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Pilot-Scale Evaluation of CO_2 Loading Capacity in AMP Aqueous Solution beside the Improvers HMDA-NH_3 under a Series of Operational Conditions

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Abstract

Nowadays, carbon dioxide removal has to be ingeniously managed because of its environmental and health effects. CO_2 as a heat-trapping greenhouse gas is pumped into the atmosphere through anthropogenic activities. This specific characteristic of CO_2 gas not only adversely impacts the environment but also imposes noxious effects on human life. In spite of all the various and potential scientific technics for CO_2 removal, gas absorption using alkanolamines solvents has played a significant role in industries in recent decades. In the present research, the equilibrium set up for measuring CO_2 solubility in aqueous solvents was assembled. CO_2 loading data in aqueous Amp and Amp (3M) activated with HMDA and NH_3 were assessed under the influence of various operational conditions of CO_2 partial pressures (8.44, 25.33, and 42.22kPa), temperatures (303, 313, and 323K) and solvent concentrations of (0.5, 1.5 and 3M) for pure AMP and (0.4, 0.8 and 1.2M) for HMDA-NH_3. The result showed that CO_2 loading of AMP activated HMDA-NH3 increases with decreasing system temperature and increasing CO_2 partial pressure. Furthermore adding the HMDA solvent into the system increased CO_2 loading before it followed a slight decrease while adding NH_3 decreased the amount. Concerning efficiency enhancement, it was comprehended that, HMDA could be considered among promising improvers while NH_3 as an additive beside AMP or as a based solvent, perform well in CO_2 absorption process only under specific operational condition.

Keywords: CO_2 solubility, AMP, Ammonia (NH_3), Loading

1 Introduction

The anthropogenic increase of greenhouse gases concentration in the atmosphere is stated to be the root cause of global warming. Among these greenhouse gases, CO_2 is believed to be highly responsible contributing to this issue. The accumulation of CO_2 in the air stems from diverse sources such as steel plants, cement industry and coal-fired power plants [1]. It is estimated that, if these large emitters continue to release CO_2 up into the atmosphere, by the year 2100 the atmosphere may will have loaded up to 570 ppm CO_2. This will then increase the mean global temperature by 1.9 C and the sea level by 3.8 m [2]. To find a solution to this severe environmental concern and to reduce the amplified greenhouse effects, several CO_2 removal methods have been designed after tremendous amounts of laboratory works. Some of them include chemical absorption, physical absorption, refrigerating methods, membrane separation and biological absorption. However gas absorption using aqueous alkanolamine solutions as a mature well-established technology has proved both efficacious and viable among others. Some of the most sought-after solutions in this category which have been exercised by many industry are monoethanolamine (MEA), diethanoleamine (DEA), and methyldiethanolamine (MDEA). Owing to a recent advancement in gas treating technology, a sterically hindered amine 2-amino-2-methyl-1-propanol (AMP) has

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been proposed as a different class of chemical absorbent [3].

Due to several supremacies in absorption capacity, absorption rate, selectivity, degradation resistance and regeneration energy over conventional alkanolamines it has been called a commercially attractive solvent [4]. Preliminary work on hindered amine solution was conducted by A.K. Chakraborty et.al. Also pahlavanzadeh and jahangiri were the priors to undertook the similar experiment with the introduced CO_2 absorption set up which showed good results [5]. Another study with AMP solvent was conducted by Anoar Ali Khan et.al to prove high loading capacity of this hindered amine [1]. Concerning efficiency enhancement, many researchers made a start on the utilization of blends of alkanolamines, or an amine based improved solution in varying concentration. They believed to produce absorbent with intensified absorption characteristics [4]. In other word, by this method it could bring together the advantages of each amine to facilitate CO_2 absorption process. For instance a mixture of primary (MEA) and tertiary amine (MDEA) could benefit from both a high absorption rate of MEA and a high equilibrium capacity of MDEA [6]. In this field, there exist several study to show the increasing interest in performing CO_2 absorption experiment using amine mixtures. As an example Yuli Artanto et.al investigated CO_2 absorption in aqueous mixture of AMP and piperazine (PZ) which showed good results compared to conventional MEA [7]. Won-Joon Choi et.al investigated CO_2 absorption into aqueous AMP/HMDA and AMP/MDEA to show the high CO2 loading capacity and high absorption rate of HMDA and MDEA additives [6].

The present research focuses on the use of amine blends which takes advantages of a hindered amine named AMP with a higher equilibrium CO_2 loading capacity in compare to conventional amines. Aqueous HMDA and NH_3 were also used beside to compensate for the low absorption rate of AMP [8]. NH_3 as an additive has several major dominances over amine solutions such as high CO_2 removal capacity, no degradation, less corrosion, low heat requirement for regeneration and the potential of capturing CO_2, SO_2 and NOx simultaneously [1]. In this regard, experiments were carried out with different molar compositions of AMP (.5, 1.5 and 3 M), AMP+HMDA (3+.4, 3+.8 and 3+1.2M) and AMP+NH3 (3+1, 3+2 and 3+3M) at three different temperatures of (303, 313, and 323K) and CO_2 partial pressures of (8.44, 25.33, and 42.22Kpa). The loading capacities of CO_2 in each blends of AMP, AMP/NH3 and AMP/HMDA were calculated under the mentioned operational conditions and the data were all registered.

2 Materials and Methods

In order to carry out the experiments, AMP, HMDA and NH_3 solvents were purchased with purity of 95%, 99% and 25% respectively, supplied by Merck Company and a certain amount of distilled water for preparing aqueous solution. CO_2-N_2 gas was prepared by SEPAHAN, industrial and medical gasses production, Company which is located in ISFAHAN

Laboratory Setup: In order to conduct the CO_2 absorption process, equilibrium set up for measuring CO_2 solubility in aqueous solvents was assembled which is illustrated in Fig. 1. This set up have several advantages over the conventional static and flow apparatus which have been applied for several years to measure CO_2 solubility data. The most important feature is the continuous contact of both phases during the experiment which practically occurs in industrial processes. Since you could have precise data for industrial designing.

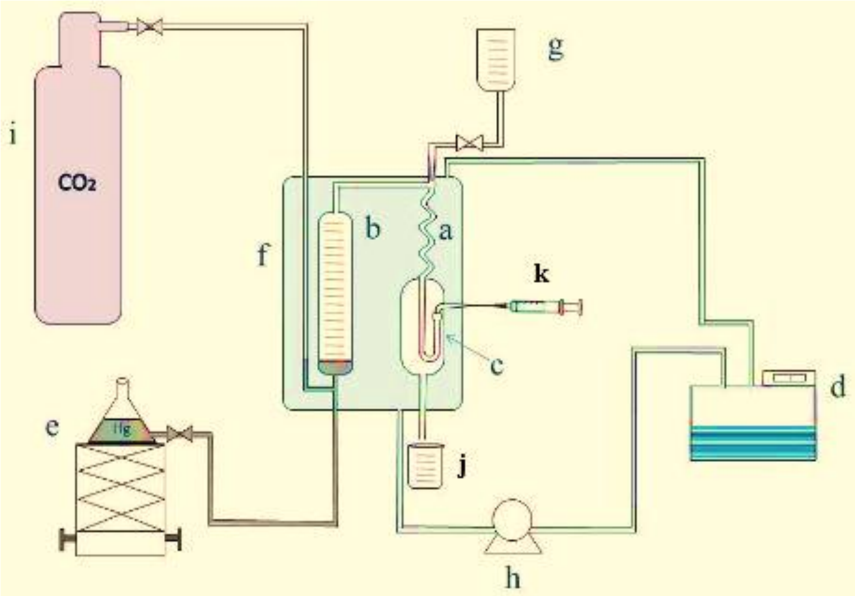

Figure 1: The apparatus for measuring the solubility of gases in liquid (a:Spiral tube, b:Scalling burette, c:Monometre, d:Water bath, e:Mercury Jack, f:Cell, g:Unloaded Solvent Container, h: Circulating Pump, i: CO_2 Capsule, J:Loaded Solvent Collector, K:H_2O injector)

The basic elements of the set up are as follows:

- **Equilibrium cell:** It is designed to make an equilibrium environment in which the equilibrium solubility of CO_2 in aqueous solvent solution could be investigated. The water which enters the equilibrium cell adjust the temperature to begin the experiments.
- **Spiral tube**: There exist number of turns which is constant. In these turns the liquid and vapor phase come into contacts with each other to begin absorption process. The solute and the solvent decide the parameters such as number of turns, the slope and the diameter of the tube. While the solubility of the gas increases, the number turns should be increased and the slope should be decreased to guarantee the equilibrium condition between the solvent and the solute at the end of the spiral tube.
- **Scaling Burette:** A scaling burette is a requisite device in order to estimate the volume of the dissolved gas into the solvent and also to maintain the gas in the set up. This burette is connected to the spiral tube at the top and to an internal valve at the bottom. The valve is in connection with a CO_2 capsule and a mercury vessel. The mercury vessel is located on a moving platform so as to adjust the level of the solution in the monometer.
- **Manometer:** A manometer is constructed at the bottom of the spiral tube. It is needed to show the pressure disagreement in the set up. The manometer is joint to the spiral tube from one end and is opened to the atmosphere from the other end.
- **Water bath:** A water bath is applied in the process in order to supply the water to the equilibrium cell at an adjusted temperature. This will provide for the temperature at which the experiments are considered to be performed.
- **Circulating pump:** This device is used to circulate the water which is supplied from the bath into and out of the equilibrium cell.
- **Solvent container:** Solvent container is used to inject the certain amount of solvent into the system at a constant rate.

CO_2 loading calculations: To obtain CO_2 loading, tests are needed to measure the amount of CO_2 gas dissolved in a certain amount of solvent. In each experiment, the amount of CO_2 dissolved during the test is obtained by reading on the burette. Then, using a proper equation of state, with having the pressure and temperature of the experiment, the volume of the gas is converted to the number of dissolved moles. Because the total pressure at which the set up works is approximately 1 atmosphere, the ideal gas equation of state is used. Molar volume of the gas could be obtained from equation 1.

$$Pv = RT \tag{1}$$

After calculating the molar volume of the gas dissolved in the test conditions, given the fact that during the test the volume of the gas is also determined based on the change in the height of the surface of the mercury, the amount of CO_2 moles can be obtained according to equation 2.

$$n = \frac{V}{\upsilon} \tag{2}$$

Determining the number o**f Solvent moles w**ith the volume, density and molecular mass of the solvent, the number of solvent moles consumed is calculated from the following equation:

$$n = \frac{Vd}{M_w} \tag{3}$$

In this regard, V is the solvent volume in milliliters, d is the solvent density in grams per ml, and MW is the solvent molecular mass in grams per mole. The number of moles consumed from each of the solvents is obtained by the following equation:

$$n_t = \frac{Vd}{M_w} \tag{4}$$

That n_t is the number of total molecules consumed for solvent mixtures, in which:

$$d = \sum_i^n x_i d_i \tag{5}$$

$$M_w = \sum_i^n x_i (M_w)_i \tag{6}$$

In these equations, xi, di and $(MW)_i$ are the solvent (i) mole fraction in the composition, the solvent (i) density, and the molecular mass of the solvent (i). The following equation is used to calculate the mole of each solvent consumed:

$$n_i = c_i n_t \tag{7}$$

By calculating the amount of CO_2 moles and the amount of solvent moles according to equations above, the amount of α which stands for CO_2 loading could be obtained by the following equation:

$$\alpha_{\exp} = \frac{mol_{CO_2}}{mol_{solvent}} \tag{8}$$

Laboratory data related to CO_2 loading in AMP + H_2O + CO_2 system: In Table 1, CO_2 loadings are calculated according to equation. The calculations were performed under different operational conditions in AMP concentrations of (.5, 1.5 and 3M), temperature (303, 313, and 323K) and CO_2 partial pressure (8.44, 25.33, and 42.22kPa). According to the data which are presented in table 1, Figure 1 displays CO_2 loading capacity of pure AMP under the mentioned operational conditions.

Laboratory data related to CO_2 loading in AMP + H_2O + CO_2 + HMDA system: In Table 2, CO_2 loadings are calculated according to equation. The calculations were performed under different operational conditions in AMP+HMDA concentrations of (3+.4, 3+1.8 and 3+1.2), temperature (303, 313, and 323K) and CO_2 partial pressure (8.44, 25.33, and 42.22kPa). According to the data which are presented in table 2, Figure 2 displays the effects of HMDA additive into AMP (3M) under the mentioned operational conditions.

Table 1: CO_2 loading in AMP+H_2O+CO_2 system

AMP Concentration M	Temp K	α_{Exp}		
		$P_{CO_2} = 8.44 kPa$	$P_{CO_2} = 25.33 kPa$	$P_{CO_2} = 42.22 kPa$
AMP (0.5M)	303	0.0207	0.1243	0.3107
AMP (0.5M)	313	0.0160	0.0722	0.2005
AMP (0.5M)	323	0.0078	0.0466	0.1166
AMP (1.5M)	303	0.0096	0.0495	0.1581
AMP (1.5M)	313	0.0080	0.0399	0.1261
AMP (1.5M)	323	0.0052	0.0232	0.0903
AMP (3M)	303	0.0062	0.0329	0.0960
AMP (3M)	313	0.0040	0.0279	0.0797
AMP (3M)	323	0.0026	0.0212	0.0643

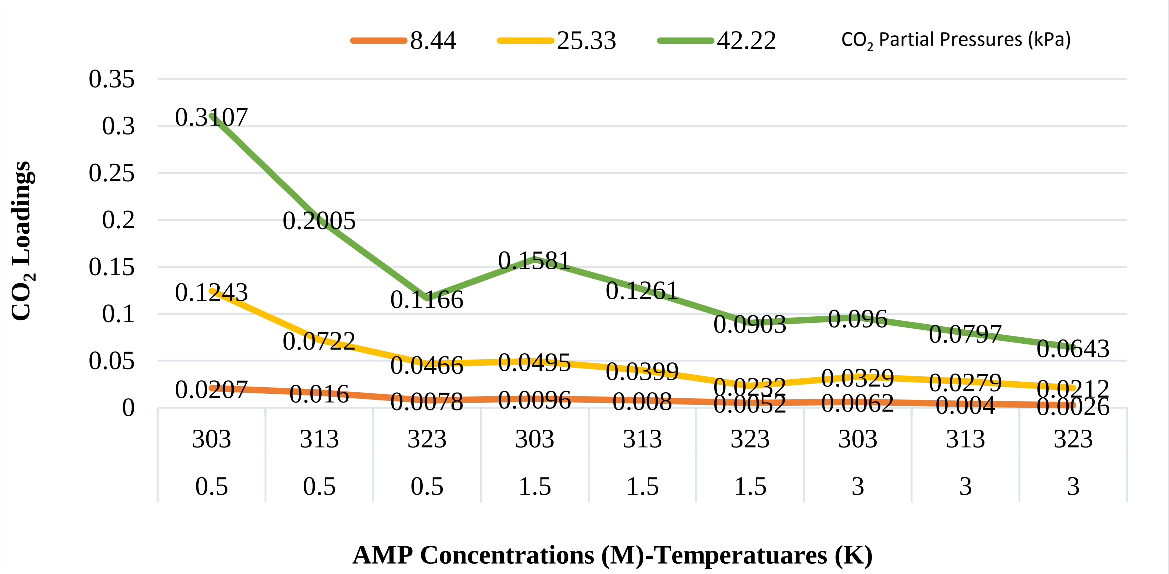

Figure 1: The influence of operational conditions on CO_2 loading in different AMP Concentrations of (0.5, 1 and 3M)

Table 2: CO_2 loading in AMP+HMDA+H_2O+CO_2 system

AMP Concentration M	Temp K	α_{Exp}		
		$P_{CO_2} = 8.44 kPa$	$P_{CO_2} = 25.33 kPa$	$P_{CO_2} = 42.22 kPa$
AMP(3M)+HMDA(0.4M)	303	0.011	0.052	0.0105
AMP(3M)+HMDA(0.4M)	313	0.009	0.042	0.096
AMP(3M)+HMDA(0.4M)	323	0.007	0.037	0.079
AMP(3M)+HMDA(0.8M)	303	0.001	0.052	0.099
AMP(3M)+HMDA(0.8M)	313	0.009	0.044	0.088
AMP(3M)+HMDA(0.8M)	323	0.007	0.039	0.073
AMP(3M)+HMDA(1.2M)	303	0.010	0.048	0.099
AMP(3M)+HMDA(1.2M)	313	0.009	0.041	0.089
AMP(3M)+HMDA(1.2M)	323	0.007	0.037	0.073

Laboratory data related to CO_2 loading in AMP+NH_3 + H_2O + CO_2 system: In Table 3, CO_2 loadings are calculated according to equation. The calculations were performed under different operational conditions in AMP+NH_3 concentrations of (3+1, 3+2 and 3+3M), temperature (303, 313, and 323K) and CO_2 partial pressure (8.44, 25.33, and 42.22kPa). According to the data which are presented in table 3, Figure 3 displays the effects of NH_3 additive into AMP (3M) under the mentioned operational conditions.

3 Results and Discussion

Experiments were carried out under the mentioned operational conditions. According to the Figures 1, 2, and 3, it was comprehended that for pure AMP, AMP+NH_3 and AMP+HMDA, CO_2 loading increased with a reduction in temperature and an increase in CO_2 partial pressures. By increasing AMP concentration, CO_2 loading decreased. In practice, during the absorption process with pure AMP, the increase in CO_2 mole numbers in the solvent is not as well as the increase in AMP solvent moles when increasing the concentration. According to equation 8, the denominator increase is much more than the numerator increase. For this reason, CO_2 loading decreases with increase in concentration, which has been observed in previous researches conducted by pure AMP to confirm the accuracy of the matter[5]. According to Figure 2 HMDA additive into AMP (3M) made an upward trend toward an enhancement in CO_2 loading capacity especially at higher CO_2 partial pressures, however it was applied in low concentrations. For aqueous NH_3 According to Figure 3, it was found that, no improvement has obtained during the absorption process while NH_3 was added to AMP system under the same operational conditions. In order to justify the behavior of ammonia solvent, Several Previous works on CO_2 absorption using aqueous ammonia were studied. It was understood that, aqueous ammonia in CO_2 absorption process has its best performance while it is applied in temperatures below 10C. In a case where the temperature exceeds, Figure 3, ammonia evaporation may occur as a result which leads to solvent loss during the experiments. Furthermore, In order to cope with solvent loss during the absorption process, some researchers have recommended the use of metal additives like Zn, Cu, Ni, and Me into the aqueous ammonia [9, 10].

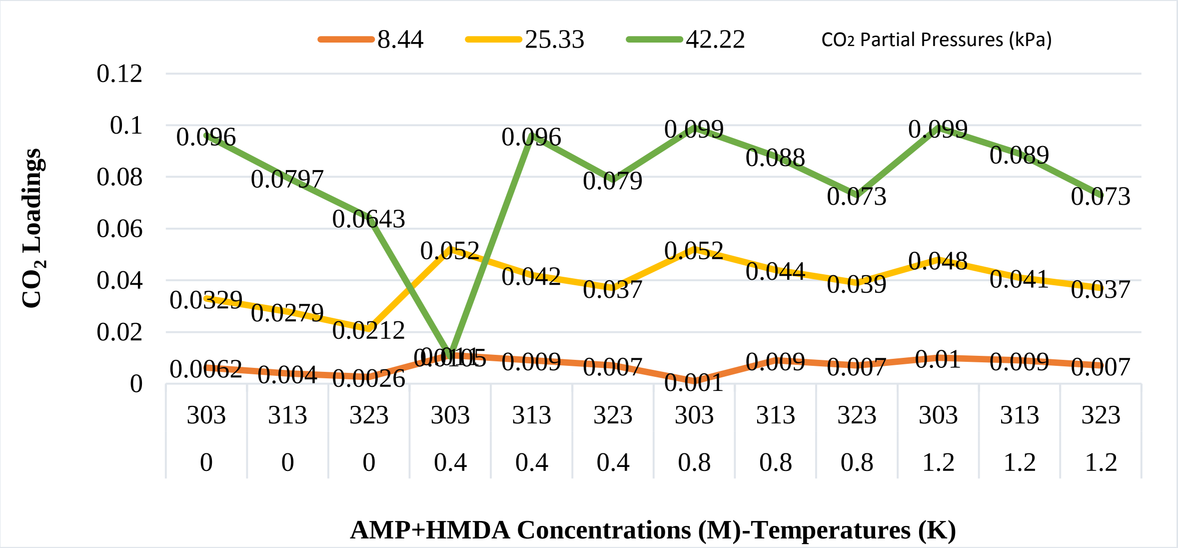

Figure 2: The influence of adding the improver (HMDA) in concentrations of (0.4, 0.8 and 1.2M) into AMP (3M) under variable operational conditions

Table 3: CO_2 loading in AMP+NH_3+H_2O+CO_2 system

AMP Concentration M	Temp K	α_{Exp}		
		$P_{CO_2} = 8.44kPa$	$P_{CO_2} = 25.33kPa$	$P_{CO_2} = 42.22kPa$
AMP(3M)+NH_3(0.4M)	303	0.0010	0.0209	0.0499
AMP(3M)+NH_3(0.4M)	313	0.0007	0.0181	0.0435
AMP(3M)+NH_3(0.4M)	323	0.0002	0.0161	0.0398
AMP(3M)+NH_3(0.8M)	303	0.0010	0.0150	0.0351
AMP(3M)+NH_3(0.8M)	313	0.0006	0.0131	0.0307
AMP(3M)+NH_3(0.8M)	323	0.0003	0.0117	0.0282
AMP(3M)+NH_3(1.2M)	303	0.0010	0.0120	0.0291
AMP(3M)+NH_3(1.2M)	313	0.0007	0.0105	0.0263
AMP(3M)+NH_3(1.2M)	323	0.0003	0.0094	0.0237

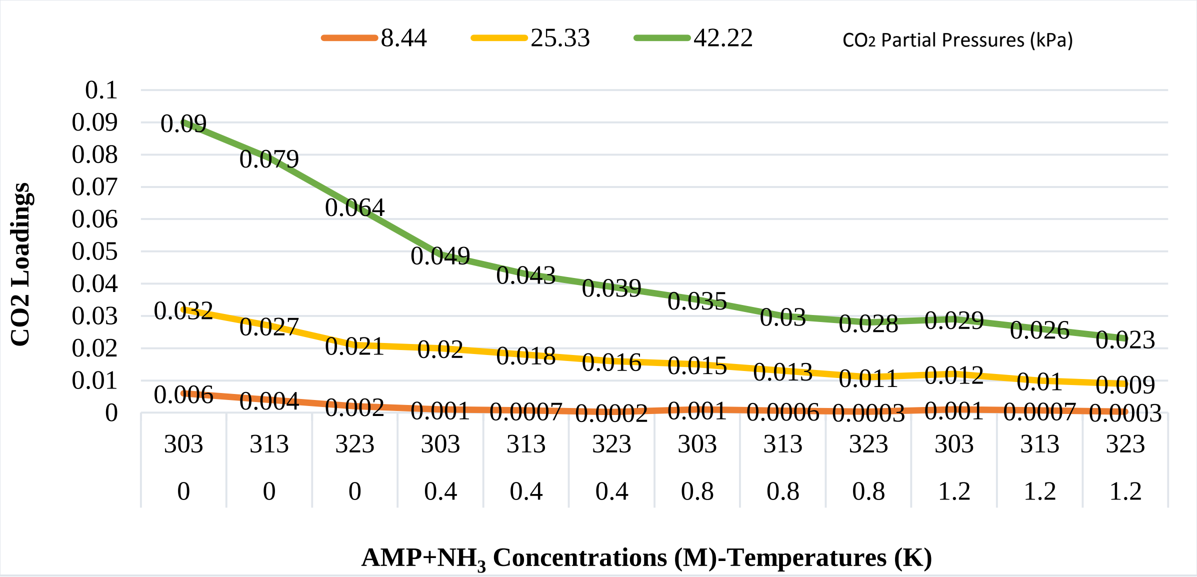

Figure 3: The influence of adding the improver (NH_3) in concentrations of (0.4, 0.8 and 1.2M) into AMP (3M) under variable operational conditions

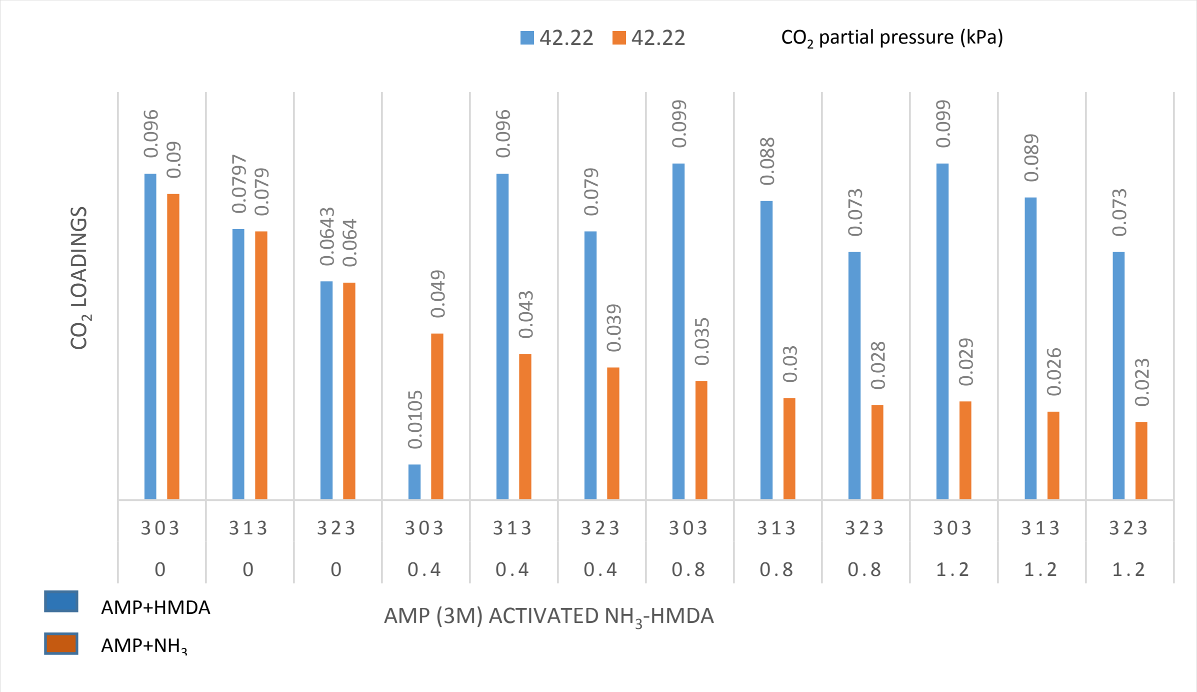

Figure 4: Experimental CO_2 loading of the mixed AMP+HMDA in comparison with AMP+NH3

4 Conclusion

In the present research CO_2 absorption by pure AMP and AMP activated NH_3-HMDA was studied under various operational conditions. HMDA additive increased CO_2 loading capacity of pure AMP while adding aqueous NH_3 to AMP did nothing to enhance the amount. In fact inappropriate selection of the operational temperature range higher than the optimum amount, led to ammonia loss during the CO_2 absorption process. That meant that no NH_3 was introduced into the system while it had been taken into consideration for CO_2 loading calculation which caused a drop in the amount.

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