CO$_2$ capture by aqueous solution of amine: experimental measurements and thermodynamic model for the enthalpy of solution.

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*Colloquium to promote experimental work in Thermophysical Properties for Scientific Research and Industry.*
Thermodynamic model for \{\text{CO}_2 - \text{H}_2\text{O} - \text{alkanolamine}\}

1/ Capture of CO\(_2\) in industrial effluents using chemical absorbents

2/ \{\text{CO}_2 - \text{water} - \text{amine}\} systems
   - Thermodynamic model
   - Correlation of solubility data
   - Enthalpy calculation

3/ Enthalpy of solution of CO\(_2\) in aqueous solution of amine
   - Experimental measurements
   - Influence of the different enthalpy contributions
CO₂ emissions responsible of global warming

70 % of anthropogenic emissions of greenhouse gases.

Option to reduce global warming:
capture and storage of CO₂ in industrial effluents
(power plant, cement plant, metallurgy …)

Fixed sources of CO₂

Industry +electricity

1/2 of CO₂ emissions
1/ Capture of CO₂ in industrial effluents

Principle of gas capture industrial process

exhaust gas

absorber

absorbent

gas saturated absorbent

CO₂

stripper

Storage

Industrial effluent

Properties required for the absorbent

Reversible reaction

High loading charge

CO₂ solubility

Low energy of regeneration

Enthalpy of solution

degradation, corrosion, heat capacity …
1/ Capture of CO2 in industrial effluents

Mature technology: absorption in aqueous solution of amines

Reference chemical absorbent: aqueous solution of amine
Reference absorbent: aqueous solution of MEA 30 wt%
Problem of capture: 60 € / tCO2

Transfer to treatment of industrial effluent

Research: reduction of economical cost

Reduction of energy for regeneration of absorbent ($H_S$)
High loading charge (gas solubility) at low $p_{CO2}$
Low vapor pressure
Low thermal degradation ….

Goal of this work: determination of enthalpy of gas dissolution

Calculation of enthalpy of solution using solubility data
Calorimetric determination
Development and test of the thermodynamic model

- $K$ for chemical reactions
- $K_H$ for physical dissolution

Literature solubility data

- $T$, $p$, $m^{\circ}_{\text{amine}}$
- $\alpha$ ($m^{\circ}_{\text{amine}} / m^{\text{dis}}_{\text{CO}_2}$)

Solubility correlation

Enthalpy calculation

Experimental enthalpy data

Interaction parameters

Speciation

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2/ Vapor liquid equilibria: Thermodynamic model

Thermodynamic VLE model

- System considered as non ideal: $\gamma - \phi$ approach

- Activity coefficients calculated from modified Pitzer equation. Interactions parameters: like charged ions, cation-anion, ion-molecule, molecule-molecule

- Fugacity coefficients calculated from truncated virial equation

- Standard states
  - CO$_2$: ideal gas
  - Amine: infinite dilution
  - Water: pure water
2/ Vapor liquid equilibria : Thermodynamic equations

Equations for vapor liquid equilibria

\[
\begin{align*}
\text{CO}_2 \text{ (liquid)} &= \text{CO}_2 \text{ (vapor)} \\
\phi_{\text{CO}_2} y_{\text{CO}_2} p &= \gamma_{\text{CO}_2} m_{\text{CO}_2} K_H(\text{CO}_2) \exp \left[ \frac{V_{\text{CO}_2} (p - p_{\text{H}_2\text{O}}^{\text{Sat}})}{RT} \right]
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} \text{ (liquid)} &= \text{H}_2\text{O} \text{ (vapor)} \\
\phi_{\text{H}_2\text{O}} y_{\text{H}_2\text{O}} p &= \gamma_{\text{H}_2\text{O}} m_{\text{H}_2\text{O}} \phi_{\text{H}_2\text{O}}^{\text{Sat}} p_{\text{H}_2\text{O}}^{\text{Sat}} \exp \left[ \frac{V_{\text{H}_2\text{O}} (p - p_{\text{H}_2\text{O}}^{\text{Sat}})}{RT} \right]
\end{align*}
\]

\[
\begin{align*}
\text{Am} \text{ (liquid)} &= \text{Am} \text{ (vapor)} \\
\phi_{\text{Am}} y_{\text{Am}} p &= \gamma_{\text{Am}} m_{\text{Am}} \phi_{\text{Am}}^{\text{Sat}} p_{\text{Am}}^{\text{Sat}} \exp \left[ \frac{V_{\text{Am}} (p - p_{\text{Am}}^{\text{Sat}})}{RT} \right]
\end{align*}
\]
Equations for chemical reactions

Ionization of \( \text{CO}_2 \)

\[ \text{CO}_2^{(aq)} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+ \]

\( \text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \)

\[ K_1 = \frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{CO}_2^{(aq)}} a_{\text{H}_2\text{O}}} = \frac{\gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-} \gamma_{\text{H}^+} m_{\text{H}^+}}{\gamma_{\text{CO}_2^{(aq)}} m_{\text{CO}_2^{(aq)}} a_{\text{H}_2\text{O}}} \]

Ionization of water

\[ \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \]

\[ K_{\text{III}} = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} = \frac{\gamma_{\text{H}^+} m_{\text{H}^+} \gamma_{\text{OH}^-} m_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} \]
2/ Vapor liquid equilibria : Thermodynamic equations

Protonation of amine

\[ \text{AMINE} + H^+ = \text{AMINEH}^+ \]

\[ K_{IV} = \frac{a_{\text{AMINEH}^+}}{a_{\text{AMINE}} a_{H^+}} = \frac{\gamma_{\text{AMINEH}^+} m_{\text{AMINEH}^+}}{\gamma_{\text{AMINE}} m_{\text{AMINE}} \gamma_{H^+} m_{H^+}} \]

Carbamate formation (for primary and secondary amine)

\[ \text{AMINE} + HCO_3^- = \text{AMINECOO}^- + H_2O \]

\[ K_V = \frac{\gamma_{\text{AMINECOO}^-} m_{\text{AMINECOO}^-} a_{H_2O}}{\gamma_{HCO_3^-} m_{HCO_3^-} \gamma_{\text{AMINE}} m_{\text{AMINE}} \gamma_{H^+} m_{H^+} \gamma_{H_2O} m_{H_2O} \gamma_{H_2O} m_{H_2O}} \]

Equations for chemical reactions

Mass balance

\[ m_{HCO_3^-} + m_{CO_3^{2-}} + m_{CO_2} = m_{CO_2}^{\text{dis}} \]

\[ m_{\text{amine}} + m_{\text{amineH}^+} = m_{\text{amine}}^{\circ} \]

Charge balance

\[ m_{HCO_3^-} + 2 m_{CO_3^{2-}} + m_{OH^-} = m_{\text{amineH}^+} + m_{H^+} \]

Vapor phase

\[ \gamma_{CO_2} + \gamma_{H_2O} + \gamma_{\text{Amine}} = 1 \]
2/ Vapor liquid equilibria: Thermodynamic model

Calculations

Data: \(T, p_i, m_{amine}, \alpha, \delta p_i\)

- Initialization of interaction parameters
- Initialization of speciation (ideal system)
- Calculation of activity and fugacity coefficients (\(\gamma, \phi\))
- Resolution of the jacobian: solve chemical and physical equations \(f(i)\) of the system (Newton-Raphson) and find speciation

\[\Sigma f(i) < \epsilon\]

- Generating new interactions parameters by optimization (MINUIT)
- \[F = \Sigma \left(\frac{p_i^{exp} - p_i^{cal}}{\delta p_i}\right)^2 < \epsilon\]

Tests:

- MDEA solubility data
- 3 literature \(K_{amine}\)

End of regression
Correlation of solubility data for \{\text{CO}_2\text{-MDEA-water}\}

Tests: 3 literature amine protonation constants

Solubility data correlation
3/ Enthalpy of solution of CO$_2$ in aqueous amine solutions

Enthalpy of solution derived from the thermodynamic model

Contribution of chemical reactions

$$\left(\frac{\partial \ln K_N}{\partial T}\right)_p = \frac{\Delta H_N^i}{RT^2} \quad \text{Ideal term}$$

$$H_i^E = -RT^2 \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_p \quad \text{Excess term}$$

Heat contribution for 1 mole of absorbed CO$_2$

$$Q_N (kJ) = \xi N \sum_i \left(\Delta H_N^i + \nu_i H_i^E \right)$$

Contribution of physical dissolution

$$\Delta H_g / (kJ \cdot mol^{-1}CO_2) = -RT^2 \left[\frac{\partial \ln H_{CO_2}^g (T, p_w^s)}{\partial T} + \frac{\partial \ln \gamma_{CO_2}}{\partial T} + \frac{\partial (\nu_{CO_2}^\infty (p - p_w^s) / RT)}{\partial T} - \frac{\partial \ln \phi_{CO_2}}{\partial T}\right]$$

Ideal term \hspace{1cm} Excess term

Total enthalpy of solution per mol of CO$_2$

$$H_s / (kJ \cdot mol^{-1}CO_2) = \Delta H_g + \frac{1}{n_{dis}^\text{CO}_2} \sum_{N=1}^V Q_N$$
3/ Enthalpy of solution of $\text{CO}_2$ in aqueous amine solutions

Experimental measurement

Flow calorimetric technique
3/ Enthalpy of solution of CO₂ in aqueous amine solutions

Experimental measurement

$$H_s = \frac{S_M - S_{LB}}{K \cdot n_i}$$
3/ Enthalpy of solution of CO$_2$ in aqueous amine solutions

**Experimental measurement**

![Graph 1](image1.png)

- Enthalpy of solution per mole of CO$_2$

![Graph 2](image2.png)

- Determination of limit of solubility
3/ Enthalpy of solution in aqueous amine solutions

Influence of protonation constant correlation

\[
\left( \frac{\partial \ln K_N}{\partial T} \right)_p = \frac{\Delta H_N^o}{RT^2}
\]

- Experimental data
- Oscarson et al.
- Kamps et al.
- Rumpf and coll.

MDEA 15 wt%

\( T = 323 \text{ K} \)

\( T = 373 \text{ K} \)

- MDEA 15 wt% 
- Rumpf and coll.
- Oscarson et al.
- Kamps et al.

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3/ Enthalpy of solution in aqueous amine solutions

Analyze of the different enthalpy contributions

Contributions (kJ·mol⁻¹ of CO₂) to the enthalpy of solution (Hₛ) at T = 333 K for MDEA 4m.
- Ternary amine: enthalpy of solution can be calculated from solubility data using $pK_a$ temperature correlation

- Primary – secondary amine: need equilibrium constant for carbamate formation

- Need speciation, composition