



## Catalytic effect of amines on a CO<sub>2</sub>BOL absorption performance

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In the scope of this work, the kinetic parameters for the reaction between CO<sub>2</sub> and promoted CO<sub>2</sub>BOLs were achieved by using stopped-flow technique. As an organic base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and as promoters MEA (monoethanolamine) and morpholine were investigated. Experiments were performed under constant DBU weight percentage by varying promoter concentration in 1-hexanol medium at 298 K. The experimental kinetic data was analysed by applying a modified termolecular reaction mechanism. Power law kinetics was performed by plotting the natural logarithm of pseudo-first order reaction rate constants ( $k_0$ , s<sup>-1</sup>) vs promoter (morpholine or MEA) concentration. The fractional reaction orders were determined to be between 1.2 and 1.4.

Keywords: Catalytic effect, CO<sub>2</sub>BOL, CO<sub>2</sub> removal, DBU, morpholine, reaction kinetics.

### Introduction

CO<sub>2</sub> is one of the major greenhouse gases (GHGs) and its emission into atmosphere is a global concern because of direct connection with global warming and climate change<sup>1,2</sup>. Also, the CO<sub>2</sub> capture process is the most important component of the technology called Carbon Capture, Utilization and Storage (CCUS), which plays an important role in addressing two important environmental problems of our time: (i) climate change and (ii) energy challenge<sup>3</sup>. CO<sub>2</sub> capture with aqueous alkanolamine solutions is preferred for post-combustion CO<sub>2</sub> capture from flue gas and industrial applications. Among solvent based CO<sub>2</sub> capture technologies, 30 wt.% aqueous monoethanolamine (MEA) solution is widely the accepted benchmark<sup>4,5</sup>. Although aqueous amine solvent systems can react with CO<sub>2</sub> rapidly and have good selectivity, they require high amount of energy while the regeneration of the CO<sub>2</sub> loaded solvent that necessitates reboiling<sup>6,7</sup>. Moreover, aqueous amine solvents are vulnerable to foaming, oxidative degradation, and they have corrosiveness nature<sup>8</sup>. Since CO<sub>2</sub> capture using aqueous amines require high energy consumption, new research studies have been conducted to investigate non-aqueous absorbents<sup>9</sup>. Carbon dioxide binding organic liquids (CO<sub>2</sub>BOLs) include a super base such as guanidine or amidine and a linear alcohol such

as 1-hexanol<sup>10</sup>. These solvent systems have high CO<sub>2</sub> capture capacities and can be regenerated by simple temperature and pressure swings without a necessity to boil. Therefore, the latent heat of evaporation can be eliminated<sup>11</sup>. However, their relatively low CO<sub>2</sub> loading rate can be enhanced by blending with promoters<sup>12</sup>. The main target of this study is to develop a high capacity and cost-effective solvent systems that also has high capture reactivity towards to CO<sub>2</sub>. In this work, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1-hexanol were selected as a amidine base and alcohol, respectively. Different concentrations of DBU in 1-hexanol were prepared. Morpholine and MEA were used to enhance the CO<sub>2</sub> absorption rate of CO<sub>2</sub>BOLs. The effect of primary linear amine (MEA) and secondary cyclic amine (morpholine) on reaction rates between CO<sub>2</sub> and CO<sub>2</sub>BOL were obtained by using the conductivity stopped-flow technique at 298 K.

### Reaction kinetics

Termolecular reaction mechanism propose that CO<sub>2</sub> and a base molecule react with an amine in a single step<sup>13</sup>. In this work, the modified termolecular reaction mechanism was suggested as given in eq. (1).

$$k_0 = k_{OH}[-OH][A] + k'_{OH}[-OH][P] + k_A[A][A] + k_P[P][P] + k_{AP}[A][P] \quad (1)$$

where,  $k$  is reaction rate constant, A is amine (DBU, here), OH is alcohol (1-hexanol) and P is promoter.

Considering that the alcohol is in excess and almost at constant concentration. Therefore,  $k = k_{OH} [OH]$  and  $k^* = k'_{OH} [OH]$  are also nearly constant. Then, eq. (1) can be rearrange in the form of eq. (2).

$$k_0 = k[A] + k^*[P] + k_A[A][A] + k_P[P][P] + k_{AP}[A][P] \quad (2)$$

$$k_0 = (k + k_A[A])[A] + (k^* + k_P[P])[P] + k_{AP}[A][P] \quad (3)$$

During an experimental run, DBU concentration [A] was kept constant – almost at its initial value of  $[A]_0$  – and promoter concentration [P] was varied.

$$k_0 = (k + k_A[A]_0)[A]_0 + (k^* + k_P[P])[P] + k_{AP}[A]_0[P] \quad (4)$$

$$k_0 = k_1 + k_2[P] + k_P[P][P] \quad (5)$$

where,  $k_1 = (k + k_A[A]_0)[A]_0$  and  $k_2 = k^* + k_{AP} [A]_0$

The forward reaction rate constants of the reaction between  $CO_2$  and promoted  $CO_2$ BOLs were calculated by using eq. (5). As seen from eq. (5),  $k_0$  is a function of the concentration of promoters.

## Materials and methods

List of chemicals and reagents used in the study were summarized in Table 1. No further purification was performed on the materials used.

**Table 1.** Specific properties of chemicals

Chemical	CAS Number	Purity (%)	Supplier
DBU	6674-22-2	98	Sigma-Aldrich
MEA	141-43-5	≥ 99	Sigma-Aldrich
Morpholine	110-91-8	≥ 99	Sigma-Aldrich
Hexanol	111-27-3	98	Sigma-Aldrich
$CO_2$	124-38-9	99.9	Linde

The stopped-flow apparatus was used to determine the fast chemical reactions kinetic parameters in terms of pseudo-first order rate constants ( $k_0, s^{-1}$ ) for homogenous reactions of  $CO_2$  into promoted  $CO_2$ BOLs at 298 K. The stopped-flow technique, which is also known as a direct technique, has several advantages such as easy operation, quick experiment run (4 0.05 s), small amount of solvent consumption for each experimental run (4 0.1 mL) and no effect of gas phase resistance<sup>14</sup>. The amine concentration were kept ten times higher than  $CO_2$  concentration in terms of pseudo-first

order conditions.  $k_0$  values were automatically generated by software installed on microprocessor. The further information can be found in previous publications<sup>15–17</sup>.

## Results and discussion

The reaction kinetic experiments were performed for the promoted  $CO_2$ BOL systems. During each experimental sets, the DBU weight percentage were kept constant at 2.5 wt% or 5 wt% while varying different concentrations of promoters (morpholine or MEA).

**Table 2.** Pseudo-first order reaction rate constants for (2.5 wt% DBU + MEA)- $CO_2$  system and (2.5 wt% DBU + Morp.)- $CO_2$  system in 1-hexanol at 298 K

wt% DBU	[MEA] (kmol m <sup>-3</sup> )	$k_0$ (s <sup>-1</sup> )	wt% DBU	[Morp.] (kmol m <sup>-3</sup> )	$k_0$ (s <sup>-1</sup> )
2.5	0	112	2.5	0	112
2.5	0.01	124	2.5	0.01	117
2.5	0.02	136	2.5	0.02	121
2.5	0.04	155	2.5	0.04	129
2.5	0.08	215	2.5	0.08	153
2.5	0.16	420	2.5	0.16	221

Table 2 shows a summary of results of  $k_0$  values obtained for the 2.5 wt% DBU-promoter: 1-hexanol systems. In order to obtain consistent  $k_0$  values, experiments were repeated at least ten times. The results give the expected positive trend as seen in Table 2. The  $k_0$  value increases progressively with an increase in the promoter concentration.

The  $k_0$  values versus promoter concentration were plotted according to eq. (5) as shown in Fig. 1. The forward reaction rate constants for (2.5 wt% DBU + promoter)- $CO_2$  systems were determined from the slope of the fitted lines.

Table 3 shows a summary of results of  $k_0$  values obtained for the 5.0 wt% DBU-promoter: hexanol systems.

In order to calculate the forward reaction rate constants of (5.0 wt% DBU + promoter)- $CO_2$  systems, the  $k_0$  values versus the promoter concentrations were plotted as seen in Fig. 2. The forwards reaction rate constants were specified from the slopes of fitted lines and they summarized in Table 4.

The natural logarithms of  $k_0$  values versus promoter concentrations were plotted to specify the order of reaction as shown in Fig. 3. Empirical power law kinetics was fitted us-

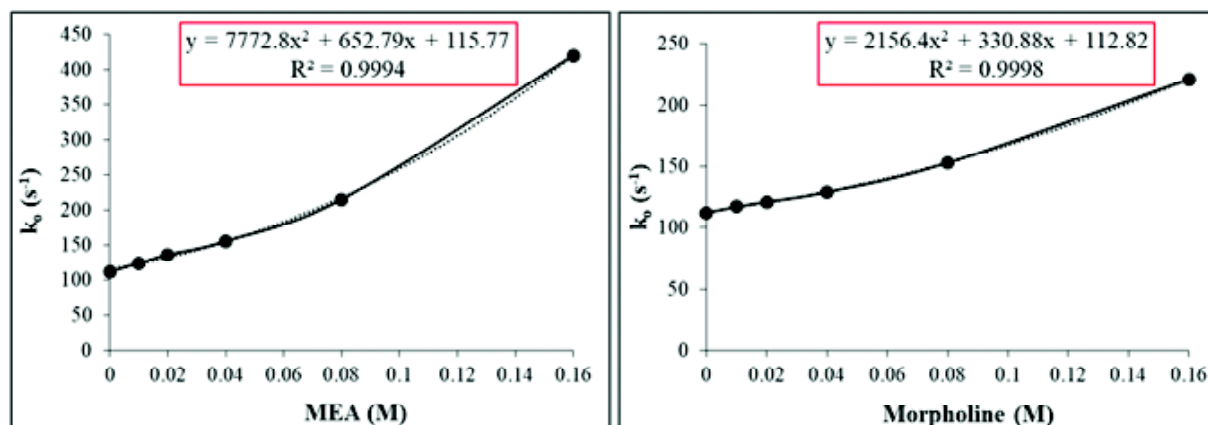


Fig. 1. Pseudo-first order rate constants for the (2.5 wt% DBU + promoter)-CO<sub>2</sub> system at 298 K in 1-hexanol.

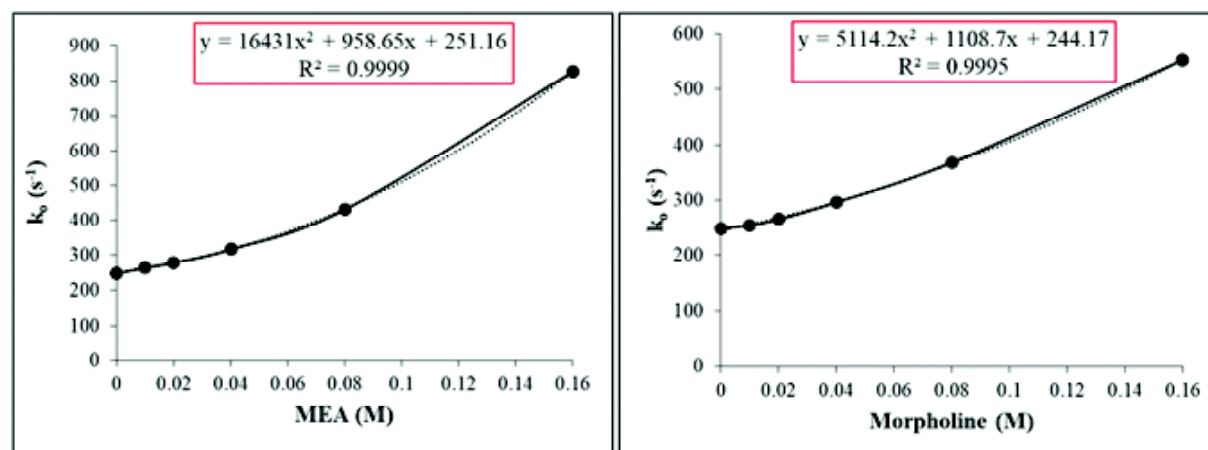


Fig. 2. Pseudo-first order rate constants for the (5.0 wt% DBU + promoter)-CO<sub>2</sub> system at 298 K in 1-hexanol.

**Table 3.** Pseudo-first order reaction rate constants for (5.0 wt% DBU + MEA)-CO<sub>2</sub> system and (5.0 wt% DBU + Morp.)-CO<sub>2</sub> system in 1-hexanol at 298 K

wt% DBU	[MEA] (kmol m <sup>-3</sup> )	k <sub>0</sub> (s <sup>-1</sup> )	wt% DBU	[Morp.] (kmol m <sup>-3</sup> )	k <sub>0</sub> (s <sup>-1</sup> )
5.0	0	248	5.0	0	248
5.0	0.01	264	5.0	0.01	254
5.0	0.02	279	5.0	0.02	265
5.0	0.04	317	5.0	0.04	296
5.0	0.08	431	5.0	0.08	368
5.0	0.16	826	5.0	0.16	552

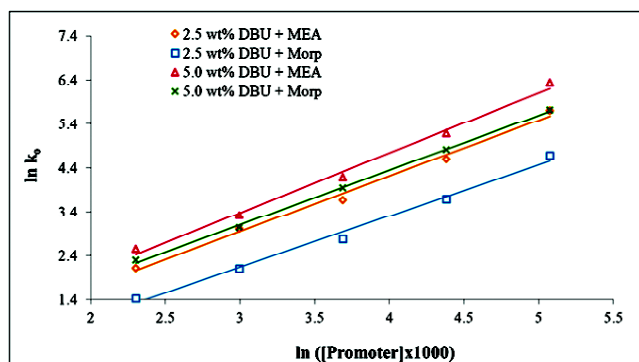
ing the least squares method and the slopes corresponds to the reaction order were presented in Table 3. The orders of the reaction between CO<sub>2</sub> and promoted CO<sub>2</sub>BOLs were found to be between 1.2 and 1.4 which indicates that the suggested modified termolecular mechanism is valid.

**Table 4.** The forward reaction rate constants and reaction orders for the promoted CO<sub>2</sub>-BOL systems at 298 K

System	k <sub>p</sub> (m <sup>6</sup> / kmol <sup>2</sup> s)	k <sub>2</sub> (m <sup>3</sup> / kmol s)	k <sub>1</sub> (s <sup>-1</sup> )	Reaction order
2.5 wt% DBU + MEA	7773	653	116	1.27
2.5 wt% DBU + Morpholine	2156	331	113	1.17
5.0 wt% DBU + MEA	16431	959	251	1.37
5.0 wt% DBU + Morpholine	5114	1109	244	1.25

## Conclusions

The removal and subsequent disposal or utilization of CO<sub>2</sub> needs to be considered a high priority because of the adverse impact of greenhouse gas emissions which are derived significantly from industrial operations and energy utilizations. The results of this study contributes an advancement to the development of novel solvent systems. The ab-



**Fig. 3.** The apparent reaction order plot for the DBU/promoter/1-hexanol systems.

sorption  $\text{CO}_2$  kinetics into promoted  $\text{CO}_2$ BOLs were analysed by using the rapid-mixing stopped-flow technique. The  $k_0$  values at various promoter concentrations were measured at 298 K. It was observed that the values of  $k_0$  increased as the promoter concentration were increased. The obtained results showed that the relatively low reaction rate between  $\text{CO}_2$  and  $\text{CO}_2$ BOLs could be considerably enhanced by adding morpholine and MEA. This study suggests that the catalytic effect of primary amine, MEA, on  $\text{CO}_2$  absorption kinetics plays more important role than cyclic secondary amine, morpholine. The suggested promoted  $\text{CO}_2$ BOLs are promising candidates for reducing the cost of  $\text{CO}_2$  removal from flue gas.

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