Absorption rate and CO_2 solubility in new PZ blends

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University of Texas at Austin / Texas Carbon Management Program

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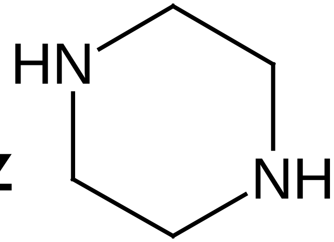
Outline

- Introduction
  - PZ blends
  - Performance criteria
- Absorption rate (k_g')
  - Effect of viscosity
- CO_2 solubility
  - Capacity
- Heat of absorption
- Conclusions

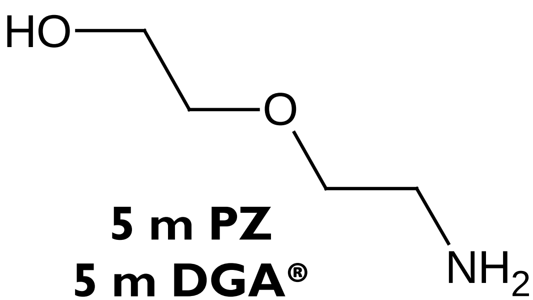
Piperazine blends (equi-molar)

8 m PZ

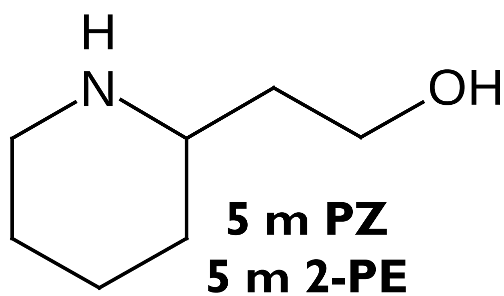


- High absorption rate
- High capacity
- Low volatility
- High stability

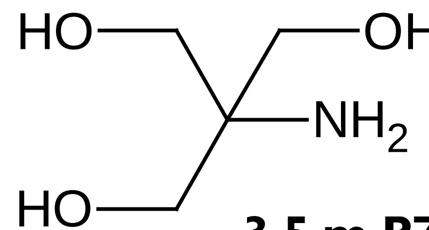
- *Moderate -H_{abs}*
- *Moderate viscosity*
- *Solid precipitation*



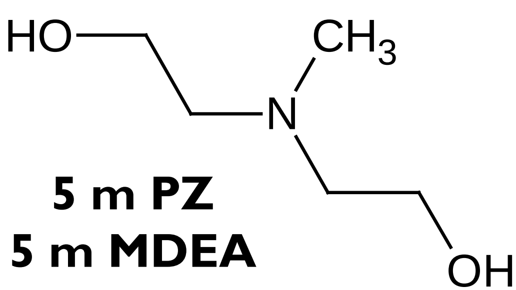
5 m PZ
5 m DGA®



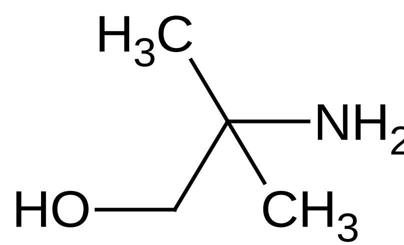
5 m PZ
5 m 2-PE



3.5 m PZ
3.5 m Tris



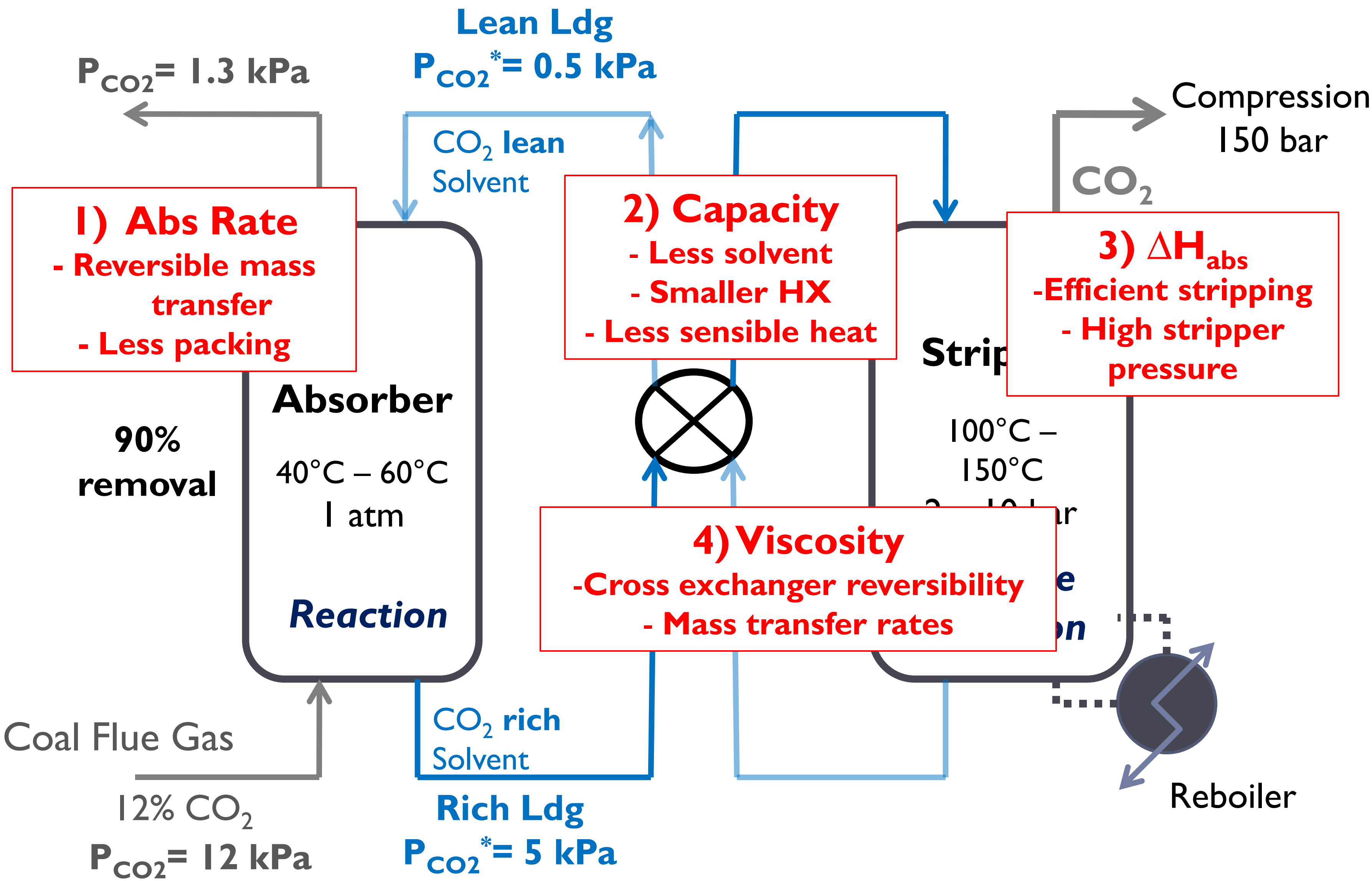
5 m PZ
5 m MDEA



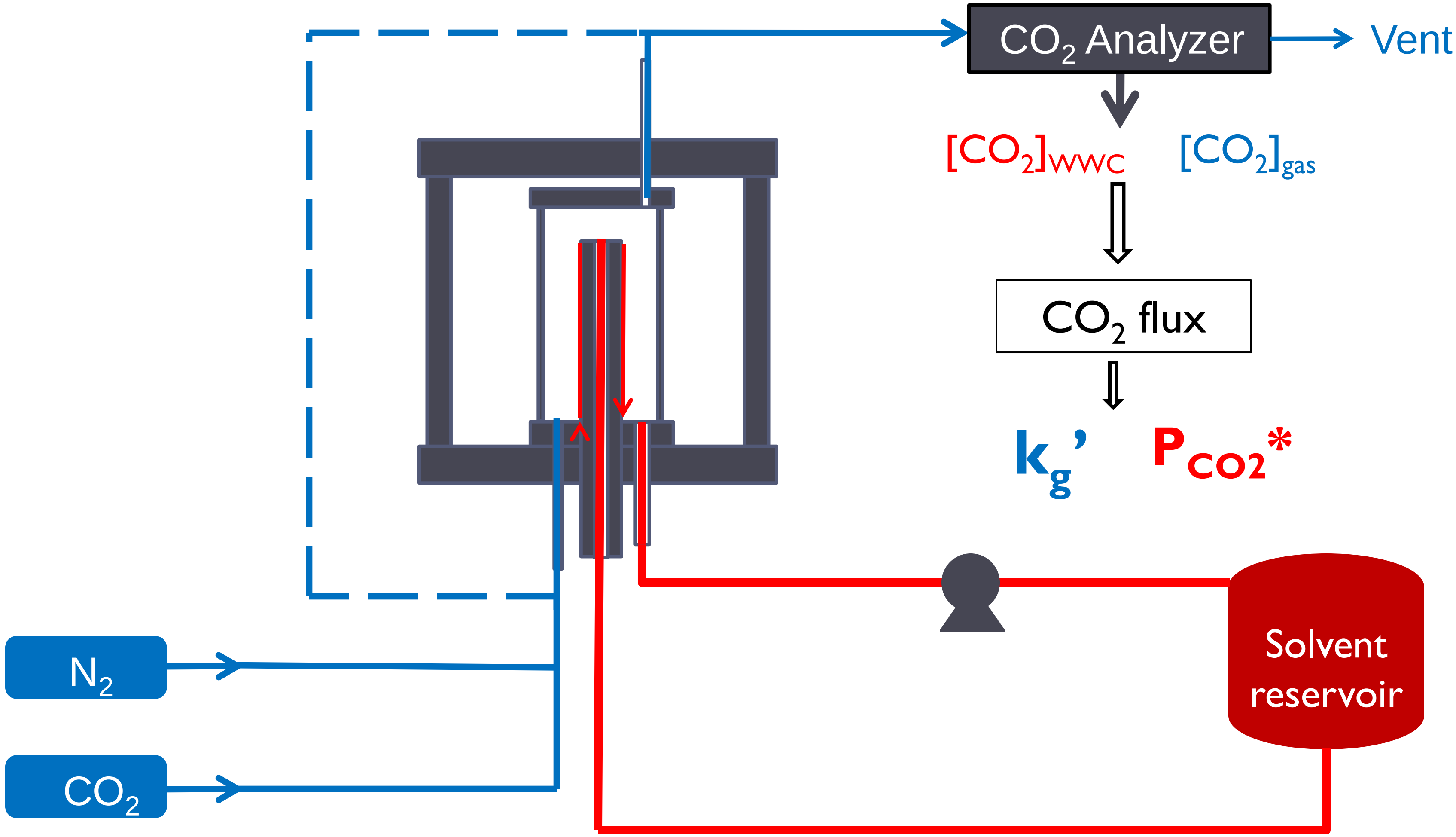
5 m PZ
2.3 m AMP

2 m PZ
4 m AMP

Background: Amine Scrubbing

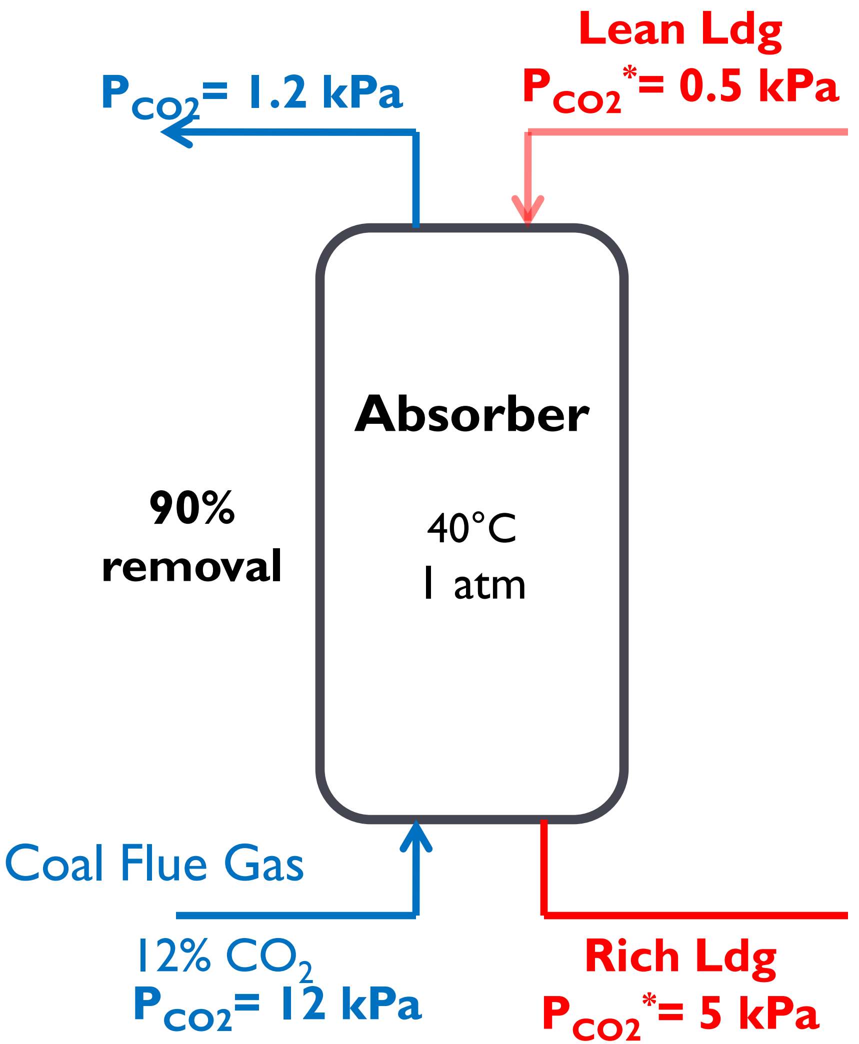


Wetted Wall Column



Absorption rate (k_g')

CO_2 Removal [mol/s] = Area · k_g' · (P_{CO2}-P_{CO2}^*)



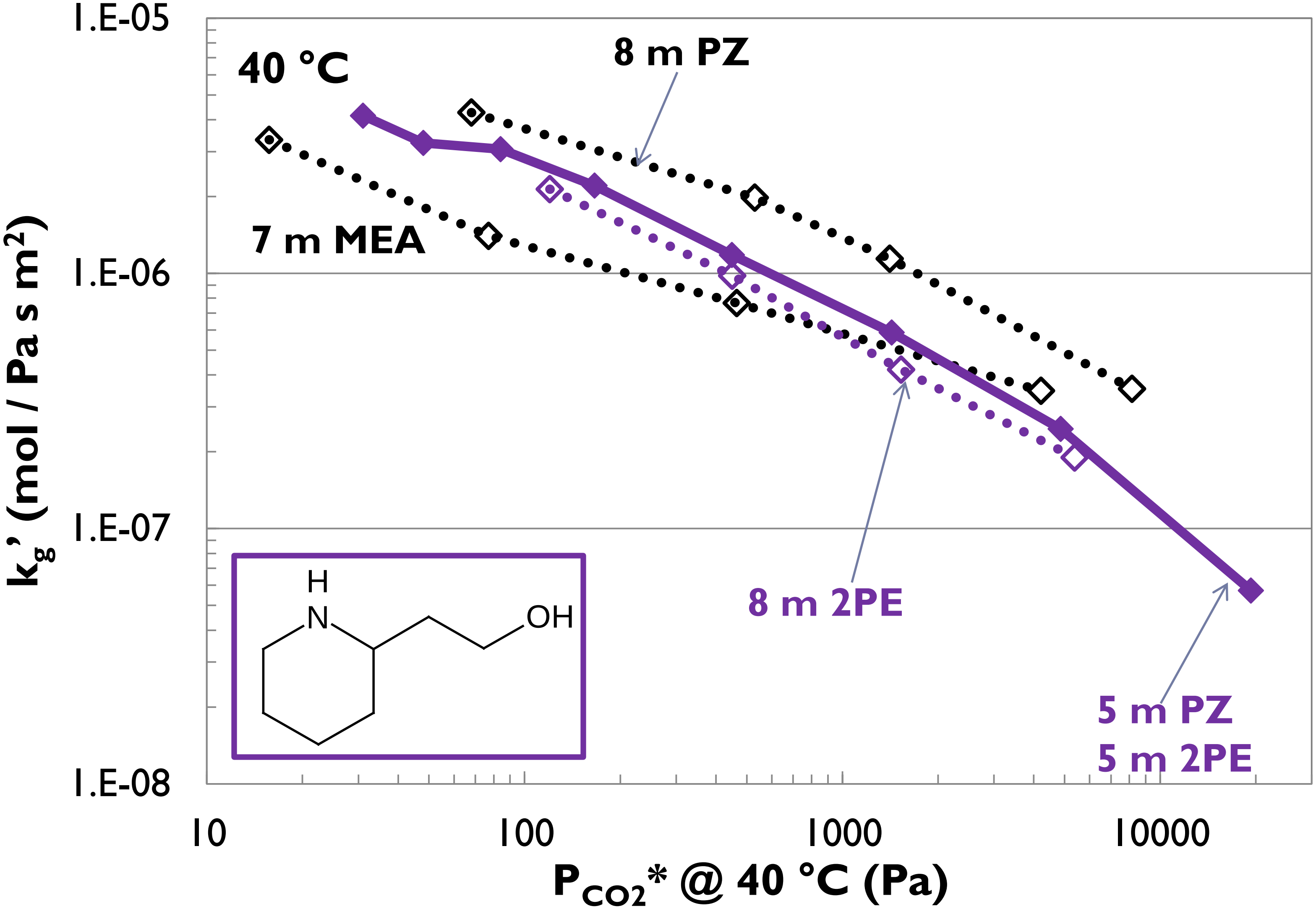
High absorption rate (k_g')

a. Less packing
b. Less exergy loss
c. Higher removal rate

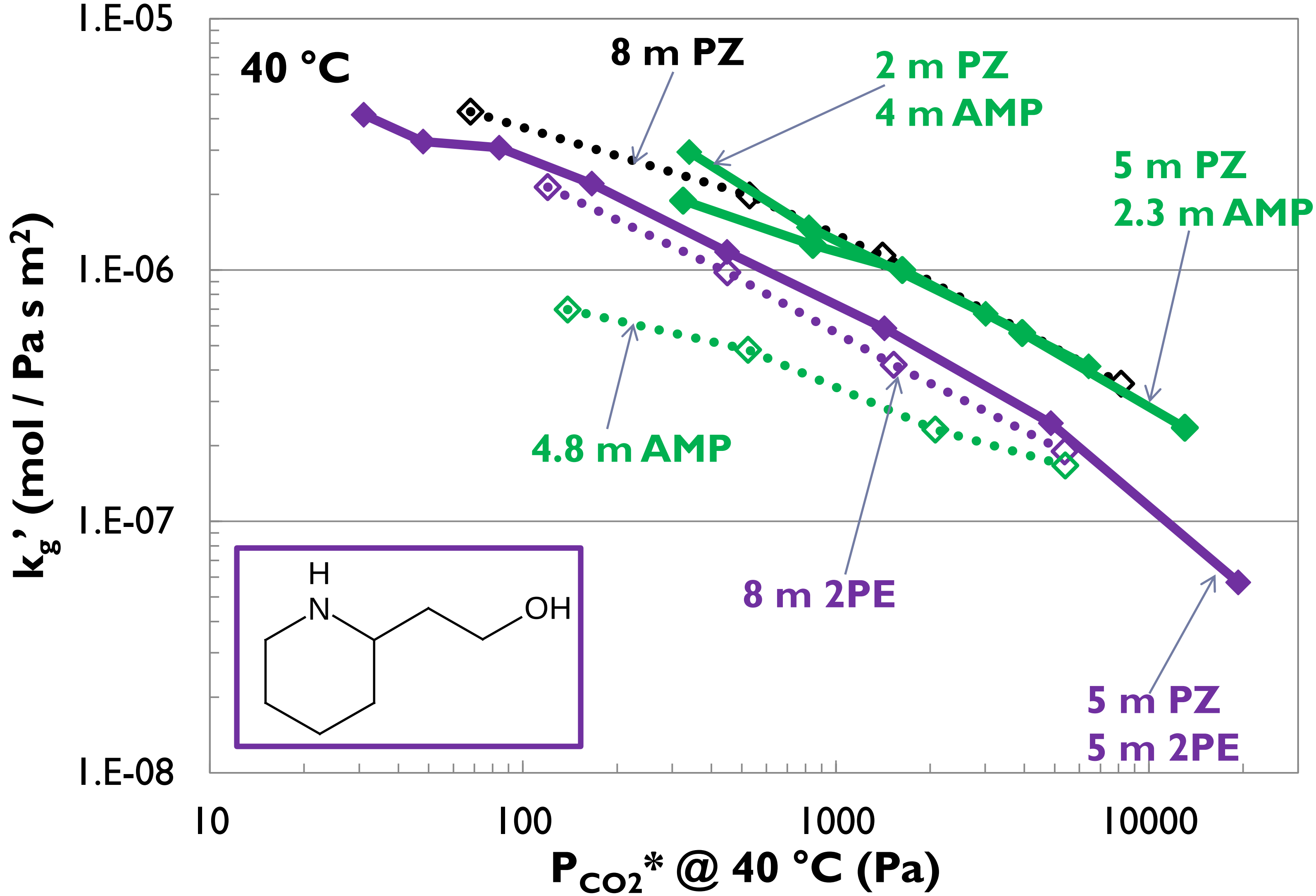
$$k_g' \approx \frac{\sqrt{D_{CO_2} k_2 [Am]_b}}{H_{CO_2}}$$

$$k_g'{}_{avg} = \frac{Flux_{CO_2,LM}}{(P_{CO_2,gas} - P_{CO_2}^*)_{LM}}$$

Absorption rates: 5 m PZ 5 m 2PE



Absorption rates: 5 m PZ 5 m 2PE



k_g' is effected by viscosity

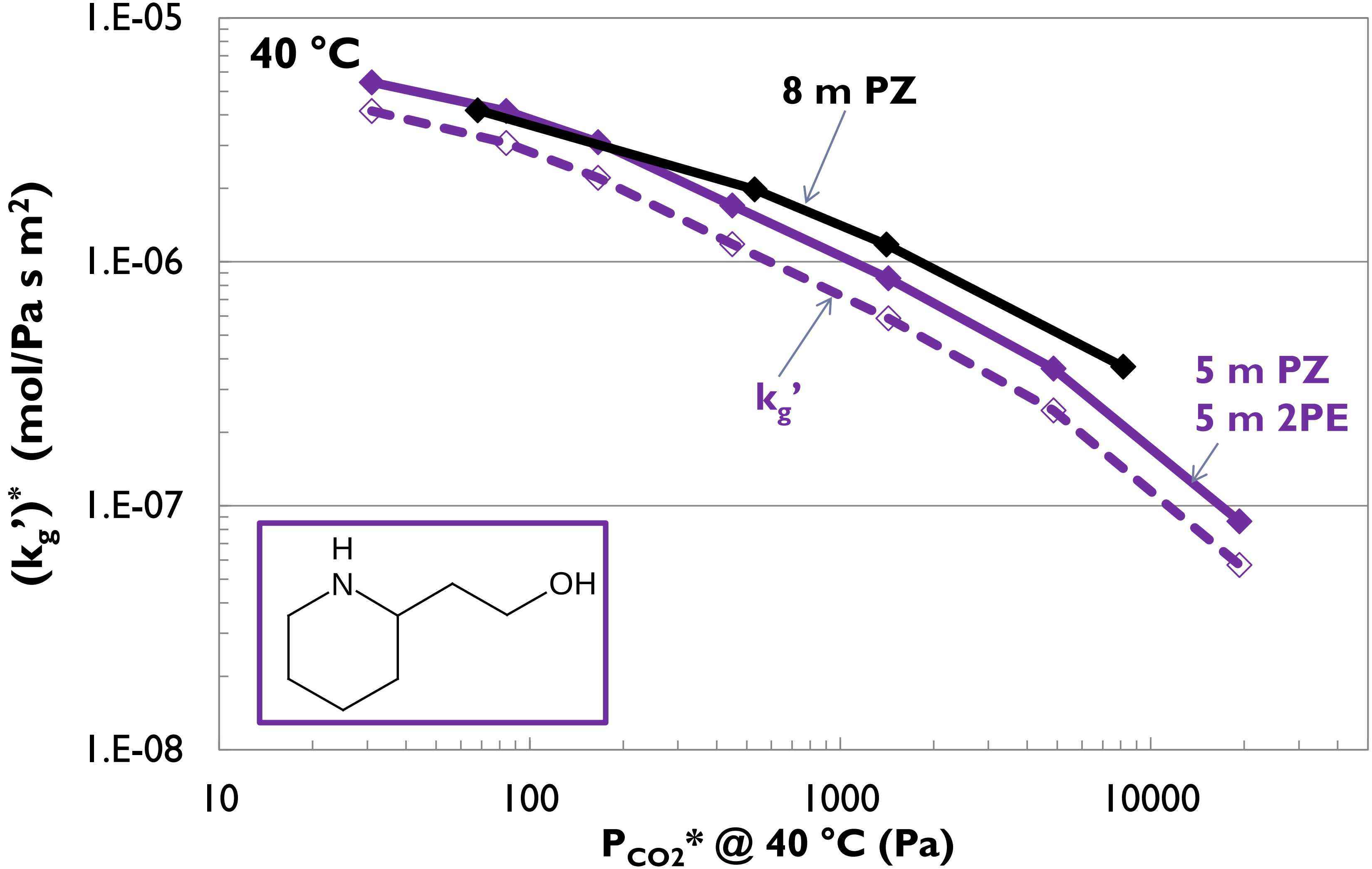
$$\left(D_{CO_2}\mu^{0.8}\right)_{solution} = \left(D_{CO_2}\mu^{0.8}\right)_{water}$$

Versteeg et al (1998)

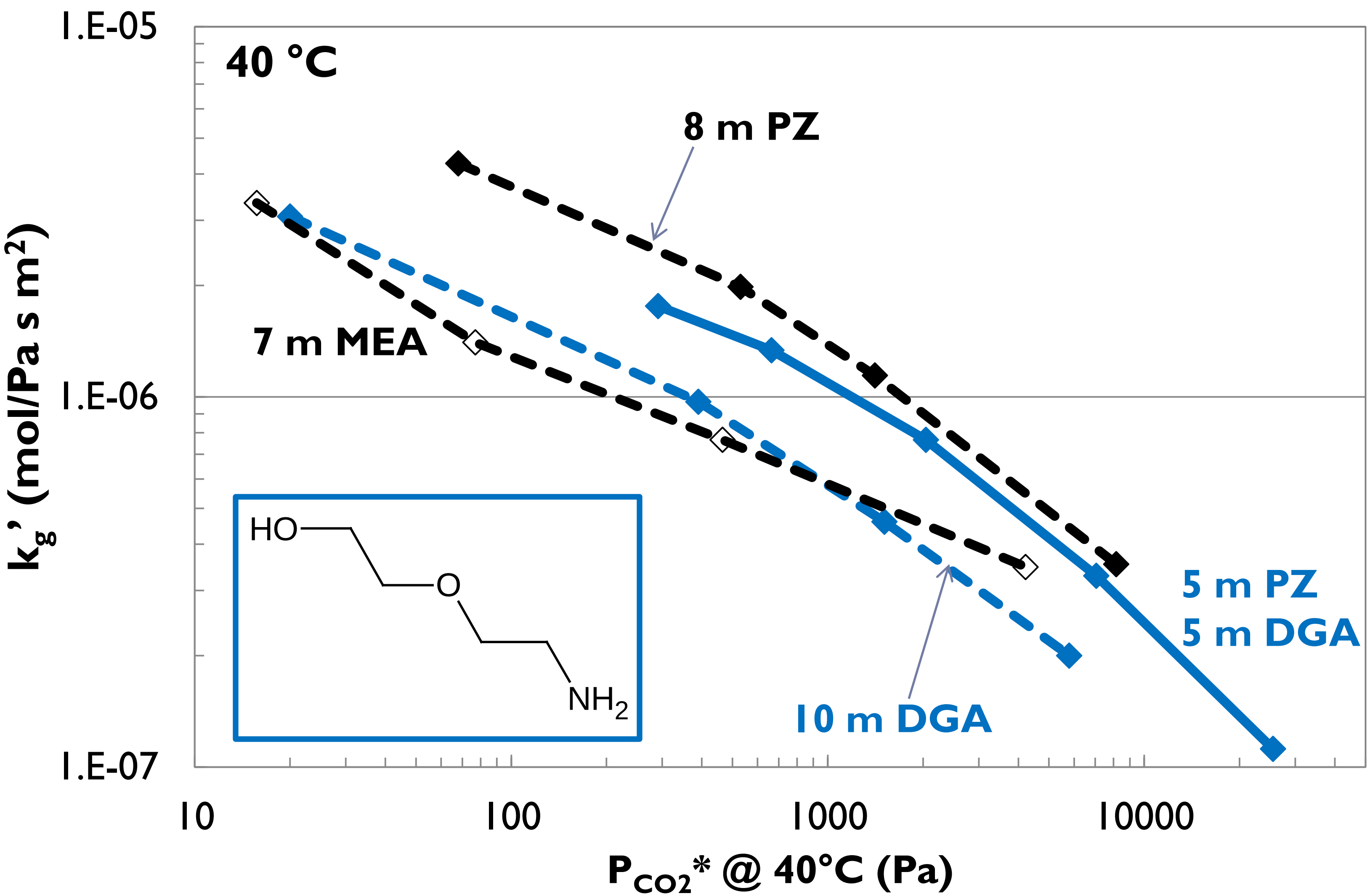
$$k_g^{'} \approx \frac{\sqrt{D_{CO_2} k_2 [Am]_b}}{H_{CO_2}} \Rightarrow \frac{(\mu)^{-0.4}\sqrt{k_2[Am]_b}}{H_{CO_2}}$$

$$\left(k_g^{'}\right)^* = \left(k_g^{'}\right)\cdot\left(\frac{\mu}{10\ cP}\right)^{0.4} = f\left(k_2, [Am]_b, H_{CO_2}\right)$$

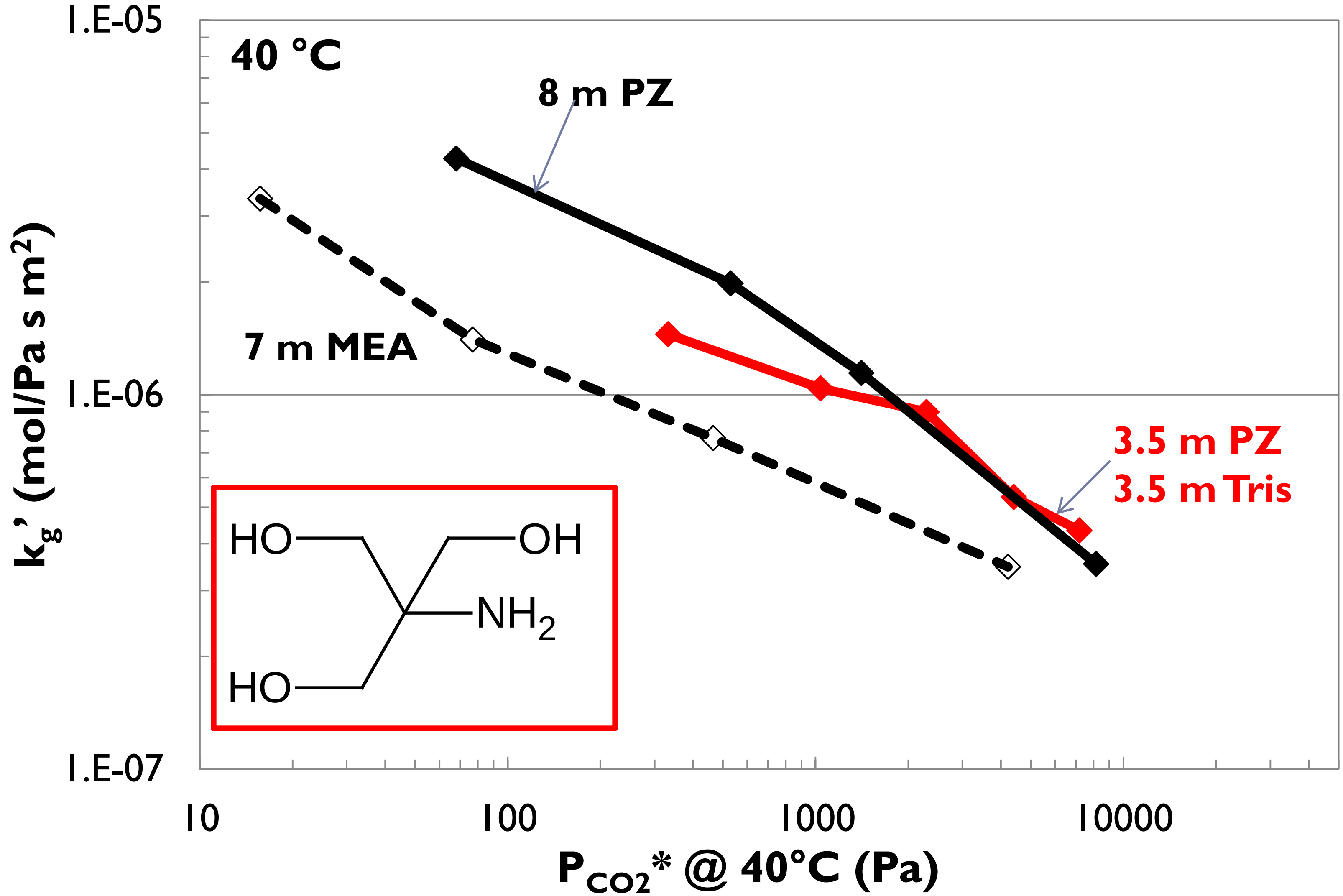
k_g' is effected by viscosity



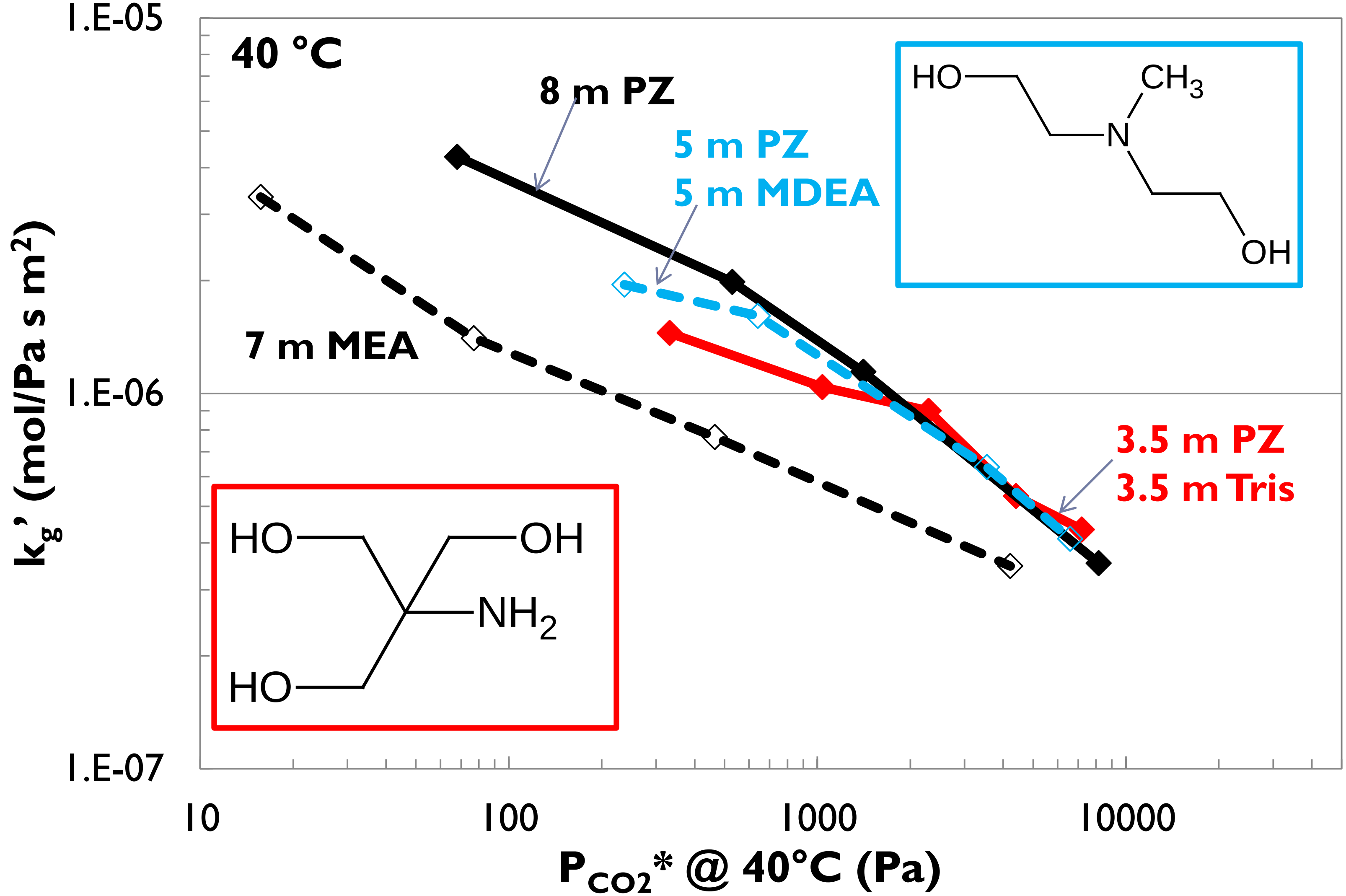
Absorption rate of 5 m PZ 5 m DGA



Absorption rate of 3.5 m PZ 3.5 m Tris



Absorption rate of 3.5 m PZ 3.5 m Tris



CO_2 Solubility: Capacity

Capacity

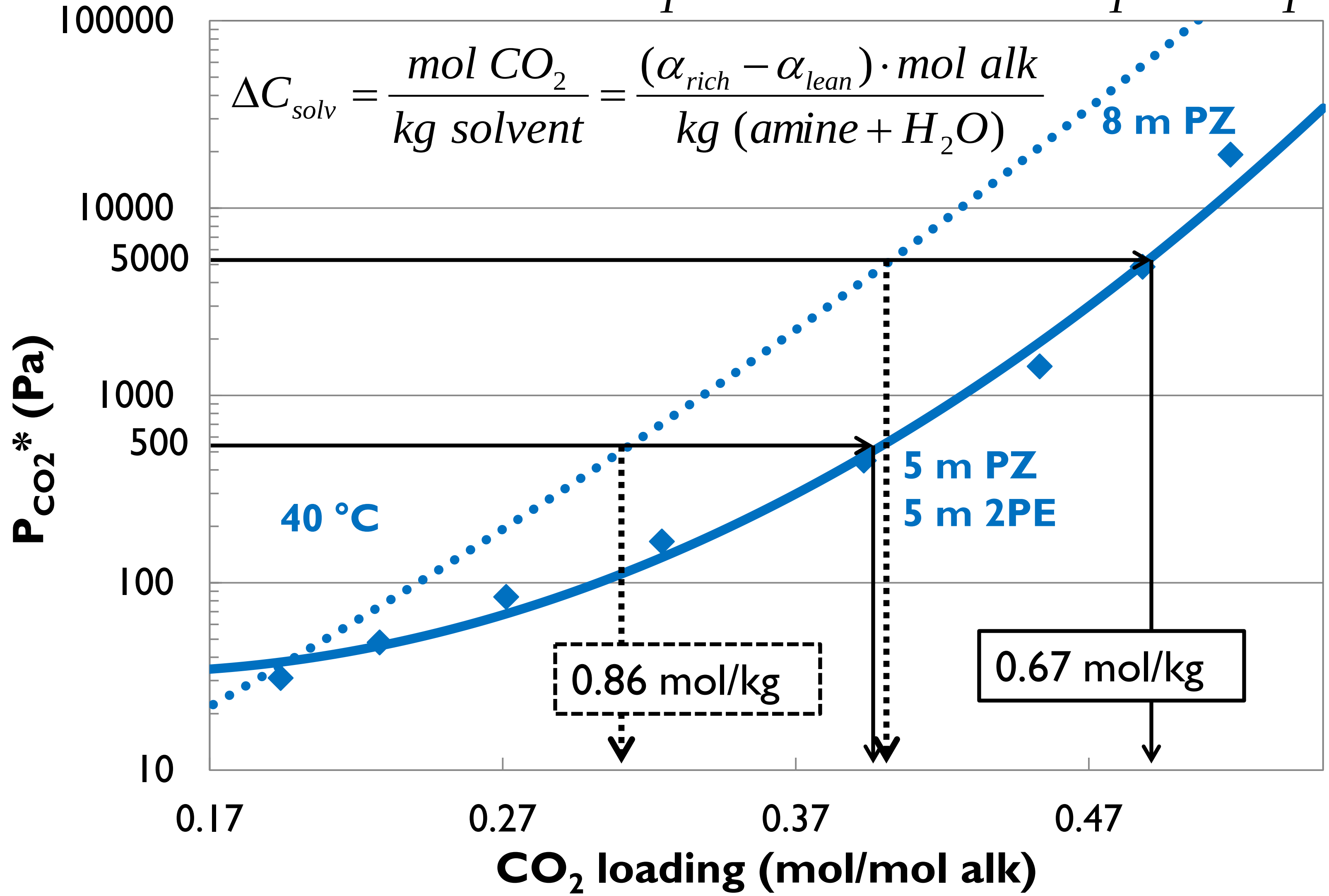
$$\Delta C_{solv} = \frac{(\alpha_{rich} - \alpha_{lean}) \cdot mol\ alk}{kg(am + H_2O)} = \frac{mol\ CO_2}{kg\ solv}$$

Thermodynamic property
- pKa
- Amine structure, hinderance
- blend: amine ratio

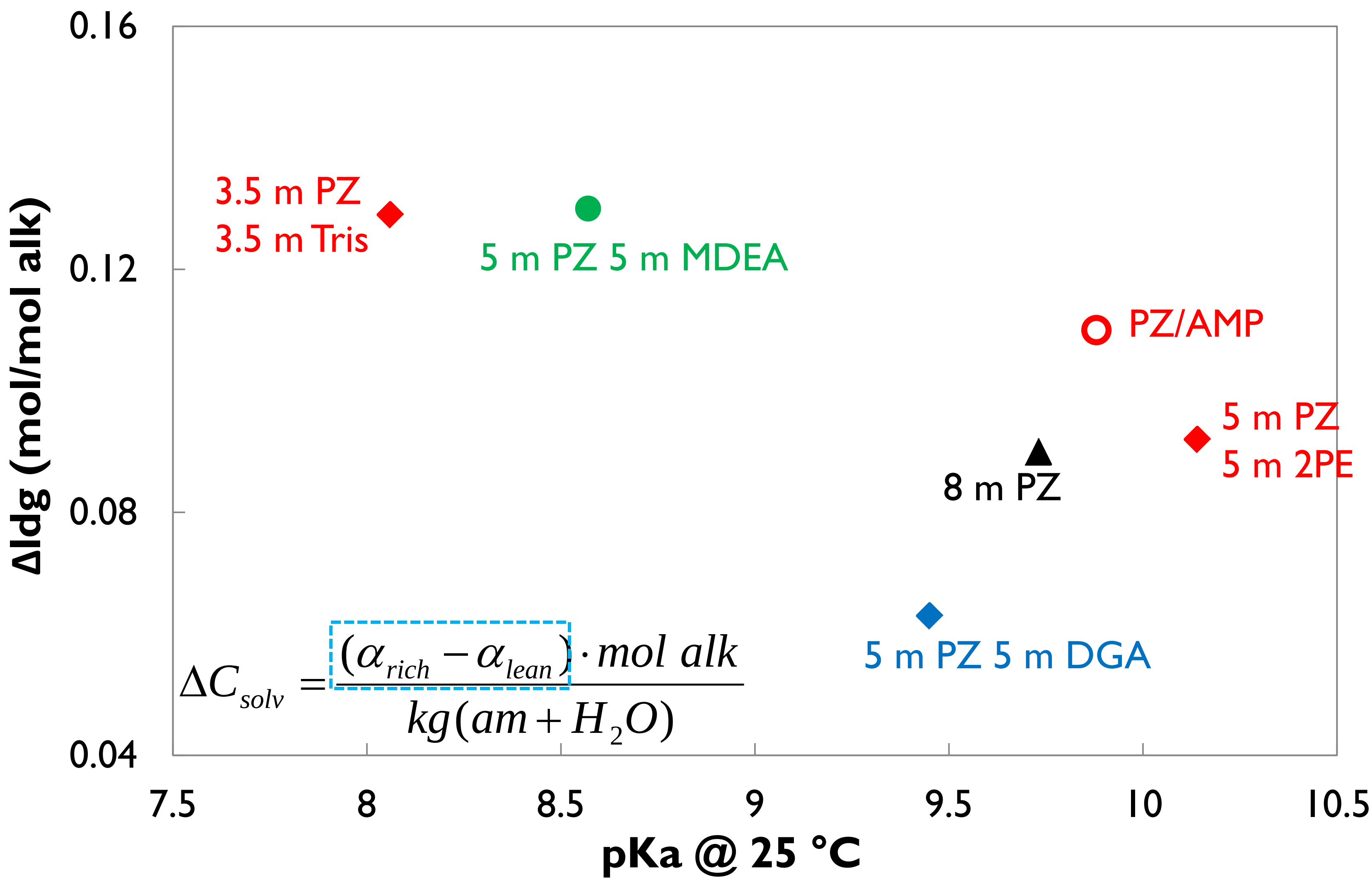
Concentration effect
- Viscosity
- Solid solubility
- Molecular weight

CO_2 solubility: Capacity

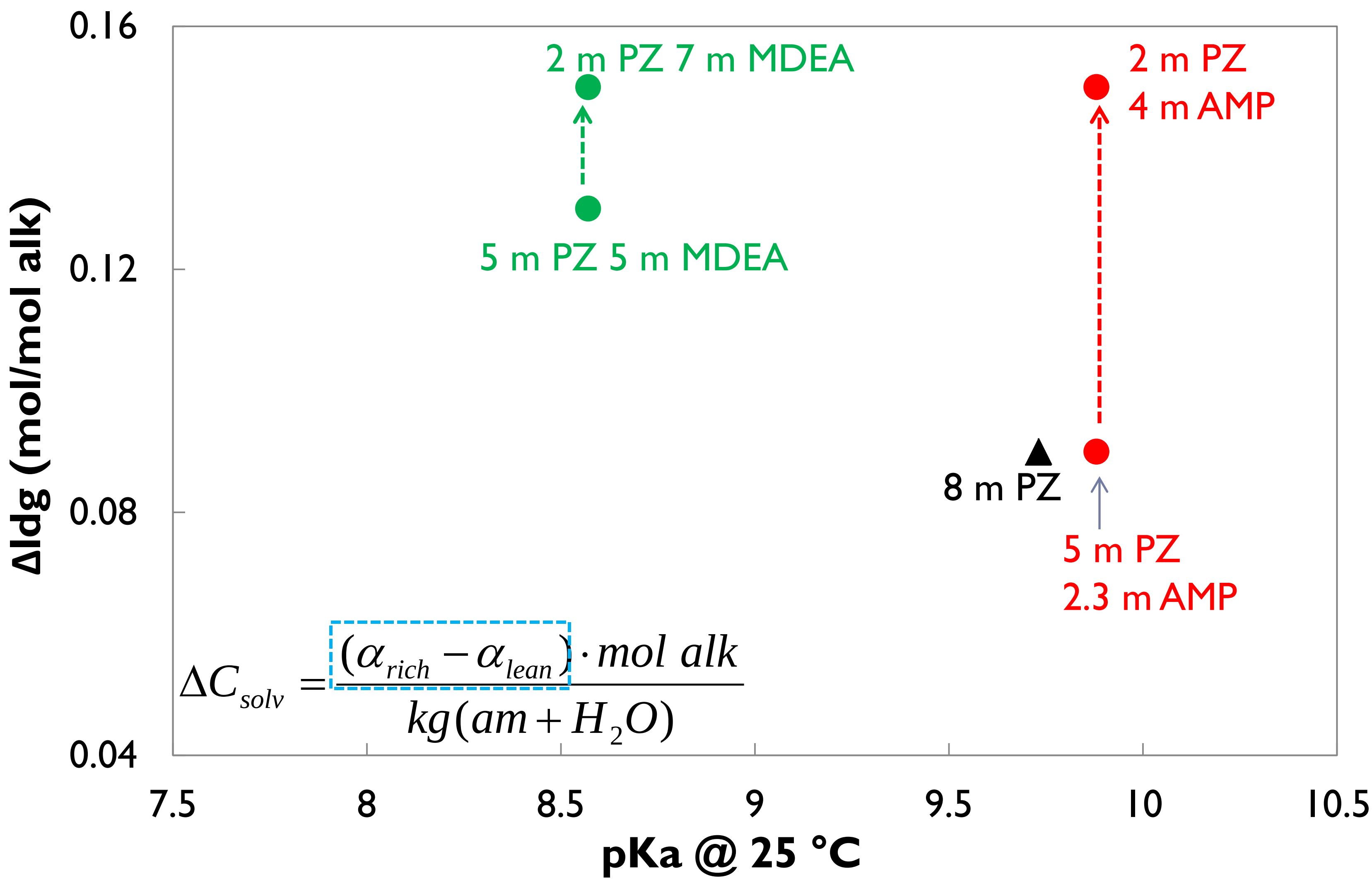
$$\ln(P^*_{CO_2}) = a + \frac{b}{T} + c\cdot\alpha_{CO_2} + d\cdot\alpha_{CO_2}{}^2 + e\cdot\frac{\alpha_{CO_2}}{T} + f\cdot\frac{\alpha_{CO_2}{}^2}{T}$$



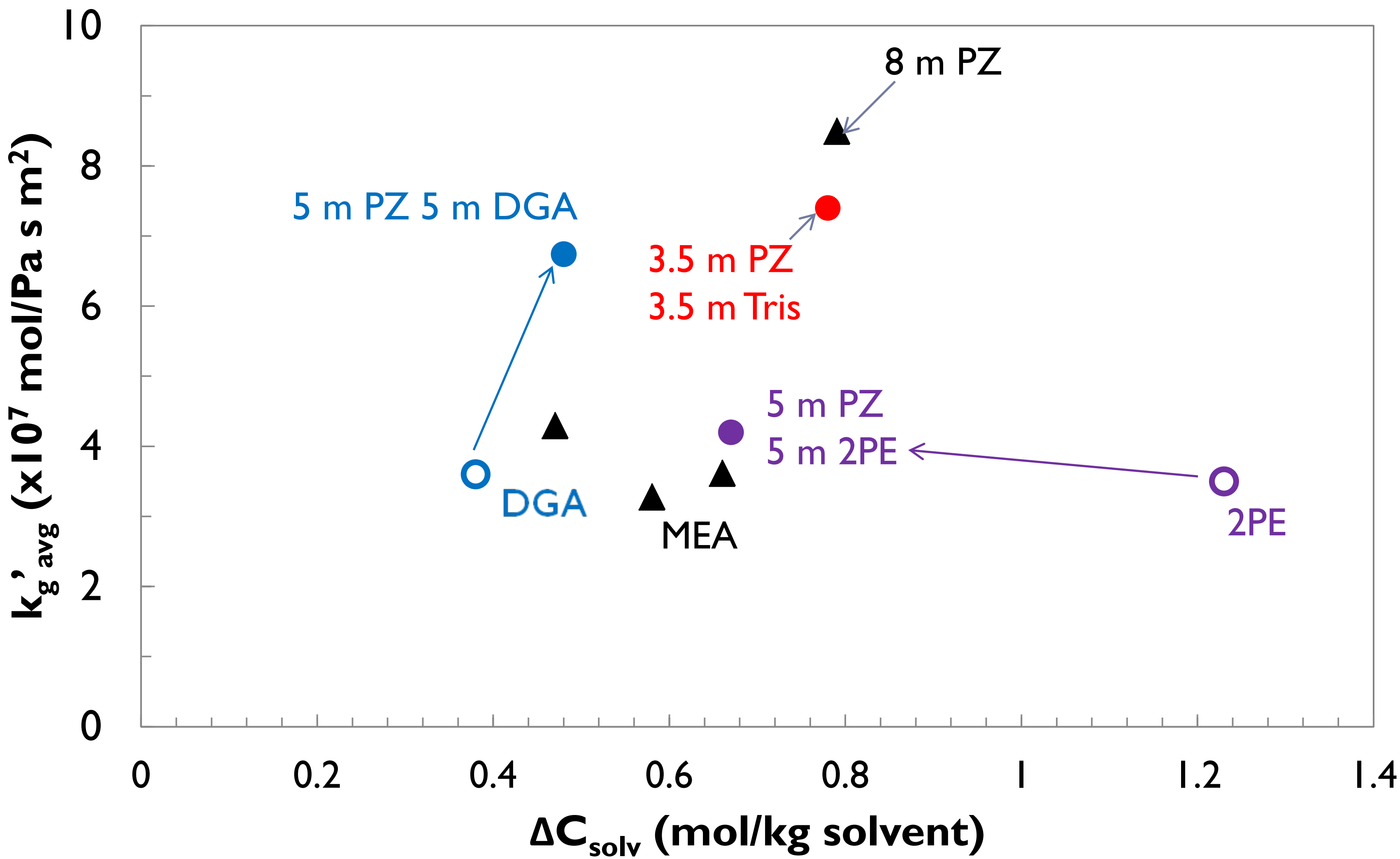
Effect of amine choice on Δldg



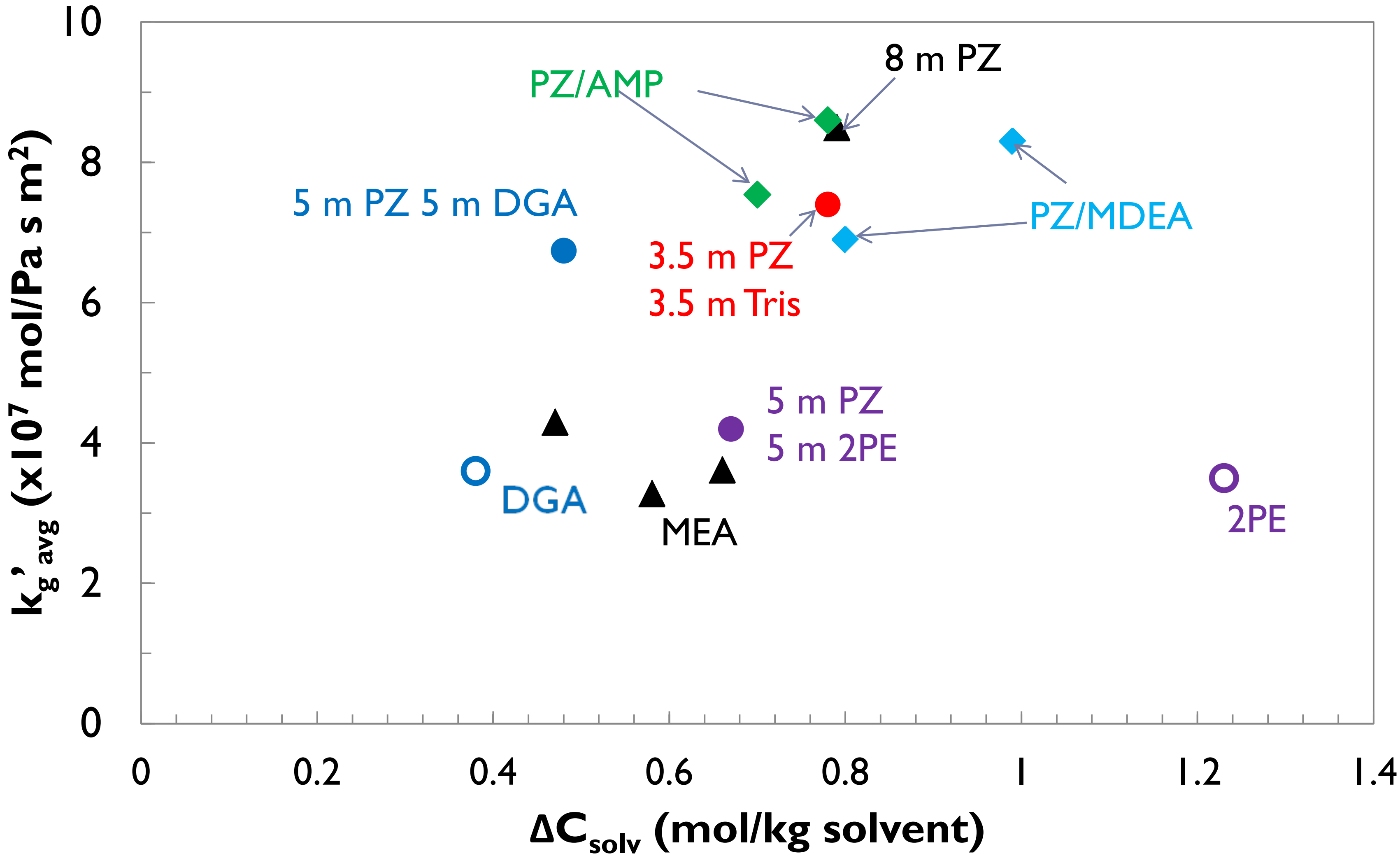
Effect of amine choice on Δldg



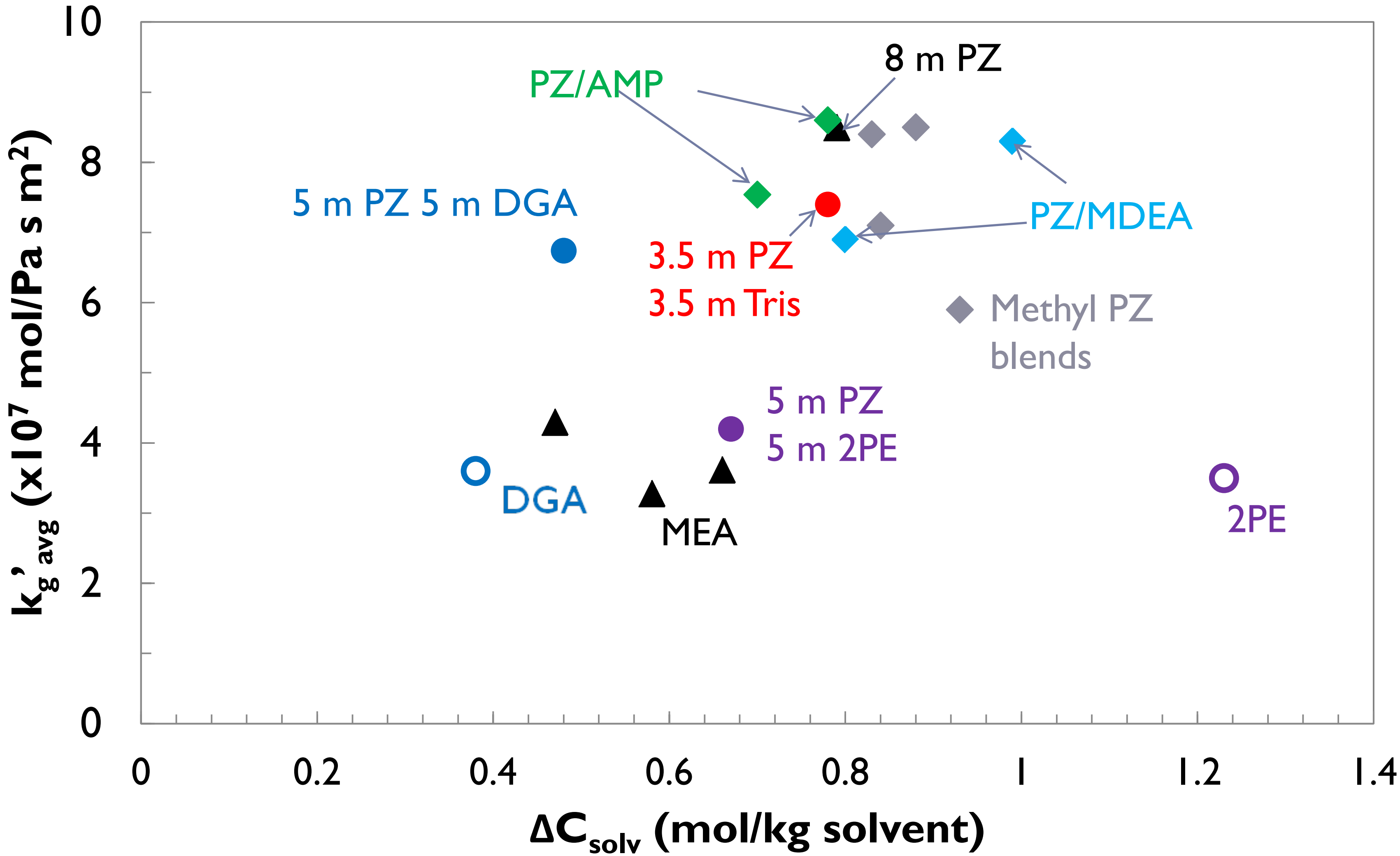
Absorption rate vs. Capacity



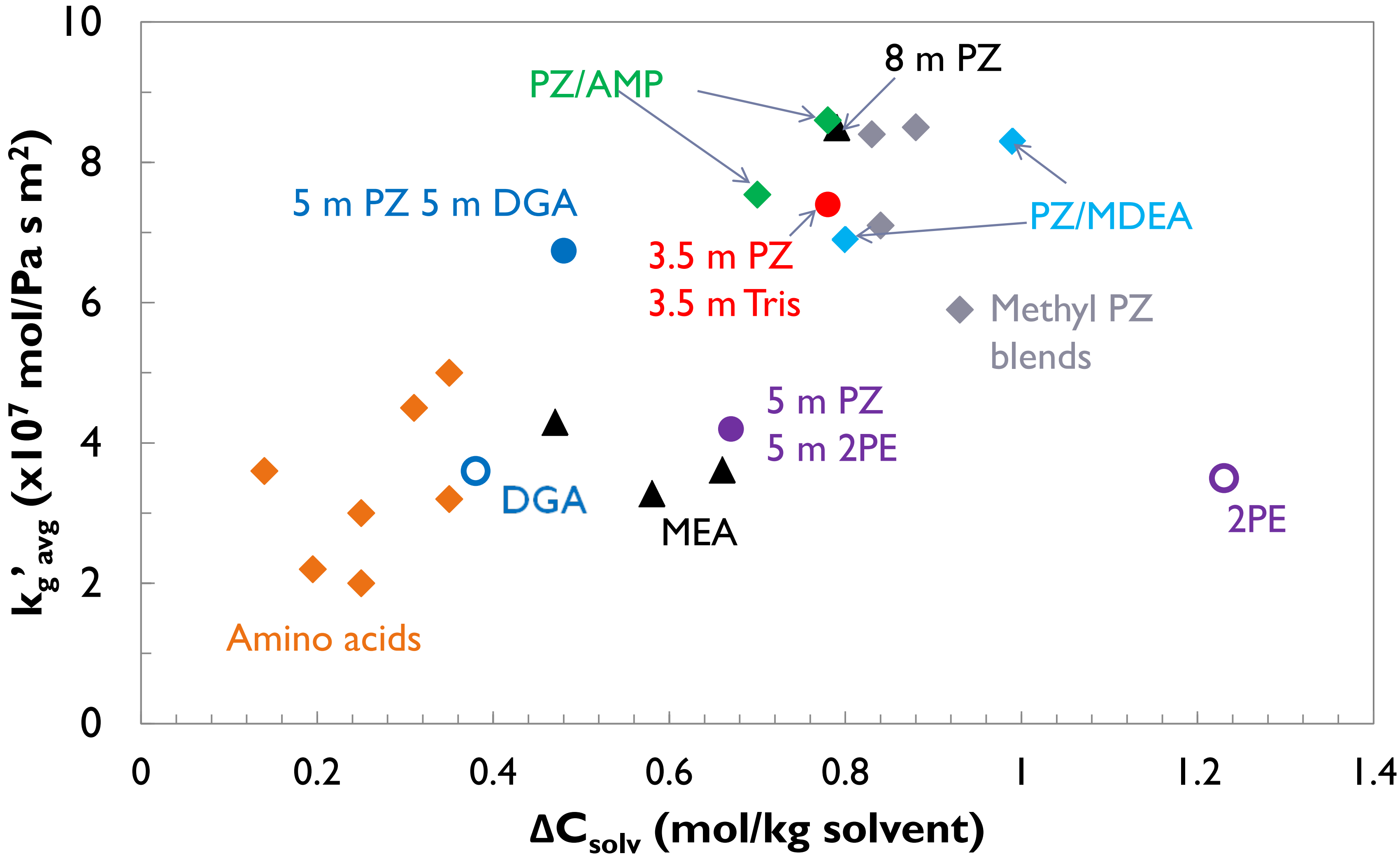
Absorption rate vs. Capacity



Absorption rate vs. Capacity

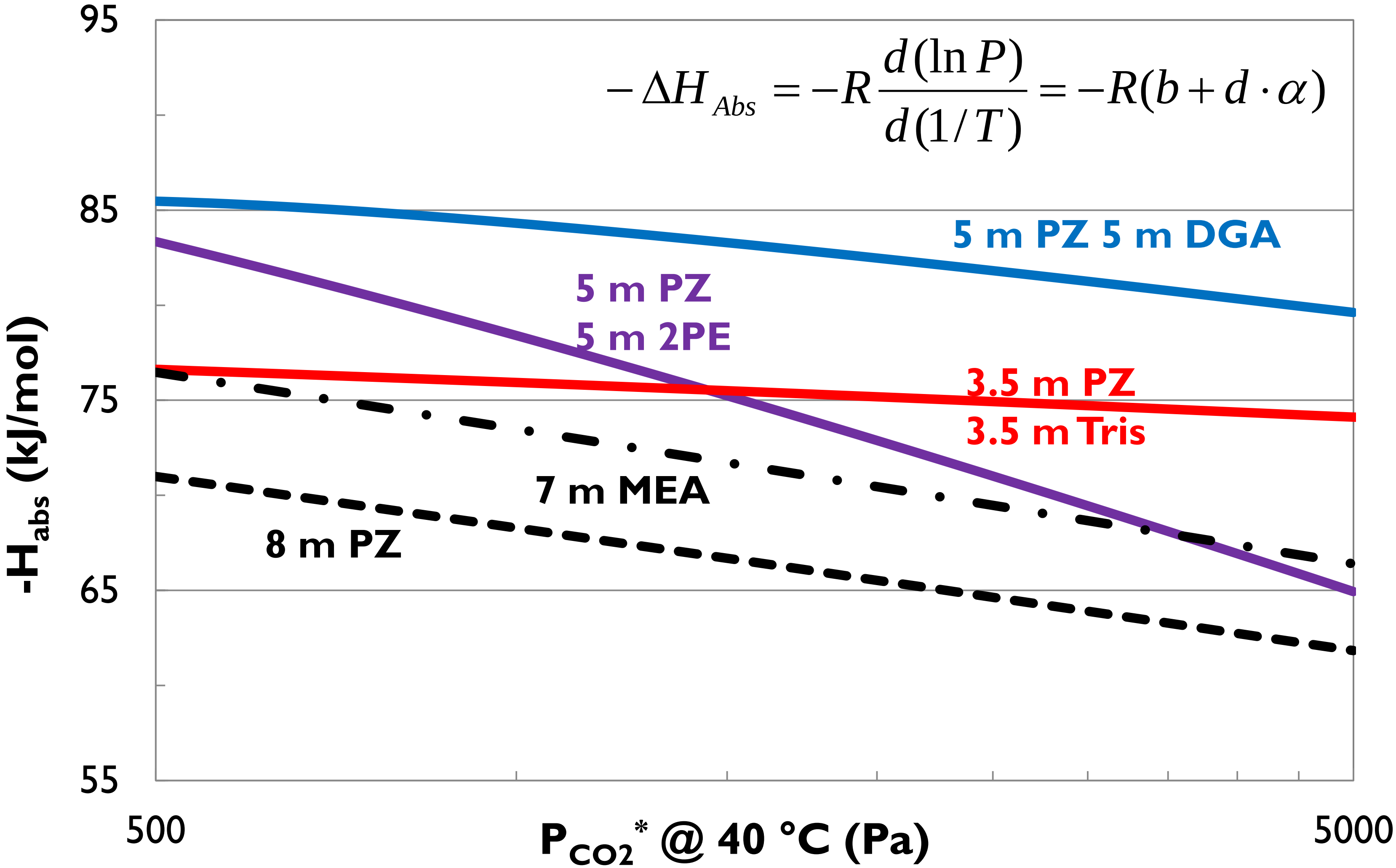


Absorption rate vs. Capacity



Heat of Absorption

Heat of Absorption of new PZ blends



$$-\Delta H_{Abs} = -R\frac{d(\ln P)}{d(1/T)} = -R(b + d\cdot\alpha)$$

Summary Table

Amine		k_{g}' avg	ΔC_{solv}	ΔC_{μ}	$-H_{abs}$ (mid ldg)	μ (mid ldg)
(m)	(m)	X 10^7 mol/Pa s m^2	mol/kg		kJ	cP
PZ (5)	2PE (5)	**4.2**	0.67	**0.53**	75	**26**
PZ (5)	DGA (5)	6.7	0.48	**0.47**	**83**	11
PZ (3.5)	Tris (3.5)	7.4	0.78	**0.89**	76	**6**
PZ (5)	MDEA (5)	8.3	0.98	0.91	74	13
PZ (2)	AMP (4)	8.5	0.77	0.90	77	5
PZ (8)		8.5	0.86	0.84	71	11

$$\Delta C_{\mu} = \frac{\Delta C_{solv}}{\left(\mu_{\alpha_{mid}} / 10cP \right)^{0.25}}$$

Conclusions

- 3.5 m PZ 3.5 m Tris
  - Competitive capacity / viscosity / heat of absorption
  - Good absorption rate
- 5 m PZ 5 m 2PE
  - High viscosity, low capacity, low absorption rate
- 5 m PZ 5 m DGA
  - Moderate absorption rate, heat of abs, viscosity
  - Low capacity
- High viscosity: reduces k_g' and ΔC_μ
- PZ blends:
  - Tertiary / Hindered amines (equi-molar): large Δldg
  - Tertiary / Hindered amines: higher amine/PZ ratio = large Δldg

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Questions?

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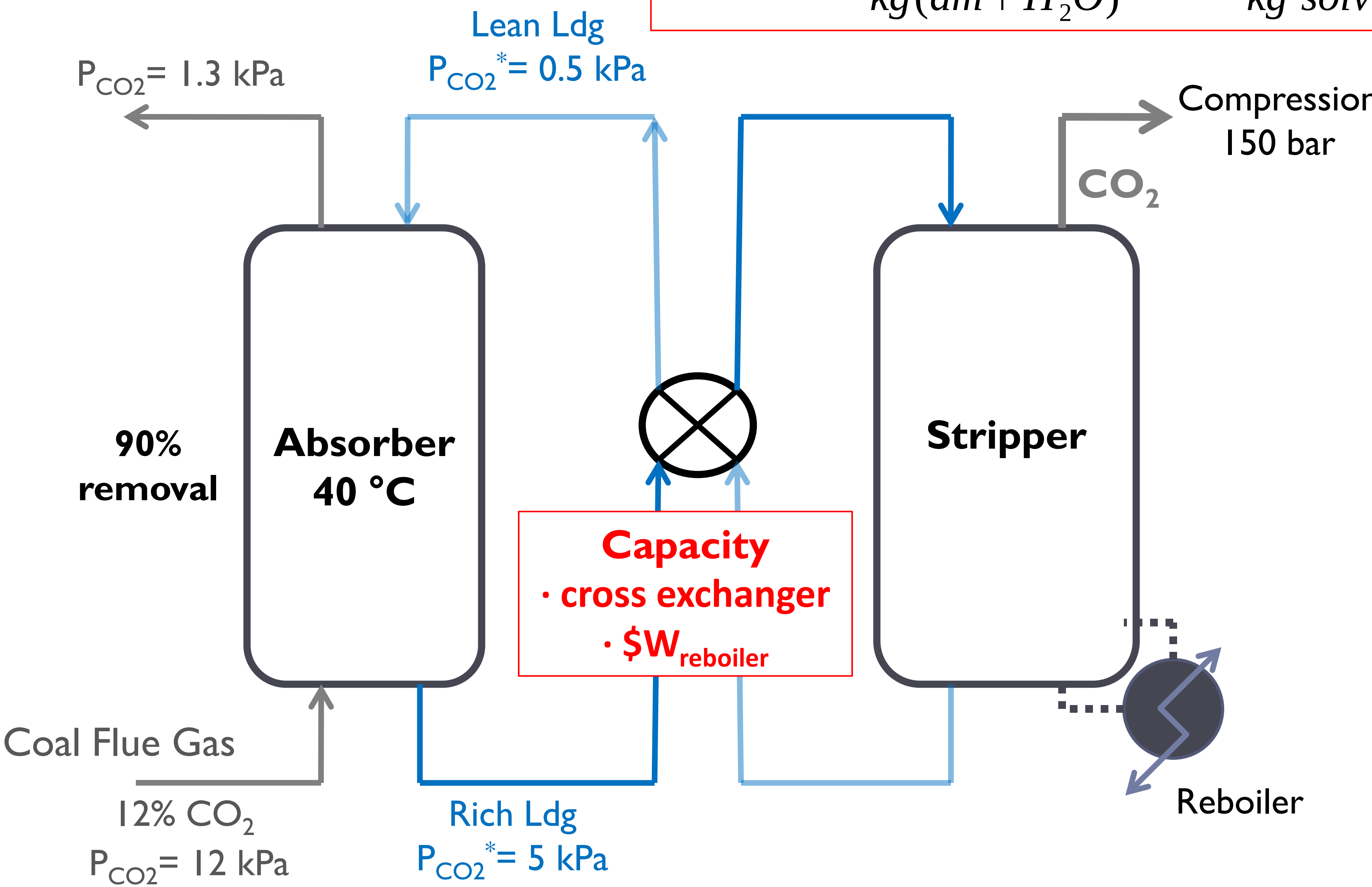
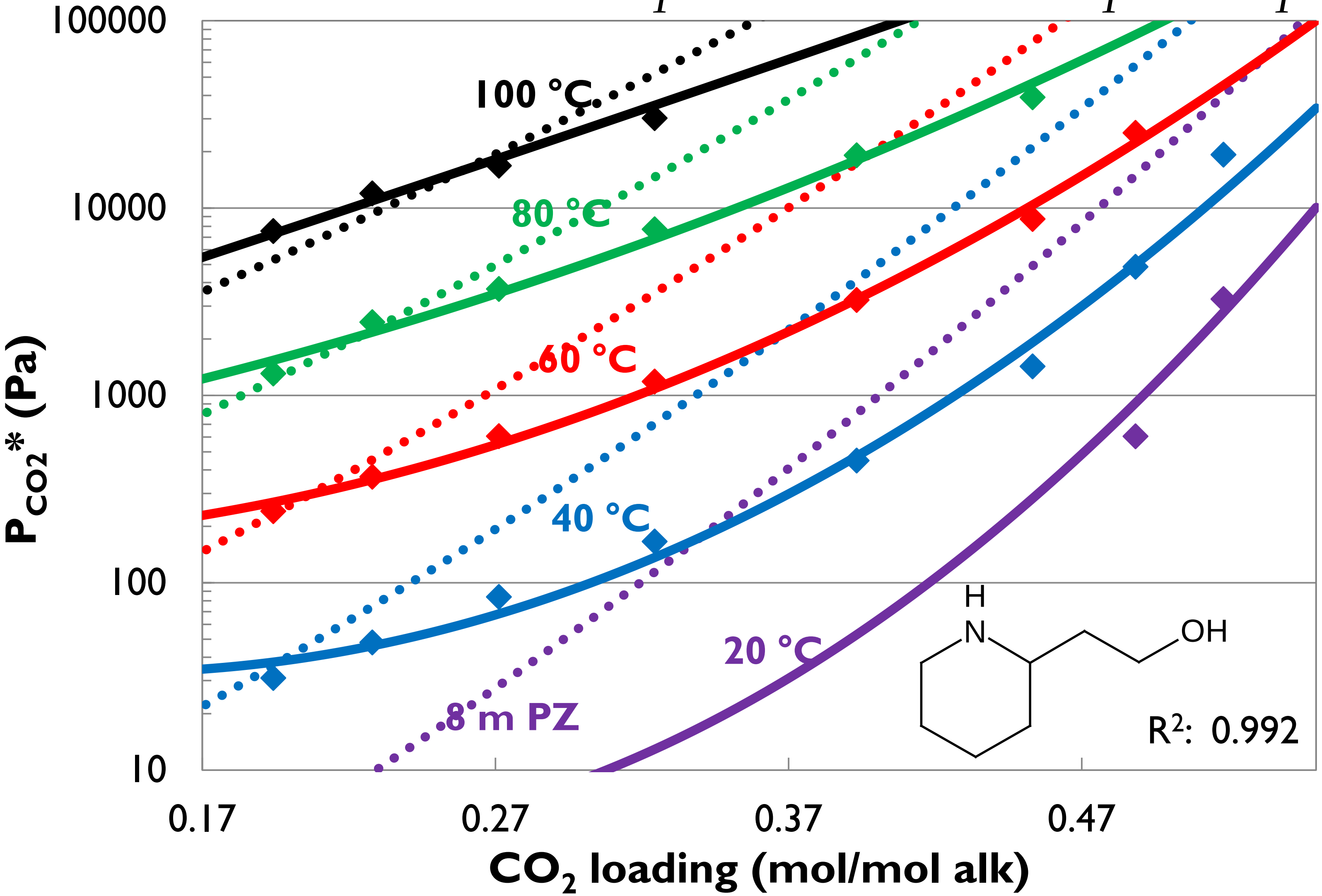
$$\Delta C_{solv} = \frac{(\alpha_{rich} - \alpha_{lean}) \cdot mol\ alk}{kg(am + H_2O)} = \frac{mol\ CO_2}{kg\ solv}$$



CO_2 solubility: 5 m PZ 5 m 2PE

$$\ln(P^*_{CO_2}) = a + \frac{b}{T} + c \cdot \alpha_{CO_2} + d \cdot \alpha_{CO_2}{}^2 + e \cdot \frac{\alpha_{CO_2}}{T} + f \cdot \frac{\alpha_{CO_2}{}^2}{T}$$



Optimized sensible heat cost

$$\left(\frac{\$Heat}{mol\ CO_2}\right)_{min} = \sqrt{\frac{0.75\cdot(\$/A)(\$/W)(T_{out}-T_{in})(T_{steam}-T_{sk})}{a\cdot T_{steam}}\left(\frac{2\cdot C_p}{\Delta C_{solv}\cdot\mu^{-0.25}}\right)}$$

Solvent	ΔC_{solv}	ΔC_{μ}	μ_{mid}
(m)	mol/kg solv		cP
8 m PZ	0.86	0.84	10.8
7 m MEA	0.5	0.67	3
2 m PZ 4 m AMP	0.77	0.90	5.4
5 m PZ 5 m MDEA	0.99	0.91	13.2

$$h = \left(\frac{0.026\cdot G^{0.8}C_p^{\ 0.3}k^{0.7}}{D^{0.2}}\right)\frac{1}{\mu^{0.5}} \cong \frac{a}{\mu^{0.5}}$$

Colburn (1933)

$$\Delta C_{\mu} = \frac{\Delta C_{solv}}{\left(\mu_{\alpha_{mid}}/10cP\right)^{0.25}}$$