Mass Transfer Performance and Correlations for CO$_2$ Absorption into Aqueous Blended of DEEA/MEA in a Random Packed Column

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Zhiwu Liang, zwliang@hnu.edu.cn

Joint International Center for CO$_2$ Capture and Storage (iCCS)
Dept. of Chemical Engineering, Hunan University, PR China
Hunan University, Changsha, China

Xi’an, Shaanxi

Hunan University, Changsha

Hong Kong

College of Chemistry and Chemical Engineering
Hunan University
Joint International Center for CO$_2$ Capture & Storage (iCCS), Hunan University, P.R.China
About iCCS in Hunan University, China

Current Members: 40
- 7 Professors
- 1 Engineer
- 2 Post-doctors
- 30 Current Graduates

Research Interests:
- Solvents for CO₂ Capture
- Kinetics & Mass Transfer
- Process Development
- CO₂ Capture Pilot Test
- CO₂ Utilization
Aqueous Amine CO$_2$ Capture at iCCS

- Amine screening & Thermodynamics
- Kinetics & Mass transfer
- Membrane & Packing Contactor
- Degradation & Corrosion
- Heat Cost of Amine Regeneration
- Process Simulation & Pilot Test
Other Research Topics at iCCS

➢ Solid Adsorption CO$_2$ Capture
➢ Oxy-fuel Process CO$_2$ Capture
➢ CO$_2$ Physical & Chemical Utilization
CCUS R & D Projects at iCCS HNU China

- National Science and Technology Support Plan (MOST of China. 2012BAC26B01) RMB 48.8M
- National Natural Science Foundation of China (NSFC. 21376067, U1362112, 21536003) RMB 7.2M
- The Innovative Research Team Development Plan- (MOE of China. IRT1238) RMB 3.0M
- Shaanxi Yanchang Petroleum Co.,LTD Technology Development, RMB 3.0M
- National 1000-Talent plan and 985-subject through Hunan University RMB 8.8M
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### Published Journal Papers

**98 Papers (2011-2017)**

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<th>Published Journal</th>
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Outline of this work

1. Background
2. Experimental section
3. Results and discussion
4. Conclusions
5. Acknowledgement
1. Background

Traditional absorption-stripping process

Key Strategies:
- Development of efficient absorbent
- Improvement of contactor
- Optimization of process configuration
1. Background

- Conflict between good CO\textsubscript{2} absorption and regeneration performance

The application of blended amines can combine the advantage of each amine

**Primary amines: MEA**

Advantages: High CO\textsubscript{2} absorption rate, low price of solvent

**Tertiary amines: DEEA**

Advantages: Low energy requirement, high resistance for degradation and corrosion; can be prepared from renewable and cheap resources (such as ethylene and ethanol)

DEEA/MEA-CO\textsubscript{2} (3 M 1:1)

Reaction mechanism for blended CO$_2$-DEEA-MEA system

DEEA + H$^+$ $\rightleftharpoons$$^{K_1}_{\text{K}_1}$ DEEAH$^+$

CO$_2$ + DEEA + H$_2$O $\rightleftharpoons$$^{K_2 k_{2,\text{MDEA}}}_{K_2 k_{2,\text{MDEA}}} \text{DEEAH}^+ + \text{HCO}_3^-$

MEA + H$^+$ $\rightleftharpoons$$^{K_3}_{\text{K}_3}$ MEAH$^+$

CO$_2$ + MEA $\rightleftharpoons$$^{K_4 k_{2,\text{MEA}}}_{K_4 k_{2,\text{MEA}}} \text{MEACOO}^- + \text{H}^+$

 MEACOO$^-$ + H$_2$O $\rightleftharpoons$$^{K_5}_{\text{K}_5} \text{MEA} + \text{HCO}_3^-$

CO$_2$ + H$_2$O $\rightleftharpoons$$^{K_6}_{\text{K}_6} \text{HCO}_3^- + \text{H}^+$

CO$_2$ + OH$^-$ $\rightleftharpoons$$^{K_7 k_{2,7}}_{K_7 k_{2,7}} \text{HCO}_3^-$

HCO$_3^-$ $\rightleftharpoons$$^{K_8}_{\text{K}_8} \text{CO}_3^{2-} + \text{H}^+$

H$_2$O $\rightleftharpoons$$^{K_9}_{\text{K}_9} \text{OH}^- + \text{H}^+$

Objectives: to know the Mass Transfer Performance
2. Experimental section

Schematic diagram of absorption experimental process
2. Experimental section

- **Determination of the mass transfer coefficient $K_G a_v$**

  Based on the two-film theory, material balance, and mass flux equation

  \[ N_A a_v = K_G a_v (P_A - P_{A*}) = K_G a_v P (y_{A,G} - y_A^*) \]

  \[ N_A a_v dh = G_1 dY_A \]

  \[ K_G a_v = \frac{G}{P (y_{A,G} - y_A^*)} \frac{dY_A}{dz} \]

  \[ K_G a_v = \frac{G}{P y_{A,G}} \frac{dY_A}{dz} \]

- **Determination of unit volume absorption rate $\Phi$**

  \[ \phi = K_G a_v P_{CO_2} \]

  \[ P_{CO_2} = \frac{P_{CO_2,in} - P_{CO_2,out}}{\ln(P_{CO_2,in} / P_{CO_2,out})} \]

  \[ \phi = \frac{G_1 \Omega (Y_1 - Y_2)}{V_r} \]
3. Results and discussion

Effect of **liquid feed temperature** on $K_G a_v$ and $\Phi$

(solvent concentration 3 kmol/m$^3$; liquid flow rate 5.85 m$^3$/m$^2$-hr; CO$_2$ loading 0.32 mol/mol; inert gas flow rate 39.17 kmol/m$^2$-hr; CO$_2$ partial pressure 15 kPa)
3. Results and discussion

Effect of lean CO₂ loading on $K_{Ga_v}$ and $\Phi$

(solvent concentration 3 kmol/m³; liquid flow rate 5.85 m³/m²-hr; inert gas flow rate 39.17 kmol/m²-hr; CO₂ partial pressure 15 kPa, liquid feed temperature 313.13 K)
3. Results and discussion

Effect of liquid flow rate on $K_G a_v$ and $\Phi$

(solvent concentration 3 kmol/m$^3$; inert gas flow rate 39.17 kmol/m$^2$-hr; CO$_2$ partial pressure 15 kPa, liquid feed temperature 313.13 K)
3. Results and discussion

Effect of CO₂ partial pressure on $K_G a_v$ and $\Phi$

(solvent concentration 3 kmol/m³; lean CO₂ loading 0.18 mol/mol; inert gas flow rate 39.17 kmol/m²-hr; liquid flow rate 5.85 m³/m²-hr; liquid feed temperature 313.13 K)
3. Results and discussion

Effect of inert gas flow rate on $K_G a_v$

(solvent concentration 3 kmol/m$^3$; lean CO$_2$ loading 0.22 mol/mol; liquid flow rate 5.85 m$^3$/m$^2$-hr; CO$_2$ partial pressure 15 kPa; liquid feed temperature 313.13 K)
3. Results and discussion

Effect of inert gas flow rate

(solvent concentration 3kmol/m³; lean CO₂ loading 0.28mol/mol; liquid flow rate 5.85m³/m²-hr; CO₂ partial pressure 10kPa; liquid feed temperature 313.13K)
3. Results and discussion

Effect of lean CO$_2$ loading

(solvent concentration 3kmol/m$^3$; liquid flow rate 5.85m$^3$/m$^2$-hr; inert gas flow rate 39.17kmol/m$^2$-hr; CO$_2$ partial pressure 15kPa, liquid feed temperature 313.13K)
3. Results and discussion

Temperature and CO$_2$ concentration profile

(solvent concentration 3kmol/m$^3$; lean CO$_2$ loading 0.13mol/mol; liquid flow rate 5.85m$^3$/m$^2$-hr; inert gas flow rate 39.17kmol/m$^2$-hr; CO$_2$ partial pressure 15kPa; liquid feed temperature 313.13K)
Correlations

An accurate correlation for the calculation of $K_G a_v$ is very essential for the design of the absorber and predicting the effects of operational parameters. $K_G a_v$ is a function of the liquid flow rate ($L$), CO$_2$ partial pressure ($P_{CO_2}$), and free amine concentration [$(\alpha_{eq}-\alpha)C$]

$$K_G a_v \propto L^b \left[ \alpha_{eq} - \alpha \right] C / P_{CO_2}$$

Result of $K_G a_v$ correlations for each section of absorber:

<table>
<thead>
<tr>
<th>No.</th>
<th>Correlated equation</th>
<th>$R^2$</th>
<th>AAD</th>
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<tr>
<td>1</td>
<td>$K_G a_v 1 = L^{0.45} \left[ 1.5816 \times (\alpha_{eq} - \alpha) C / P_{CO_2} + 0.0526 \right]$</td>
<td>0.8627</td>
<td>10.4%</td>
</tr>
<tr>
<td>2</td>
<td>$K_G a_v 2 = L^{0.45} \left[ 1.6524 \times (\alpha_{eq} - \alpha) C / P_{CO_2} - 0.0172 \right]$</td>
<td>0.9408</td>
<td>10.2%</td>
</tr>
<tr>
<td>3</td>
<td>$K_G a_v 3 = L^{0.45} \left[ 1.7196 \times (\alpha_{eq} - \alpha) C / P_{CO_2} - 0.0329 \right]$</td>
<td>0.8849</td>
<td>11.1%</td>
</tr>
<tr>
<td>4</td>
<td>$K_G a_v 4 = L^{0.45} \left[ 1.8896 \times (\alpha_{eq} - \alpha) C / P_{CO_2} + 0.0642 \right]$</td>
<td>0.8795</td>
<td>9.8%</td>
</tr>
<tr>
<td>5</td>
<td>$K_G a_v 5 = L^{0.45} \left[ 0.3935 \times (\alpha_{eq} - \alpha) C / P_{CO_2} + 0.0192 \right]$</td>
<td>0.7991</td>
<td>4.9%</td>
</tr>
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</table>
Correlations

Comparison between $y_{\text{out}}$ values calculated from proposed correlation and those from experimental results

Outlet gas concentration ($y_{\text{out}}$) is a key parameter for column design and simulation of the process.

\[
P_{\text{CO}_2} = P \left( \frac{y_{\text{CO}_2,\text{in}} - y_{\text{CO}_2,\text{out}}}{\ln\left(\frac{y_{\text{CO}_2,\text{in}}}{y_{\text{CO}_2,\text{out}}}\right)} \right)
\]

\[
\ln y_{\text{out}} = \ln y_{\text{in}} - \frac{PV}{G\Omega} K_G a_v
\]

\[
\ln y_{\text{out}} = \ln y_{\text{in}} - \frac{1}{5} \frac{PV}{G\Omega} L^{0.45} \left( K_G a_v 1 + K_G a_v 2 + K_G a_v 3 + K_G a_v 4 + K_G a_v 5 \right)
\]

AAD=8.4%
4. Conclusions

➢ The overall mass transfer coefficient ($K_G a_v$) and unit volume absorption rate $\Phi$ increases as liquid feed temperature and liquid flow rate increase, and decreases with increasing CO$_2$ loading, while changes in inert gas flow rate have little effect.

➢ The bottom temperature of the column ($T_{bot}$) increases with CO$_2$ partial pressure and decreases with increasing CO$_2$ loading and liquid flow rate.

➢ The correlations between $K_G a_v$ and operating parameters were proposed in DEEA/MEA-CO$_2$ system.

➢ The $y_{out}$ correlation was also studied in this work and found to be in satisfactory agreement with experimental results with AAD of 8.4%.
5. Acknowledgements

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Thank you

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