Oxygen solubility and mass transfer in amine solutions for applications in post-combustion CO₂ capture

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1. Introduction and state of the art
2. Dissolved O\textsubscript{2} concentration
3. Mass transfer
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1. Introduction

Solvent degradation in post-combustion CO₂ capture

• Process operating costs:
  - Solvent replacement: up to 22% of the CO₂ capture OPEX[^1]!
  - Removal and disposal of toxic degradation products

• Process performance:
  - Decrease of the solvent loading capacity
  - Increase of viscosity, foaming, fouling…

• Capital costs
  - Corrosion

• Environmental balance
  - Emission of volatile degradation products!

1. Introduction

**Question 1:** Representativity of *lab* accelerated degradation\(^1\) versus *industrial* degradation? 

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Mass transfer\(^2\)? \(k_{La}\) ?

Pressure ?
Temperature ?

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1. Introduction

Solvent degradation in post-combustion CO$_2$ capture

=> Representativity ok, but where does it come from?
=> Focus on oxidative degradation of MEA

1. Introduction

**Question 2:** $O_2$ solubility in 30 wt% MEA, depending on Pressure and Temperature?

- **Henry’s law**:

  
  \[
  [O_2] = H(T). P_{O_2}
  \]

  where $H(T) = K. \exp\left(-\frac{\Delta H}{R}. \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$

  Constants for $O_2$ in pure water available\(^1\), but no data for $O_2$ in MEA…

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\(^1\) Sander, 1999. Air Chemistry Department, Max-Planck Institute for Chemistry. www.henrys-law.org
1. Introduction

- **Experimental measurements**

  - Empirical correlation for $\text{O}_2$ in 20 wt% MEA$^1$
    
    $$[\text{O}_2] = -2.545 + 0.807 \times 10^{-2} T - 84.14 P + 2.096 \times 10^{-4} PT^2 + 2.322 \times 10^4 PT^{-1} + 1.027 P^2 - 3.911 \times 10^2 P^2T^{-1}$$
    
    However, this correlation overestimates the solubility of $\text{O}_2$

  - Measurements for $\text{O}_2$ in 30 wt% MEA$^2$
    
    No variation of the $\text{O}_2$ partial pressure, no correlation proposed

  => *Few experimental data available*

[2] Wang et al., 2013. dx.doi.org/10.1021/je301077y
2. Dissolved O₂ concentration

Use of a galvanic probe to determine the O₂ concentration

- Operating mode: the gas flow is sparged into 400 gr of MEA 30 wt% until reaching a constant concentration in dissolved O₂
- 20°C < T < 40°C
- 200 Nml/min gas flow
- Atmospheric pressure
- 9,500 < Pₐ₉ < 50,000 Pa
- 600 rpm
2. Dissolved $O_2$ concentration

- Influence of the temperature on $C^{*}_{O2}$
  $P_{O2} \sim 20,000$ Pa

![Graph showing the influence of temperature on dissolved oxygen concentration](image-url)
2. Dissolved $O_2$ concentration

- Influence of $P_{O_2}$ on $C^*_{O_2}$

![Graph showing the influence of $P_{O_2}$ on $C^*_{O_2}$]
2. Dissolved O$_2$ concentration

• Resulting correlation:

\[
C_{O_2}^* (T, P_{O_2}) = \left( 2.03 \times 10^{+11} \cdot e^{-\frac{19666}{RT}} \right)^{-1} P_{O_2}
\]

$P_{O_2}$ in Pa, $T$ in K and $C_{O_2}^*$ in mol/L

• This correlation is based on own experimental results and on results retrieved from Wang et al., 2013

• Range of validity:
  - MEA 30 wt% ($C_{O_2}^*$ does not vary with concentration$^1$)
  - $10 < T < 60^\circ C$
  - $9,500 < P_{O_2} < 50,000$

[1] Wang et al., 2013. dx.doi.org/10.1021/je301077y
3. Mass transfer

$k_L a$ is representative of the quality of the mass transfer.

$$\frac{dC_A}{dt} = K_L a \left( C_A^* - C_A \right)$$

It depends on:

• Physico-chemical system
• Chemical reaction (neglected)
• Process hydrodynamics
• Column packing / experimental set-up

• Determination of the $k_L a$ with consideration of the probe response time $\tau_P$

$$\frac{C^* - C_P}{C^* - C_0} = \frac{1}{1 - \tau_P K_L a \left( e^{-K_L a \cdot t} - \tau_P K_L a \cdot e^{-\tau_P} \right)}$$
3. Mass transfer

Dynamic degassing/regassing to determine the $k_La$

- Nitrogen sparging to remove any $O_2$ from the solution
- $O_2$ sparging into the solution
- Step changes in $P_{O_2}$
- Stabilisation of the dissolved $O_2$ measurement
3. Mass transfer

• Influence of the temperature

\[ K_{La_{600 \text{ RPM}}} (T) = -2.49 \times 10^{-2} \frac{T}{273.15} + 2.97 \times 10^{-2} \]
4. Relevance for oxidative degradation

Study of oxidative degradation in semi-batch conditions

⇒ Accelerated conditions (base case):

- 300 g of 30 wt% MEA
- 55-140°C, 4 barg, 600 rpm
- 7 days
- Continuous gas flow: 160 Nml/min, 2.5 – 5 – 10% O₂ in N₂
4. Relevance for oxidative degradation

Influence of operating variables:

- \( P_{O_2} \)
- Temperature

\[ -r_{MEA} = 1.36 \times 10^6 \exp(55111/RT) [O_2]^{1.03} \]

\[ \text{[mol]} \]

\[ \text{O}_2 \text{ partial pressure [Pa]} \]

\[ \text{[mol]} \]

\[ \text{Temperature [K]} \]

4. Relevance for oxidative degradation

Comparison of the laboratory degradation with degradation in industrial pilot plants:

- Similar degradation products (GC spectra)
- Faster degradation:
  21% MEA loss in 7 days (lab) vs. 4% loss in 45 days (Pilot)

4. Relevance for oxidative degradation

Comparison of the laboratory degradation with degradation in industrial pilot plants

<table>
<thead>
<tr>
<th>Unit</th>
<th>Industrial conditions</th>
<th>Lab conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradation rate</td>
<td>wt-%/day</td>
<td>0.026</td>
</tr>
<tr>
<td>$k_La$</td>
<td>s$^{-1}$</td>
<td>0.01 &lt; $k_La$ &lt; 0.04$^{[1]}$</td>
</tr>
<tr>
<td>$P_{O2}$</td>
<td>Pa</td>
<td>~ 6,000</td>
</tr>
<tr>
<td>$T$</td>
<td>°C</td>
<td>40-60</td>
</tr>
</tbody>
</table>

=> Temperature is the main parameter that has been used for the accelerated degradation experiments

$^{[1]}$ Typical $k_La$ in Mellapak structured packing depending on packing geometry and hydrodynamics: De Brito M., 1991. PhD thesis n° 984, EPFL.
5. Conclusion & perspectives

• Measurements of dissolved $O_2$ concentrations in 30 wt% MEA

• A correlation is proposed as an alternative to the correlation of Rooney & Daniels (1998)

• This correlation has been used to build an Aspen Plus model of PCCC with assessment of oxidative (and thermal) degradation.

• The Aspen Plus model predicts a degradation rate that is in the same range as reported degradation from pilot plants\(^2\)

\[\text{[2] Léonard G. et al., 2015. DOI: 10.1016/j.compchemeng.2015.05.003.}\]
5. Conclusion & perspectives

• The $k_L a$ of the experimental Degradation Test Rig is determined at 600 rpm

• It appears to be smaller than typical $k_L a$ for structured packing used in industrial conditions

• The acceleration of the oxidative degradation rate was mainly due to the higher temperature and $P_{O_2}$

• This appears as an alternative to the degradation acceleration induced by a high agitation rate
Thank you for your attention!