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ENVIRONMENTAL PROGRESS & SUSTAINABLE ENERGY

ORIGINAL RESEARCH

Remediation and Treatment

CO_2 capture by aqueous mixture of 1,8-diaminooctane promoted MDEA and MEA: CO_2 loading, kinetic study, and regenerability

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Abstract

The main aim of the current research is to determine the kinetics, CO_2 loading, absorption rate, and regenerability of 1,8-diaminooctane (DAO) promoted MEA and MDEA solvents in a lab-scale experimental setup. The DAO is a linear diamine molecule with a long distance between amine groups and low vapor pressure. In the first step, the CO_2 loading and rate of solutions are measured in a well-mixed isothermal batch reactor at the CO_2 pressure range 0.2–1.2 bar, the temperature range of 303–313 K, and promoter volume fraction of 0%–10%. It appears the equilibrium loading of MEA is less sensitive to an increase in dissolved CO_2 concentration compared to the promoted samples due to the stability of MEA carbamate. Afterward, to investigate the regenerability of the prepared solutions, the effective loading of samples is determined through the designed regeneration test. The results show that the addition of a small quantity of 1,8-diaminooctane reveals a considerable enhancement in the rate and CO_2 loading of the base solutions. The maximum loading of 0.95 mol CO_2 per mol amine is obtained by 1,8-diaminooctane promoted MDEA (10%) at equilibrium temperature 313.15 K, and pressure 1.01 bar.

KEYWORDS
absorption rate, CO_2 solubility, diaminooctane, effective loading

1 | INTRODUCTION

Currently, the energy supply, sustainable development, and climate change are the main challenges in the world. Applying fossil fuels as a non-renewable resource to generate energy has increased the concentration of greenhouse gases in the atmosphere. The greenhouse gases absorb and emit radiant energy toward the Earth within the thermal infrared range. At the equilibrium condition, this process maintains the Earth's temperature at the desired level and makes it suitable for plants, animals, and humans. However, increasing the concentration of greenhouse gases in the atmosphere decreases the rate of heat emission from the earth and results in climate change.[1,2] It promotes water deficits and light stress and imposes harmful effects on the earth.[3]

Among the greenhouse gases, carbon dioxide has a high emission rate and lifetime in the atmosphere, so it has a significant outcome on worldwide warming.[4] In this regard, there is a significant interest to develop efficient technologies to capture the produced CO_2 in industrial resources such as power stations, chemical and petrochemical plants, gas and oil refineries, and cement production plants.[5] Among the developed technologies, the CO_2 absorption by alkanolamines such as MEA, DEA, and MDEA is more relevant and has been commercialized to separate CO_2 from gas mixture in industrial plants.[6,7] However, the conventional alkanolamines cannot fulfill the desired absorption specifications including high reactivity, capacity, selectivity, stability, regenerability, and low heat of absorption. In this regard, the promotion of alkanolamines by super effective chemicals is a practical route to achieve the desired

performance. The promoter selection requires a fundamental understanding of chemistry and reaction kinetic to determine solvent reactivity, stability, CO_2 solubility, and interactions. Among common promoters, diamines with two amine functional groups in a molecule have been proposed for the promotion of conventional alkanolamines.[8] At the moment, the piperazine-activated MDEA is used to remove CO_2 and H_2S from the natural gas stream in gas absorption plants.[9] Piperazine is a cyclic diamine that consists of two amine functional groups and could enhance the absorption capacity and rate of MDEA. Mudhasakul et al. showed that the solution contains 5% piperazine and 45% MDEA is the most suitable case to apply in the gas absorption units.[10] Xiao investigated the potential of kinetic promoters including aliphatic linear and cyclic diamines in CO_2 absorption and desorption processes.[8] The effect of additives on the chemical speciation including carbamate and bicarbonate was investigated using NMR results. It was claimed that absorption rate, equilibrium loading, and cyclic capacity were enhanced in the presence of diamine promoters in the aqueous solution of MEA. Yu et al. investigated the kinetic and absorption capacity of different diamines including ethylenediamine, propanediamine, methylpropane diamine, methylethylenediamine, and diethylamino-ethylamine in a bubble column absorber.[11] The results showed that all the studied diamines had higher CO_2 absorption and rate than the monoamines. In addition, increasing the carbon chain length between diamine groups increased the initial absorption rate in diamines considerably. Although the replacement of the primary amine functional group with one tertiary group had a small effect on the equilibrium loading, it decreased the initial absorption rate significantly. Singh et al. reported that increasing the chain length between amine functional groups in diamines enhanced the CO_2 loading of solution due to the decline of the stability of the carbamate.[12] Azhgan et al. performed a set of experiments to compare the CO_2 loading and regenerability of MEA and MDEA promoted by methyl diaminopantane (MDAP) and diaminohexane (DAH) at low-pressure conditions.[13] Despite similar carbon numbers, DAH was more effective to enhance the CO_2 loading and rate of MEA and MDEA in comparison to DAMP. Hamidi et al. investigated the CO_2 solubility in the ternary mixtures of MDEA, MEA, and methyldiaminopentane (MDAP).[14] The experimental results showed that increasing MDAP concentration in the mixture improved the CO_2 solubility and reactivity. The results of cyclic loading showed that the base and promoted solvents released about 80% of absorbed CO_2 through regeneration tests at 343 K. In general, the thermal degradation of solvent has a significant impact on operational cost and induces operational difficulties in the CO_2 absorption units such as raising foaming tendency and contributing to corrosion.[15] Huang et al. compared the thermal stability of diamines, amino acid salt, and alkanolamines.[16] The results showed that diamines are more thermally stable compared to the alkanolamines and amino acid salts. In addition, for alkanolamine and diamine structural isomers, the primary amines were greatly more stable than the secondary amines.

Although many studies have been conducted on the CO_2 solubility of diamines and alkanolamines such as MEA, DEA, and MDEA, further understanding of molecular interaction, absorption rate, and capacity of promoted alkanolamines by diamines is needed. In this regard, the main objectives of the current research are to investigate the equilibrium loading, initial absorption rate, and effective loading of CO_2 in binary blends of MDEA, MEA, and 1,8-diaminooctane (DAO). Based on the presented data in the literature, the diamine molecules such as diaminooctane are good candidates for CO_2 absorption due to a long chain distance between amine groups, thermal stability, and linear structure. The presented study has been organized into four sections. In the Section 2, the supplied materials, designed set up, and considered testing procedure are briefly cleared. The CO_2 loading and regenerability of binary mixtures are presented in the Section 3. The conclusions are presented in the Section 4.

2 | EXPERIMENTAL METHOD

2.1 | Materials

The 1,8-diaminooctane, CAS NO 110-60-1, was provided from MERCK Chemical Company. The MEA and MDEA, Catalog NO 5593-4400 and 5696-4105, were supplied from DAEJUNG Company. Besides, the CO_2 cylinder with 99.9% purity was provided by domestic producers. Table 1 shows the physical properties of DAO, MDEA, and MEA.[17]

2.2 | Experiment procedure

In this section, the designed experimental setup to measure the absorption rate and the CO_2 loading of prepared mixtures is presented briefly. The amine solutions are prepared by dissolving the appropriate quantity of amines in volumetric glassware and making up to volume with deionized water. The total concentration of 2.5 mol L^{-1} is selected for the solutions. Figure 1 shows the planned setup to measure the CO_2 loading of samples. The developed setup consists of a glass reactor, a magnetic stirrer, pressure and temperature transmitters, a water bath, a data logger, and a vacuum pump. The volume of the applied reactor is 250 cc. The reactor is placed in the isothermal water bath to regulate the temperature at the desired level. The reactor pressure is measured by an industrial transmitter manufactured by Trafag Company. The range and accuracy of the applied pressure transmitter are ±0.5% and 0–2.5 bar. The measured pressure is saved in the computer using a data logger manufactured by Advantech Company. To obtain the inherent reaction rate and elimination of mass transfer resistance in the gas and liquid phases, pure CO_2 is applied in the reactor, and the liquid is stirred at 300 rpm by a magnetic stirrer.

To perform tests, the air is removed from the reactor through a two-step procedure containing injection of CO_2 over 30 s and discharging the gas from the reactor by a vacuum pump. In the second

step, the supplied CO_2 gas is injected into the batch reactor and the vessel pressure is regulated at an adequate level. In the next step, the prepared aqueous blend feeds into the batch reactor and the vessel pressure is logged. The volume of applied solvent into the reactor is 5 cc. Using the ideal gas assumption, the CO_2 loading is obtained as follows:

$$\alpha = \frac{(V_R - V_S)}{RT} \frac{\Delta P_{CO_2}}{N_s}, \quad (1)$$

Where R, V_R, V_S, T, and N_S are the gas constant, the effective volume of bath reactor, the volume of applied solvent, equilibrium temperature, and moles of applied solvent in the setup, respectively. To examine the regenerability of the rich solution and to obtain the effective loading of samples, the blend is saturated at 30°C and then the temperature is raised to 70°C to release the absorbed CO_2. The effective loading is computed as follows:

$$\epsilon = \frac{(V_R - V_S)}{RN_s} \left(\frac{P_{CO_2}}{T}\bigg|_{343} - \frac{P_{CO_2}}{T}\bigg|_{303} \right), \quad (2)$$

TABLE 1 The physical properties of DAO, MDEA and MEA

Properties	DAO	MEA	MDEA
Physical state	**Solid**	**Liquid**	**Liquid**
Molecular weight (gr mol^{-1})	144.26	61.08	119.16
Melting point (°C)	50	10.3	−21
Boiling point (°C)	225	170	247
Vapor pressure at 20°C (Pa)	5	60	1
Solubility in water (g l^{-1})	534	Miscible	Miscible
Density at 20°C (gr ml^{-1})	0.98	1.01	1.04

3 | RESULTS AND DISCUSSIONS

3.1 | Setup accuracy

To investigate the accuracy of setup and planned test method, the CO_2 loading of MDEA solution at total concentration 2.5 M is measured at equilibrium temperature 40°C and compared with the available data in the literature (see Figure 2).[18,19] The presented data in Figure 2 reveals that there is an acceptable agreement between the measured and reported CO_2 loading in the literature.

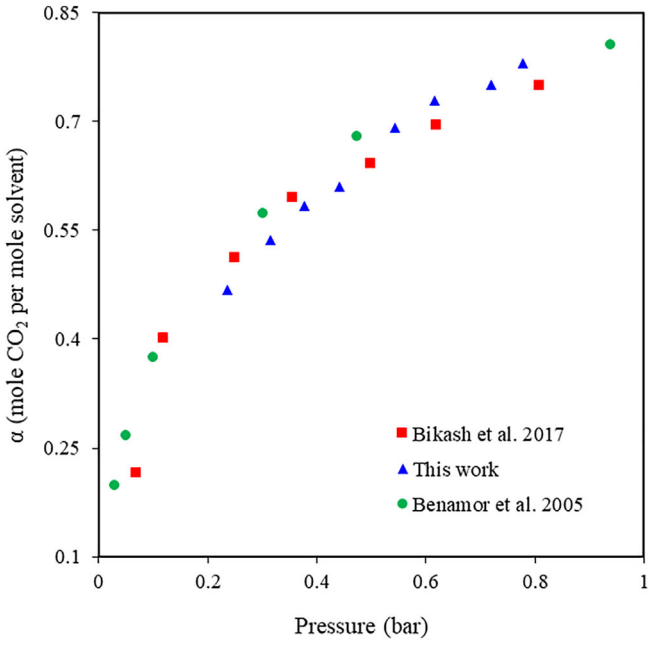

FIGURE 2 CO_2 solubility of aqueous solution of MDEA at 40°C

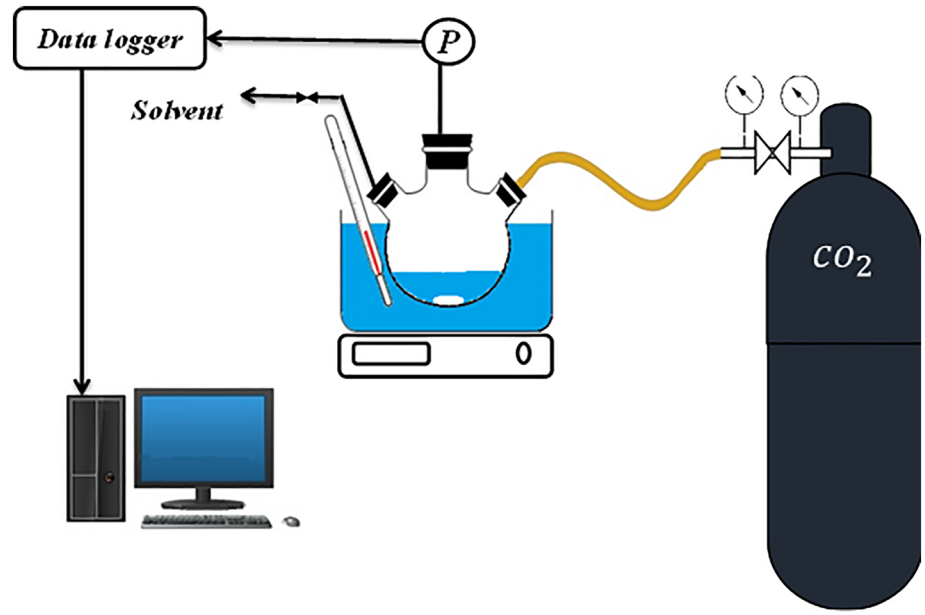

FIGURE 1 The schematic diagram of experimental setup

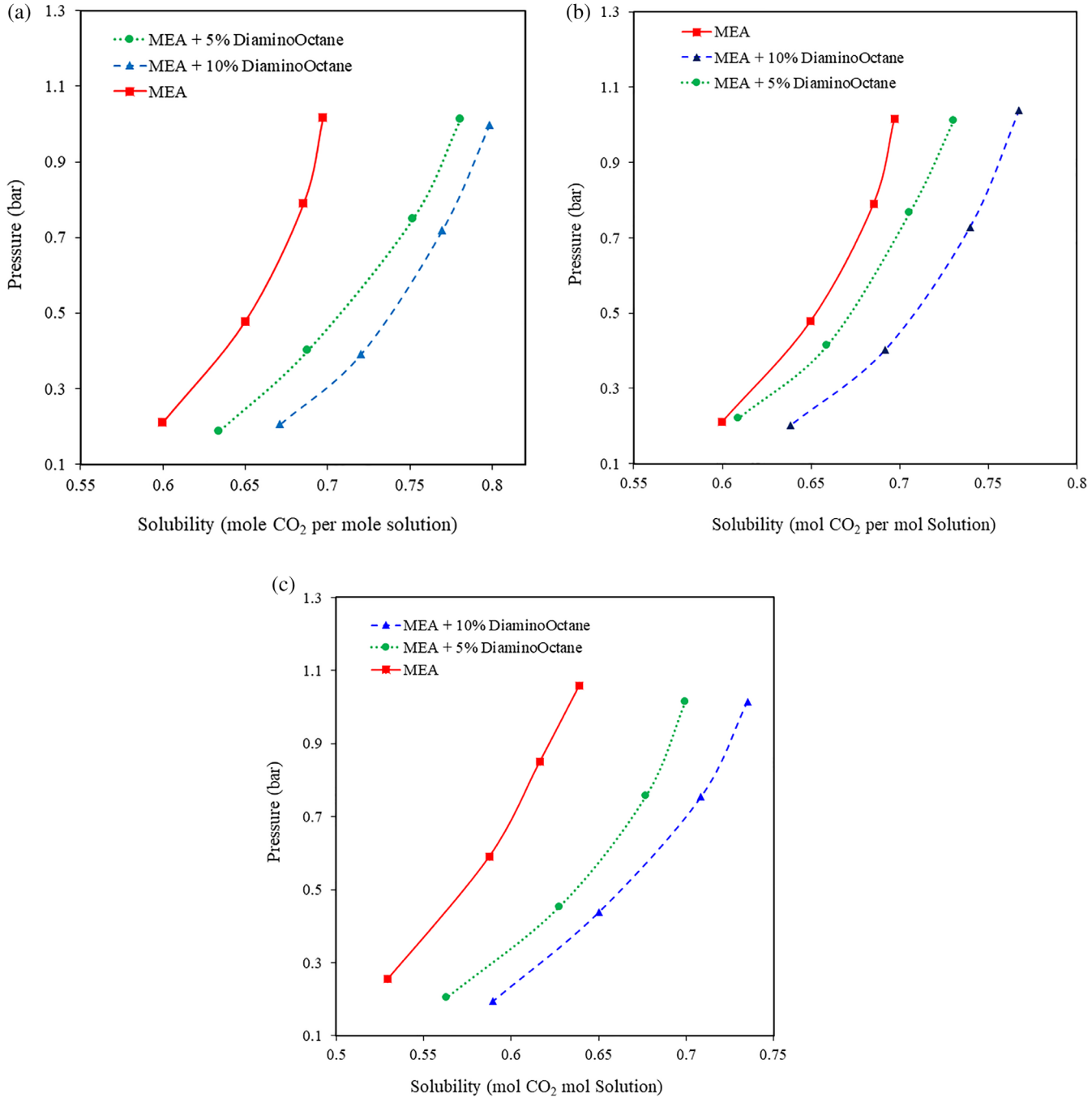

FIGURE 3 CO_2 solubility in mixture of MEA and DAO at (a) 20°C, (b) 30°C and (c) 40°C

3.2 | MEA promoted by DAO

This section presents the CO_2 loading of MEA and MEA promoted by DAO at the pressure range of 0.2 to 1.2 bar and promoter volume fraction of 0%–10%. Conventional alkanolamines such as MEA and MDEA are industrially approved for CO_2 absorption. Unlike diaminooctane, alkanolamines are cheap, safe to handle, and available. Thus, DAO has been considered as the promoter to enhance the rate and capacity of MEA and MDEA. Figure 3a–c presents the CO_2 loading of prepared mixtures at temperatures 293, 303, and 313 K. From the kinetic viewpoint, the CO_2 molecules react with the solvent in the liquid phase. Increasing CO_2 partial pressure in the gas phase enhances the CO_2 solubility in the liquid and changes the reaction (1) toward the right side. It appears the equilibrium loading of MEA is less sensitive to an increase in dissolved CO_2 concentration compared to the promoted samples due to the stability of MEA carbamate. This effect is reduced with decreasing concentration of MEA and increasing DAO concentration in the blend. The long-chain length between functional groups in the DAO molecule decreases the interaction of functional groups to absorb CO_2 and enhances the reactivity and CO_2

loading. It appears that the CO_2 absorption capacity of MEA and MEA promoted by 5% and 10% DAO at the equilibrium pressure 1 bar and temperature 20°C are 0.696, 0.772, and 0.786 mol CO_2 per mol solution, respectively. Increasing promoter volume fraction in the MEA solution up to 5% and 10% enhances the CO_2 loading by 10.9% and 12.9% compared to the MEA solution. Also, the CO_2 solubility in MEA and MEA promoted by 5% and 10% DAO at equilibrium pressure 1 bar and temperature of 40°C are 0.632, 0.678, and 0.698 mol CO_2 per mol solution, respectively. Although applying high-temperature shifts the reaction of CO_2 and amine molecules toward the CO_2 regeneration and reduces the equilibrium loading, it increases the kinetic constant and significantly improves the absorption rate from the kinetic viewpoint.

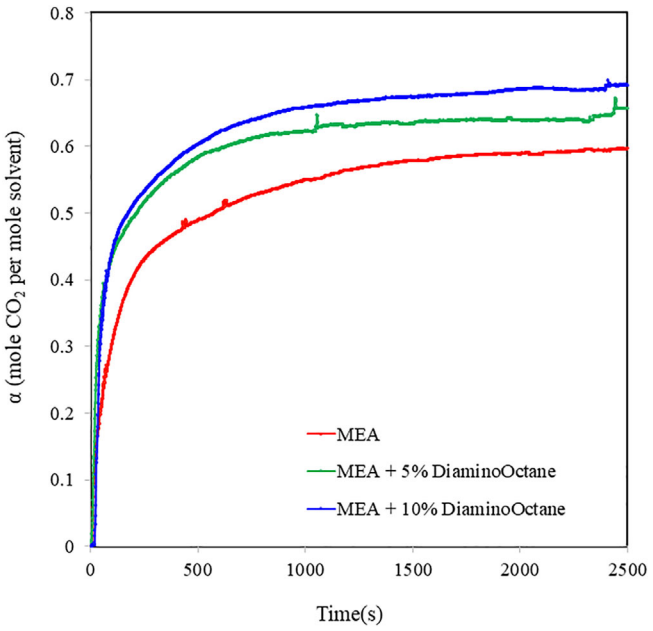

FIGURE 4 CO_2 absorption rate of aqueous solutions of MEA and mixture of MEA and DAO at 20°C

Figure 4 presents the CO_2 loading of MEA, and MEA promoted by 5% and 10% DAO solutions at temperature 20°C during the test run. In general, the rate of CO_2 absorption could be controlled by mass transfer or reaction kinetics limitations. Since the applied gas in the reactor is pure and the liquid phase is stirred continuously, the mass transfer resistance in the gas and liquid phases are negligible and CO_2 absorption is under kinetic control. It appears the CO_2 loading increases during the test run and approaches the equilibrium value in all samples. The maximum absorption rate is appeared at the start-up condition because of higher CO_2 partial pressure. Although the type of functional groups in MEA and DAO are similar, the attendance of two reactive functional groups permits the absorption of two molecules of CO_2 per one molecule of DAO. The results show that the initial reaction rate of CO_2 in MEA and MEA promoted by 5% and 10% DAO within the initial 50 s of CO_2 absorption are 0.009, 0.011 and 0.013 mol s^{-1} cc^{-1}, respectively. To determine the rate of reaction, the concentration of CO_2 in the gas phase is calculated during the test run based on the partial pressure of CO_2 in the reactor. Then, the slope of the curve of CO_2 concentration versus time is determined and divided into the volume of applied solvent in the reactor. In general, the solution of MEA promoted by DAO has a higher reactivity compared to MEA at the same equilibrium temperature. A faster absorption rate removes the same CO_2 within a smaller amount of packing, thereby reduces the capital cost.

In this part, the effective loading of solutions is measured based on the considered regeneration tests. To collect the regeneration data,

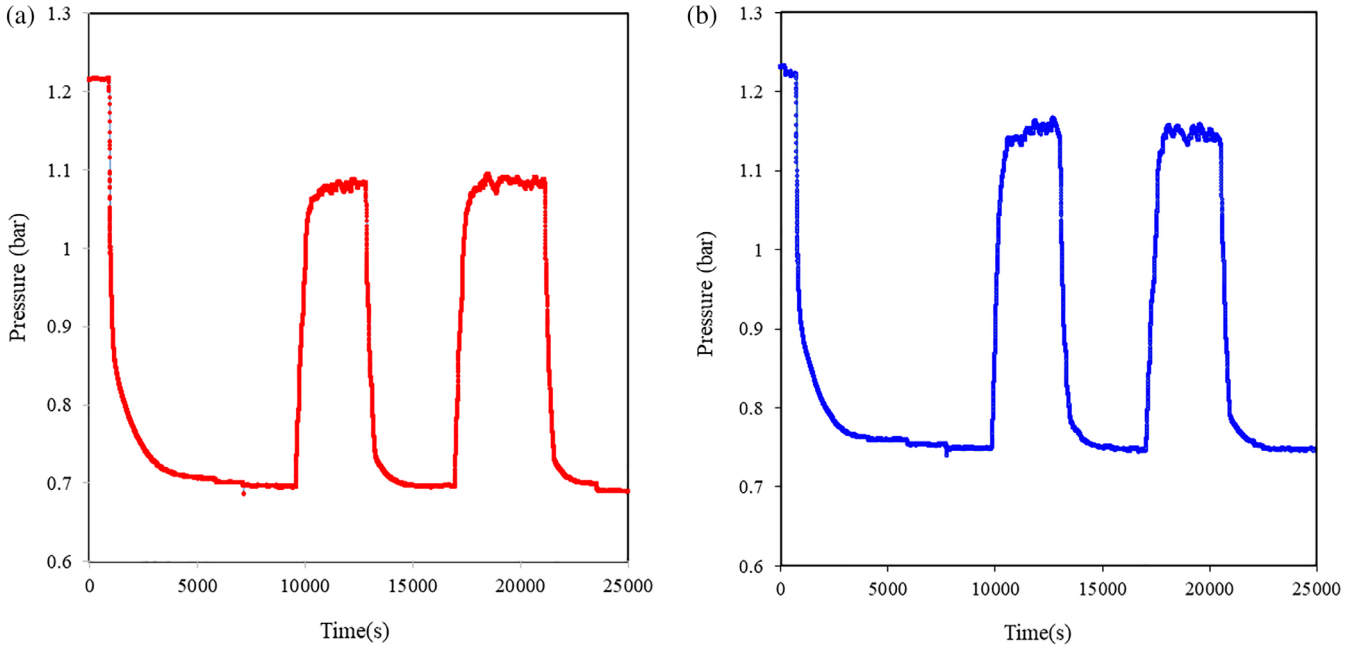

FIGURE 5 Cyclic loading of (a) MEA and (b) 90%MEA+10%DAO solutions

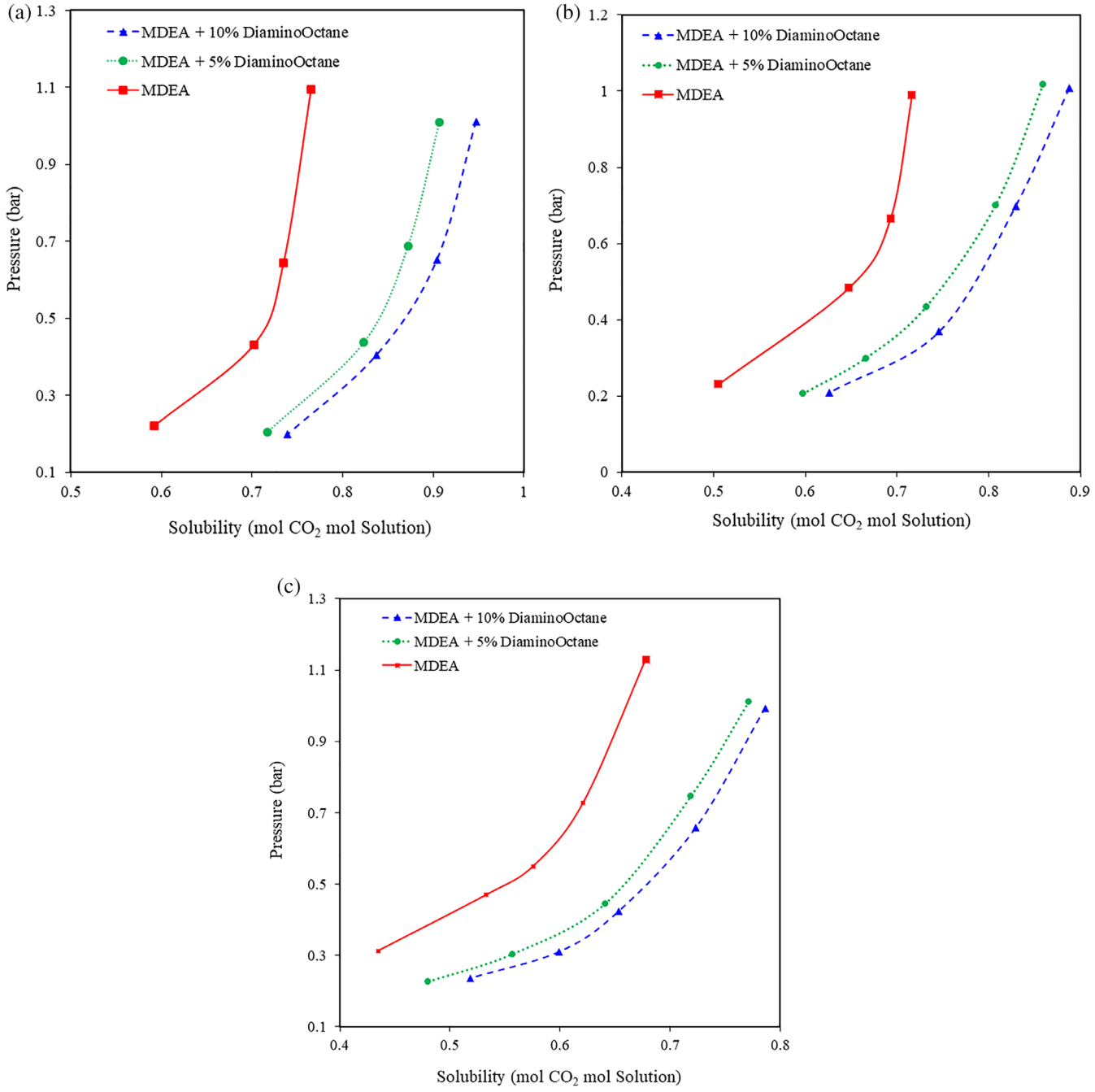

FIGURE 6 CO_2 solubility in mixture of MDEA and DAO at (a) 20°C, (b) 30°C and (c) 40°C

the blend is saturated with CO_2 at equilibrium temperature 30°C and then is heated up to 70°C. Figures 5a,b show the pressure of the reactor during the cyclic absorption and desorption tests applying MEA and MEA promoted by 5% and 10% DAO, respectively. Since the reaction CO_2 and amine is reversible and exothermic, applying high-temperature shifts the reaction toward the zwitterion decomposition to CO_2 and origin amine. Based on the presented data in Figure 5, the effective loading of MEA, MEA promoted by 5% and 10% DAO are 0.32, 0.41, and 0.43 mol CO_2 per mol solution, respectively. It appears the MEA promoted by 10% DAO has a higher effective loading and it is more efficient to absorb CO_2 compared to other samples. Due to the low vapor pressure of DAO compared to MEA, increasing DAO volume fraction in the base solution decreases the rate of solvent loss in the industrial process.

3.3 | MDEA promoted by DAO

The equilibrium loading is a key parameter in the evaluation of solvent performance for CO_2 capture. This property is dictated by the equilibrium state of the investigated system and is influenced by temperature, CO_2 partial pressure in the gas phase, and the concentration and

chemistry of solvent. Figure 6a–c shows the CO_2 loading of MDEA and MDEA promoted by 5% and 10% DAO at the low-pressure condition and the temperature range 293–313 K. Although the aqueous solution of MDEA has higher equilibrium CO_2 loading compared to MEA, the main drawback of the MDEA solution is the slow CO_2 absorption rate. Since the reaction rate of CO_2 and primary amine molecules is faster compared to the ternary amines, increasing the DAO volume fraction in the aqueous solution of MDEA makes the mixture more reactive to absorb CO_2. According to the experimental data, the absorption capacity of MDEA and MDEA promoted 5% and 10% DAO are 0.718, 0.812, and 0.835 mol CO_2 per mol solution at pressure 1 bar and temperature 30°C, respectively. It appears increasing DAO volume fraction in the MDEA solution to 5% and 10% enhances the CO_2 loading by 13.1% and 16.3% at equilibrium temperature 30°C, respectively.

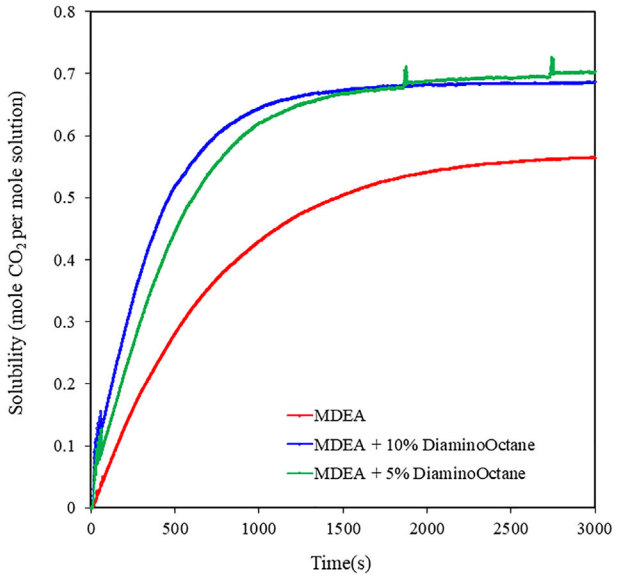

FIGURE 7 CO_2 absorption rate of aqueous solutions of MDEA and mixture of MDEA and DAO at 20°C

Figure 7 shows the CO_2 loading of MDEA and MDEA promoted by 5% and 10% DAO at equilibrium temperature 20°C during the test run time. From a kinetic viewpoint, CO_2 and the primary amine molecules react directly and carbamate is produced from the zwitterion intermediate, while the tertiary amine molecules cannot directly react with CO_2 and lone catalyzes the CO_2 hydration reaction as a slow reaction to produce bicarbonate. Thus, MDEA promoted by the DAO solution has a higher reactivity compared to the base solution to absorb CO_2. The initial absorption rate of CO_2 in MDEA and MDEA promoted by 5% and 10% DAO are 0.0007, 0.0011, and 0.0015 mol cc^{-1} s^{-1}, respectively.

Figure 8a,b show the pressure of the reactor during the cyclic absorption and desorption tests applying MDEA and MDEA promoted by 5% and 10% DAO, respectively. It appears that the rate of CO_2 absorption is slow at temperature 30°C, while the absorbed CO_2 is released quickly at temperature 70°C. Based on the presented data in Figure 8, the effective loading of MDEA, and MDEA promoted by 5% and 10% DAO are respectively 0.51, 0.57, and 0.59 mol CO_2 per mol solution, and the effective loading of blends do not change in the cyclic operation. It concludes the aqueous solution of MDEA promoted by DAO is more effective and regenerable in comparison with the MEA and MDEA solutions at the same condition. Based on the presented data, maximum loading 0.95 mol CO_2 per mol amine is obtained by MDEA promoted by 10% DAO at equilibrium temperature 313.15 K, and pressure 1.01 bar.

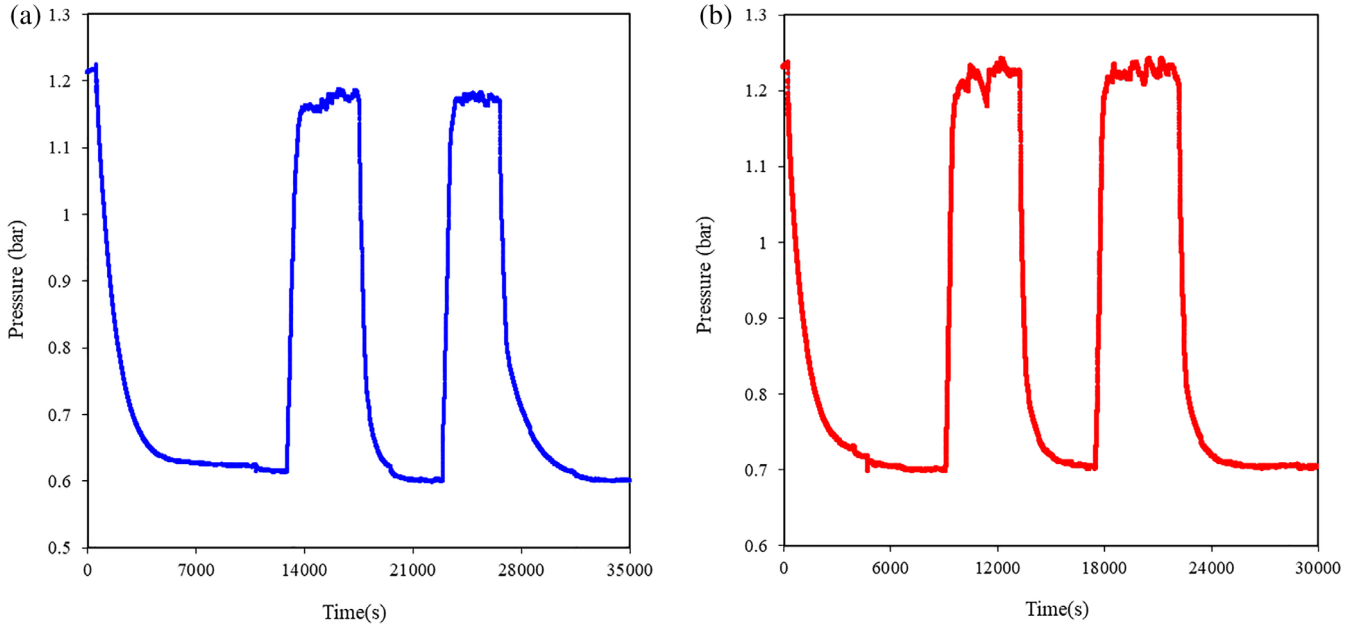

FIGURE 8 Cyclic loading of (a) MDEA and (b) 90%MDEA+10%DAO solutions

4 | CONCLUSIONS

In the current experimental study, the reaction kinetics, equilibrium CO_2 loading, absorption rate, and the effective loading of MEA and MDEA promoted by DAO were measured in a well-mixed isothermal reactor at the pressure range of 0.2–1.2 bar and equilibrium temperature range of 303–313 K. It was concluded the long distance between amine functional groups, linear structure, and the low vapor pressure made DAO an efficient chemical to enhance the CO_2 loading of conventional alkanolamines. Increasing DAO volume fraction up to 10% in the MEA solution improved CO_2 loading up to 12.9% at pressure 1 bar and temperature 20°C. The effective loading of MDEA and MDEA promoted by 10% DAO were 0.51 and 0.59 mol CO_2 per mol solution, while in MEA and MEA promoted by 10% DAO solutions were 0.32 and 0.43 mol CO_2 per mol solution, respectively. It was concluded that increasing the DAO volume fraction in MDEA could rise the effective loading, reactivity, and capacity of the base solution. Indeed, the aqueous solution of MDEA promoted by DAO was more effective and regenerable compared to other samples.

AUTHOR CONTRIBUTIONS

M. Gholidoust: Investigation (supporting); methodology (equal); validation (equal). **Mohammad Farsi:** Conceptualization (lead); data curation (lead); funding acquisition (equal); methodology (lead); project administration (lead); supervision (lead); validation (equal); writing – original draft (lead); writing – review and editing (lead). **P. Setoodeh:** Funding acquisition (equal); methodology (supporting); project administration (equal); writing – review & editing (supporting).

DATA AVAILABILITY STATEMENT

No data are available.

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