ISSN: 1813-162X (Print) ; 2312-7589 (Online)

Tikrit Journal of Engineering Sciences

available online at: http://www.tj-es.com

College of Engineering

TJES
Tikrit Journal of Engineering Sciences

Saleh SR, Wiheeb AD. Kinetic study of carbon dioxide reaction with binding organic liquids. *Tikrit Journal of Engineering Sciences* 2019; **26**(1):26-32.

Kinetic Study of Carbon Dioxide Reaction with Binding Organic Liquids

Sanaa Rabie Saleh

Ahmed Daham Wiheeb *

Department of Chemical Engineering
College of Engineering
Tikrit University
Tikrit
Iraq

***Keywords*:**

Carbon dioxide capture
binding organic liquids
amidine
methyldiethanolamine

ARTICLE INFO

Article history:

Received	30 December 2018
Accepted	03 February 2019
Available online	01 March 2019

ABSTRACT

Binding organic liquids are strong base of amidine have been used for CO_2 capture. Up to now, there is no known datum on the reaction kinetics of CO_2 with 1.5-Diazabicyclo [4.3.0] non-5-ene (DBN). In this paper, Kinetics of reaction between CO_2 and DBN/MDEA in 1-Pentanol was performed utilizing the stirred cell reactor with DBN concentration (2 – 2.9 M) and at room temperature. The reaction path was qualified using zwitterion and the termolecular mechanism. From the kinetic datum with DBN concentrations (2 - 2.9 M), it was found that the capturing process happened in a fast reaction system with a second-order reaction kinetics of DBN/MDEA and first order with CO_2. In addition, CO_2 absorption was achieved using gas-liquid contact system. CO_2 absorption rate was $(2 \times 10^{-5} - 2.8 \times 10^{-5}\,\mathrm{kmol/m^2 . sec})$ at DBN concentration (2 – 2.9 M). Finally, it is known that DBN/MDEA/1-Pentanol/CO_2 system is easily switchable and can be used both CO_2 capture and for other applications that require rapid change of medium from nonionic to ionic liquid.

DOI: http://dx.doi.org/10.25130/tjes.26.1.04

دراسة ميكانيكية تفاعل ثاني اوكسيد الكاربون مع السوائل العضوية الملزمة

الخلاصة

السوائل العضوية الملزمة هي قاعدة قوية من الاميدين تستخدم لالتقاط CO_2. لحد الآن، لا توجد بيانات معروفة عن حركية تفاعل ثاني أكسيد الكربون مع (DBN). في هذه الورقة، تم دراسة آلية التفاعل والحركية باستخدام خلية تفاعل مع تركيز (DBN) (2 – 2.9 مولاري) عند درجة حرارة الغرفة. تم وصف مسار التفاعل باستخدام زيوترن والآلية الجزئية. من البيانات الحركية ل DBN بتراكيز M (2 - 2.9) ، وجد أن عملية الامتصاص تحدث في نظام تفاعل سريع مع حركية تفاعل من الدرجة الثانية مع DBN/MDEA و الدرجة الأولى مع CO_2. اضافة الى ذلك فان امتصاص غاز CO_2 كان $(2 \times 10^{-5} - 2.8 \times 10^{-5})$ كيلومول/م.ثا عند تركيز DBN (2.9 – 2 مولاري). اخيرا، كما هو معروف فان نظام DBN/MDEA/1-Pentanol/CO_2 سهل التحول ومن الممكن استخدامه لالتقاط CO_2 وتطبيقات اخرى تحتاج لتغير السريع للوسط من لاايوني الى ايوني.

---

[*] *Corresponding author: E-mail:* chahmed@tu.edu.iq

1. INTRODUCTION

There was a great importance for the increased capture of CO_2 and storage studies over the past decades as a result of the global warming problem. At the present time, all the components of the CO_2 capture industry are available and stored, so far these components have not yet been used in the concept of CO_2 capture and storage. The direct reason behind this, is the operational cost of the absorption/adsorption processes and thus the inability to expand absorption capacities [1-4]. Generally, the process of CO_2 capture requires high power consumption due to the need to re-boil conventional processing. The researchers are focusing their attention on the development of the solvent and finding a new solvent that is less energy intensive when the solvent is regeneration. They proposed several solvents, the most important of which was the binding organic liquids (CO_2BOLs).

List of symbols

M	Molar
CO_2	Carbon dioxide
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene
MDEA	Methyldiethanolamine
CO_2BOLs	Binding organic liquids
MEA	Monoethanolamine
TMG	Tetramethylguanidine
K_{obs}	Observe reaction rate constant
K_1	Forward reaction rate in Eq. (10)
K_2	Forward reaction rate in Eq. (2)
K_3	Reverse reaction rate constant in Eq. (2)
K_4,K_3	Forward reaction rate in Eq. (11) and Eq. (12)
K_{BM}	Deprotonation reaction rate constant of the zwitterion by a base
BM	Base
R_{CO_2}â	Absorption rate
V_G	The volume of gas inside the cell reaction
V_L	The volume of liquid inside the cell reaction
R	Gas constant
T	Temperature
D_{CO_2}	Diffusivity of CO_2 in solvent
H_{CO_2}	Solubility of CO_2 in solvent

CO_2BOLs are a liquid solution consisting of a linear alcohol and strong base of amidine or guanidine that captures CO_2 [5, 6]. When the CO_2 is captured by the CO_2BOLs the output of the CO_2 interaction with CO_2BOLs an amidinium or guanidinium alkylcarbonate depending on the base. Furthermore, CO_2BOLs has a significant advantage compared with the traditional alkalonamine in terms of CO_2-binding enthalpy. Carbonate and bicarbonate salts that produced from CO_2 reaction with alkalonamine have a lower hydrogen bonds compared with the alkylcarbonate salts that produced by the CO_2 reaction with CO_2BOLs [7, 8]. This means that the renewing process of CO_2BOLs requires less energy compared with the traditional amine system. In fact, CO_2BOLs has many advantages compared with the alkalonamine, such as the widely used monoethanolamine (MEA) for CO_2 capture. Specifically, CO_2BOLs has a high boiling point, low vapor pressure, perfect physical and chemical properties, low thermal capacity compared with water and no corrosion problems [8].

Before proposing CO_2 BOLs was to capture CO_2, these solvents were labeled as ″reverse ionic liquids″ and were also bringing to light to be able to replace their polarity using CO_2 [8]. CO_2 is able to switch the polarity of non-ionic solvents to ionic solvents by passing CO_2 to the solvent and returning it to a polarizer by striping of the solvent at a temperature much below the solvent boiling point [6, 9]. Therefore, CO_2BOLs has many applications that have emerged in recent years, while there are a limited number of studies including the study of the kinetics reaction of CO_2BOLs with CO_2 such as: the combination of 1,8-diazabicyclo [5,4,0] undec-7-ene (DBU) amidine base in 1-Hexanol or 1-Propanol [10] and 1,1,3,3-Tetramethylguanidine (TMG) guanidine base in 1-hexanol and 1-propanol with CO_2 [11, 12]. In the light of all these advantages for CO_2BOLs, this paper aimed to study the kinetics and the reaction mechanism of CO_2 reaction with DBN/MDEA in 1-Pentanol.

2. THEORY

2.1. Reaction Pathways

The base of CO_2BOLs does not immediatly react with CO_2 as the amine is formed carbamate. The alcohol group was found in CO_2BOLs first it react to be alkylcarbonic acid, which then protonates the base to form a liquid alkylcarbnate [5, 13]. Where CO_2BOLs interacts with CO_2 and forming alkylecarbonate salts, as shown in the following interaction:

$$\mathrm{DBU} + \mathrm{ROH} + \mathrm{CO_2} \rightarrow [\mathrm{DBUH^+}][\mathrm{ROCO2^-}] \qquad (1)$$

2.2. Zwittrion Mechanism

This mechanism was suggested by Caplow and Danckwert [14, 15]. Zwitterions mechanism assumes that CO_2 interact with amine and form zwitterions as an intermediary:

$$\mathrm{CO}_{\ 2} + \ \mathrm{R`RNH} \xleftrightarrow{K_2,K_3} \mathrm{R`RNH} + \mathrm{COO^-} \qquad (2)$$

The zwitterion passed through deprotonation by base (or bases) BM, forming carbamate as shown in the reaction below:

$$\mathrm{R`RNH^+COO^-} + \mathrm{BM} \xrightarrow{K_{BM}} \mathrm{R`RNCOO^-} + \mathrm{BMH^+} \qquad (3)$$

The reaction rate could be express as folow:

$$R_{CO_2} = \frac{CO_2\,[CO_2][R`RNH]}{1 + \frac{k_3}{k_B[BM]}} \qquad (4)$$

where: k_{BM} [BM]: kinetic constant represents deprotonation of the zwitterions by base such as (H_2O, OH^-, or DBN, or by combination of bases). Eq. (4) displays a fractions order between one and two with respect to DBN concentration. Eq. (4) becomes:

$$R_{CO_2} = K_{obs}[CO_2] \qquad (5)$$

K_{obs}: is the observed reaction rate constant and represent via:

$$K_{obs} = \frac{[R`RNH]}{\frac{1}{k_2} + \frac{k_3}{k_2 k_B[BM]}} \qquad (6)$$

where:

$$k_B[BM] = \frac{k_2 k_B[BM]}{k_3} \qquad (7)$$

When deprotonation is near quick contrast to reverberate interaction in its Eq. (1) ($k_3 << k_B$[BM]) and zwitterion formation is rate-determining, Eq. (5) pick the compose:

$$R_{CO_2} = k_2[CO_2][R`RNH] \qquad (8)$$

Indicating that the reaction is the first order of both the CO_2 and the amine, and hence, overall of the second order.
When zwitterion deprotonation is rate-determining (k_3 >>k_B[BM]) Eq. (5) become:

$$R_{CO_2} = \frac{k_2 k_B[BM]}{K_3}[CO_2][R`RNH] \qquad (9)$$

Similar to Eq. (4), suggested the final expression reaction order between one and two for concentration amines. In the specific state where the concentration of the amine is the most important contribution in zwitterion deprotonation of those base such as H_2O and OH^-, the overall reaction is a second order with the amine [16]. However, the zwitterions is not sufficient to explain the laboratory results when the solvent is composed of two more reactants [17, 18]. So the researchers adjusted termolecular mechanism for blends and found it satisfactory since then [19-21].

2.3. Termolecular Mechanism

This mechanism is offer via Crooks and Donnellan [22]. It is assumed that reaction of CO_2 molecule with amine molecule (DBN) and the base molecule (BM) to form loosely bound encounter complex in a single step as shown in Fig. 1

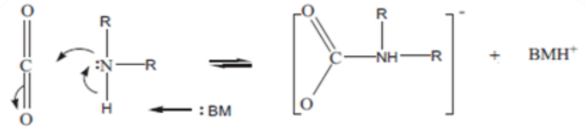

Fig. 1. Single step reaction.

The net reaction of this mechanism is:

$$CO_2 + RNH_2 \ldots BM \xleftrightarrow{K_1,K_2} RNHCOO^- \ldots . BMH^+ \qquad (10)$$

(BM) is represents either one of two reactants (such as, two various amine for a dual blend) and dissolvent molecule. BM stands for base and $RNH_2$is the amine. Regardless of the amine. The controlling base may be water or ion hydroxyl in aqueous systems or a liner alcohol in non-aqueous solution. This mechanism assumes the correlation between the amine molecule and CO_2 molecule and transfer the proton as shown in Fig. 1, whereas the binding middle part weak and transformed into reactors. The remaining part interacts with one other amine and forms ionic productions. As in reactions below:

$$RNHCOO^- \ldots BMH^+ + RNH_2 \overset{K_3}{\rightarrow} RNHCOO^- + {RNH_3}^+ + BM \qquad (11)$$

$$RNHCOO^- \ldots BMH^+ + H_2O \overset{K_4}{\rightarrow} {HCO_3}^- + {RNH_3}^+ + BM \qquad (12)$$

Utilize the pseudo first – steady state on the ionic intermediary created in Eq. (10) [11, 23]. The reaction rate in Eq. (11) and (12) could be written:

$$r_2 = \frac{k_1 k_3\,[CO_2][RNH_2 \ldots BM][H_2O]}{k_2 + k_3[RNH_2] + k_4[H_2O]} \qquad (13)$$

$$r_3 = \frac{k_1 k_4\,[CO_2][RNH_2 \ldots BM][H_2O]}{k_2 + k_3[RNH_2] + k_4[H_2O]} \qquad (14)$$

Assuming that [RNH_2…BM] = K[RNH_2], where K is a fixed and the overall reaction rate is:

$$R_{CO_2} = r_2 + r_3 \qquad (15)$$

Thus the R_{CO2} is:

$$R_{CO_2} = \left(\frac{K\,k_1 k_3\,[RNH_2] + K\,k_1 k_3[H_2O]}{k_2 + k_3[RNH_2] + k_4[H_2O]}\right)[RNH_2][CO_2] \qquad (16)$$

The interaction in Eq. (10) is a quick, two-way interaction where the result is intermediary and short. So that k_1 and k_2 much larger than $k_3$and k_4 in Eqs. (11) and (12), So it can be assumed that k_2 is dominate on $k_3[RNH_2]$ and $k_4[H_2O]$ to simplify the Eq. (16) by K k_1, $k_3 = k_{RNH_2}$and K k_1, $K_4 = k_{H_2O}$ to obtain reaction rate:

$$R_{CO_2} = \left(k_{RNH_2}[RNH_2] + k_{H_2O}[H_2O]\right)[RNH_2][CO_2] \qquad (17)$$

replacing water with a linear alcohol, Eq. (12) becomes as follows [24, 25]:

$$RNHCOO^- \ldots BMH^+ + ROH \rightleftharpoons {RCO_3}^- + {RNH_3}^+ + BM \qquad (18)$$

And reaction rate could be expressed:

$$R_{CO_2} = \left(k_{RNH_2}[RNH_2] + k_{ROH}[ROH]\right)[RNH_2][CO_2] \qquad (19)$$

For pseudo first order condition wherever the solvent (i.e amine or amine blend and liner alcohol) would be in overabundance, the reaction rate could be represented as in Eq. (20):

$$R_{CO_2} = K_{obs}\,[CO_2] \tag{20}$$

Where:
K_{obs} is the observed reaction rate constant and could be expressed as:

$$K_{obs} = \left(k_{RNH_2}[RNH_2] + k_{ROH}[ROH]\right)[RNH_2] \tag{21}$$

Whether the amine (DBN blend in this research) is the controlling base, the interaction was ranked second with the amine and Eq. (21) becomes:

$$K_{obs} = k_{DBN}[DBN]^2 \tag{22}$$

And the overall reaction rate is:

$$R_{CO_2} = K_{DBN}\,[DBN]^2\,[CO_2] \tag{23}$$

If alcohol is the controlling base, reaction rate constant becomes:

$$K_{obs} = k_{ROH}[ROH][DBN] \tag{24}$$

And the interaction was ranked second with respect to [DBN] and the overall reaction rate is:

$$R_{CO_2} = K_{ROH}\,[ROH][DBN][CO_2] = K\,[CO_2][DBN] \tag{25}$$

where: $K = k_{ROH}[ROH]$.

3. EXPERIMENTAL WORK

3.1. Materials

1,5-Diazabicyclo [4.3.0] non-5-ene (DBN) (purity ≥ 98%), Methyldiethanolamine (MDEA) (purity 99%) and 1-Pentanol (purity 99%) used in experiments which were purchased from TCL. Carbon dioxide and nitrogen gases with a pureness of 99.95% from SDI Samarra .

3.2. Experimental Procedure

The metering device is consisting of a glass stirred cell 100 ml, and a pressure transducer (0 – 1) bar. Fig. 2 illustrates schematically the diagram of the stirred cell set up. The CO_2 reaction kinetics are measured for the DBN/MDEA/1-Pentanol where 40 ml of solvent was placed at the designed concentration in the reactor-cell and the solution was mixed by stirring vigorously. Pure CO_2 gas was controlled by a flow meter and then pumped into the reactor after ensuring closing all outlets reactor-cell. This is starting point the experiment and the pressure starts to decrease. The pressure was measured by the pressure transducer during each half minute. The recorded partial pressure of CO_2 (P_{CO2}) was drawn with time and inclination represented ($-\frac{dP_{CO_2}}{dt}$) by using the relationship :

$$R_{CO_2}\hat{a} = -\left[\frac{V_G}{V_L RT}\,\frac{dP_{CO_2}}{dt}\right] \tag{26}$$

Where: $R_{CO_2}\hat{a}$: is the reaction rate of CO_2 (kmol/m^2. s), V_G: is the volume of gas inside reactor (m^3), V_L: is the liquid volume inside the reactor (m^3), R: is gas constant (m^3 kPa/kmol. K), T: is temperature (K), t: is time (sec), P_{CO_2}: is partial pressure of CO_2 in bulk gas phase (kPa) and $-\frac{dP_{CO_2}}{dt}$: represent the slope which represents the absorption rate.

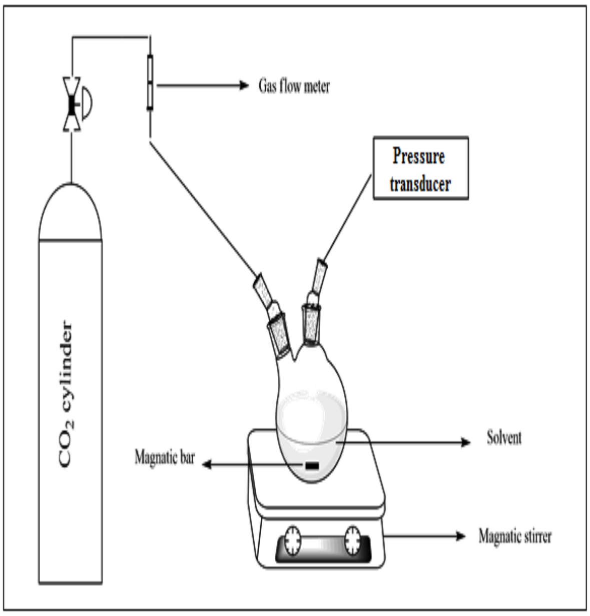

Fig. 2. The schematic of the stirred-cell apparatus.

The calculated R_{CO_2} was used to evaluate the observed reaction rate constant (k_{abs}) using the following relationship:

$$R_{CO_2} = [CO_2]\sqrt{D_{CO_2}k_{abs}} = P_{CO_2}H_{CO_2}\sqrt{D_{CO_2}k_{obs}} \tag{27}$$

where: $[CO_2]$: is the interfacial concentration of CO_2 (kmol/m^3), D_{CO_2}: is diffusivity of CO_2 in solvent (m^2/sec) and H_{CO_2}: is solubility of CO_2 in solvent (kmol/m^3. kPa).

4. RESULTS AND DISCUSION

The CO_2 interaction with DBN/MDEA/1-Pentanol is studied at room temperature with DBN concentrations of (2 - 2.9) M by calculating the CO_2 reaction rate with DBN/MDEA/1-Pentanol mixture. As shown in fig. 3, the reduction of the CO_2 partial pressure was gradually over time indicates the CO_2 interaction with DBN/MDEA/1-Pentanol. The reaction rate of CO_2 $\left(R_{CO_2}\hat{a}\right)$ were illustrated in Table 1. R_{CO_2} was plotted against $[DBN]_0$ at room temperature as shown in Fig. 4. Using linear regression, it found that the R-squared value is poor ($R^2 = 0.9$) and the relationship is not-linear. Therefore, the system is not the first order [16] .

Table 1
Reaction rate of CO_2 $\left(R_{CO_2}\hat{a}\right)$ in $[DBN]_0$ at room temperature.

[DBN]₀, KPa/m³	**P_{CO_2}, KPa**	**$R_{CO_2} \times 10^5$, kmole/m².sec**
2	20	2.26
2.3	15	2.45
2.5	10	2.63
2.7	8	2.71
2.9	6	2.78

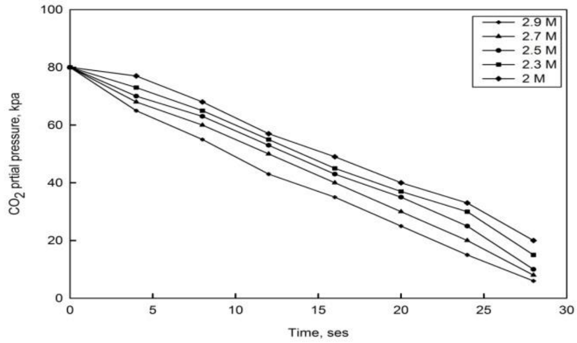

Fig.3. CO_2 Partial pressure of DBN/MDEA/1-Pentanol with different concentration of DBN.

Fig. 5 shows a plot of $(R_{CO_2}\hat{a})$ against the partial pressure of CO_2 $(R_{CO_2}\hat{a})$ at room temperature. If it is assumed that the reaction is the first-order and is the slope for the plot of Fig. 4 which is equal to 2.64×10^{-6} kmol/m².s.kPa. This slope represents $H_{CO_2}\sqrt{D_{CO_2}k_{obs}}$ at room temperature. Using the solubility and the diffusivity values of CO_2 according to Versteeg and Van Swaaij [26], (i.e $H_{CO_{2-}\,solvent} = 0.019\ \mathrm{kmol/kPa.m^3}$ and $D_{CO_2-solvent} = 1.87\ \times 10^{-11}\ \mathrm{m^2/sec}$, k_{obs} was found to be equal $1025\ \mathrm{sec^{-1}}$.

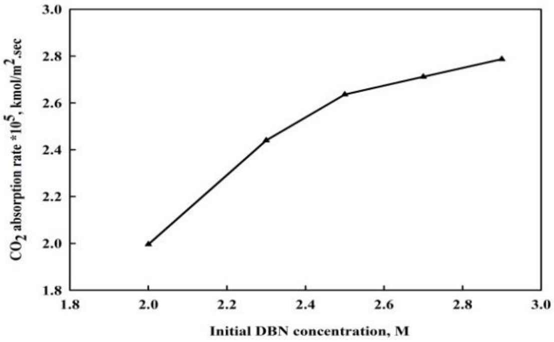

Fig. 4. R_{CO_2} vs. $[DBN]_0$ at 308K.

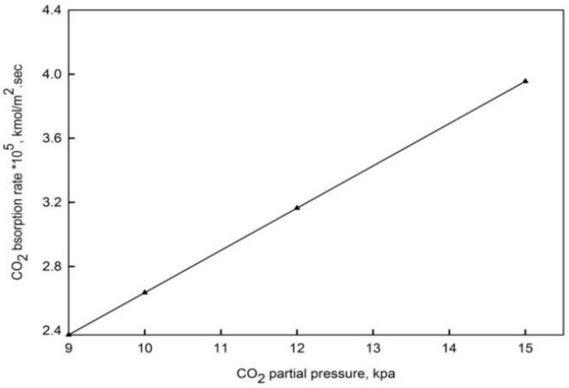

Fig.5. R_{CO_2} vs. P_{CO_2}at room temperature ($[DBN]_0 =$ 2.9 M).

A comparison with other previous studies was revealed in Table 2. It could be noticed that this work value of $\mathbf{k_{obs}}$ is higher than that reported in the literature because DBN concentration was 2.9 M higher than the other studies

Table 2
Values of k_{obs} for CO_2- binding organic liquids at 308K.

Solvent	**Wt%**	**k_{obs}, sec**	**Ref.**
DBN/1-Hexanol	20	891	[27]
DBN/1-Propanol	15	763.1	[28]
DBN/MDEA/1-Pentanol	38	1025	this work

Impose second-rank kinetics for DBN, and later, overall third-rank kinetics, Eq. (27) could be appeared as:

$$R_{CO_2}\hat{a} = H_{CO_2}P_{CO_2}\sqrt{D_{CO_2}K_2[DBN]_0^2} \tag{28}$$

Fig. 6 shows a plot of R_{CO_2}/P_{CO_2} against the DBN concentration. The slope of the line in Fig. 6 appears, $H_{CO_2}\sqrt{D_{CO_2}k_2}$, at room temperature and which is equal to $3.9\ \times 10^{-6}\ \mathrm{m/kPa.sec}$. Familiarity the solubility values and diffusivity of CO_2 [26], k_2 was found to be equal to $6532\ \mathrm{m^3/kmol.sec}$, which is higher than the values in the previous studies as shown in Table 3. The reason for the low rate reaction constant (k_2) is the inaccuracy of the values of physical properties in this study and the other reasons are the difference in the practical experiments used to study the kinetics of the reaction (such as the inverted cell and stalled flow technique) .

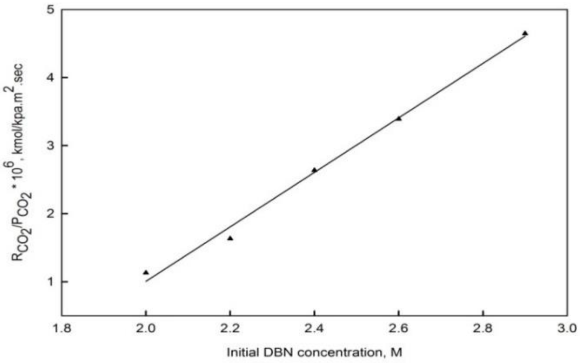

Fig. 6. (R_{CO_2}/P_{CO_2}) vs. $[DBN]_0$ at room temperature.

Table 3
Kinetic comparison of different CO_2 capture.

Solvent	**Reaction order**	**k_2, m³/kmol.sec**	**Ref.**
DBN/MDEA/1-Pentanol	2	6532	This work
DBU/1-Hexanol	1.21	627	[10]
AMP	1.15	502	[29]
MEA	1.04	5545	[29]

It is important to note that in the event the two-step zwitterions are suitable, k_{obs} can be written as follows:

$$k_{obs} = \frac{k_2\,[DBN]}{1 + \dfrac{k^{-1}}{k_{DBN}[DBN] + k_{H_2O}[H_2O] + k_{OH^{-1}}\,[OH^{-1}]}} \quad (29)$$

The results show that the reliability of the capturing rate on the DBN concentration was second rank. It is clear that both the zwitterion formation and deprotonation are significant in the overall reaction. On the top of all, the DBN contribution to deprotonation is a task. This is compatible with other studies [30]. Observe reaction rate constant (k_{obs}) equal to k_2 $[DBN]^2$ when termolecular mechanism is suitable. It is clear that DBN is the controlling base. Thus k_{obs} is equal to k_{DBN} $[DBN]^2$. Therefore, the CO_2/DBN reaction system could be appear evenly well by both zwitterion and termolecular mechanism

5. CONCLUSIONS

In this paper, the kinetic reaction of the CO_2 reaction with CO2BOLs system (DBN/MDEA/1-Pentanol) at concentrations (2.0 – 2.9 M) and room temperature was performed in a stirred-cell reactor. It was found that the increase the initial concentration values of DBN give increase in the capturing rates of CO_2. The two-steps zwitterion and the single-step termolecular mechanism were used to describe the carbonate formation. The CO_2 reaction with DBN/MDEA/1-Pentanol system was found to be of the second order. The observed reaction rate constant was evaluated at 308 K and its value 1025 sec^{-1} which is within the range of the previous studies.

REFERENCES

[1] Herzog HJ. Peer reviewed: what future for carbon capture and sequestration?: *ACS Publications*; 2001.

[2] Herzog HJ. Scaling up carbon dioxide capture and storage: From megatons to gigatons. *Energy Economics* 2011;**33**:597-604.

[3] Wiheeb AD, Shamsudin IK, Ahmad MA, Murat MN, Kim J, Othman MR. Present technologies for hydrogen sulfide removal from gaseous mixtures. Reviews in *Chemical Engineering* 2013;**29**:449-70.

[4] Wiheeb A, Helwani Z, Kim J, Othman M. Pressure swing adsorption technologies for carbon dioxide capture. *Separation & Purification Reviews* 2016;**45**:108-21.

[5] Heldebrant DJ, Yonker CR, Jessop PG, Phan L. Organic liquid CO_2 capture agents with high gravimetric CO_2 capacity. *Energy & Environmental Science* 2008;**1**:487-93.

[6] Heldebrant DJ, Koech PK, Rainbolt JE, Zheng FR. CO_2-binding organic liquids, an integrated acid gas capture system. *Energy Procedia* 2011;**4**:216-23.

[7] Peeters A, Faaij A, Turkenburg W. Techno-economic analysis of natural gas combined cycles with post-combustion CO_2 absorption, including a detailed evaluation of the development potential. *International Journal of Greenhouse Gas Control* 2007;**1**:396-417.

[8] Heldebrant DJ, Yonker CR, Jessop PG, Phan L. CO_2-binding organic liquids (CO_2 BOLs) for post-combustion CO_2 capture. *Energy Procedia* 2009;**1**:1187-95.

[9] Jessop PG, Heldebrant DJ, Li X, Eckert CA, Liotta CL. Green chemistry: Reversible nonpolar-to-polar solvent. *Nature* 2005;**436**:1102.

[10] Öztürk MÇ, Ume CS, Alper E. Reaction Mechanism and Kinetics of 1, 8-Diazabicyclo [5.4. 0] undec-7-ene and Carbon Dioxide in Alkanol Solutions. *Chemical Engineering&Technology* 2012;**35**:2093-8.

[11] Ozturk MC, Orhan OY, Alper E. Kinetics of carbon dioxide binding by 1, 1, 3, 3-tetramethylguanidine in 1-hexanol. *International Journal of Greenhouse Gas Control* 2014;**26**:76-82.

[12] YÜKSEL Ö, ÖZTÜRK MÇ, ŞEKER A, ALPER E. Kinetics and performance studies of a switchable solvent TMG (1, 1, 3, 3-tetramethylguanidine)/1-propanol/carbon

[13] dioxide system. *Turkish Journal of Chemistry* 2015;**39**:13-24.

[14] Mathias PM, Afshar K, Zheng F, Bearden MD, Freeman CJ, Andrea T, et al. Improving the regeneration of CO_2-binding organic liquids with a polarity change. *Energy & Environmental Science* 2013;**6**:2233-42.

[15] Caplow M. Kinetics of carbamate formation and breakdown. *Journal of the American Chemical Society* 1968;**90**:6795-803.

[16] Danckwerts P. The reaction of CO_2 with ethanolamines. *Chemical Engineering Science* 1979;**34**:443-6.

[17] Sutar PN, Jha A, Vaidya PD, Kenig EY. Secondary amines for CO_2 capture: A kinetic investigation using N-ethylmonoethanolamine. *Chemical engineering Journal* 2012;**207**:718-24.

[18] Ali SH. Kinetics of the reaction of carbon dioxide with blends of amines in aqueous media using the stopped-flow technique. *International Journal of Chemical Kinetics* 2005;**37**:391-405.

[19] Vaidya PD, Kenig EY. A Study on CO_2 Absorption Kinetics by Aqueous Solutions of N, N-Diethylethanolamine and N-Ethylethanolamine. *Chemical Engineering&Technology* 2009;**32**:556-63.

[20] Orhan OY, Alper E. Kinetics of carbon dioxide binding by promoted organic liquids. *Chemical Engineering & Technology* 2015;**38**:1485-9.

[21] Ozkutlu M, Orhan OY, Ersan HY, Alper E. Kinetics of CO_2 capture by ionic liquid—CO_2 binding organic liquid dual systems. *Chemical Engineering and Processing: Process Intensification* 2016;**101**:50-5.

[22] Ume CS, Ozturk MC, Alper E. Kinetics of CO_2 absorption by a blended aqueous amine solution. *Chemical Engineering & Technology* 2012;**35**:464-8.

[23] Crooks JE, Donnellan JP. Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution. *Journal of the Chemical Society, Perkin Transactions* 2 1989:331-3.

[24] Orhan OY, Alper E. Kinetics of reaction between CO_2 and ionic liquid-carbon dioxide binding organic liquid hybrid systems: Analysis of gas-liquid absorption and stopped flow experiments. *Chemical Engineering Science* 2017;**170**:36-47.

[25] Sada E, Kumazawa H, Han Z, Matsuyama H. Chemical kinetics of the reaction of carbon dioxide with ethanolamines in nonaqueous solvents. *AIChE Journal* 1985;**31**:1297-303.

[26] Vaidya PD, Kenig EY. Termolecular Kinetic Model for CO_2-Alkanolamine Reactions: An Overview. *Chemical Engineering& Technology* 2010;**33**:1577-81.

[27] Versteeg GF, Van Swaaij WP. Solubility and diffusivity of acid gases (carbon dioxide, nitrous oxide) in aqueous alkanolamine solutions. *Journal of Chemical & Engineering Data* 1988;**33**:29-34.

[28] Orhan OY, Tankal H, Kayi H, Alper E. Kinetics of CO_2 capture by carbon dioxide binding organic liquids: Experimental and molecular modelling studies. *International Journal of Greenhouse Gas Control* 2016;**49**:379-86.

[29] Tankal H, Orhan ÖY, Alper E, Özdoğan T, Kayi H. Experimental and theoretical investigation of the reaction between CO $ _ {2} $ and carbon dioxide binding organic liquids. *Turkish Journal of Chemistry* 2016;**40**:706-19.

[30] Alper E. Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1-propanol and carbon dioxide. *Industrial & Engineering Chemistry Research* 1990;**29**:1725-8.

[31] Li J, Henni A, Tontiwachwuthikul P. Reaction kinetics of CO_2 in aqueous ethylenediamine, ethyl ethanolamine, and diethyl monoethanolamine solutions in the temperature range of 298− 313 K, using the stopped-flow technique. *Industrial & Engineering Chemistry Research* 2007;**46**:4426-34.