Thermodynamics and ANN models for correlation and predication of the equilibrium $CO_2$ solubility of seven tertiary amine solvents

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Outline

1. Introduction
2. Theory
3. Experiment
4. Results and discussion
5. Conclusion
6. Acknowledgements
CCS Research ?
Key technologies for reducing global CO$_2$ emissions under Blue Map scenario

A wide range of technologies will be necessary to reduce energy-related CO$_2$ emissions substantially.
Introduction

Post-combustion Carbon Capture

Optimization of process

Columns and Packs 30-50% CAPEX

Solvent Flow Rate 5-10% OPEX

Solvent

Absorber

Lean Amine Cooler

Rich Pump

Lean Pump

Condenser

Reboiler

Rich/Lean Exchanger

Water Wash

Exhaust Gas

Contactors

Flue Gas

Feed Gas Cooler

Feed Gas

Rich Pump

Lean Pump

Rich

CO2 Product Gas

Regeneration Heat 50-60% OPEX

Reboiler

Solvent Makeup

Post-combustion Carbon Capture

Flue Gas

Feed Gas Cooler

Feed Gas

Rich Pump

Lean Pump

Rich

CO2 Product Gas

Regeneration Heat 50-60% OPEX
Introduction

Solvent

Reactions
- Reaction rate
- Reaction heat

CO₂ capacity

Physical property

- CO₂ loading/mol CO₂:mol amine⁻¹
- Molar CO₂ partial pressure (kPa)
Several performance criteria's of an optimized amine solution.
History of Solvent Development
Use of Amine Solvents

- **CCS Applications and ....**
  - *Gas Processing*
  - *Refinery gas*
  - *Landfill gas*
  - *Bio gas*
  - *Solution gas*
  - *EOR gas*
  - *Etc.*
In the 1960’s and 1970’s

Gas-Liquid Reactions

P. V. Danckwerts, F.R.S.

Shell Professor of Chemical Engineering
University of Cambridge
In the 1980’s

GAS TREATING WITH CHEMICAL SOLVENTS

GIANNI ASTARITA
University of Naples and University of Delaware

DAVID W. SAVAGE
Exxon Research and Engineering Company

ATTILIO BISIO
Exxon Research and Engineering Company
Sterically Hindered Amines for CO₂ Removal from Gases

Guido Sartori* and David W. Savage

Corporate Research, Exxon Research and Engineering Company, Linden, New Jersey 07036

Steric hindrance and basicity are shown to control CO₂-amine reactions. In aqueous amino alcohols, steric hindrance is the dominant factor giving high thermodynamic capacity and fast absorption rates at high CO₂ loadings. Introducing steric hindrance by a bulky substituent adjacent to the amino group lowers the stability of the carbamate formed by CO₂-amine reaction. Reduced carbamate stability allows thermodynamic CO₂ loadings to exceed those attainable with conventional, stable-carbamate amines. Lowering carbamate stability also leads to high free-amine concentration in solution; therefore fast amine–CO₂ reaction rates are obtained despite some reduction of the rate constant owing to steric interference. Hindered amines show capacity and absorption rate advantages over conventional amines for CO₂ removal from gases by absorption in aqueous amine solutions and amine-promoted hot potassium carbonate. Cyclic capacity broadening of 20–40% and absorption rate increases up to 100% or more are possible with certain hindered amines.
Table II. Examples of Sterically Hindered Amines

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

1,8-\(p\)-menthanediamine (MDA)

2-piperidineethanol (PE)
In 2000’s to now

- *PCCC Conferences*
- GHGT Conferences
- and much more ....
United States Patent
Tontiwachwuthikul et al.

Method of Capturing Carbon Dioxide from Gas Streams

Inventors: Paitoon Tontiwachwuthikul, Regina (CA); Andrew G. H. Wee, Regina (CA); Raphael Idem, Regina (CA); Kreangkrai Maneerintr, Regina (CA); Gao-jun Fan, Regina (CA); Amornvadee Veawab, Regina (CA); Amr Henni, Regina (CA); Adisorn Aroonwilas, Regina (CA); Amit Chakma, Waterloo (CA)

Assignee: University of Regina, Regina, Saskatchewan (CA)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154.

References Cited

U.S. PATENT DOCUMENTS

4,273,326 A 3/1981 Canadian
“Developed based on a systematic modification of the structure of amino alcohols by an appropriate placement of the substituent, especially hydroxyl function and relative position of amino group”  

(US Patent 7,910,078 – B2)
Synthesis of new amines for enhanced carbon dioxide (CO₂) capture performance: The effect of chemical structure on equilibrium solubility, cyclic capacity, kinetics of absorption and regeneration, and heats of absorption and regeneration

Sudkanueng Singto a, Teeradet Supap b, *, Raphael Idem b, *, Paitoon Tontiwachwuthikul b, *, Supawan Tantayanon a, c, *, Mohammed J. Al-Marri d, Abdelbaki Benamor d

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d Gas Processing Center, Qatar University, Doha, Qatar
Equlibrium Solubility – One of the key parameters

Equilibrium Solubility of CO₂

DEAB~PZ>AMP>MDEA>MEA >DEA

Math model for Equilibrium Solubility of CO₂

(AAD=7.3%)

Equilibrium constant

\[
\text{CO}_2 + R\text{R}_2'\text{N} + \text{H}_2\text{O} \xrightleftharpoons{K_2} R\text{R}_2'\text{NH}^+ + \text{HCO}_3^{-}
\]

\[
K_2 = \frac{[R\text{R}_2'\text{NH}^+][\text{HCO}_3^-]}{[\text{CO}_2][R\text{R}_2'\text{N}]}
\]

\[
K_i = \exp \left[ -193 + \frac{(-1.685 \times 10^4)}{T} + 67.85 \ln T - 0.4325T \right]
\]

(Sema et al., Ind. Eng. Chem. Res. 2011, 50, 14008-14015)
Why do we need this information?

Column performance at high loading. AMP (Run T28 - solid circles) vs MEA (Run T18 - open squares). Operating conditions: gas flow rate = 14.8 mol/m²·s; liquid flow rate = 9.5 m³/m²·hr; total amine concentration = 2.0 kmol/m²; inlet gas CO₂ concentration = 19.15%; outlet CO₂ loading = 0.583 moles of CO₂/mole of amine. The lines represent smoothed experimental values.
\[
\begin{align*}
RNH_3^+ &= H^+ + RNH_2 & (1) \\
RNHCOO^- + H_2O &= RNH_2 + HCO_3^- & (2) \\
H_2O + CO_2 &= H^+ + HCO_3^- & (3) \\
H_2O &= H^+ + OH^- & (4) \\
HCO_3^- &= H^+ + CO_3^{2-} & (5)
\end{align*}
\]

\[
K_1 = \frac{[H^+][RNH_2]}{[RNH_3^+]}, \quad K_3 = \frac{[H^+][HCO_3^-]}{[CO_2]} \\
K_4 = [H^+][OH^-], \quad K_5 = [H^+][CO_3^{2-}] / [HCO_3^-]
\]

\[
[AMP] = [RNH_2] + [RNH_3^+] \quad (10)
\]

\[
\alpha[AMP] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (11)
\]

\[
[RNH_3^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad (12)
\]
Theory-thermodynamic model

➢ Tertiary amine and steric hindrance amine

![Chemical Reactions](image)

**Liquid phase**

**Chemical Reactions**

\[
R_1R_2R_3H^+ \rightleftharpoons K_1 \rightarrow R_1R_2R_3N + H^+
\]

\[
CO_2 + R_1R_2R_3 + H_2O \rightleftharpoons K_{2,3,2} \rightarrow R_1R_2R_3H^+ + HCO_3^-
\]

\[
H_2O + CO_2 \rightleftharpoons K_1 \rightarrow H^+ + HCO_3^-
\]

\[
CO_2 + OH^- \rightleftharpoons K_4 \rightarrow HCO_3^-
\]

\[
HCO_3^- \rightleftharpoons K_5 \rightarrow H^+ + CO_3^{2-}
\]

\[
H_2O \rightleftharpoons K_6 \rightarrow H^+ + OH^-
\]

➢ Primary and secondary amine

**Balance equation**

\[
[R_1R_2R_3]_0 = [R_1R_2R_3NH^+] + [R_1R_2R_3N]
\]

\[
\alpha[R_1R_2R_3N]_0 = [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}]
\]

\[
[R_1R_2R_3NH^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]
\]

---where \( \alpha \) denotes CO\(_2\) loading

**Henry’s Law**

\[
P_{CO_2} = He_{CO_2}[CO_2(aq)]
\]

**Gas-Liquid phase**

**Gas phase**

\( CO_2, N_2 \)
Theory-thermodynamic model

Expressions of $K_i$ (i=3,5,6) and $H_{CO_2}$

$$K_i \text{ or } H_{CO_2}^0 = \exp \left( a + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3} + \frac{e}{T^4} \right) \quad H_{CO_2} = \frac{H_{CO_2}^0}{7.50061}$$

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
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<td>$K_5$</td>
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<td>$K_6$</td>
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<td>691.346E4</td>
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</tbody>
</table>

Dominate reaction

$$\text{CO}_2 + R_1R_2R_3 + \text{H}_2\text{O} \rightleftharpoons K_{2,k_2,k_2,k_2} R_1R_2R_3\text{H}^+ + \text{HCO}_3^-$$

Equilibrium Constant $K_2$

- Temperature
- CO2 partial pressure
- Amine concentration
- Total pressure

Data source: Kent and Elsenberg, *Hydrocarbon processing*, 1976
Theory-thermodynamic model

Input experimental value:
Temperature, CO2 partial pressure, amine concentration, total pressure etc.

Concentration of all species
Obtain Value of \( K_2 \)
Correlate \( K_2 \) with parameters
Nonlinear regression of \( K_2 \)
Prediction of CO2 loading

Compare with experimental value
Acceptable deviation

Output \( K_2 \)

Expression of \( K_2 \)

KE model
\[
K_i = \exp\left( A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \frac{E}{T^4}\right)
\]

Heli-Liu model
\[
K_i = \exp\left( B_1 + \frac{B_2}{T} + B_3 \ln T + B_4 T\right)
\]

Hu-Chakma
\[
K_i = \exp\left( D_1 + D_2 T + D_3 [CO_{2aq}] + D_4 \ln[A \min e]\right)
\]

Li-Shen model
\[
K_i = \exp\left( A_1 + \frac{A_2}{T} + \frac{A_3}{T} + C_1 \alpha + \frac{C_2}{\alpha} + \frac{C_3}{\alpha} + C_4 \ln[A \min e]\right)
\]

Liu et.al model
\[
K_2 = \exp\left( E_1 + E_2 T + E_3 [CO_{2aq}] + E_4 \ln[A \min e] + \frac{E_5}{P_{total}}\right)
\]
Theory-ANN model

(a) The basic structure of RBFNN with multi-input parameters

(b) the basic structure of BPNN
A taxonomy of feed-forward and recurrent/feedback network architecture (Jain & Mao, 1996)
Experiment

Structure and abbreviation

Schematic diagram of the experimental setup for CO₂ loading measurement
Synthesis of new amines for enhanced carbon dioxide (CO₂) capture performance: The effect of chemical structure on equilibrium solubility, cyclic capacity, kinetics of absorption and regeneration, and heats of absorption and regeneration

Sudkanueng Singto a, Teeradet Supap b,*, Raphael Idem b,*, Paitoon Tontiwachwuthikul b,*, Supawan Tantayanon a, c,*, Mohammed J. Al-Marri d, Abdelbaki Benamor d

a Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
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c Green Chemistry Research Lab, Faculty of Science, Department of Chemistry, Chulalongkorn University, Bangkok 10330, Thailand
d Gas Processing Center, Qatar University, Doha, Qatar
Results and discussions

Higher CO₂ partial pressure → increase CO₂ loading

Higher temperature → decrease CO₂ loading

Graphs show the relationship between CO₂ partial pressure and CO₂ loading/mol CO₂·mol amine⁻¹ for different temperatures and concentrations.

2 M DE-1,2-PD

2 M 1-(2-HE)PRLD

2 M 1-(2-HE)PP
Results and discussions

\[ K_2 = \exp(E_1 + E_2 T + E_3 [CO_{aq}] + E_4 \ln[A \text{ min e}] + \frac{E_5}{P_{\text{total}}}) \]

<table>
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<tr>
<th>Parameters</th>
<th>Values</th>
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<td>(4.300501)</td>
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<tr>
<td>( E_4 )</td>
<td>(-27.8278)</td>
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<td>( E_5 )</td>
<td>(0.453665)</td>
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</table>
Results and discussions

HEMAB (8.3%)  
DMAB (5.4%)  
HEEAB (4.2%)

\[ K_2 = \exp(E_1 + E_2 T + E_3 [CO_{2aq}] + E_4 \ln[A \text{ min e}] + \frac{E_5}{P_{total}}) \]

<table>
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<th>Parameters</th>
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<td>( E_4 )</td>
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<td>( E_5 )</td>
<td>0.036432</td>
<td>0.667424</td>
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</table>

Data source: Singto et al., *Separation and Purification Technology*, 2016
Results and discussions

DPAB 24.7%

Fail to give reasonable result

➢ The expression of $K_2$ is not suitable at low CO$_2$ loading region

➢ The absolute deviation is small although the relative deviation is large

$$K_2 = \exp(E_1 + E_2 T + E_3 [\text{CO}_2\text{aq}] + E_4 \ln[A \text{min e}] + \frac{E_5}{P_{\text{total}}})$$

<table>
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Results and discussions

The summarize of all prediction results for investigated amines
Results and discussions - ANN
Results and discussions - ANN

Graphs showing the predicted CO₂ solubility versus experimental CO₂ solubility for different amines and ANN models. The graphs compare the performance of BPNN and RBFNN for HEEAB and HEMAB, with AAD values given for each model.
## Results and discussions

<table>
<thead>
<tr>
<th>Amine(s)</th>
<th>Kent-Eisenberg model</th>
<th>Austgen Model</th>
<th>Liu-Helei model</th>
<th>Li-Shen model</th>
<th>Hu-Chakma model</th>
<th>Liu et al model</th>
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<th>RBFNN model</th>
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<td>DMAB</td>
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<td>1.4</td>
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</table>
The CO₂ loading of some tertiary amine solvents was measured at various temperature and CO₂ partial pressure.

A novel model was developed for predicting CO₂ loading. It was found that the model was able to give reasonable predictions for most of investigating amines.

ANN models were developed for predicting CO₂ loading with the excellent AADs.

The solvents presented need to be used with other mixtures to get good results for CO₂ capture.
Good solvents need more than one ingredients!
Advancement and new perspectives of using formulated reactive amine blends for post-combustion carbon dioxide (CO₂) capture technologies

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