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Absorption of Carbon Dioxide in Aqueous Solutions of *N*-methyldiethanolamine Mixtures

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Abstract. Carbon dioxide (CO₂) is one of the greenhouse gases (GHG) that has contributed to the global warming problem. Carbon dioxide is produced in large quantity from coal-fired power plants, iron and steel production, cement production, chemical and petrochemical industries, natural gas purification, and transportation. Some efforts to reduce the CO₂ emissions to the atmosphere are then required. Amine-based absorption may be an option for post-combustion capture. The objective of this study is to measure the effect of promoter addition as well as MDEA concentration for the CO₂ absorption into the aqueous solutions of MDEA to improve its performances, i.e. increasing the absorption rate and the absorption capacity. Absorption of CO₂ in aqueous solutions of MDEA mixtures were measured at 40 °C in a bubble tank reactor. The systems tested were the mixtures of 30 wt% MDEA with 5 and 10 wt% BEA and the mixtures of 40 and 50 wt% MDEA with 6 wt% AEEA. It was found that for MDEA-BEA-H₂O mixtures, the higher the promoter concentration the higher the CO₂ absorption rate, while for the MDEA-AEEA-H₂O mixtures, the higher the MDEA concentration the lower the CO₂ absorption rate.

1. Introduction

Carbon dioxide is known as one of the major contributors to the global warming problem. Carbon dioxide is produced in large quantities from coal-fired power plants, iron and steel industries, petrochemical industries, cement production, and natural gas purification as well as the exhaust gas from the transportation sectors [1, 2]. CO₂ emissions seem to rise from year to year. In 2005, 26.3 Gt of CO₂ were emitted globally and reached 32 Gt in 2010 [3]. Aqueous solutions of alkanolamines are the most commonly used absorbents for the removal of acidic gases from natural, refinery, and synthesis gas streams, such as monoethanolamine [MEA – H₂N(CH₂)₂OH], diethanolamine [DEA – HN(CH₂CH₂OH)₂], and *N*-methyldiethanolamine [MDEA – CH₃N(CH₂CH₂OH)₂]. A chemical that is used as a commercial absorbent should meet some criteria such as high net cyclic capacity, high absorption rate, low regeneration energy requirement, reasonable thermal stability, etc. In addition, other criteria that need to consider in selecting CO₂ capturing solvents can also be found in [4].

MDEA is a tertiary amine. This solvent has been widely used for high-pressure CO₂ removal and for selective removal of hydrogen sulfide (H₂S) from gas streams containing both CO₂ and H₂S. The advantages of MDEA over primary and secondary amines are, besides the selectivity for H₂S, a lower enthalpy of reaction with the acidic gases which leads to lower energy requirements for regeneration, a lower corrosiveness, better thermal and chemical stability, and a lower vapor pressure. Because of its low vapor pressure, the concentrations of aqueous solutions of MDEA can be used up to 60 wt% without appreciable evaporation losses [5]. The limitations of MDEA include a slower reaction rate with CO₂ and a lower absorption capacity at low CO₂ concentrations. To encounter the MDEA



limitations, the addition of promoter may, therefore, be required. The objective of this work is to measure the effect of promoter addition and MDEA concentration for the CO₂ absorption into the aqueous solution of MDEA to improve its performances, e.g. increasing the absorption rate and the absorption capacity.

2. Materials and Method

2.1. Materials

The CO₂ (min. 99.99 mol %) and N₂ (min. 99.6 mol %) gases were obtained from AGA Gas GmbH. The alkanolamines used were MDEA min. 98.5%, BEA min. 98% [2-(butylamino)ethanol – CH₃(CH₂)₃NH(CH₂)₂OH], and AEEA min. 97% [2-(2-aminoethyl-amino)ethanol – H₂N(CH₂)₂NH(CH₂)₂OH]. They were obtained from Acros Organics and were used without further purification.

2.2. Apparatus and Method

The experiments were conducted using a similar screening apparatus used by [6] as shown in figure 1. According to [6], the apparatus was designed to operate at atmospheric pressure and temperatures up to 80 °C. It consists of six 1-L glass absorbers including six water saturators, six K-type thermocouples, a HETO circulating heater (Type 02 T 623), a Hartmann & Braun Uras 3G IR CO₂ analyzer, and a BRONKHORST HI-TEC N₂/CO₂/H₂S mass flow controller (Type E-7100). The data acquisition system uses LabVIEW. Before starting the experiment, a CO₂-N₂ gas mixture containing 10 vol% CO₂ with flowrate of 5 NL/min was circulated through a by-pass valve to calibrate the analyzer. Once the process started, the by-pass valve closed automatically. The gas mixture was passed through a water saturator and then to the absorber containing 750 mL of the absorbent. The gas phase leaving the absorber was cooled and the CO₂ concentration was directly measured by the IR CO₂ analyzer. The temperature of the water bath was maintained at 40 ± 0.1 °C. The gas CO₂ content, the temperatures, and the gas flowrates were collected by the LabVIEW data acquisition system. The process automatically terminated when the concentration of CO₂ in the outlet reached 9.5 vol% (9.5 kPa CO₂ partial pressure).

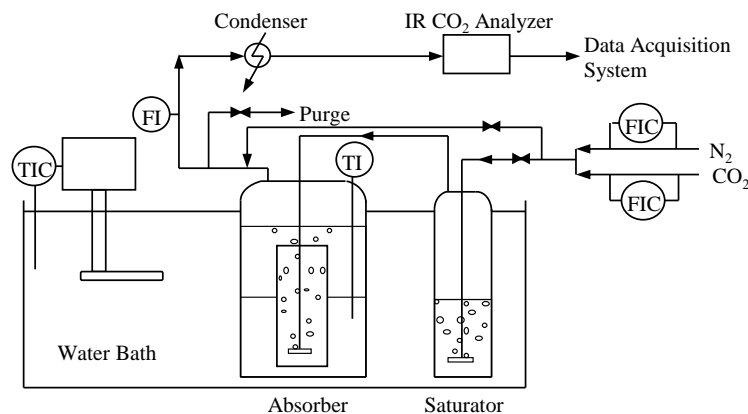


Figure 1. Experimental setup for CO₂ absorption.

2.3. Gas and Liquid Analyses

The vapor bleed extracted for CO₂ concentration measurement was cooled to about 10 °C to condense water, MDEA, BEA, and AEEA. The CO₂ content was directly determined by IR analysis. The vapor phase in the IR analyzer, therefore, consists of N₂, CO₂, and little amounts of H₂O and alkanolamines (MDEA, BEA, and AEEA). The concentration of CO₂ in the IR analyzer is calculated as follows:

$$y_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{CO}_2} + n_{\text{N}_2} + n_{\text{H}_2\text{O}} + n_{\text{MDEA}} + n_{\text{BEA/AEEA}}} \quad (1)$$

where the n 's denote molar flow (mol/s). Due to the low vapor pressures of MDEA, BEA and AEEA at 10 °C, i.e. $P_{\text{MDEA}}^0 = 0.007$ Pa, $P_{\text{BEA}}^0 = 3.395$ Pa and $P_{\text{AEEA}}^0 = 0.020$ Pa [7, 8], thus MDEA, BEA and AEEA contents in the vapor phase through the analyzer can then be disregarded. After terminating the experiment, a liquid sample was then analyzed by the barium chloride (BaCl_2) method [9]. The amount of HCl that was not used to dissolve BaCO_3 was titrated by 0.1 M NaOH carried out with an automatic titrator (Metrohm 702 SM Titrino) with an endpoint at pH 5.2.

3. Results and Discussion

Absorption rates of CO_2 in aqueous solutions of MDEA mixtures were measured at 40 °C. The objective of this work is to evaluate the effect of promoter addition, i.e. BEA and AEEA, and MDEA concentration to improve MDEA performances such as increasing the absorption rate and the absorption capacity. BEA and AEEA were selected in this study because they give, according to [6], better CO_2 absorption rates and capacities in comparison to those of MDEA. To calculate the CO_2 absorption rate, equation (2) below was used.

$$r_{\text{CO}_2} = \frac{1}{V} \left[n_{\text{CO}_2}^{\text{in}} - \frac{y_{\text{CO}_2}^{\text{out}} n_{\text{N}_2}}{(1 - y_{\text{CO}_2}^{\text{out}})} \right] \quad (2)$$

where V is the volume of the solution (L), n is molar flow (mol/s), and y is mole fraction of CO_2 in the gas phase measured by the CO_2 IR analyzer. Ma'mun *et al.* [6] tested 30 wt% MDEA solution and the result showed poor performance in terms of CO_2 absorption rate. Therefore, addition a promoter may be required to eliminate its drawback. To evaluate the effect of BEA as a promoter, aqueous solutions of 30 wt% MDEA were mixed by 5 and 10 wt% BEA. In addition, mixtures of 40 wt% MDEA + 6 wt% AEEA and 50 wt% MDEA + 6 wt% AEEA were tested. These additional data were run to evaluate the effect of MDEA concentration and AEEA addition as a promoter. However, direct comparison can only be evaluated between 30 wt% MDEA + 5 wt% BEA and 30 wt% MDEA + 10 wt% BEA mixtures, and between 40 wt% MDEA + 6 wt% AEEA and 50 wt% MDEA + 6 wt% AEEA mixtures. The last mixtures were tested to evaluate the effect of MDEA concentration at constant AEEA concentration.

Table 1 shows the experimental data of CO_2 absorption in the aqueous mixture of 30 wt% MDEA + 5 wt% BEA at 40 °C. The CO_2 - N_2 gas mixture that was bubbled into the reactor contains 9.74 vol% CO_2 with the flowrate of 5.11 NL/min. It can be seen from table 1 that the CO_2 absorption rate at the beginning reached 2.717×10^{-4} kmol/ m^3 /s. This value is much higher compared to the absorption rate of CO_2 into 30 wt% MDEA solution which is only about 1.87×10^{-4} kmol/ m^3 /s [6]. This indicates that the addition of BEA as a promoter was able to improve the CO_2 absorption rate into the MDEA solution, i.e. ~45% increase). Moreover, the accumulated CO_2 that can be absorbed was found to significantly increase from 0.77 to 0.99 mol CO_2 /L. The concentration of CO_2 in the outlet reached 9.5 vol% after the experiment was run for 159 minutes. Figure 2 shows the results of this study. It can be seen that for 30 wt% MDEA solutions, the higher the promoter concentration, the higher the CO_2 absorption rate. According to Ma'mun *et al.* [6], the CO_2 absorption rate into BEA solution are higher than that into MDEA. That is why addition of BEA to MDEA solution will improve MDEA performance, i.e. CO_2 absorption rate. In addition, the effect of MDEA concentration was studied. It can be seen from figure 2 that the CO_2 absorption rate into 40 wt% MDEA + 6 wt% AEEA mixture is relatively higher than that into 50 wt% MDEA + 6 wt% AEEA mixture for the first two hours, but it becomes lower afterwards. Since the CO_2 absorption into the MDEA solution is relatively low, therefore, increasing MDEA concentration in a mixture may lead to decreasing the overall absorption rate. It should be noted that the comparison is semi-quantitative, in the sense that there is, according to [6], no guarantee that the bubble structure, and therefore the gas-liquid interfacial area was exactly the same during all experiments. However, the superficial gas velocity was the same, so differences would arise mainly due to variations in interfacial tension, bubble coalescence properties, and viscosity.

Table 1. Experimental data of CO₂ absorption in aqueous mixture of 30 wt% MDEA + 5 wt% BEA at 40 °C.

Time, min	$y_{\text{CO}_2\text{-out}}$, vol%	$[\text{CO}_2]_{\text{absorbed}}$, mol/L	CO ₂ loading, mol CO ₂ /mol amines	$r_{\text{CO}_2} \times 10^5$, kmol/m ³ /s
1	4.59	0.008	0.003	27.17
5	5.21	0.069	0.022	24.19
10	5.48	0.139	0.045	22.90
15	5.65	0.206	0.066	21.91
20	5.87	0.270	0.087	20.82
25	6.09	0.331	0.106	19.63
30	6.34	0.376	0.121	18.34
35	6.61	0.429	0.138	17.05
40	6.87	0.478	0.153	15.57
45	7.11	0.523	0.168	14.28
50	7.32	0.564	0.181	13.09
55	7.49	0.602	0.193	12.29
60	7.66	0.638	0.205	11.40
65	7.81	0.671	0.215	10.51
70	7.97	0.702	0.225	9.82
75	8.10	0.730	0.234	9.12
80	8.22	0.756	0.243	8.53
85	8.34	0.780	0.250	7.63
90	8.46	0.802	0.257	7.04
95	8.53	0.819	0.263	6.74
100	8.62	0.838	0.269	6.35
105	8.70	0.856	0.275	5.75
110	8.77	0.872	0.280	5.25
115	8.84	0.888	0.285	5.16
120	8.90	0.902	0.290	4.56
125	8.96	0.916	0.294	4.36
130	9.01	0.928	0.298	4.06
135	9.06	0.940	0.302	3.67
140	9.10	0.951	0.305	3.67
145	9.15	0.962	0.309	3.27
150	9.19	0.971	0.312	3.17
155	9.23	0.980	0.315	2.78
159	9.25	0.987	0.317	2.68

Figure 3 shows the CO₂ absorption rates as a function of CO₂ loading. It can be seen that all the mixtures give higher absorption rates up to a CO₂ loading of 0.30, except for the mixture of 50 wt% MDEA + 6 wt% AEEA. The maximum CO₂ loading, i.e. at equilibrium, that could be achieved by the mixtures of 30 wt% MDEA + 5 wt% BEA, 30 wt% MDEA + 10 wt% BEA and 40 wt% MDEA + 6 wt% AEEA is about 0.34, while the 50 wt% MDEA + 6 wt% AEEA mixture could achieve the maximum CO₂ loading of 0.28. It can also be seen that for the MDEA-BEA-H₂O mixtures, the higher the promoter concentration the higher the CO₂ absorption rate, while for the MDEA-AEEA-H₂O mixtures, increasing MDEA concentration leads to lower absorption rate. In general, the addition of promoters has improved the MDEA performances.

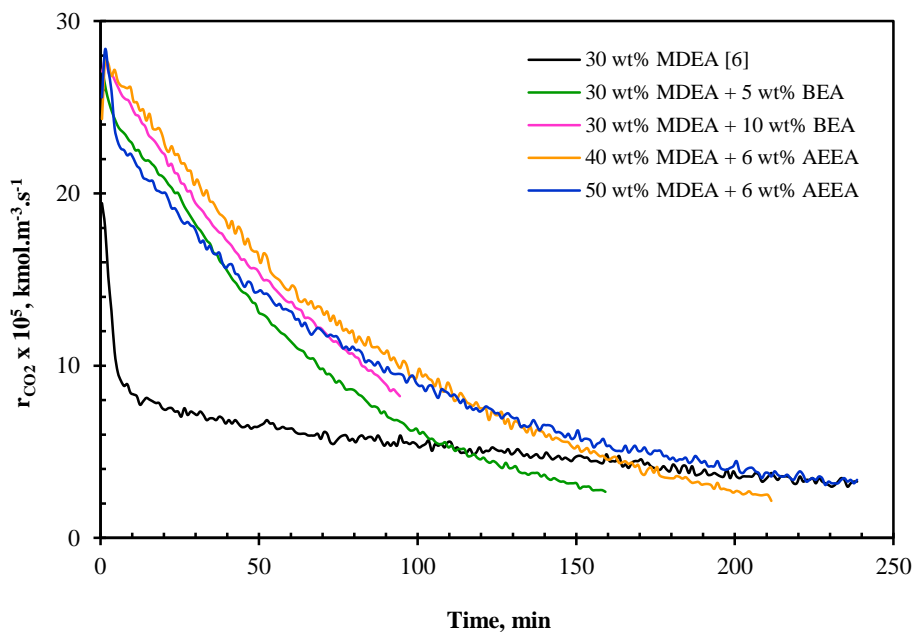


Figure 2. Absorption rates of CO₂ in aqueous solutions of MDEA at 40 °C.

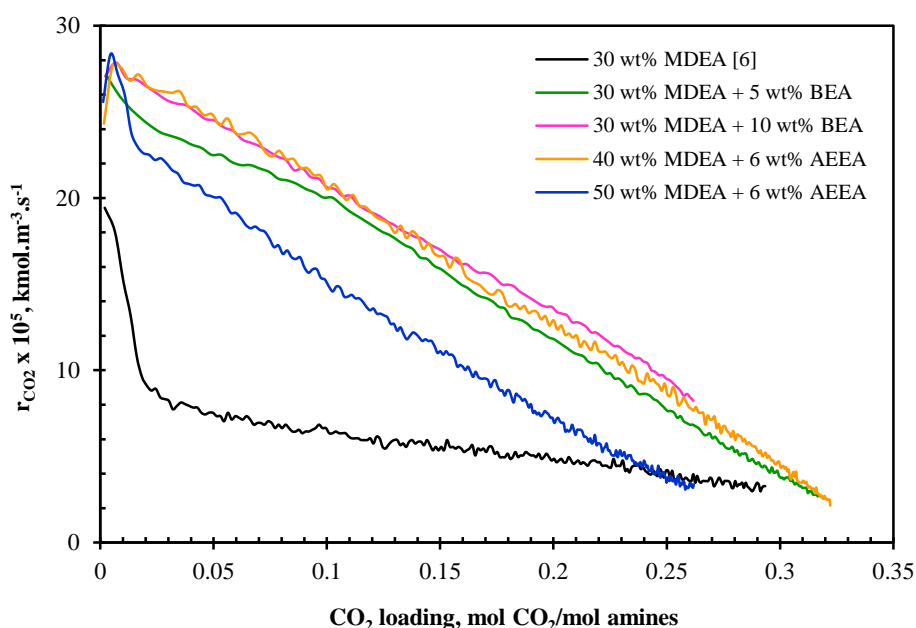
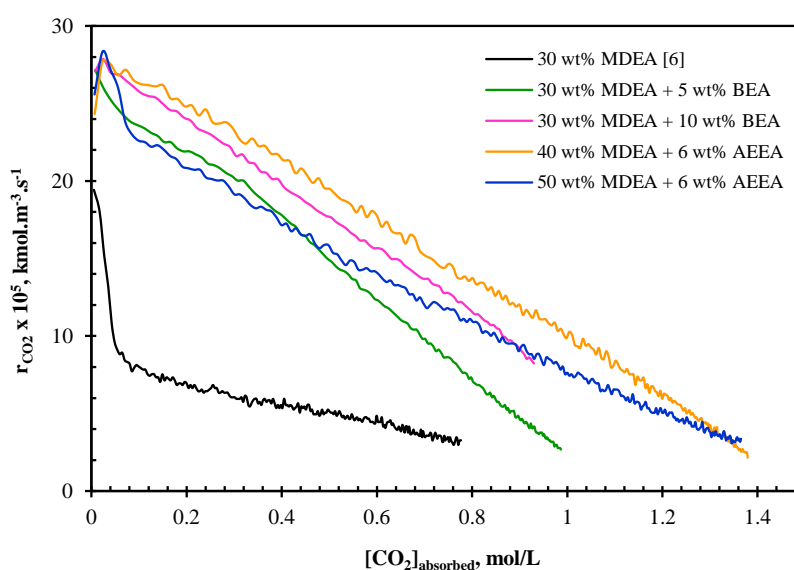


Figure 3. Absorption rates of CO₂ at different CO₂ loadings at 40 °C.

Figure 4 shows the effect of promoter addition on the MDEA performances in terms of the total CO₂ that can be absorbed. It can be seen that the aqueous solution of 40 wt% MDEA + 6 wt% AEEA mixture gives relatively higher absorption rates compared to the other mixtures up to the total CO₂ absorbed of about 1.35 mol CO₂/L. Table 2 shows the total CO₂ absorbed for all systems at 9.5 kPa CO₂ partial pressure. The total CO₂ absorbed that were determined by both the liquid analysis and by the IR analyzer were found to be slightly different where the results from the analyzer were relatively higher than those determined by the liquid analysis. This might occur due to dilution of the solution in the reactor by water condensate from the cooler. The CO₂ concentration in the solution that was determined by the analyzer was calculated from the CO₂ mass balance.

Table 2. Gas and liquid analyses for the CO₂ absorption in aqueous solutions of MDEA mixtures.

System	[CO ₂] _{absorbed} , mol/L				Difference, %
	Liquid analysis			CO ₂ gas analyzer	
	Parallel 1	Parallel 2	Average		
30 wt% MDEA	0.693	0.695	0.694	0.777	10.58
30 wt% MDEA + 5 wt% BEA	0.967	0.955	0.961	0.987	2.60
30 wt% MDEA + 10 wt% BEA	0.921	0.918	0.919	0.930	1.15
40 wt% MDEA + 6 wt% AEEA	1.330	1.324	1.327	1.379	3.76
50 wt% MDEA + 6 wt% AEEA	1.231	1.233	1.232	1.365	9.76

**Figure 4.** Absorption rates of CO₂ vs total CO₂ absorbed at 40 °C.

4. Conclusion

Absorptions of CO₂ in aqueous solutions of MDEA mixtures were measured at 40 °C in a bubble tank reactor. The systems tested were 30 wt% MDEA + 5 wt% BEA, 30 wt% MDEA + 10 wt% BEA, 40 wt% MDEA + 6 wt% AEEA and 50 wt% MDEA + 6 wt% AEEA. It was found that for MDEA-BEA-H₂O mixtures, the higher the promoter concentration the higher the CO₂ absorption rate, while for the MDEA-AEEA-H₂O mixtures, the higher the MDEA concentration the lower the CO₂ absorption rate. For all systems, in comparison to the 30 wt% MDEA solution, the addition of promoters has improved the MDEA performances.

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