Modelling CO$_2$ capture with AMP in NMP

SANKU, M., DR. SVENSSON, H.
Outline

• Background of our research

• Model
  o Work so far / Shortcomings / Proposed improvements

• Remaining properties
  o Gaps: data in aqueous medium (literature)
  o Gaps: data in NMP medium (experimental)
  o Properties of precipitate
  o Properties of transfer

• Future work
The system

Solvent:

\[
\text{NMP} \quad \text{(N-methyl-2-pyrrolidone)}
\]

Amine:

\[
\text{AMP} \quad \text{(2-amino-2-methyl-1-propanol)}
\]

Note: AMP is sterically hindered
Reaction mechanism

\[
\begin{align*}
\text{CO}_2 (g) & \leftrightarrow \text{CO}_2 (\text{sol}) \\
\text{CO}_2 (\text{sol}) + \text{RNH}_2 (\text{sol}) & \leftrightarrow \text{RNH}_2^+ \text{COO}^- (\text{sol}) \\
\text{RNH}_2^+ \text{COO}^- (\text{sol}) + \text{RNH}_2 (\text{sol}) & \leftrightarrow \text{RNH}_3^+ (\text{sol}) + \text{RNHCOO}^- (\text{sol}) \\
\text{RNH}_3^+ (\text{sol}) + \text{RNHCOO}^- (\text{sol}) & \leftrightarrow \text{RNH}_3^+ \text{RNHCOO}^- (s)
\end{align*}
\]
Model: What we want to do?

- Predict the lean and rich stream loading
- Energy requirements for the plant
- Test different plant configurations
What we have done?

Absorption column

Crystallisation unit

Regeneration unit

Simplifications

- Equilibrium model
- Literature data - CO₂, AMP, NMP, AMP+
- No solid data or ternary data
- Approximations when data unavailable
- Not heat integrated yet

ENRTL-RK
# Model vs experimental

## Energy requirement (25w% AMP in NMP)

<table>
<thead>
<tr>
<th>Model</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 GJ/ton CO$_2$</td>
<td>14.4 GJ/ton CO$_2$</td>
</tr>
<tr>
<td>1.01 bar a</td>
<td>7 bar a</td>
</tr>
<tr>
<td>$T_{\text{abs}}=50$ °C</td>
<td>$T_{\text{abs}}=45$ °C</td>
</tr>
<tr>
<td>$T_{\text{reg}}=75$ °C</td>
<td>$T_{\text{reg}}=75$ °C</td>
</tr>
<tr>
<td>No crystallisation</td>
<td>Crystallisation Heating of the reactor</td>
</tr>
</tbody>
</table>
Total pressure at 85 °C, AMP in NMP

<table>
<thead>
<tr>
<th>Solution</th>
<th>Model (bar a)</th>
<th>Experiment (bar a)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>15w% AMP in NMP</td>
<td>0.022</td>
<td>0.037</td>
</tr>
<tr>
<td>25w% AMP in NMP</td>
<td>0.025</td>
<td>0.075</td>
</tr>
</tbody>
</table>

* "Regeneration of Non-Aqueous Precipitating Amine Solvents” by Hanna K. Karlsson at PCCC-4, Birmingham, Alabama

Assumed binary NRTL parameters
Outlet of regeneration

<table>
<thead>
<tr>
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<th>Unit</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>85</td>
</tr>
<tr>
<td>Pressure</td>
<td>bar a</td>
<td>2.52</td>
</tr>
<tr>
<td>H₂O</td>
<td>kmol/hr</td>
<td>1.00E-10</td>
</tr>
<tr>
<td>CO₂</td>
<td>kmol/hr</td>
<td>0.014465</td>
</tr>
<tr>
<td>AMP</td>
<td>kmol/hr</td>
<td>0.1261</td>
</tr>
<tr>
<td>NMP</td>
<td>kmol/hr</td>
<td>0.8586</td>
</tr>
<tr>
<td>AMP⁺COO⁻</td>
<td>kmol/hr</td>
<td>1.73E-34</td>
</tr>
<tr>
<td>AMP⁺</td>
<td>kmol/hr</td>
<td>0.0211</td>
</tr>
<tr>
<td>AMPCOO⁻</td>
<td>kmol/hr</td>
<td>0.0211</td>
</tr>
<tr>
<td>SOLID</td>
<td>kmol/hr</td>
<td>0</td>
</tr>
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Inlet:
15w% AMP in NMP
CO₂ loading=0.2
Outlet of regeneration

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Inlet: 15w% AMP in NMP CO$_2$ loading=0.2

Species in the liquid phase (about 60 mole% CO$_2$)
Outlet of regeneration

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Inlet: 15w% AMP in NMP CO₂ loading=0.2

**Experiment:**
At the same conditions, the solution has much lower CO₂*

Species in the liquid phase (about 60 mole% CO₂)

* "Regeneration of Non-Aqueous Precipitating Amine Solvents" by Hanna K. Karlsson at PCCC-4, Birmingham, Alabama
Approximations

• Dielectric constant of NMP is constant with temperature

• Properties of $\text{RNH}_2^+\text{COO}^- (aq) \approx \text{H}^+\text{PZCOO}^- (aq)$, $\text{RNHCOO}^- (aq) \approx \text{PZCOO}^- (aq)$

• Binary NRTL parameters approximated

• He constant for CO$_2$ in AMP assumed same as CO$_2$ in NMP

• No solid or ternary data

• Approximated infinite dilution heat capacity of the ions for our system
## Improvements

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of vaporization</td>
<td>Vapor pressure of pure solvents</td>
</tr>
<tr>
<td>Binary parameters</td>
<td>Vapor pressure of mixtures – loaded and unloaded</td>
</tr>
<tr>
<td>Henry’s constant</td>
<td>Measured in NMP, will be measured in AMP with N$_2$O</td>
</tr>
<tr>
<td>Heat capacity of solid</td>
<td>Measure with solid calorimetry</td>
</tr>
<tr>
<td>Molar volume of solid</td>
<td>Density of a whole crystal</td>
</tr>
</tbody>
</table>
What would still be missing?

- Properties of $\text{RNH}_2^+\text{COO}^-$, $\text{RNHCOO}^-$
- Properties of the precipitate
- Dielectric constant of NMP with temperature
- Ternary data
- Infinite dilution heat capacity of the ions for our system
Simplifications

\[ \text{CO}_2 (g) \leftrightarrow \text{CO}_2 (\text{sol}) \]
\[ \text{CO}_2 (\text{sol}) + 2\text{RNH}_2 (\text{sol}) \leftrightarrow \text{RNH}_3^+ (\text{sol}) + \text{RNHCOO}^- (\text{sol}) \]
\[ \text{RNH}_3^+ (\text{sol}) + \text{RNHCOO}^- (\text{sol}) \leftrightarrow \text{RNH}_3^+ \text{RNHCOO}^- (s) \]

**Assumptions:**

- Zwitterion concentration and impact is negligible
- The precipitate completely dissociates to ions
- Single solid phase
Pure component properties (aq)

\[ \text{CO}_2(aq) + 2\text{RNH}_2(aq) \rightleftharpoons \text{RNH}_3^+(aq) + \text{RNHCOO}^- (aq) \]
Pure component properties (aq)

Pure component data available

$$\text{CO}_2(\text{aq}) + 2\text{RNH}_2(\text{aq}) \iff \text{RNH}_3^+(\text{aq}) + \text{RNHCOO}^- (\text{aq})$$
Pure component properties (aq)

Pure component data available

\[
\text{CO}_2(aq) + 2\text{RNH}_2(aq) \overset{K_1}{\leftrightarrow} \text{RNH}_3^+(aq) + \text{RNHCOO}^- (aq)
\]

\[
\text{RNH}_2(aq) + \text{H}^+ (aq) \overset{K_p}{\leftrightarrow} \text{RNH}_3^+ (aq)
\]
Pure component properties (aq)

Pure component data available

CO$_2$(aq) + 2RNH$_2$(aq) $\overset{K_1}{\leftrightarrow}$ RNH$_3^+$(aq) + RNHCOO$^-$ (aq)

Unsymmetrical properties calculable

Data available

RNH$_2$(aq) + H$^+$(aq) $\overset{K_p}{\leftrightarrow}$ RNH$_3^+$(aq)
Pure component properties (aq)

Pure component data available

$\text{CO}_2(aq) + 2\text{RNH}_2(aq) \leftrightarrow \text{RNH}_3^+(aq) + \text{RNHCOO}^- (aq)$

Data available

$\text{RNH}_2(aq) + \text{H}^+ (aq) \leftrightarrow \text{RNH}_3^+(aq)$

Unsymmetrical properties calculable

$K_t$

Missing

$K_p$
Pure component properties (aq)

\[ \text{CO}_2(aq) + 2\text{RNH}_2(aq) \leftrightarrow \text{RNH}_3^+(aq) + \text{RNHCOO}^-(aq) \]

Pure component data available

Unsymmetrical properties calculatable

Data available

Note: aqueous medium
Pure component properties (NMP)

\[
\begin{align*}
\text{CO}_2 (g) & \underset{H}{\overset{K_1}{\rightleftharpoons}} \text{CO}_2 (sol) \\
\text{CO}_2(sol) + 2\text{RNH}_2(sol) & \rightleftharpoons \text{RNH}_3^+(sol) + \text{RNHCOO}^- (sol) \\
\Delta H_r & = \Delta H_{\text{CO}_2} + \Delta H_{r1}
\end{align*}
\]

Experiments: without precipitation
Pure component properties (NMP)

Without precipitation

\[ \text{CO}_2 (g) \rightleftharpoons \text{CO}_2 (\text{sol}) \]

\[ \text{CO}_2(\text{sol}) + 2\text{RNH}_2(\text{sol}) \rightleftharpoons \text{RNH}_3^+(\text{sol}) + \text{RNHCOO}^- (\text{sol}) \]

Measured separately

\[ \Delta H_r = \Delta H_{\text{CO}_2} + \Delta H_{r1} \]
Pure component properties (NMP)

Without precipitation

\[ \text{CO}_2 (g) \rightleftharpoons \text{CO}_2 (\text{sol}) \]

Measured separately

\[ \text{CO}_2(\text{sol}) + 2\text{RNH}_2(\text{sol}) \rightleftharpoons \text{RNH}_3^+(\text{sol}) + \text{RNHCOO}^- (\text{sol}) \]

Measured

\[ \Delta H_r = \Delta H_{\text{CO}_2} + \Delta H_{r1} \]

Calculatable

Measured separately

\[ H \]

\[ K_1 \]
Pure component properties (NMP)

Without precipitation

\[ \text{CO}_2 (g) \rightleftharpoons \text{CO}_2 (\text{sol}) \]

\[ \text{CO}_2 (\text{sol}) + 2\text{RNH}_2 (\text{sol}) \rightleftharpoons \text{RNH}_3^+ (\text{sol}) + \text{RNHCOO}^- (\text{sol}) \]

Measured

\[ \Delta H_r = \Delta H_{\text{CO}_2} + \Delta H_{r1} \]

Measured separately

\[ \frac{d \ln K_1}{dT} = \frac{\Delta H_{r1}}{RT^2} \] at constant pressure

Properties of \text{RNHCOO}^- (\text{NMP})

Properties of \text{CO}_2, \text{RNH}_2, \text{RNH}_3^+ in \text{NMP}

Missing: \ln K_1 at any \text{T}
Pure component properties (NMP)

**Without precipitation**

$$\text{CO}_2 (g) \rightleftharpoons \text{CO}_2 (\text{sol})$$

$$\text{CO}_2 (\text{sol}) + 2\text{RNH}_2 (\text{sol}) \ rightleftharpoons \text{RNH}_3^+ (\text{sol}) + \text{RNHCOO}^- (\text{sol})$$

**Measured separately**

$$\Delta H_r = \Delta H_{\text{CO}_2} + \Delta H_{r1}$$

**Measured**

$$\frac{d \ln K_1}{dT} = \frac{\Delta H_{r1}}{RT^2}$$ at constant pressure

**Calculatable**

**Properties of RNHCOO\(^-\) (NMP)**

Assumptions:

- \(\text{CO}_2 (\text{sol})\) in the solution is same as in the absence of AMP
- \(\text{CO}_2 (\text{sol})\) in AMP will be measured
Properties of the solid

\[
\begin{align*}
\text{CO}_2 (g) & \rightleftharpoons \text{CO}_2 (sol) \\
\text{CO}_2 (sol) + 2\text{RNH}_2 (sol) & \rightleftharpoons \text{RNH}_3^+ (sol) + \text{RNHCOO}^- (sol) \\
\text{RNH}_3^+ (sol) + \text{RNHCOO}^- (sol) & \rightleftharpoons \text{RNH}_3^+ \text{RNHCOO}^- (s)
\end{align*}
\]

\[\Delta H_r = \Delta H_{\text{CO}_2} + \Delta H_{r1} + \Delta H_{r2}\]

Experiments with precipitation
Properties of the solid

\[
\begin{align*}
\text{With precipitation} & \quad \text{Measured separately} \\
\text{Measured} & \quad \Delta H_r = \Delta H_{CO_2} + \Delta H_{r1} + \Delta H_{r2} \\
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2 (g) & \rightleftharpoons \text{CO}_2 (sol) \\
\text{CO}_2 (sol) + 2\text{RNH}_2 (sol) & \rightleftharpoons \text{RNH}_3^+ (sol) + \text{RNHCOO}^- (sol) \\
\text{RNH}_3^+ (sol) + \text{RNHCOO}^- (sol) & \rightleftharpoons \text{RNH}_3^+ \text{RNHCOO}^- (s) \\
\end{align*}
\]
Properties of the solid

With precipitation

\[ \text{CO}_2 (g) \overset{H}{\rightleftharpoons} \text{CO}_2 (sol) \]

\[ \text{CO}_2 (sol) + 2\text{RNH}_2 (sol) \overset{K_1}{\rightleftharpoons} \text{RNH}_3^+ (sol) + \text{RNHCOO}^- (sol) \]

\[ \text{RNH}_3^+ (sol) + \text{RNHCOO}^- (sol) \overset{K_2}{\rightleftharpoons} \text{RNH}_3^+ \text{RNHCOO}^- (s) \]

Measured separately

\[ \Delta H_r = \Delta H_{\text{CO}_2} + \Delta H_{r1} + \Delta H_{r2} \]

Measured

Calcuatable

\[ \frac{d \ln K_2}{dT} = \frac{\Delta H_{r2}}{RT^2} \text{ at constant pressure} \]
Properties of the solid

With precipitation

\[ \text{CO}_2 \ (g) \overset{H}{\leftrightarrow} \text{CO}_2 \ (\text{sol}) \]

\[ \text{CO}_2 \ (\text{sol}) + 2\text{RNH}_2 \ (\text{sol}) \overset{K}{\leftrightarrow} \text{RNH}_3^+ \ (\text{sol}) + \text{RNHCOO}^- \ (\text{sol}) \]

\[ \text{RNH}_3^+ \ (\text{sol}) + \text{RNHCOO}^- \ (\text{sol}) \overset{K_2}{\leftrightarrow} \text{RNH}_3^+ \text{RNHCOO}^- \ (s) \]

Measured

\[ \Delta H_r = \Delta H_{\text{CO}_2} + \Delta H_{r1} + \Delta H_{r2} \]

Calculatable

Missing: \( \ln K_2 \) at any \( T \)

\[ \frac{d \ln K_2}{dT} = \frac{\Delta H_{r2}}{RT^2} \] at constant pressure

Properties of \( \text{RNH}_3^+, \text{RNHCOO}^- \) in NMP

Properties of \( \text{RNH}_3^+ \text{RNHCOO}^- \ (s) \)
**Properties of the solid**

With precipitation:

\[
\text{CO}_2 (g) \rightleftharpoons \text{CO}_2 (\text{sol})
\]

\[
\text{CO}_2 (\text{sol}) + 2\text{RNH}_2 (\text{sol}) \rightleftharpoons \text{RNH}_3^+ (\text{sol}) + \text{RNHCOO}^- (\text{sol})
\]

\[
\text{RNH}_3^+ (\text{sol}) + \text{RNHCOO}^- (\text{sol}) \rightleftharpoons \text{RNH}_3^+ \text{RNHCOO}^- (s)
\]

Measured separately:

\[
\Delta H_r = \Delta H_{\text{CO}_2} + \Delta H_{r1} + \Delta H_{r2}
\]

Measured:

\[
\frac{d \ln K_2}{dT} = \frac{\Delta H_{r2}}{RT^2}
\]

at constant pressure

Properties of \(\text{RNH}_3^+ \text{RNHCOO}^- (s)\)

Properties of \(\text{RNH}_3^+ , \text{RNHCOO}^- \text{in NMP}\)

Missing: \(\ln K_2\) at any \(T\)

Note: AMP-NMP heat of mixing not in heat of reaction
Summary of missing properties

• Properties of transfer

• $\ln K_2$ at any $T$

• $\ln K_1$ at any $T$
Properties of transfer

- Properties of RNH$_3^+$ in water
- Properties of RNH$_3^+$ in NMP
- Properties of RNHCOO$^-$ in water
- Properties of RNHCOO$^-$ in NMP

Missing: Properties of transfer NMP $\rightarrow$ water

Aspen plus requires properties in water

Evaluation of experimental data needs properties in NMP
Properties of CO\(_2\) and AMP in NMP

- Directly measured

- CO\(_2\) in NMP: Using Henry’s constants & enthalpy for CO\(_2\) physical absorption

- AMP in NMP: Enthalpy of mixing & vapor pressure of mixtures
How to get Properties of transfer

\[
\ln \gamma_{i,t}^m = \frac{\mu_{i,NMP}^m - \mu_{i,water}^m}{RT}
\]

Transfer properties of the salt
- Solubility product
- Properties of ions separately and then combine
- Born equation
How to get properties of transfer?

$$\text{RNH}_3^+(sol) + \text{RNHCOO}^- (sol) \xleftrightarrow{\ K_2\ } \text{RNH}_3^+\text{RNHCOO}^- (s)$$

$$\ln \gamma_{\pm,t} = \ln \frac{K_{2,water}}{K_{2,NMP}}$$

Transfer properties of the salt

- Solubility product
- Properties of ions separately and then combine
- Born equation
How to get properties of transfer?

\[
\text{RNH}_3^+(sol) + \text{RNHCOO}^- (sol) \rightleftharpoons \text{RNH}_3^+\text{RNHCOO}^- (s)
\]

\[
\ln \gamma_{\pm,t} = \ln \frac{K_{2,\text{water}}}{K_{2,\text{NMP}}}
\]

In water, the salt forms bicarbonate!

**Transfer properties of the salt**
- Solubility product
- Properties of ions separately and then combine
- Born equation
How to get Properties of transfer

Transfer properties of the salt

- Solubility product
- Properties of ions separately and then combine
- Born equation

Not enough data
How to get Properties of transfer

\[ \ln \gamma_{\pm,t}^* = \frac{q^2}{2} \left\{ \left( \frac{1}{R_{c2}D_2} - \frac{1}{R_{c1}D_1} \right) + \left( \frac{1}{R_{c1}} - \frac{1}{R_{c2}} \right) \right\} \]

Radius of cavity  \hspace{1cm}  Dielectric constant

**Transfer properties of the salt**

- Solubility product
- Properties of ions separately and then combine
- Born equation

How to get Properties of transfer

$$\ln \gamma_{\pm,t} = \frac{q^2}{2} \left\{ \left( \frac{1}{R_{c2}D_2} - \frac{1}{R_{c1}D_1} \right) + \left( \frac{1}{R_{c1}} - \frac{1}{R_{c2}} \right) \right\}$$

Radius of cavity
Dielectric constant

Missing
Measurable

Transfer properties of the salt
- Solubility product
- Properties of ions separately and then combine
- Born equation

Missing data

• Measuring or estimating radius of cavity

• $\ln K_2$ at any $T$

• $\ln K_1$ at any $T$
Future work

• Equilibrium constants at one temperature
• Further studies on estimating radius of cavity
• Experimental determination of the mentioned properties
• Infinite dilution heat capacity of the ions for our system
• Ternary data
• Tweeking binary data to better fit the ternary data
• Accounting for two solid phases
• Using ENRTL-RK or extended-UNIQUAC
• Validation of properties, plant simulation with continuous setup and batch calorimetry