INVESTIGATIONS OF CARBON DIOXIDE ABSORPTION INTO AQUEOUS POTASSIUM CARBONATE SOLUTIONS CONTAINING PRIMARY AND SECONDARY ALKANOLAMINES

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Dedicated to Prof. Ryszard Pohorecki on the occasion of his 80th birthday

In the paper the results of measurements of CO₂ absorption rate in aqueous potassium carbonate solutions containing cyclohexylamine, diethanolamine, 2-methylaminoethanol and triethylenetetramine as activators have been presented. Enhancement mass transfer factors as well as reaction rate constants have been determined. Results show that among the tested activators triethylenetetramine and 2-methyl-aminoethanol may be used (instead of diethanolamine) as new promotors in a modified BENFLIELD process.

Keywords: carbon dioxide absorption, alkanolamines, potassium carbonates, laminar jet

1. INTRODUCTION

The absorption of carbon dioxide from synthesis gases by water has been practiced for many years, but it is now being superseded by the use of more specific absorbents. Several solvents such as propylene carbonate, methanol, N-methyl-2-pyrrolidine have been investigated, but only diethylene glycol acetate have been employed on a commercial scale. The removal of carbon dioxide from gas mixtures by contacting gases with a liquid solution exemplifies a class of chemical reactions that is both of theoretical and practical importance. Chemically reactive solvents usually have higher capacity and higher mass transfer rates than those based solely on physical absorption.

Capital investments (mainly solvent cost and equipment cost) and energy requirements for solvent regeneration are the two most important factors to be considered in selecting an appropriate process.

The most widely used chemical solvents employed for removal of acid gases such as CO₂, H₂S and COS are:

- aqueous solution of alkanolamines such as MEA, DEA TEA, MDEA and DIPA (Vaidya and Kenig, 2010),
- potassium carbonate solution with addition of alkanolamines.

The use of a promoted potassium carbonate solution at a temperature of ca. 100°C has the advantage over an aqueous solution of alkanolamines in terms of its lower cost and better suitability for regeneration purposes, because it requires less steam for stripping than the cold solvent. A hot
carbonate process with DEA as an activator was originally developed by Benson et al. in late 1950s (BENFIELD process).

Several research groups have investigated new alkanolamines activators for CO$_2$ absorption into potassium carbonate solutions (Bińczak et al., 2013; Cullinane and Rochelle, 2004; Kim et al., 2012; Pohorecki et al. 1988; Tseng et al., 1988; Yih and Sun, 1987).

The aim of this work was to evaluate the suitability of new alkanolamines activators (such as cyclohexylamine, 2-methylaminoethanol and triethylenetetramine) for synthesis gases purification in the modified BENFIELD process. The work is a part of a wider experimental program aimed at the development of a new activator in the process of CO$_2$ absorption during ammonia synthesis.

2. ABSORPTION MODEL

The following reactions occur during the CO$_2$ absorption into aqueous potassium carbonate solutions with alkanolamines used as activators

\[
\begin{align*}
\text{CO}_2(g) & \rightleftharpoons \text{CO}_2(aq) \quad (1) \\
\text{CO}_2(aq) + \text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad (2) \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- \quad (3) \\
\text{CO}_2(aq) + \text{OH}^- & \rightleftharpoons \text{HCO}_3^- \quad (4) \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad (5) \\
2\text{RR}^'\text{NH} + \text{CO}_2(aq) & \rightleftharpoons \text{RR}^'\text{NCOO}^- + \text{RR}^'\text{NH}_2^+ \quad (6) \\
\text{RR}^'\text{NCOO}^- + \text{H}_2\text{O} & \rightleftharpoons \text{RR}^'\text{NH} + \text{HCO}_3^- \quad (7) \\
\text{RR}^'\text{NH}_2^+ & \rightleftharpoons \text{RR}^'\text{NH} + \text{H}^+ \quad (8)
\end{align*}
\]

As can be seen, CO$_2$aq reacts in three parallel reactions with H$_2$O, OH$^-$ ions and alkanolamines. The reaction with water is first-order, whereas reactions with OH$^-$ ions and alkanolamines are second-order. For the pseudo-first order chemical reaction (see adequate criterion in Appendix) the reaction rate constant $k_1$ can be expressed as in Eq. (9):

\[
k_1 = k_{\text{H}_2\text{O}} + k_{\text{OH}^-} \left[\text{OH}^-\right] + k_{\text{Am}}[\text{Am}] \quad (9)
\]

The rate constant $k_{\text{H}_2\text{O}}$ for the reaction (2) does not depend on the ionic strength of the solution and may be calculated from Eq. (10) (Danckwerts and Sharma, 1966)

\[
\log k_{\text{H}_2\text{O}} = 329.85 - 110.541 \log T - \frac{17265.4}{T} \quad (10)
\]

From equilibrium constants of the reaction (5)

\[
K_2 = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (11)
\]

and reaction (3)

\[
K_w = \left[\text{OH}^-\right] [\text{H}^+] \quad (12)
\]
we get:
\[ [\text{OH}^-] = \frac{K_w}{K_2} \left( \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right) = \frac{K_w}{K_2} \left( \frac{1-\alpha}{2\alpha} \right) \]  
(13)

where the carbonisation ratio \( \alpha \) is defined as in Eq. (14):
\[ \alpha = \frac{[\text{HCO}_3^-]}{2([\text{CO}_3^{2-}]+[\text{HCO}_3^-])} \]  
(14)

The product \( k_{\text{OH}} [\text{OH}^-] \) can be expressed as in Eq. (15):
\[ k_{\text{OH}} [\text{OH}^-] = k_{\text{OH}} \frac{K_w}{K_2} \frac{1-\alpha}{2\alpha} = K_R \frac{1-\alpha}{2\alpha} \]  
(15)

where the kinetic coefficient \( K_R \) is expressed by the Eq. (16):
\[ K_R = k_{\text{OH}} \frac{K_w}{K_2} \]  
(16)

and can be calculated from the following relation (Pohorecki and Kucharski, 1991)
\[ \ln K_R = 27.821 - \frac{8514}{T} + 0.5456I - 0.0276I^2 \]  
(17)

3. EXPERIMENTS AND METHOD OF CALCULATIONS

The measurements of the CO\(_2\) absorption rate were carried out at a normal pressure using a laminar jet absorber. The experimental apparatus is shown in Fig.1. A detailed description of the apparatus and the measuring technique can be found elsewhere (Pohorecki, 1972; Bińczak et al., 2013).

![Scheme of the experimental apparatus](image-url)
The measurements were carried out in the temperature range of 20–40°C at atmospheric pressure. Total concentration of carbonates (expressed as equivalent weight fraction of \( K_2CO_3 \)) was 8 wt%, with carbonisation ratio of 0.4. The following activators were used: cyclohexylamine (CHA) 3 wt%; diethanolamine (DEA) 1–3 wt%; 2-methylaminoethanol (2-MAE) 1–3 wt% end triethylenetetramine (TETA) 1–3 wt%. CHA is a primary amine; DEA and 2-MAE are secondary amines; TETA has got two groups of primary amines (-NH2) and two groups of secondary amines (-NH-).

In the absorption process with a reversible chemical reaction, the molar flux \( N_A \) of the absorbed component is expressed as:

\[
N_A = k_L^* (C_{Ai} - C_{Ar}) \tag{18}
\]

and the absorption rate \( R \) is:

\[
R = N_A a = k_L^* (C_{Ai} - C_{Ar}) a \tag{19}
\]

For the laminar jet absorber the interfacial area \( a \) may be assumed according to Eq. (20):

\[
a = \pi dl \tag{20}
\]

The measured absorption rate \( R \) is:

\[
R = \frac{V_g p_{CO_2}}{R T} \tag{21}
\]

The concentration of \( CO_2 \) at the interface can be calculated from the Henry’s law:

\[
C_{Ai} = H p_{Ai} \tag{22}
\]

In the experiments, pure \( CO_2 \) (saturated only with water vapour) was used.

\[
p_{Ai} = p_{A0} = P - p_{H_2O} \tag{23}
\]

The Henry’s constant for \( CO_2 \)-aqueous potassium carbonate solutions can be calculated from the following relations (Barrett, 1966; Danckwerts, 1970):

\[
\log \frac{H}{H_w} = -\sum I_i h_i \tag{24}
\]

\[
h_i = h_+ + h_- + h_g \tag{25}
\]

\[
\log H_w = 9.1229 - 5.9044 \times 10^{-2} T + 7.8857 \times 10^{-5} T^2 \tag{26}
\]

From equilibrium constants of the reactions (5), \( K_2 \) and (2), \( K_1 \)

\[
K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \tag{27}
\]

we have

\[
[CO_2] = C_{Ar} = \frac{K_2}{K_1} \left[ \frac{HCO_3^-}{2} \right]^2 \tag{28}
\]

Making use of Eq. (14), we obtain:

\[
C_{Ar} = \frac{4\alpha^2 K_2}{1 - \alpha K_1} \left[ \left[ CO_3^{2-} \right] + \frac{1}{2} \left[ HCO_3^- \right] \right] \tag{29}
\]

The equilibrium partial pressure of \( CO_2 \) is equal to:
\[ p_{Ar} = \frac{C_{Ar}}{H} = \frac{4x^2 K_2}{1-\kappa K_1 H} \left( \left[ \text{CO}_3^{2-} \right] + \frac{1}{2} \left[ \text{HCO}_3^- \right] \right) = \frac{1}{K_p} \frac{4x^2}{1-\kappa} \left( \left[ \text{CO}_3^{2-} \right] + \frac{1}{2} \left[ \text{HCO}_3^- \right] \right) \]  

(30)

where the equilibrium coefficient \( K_p \) is defined as:

\[ K_p = \frac{K_1 H}{K_2} \]  

(31)

and can be calculated from the following relation (Pohorecki and Kucharski, 1991)

\[ \ln K_p = -3.154 + \frac{2311}{T} - 0.068 I + 0.0138 I^2 \]  

(32)

Making use of the experimental values of the absorption rate \( R \) in Eq. (21), the values of the mass transfer coefficient with chemical reaction, \( k_L^* \) were calculated from Eq. (19).

For fast, pseudo-first order chemical reactions, the mass transfer coefficient with a chemical reaction is equal to (see relevant criteria in the Appendix):

\[ k_L^* = \sqrt{D_A k_1} \]  

(33)

The diffusivity of \( \text{CO}_2 \) in aqueous potassium carbonate solutions was calculated from the following relations (Barrett, 1966)

\[ (D_A \mu)_T = (D_{w \mu_w})_T \]  

(34)

\[ \log D_w = -8.1764 + \frac{712.5}{T} - \frac{2.591 \times 10^5}{T^2} \]  

(35)

The viscosity of the solution was calculated using the relation proposed by Moniuk and Pohorecki (Moniuk and Pohorecki, 1991):

\[ \log \mu = \frac{844.279}{T} - 2.8653 + 0.1458 S + 0.0243 \alpha \]  

(36)

where:

\[ \log \mu = \frac{844.279}{T} - 2.8653 + 0.1458 S + 0.0243 \alpha \]  

(37)

The values of pseudo-first order reaction rate constant \( k_1 \) were calculated from Eq. (33) and values of second-order reaction rate \( k_{Am} \) were calculated from Eq. (9).

4. RESULTS AND DISCUSSION

The determined values of mass transfer with a chemical reaction, \( k_L^* \) were used for the calculation of the enhancement factor, \( E \) using the following relation:

\[ E = \frac{k_L^*}{k_L} \]  

(38)

For the laminar-jet absorber, the physical mass transfer coefficient in the liquid phase may be calculated from the relation below (Higbie model)

\[ k_L = 2 \sqrt{\frac{D_A}{\pi \tau}} \]  

(39)

where the contact time \( \tau \) is given as:

\[ \tau = \frac{l}{u} = \frac{\pi d^2 l}{4V_L} \]  

(40)
In Fig. 2 the values of the enhancement factor, $E$, for the activators at 40°C are presented. As can be seen, the value of $E$ for CHA as an activator is lower than that for DEA. However, the values of $E$ for TETA and 2-MAE as activators are significantly higher than those for DEA.

In Fig. 3 in Arrhenius plot ($\ln k_{Am} = f \left(\frac{1}{T}\right)$) for CO$_2$–CHA system is presented. The straight line can be described by the relation:

$$\ln k_{Am} = 20.439 - \frac{3681.6}{T}$$

(41)

Due to the low activation properties of CHA we present only results for its highest investigated concentration.
In the literature there are no data on the kinetics of the reaction between CO₂ and CHA. It has been only mentioned (Cwalina and Kubicki, 1977) that CHA may be used as an activator in CO₂ absorption into aqueous potassium carbonate solutions.

In Fig. 4 Arrhenius plots \( \ln k_1 = f \left( \frac{1}{T} \right) \) for the CO₂ – DEA system for different values of activator concentrations (1-3 wt%) are presented. The results reveal that the values of the pseudo-first order reaction rate constants, \( k_1 \), significantly depend on the activator concentrations.

\[
\ln k_1 = 7.1431 - \frac{1048.9}{T}
\]  

(42)

In Fig. 5 an Arrhenius plot \( \ln k_{Am} = f \left( \frac{1}{T} \right) \) for the CO₂ – DEA system is presented. The data show that the values of the reaction rate constant, \( k_{Am} \), practically do not depend on the activator concentrations. The straight line can be described by the following relation (42).

\[
\ln k_{Am} = 8.80
\]

(42)
Table 1. Literature data on the kinetics for the reaction between CO₂ and aqueous DEA

<table>
<thead>
<tr>
<th>Author</th>
<th>T, K</th>
<th>DEA, kmol/m³</th>
<th>k_{DEA}, m³/(kmol·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sharma, 1964</td>
<td>298</td>
<td>1</td>
<td>1240</td>
</tr>
<tr>
<td>Sada et al., 1976</td>
<td>298</td>
<td>0 – 1.922</td>
<td>1340</td>
</tr>
<tr>
<td>Donaldson and Nguyen, 1980</td>
<td>298</td>
<td>0 – 0.88</td>
<td>1400</td>
</tr>
<tr>
<td>Blanc and Demarais, 1981</td>
<td>298</td>
<td>0 – 4</td>
<td>655</td>
</tr>
<tr>
<td>Barth et al., 1983</td>
<td>298</td>
<td>0.021</td>
<td>110</td>
</tr>
<tr>
<td>Laddha and Danckwerts, 1981</td>
<td>298</td>
<td>0 – 2.88</td>
<td>1410</td>
</tr>
<tr>
<td>Blauwhoff et al., 1983</td>
<td>298</td>
<td>0 – 2.38</td>
<td>7300</td>
</tr>
<tr>
<td>Versteeg and Oyevaar, 1989</td>
<td>298</td>
<td>0 – 4.358</td>
<td>3240</td>
</tr>
<tr>
<td>Jensen et al., 1954</td>
<td>291</td>
<td>0 – 0.3</td>
<td>5900</td>
</tr>
</tbody>
</table>

DEA as an activator is commonly used in a number of industrial plants (BENFIELD process) and many studies have been performed on the kinetics of the reaction between CO₂ and DEA. As it becomes evident from Table 1, discrepancies between results obtained by various authors (at 298 K) are very large (110-7300 m³/(kmol·s)). At this temperature $k_{Am}$ determined from the relation (42) amounts to 4200 m³/(kmol·s).

In Fig. 6 Arrhenius plots $\ln k_1 = f \left( \frac{1}{T} \right)$ for the CO₂ – 2-MAE system for a different values of activator concentrations (1-3 wt%) are presented. The results reveal that the values of the pseudo-first order reaction rate constants, $k_1$ significantly depend on the activator concentrations.

In Fig. 7 an Arrhenius plot $\ln k_{Am} = f \left( \frac{1}{T} \right)$ for the CO₂ – 2-MAE system is presented. The data show that the values of the reaction rate constant, $k_{Am}$ practically are independent of the activator concentration. The straight line can be described by the following relation (43).
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\[
\ln k_{Am} = 29.925 - \frac{6295.6}{T}
\]  

\( (43) \)

Mimura et al. (1988) investigated the kinetics of the reaction between CO\(_2\) and 2-MAE in aqueous solutions of 2-MAE (0.9-2.5 kmol/m\(^3\)). At 298 K, the value of the reaction rate constant, \( k_{Am} \) amounts to 7940 m\(^3\)/(kmol·s). From Eq. (43) \( k_{Am} \) is 6604 m\(^3\)/(kmol·s).

In Fig. 7 Arrhenius plots \( \ln k_{Am} = f \left( \frac{1}{T} \right) \) for the CO\(_2\)–2-MAE system

In Fig. 8 Arrhenius plots \( \ln k_1 = f \left( \frac{1}{T} \right) \) for the CO\(_2\)–TETA system for different values of the activator concentrations (1-3 wt%) are presented. The results reveal that the values of the pseudo-first order reaction rate constants, \( k_1 \) significantly depend on the activator concentrations.
In Fig. 9 an Arrhenius plot \( \ln k_{Am} = f \left( \frac{1}{T} \right) \) for the CO\(_2\)–TETA system is presented. As can be seen, the values of the reaction rate constant, \( k_{Am} \), are practically independent of the activator concentrations. The straight line can be described by the following relation (44):

\[
\ln k_{Am} = 22.500 - \frac{4017.5}{T}
\]  

(44)

Singh et al. (2009) investigated relationships between the structure the number of amine groups) and the activity of amine-based CO\(_2\) absorbents.

For the CO\(_2\)–TETA system the total capacity of aqueous solutions is high and amounts to 2.51 mol CO\(_2\)/mol amine or 17.15 mol CO\(_2\)/kg amine (Singh et al., 2009).

![Fig. 9. Arrhenius plot \( \ln k_{Am} = f \left( \frac{1}{T} \right) \) for the CO\(_2\)–TETA system](image)

5. CONCLUSIONS

Measurements of a CO\(_2\) absorption rate were carried out in aqueous potassium carbonate solutions containing alkanolamines (cyclohexylamine, diethanoloamine, 2-ethyl-aminoethanol and triethylenetetramine) using the laminar-jet technique. Enhancement mass transfer factors as well as reaction rate constants between CO\(_2\) and alkanolamines were determined. Results clearly show that triethylenetetramine and 2-methyl-aminoethanol may be used (instead of diethanolamine) as new activators of aqueous potassium carbonate/bicarbonate solution in a modified BENFLIELD process.

**SYMBOLS**

- \( a \) interfacial area, m\(^2\)
- \( a \) concentration of carbonate ion Eq. (A2), kmol/m\(^3\)
- \( b \) concentration of bicarbonate ion Eq. (A2), kmol/m\(^3\)
- \( C_A \) molar concentration of component A, kmol/m\(^3\)
- \( D_A \) diffusivity of the absorbed gas in the liquid phase, m\(^2\)/s
- \( d \) nozzle diameter, m
- \( E \) enhancement factor
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\[ H \]  Henry’s constant, kmol/(m\(^3\)-bar)
\[ h_i, h_+, h_-, h_g \]  contributions of compound, cation, anion and gas respectively, m\(^3\)/kmol
\[ I \]  ionic strength of solution, kmol/m\(^3\)
\[ K_2 \]  equilibrium constant reaction (5), kmol/m\(^3\)
\[ K_p \]  equilibrium coefficient, kmol/(m\(^3\)-atm)
\[ K_R \]  kinetic coefficient defined by Eq. (16), 1/s
\[ K_w \]  ionic product of water, kmol\(^2\)/m\(^6\)
\[ k_{f1} \]  pseudo-first order reaction rate constant, 1/s
\[ k_{am} \]  reaction rate constant, m\(^3\)/(kmol-s)
\[ k_{H2O} \]  reaction rate constant, m\(^3\)/(kmol-s)
\[ k_L \]  liquid-film mass transfer coefficient, m/s
\[ k'_L \]  liquid-film mass transfer coefficient with chemical reaction, m/s
\[ k_{OH^-} \]  reaction rate constant, m\(^3\)/(kmol-s)
\[ l \]  jet length, m
\[ N_A \]  molar flux, kmol/m\(^2\)-s
\[ P \]  total pressure, bar
\[ p \]  partial pressure, bar
\[ R \]  rate of absorption, kmol/s
\[ \bar{R} \]  gas constant, J/(mol·K)
\[ S \]  total concentration of carbonates defined by Eq. (37), kmol/m\(^3\)
\[ T \]  temperature, K
\[ u \]  linear liquid velocity, m/s
\[ V \]  volumetric flow rate, m\(^3\)/s

Greek symbols
\[ \alpha \]  carbonisation ratio defined by Eq. (14)
\[ \mu \]  viscosity, mPa·s
\[ \tau \]  contact time, s

Subscripts
\[ A \]  absorbed gas
\[ g \]  gas
\[ i \]  interface
\[ L \]  liquid
\[ r \]  chemical equilibrium
\[ w \]  water

REFERENCES


APPENDIX

1. Criterion for pseudo-first order reaction (Leder, 1971)

\[
1 + \frac{[RR'NH]}{C_{dR}} \gg \sqrt{1 + \frac{D_i k}{k_L} \left[ \text{OH}^- \right] + \frac{D_i k_{dm}[Am]}{k_L}}
\]  
(A1)

\[
1 + \frac{1}{C_{dR}(\frac{1}{a_1} + \frac{b}{2})} \gg \sqrt{1 + \frac{D_i k}{k_L} \left[ \text{OH}^- \right] + \frac{D_i k_{dm}[Am]}{k_L}}
\]  
(A2)

Both these criteria (A1) and (A2) must be met.

2. Criterion for fast reaction (Pohorecki and Wroński, 1977)

\[
\frac{\sqrt{D_i k_1}}{k_L} \gg 1
\]  
(A3)