Mass transfer in semi-aqueous MEA for CO_2 Capture

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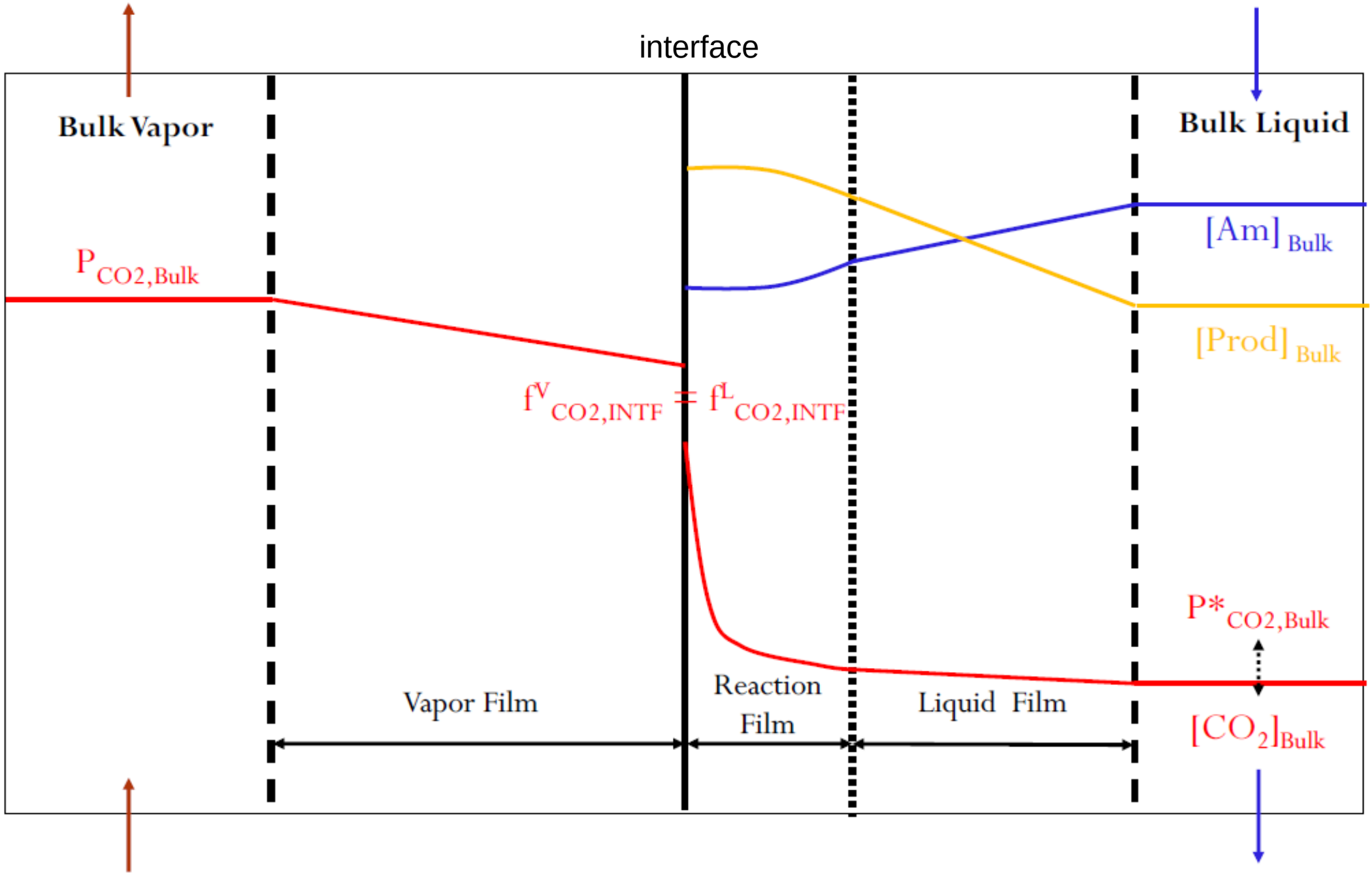
- **Introduction:**
  - CO_2 diffuse and react with amine
  - $MEA_{(semi\text{-}aq)}$: MEA-physical solvent-water
- **Theory**
- **Experiment Method**
  - WWC, FTIR, N_2O analogy
- **Results**
- **Conclusion**

Mass transfer with fast and finite rate reaction



Mass balance: CO_2 reacts with amine

$$CO_2 + 2\,MEA \overset{K_{eq}}{\longleftrightarrow} MEACOO^- + MEAH^+$$

$$\frac{dc_i}{dt} = -Di\ \frac{d^2c_i}{dx^2} + V_i * R$$

$$R = k_3 * a_{CO2} * a_{MEA}^2 - \frac{k_3}{K_{eq}} a_{MEACOO} * a_{MEAH}$$

$$a_i = \gamma_i * C_i$$

- i = CO_2, MEA, $MEACOO^-$, $MEAH^+$
- Can’t solve analytically
- Can be solved with assumptions (PFO)

Solve k_g' by film theory and PFO (Danckwarts,1970)

- [amine] >> [CO_2], constant
- Pseudo First Order (PFO)

$$D_{co2}\frac{\partial^2[CO_2]}{\partial x^2} - k[Am]^2[CO_2] = 0$$

$$N_{CO2} = \frac{\sqrt{D_{CO2}k} * [Am]}{H_{CO2-solution}}(P_{CO2,i} - P^*_{CO2,b})$$

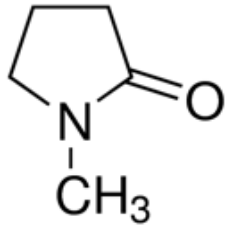
$$k_g{}' = \frac{\sqrt{D_{CO2}k_3} * [Am]}{\gamma_{CO2}H_{CO2}}$$

activity based

$$k_g{}' = \frac{\sqrt{D_{CO2}\,k_3} * a_{am}}{\gamma_{CO2}{}^{0.5}H_{CO2}}$$

Semi-aqueous amine, Why higher k_g' ?

Amine-water-physical solvent (NMP)



$$k_g{}' = \frac{\sqrt{D_{CO2}\, k_3} * a_{am}}{\gamma_{CO2}{}^{0.5} H_{CO2}}$$

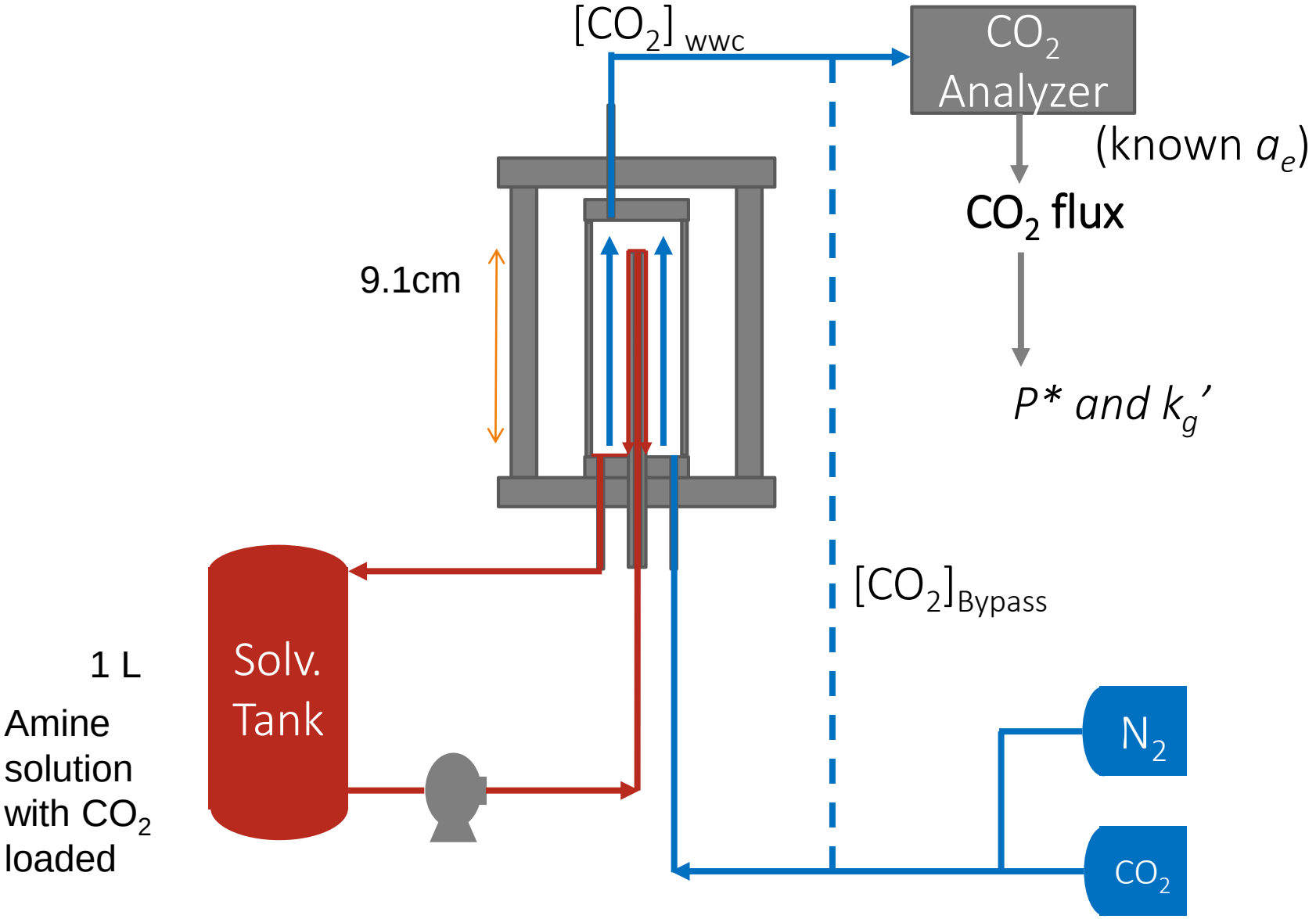
Hypothesis

- γ_{CO2} reduced, k_g' increase
- a_{am} increase, k_g' increase
- Viscosity increase, D_{CO2} decrease, k_g' decrease

Experiment method

- k_g' & P^*_{CO2}
  by the WWC
- γ_{CO2},
  by N_2O analogy
- $a_{am,}$
  by FTIR

Wetted Wall Column (WWC)



Measuring CO_2 physical solubility using N_2O analogy (Versteeg 1988)

$$H_{CO2-solution} = \frac{H_{CO2\ in\ water}}{H_{N2O\ in\ water}} * H_{N2O-solution}$$

Known, 0.73

measured

$$H_{CO2-solution} = \gamma_{CO2} H_{CO2}$$

H_{CO2} is the Henry's constant (std.)

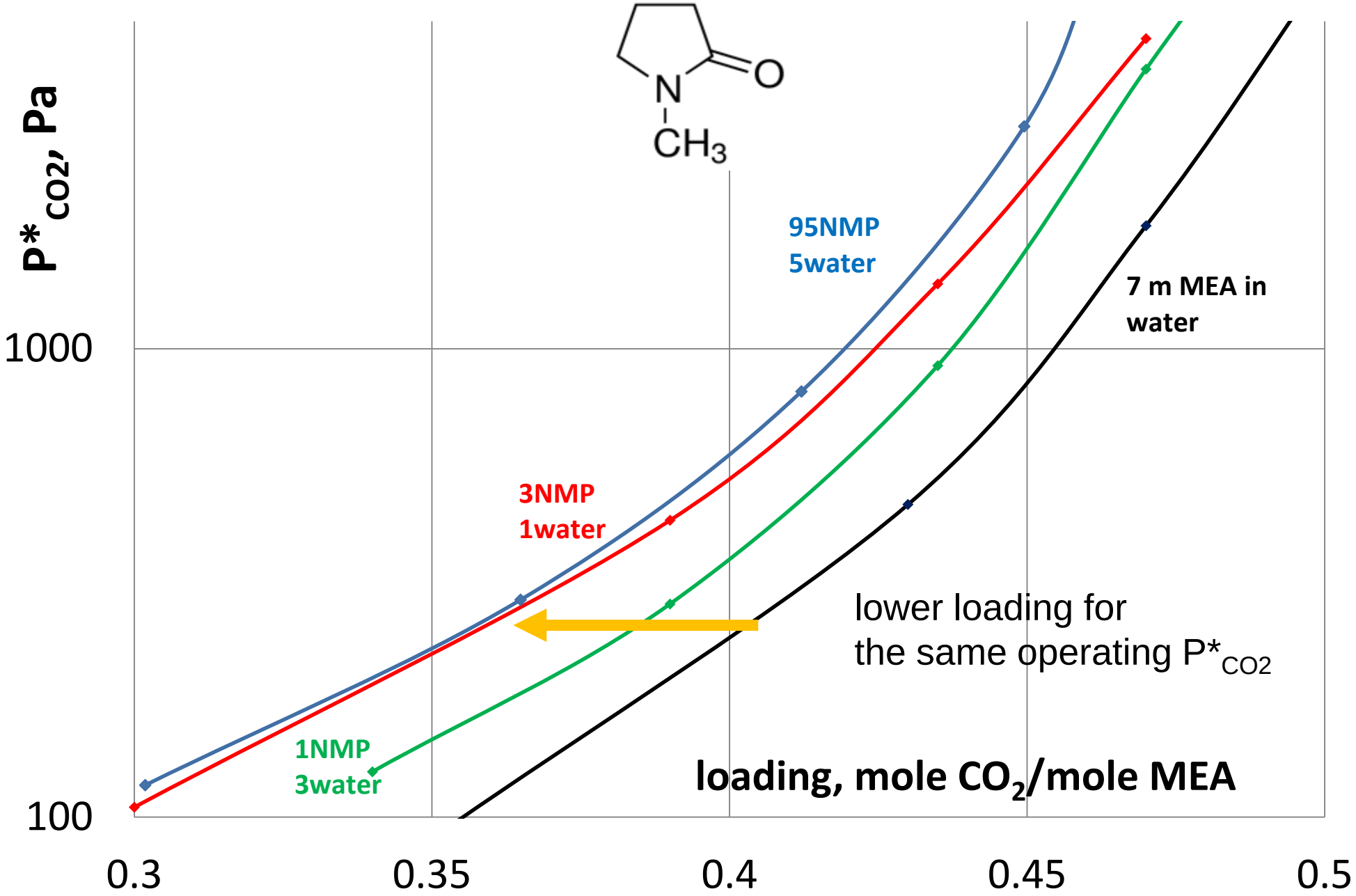
Activity of amine

- $P_{am} = H_{am}\gamma_{am}x_{am} = H_{am}a_{am}$
- $a_{am} = P_{am} / H_{am}$

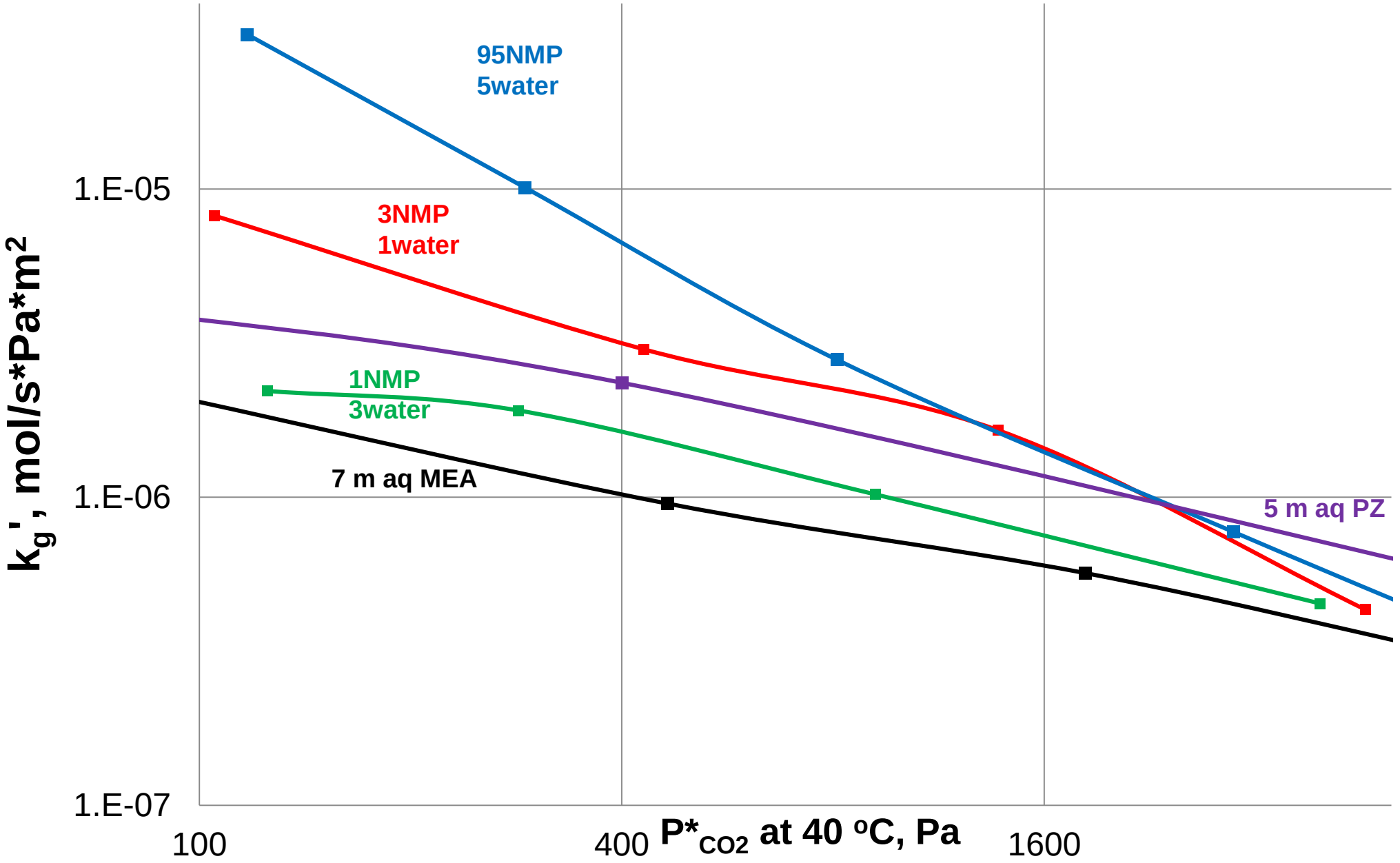
  - H_{am} is the Henry's constant (std.)
  - γ_{am} is the activity coefficient
  - a_{am} is the activity of the amine.

- $$\frac{P_{am,2}}{P_{am,1}} = \frac{a_{am,2}}{a_{am,1}}$$

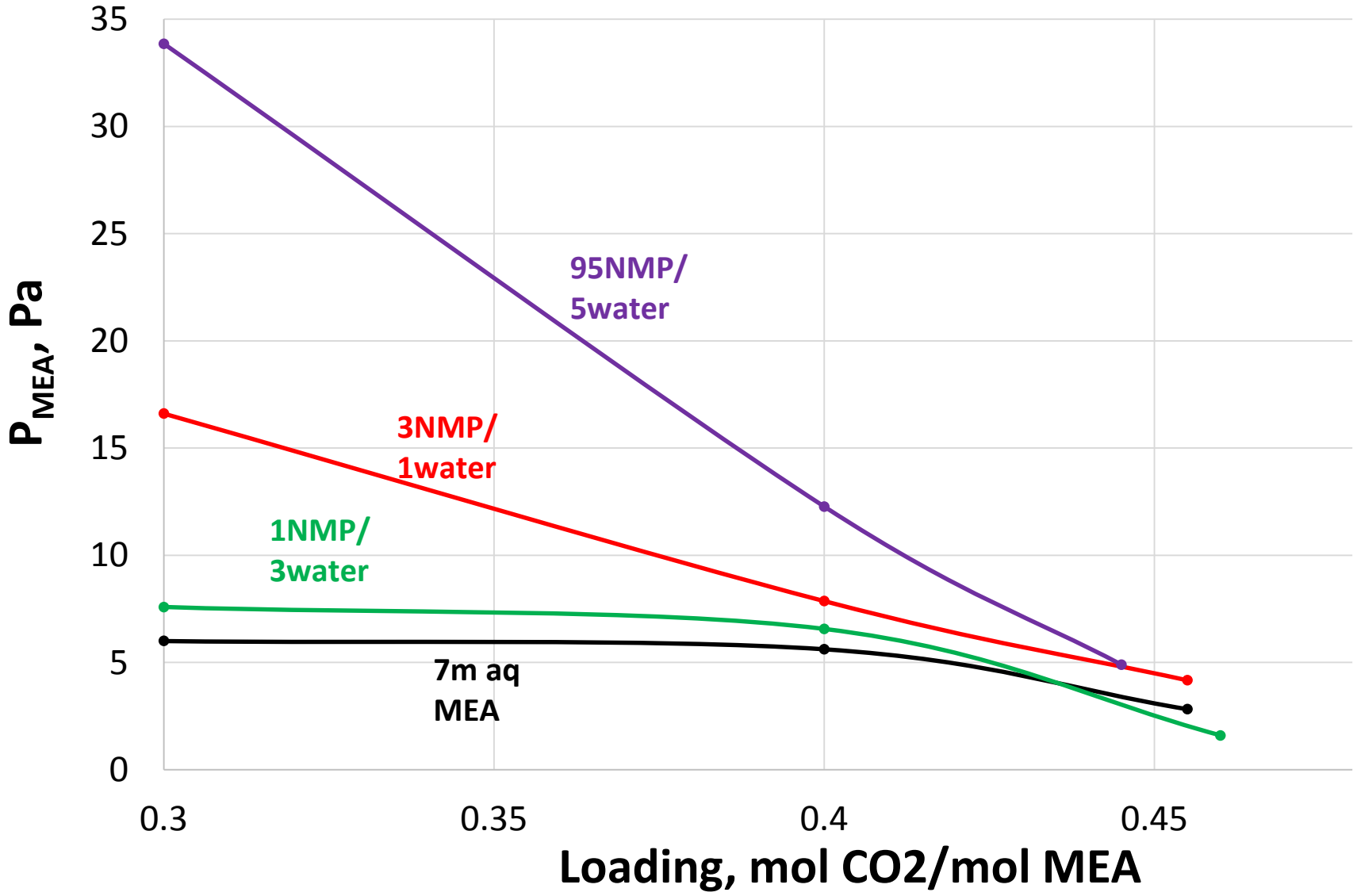
CO_2 solubility with different NMP/water ratios at 40 °C



k_g' of 7 m MEA in different solvents at 40 °C by WWC



P_{MEA} above different 7 m semi-aqueous MEA at 40 °C by FTIR



$$\frac{P_{am,2}}{P_{am,1}} = \frac{a_{am,2}}{a_{am,1}}$$

Numerical solution of penetration theory by MATLAB

$$CO_2 + 2\,MEA \overset{K_{eq}}{\longleftrightarrow} MEACOO^- + MEAH^+$$

$$\frac{dc_i}{dt} = -Di\,\frac{d^2c_i}{dx^2} + V_i * R$$

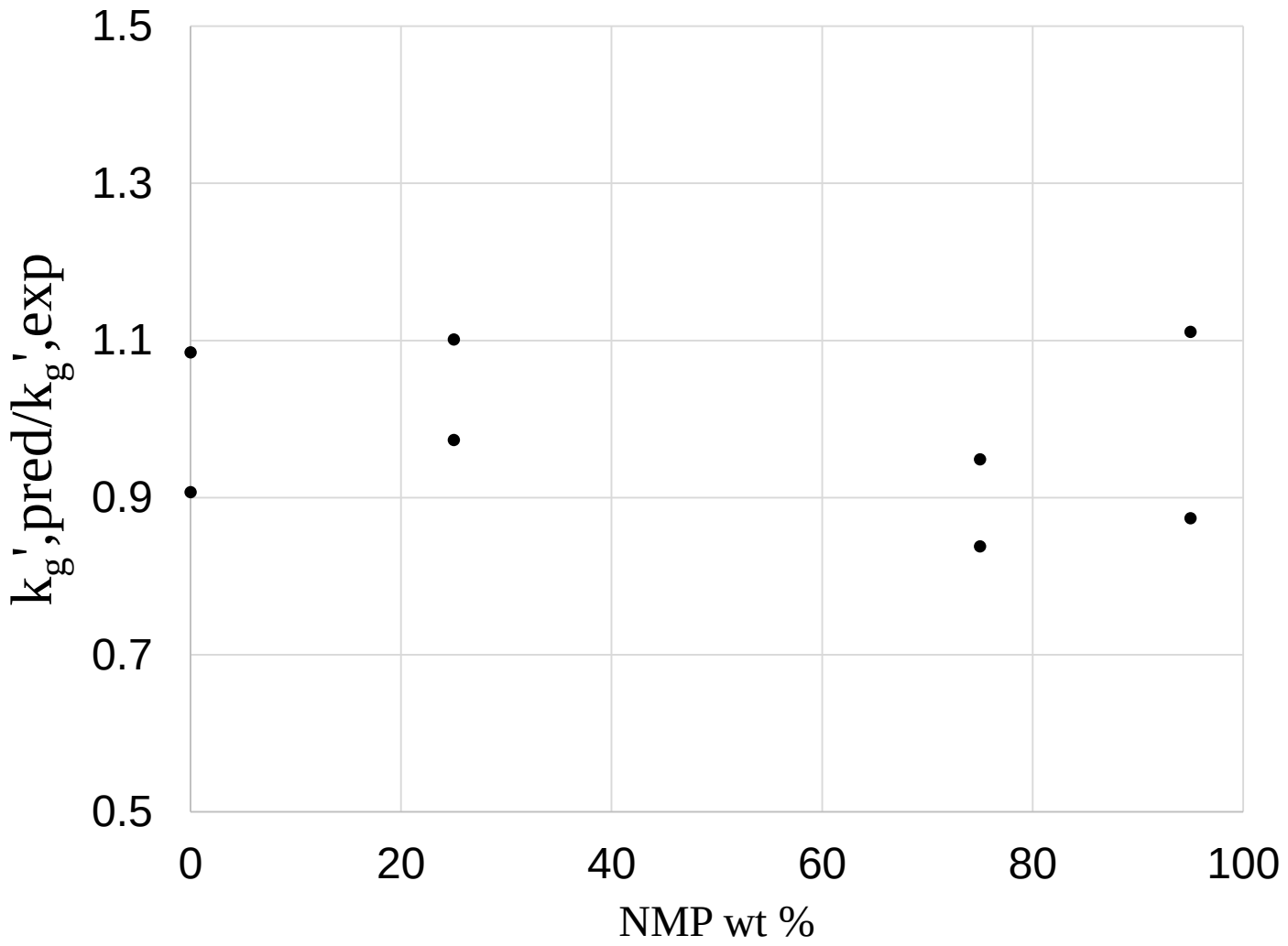
$$R = k_3 * a_{CO2} * a_{MEA}^2 - \frac{k_3}{K_{eq}}\,a_{MEACOO} * a_{MEAH}$$

$$a_i = \gamma_i * C_i$$

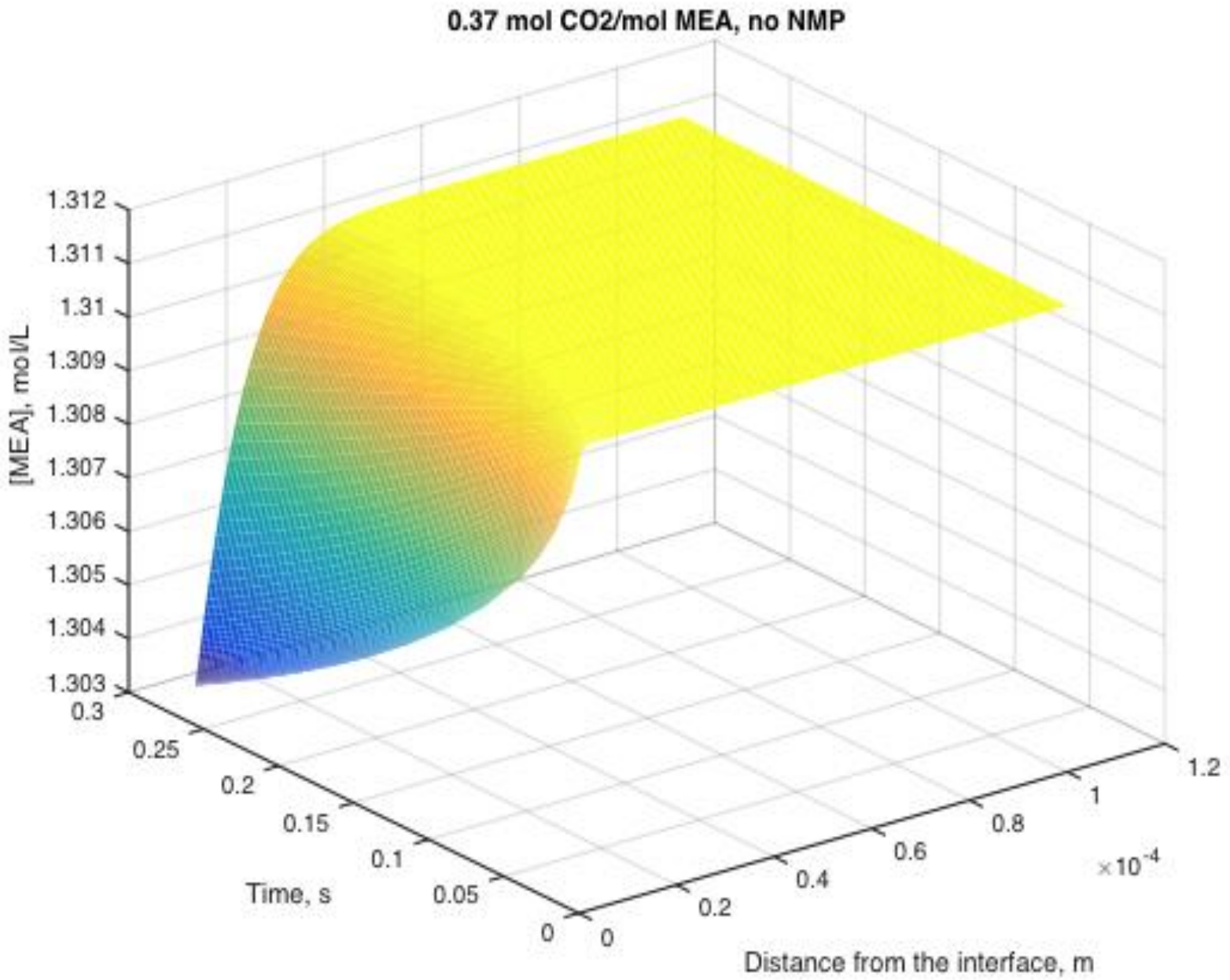
regressed parameters

$$k_3 = 12711\ \frac{m^6}{mol^2 * s}$$

$$D_{co2} = D_{co2,aq}\,(\frac{\mu}{\mu_{aq}})^{-0.52}$$

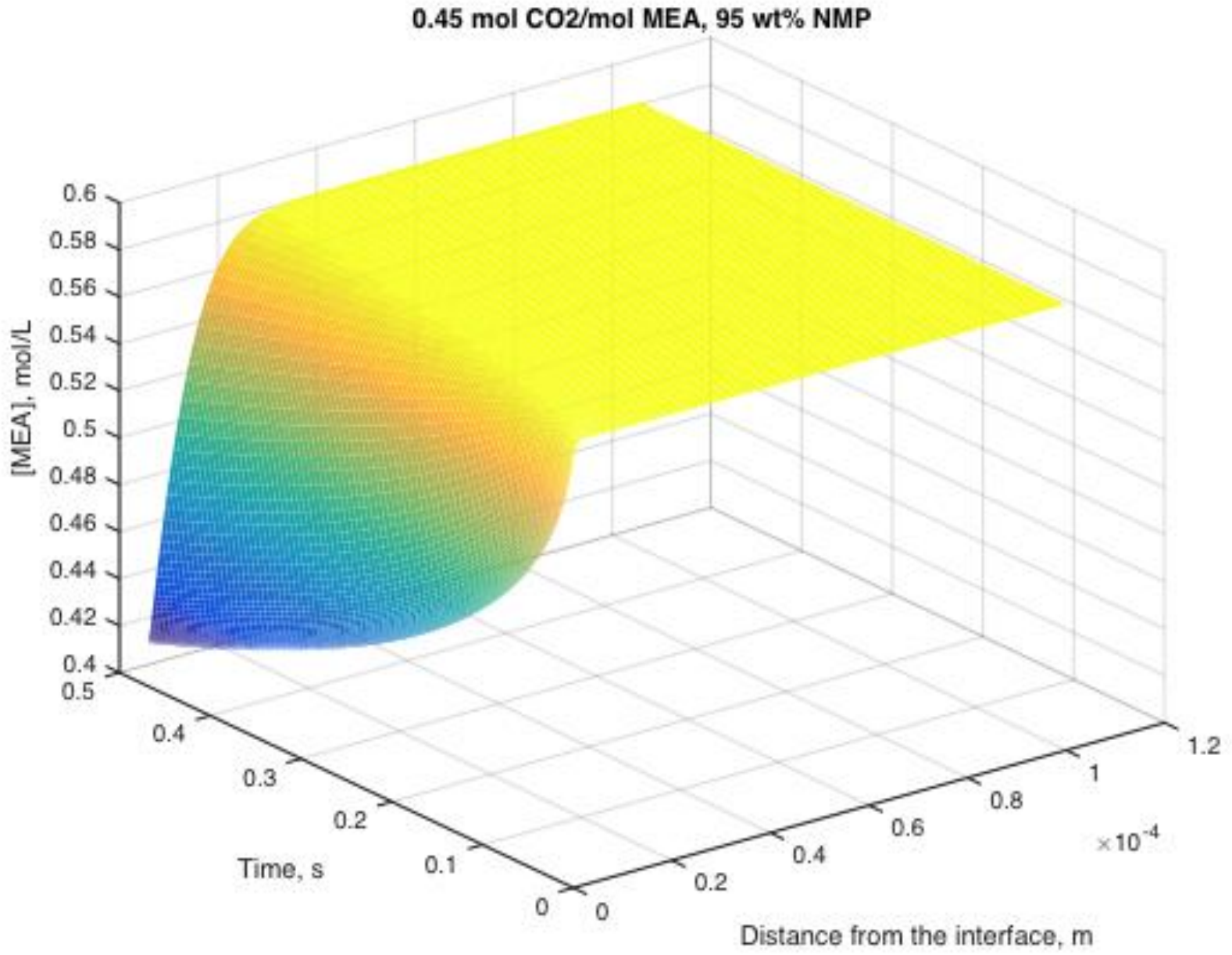


MEA concentration profile by MATLAB



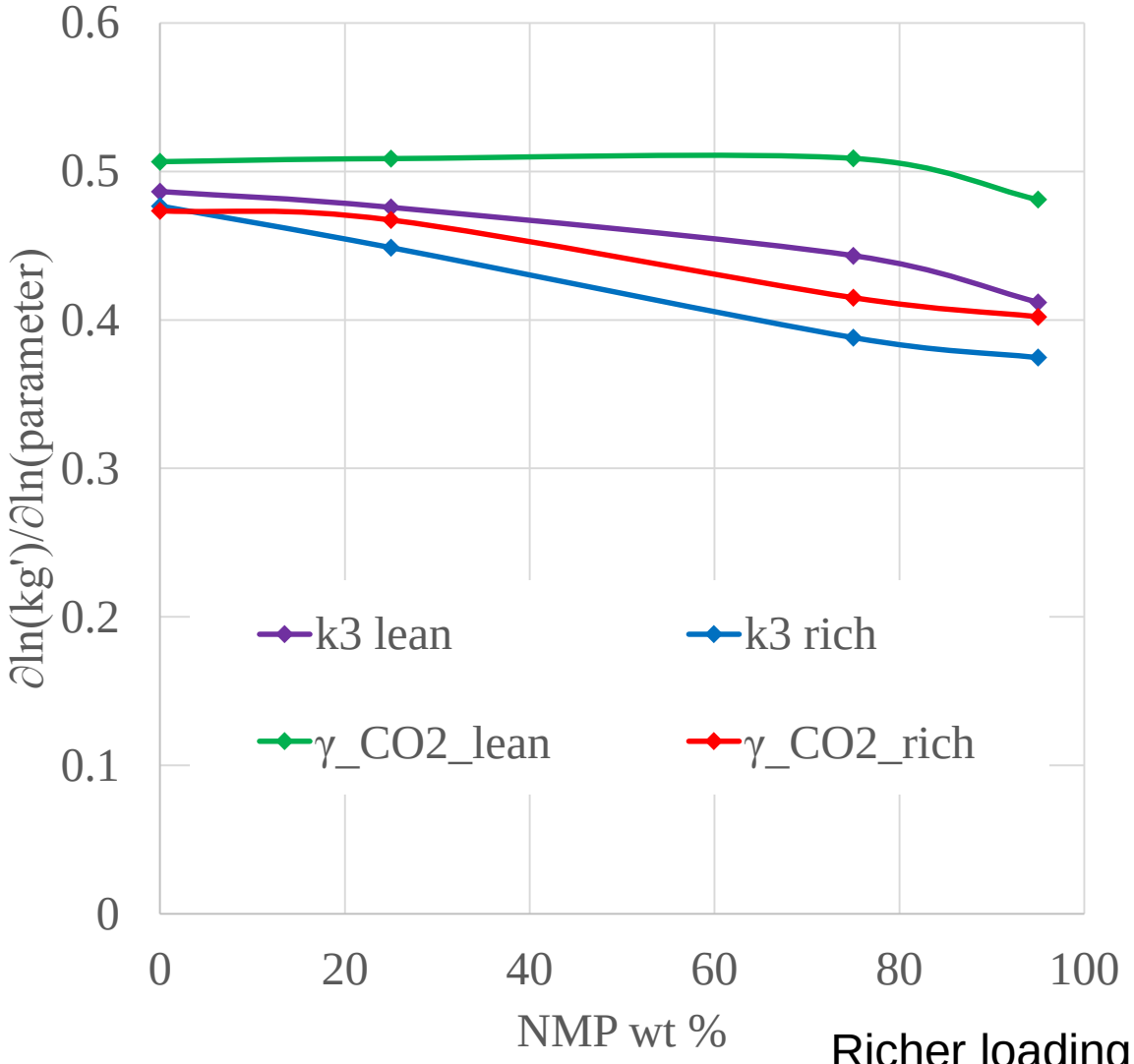
PFO approximation is adequate

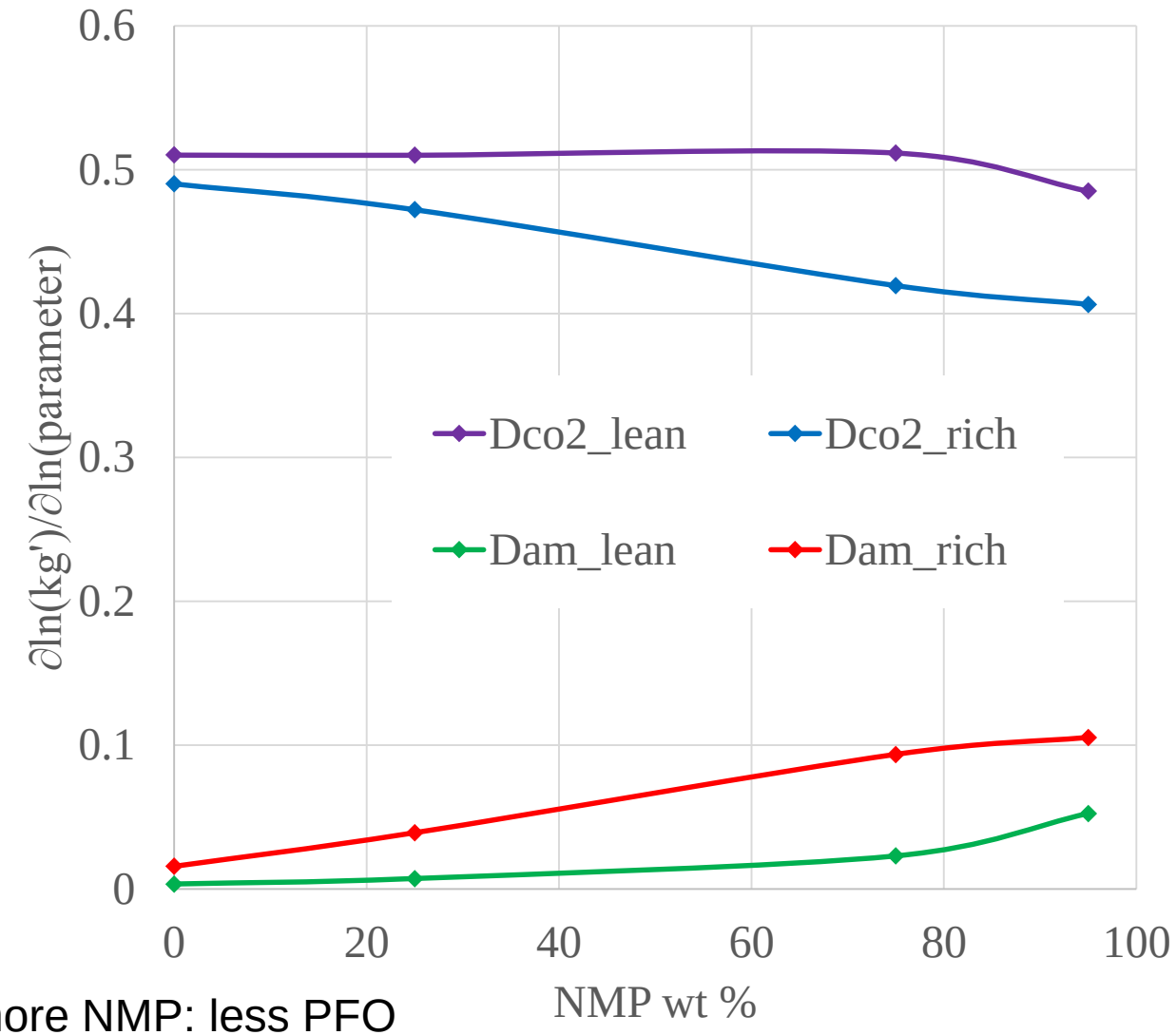
MEA concentration profile by MATLAB



Rich loading, more NMP:
PFO is not accurate

Sensitivity analysis: $\frac{\partial \ln k_g'}{\partial\ ln\ parameter}$, deviation from $k_g{}' = \frac{\sqrt{D_{CO2}\ k_3} * a_{am}}{\gamma_{CO2}{}^{0.5} H_{CO2}}$





Richer loading, more NMP: less PFO

Explain the rate increase by PFO

$$k_g' = \frac{\sqrt{D_{CO2}\, k_3} * a_{am}}{\gamma_{CO2}^{0.5} H_{CO2}}$$

Lean:0.37 mol CO_2/mol MEA

$D_{CO2} \propto \mu^{-0.52}$

Solvent mass ratio		μ, 40 °C	γ_{CO2}	γ_{MEA}	k_g', exp	k_g', predict
NMP	water					$a_{MEA} * \mu^{-0.26} * \gamma_{CO2}^{-0.5}$
0	1	1	1	1	1	1.0
1	3	1.84	0.95	1.60	1.2	1.4
3	1	6.08	0.58	2.67	2.1	2.2
95	5	5.76	0.28	4.44	5.2	5.3

Rich loading: not PFO, must use the MATLAB model

Conclusion

- At lean loading (P^*_{CO2} at 40 ^oC = 100 Pa) , k_g' of 7 m MEA in 3 water/1 NMP, 1 water/3 NMP, and 5 water/95 NMP is 1.25 times, 4 times, and 17 times that of 7 m MEA(aq), respectively.
- Adding NMP increases k_g': lower loading, higher physical solubility, higher MEA activity.
- A MATLAB mass transfer model was built for semi-aqueous MEA.
- PFO approximation is adequate to represent the CO_2 mass transfer in aqueous MEA but not accurate for semi-aqueous MEA.

Thanks

Comments & Questions?

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