Mass transfer in semi-aqueous MEA for CO$_2$ Capture

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• Introduction:
  • CO\textsubscript{2} diffuse and react with amine
  • MEA\textsubscript{(semi-aq)}: MEA-physical solvent-water

• Theory

• Experiment Method
  • WWC, FTIR, N\textsubscript{2}O analogy

• Results

• Conclusion
Mass transfer with fast and finite rate reaction
Mass balance: CO$_2$ reacts with amine

$$CO_2 + 2 MEA \leftrightarrow MEACOO^- + MEAH^+$$

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

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

$$a_i = \gamma_i * C_i$$

- 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\textsubscript{2}], constant
- Pseudo First Order (PFO)

\[ D_{\text{CO}_2} \frac{\partial^2 [\text{CO}_2]}{\partial x^2} - k[\text{Am}]^2[\text{CO}_2] = 0 \]

\[ N_{\text{CO}_2} = \sqrt{D_{\text{CO}_2} k \cdot [\text{Am}]} \frac{H_{\text{CO}_2-solution}}{(P_{\text{CO}_2,i} - P_{\text{CO}_2,b}^*)} \]

\[ k_g' = \frac{\sqrt{D_{\text{CO}_2} k_3 [\text{Am}]}}{\gamma_{\text{CO}_2 H_{\text{CO}_2}}} \]

activity based

\[ k_g' = \frac{\sqrt{D_{\text{CO}_2} k_3 \cdot a_{\text{am}}}}{\gamma_{\text{CO}_2^{0.5} H_{\text{CO}_2}}} \]
Semi-aqueous amine, Why higher $k_g$’?

Amine-water-physical solvent (NMP)

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

Hypothesis

- $\gamma_{CO2}$ 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

- $\gamma_{CO2}$,
  - by $N_2O$ analogy

- $a_{am}$,
  - by FTIR
Wetted Wall Column (WWC)

- CO$_2$ Analyzer
- CO$_2$ flux
- $P^*$ and $k_g'$ (known $\alpha_e$)
- [CO$_2$]$_{\text{wwc}}$
- [CO$_2$]$_{\text{Bypass}}$

- Solv. Tank
- 1 L
- Amine solution with CO$_2$ loaded

- N$_2$
- CO$_2$
Measuring CO₂ physical solubility using N₂O analogy (Versteeg 1988)

\[ H_{CO2\text{-solution}} = \frac{H_{CO2 \text{ in water}}}{H_{N2O \text{ in water}}} \times H_{N2O\text{-solution}} \]

Known, 0.73

\[ H_{CO2\text{-solution}} = \gamma_{CO2} H_{CO2} \]

\( H_{CO2} \) is the Henry's constant (std.)
Activity of amine

- \( P_{am} = H_{am} \gamma_{am} x_{am} = H_{am} a_{am} \)
- \( a_{am} = \frac{P_{am}}{H_{am}} \)

- \( H_{am} \) is the Henry's constant (std.)
- \( \gamma_{am} \) 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

![Graph showing CO$_2$ solubility with different NMP/water ratios at 40 °C.](image)

- $P^*_\text{CO}_2$, Pa
- 3NMP, 1water
- 95NMP, 5water
- 7 m MEA in water
- lower loading for the same operating $P^*_\text{CO}_2$

loading, mole CO$_2$/mole MEA

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

$P*_{CO2}$ at 40 °C, Pa

1.0E-06

1.0E-05

1.0E-07

7 m aq MEA

5 m aq PZ
$P_{\text{MEA}}$ 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

$$CO_2 + 2 MEA^{K_{eq}} MEACOO^- + MEAH^+$$

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

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

$$a_i = \gamma_i * C_i$$

regressed parameters

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

$$D_{CO2} = D_{CO2,aq} \left( \frac{\mu}{\mu_{aq}} \right)^{-0.52}$$
PFO approximation is adequate
Rich loading, more NMP: PFO is not accurate
Sensitivity analysis: \[ \frac{\partial \ln k'_g}{\partial \ln \text{parameter}}, \] deviation from \[ k'_g = \sqrt{D_{CO2} k_3 a_{am}} \gamma_{CO2}^{0.5} H_{CO2} \]
Explain the rate increase by PFO

Lean: 0.37 mol CO₂/mol MEA

\[ k'_g = \frac{\sqrt{D_{CO2} k_3 a_{am}}}{\gamma_{CO2}^{0.5} H_{CO2}} \]

\[ D_{CO2} \propto \mu^{-0.52} \]

<table>
<thead>
<tr>
<th>Solvent mass ratio</th>
<th>( \mu, 40^\circ C )</th>
<th>( \gamma_{CO2} )</th>
<th>( \gamma_{MEA} )</th>
<th>( k'_g ), exp</th>
<th>( k'_g ), predict</th>
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</table>

Rich loading: not PFO, must use the MATLAB model
Conclusion

• At lean loading ($P^*_{CO2}$ at 40 °C = 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?