



Catalytic effect of amines on a CO₂BOL absorption performance

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In the scope of this work, the kinetic parameters for the reaction between CO₂ and promoted CO₂BOLs 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_o , s⁻¹) vs. promoter (morpholine or MEA) concentration. The fractional reaction orders were determined to be between 1.2 and 1.4.

Keywords: Catalytic effect; CO₂BOL; CO₂ removal; DBU; morpholine; reaction kinetics

Introduction

CO₂ 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^{1,2}. Also, the CO₂ 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 challenge³. CO₂ capture with aqueous alkanolamine solutions is preferred for post-combustion CO₂ capture from flue gas and industrial applications. Among solvent based CO₂ capture technologies, 30 wt. % aqueous monoethanolamine (MEA) solution is widely the accepted benchmark^{4,5}. Although aqueous amine solvent systems can react with CO₂ rapidly and have good selectivity, they require high amount of energy while the regeneration

of the CO₂ loaded solvent that necessitates reboiling^{6,7}. Moreover, aqueous amine solvents are vulnerable to foaming, oxidative degradation, and they have corrosiveness nature⁸. Since CO₂ capture using aqueous amines require high energy consumption, new research studies have been conducted to investigate non-aqueous absorbents⁹. Carbon dioxide binding organic liquids (CO₂BOLs) include a super base such as guanidine or amidine and a linear alcohol such as 1-hexanol¹⁰. These solvent systems have high CO₂ 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 eliminated¹¹. However, their relatively low CO₂ loading rate can be enhanced by blending with promoters¹². 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 CO₂. 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 CO₂ absorption rate of CO₂BOLs. The effect of primary linear amine (MEA) and secondary cyclic amine (morpholine) on reaction rates between CO₂ and CO₂BOL were obtained by using the conductivity stopped-flow technique at 298 K.

Reaction Kinetics

Termolecular reaction mechanism propose that CO₂ and a base molecule react with an amine in a single step¹³. In this work, the modified termolecular reaction mechanism was suggested as given in Equation 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, Equation 1 can be rearrange in the form of Equation 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 CO₂ and promoted

CO₂BOLs were calculated by using Equation 5. As seen from Equation 5, k₀ 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.

The stopped-flow apparatus was used to determine the fast chemical reactions kinetic parameters in terms of pseudo-first order rate constants (k₀, s⁻¹) for homogenous reactions of CO₂ into promoted CO₂BOLs 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 (~ 0.05 s), small amount of solvent consumption for each experimental run (~ 0.1 mL) and no effect of gas phase resistance¹⁴. The amine concentration were kept ten times higher than CO₂ concentration in terms of pseudo first-order conditions. k₀ values were automatically generated by software installed on microprocessor. The further information can be found in previous publications¹⁵⁻¹⁷.

Results and discussion

The reaction kinetic experiments were performed for the promoted CO₂BOL 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 shows a summary of results of k₀ values obtained for the 2.5 wt% DBU-promoter: 1-hexanol systems. In order to obtain consistent k₀ 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

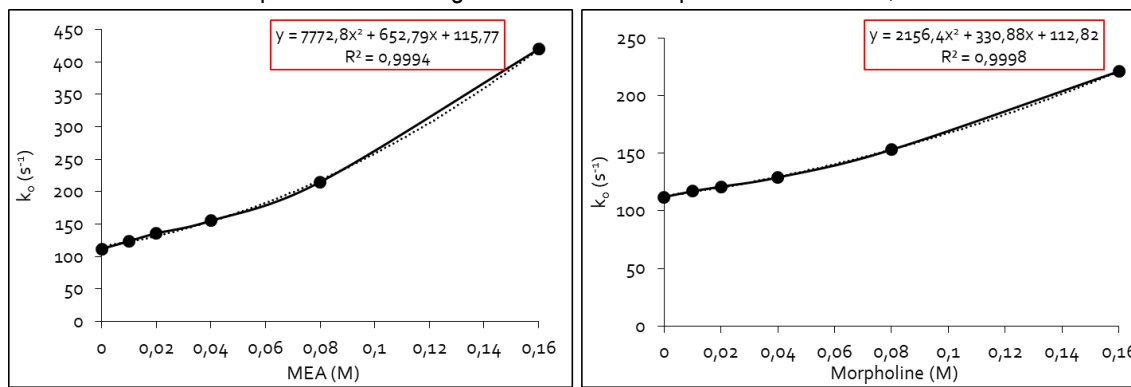


Fig. 1. Pseudo-first order rate constants for the (2.5 wt% DBU + Promoter)–CO₂ system at 298 K in 1-hexanol

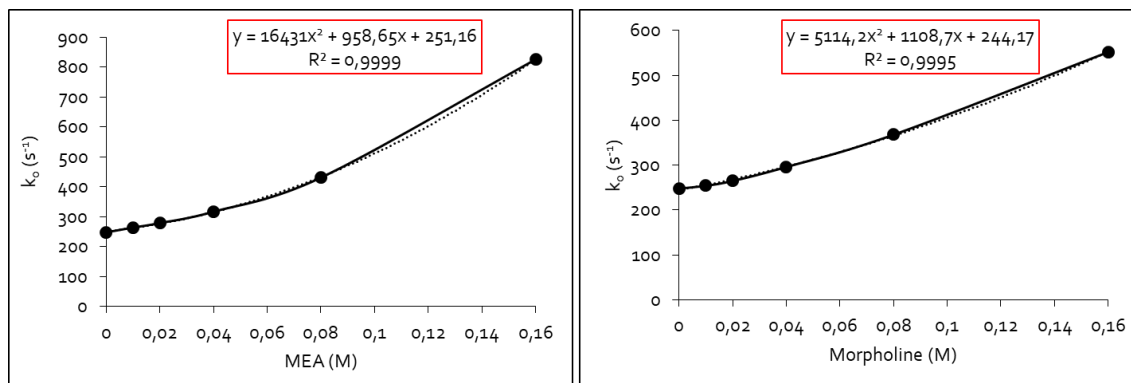


Fig. 2. Pseudo-first order rate constants for the (5.0 wt% DBU + Promoter)–CO₂ system at 298 K in 1-hexanol

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)–CO₂ systems, the k_0 values versus the promoter concentrations were plotted as seen in Figure 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

Equation 5 as shown in Figure 1. The forward reaction rate constants for (2.5 wt% DBU + promoter)–CO₂ systems were determined from the slope of the fitted lines,.

Figure 3. Empirical power law kinetics was fitted using the least squares method and the slopes corresponds to the reaction order were presented in Table 3. The orders of the reaction between CO₂ and promoted CO₂BOLs were found to be between 1.2 and 1.4 which indicates that the suggested modified termolecular mechanism is valid.

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

wt% DBU	[MEA] (kmol.m ⁻³)	k _o (s ⁻¹)	wt% DBU	[Morp.] (kmol.m ⁻³)	k _o (s ⁻¹)
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

wt% DBU	[MEA] (kmol.m ⁻³)	k _o (s ⁻¹)	wt% DBU	[Morp.] (kmol.m ⁻³)	k _o (s ⁻¹)
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

Conclusions

The removal and subsequent disposal or utilization of CO₂ 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 absorption CO₂ kinetics into promoted CO₂BOLs were analysed by using the rapid-mixing stopped-flow technique.

Table 4. The forward reaction rate constants and reaction orders for the promoted CO₂-BOL systems at 298 K.

System	k_p (m ⁶ /kmol ² .s)	k_2 (m ³ /kmol s)	k_1 (s ⁻¹)	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

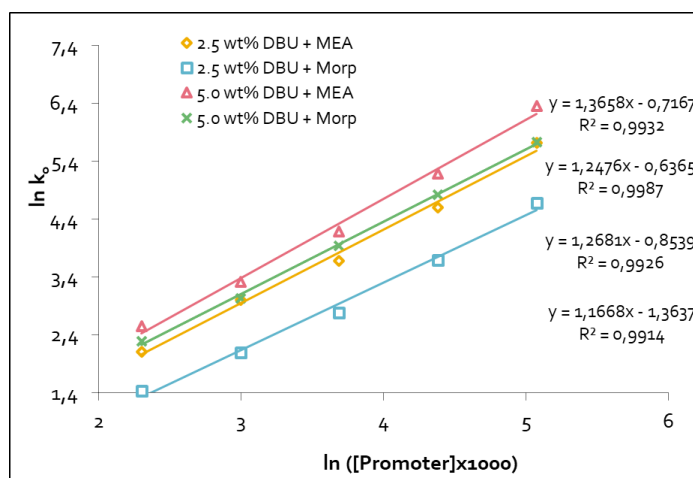


Fig. 3. The apparent reaction order plot for the DBU/promoter/1-hexanol systems

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 CO₂ and CO₂BOLs could be considerably enhanced by adding morpholine and MEA. This study suggests that the catalytic effect of primary amine, MEA, on CO₂ absorption kinetics plays more important role than cyclic secondary amine, morpholine. The suggested promoted CO₂BOLs are promising candidates for reducing the cost of CO₂ removal from flue gas.

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