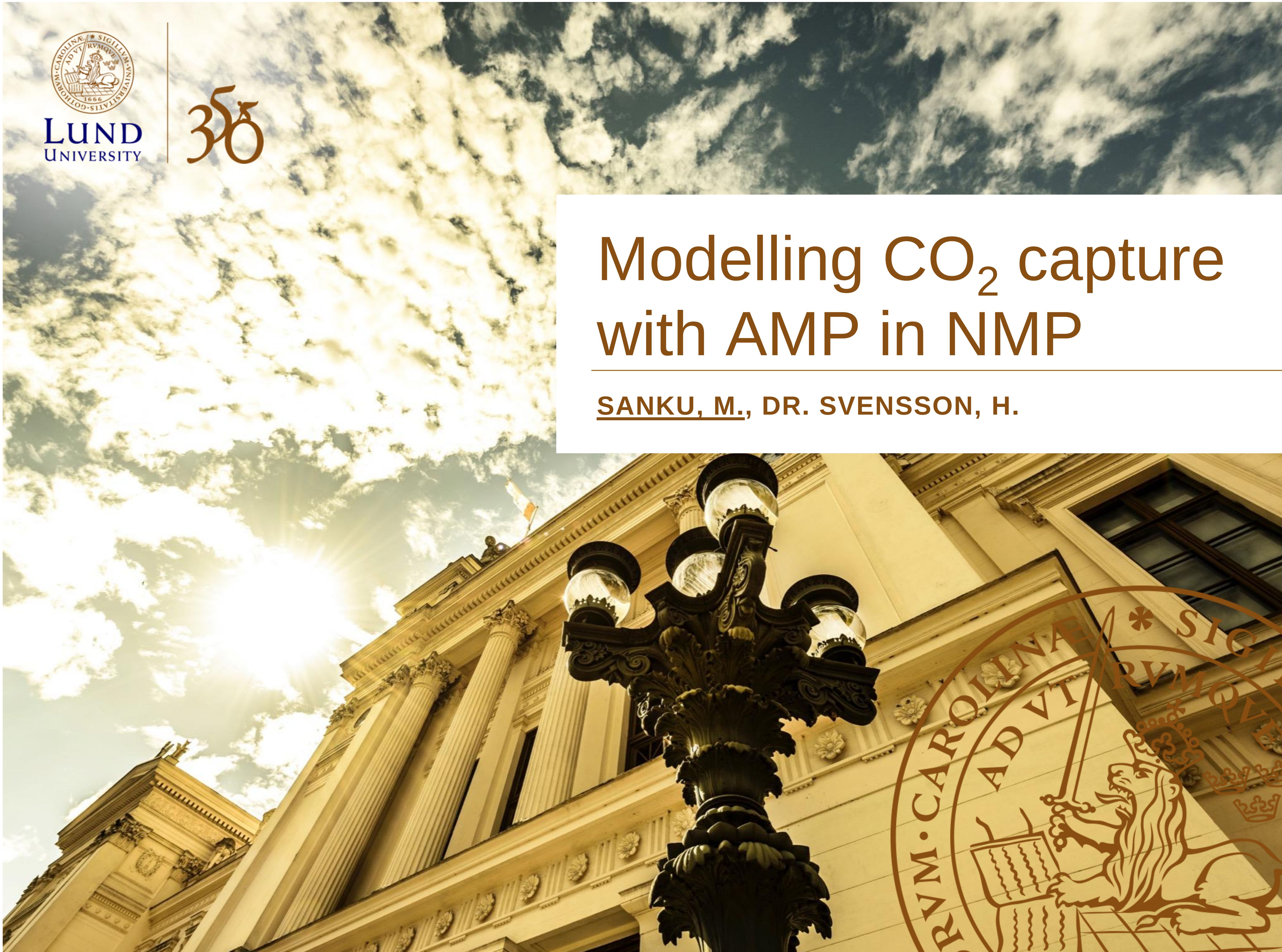


Modelling CO_2 capture with AMP in NMP

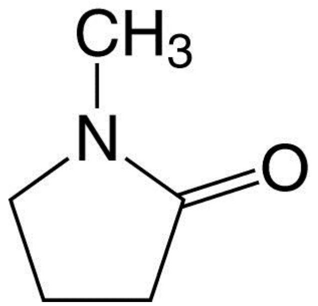
SANKU, M., DR. SVENSSON, H.

Outline

- Background of our research
- Model
  - Work so far / Shortcomings / Proposed improvements
- Remaining properties
  - Gaps: data in aqueous medium (literature)
  - Gaps: data in NMP medium (experimental)
  - Properties of precipitate
  - Properties of transfer
- Future work

The system

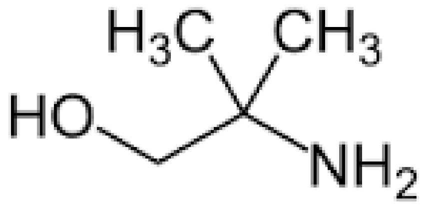
Solvent:



NMP

(N-methyl-2-pyrrolidone)

Amine:



AMP

(2-amino-2-methyl-1-propanol)

Note: AMP is sterically hindered

Reaction mechanism

$$\mathrm{CO_2}\ (g) \leftrightarrow \mathrm{CO_2}(sol)$$

$$\mathrm{CO_2}(sol) + \mathrm{RNH_2}(sol) \leftrightarrow \mathrm{RNH_2^+COO^-}(sol)$$

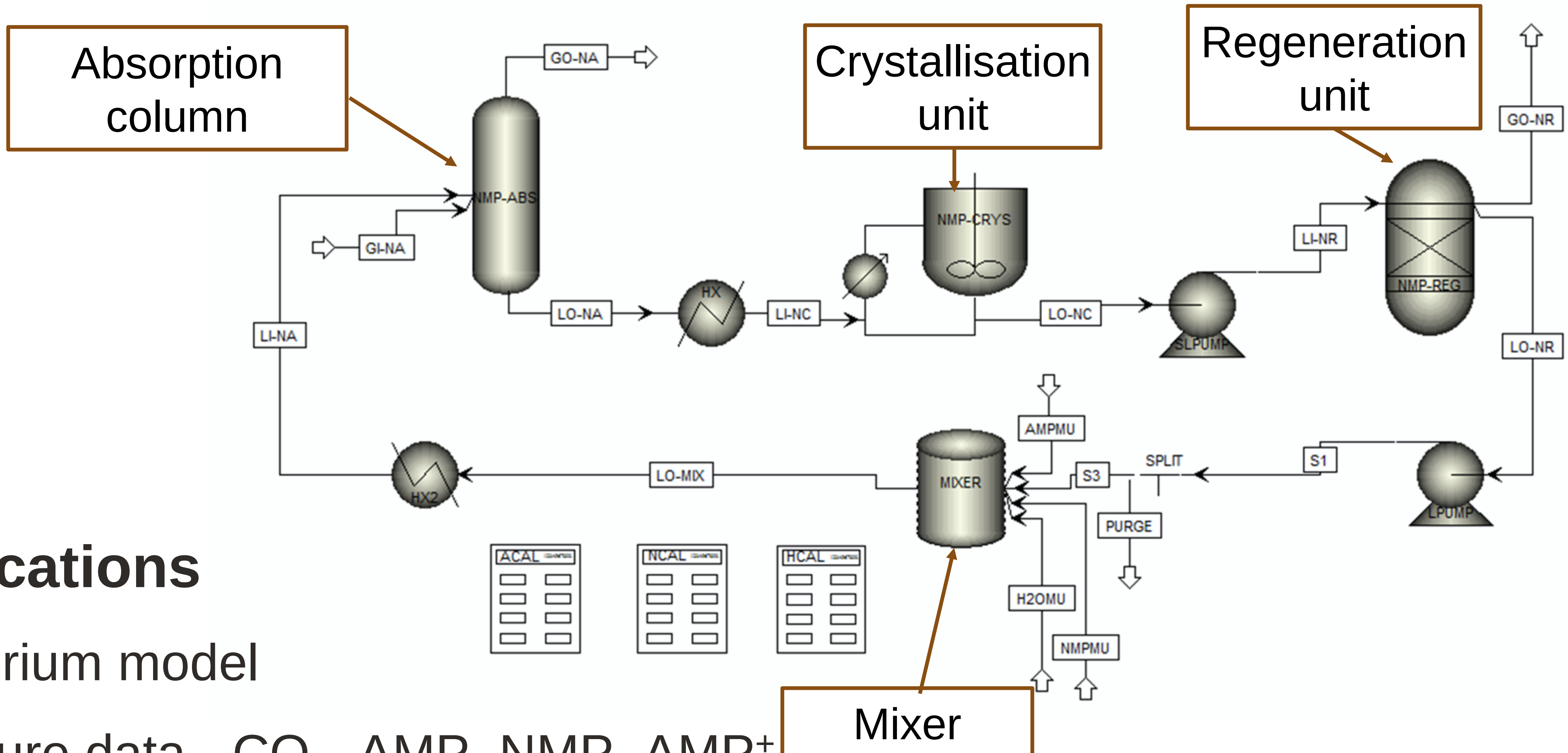
$$\mathrm{RNH_2^+COO^-}(sol) + \mathrm{RNH_2}(sol) \leftrightarrow \mathrm{RNH_3^+}(sol) + \mathrm{RNHCOO^-}(sol)$$

$$\mathrm{RNH_3^+}(sol) + \mathrm{RNHCOO^-}(sol) \leftrightarrow \mathrm{RNH_3^+RNHCOO^-}(s)$$

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?



Simplifications

- Equilibrium model
- Literature data - CO_2, 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)

Model	Experiment
8.1 GJ/ton CO_2	14.4 GJ/ton CO_2
1.01 bar a T_{abs}=50 °C T_{reg}=75 °C	7 bar a T_{abs}=45 °C T_{reg}=75 °C
No crystallisation	Crystallisation Heating of the reactor

Total pressure at 85 °C, AMP in NMP

Solution	Model (bar a)	Experiment (bar a)*
15w% AMP in NMP	0.022	0.037
25w% AMP in NMP	0.025	0.075

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

Assumed binary NRTL parameters

Outlet of regeneration

	Unit	Model
Temperature	°C	85
Pressure	bar a	2.52
H_2O	kmol/hr	1.00E-10
CO_2	kmol/hr	0.014465
AMP	kmol/hr	0.1261
NMP	kmol/hr	0.8586
AMP^+COO^-	kmol/hr	1.73E-34
AMP^+	kmol/hr	0.0211
$AMPCOO^-$	kmol/hr	0.0211
SOLID	kmol/hr	0

Inlet:
15w% AMP in NMP
CO_2 loading=0.2

Outlet of regeneration

	Unit	Model
Temperature	°C	85
Pressure	bar a	2.52
H_2O	kmol/hr	1.00E-10
CO_2	kmol/hr	0.014465
AMP	kmol/hr	0.1261
NMP	kmol/hr	0.8586
AMP^+COO^-	kmol/hr	1.73E-34
AMP^+	kmol/hr	0.0211
$AMPCOO^-$	kmol/hr	0.0211
SOLID	kmol/hr	0

Inlet:
15w% AMP in NMP
CO_2 loading=0.2

Species in the liquid phase
(about 60 mole% CO_2)

Outlet of regeneration

	Unit	Model
Temperature	°C	85
Pressure	bar a	2.52
H_2O	kmol/hr	1.00E-10
CO_2	kmol/hr	0.014465
AMP	kmol/hr	0.1261
NMP	kmol/hr	0.8586
AMP^+COO^-	kmol/hr	1.73E-34
AMP^+	kmol/hr	0.0211
$AMPCOO^-$	kmol/hr	0.0211
SOLID	kmol/hr	0

Inlet:
15w% AMP in NMP
CO_2 loading=0.2

Experiment:
At the same conditions, the solution has much lower CO_2*

Species in the liquid phase (about 60 mole% CO_2)

* ”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 $\mathrm{RNH_2^+COO^-}(aq) \approx \mathrm{H^+PZCOO^-}(aq)$, $\mathrm{RNHCOO^-}(aq) \approx \mathrm{PZCOO^-}(aq)$
- 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

Property	Method
Heat of vaporization	Vapor pressure of pure solvents
Binary parameters	Vapor pressure of mixtures – loaded and unloaded
Henry's constant	Measured in NMP, will be measured in AMP with N_2O
Heat capacity of solid	Measure with solid calorimetry
Molar volume of solid	Density of a whole crystal

What would still be missing?

- Properties of $RNH_2^+COO^-, RNHCOO^-$
- Properties of the precipitate
- Dielectric constant of NMP with temperature
- Ternary data
- Infinite dilution heat capacity of the ions for our system

Simplifications

$$CO_2\ (g) \leftrightarrow CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \leftrightarrow RNH_3^+(sol) + RNHCOO^-(sol)$$

$$RNH_3^+(sol) + RNHCOO^-(sol) \leftrightarrow RNH_3^+RNHCOO^-(s)$$

Assumptions:

- Zwitterion concentration and impact is negligible
- The precipitate completely dissociates to ions
- Single solid phase

Pure component properties (aq)

$$\mathrm{CO_2}(aq) + 2\mathrm{RNH_2}(aq) \overset{\mathrm{K_1}}{\leftrightarrow} \mathrm{RNH_3^+}(aq) + \mathrm{RNHCOO^-}(aq)$$

Pure component properties (aq)

Pure component data available

$$CO_2(aq) + 2RNH_2(aq) \overset{K_1}{\leftrightarrow} RNH_3^+(aq) + RNHCOO^-(aq)$$

Pure component properties (aq)

Pure component data available

$$CO_2(aq) + 2RNH_2(aq) \overset{K_1}{\leftrightarrow} RNH_3^+(aq) + RNHCOO^-(aq)$$

$$RNH_2(aq) + H^+(aq) \overset{K_p}{\leftrightarrow} RNH_3^+(aq)$$

Pure component properties (aq)

Pure component data available

$$\mathrm{CO_2}(aq) + 2\mathrm{RNH_2}(aq) \overset{K_1}{\leftrightarrow} \mathrm{RNH_3^+}(aq) + \mathrm{RNHCOO^-}(aq)$$

Unsymmetrical properties calculatable

Data available

$$\mathrm{RNH_2}(aq) + \mathrm{H^+}(aq) \overset{K_p}{\leftrightarrow} \mathrm{RNH_3^+}(aq)$$

Pure component properties (aq)

Pure component data available

Missing

$$CO_2(aq) + 2RNH_2(aq) \overset{K_1}{\leftrightarrow} RNH_3^+(aq) + RNHCOO^-(aq)$$

Unsymmetrical properties calculatable

Data available

$$RNH_2(aq) + H^+(aq) \overset{K_p}{\leftrightarrow} RNH_3^+(aq)$$

Pure component properties (aq)

Pure component data available

Missing

$$CO_2(aq) + 2RNH_2(aq) \overset{K_1}{\leftrightarrow} RNH_3^+(aq) + RNHCOO^-(aq)$$

Unsymmetrical properties calculatable

Data available

$$RNH_2(aq) + H^+(aq) \overset{K_p}{\leftrightarrow} RNH_3^+(aq)$$

Note: aqueous medium

Pure component properties (NMP)

$$CO_2\ (g) \overset{H}{\leftrightarrow} CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

$$\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1}$$

Experiments: without precipitation

Pure component properties (NMP)

Without precipitation

Measured separately

$$CO_2\ (g) \overset{H}{\leftrightarrow} CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

Measured

$$\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1}$$

Pure component properties (NMP)

Without precipitation

Measured separately

$$CO_2\,(g) \overset{H}{\leftrightarrow} CO_2\,(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

Measured

$$\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1}$$

Calculatable

Pure component properties (NMP)

Without precipitation

Measured separately

$$CO_2\ (g) \overset{H}{\leftrightarrow} CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

Measured → $\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1}$ → Calculatable

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

Missing: $\ln K_1$ at any T

Properties of $RNHCOO^-(NMP)$

Properties of CO_2, RNH_2, RNH_3^+ in NMP

Pure component properties (NMP)

Without precipitation

Measured separately

$$CO_2\ (g) \overset{H}{\leftrightarrow} CO_2\ (sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

Measured → $\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1}$ → Calculatable

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

Missing: $\ln K_1$ at any T

Properties of $RNHCOO^-(NMP)$

Properties of CO_2, RNH_2, RNH_3^+in NMP

Assumptions:

$CO_2(sol)$ inthe solution is same as in the absence of AMP

$CO_2(sol)$ in AMP will be measured

Properties of the solid

$$CO_2\ (g) \overset{H}{\leftrightarrow} CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

$$RNH_3^+(sol) + RNHCOO^-(sol) \overset{K_2}{\leftrightarrow} RNH_3^+RNHCOO^-(s)$$

$$\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1} + \Delta H_{r2}$$

Experiments with precipitation

Properties of the solid

With precipitation

Measured separately

$$CO_2\,(g) \overset{H}{\leftrightarrow} CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

$$RNH_3^+(sol) + RNHCOO^-(sol) \overset{K_2}{\leftrightarrow} RNH_3^+RNHCOO^-(s)$$

Measured

$$\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1} + \Delta H_{r2}$$

Calculatable

Properties of the solid

With precipitation

Measured separately

$$CO_2\,(g) \overset{H}{\leftrightarrow} CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

$$RNH_3^+(sol) + RNHCOO^-(sol) \overset{K_2}{\leftrightarrow} RNH_3^+RNHCOO^-(s)$$

Measured → $\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1} + \Delta H_{r2}$ ← Calculatable

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

Properties of the solid

With precipitation

Measured separately

$$CO_2\ (g) \overset{H}{\leftrightarrow} CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

$$RNH_3^+(sol) + RNHCOO^-(sol) \overset{K_2}{\leftrightarrow} RNH_3^+RNHCOO^-(s)$$

Measured

$$\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1} + \Delta H_{r2}$$

Calculatable

Missing: $\ln K_2$ at any T

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

Properties of $RNH_3^+, RNHCOO^-$ in NMP

Properties of $RNH_3^+RNHCOO^-(s)$

Properties of the solid

With precipitation

Measured separately

$$CO_2\,(g) \overset{H}{\leftrightarrow} CO_2(sol)$$

$$CO_2(sol) + 2RNH_2(sol) \overset{K_1}{\leftrightarrow} RNH_3^+(sol) + RNHCOO^-(sol)$$

$$RNH_3^+(sol) + RNHCOO^-(sol) \overset{K_2}{\leftrightarrow} RNH_3^+RNHCOO^-(s)$$

Measured

$$\Delta H_r = \Delta H_{CO_2} + \Delta H_{r1} + \Delta H_{r2}$$

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 $RNH_3^+, RNHCOO^-$ in NMP

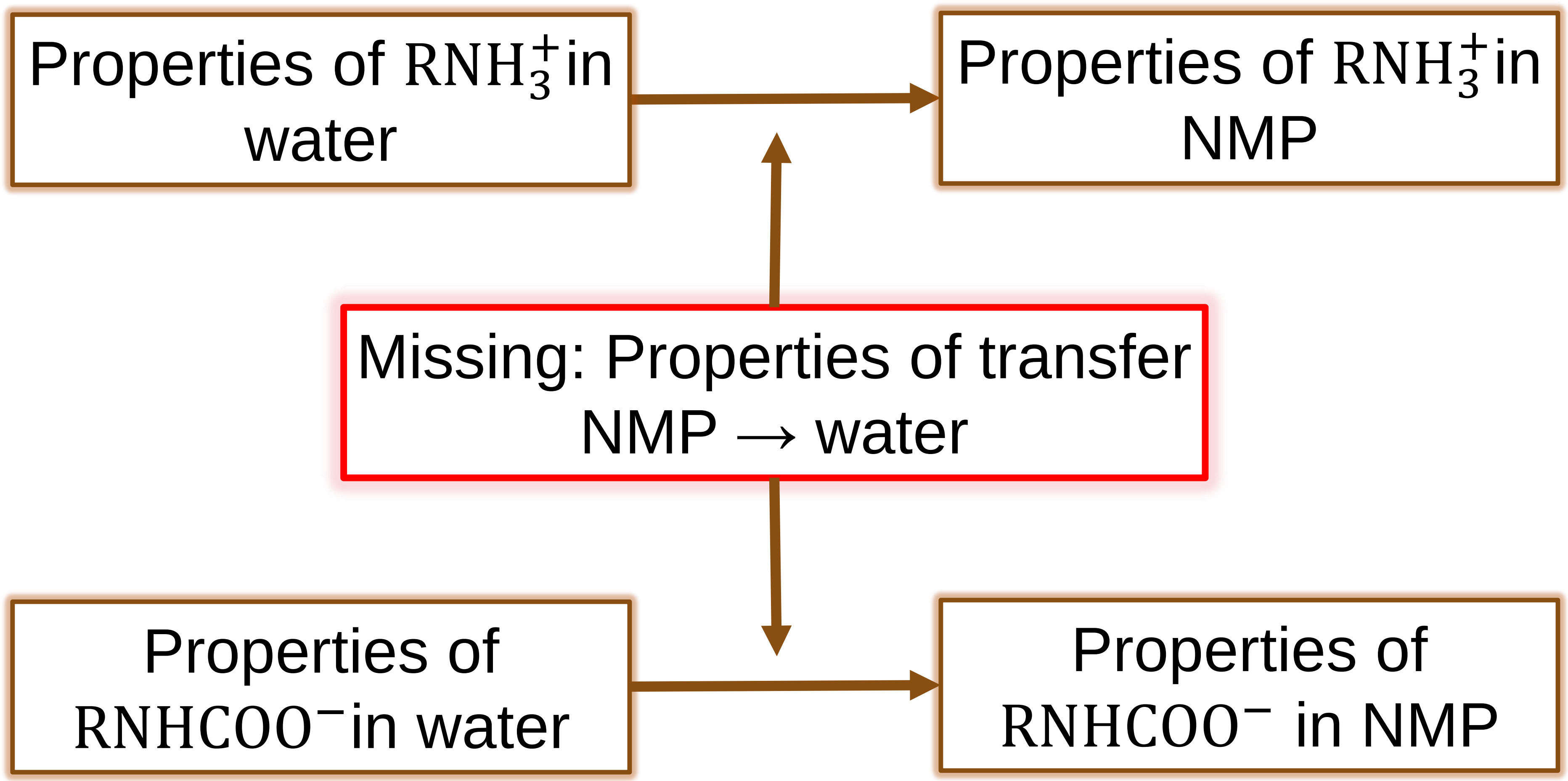
Properties of $RNH_3^+RNHCOO^-(s)$

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



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

Molality scale

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

Solute i

Transfer

Transfer properties of the salt

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

How to get properties of transfer?

$$\mathrm{RNH_3^+}(sol) + \mathrm{RNHCOO^-}(sol) \overset{\mathrm{K_2}}{\leftrightarrow} \mathrm{RNH_3^+RNHCOO^-}(s)$$

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

Transfer properties of the salt

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

How to get properties of transfer?

$$\mathrm{RNH_3^+}(sol) + \mathrm{RNHCOO^-}(sol) \overset{\mathrm{K_2}}{\leftrightarrow} \mathrm{RNH_3^+RNHCOO^-}(s)$$

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

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

Not enough data

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

<u>Transfer properties of the salt</u>

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

"Reevaluation of the Born model of ion hydration" by Rashin and Honig *J. Phys. Chem.*, 1985, *89* (26), pp 5588–5593

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 → Missing

Dielectric constant → Measurable

Transfer properties of the salt

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

"Reevaluation of the Born model of ion hydration" by
Rashin and Honig *J. Phys. Chem.*, 1985, *89* (26), pp 5588–5593

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

LUND UNIVERSITY

350