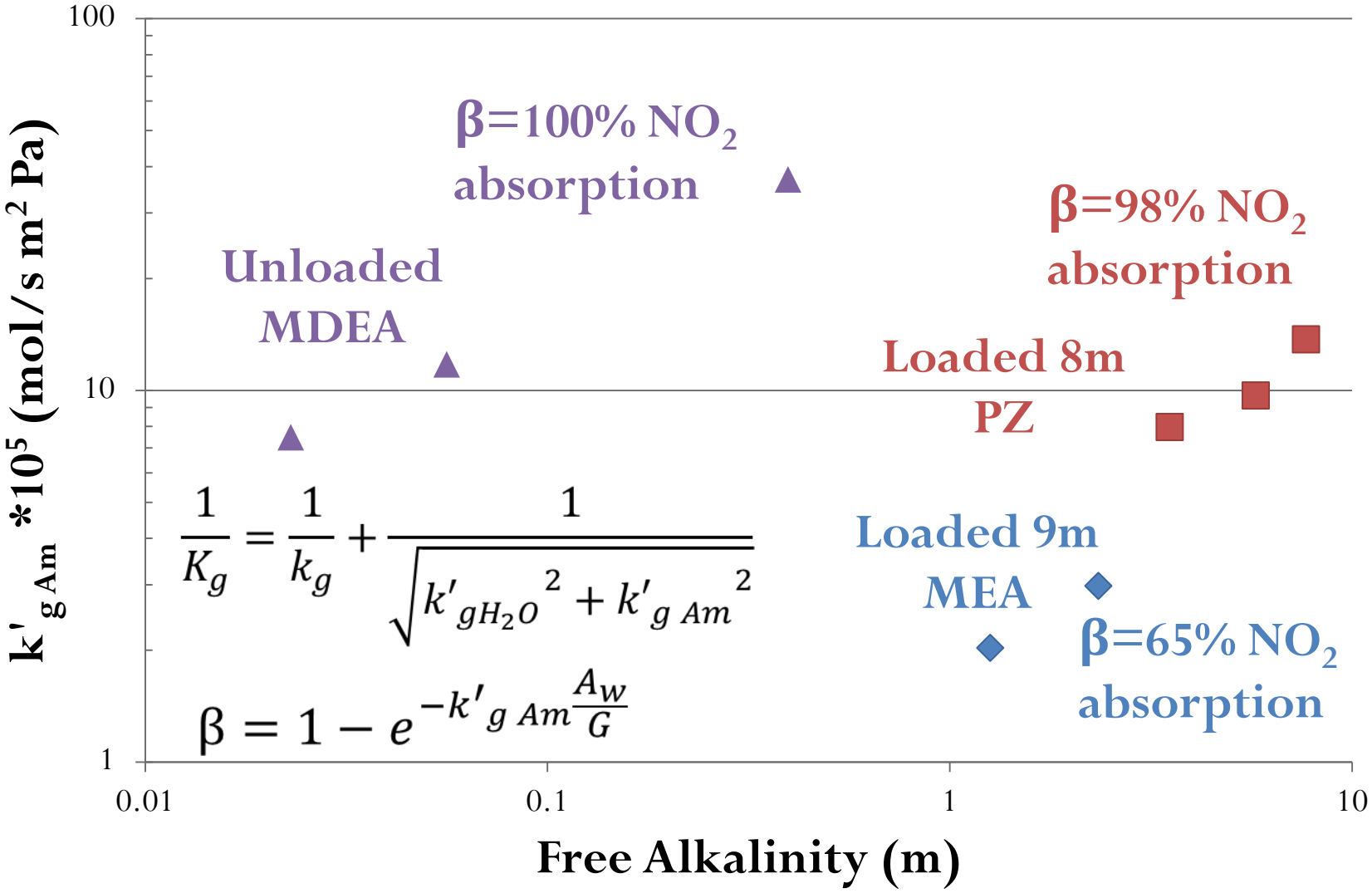
NO_2 Absorption into Water



NO_2 Absorption into MEA



NO_2 Absorption Into Amines

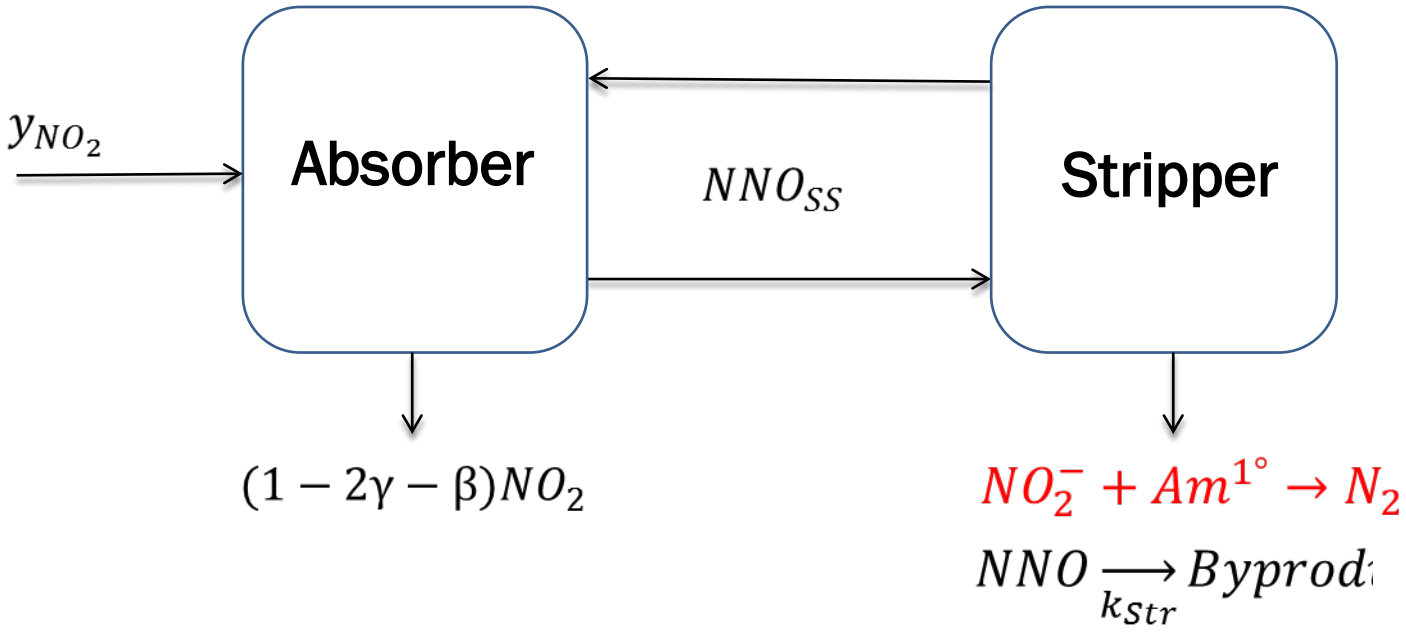


Nitrosation from Nitrite

$$\boldsymbol{\beta NO_2 + Am \rightarrow NO_2^- + Am\cdot}$$

$\delta NO_2^- + Am^{2^\circ} \rightarrow AmNO$

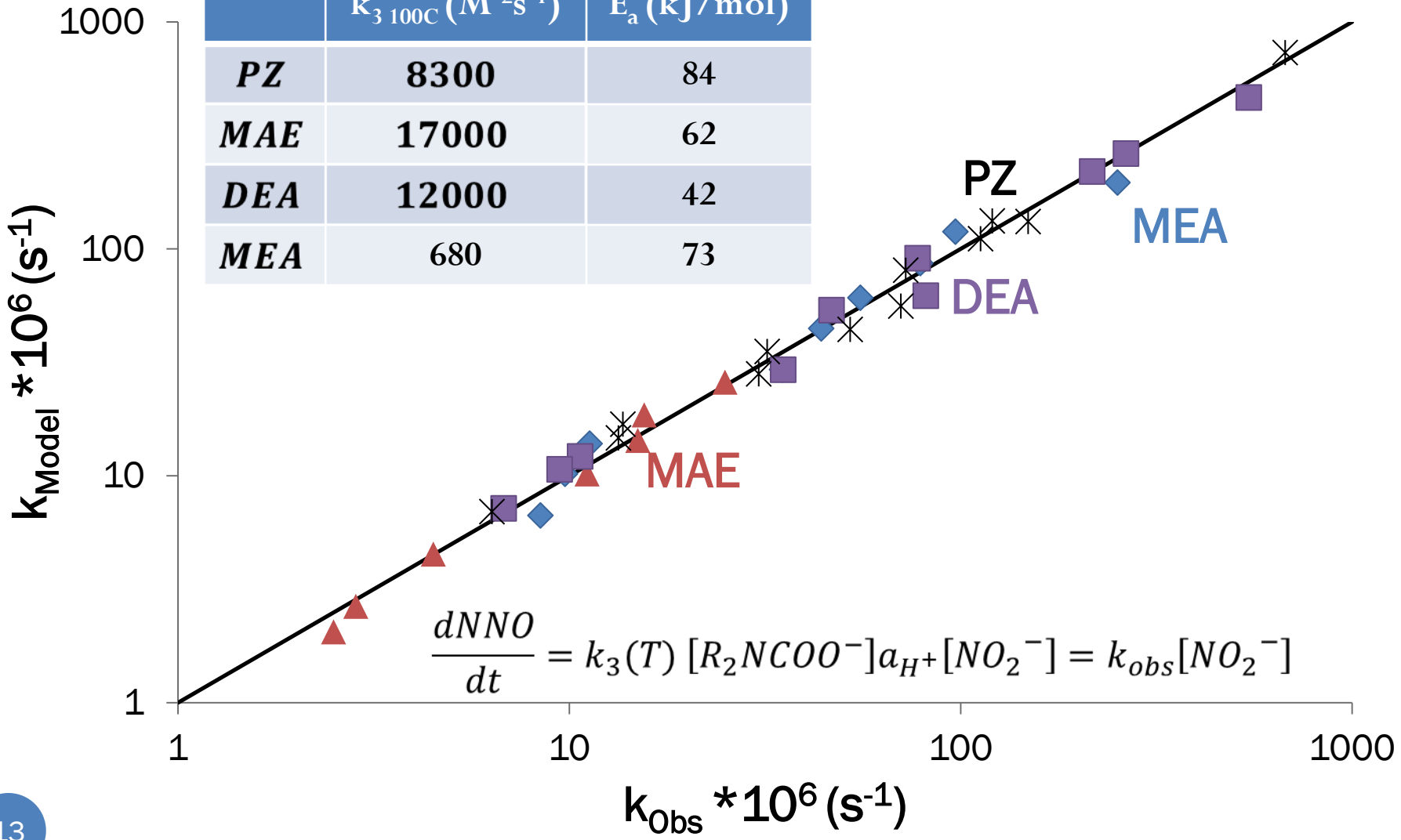
$\gamma 2NO_2 + Am \rightarrow AmNO + NO_3^-$



$$NNO_{SS} \approx y_{NO_2} \frac{G}{L} * \left(\frac{\delta\beta}{k_{Str}\tau_{Str}} \right)$$

Nitrosation of 1°/2° Amines with Nitrite

	$k_{3\ 100C}$ ($M^{-2}s^{-1}$)	E_a (kJ/mol)
PZ	**8300**	84
MAE	**17000**	62
DEA	**12000**	42
MEA	680	73



Nitrosamine yield: 1° Amines

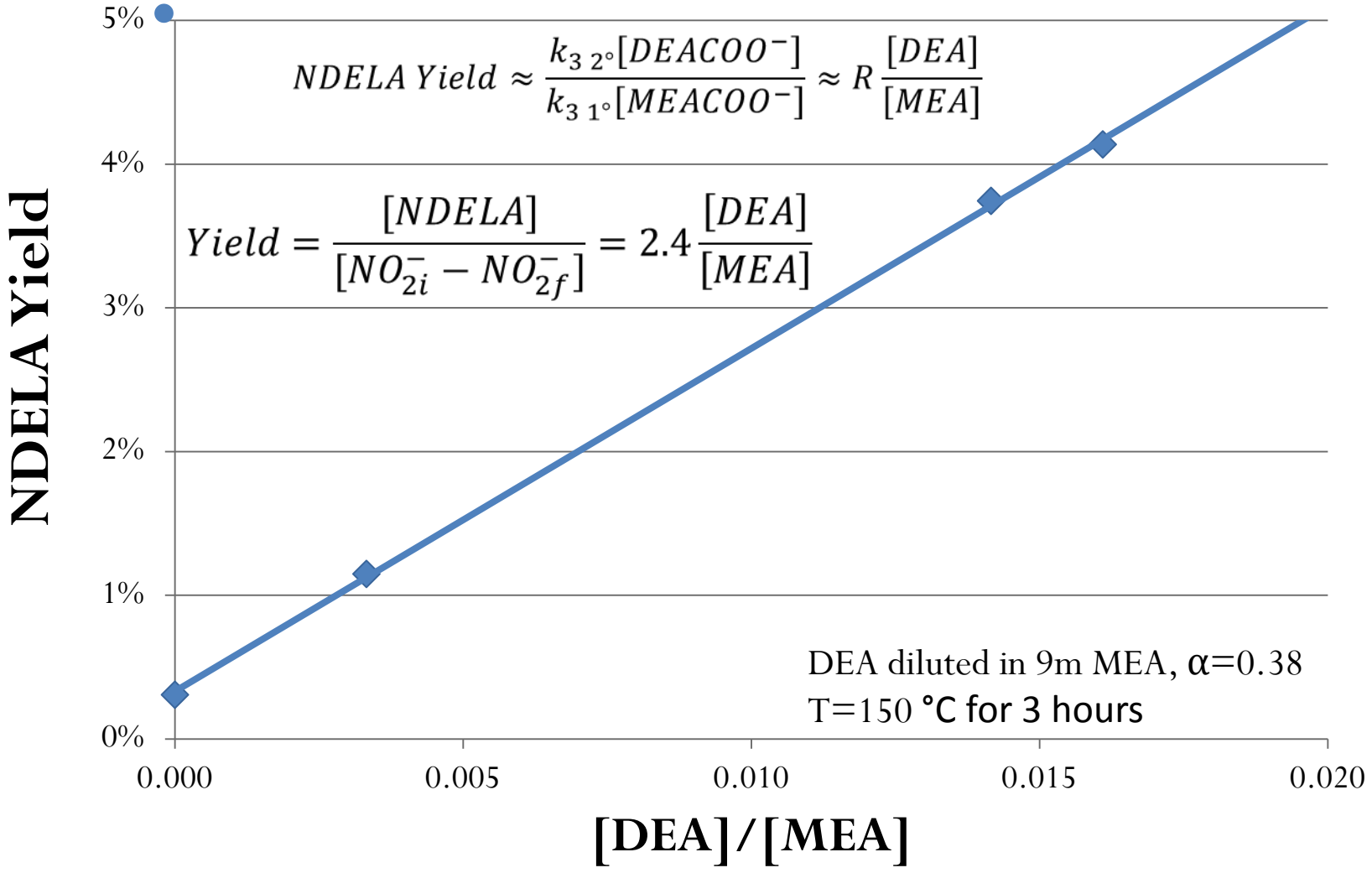
- Yield determined by competing 1° and 2° amine reactions
- Loading affects yield by changing carbamate speciation

$$NNO\ Yield = \frac{k_{3\ 2^\circ}[2^\circ AmCOO^-]}{k_{3\ 1^\circ}[1^\circ AmCOO^-] + k_{3\ 2^\circ}[2^\circ AmCOO^-]}$$

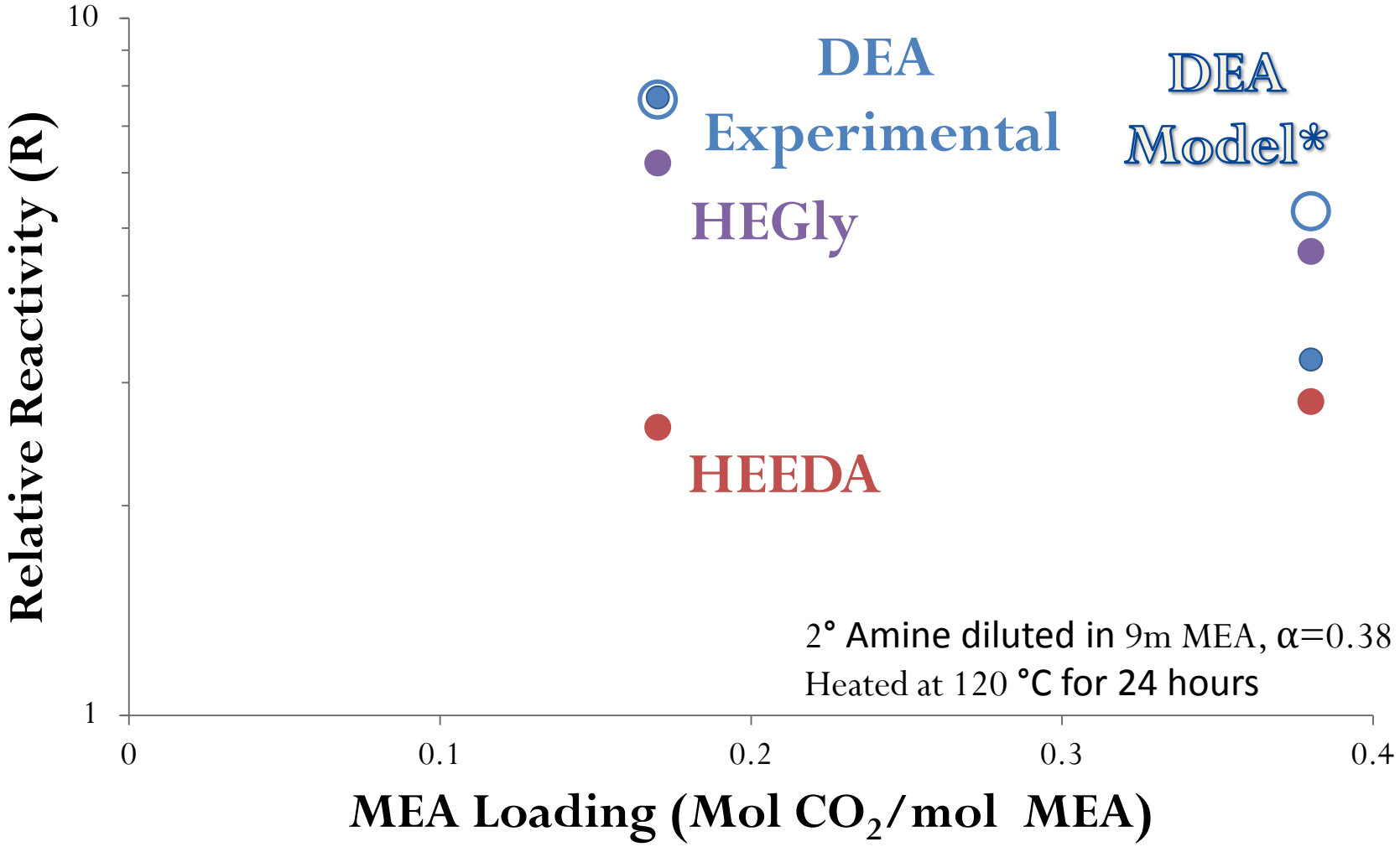
$$1^\circ Am + 2^\circ AmCOO^- \underset{\frac{K_c 1^\circ Am}{K_c\ 2^\circ Am}}{\longleftrightarrow} 1^\circ AmCOO^- + 2^\circ Am$$

$$1^\circ Am + 2^\circ AmH^+ \underset{\frac{K_a 1^\circ Am}{K_a 2^\circ Am}}{\longleftrightarrow} 1^\circ AmH^+ + 2^\circ Am$$

Dilute DEA in MEA



Reactivity in 9m MEA



*Carbamate and protonate stability for DEA/MEA extrapolated from 40 °C

Nitrosamine yield: 2°/3° Amine Blends

- Tertiary amines do not form carbamates
  - Nitrosate very slowly
  - Yield from 2° amine nitrosation is close to unity at promoter concentrations

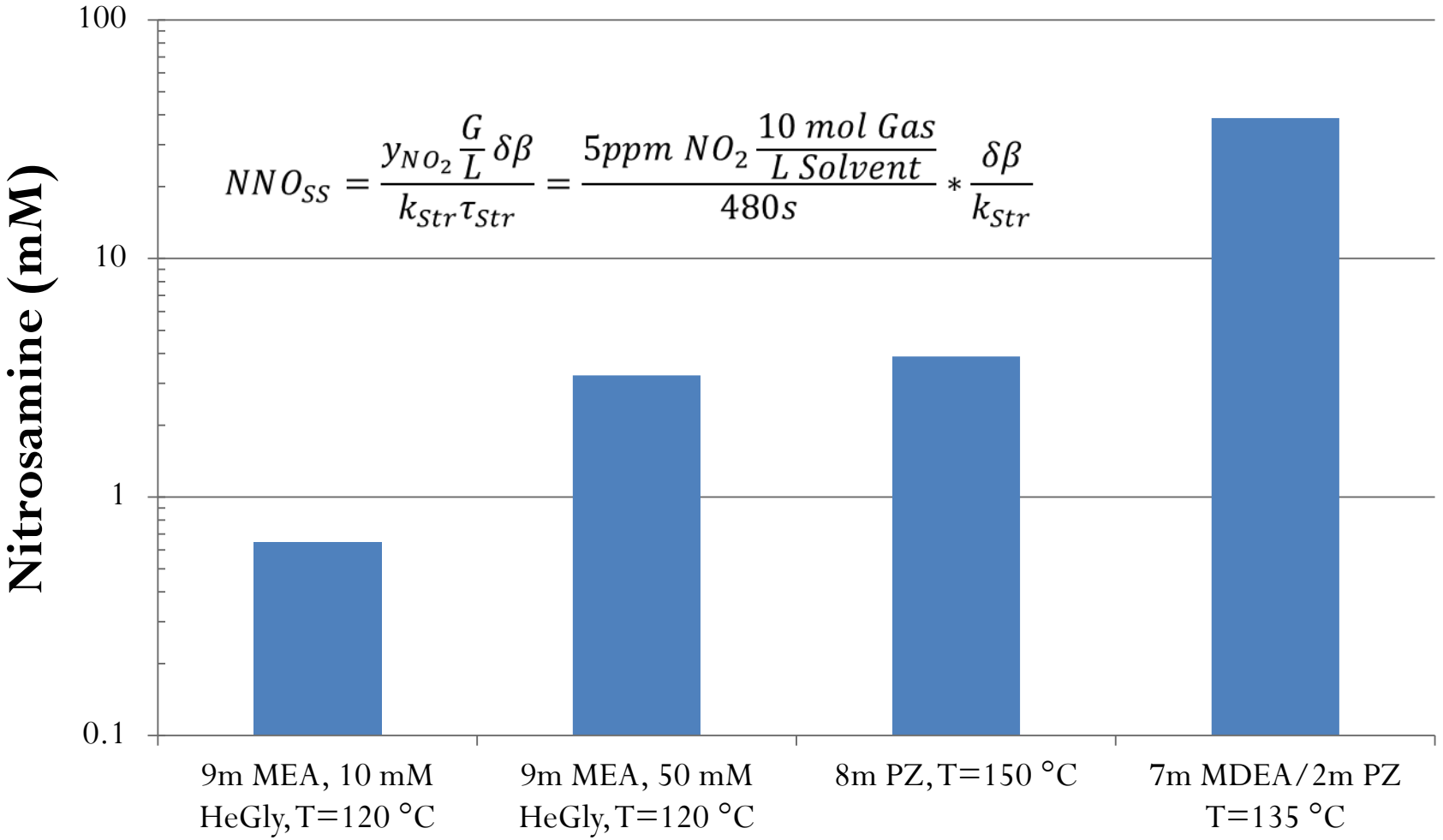
Blend	MNPZ Yield (%)
0.1-8m PZ	**95±11**
PZ/Methyldiethanolamine (MDEA)	**85**
PZ/Triethanolamine (TEA)	**102**
PZ/Dimethylaminopropanol (DMAP)	**93**
PZ/Diethylaminoethanol (DEAE)	**96**

2m PZ / 7m 3° amine; α=0.25; Heated for 3 hours at T = 150 °C

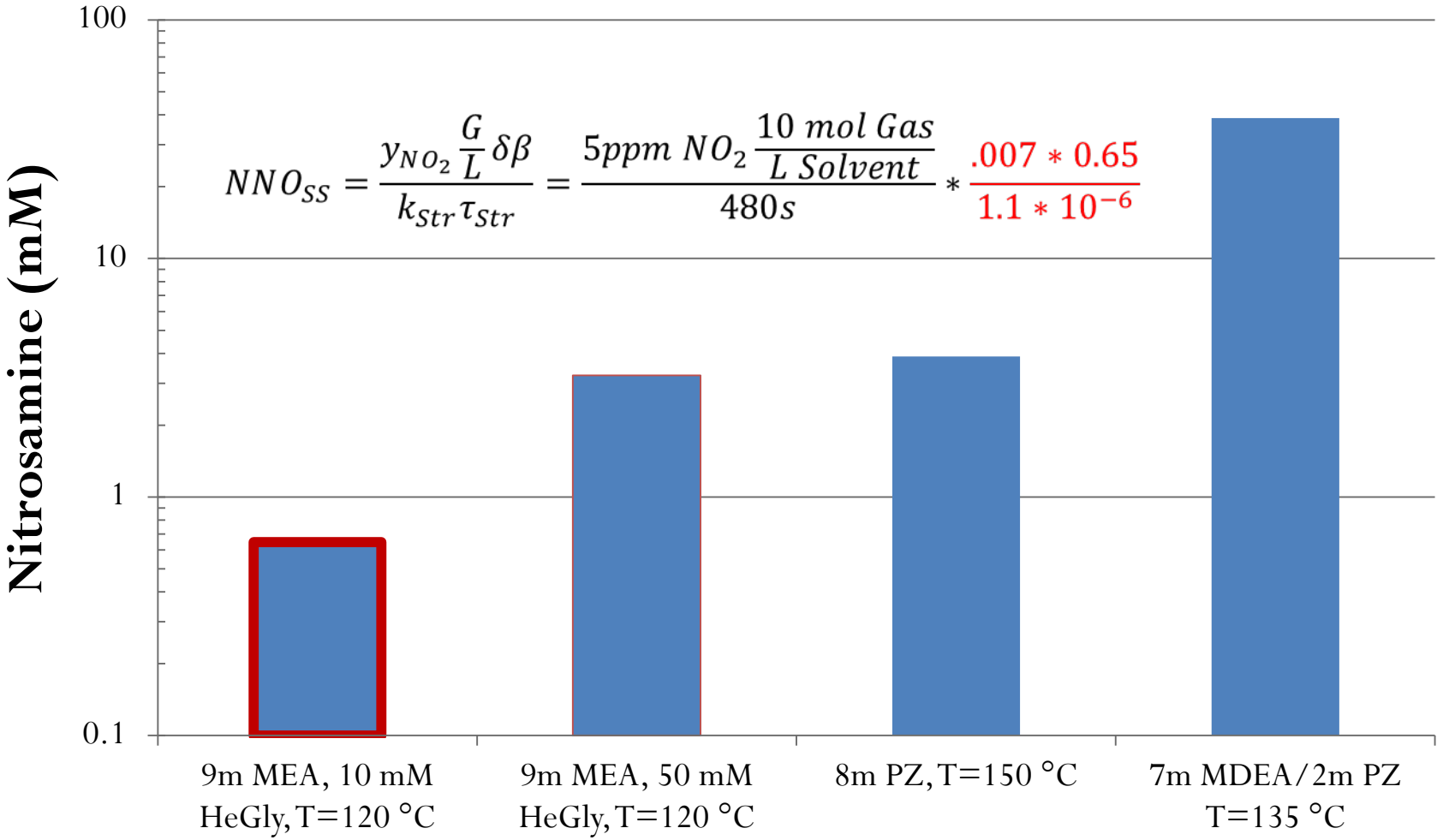
Nitrosamine Accumulation

Balancing NO_2 absorption and nitrosation with nitrosamine decomposition

Nitrosamine Accumulation



Nitrosamine Accumulation



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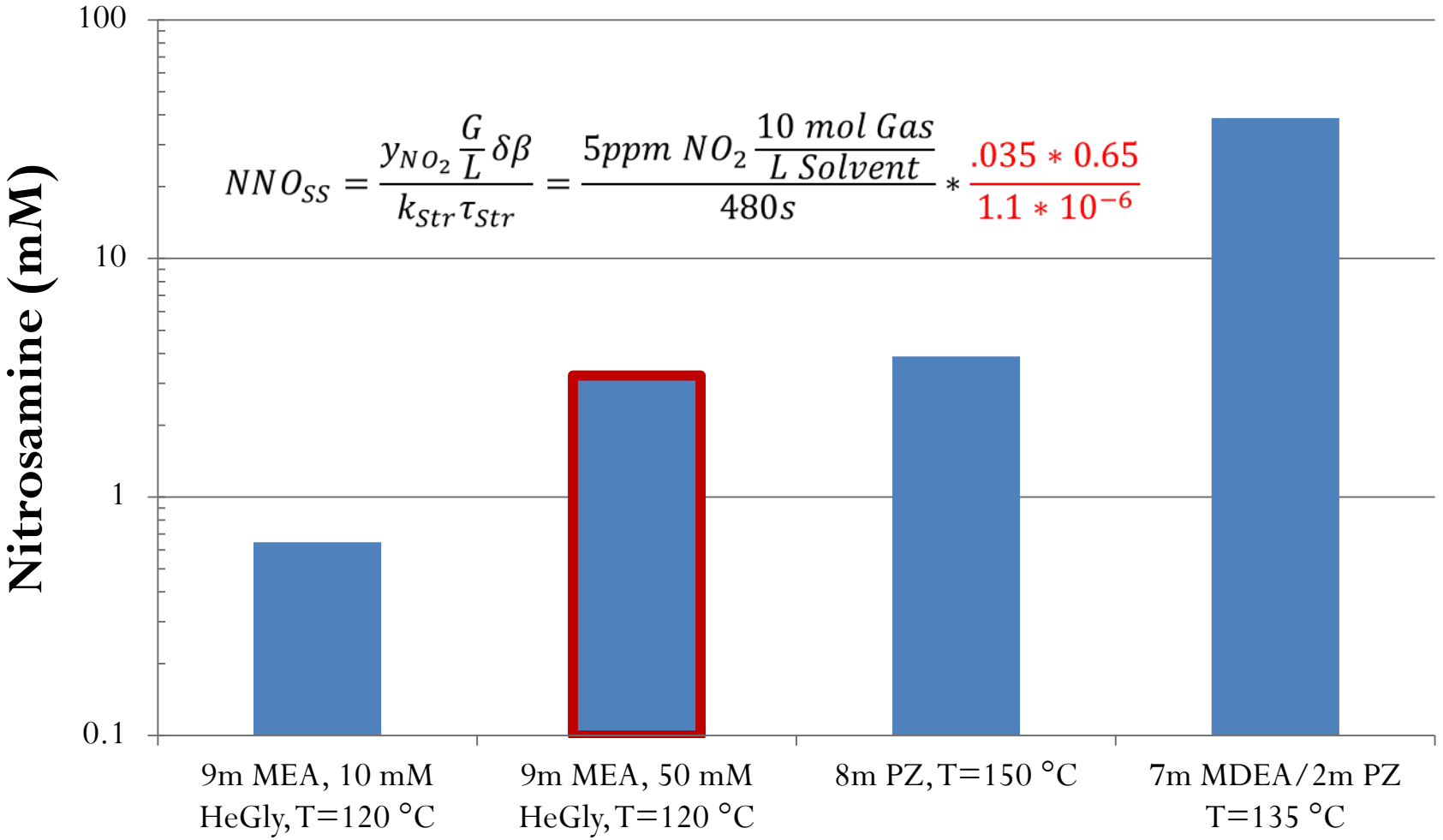

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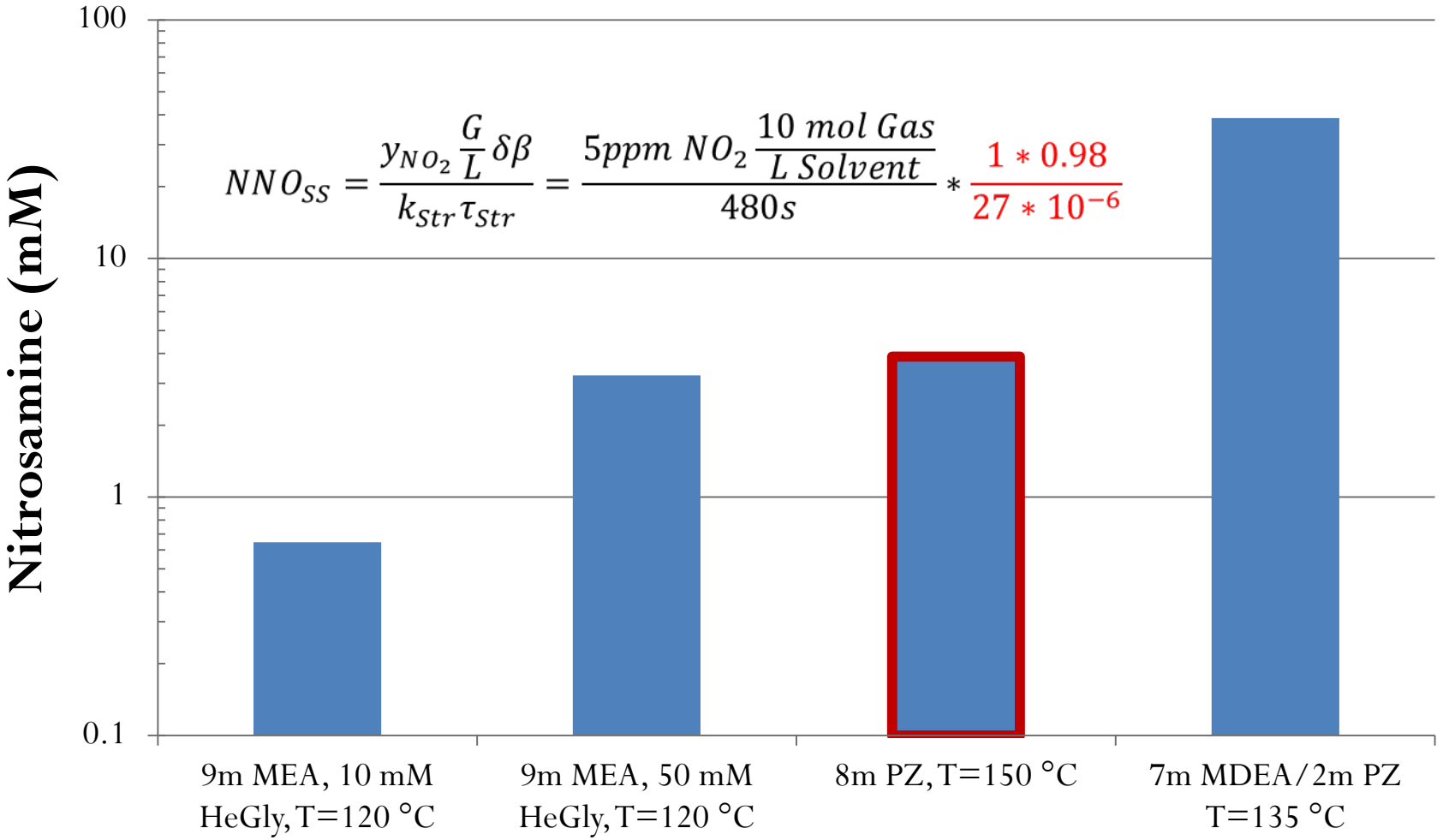
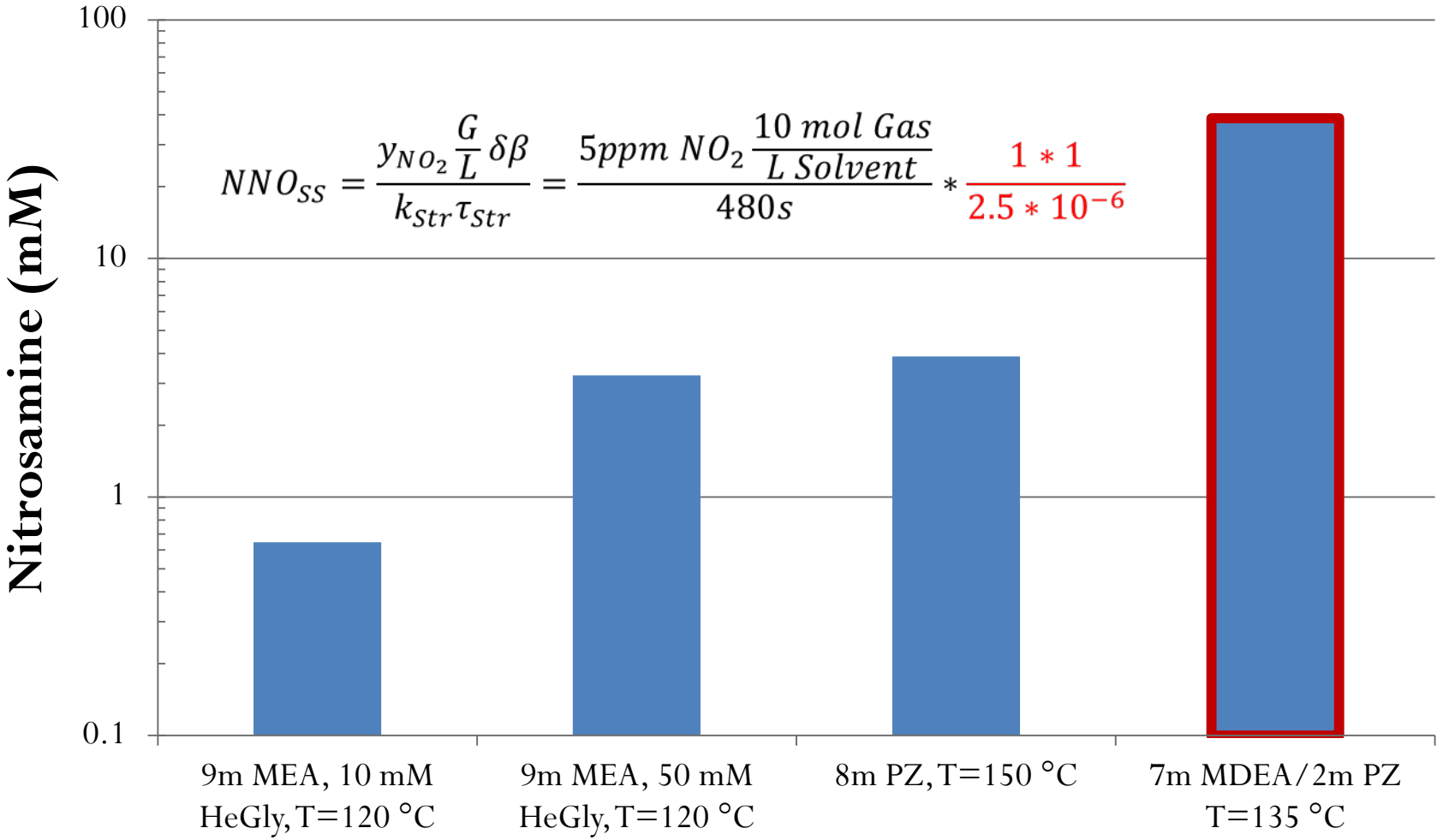


Nitrosamine Accumulation



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Thermal Cylinder Experiments

- Solution Preparation
  - 0.1-8m amine, α=0.1-0.4
  - 50 mmol/kg $NaNO_2$

- Batch Experiment
  - Loaded in \ inch Swagelok thermal cylinders
  - Convection oven at 80-150°C
  - Quenched in water bath at 21 °C
  - Stored in amber vials and analyzed within a week
- Pseudo-first order observed rate determined from nitrite disappearance