Phase Equilibrium in Amino Acid Salt Systems for CO2 Capture

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Phase Equilibrium in Amino Acid Salt Systems for CO₂ Capture

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Outline

- General introduction
- Experimental data for amino acid salt systems
- Methionine as a case study

Carbonate-Methionine system
- Equilibrium constants
- Vapor-Liquid equilibrium data
- Freezing point depression data
- Thermodynamic modelling

Comparison of absorbents
- Absorber conditions
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- Heat of desorption
- Conclusion
Introduction

Advantages in using amino acid salts instead of alkanolamines:
• Might be less prone to degradation in oxygen rich environments
• Less volatile than alkanolamines due to their ionic nature
• Same affinity towards CO₂ as alkanolamines
• Form carboxamates

Amino acids participate in the transportation of CO₂ in the blood by the formation of carboxamate

Problems and drawbacks:
• More expensive
• Limited solubility of amino acids in water
• Limited amount of experimental data available in literature
Experimental data for amino acid salt solutions

- **CO₂ Equilibrium data**
  - Potassium taurate – Kumar *et al.* (2003) **38 data points**, T=25 and 40°C
  - Potassium glycinate (Portugal *et al.* 2009) **103 data points**, T= 20-50°C
  - Potassium methionate (Kumelan *et al.* 2010) **65 data points**, T= 80-120°C
  - Potassium sarcosinate (Aronu *et al.* 2010) graph with 55 points, T=40-120°C
  - Potassium prolinate (unpublished, DTU, UTwente)

- **Absorption kinetics**
  - Kumar *et al.* (2003) (potassium salt of taurine and glycine)
  - Van Holst *et al.* 2009 (potassium salts of 7 different amino acids)
  - Prakash *et al.* 2010 (potassium salts of taurine and glycine)

- **Equilibrium constants**
  - Sharma *et al.* 2003
  - Hamborg *et al.* 2007

- **Heat capacity and other thermal properties - none**

- **Freezing point depression data**
  - Sengeløv (2010) (loaded and unloaded potassium salt of methionine) **20 data points** -14 to 0°C
Methionine, $\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$

- Molar mass 149.21 g/mol
- Decomposition temperature 281°C
- Solubility in water at 25°C: 0.38 molal
- pKa 2.28 and 9.21
- Found in cereal grains and in nuts
Iso-electric point of methionine

Isoelectric point: 5.74

pK\text{a}=2.28

pK\text{a}=9.21
Solubility of methionine in water ○ and in NaCl solution ×

Hill and Robson, Biochemical Journal, 28(1934)1008-1013
Potassium salt of methionine – Equilibrium constants

- Sharma VK; Zinger A; Millero FJ; De Stefano C; *Dissociation constants of protonated methionine species in NaCl media*, Biophysical Chemistry, 105(2003)79-87
  - Determined in temperature range 5 – 45°C
- Hamborg ES; Niederer JPM; Versteeg GF; *Dissociation constants and thermodynamic properties of amino acids used in CO₂ absorption from (293 to 353) K*, J. Chem. Eng. Data, 52(2007)2491-2502
  - Determined in temperature range 20 – 80°C
- Equilibrium constant for the carbamate formation of methionine not available
- Equilibrium constant for the protonated form of methionine not relevant at pH above 6
Potassium salt of methionine – experimental data

  - VLE-data for the system CO₂-H₂O-K₂CO₃-Methionine at 80-120°C
  - It corresponds to loaded solutions of potassium salt of methionine
  - Some precipitation in experiments at 80°C with 2.5 molal K₂CO₃ and 0.83 molal methionine

- Sengeløv L., Bachelor Thesis, Technical University of Denmark, 2010
  - Freezing point depression data for potassium salt of methionine and for loaded solutions of this salt
Results for the CO$_2$-H$_2$O-$K_2$CO$_3$-Methionine system
(Eq. constant from Sharma et al.)
Results for the \( \text{CO}_2-\text{H}_2\text{O}-\text{K}_2\text{CO}_3-\text{Methionine} \) system
(Equilibrium constant from Sharma et al.)

Extended UNIQUAC model

\[
\begin{align*}
\text{K}_\text{m(K}_2\text{CO}_3\text{)} & \approx 1.27 \text{ mol/(kg H}_2\text{O)} \\
\text{K}_\text{m(Met)} & \approx 0.42 \text{ mol/(kg H}_2\text{O)}
\end{align*}
\]
Measurements of freezing point depressions for mixtures of 1:1 (mole ratio) aqueous Met-KOH and 1:3 (mole ratio) aqueous Met-K$_2$CO$_3$
Freezing point depressions: Results and model correlation (Equilibrium constant from Sharma et al.)

**mol ratio methionine:\(K_2\text{CO}_3\) 1:3**

**mol ratio methionine:KOH 1:1**

**Experimental**

**Extended UNIQUAC**
The potassium salt of methionine as an absorbent in post-combustion contra MEA, MDEA and K₂CO₃

Absorber conditions

Equilibrium constant from Sharma et al.

Equilibrium constant from Hamborg et al.
The potassium salt of methionine as an absorbent in post-combustion contra MEA, MDEA and $\text{K}_2\text{CO}_3$

**Desorber conditions**

Equilibrium constant from Sharma et al.
The potassium salt of methionine as an absorbent in post-combustion contra MEA, MDEA and $K_2CO_3$

Desorber conditions

Equilibrium constant from Hamborg et al.
Conclusion I

• The extreme difference between the properties of the potassium salt of methionine at absorber conditions and at desorber conditions indicates:
  – A strong temperature dependence of the equilibrium constant of methionine
  – Acidic properties of methionine strongest at desorber temperature

• Portugal et al. found that the carbon dioxide solubility in potassium glycinate did not change much in the temperature range investigated (20-50°C)
Conclusion II

• Due to the limited amount of experimental data available, it is possible to model CO₂ solubility in amino acid salt solutions without taking carbamate formation into account

• The potassium salt of methionine seems to have very interesting properties for post-combustion usage. However VLE-data at absorber column conditions are needed to validate the results

• The limited solubility and risk of precipitation provide challenges in the use of the potassium salt of methionine and must be investigated further
  – The 2 molal solutions for which calculations were shown here might be precipitating!

• More research is required to clarify the role of methionine in the absorption process: Especially regarding carbamate formation and kinetics

• Much more research is required on amino acid salt solutions. They have very interesting properties and could be real alternatives to alkanolamines.