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Research Article

Evaluating the Ability of Methyldiethanolamine/Piperazine Microemulsion in CO₂ Absorption

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ABSTRACT

In this study the CO₂ absorption into aqueous droplets of N-methyl-diethanolamine (MDEA) in water-in-oil (w/o) and oil-in-water (o/w) emulsions were investigated in batch-stirred reactor at 298K and different CO₂ partial pressure in the range of 0.1-0.5 bar. The effects of aqua phase concentration, emulsion type, CO₂ partial pressure and the amount of piperazine as a promoter on the absorption percentage and loading amount of CO₂ (mole of absorbed CO₂/mole of amines) were studied. All microemulsion samples were prepared by titration method. The CO₂ loading amounts of all experiments were calculated and the results showed that water in oil samples have better absorption performance and higher CO₂ loading values. The loading values in samples were improved in both emulsion types with increasing CO₂ partial pressure. Also, in water in oil samples concluding different concentration of piperazine or MDEA solution, the absorption and loading of CO₂ improved as amine concentration increased.

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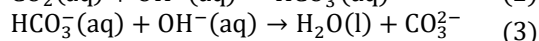
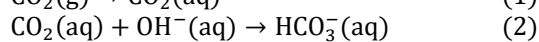
1. Introduction

Global temperatures have been recorded from the 19th century by many organizations, the Goddard Institute for Space Studies (GISS) understood that global warming was on course as early as 1980. Their recent data indicate a global temperature growth of at least 0.8 °C since 1951, with the increase ongoing into the 21st century. In parallel, there has been an increase in the discharge of greenhouse gases over the past century of human activity, with carbon dioxide being the most important gas [1]. So, global warming is a gradually upsetting subject for the international community [2]. The idea of CO₂ capture and storage has lately concerned large attention in the lessening of industrial CO₂ emissions [3]. Synthetic membranes have been an issue of excessive attention in recent years for their possible applications. One of the most exciting classes of synthetic membranes is the liquid membrane. In general, there are two types of liquid membrane classifications including emulsion-type liquid membrane and supported liquid membrane. Emulsion-type liquid membrane is prepared by forming emulsions of immiscible liquid phase by dispersing it in another phase which is called continuous phase. The emulsion is stabilized by surfactants [4]. A surfactant, a surface-active agent, is a compound that adsorbs on the air-water surface or oil-water interface [5, 6] and is used in almost all chemical, agricultural, pharmaceutical and food production processes [7]. The dispersed phase in water-in-oil (w/o) emulsion can improve the mass transfer of a dissolved gas in a gas-liquid system. The description of this phenomenon can be written as small droplets of a liquid which is immiscible with the continuous phase absorbing the gas in the hydrodynamic mass-transfer film, after which desorption of the gas takes place in the gas-poor bulk of the liquid [4].

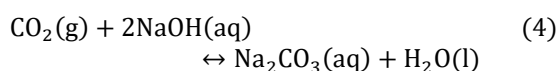
Bruining et al. have studied the absorption of oxygen into o/w emulsions. It has been revealed that the amount of mass transfer of oxygen into an aqueous sulfite solution can be enhanced by the existence of small quantities of a dispersed organic phase [8]. Salmon et.al compared a traditional packed column and a novel membrane contactor for CO₂ absorption. In their study, the influence of the concentration and the flow rates of gas and the alkaline absorbent (NaOH) were investigated. Their results showed the membrane contactor presented very reasonable results with the conventional absorption column, even though the highest mass transfer coefficient was found in the membrane equipment [9]. As stated above, the dispersed phase plays the role of a carrier that carries the dissolved gas from the gas-liquid interface to the bulk form of the liquid and the reaction of the dissolved gas with reactant happens in the continuous phase. If the absorption system is w/o emulsion that the dispersed phase is the aqueous-solution having reactant, and the continuous phase is the organic solvent having greater solubility of gas than water, then the particular rate of absorption may be improved because of higher solubility and chemical reaction [10]. Therefore, increasing the extent of gas dissolution in the liquid phase may increase the total absorption rate. This can be completed by growing the contact surface zone of the gas and the liquid phases by small droplets of liquids using an emulsion phase having two immiscible liquids [10]. Therefore, gas-liquid-liquid systems such as gas absorption by oil-in-water (O/W) emulsions have gained interest in recent studies [11-14]. It should be noted, absorption of CO₂ into W/O emulsions has been studied widely. In order to increase the mass transfer between the gas and the dispersed liquid phases in a W/O emulsion, it is essential to use a continuous liquid phase that has higher physical solubility of the gas compared to the aqueous

dispersed phase. As solubility of CO₂ in the organic solvents is more than in water, organic solvents can be applied as the continuous phase of the emulsion [10]. Due to carbon dioxide solubility, different absorbents could be selected for CO₂ capture and absorption. So, alkaline materials such as NaOH solutions and different kinds of amines can be used as an absorbent phase of emulsion. Here, we investigate the mechanism of carbon dioxide absorption in NaOH and amines. The total mechanism can be explained as:

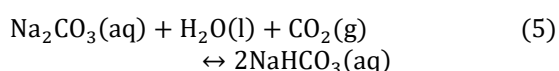
Mass transfer of CO₂ from the gas stream to the droplet surface, then CO₂ reacts with OH⁻ at the droplet surface to generate HCO₃⁻ and CO₃²⁻ (Eq.1-3) [15]:



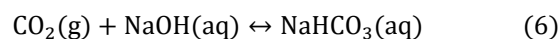
Eq. 2 is a second order reaction that can be considered as a pseudo first order one, because the carbon dioxide concentration is constant so Eq.2 and Eq.3 are reversible with very fast rates in high pH values [16, 17]. Aqueous CO₂ is not present in the solution during the overall reaction because it reacts with OH⁻ instantly and OH⁻ rapidly decreases by Eq.2 and Eq.3. Also, Eq. 3 is dominant primarily in the reaction as the absorbent is kept with a very high alkalinity, which increases the CO₃²⁻ concentration relative to that of HCO₃⁻. Therefore, while pH is quickly reduced during the first reaction period, the CO₃²⁻ concentration is increased. Eq. 4 shows chemical reaction between CO₂ and NaOH as an alkaline solution:



Na₂CO₃ is dissociated Na⁺ and CO₃²⁻ in the absorbent as Eq. 5:

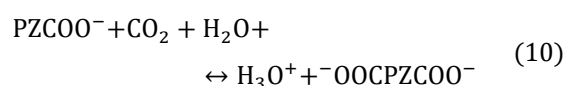
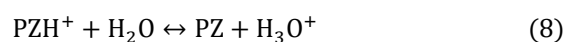
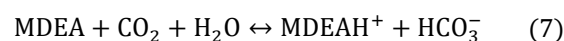


In general, the total chemical reaction can be written in a simple form as Eq. 6 [18]:



By adding small quantities of the primary or secondary amine, a high rate of absorption is realized in the absorber.

One such combination of amines is piperazine (PZ) activated methyldiethanolamine (MDEA). These absorbents have been used effectively for high-capacity carbon dioxide removal processes [19]. MDEA is a tertiary amine contains three alkyl functional groups and piperazine is an organic compound with two nitrogen atoms which react with CO₂ as Eq. 7-10:



It should be noted that, the second pK_a of piperazine to form deprotonated piperazine is 5.3 and is low enough that it can be neglected. In this study, the absorption of CO₂ in W/O and O/W emulsions was studied in a batch reactor under 1 bar total pressure. The aim of present research is to study the effect of emulsion type, CO₂ partial pressure on the rate of carbon dioxide absorption and the loading amount (mol CO₂/mole amine) of CO₂. Also, the effect of additives on efficiency was studied by adding NaOH as an alkaline factor and piperazine as a promoter to investigate their ability in improvement of the absorption performance.

2. Experimental procedure

2.1. Materials

Kerosene and N-methyl-diethanolamine (MDEA) were used as oil phase and aqueous phase, respectively. A non-ionic surfactant, Polyoxyethylene (20) Sorbitan monooleate commercially called Tween 20, was considered as surfactant to prepare microemulsions. A suitable co-surfactant

blended with surfactant was n-Butanol alcohol. All materials were purchased from Merck company in Germany.

2.2. Microemulsion preparation Method

At first a certain amount of Tween 20 and n-Butanol were weighed while the surfactant/co-surfactant ratio was equal to 2, then a desired mass amount of Kerosene was added to it. The mixture was then stirred for 15 min at 1000rpm to mix completely. After that, the pre-emulsion was titrated by a certain amount of aqua phase and stirred for 15 minutes at 1000 rpm to obtain a homogeneous mixture. The microemulsion samples were analyzed by dynamic light scattering (DLS) to ensure about the droplet diameters. Table 1 shows the composition of water-in-oil and oil-in-water micro-emulsions. During our experiments, the aqua phase composition changed as discussed in result and discussion section. The reason for choosing this combination of materials for the synthesis of the microemulsion samples is that, as shown in the ternary phase diagram (Fig. 1), the selected percentages of material are in the Winsor IV range shown in the diagram. According to the electrical conductivity measured for these two samples and as the electrical conductivity of O/W microemulsion is higher than W/O ones, W/O and O/W samples were used for experiments. The electrical conductivity values of O/W and W/O samples are 150.66 and 19.23 $\mu\text{S}/\text{cm}$ respectively.

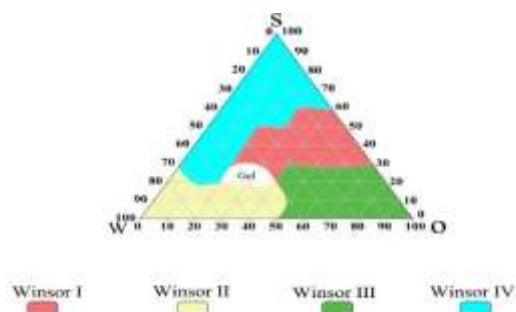


Fig.1. The ternary phase diagram of the kerosene-Tween 20/n-Butanol-water system (S:C=2:1)

Table 1. Composition of microemulsion of Oil, surfactant/co-surfactant, and Aqua (S:C ratio was 2:1)

Emulsion type	Oil phase	Surfactant phase		Aqueous phase
	(% w/w)	Surfactant (% w/w)	Co-surfactant (% w/w)	(% w/w)
O/W	5	30	15	50
W/O	18	48	24	10

2.3. Experimental procedure

A schematic diagram of the setup applied in this study is shown in Fig. 2. The main core of the setup consists of a batch reactor equipped with a pressure transmitter, pH/EC meters and thermocouple. A magnet is used as a mixer. First, the inside of the reactor evacuated by a vacuum pump, then the micro-emulsion sample injected by a syringe. After that the vessel next to the reactor is filled with pure nitrogen and pure carbon dioxide from gas cylinders depended on CO_2 partial pressure. The gas vessel is then connected to the reactor and gases entered into the reactor and injection continued until the total pressure arrived 1 bar. It means that at first, CO_2 injected to desired partial pressure and the residual capacity of reactor filled by N_2 as inert gas until total 1 bar pressure achieved. The system is allowed to reach to the equilibrium between two phases. As N_2 is insoluble in microemulsion sample, so the pressure dropping shows the carbon dioxide gas absorption.

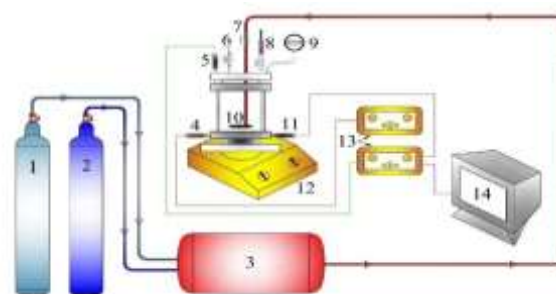


Fig. 2. The schematic of applied setup (1) CO_2 gas cylinder (2) N_2 gas cylinder (3) mixture of gas vessel (4) EC sensor (5) temperature sensor (6) vacuum port (7) gas inlet port (8) sample injection port (9) digital pressure gauge (10) magnet (11) pH sensor (12) digital stirrer (13) data logger (14) computer system.

3. Results and discussion

3.1. Effect of aqua phase on capacity of CO₂ absorption

As mentioned above, different aqua phases were used to investigate the aqua phase effect on CO₂ absorption capacity. MDEA solutions concluding 1,2,3 molal concentration of amine were used as aqua phase in the W/O and O/W emulsions at the partial pressure equal to 0.5 bar of CO₂. Fig. 3 shows that the absorption percentage is improved by increasing amine concentration in the aqua phase. As CO₂ endures chemical reaction with the amine solution, some kind of ion types are shaped in the solution. This leads to an increase in the ionic power of the solution and as a result fewer CO₂ have a tendency to stay in the solution i.e. a kind of salting out effect happens [20]. Table 2 shows the composition of microemulsion which contact to CO₂ gas to investigate the effect of aqua phase on gas absorption percentage and the CO₂ loading value. So

as showed in Fig. 3 and Fig. 4, MDEA 3m solution selected as aqua phase for following tests due to its higher absorption percentage. As the concentration of MDEA solution increased, CO₂ gas reacted with more accessible MDEA moles so the absorption percentage could be increased. The CO₂ loading value can be explained as moles of absorbed CO₂ per moles of amines so by increasing the mole of amines the loading amount is decreased. Therefore, the loading amount of the microemulsion sample made by MDEA 1m solution as aqua phase is higher than sample made by MDEA 3m solution, but the absorption percentage of sample made by MDEA 1m is lower than sample made by MDEA 3m. As mentioned before, the solubility of CO₂ in continuous phase in W/O microemulsion is higher than O/W. As CO₂ is absorbed in the dispersed phase in W/O, it can be confined by the oil phase, which helps by controlling internal phase corrosion to prevent equipment damage.

Table 2. Composition of microemulsion, absorption percentage, loading values with different aqueous phase

Emulsion type	Sample	Oil phase			Aqueous phase (%w/w)	Absorption percentage	Loading (mole CO ₂ /mole MDEA)
		Kerosene (% w/w)	Surfactant (%w/w)	n-Butanol (% w/w)			
O/W	ME water	5	30	15	50 water	23	-
	ME MDEA 1m	5	30	15	50 MDEA 1m	26	0.05
	ME MDEA 2m	5	30	15	50 MDEA 2m	30	0.03
	ME MDEA 3m	5	30	15	50 MDEA 3m	42	0.02
W/O	ME water	18	48	24	10 water	14	-
	ME MDEA 1m	18	48	24	10 MDEA 1m	15	0.15
	ME MDEA 2m	18	48	24	10 MDEA 2m	21	0.12
	ME MDEA 3m	18	48	24	10 MDEA 3m	27	0.10

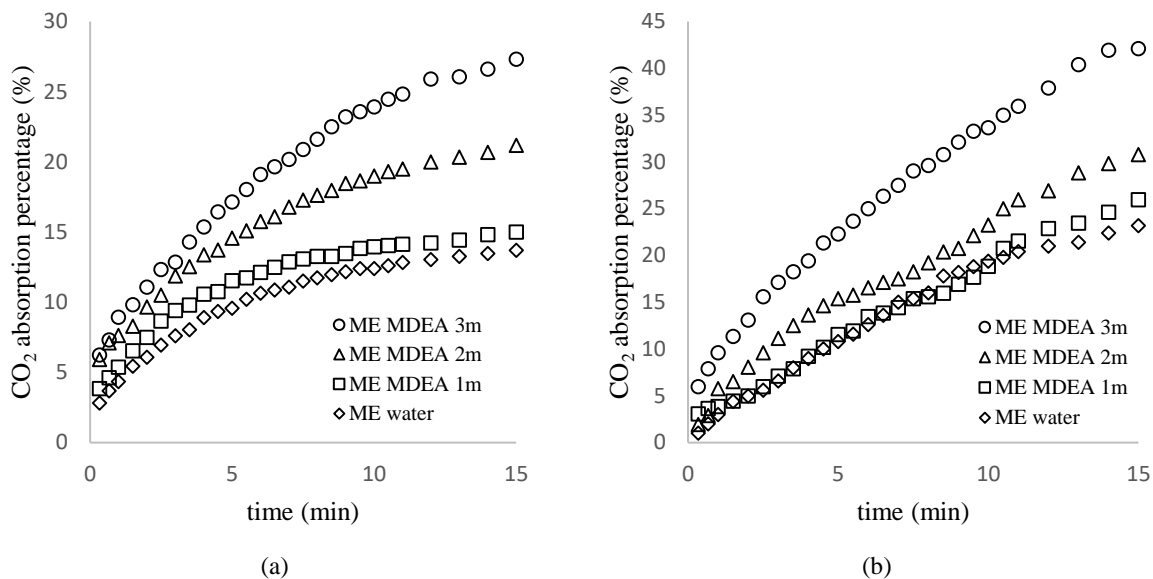


Fig. 3. CO₂ absorption percentage diagrams (a) W/O (b) O/W samples consist different aqua phase (water,MDEA 1,2,3 molal)

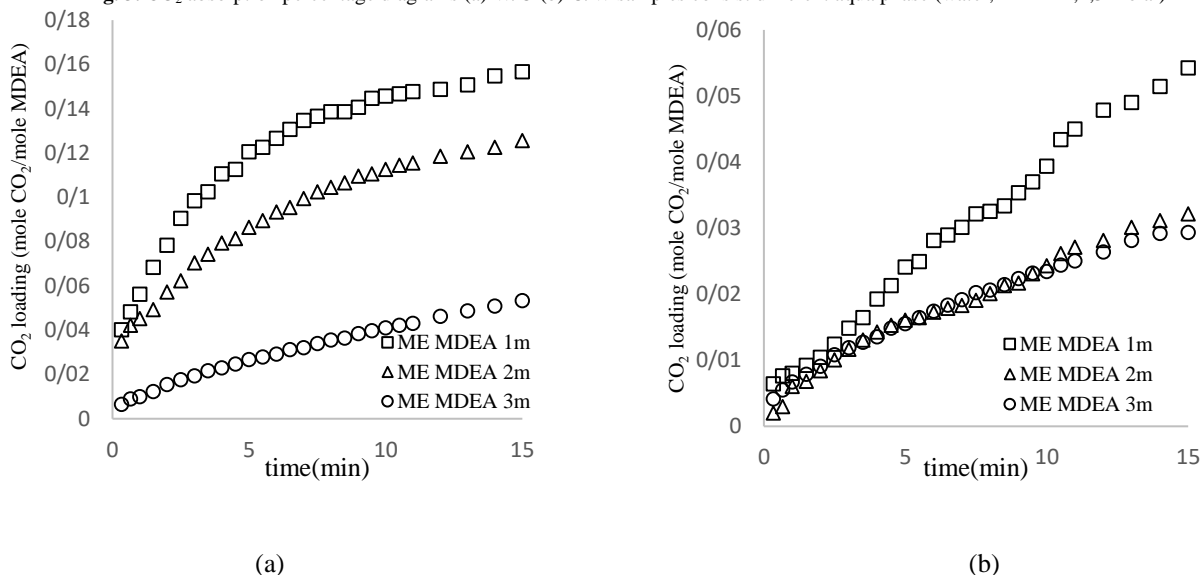


Fig. 4. CO₂ loading diagrams (a) W/O (b)O/W samples consist different aqua phase (water,MDEA 1,2,3 molal)

3.2. Effect of partial pressure on capacity of CO₂ absorption

Fig. 5, and Fig. 6 show absorption percentage and loading values of carbon dioxide at different CO₂ partial pressures which differs from 0.1-0.5 bar. As shown, absorption performance and the amount of CO₂ loading are improved in both emulsion types with increasing CO₂ partial pressure. To investigate this effect more precisely, absorption capacities of

MDEA solution in microemulsions at different CO₂ partial pressures are shown separately for both water-in-oil and oil-in-water microemulsions. It may be established that growing absorption capacities of the microemulsions are mostly due to the increase in physical absorption in the continuous phase. Table 3 shows the composition of microemulsion which contact to CO₂ gas injection.

Table 3. Composition of microemulsion, absorption percentage, loading value at different CO₂ partial pressure

Emulsion type	Oil phase			Surfactant phase		Aqueous phase		CO ₂ Partial pressure (bar)	Absorption percentage (%)	Loading (mole CO ₂ /mole MDEA)	D _i (nm)
	Kerosene (% w/w)	Surfactant (% w/w)	n-Butanol (% w/w)	50 MDEA 3m (% w/w)		(% w/w)					
O/W	5	30	15	50 MDEA 3m				0.5	44	0.029	71
	5	30	15	50 MDEA 3m				0.4	30	0.016	71
	5	30	15	50 MDEA 3m				0.3	26	0.010	71
	5	30	15	50 MDEA 3m				0.2	19	0.006	71
	5	30	15	50 MDEA 3m				0.1	15	0.002	71
W/O	18	48	24	10 MDEA 3m				0.5	27.5	0.100	116
	18	48	24	10 MDEA 3m				0.4	20	0.054	116
	18	48	24	10 MDEA 3m				0.3	18.5	0.042	116
	18	48	24	10 MDEA 3m				0.2	14	0.025	116
	18	48	24	10 MDEA 3m				0.1	9	0.006	116

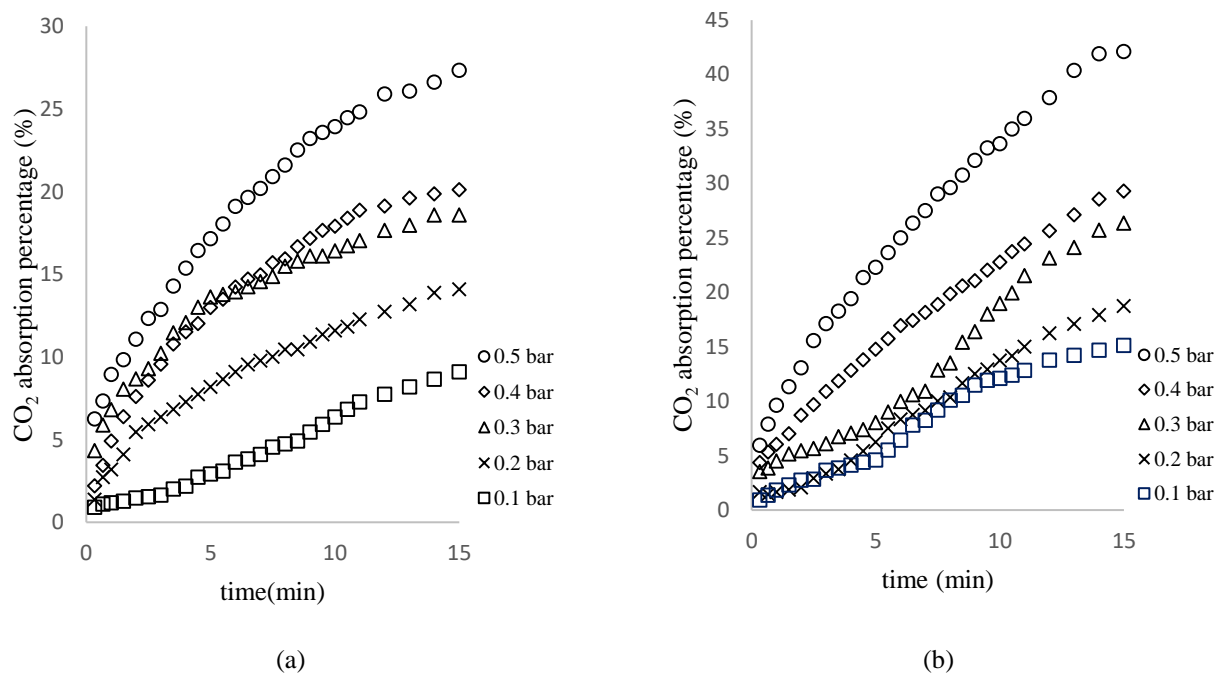


Fig. 5. CO₂ absorption percentage diagrams (a) W/O (b)O/W samples at different partial pressure of CO₂ (0.1-0.5bar)

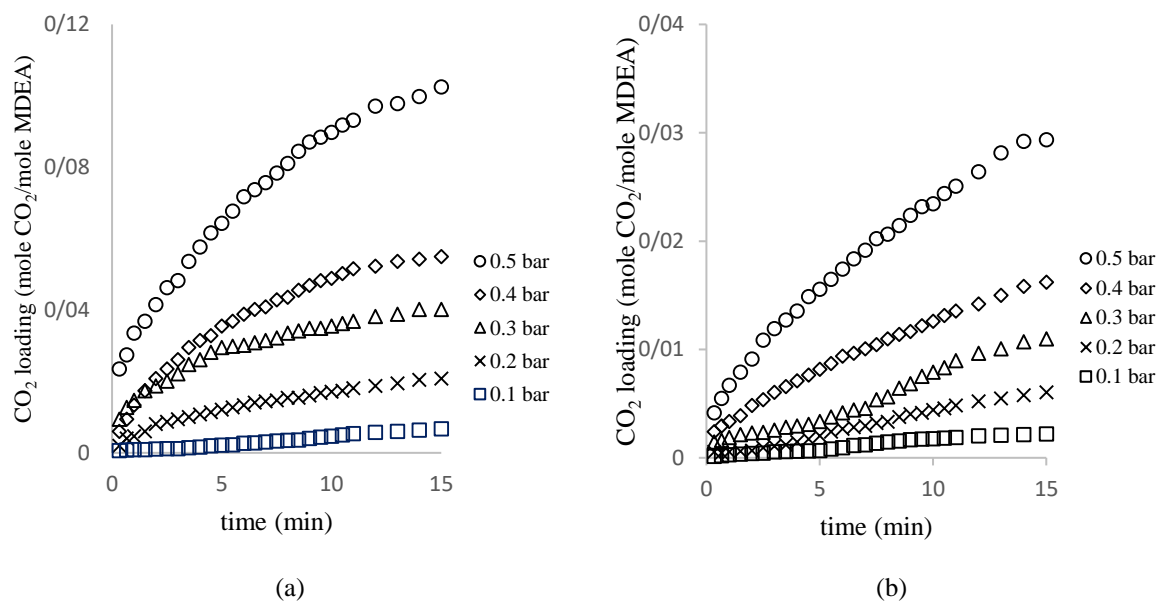


Fig. 6. CO₂ loading (mole CO₂/mole MDEA) diagrams (a) W/O (b)O/W samples at different partial pressure of CO₂ (0.1-0.5bar)

3.3. Effect of pH on capacity of CO₂ absorption

Due to the theory of carbon dioxide absorption, OH⁻ ions are essential for the absorption process therefore pH increasing could improves the capacity of CO₂ absorption. In this research we used sodium hydroxide (NaOH) as an alkaline source to increase pH value. Accordingly, we add 0.1 molal NaOH solution to our sample’s aqua phase and repeat section 3.2 experiments with different aqua phase composition.

Table 4 shows the composition of microemulsion which contact to CO₂ injection. Fig. 7 and Fig. 8 show the CO₂ absorption percentage and loading curves of experiments. As the pH of sample increased, the absorption performance improved because of OH⁻ ion existence growth. Comparing Table 3 and Table 4 results show that the loading amount of samples increased by pH increasing which means, 1 mole of MDEA absorbed higher amounts of CO₂ moles on NaOH existence.

Table 4. composition of microemulsion, absorption percentage, loading amount and droplet diameter

Emulsion type	Oil phase			Surfactant phase		Aqueous phase		CO ₂ Partial pressure (bar)	Absorption percentage (%)	Loading (mole CO ₂ /mole MDEA)	D (nm)
	Kerosene (% w/w)	Surfactant (% w/w)	n-Butanol (% w/w)	(% w/w)							
O/W	5	30	15	50(MDEA 3m, NaOH 0.1m)		0.5	49	0.033	1502		
	5	30	15	50(MDEA 3m, NaOH 0.1m)		0.4	53	0.029	1502		
	5	30	15	50(MDEA 3m, NaOH 0.1m)		0.3	76	0.030	1502		
	5	30	15	50(MDEA 3m, NaOH 0.1m)		0.2	83	0.023	1502		
	5	30	15	50(MDEA 3m, NaOH 0.1m)		0.1	98	0.014	1502		
W/O	18	48	24	10(MDEA 3m, NaOH 0.1m)		0.5	35	0.122	3870		
	18	48	24	10(MDEA 3m, NaOH 0.1m)		0.4	37	0.112	3870		
	18	48	24	10(MDEA 3m, NaOH 0.1m)		0.3	74	0.140	3870		
	18	48	24	10(MDEA 3m, NaOH 0.1m)		0.2	88	0.124	3870		
	18	48	24	10(MDEA 3m, NaOH 0.1m)		0.1	95	0.070	3870		

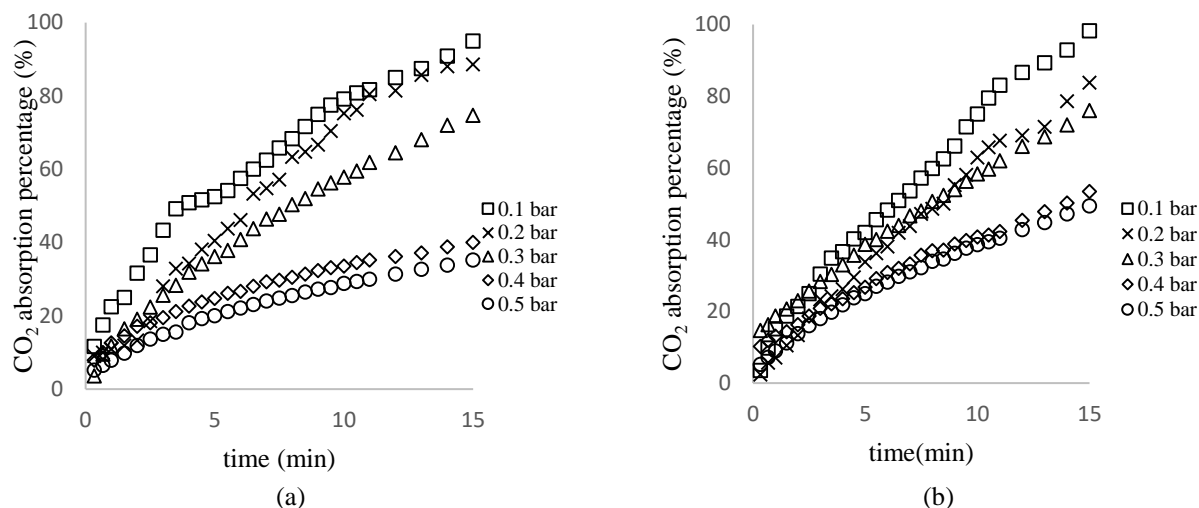


Fig. 7. CO₂ absorption percentage diagrams (a) W/O (b)O/W samples at high pH

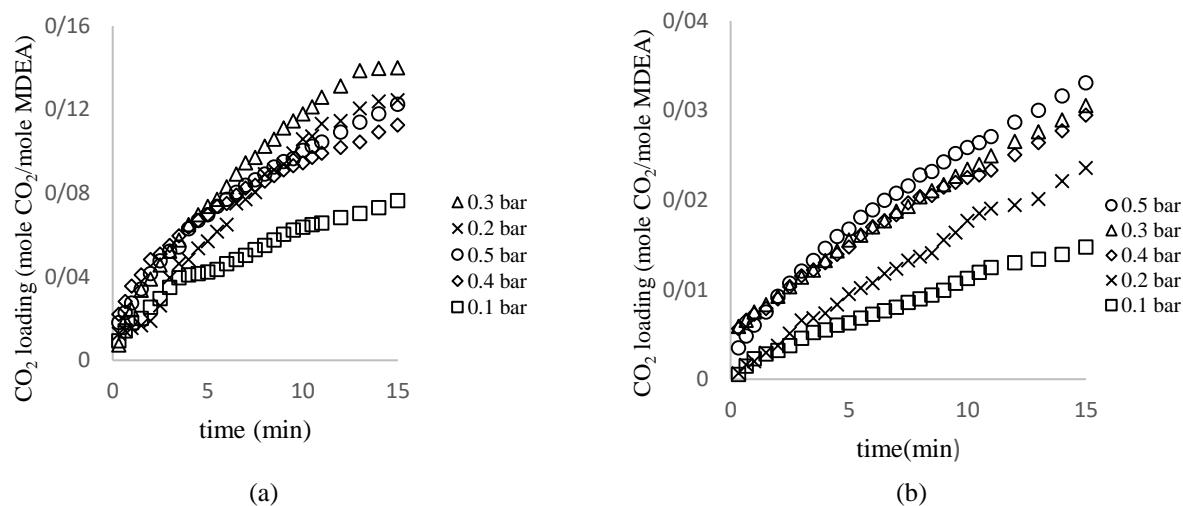


Fig. 8. CO₂ loading (mole CO₂/mole MDEA) diagrams (a) W/O (b)O/W samples at high pH

As shown in Table 4, the loading amounts of samples with aqua phase including MDEA and NaOH are higher than the samples concluding MDEA aqua phase. Also, as shown in Fig. 8, the loading values of W/O types are higher compared to O/W samples. As mentioned before, due to high corrosion of NaOH used in aqua phase, the water in oil microemulsion preferred because the aqua phase is the inner phase and surrounded by external phase and does not directly contact with the equipment.

3.4. Effect of Piperazine on capacity of CO₂ absorption

The common problem of tertiary amines is their low CO₂ absorption rate compared to primary and secondary amines [21]. To rectify this lack,

promoters such as piperazine (PZ) is naturally merged with tertiary amines to improve their CO₂ absorption rates [22-24]. Based on Lawal et al. MDEA is tending to oxidative degradation, leading to the weakening of CO₂ absorption capacity [25]. Therefore, piperazine as an activator added to microemulsion structure. Three different concentration of piperazine solution including 0.3, 0.6 and 0.9 molal were added to the aqua phase of W/O microemulsions. The results shown in Table 5 and Fig. 9. As shown, the absorption and loading of CO₂ improved by adding piperazine as a promoter. It should be noted that, Eq. 11, written based on mass balance, shows that the loading relationship with the mole fraction of piperazine is linear.

$$\alpha = \alpha_{AM} + (\alpha_{PZ} - \alpha_{AM})x_{PZ} \tag{11}$$

Where α is the total loading amount of CO₂ and α_{AM} and α_{PZ} are the loading amount of CO₂ by MDEA and PZ amines respectively and x_{PZ} is the mole fraction of piperazine. To validate the experimental data with Eq. 11 at a pressure of 0.5 bar, the

following relationship (Eq. 12) is obtained with a regression coefficient (R^2) equal to 0.936, which indicates a significant fitting between the experimental data and the relationship of Eq. 11:

$$\alpha = 0.0895 + 0.2291x_{PZ} \tag{12}$$

Table 5. Composition of microemulsion, absorption percentage, loading amount and droplet diameter at different concentration of piperazine

Oil phase	Surfactant phase		Aqueous phase	CO ₂ Partial pressure	Absorption percentage	Loading (mole CO ₂ /mole MDEA)	D (nm)
(% w/w)	Surfactant (% w/w)	n-Butanol (% w/w)	(% w/w)	(bar)	(%)		
Kerosene	48	24	10(MDEA 3m, PZ 0.3m)	0.5	32	0.0950	387
	48	24	10(MDEA 3m, PZ 0.6m)	0.5	44	0.1256	581
	48	24	10(MDEA 3m, PZ 0.9m)	0.5	64	0.1428	772

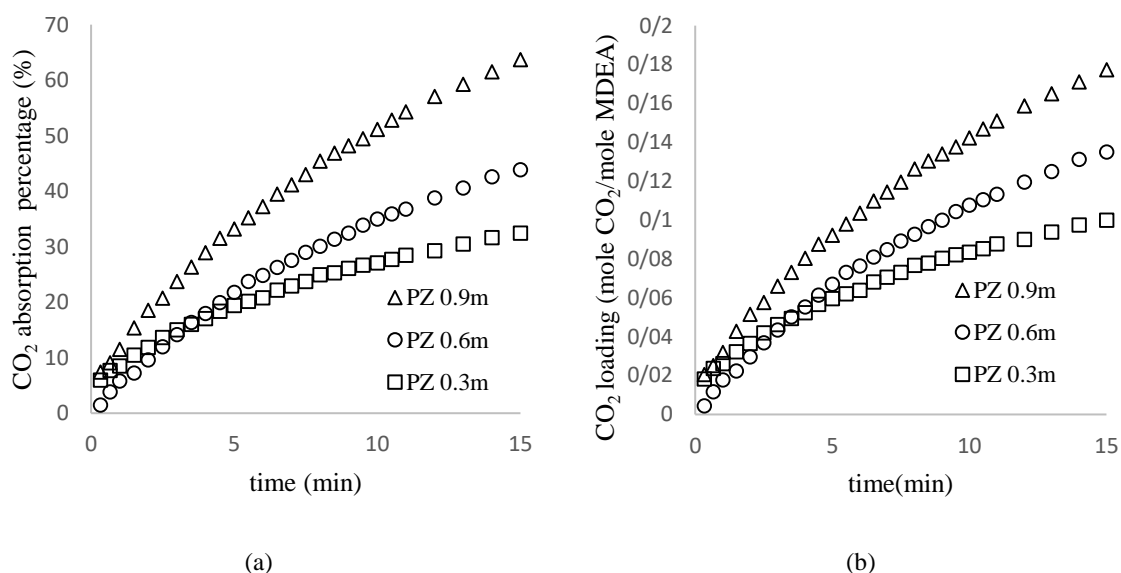


Fig. 9. (a) CO₂ absorption percentage. (b) CO₂ loading (mole CO₂/mole MDEA+PZ) vs time diagrams for W/O samples

4. Conclusion

Different microemulsion samples were prepared by titration method which varies in microemulsion formula. Five different CO₂ partial pressure were used to investigate the operation parameters effects on carbon dioxide absorption percentage and loading values. Two types of emulsion concluding oil in water and water in oil were used and finally water in oil microemulsion preferred due to its corrosion control ability. Microemulsion with

different aqua phase were tested and the microemulsion that consists higher concentration of MDEA solution in aqua phase showed higher CO₂ absorption. Piperazine were added to samples due to its promoting property and performance improvements were established. Finally, it was observed that the microemulsion sample with the highest loading value is the water-in-oil microemulsion sample containing MDEA 3m and PZ 0.9m as an aqueous phase in its formula.

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