New Experimental Data on Equilibrium CO_2 Loading into Aqueous 3-Dimethyl Amino-1-propanol and 1,5-Diamino-2-methylpentane Blend: Empirical Model and CO_2 Absorption Enthalpy

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ABSTRACT: This research was targeted to determine the equilibrium CO_2 loading in the novel aqueous 3-dimethyl amino-1-propanol (3-DMA-1-P) and 1,5-diamino-2-methylpentane (1,5-DA-2-MP) blend accomplished in the bubble absorption column of a lab-scale experimental setup. The experiments were conducted at a total concentration of the aqueous amine blend (C_T) within 10–30 wt %, the weight fraction of 1,5-DA-2-MP in the amine blend (3-DMA-1-P + 1,5-DA-2-MP) in the range of 0.05–0.2, the temperature of the aqueous amine blend system from 293.15 to 323.15 K, and the partial pressure of CO_2 ranging from 10.13 to 25.33 kPa, and all of these were executed at atmospheric pressure. The addition of a small quantity of activator 1,5-DA-2-MP revealed significant increase in the performance of CO_2 absorption. Maximum CO_2 loading α_{max} 0.97 mol CO_2/mol amine was obtained by this blend under the operating condition of C_T 10 wt %, $w_{1,5-DA-2-MP}$ 0.2, p_{CO_2} 20.27 kPa, T 313.15 K, and P 101.325 kPa. The empirical model for the equilibrium CO_2 loading in the amine blend was developed with the correlation of the experimental data. The average absolute relative deviation % was 2.7 for this empirical model. The Gibbs Helmholtz equation was employed for calculation of the CO_2 absorption enthalpy (−67.3 kJ/mol) for this amine blend, which was considerably lower than the absorption enthalpy (−83.7 kJ/mol) of conventionally used monoethanolamine.
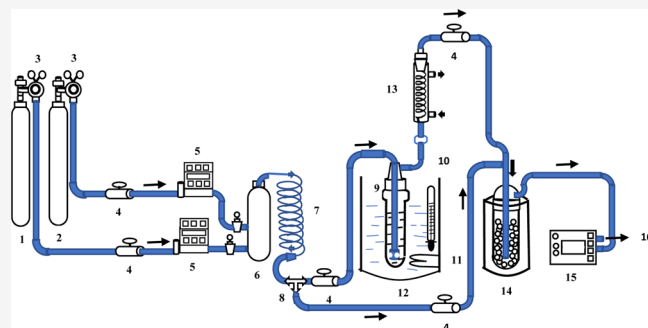
1. INTRODUCTION

Because of the inclination toward the enormous industrial development, fossil fuels are rapidly used, which result in the release of CO_2, water vapor, NO_x, SO_X, carbon monoxide, particulates, and traces of some other compounds; CO_2 is the prime contributing greenhouse gas (GHG) among them. These gases give rise to significantly important issues. Global warming, ensued global climatic condition changes, rise of the sea level, pediatric health, and equity are the issues resulting mainly from anthropogenic GHGs emissions (83%) have become great concern over some years.[1,2] The rise of CO_2 emissions globally from fossil fuel combustion will shoot up from 31.3 to 37.2 Gt from year 2011 to 2035 unless substantial endeavors are made to check the CO_2 emissions.[1] Until the year 2040, the rise in energy demand will grow by 1.3% every year.[3] The IPCC panel in its latest report stated that to reduce the Earth's temperature rise to 1.5 °C, there should be 45% reduction in CO_2 emissions of the 2010 level by 2030, and hence, at this rate, we can reach the condition of 'net zero' by 2050.[4]

As a consequence, carbon capture has been found as a key solution to minimize the CO_2 emission to the atmosphere; various techniques and technologies have been developed so far, and further research is going on.[5] There are mainly three considerable approaches of CO_2 capture, that is, oxyfuel combustion, postcombustion, and precombustion. Various techniques such as absorption, adsorption, chemical looping combustion, cryogenic separation, and membrane separation are generally used. The selection of a particular technology and technique for any process is the matter of optimum decrease in the concentration level of CO_2 and technoeconomical aspects. Because of the flexibility in the application and retrofitting with any established plant, postcombustion technology has been used frequently. Consequently, postcombustion technology with the absorption technique is the most competent, advanced, and efficient one, which has been effectively commercialized.[6−8]
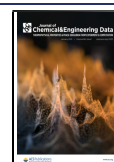
Vaidya and Kenig (2007)[9] investigated that up to a CO_2 solubility of 1 mol CO_2/mol amine was attained by the tertiary amines, which was relatively higher than primary or secondary amines, which could only reach up to 0.5 mol CO_2/mol amine. However, there was release of a large amount of energy of absorption because of formation of carbamates by primary or secondary amines with the zwitterion mechanism and less absorption heat was released because of formation of bicarbonates by tertiary amines with the base-catalytic CO_2 hydration mechanism.[9] There were several amines and amine blends which have been investigated to date, but there seem to be shortcomings in them with respect to absorption capacity, large amount of energy consumption, and economical aspects. Therefore, new amine blends are further developed with high CO_2 capture performance, lower energy utilization, economical nature, and as efficient alternative to the conventional amines.[6,7,10,11]

Chakma et al. (1997) and Idem et al. (2006) discovered that the monoethanolamine (MEA) showed fast kinetics, while methyldiethanolamine (MDEA) showed slow kinetics. Hence, when blended together, MEA results in acceleration of intermediate formation and transfer of this CO_2 intermediate in MDEA, and in consequence, MEA proves to be a promising activator.[12,13]

In recent studies, 3-dimethyl amino-1-propanol (3-DMA-1-P), a tertiary amine, demonstrated to be a potential solvent instead of the usually used MDEA. Bernhardsen et al. (2019)[14] in a recent study showed that 3-DMA-1-P appeared to be a competent solvent on the basis of VLE behavior and volatility results as an option or replacement for diethylethanolamine (DEEA).[14] At a total concentration of 1−3 mol/L, temperature of 298−323 K, and partial pressure of CO_2 of 3−101 kPa, CO_2 solubility of aqueous 3-DMA-1-P at equilibrium was estimated and fitted with various thermodynamic models in the work of Li et al. (2017).[15] Studies by Afkhamipour et al. (2018)[16] showed that the 3-DMA-1-P aqueous system does not form an azeotrope. Idris et al. (2016)[17] reported that both CO_2-loaded and -unloaded 3-DMA-1-P solutions showed decrease in their densities with temperature; unloaded amine had lower density, and its density increased with CO_2 loading. Density increases for the unloaded amine with its mole fraction. Martin et al. (2012)[18] showed that degradation induced by CO_2, degradation due to temperature, and degradation due to oxidation had lower value for aqueous 3-DMA-1-P than MEA solution. Kadiwala et al. (2012)[19] showed that 3-DMA-1-P had twice the reaction rate with CO_2 as compared to 1-dimethyl amino-2-propanol (1DMA2P). Both 1DMA2P and 3-DMA-1-P had a high value of rate constants of the second-order reaction and CO_2 equilibrium solubility than that of commonly used MDEA and triethanolamine. Xaio et al. (2016, 2018)[20,21] showed that 3-DMA-1-P (21.0 wt %) has a CO_2 loading of 0.794 mol CO_2/mol amine at p_{CO_2} 15 kPa and T 303.15 K. The dissociation coefficient value (pK_a) of 3-DMA-1-P is 9.8 at 298 K, and the second-order reaction rate constant (k_2) is 0.032 m^3/mol·s at 298 K that are better than those of 23.5 wt % MDEA (α = 0.523 mol CO_2/mol amine, pK_a = 8.4, and k_2 = 0.012).[20−22]

1,5-Diamino-2-methylpentane (1,5-DA-2-MP), is a novel diamine consisting of two primary amine groups; at different total concentrations of the solvent, temperature of 303−323 K, and pressure of 5−150 kPa, the maximum CO_2 solubility of aqueous 1,5-DA-2-MP was 0.86, 2.5 M MEA was 0.54, and 2.5

M MDEA was 0.43 mol CO_2/mol amine. This revealed that 1,5-DA-2-MP possesses higher CO_2 equilibrium solubility and CO_2 absorption rate, low vapor pressure, and high cyclic capacity against MEA. Because of low vapor pressure, it had less solvent loss than MEA in the regeneration process.[23] Hamidi et al. (2018)[24] implied that there was great hype in the absorption efficiency of the aqueous blend of MEA + MDEA + 1,5-DA-2-MP with respect to MEA + MDEA, but it did not have much effect on the desorption performance. The single amine performance study of MEA, MDEA, and 1,5-DA-2-MP showed the effective and efficient ability of 1,5-DA-2-MP as an activator with the commonly utilized amines to enhance their potential.[24] CO_2 capture using the aqueous 2-(amino)-methylpropanolamine + 1,5-DA-2-MP blend showed enhancement in CO_2 absorption and desorption performances with less energy consumption and cost as compared to MEA.[25,26] The aqueous MDEA + 1,5-DA-2-MP blend also showed amplification in CO_2 absorption and regeneration performances, and it can be efficiently and economically compared to the aqueous MDEA + piperazine blend from the hydrogen (H_2)-producing process plant.[27] Not many studies of the blend of 1,5-DA-2-MP have been carried out so far, and from the results of previous studies, it can be presumed to be a promising activator.

Therefore, the intent of this research work was to experimentally study the aqueous blend of 3-DMA-1-P + 1,5-DA-2-MP at a total concentration of the blend from 10 to 30 wt %,weight fraction of 1,5-DA-2-MP in the amine blend (3-DMA-1-P + 1,5-DA-2-MP) of 0.05−0.2, temperature of 293.15−323.15 K, partial pressure of CO_2 of 10.13−25.33, and 101.325 kPa total pressure to (1) explore the absorption performance, (2) establish the empirical model correlating the experimental data, and (3) determine the CO_2 absorption enthalpy value.

2. EXPERIMENTAL DESCRIPTION

2.1. Materials and Equipment Description. 1,5-DA-2-MP and 3-DMA-1-P amines were used in the present work. 1,5-DA-2-MP ($C_6H_{16}N_2$) and 3-DMA-1-P ($C_5H_{13}NO$) with molecular weights of 116.21 and 103.17, respectively, were purchased from Tokyo Chemical Industry Co. Ltd, Tokyo, Japan. MEA with a molecular weight of 61.08 and molecular formula of C_2H_7NO, was purchased from Sigma-Aldrich, St. Louis, USA. All three, 3-DMA-1-P, 1,5-DA-2-MP, and MEA, were utilized with initial purity supplied by the manufacturer. Details about used chemicals are given in Table 1. The aqueous solution of amines was prepared with double distilled water. Double distilled water was produced in our laboratory itself by using double distillation. Others materials such as hydrochloric acid (HCl), carbon dioxide gas (CO_2), and nitrogen (N_2) were also used. HCl was purchased from SD Fine Chemical Limited, Mumbai, India. CO_2 and N_2 were supplied by Linde India Limited. CO_2 and N_2 gases from cylinders were simulated through a gas flow controller (MC-500SCCM-D, Alicat Scientific, New Delhi, India, accuracy ±0.6%) and were mixed well. A lab-scale borosilicate bubble absorption column was employed. The CO_2 concentration in the gas stream was measured through a portable infrared flue gas analyzer (Gasboard-3800P, Wuhan Cubic Optoelectronics Co. Ltd., Wuhan, China, CO_2 range 0−100% V/V, accuracy ±0.1%). To maintain the temperature of the aqueous amine solution while performing the experiment, a water bath incubator shaker with a temperature controller was used with

Table 1. Chemicals Used in the Experimentation

chemical name	CAS number	source	final purity (%)	purification method
1,5-DA-2-MP[a]	15520-10-2	Tokyo Chemical Industry Co. Ltd, Tokyo, Japan	>98[g]	none
3-DMA-1-P[b]	3179-63-3	Tokyo Chemical Industry Co. Ltd, Tokyo, Japan	>98[g]	none
MEA[c]	141-43-5	Sigma Aldrich, St. Louice, USA	>99[g]	none
HCl[d]	7647-01-0	SD Fine chemical limited, Mumbai, India	35−38[g]	none
water	7732-18-5	Our laboratory	99.9[e]	double distillation
CO_2[e] gas	124-38-9	Linde India Ltd.	99.99[h]	none
N_2[f] gas	7727-37-9	Linde India Ltd.	99.99[h]	none

[a]1,5-Diamino-2-methylpentane. [b]3-Dimethyl amino-1-propanol. [c]Monoethanolamine. [d]Hydrochloric acid. [e]Carbon dioxide. [f]Nitrogen. [g]Mass fraction. [h]Volume fraction.

an accuracy of ±1 K. HCl was used for titration with a magnetic stirrer to estimate the amount of CO_2 in the aqueous amine solution sample.

2.2. Equilibrium CO_2 Loading Measurement. 3-DMA-1-P + 1,5-DA-2-MP aqueous solution was utilized for absorbing CO_2, and the equilibrium CO_2 loading in this blend was measured experimentally in this work. The significant potential of the 3-DMA-1-P-based blend is shown in literature.[22] For the measurement of the amount of absorbed CO_2 in the aqueous amine blend, the experimental setup is shown in Figure 1. The absorption experiment was conducted at atmospheric pressure and temperatures from 293.15 to 323.15 K. There were two cylinders, one of CO_2 (99.99 V % purity) and the other of nitrogen (99.99 V % purity), which were connected to the gas flow meters and pressure gauges. A simulated gas stream of CO_2 was used in the experiment with a total flowrate of 240 mL per min. First, the required composition of CO_2 and N_2 were maintained by mixing

them in the mixing chamber and checked using an infrared flue gas analyzer for sustaining uniform composition for further use. A laboratory-scale borosilicate bubble absorption column of capacity 200 mL in semibatch operation mode was employed for the absorption of CO_2 in the aqueous amine solution from simulated gas stream. Second, the bubble column was filled with aqueous amine solution and was placed in the water bath incubator shaker with a thermocouple as the temperature sensor, and the in-built temperature controller maintained the desired temperature of the aqueous amine solution or system. Third, the continuous flow of stimulated gas stream was bubbled into the aqueous amine blend until its saturation. The check upon the saturation level of aqueous amine solution was kept by examining the exit concentration of CO_2 at every 10 min by the flue gas analyzer. Lastly, when the outlet concentration of CO_2 approached that of the entrance or introducing concentration of CO_2 in the bubble column, the equilibrium CO_2 loading in the aqueous amine solution was reached. Prior to the measurement of the concentration of CO_2 in the outlet gas stream by the flue gas analyzer, it was passed into the condenser to condense the vaporized amine solution by circulating chilled water and then through the silica gel column to remove the remaining moisture content. The CO_2 loading was calculated by titrating the CO_2-absorbed amine sample utilizing 1 M HCl and methyl orange (0.1 wt % aqueous) as indicators in moles of CO_2 per mole of the amine blend by employing the Chittick apparatus. The experiment under the same operating condition was repeated 3 times, and the average value of CO_2 loading is reported in this paper.

3. RESULTS AND DISCUSSION

3.1. Equilibrium CO_2 Loading in the Aqueous 3-DMA-1-P + 1,5-DA-2-MP Blend. The different parameters and conditions at atmospheric pressure utilized were the activator weight fraction in the amine blend (3-DMA-1-P + 1,5-DA-2-MP) from 0.05 to 0.2 (0.05, 0.10, 0.15, and 0.20), total concentration of solution from 10 to 30 wt % (10, 15, 20, 25,, and 30 wt %), temperature from 293.15 to 323.15 K (293.15,
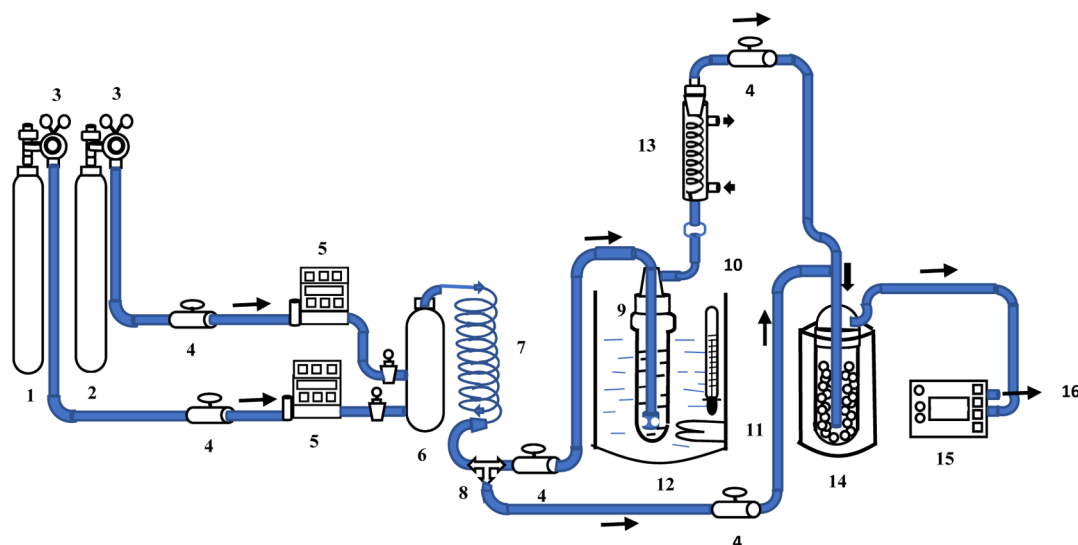
Figure 1. Diagrammatic representation of the experimental setup used for measuring CO_2 absorption: (1) CO_2 gas cylinder, (2) N_2 gas cylinder, (3) pressure controller, (4) stainless steel valve, (5) flow controller, (6) gas mixing cylinder, (7) gas mixing coils, (8) T-joint, (9) bubble absorption column filled with amine solution, (10) temperature sensor, (11) heating coils, (12) water bath with temperature controller, (13) condenser with cooling water inlet and outlet, (14) silica bed drying outlet stream, (15) portable infrared flue gas analyzer, and (16) outlet stream to the vent.

303.15, 313.15 and 323.15 K), and CO_2 partial pressure from 10.13 to 25.33 kPa (10.13, 15.2, 20.27, and 25.33 kPa) for the 3-DMA-1-P + 1,5-DA-2-MP aqueous blend in this study. To validate the lab-scale experimental setup, CO_2 loading for MEA was measured at 313.15 K and at different partial pressures of CO_2 (p_{CO_2}) (12.8, 15.20, and 20.27 kPa) and compared with available literature with the same operating condition.[28−30] Results are shown in Table 2. Average relative deviation % and

Table 2. Comparison of Experimentally Measured and Literature Data of CO_2 Loading in Aqueous MEA ($w = 30$ wt %) at 313.15 K, Different CO_2 Partial Pressure (p_{CO_2}), and Atmospheric Pressure[a]

p_{CO_2} (kPa)	α_{exp} (mol CO_2/mol amine)	α_{lit} (mol CO_2/mol amine)	ARD %
12.80	0.530	0.512[b]	4
15.20	0.540	0.564[c]	4
20.27	0.558	0.540[d]	3
		AARD %	3.7

[a]Standard uncertainties u is $u(T) = 1$ K, $u(p_{CO_2}) = 0.05$ kPa, $u(C_T) = 1$ wt %, and expanded uncertainty at 95% confidence level is $U(\alpha) = 0.01\alpha$ mol $CO_2 \cdot$mol amine^{-1}. [b]Reference 28. [c]Reference 30. [d]Reference 29.

absolute deviation % between experimental CO_2 loading (α_{exp}) data and literature data (α_{lit}) were calculated and are reported in Table 2. Average absolute relative deviation % (AARD %) 3.7 indicated that the setup assembled can be effectively used for further experimentation.

Equilibrium CO_2 loading data of the aqueous 3-DMA-1-P + 1,5-DA-2-MP blend at T (293.15−323.15) K and atmospheric pressure is given in Table 3. The effects of various operating parameters on the equilibrium CO_2 loading are discussed in following subsections.

3.1.1. Effect of Weight Fraction of Activator 1,5-DA-2-MP in the Amine Blend (3-DMA-1-P + 1,5-DA-2-MP) on CO_2 Loading. It can be seen from the results shown Figure 2 that as the weight fraction of 1,5-DA-2-MP increased from 0.05 to 0.20, the CO_2 loading in the aqueous amine blend also increased. It is known from literature[31] that most of the primary and secondary amines gave an equilibrium loading of CO_2 up to 0.5 mol CO_2/mol amine and that of tertiary amines up to 1 mol CO_2/mol amine. Thus, the blend of the primary or secondary and tertiary amine was devised to get such a blend, which possessed the efficient capabilities of the two blended amines. In this study, the primary or secondary amine enhanced the reaction kinetics, and because of the tertiary amine, the blend showed high CO_2 absorption capacity and low desorption energy.[9] As an activator, 1,5-DA-2-MP consisted of two primary amine groups, which provided more reactive sites to CO_2 absorption, hence resulting in increase in CO_2 loading with increasing 1,5-DA-2-MP weight fraction in this amine blend. However, the weight fraction of 1,5-DA-2-MP was used up to 0.20 because of 1,5-DA-2-MP as the polyamine, and polyamines have high heat of absorption. Further increase of weight fraction of 1,5-DA-2-MP could increase overall heat of absorption of the aqueous amine blend (3-DMA-1-P + 1,5-DA-2-MP).

3.1.2. Effect of the Total Concentration of the Aqueous 3-DMA-1-P + 1,5-DA-2-MP Blend on CO_2 Loading. It can be seen in the graph plotted in Figure 3 that with increase in the

total concentration from 10 to 30 wt % at $w_{1,5-DA-2-MP}$ of 0.1 and 0.2 in the amine blend (3-DMA-1-P + 1,5-DA-2-MP), the CO_2 loading continuously declined over the range of total wt % (10−30 wt %) evaluated. As the weight fraction of 1,5-DA-2-MP changes from 0.1 to 0.2, the value of CO_2 loading was enhanced substantially. Xiao et al. (2018)[21] investigated that the presence of the electron providing the methyl group to the nitrogen atom-active sites of 3-DMA-1-P enables its better performance. The presence of the hydroxyl group at γ-carbon exhibits as a weak electron-extracting group in 3-DMA-1-P than DEEA in which the hydroxyl group was present at the β-carbon position possessing strong inductive effect. The electron-removing effect of the hydroxyl group was experienced at a short range, and thus, this effect can be reduced by the presence of a long series of carbons between amine and hydroxyl groups, as in 3-DMA-1-P.[21] The increase in the total concentration prevented the carbamate conversion into bicarbonates at higher concentrations of amine solution.[32] The results represented the better condition in terms of CO_2 loading at a $w_{1,5-DA-2-MP}$ of 0.2 and total concentration of 10 wt %.

3.1.3. Effect of the Temperature of the Aqueous 3-DMA-1-P + 1,5-DA-2-MP Blend on CO_2 Loading. It is well known that dynamic equilibrium is established in the dissolution process, and for this, Le Chatelier's principle states that in the exothermic dissolution process, the solubility of the gas in a solution decreases as the temperature of the solution increases. The results from the plotted graph in Figure 4 showed moderate or nominal decrease in the rate of CO_2 loading up to 313.15 K, and after that, steep decrease in the rate can be seen. It also showed that there was a decreasing pattern in CO_2 loading with enrichment of the amine in the aqueous blend. Here, with the rise in the temperature of the blend solution, the dissolving capacity of CO_2 was reduced in the aqueous amine blend because the reaction between CO_2 gas and the aqueous amine blend was reversible and exothermic; hence, increase in temperature does not favor the absorption of gas but benefits the desorption of gas. There was desorption of absorbed CO_2 from the rich aqueous amine blend on heating because the chemical bond breaks off, which ultimately reduces CO_2 solubility.

3.1.4. Effect of CO_2 Partial Pressure on CO_2 Loading. The results given in Figure 5 show that as the partial pressure of the CO_2 was enhanced, the dissolving capacity of CO_2 in the aqueous amine blend also increased. The extent of the gas that would dissolve in any solvent was estimated by the dynamic equilibrium between the dissolved gas in the solvent and the undissolved gas. The gas solubility in a liquid is proportional to the partial pressure of the gas present above the surface of the liquid or solution at a constant temperature, as stated by Henry's law. Therefore, the concentration of the gas in the solution increases as there is increase in the partial pressure of the gas. At higher CO_2 partial pressure, more CO_2 was available in the liquid in a dissolved form so that more amount of carbamates, bicarbonate, and carbonate formed, and CO_2 loading increased by increasing the partial pressure.[33] The graph plotted shows the growth in CO_2 loading with the rise in CO_2 concentration in gas stream for different total concentrations of the blend. There was steep growth in the rate of CO_2 loading up to 20.27 kPa, and thereafter, moderate growth rate followed. The experiment of Xiao et al. (2018) showed that for dimethylethanolamine, DEEA, and 3-DMA-1-P, with increase in the CO_2 partial pressure up to 20.27 kPa,

Table 3. Experimental Equilibrium CO_2 Loading (α_{exp}) and Estimated Equilibrium CO_2 Loading (α_{est}) Data of Aqueous 3-DMA-1-P + 1,5-DA-2-MP Blend at Different Operating Conditions Such as Temperature T/K, CO_2 Partial Pressure p_{CO_2}/kPa, Total Aqueous Amine Blend Concentration C_T/wt %, and 1,5-DA-2-MP Weight Fraction in the Total Amine Blend/$w_{1,5-DA-2-MP}$ at Atmospheric Pressure[a]

serial number	T (K)	p_{CO_2} (kPa)	$w_{1,5-DA-2-MP}$	C_T (wt %)	α_{exp} (mol CO_2·mol amine^{-1})	α_{est} (mol CO_2·mol amine^{-1})	ARD %
1	313.15	20.27	0.05	10	0.702	0.747	6.5
2	313.15	20.27	0.10	10	0.811	0.791	2.5
3	313.15	20.27	0.15	10	0.899	0.862	4.1
4	303.15	20.27	0.20	10	1.011	1.050	3.8
5	313.15	20.27	0.20	10	0.970	0.963	0.7
6	313.15	10.13	0.20	10	0.775	0.757	2.4
7	313.15	15.20	0.20	10	0.875	0.873	0.2
8	313.15	25.33	0.20	10	1.020	1.027	0.6
9	323.15	20.27	0.20	10	0.743	0.755	1.6
10	313.15	20.27	0.10	15	0.795	0.773	2.8
11	313.15	20.27	0.20	15	0.953	0.945	0.8
12	313.15	20.27	0.05	20	0.650	0.706	8.5
13	313.15	20.27	0.10	20	0.771	0.749	2.9
14	313.15	20.27	0.15	20	0.872	0.821	5.9
15	293.15	20.27	0.20	10	1.030	1.016	1.4
16	293.15	20.27	0.20	20	0.975	0.974	0.1
17	303.15	20.27	0.20	20	0.962	1.008	4.8
18	313.15	20.27	0.20	20	0.933	0.921	1.3
19	313.15	10.13	0.20	20	0.715	0.715	0.0
20	313.15	15.20	0.20	20	0.824	0.831	0.9
21	313.15	25.33	0.20	20	0.980	0.985	0.5
22	323.15	20.27	0.20	20	0.694	0.713	2.8
23	313.15	20.27	0.10	25	0.745	0.719	3.5
24	313.15	20.27	0.20	25	0.900	0.892	0.9
25	313.15	20.27	0.05	30	0.582	0.641	10.1
26	313.15	20.27	0.10	30	0.711	0.684	3.8
27	313.15	20.27	0.15	30	0.809	0.756	6.6
28	293.15	20.27	0.20	30	0.931	0.909	2.4
29	303.15	20.27	0.20	30	0.912	0.943	3.4
30	313.15	20.27	0.20	30	0.862	0.856	0.7
31	313.15	10.13	0.20	30	0.640	0.650	1.6
32	313.15	15.20	0.20	30	0.750	0.766	2.2
33	313.15	25.33	0.20	30	0.924	0.920	0.4
34	323.15	20.27	0.20	30	0.642	0.648	1.0
						AARD %	2.7

[a]Standard uncertainties u are $u(T)$ = 1 K, $u(p_{CO_2})$ = 0.05 kPa, $u(w_{1,5-DA-2-MP})$ = 0.01, $u(C_T)$ = 1 wt %; and expanded uncertainty at 95% confidence level is $U(\alpha)$ = 0.01α mol CO_2·mol amine^{-1}.

the rise in the equilibrium CO_2 loading was evident, but for CO_2 partial pressure greater than 20.27 kPa, this rise was nominal.[21] This outcome unfolded the distinct reaction behavior of the solvent and its suitability for the usage in thermal power plants in which flue gas has a partial pressure of CO_2 up to 14 V %.[6]

Comparison of the equilibrium CO_2 loading of 5 M MEA (0.5641 mol CO_2/mol amine), MEA + MDEA (0.5332 mol CO_2/mol amine), and MEA + 3-DMA-1-P (0.5472 mol CO_2/mol amine)[29] at C_T 10 wt % and $w_{1,5-DA-2-MP}$ 0.2 with the studied amine blend in this paper showed that it indeed presented an appreciably higher value of α (0.9 mol CO_2/mol amine) among them at p_{CO_2} 15 kPa, T 313.15 K, and P 101.325 kPa.

3.2. Empirical Model Development for CO_2 Loading at Equilibrium. Equation 1 written below represents the empirical model for the 3-DMA-1-P + 1,5-DA-2-MP system to determine CO_2 loading at equilibrium. In this equation,

variables were temperature of the aqueous blend solution (T), CO_2 partial pressure in simulated gas stream (p_{CO_2}), activator 1,5-DA-2-MP weight fraction ($w_{1,5-DA-2-MP}$), and total concentration of the blend (C_T) at atmospheric pressure. Variable limits were T from 293.15 to 323.15 K, p_{CO_2} from 10.13 to 25.33 kPa, $w_{1,5-DA-2-MP}$ from 0.05 to 0.2, and C_T from 10 to 30 wt % at P of 101.325 kPa. The equation of the empirical model is expressed as

$$\alpha = x_1 + x_2 t + x_3 t^2 + x_4 p_{CO_2} + x_5 p_{CO_2}^2 + x_6 w_{1,5-DA-2-MP}$$
$$+ x_7 w_{1,5-DA-2-MP}^2 + x_8 C_T + x_9 C_T^2 \qquad (1)$$

where α is the CO_2 loading at equilibrium in the aqueous 3-DMA-1-P + 1,5-DA-2-MP system in mol CO_2/mol amine, t is the temperature of the aqueous amine blend in °C, p_{CO_2} is the CO_2 partial pressure in kPa, $w_{1,5-DA-2-MP}$ is the 1,5-DA-2-MP weight fraction in the amine blend (3-DMA-1-P + 1,5-DA-2-
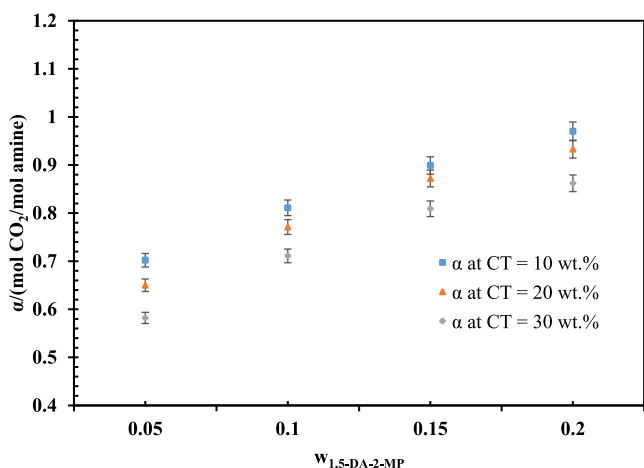
Figure 2. Effect of weight fraction of 1,5-DA-2-MP on CO_2 loading at constant p_{CO_2} 20.27 kPa, T 313.15 K, and at different C_T 10, 20, and 30 wt %.

Figure 4. Effect of temperature on CO_2 loading at constant $w_{1,5-DA-2-MP}$ 0.2, p_{CO_2} 20.27 kPa, and at different C_T 10, 20, and 30 wt %.
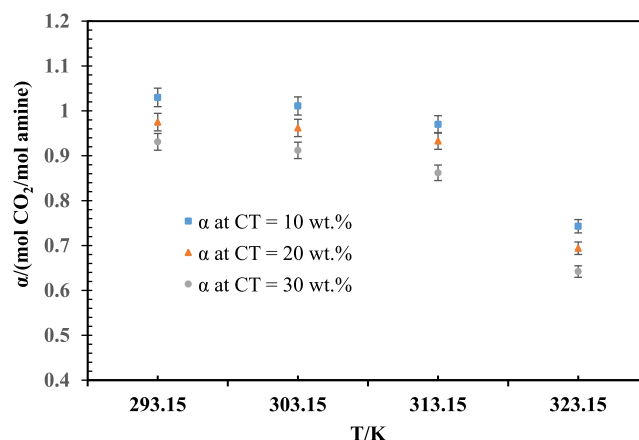
MP), C_T is the total concentration of the blend in wt %, and x_1-x_9 are the coefficients of the empirical model for this system.

With the use of experimental data under defined operating conditions, the values of the coefficients of eq 1 were determined using Excel solver and are given in Table 4. The concurrence of the experimental data was obtained by this empirical model. The estimated values of CO_2 loading at equilibrium were generated by this model within specified operating ranges. % Absolute relative deviation (ARD) and % AARD between experimental (α_{exp}) and estimated values (α_{est}) of CO_2 loading were measured by following eqs 2a and 2b
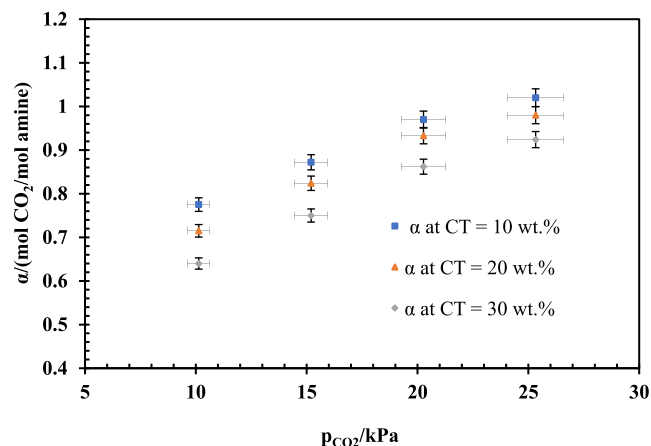
$$\% \; ARD = \frac{|\alpha_{exp} - \alpha_{est}|}{\alpha_{exp}} \times 100 \tag{2a}$$

$$\% \; AARD = \frac{100}{n} \times \sum_{i=1}^{n} \frac{|\alpha_{exp} - \alpha_{est}|}{\alpha_{exp}} \tag{2b}$$

where, n is the number of experimental data points, α_{exp} is the experimentally measured CO_2 loading at equilibrium, and α_{est}

**Figure 5.** Effect of CO_2 partial pressure on CO_2 loading at constant $w_{1,5-DA-2-MP}$ 0.2, T 313.15 K, and at different C_T 10, 20, and 30 wt %.
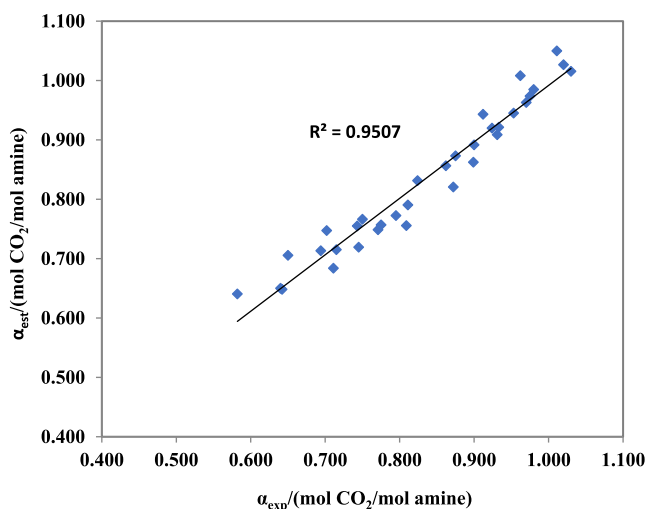
is the estimated CO_2 loading at equilibrium by the empirical model. All the experimental data were plotted with empirically estimated data in Figure 6 and an AARD of 2.7% was obtained, which indicated the reliability and good agreement of the data
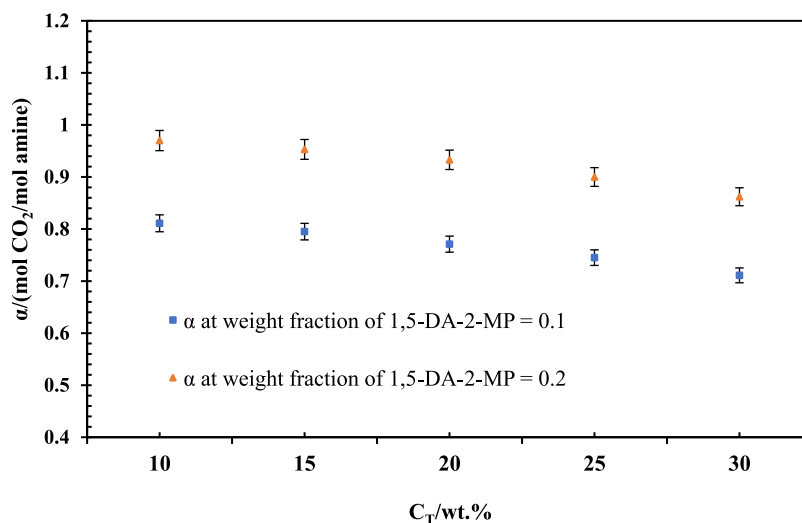
Figure 3. Effect of total concentration on CO_2 loading at constant p_{CO_2} 20.27 kPa, T 313.15 K, and at different $w_{1,5-DA-2-MP}$ 0.1 and 0.2.

Table 4. Values of Coefficients of the Empirical Model Eq 1

| coefficient	value	coefficient	calue	coefficient	value
x_1	−0.146263	x_4	0.035942	x_7	5.742445
x_2	0.033736	x_5	−0.000513	x_8	−0.000695
x_3	−0.000606	x_6	0.002869	x_9	−0.000116

Figure 6. Estimated (α_{est}) by eq 1 vs experimental (α_{exp}) CO_2 loading values at equilibrium.

of CO_2 loading at equilibrium generated by the empirical model with experimental results within defined operating ranges.

3.3. CO_2 Absorption Enthalpy. Higher reactivity was shown by primary amines and secondary amines on reaction with CO_2, and it also released a high reaction heat of ≈80 kJ/mol CO_2 because carbamates were formed. During the desorption process, the energy requirement for breaking off these carbamates was high and depended largely upon the reaction heat of absorption. Lesser energy was required for desorption of the tertiary amines, which releases an absorption heat of ≈60 kJ/mol CO_2 on reaction with CO_2 because bicarbonates formed during CO_2 absorption needed less energy for breaking off than carbamates needed for breakdown.[34] For regeneration of the chemical solvent, 60% of the total energy is required.[10] Major contributing operating cost was because of the solvent regeneration energy, which was significantly dependent on CO_2 absorption enthalpy; therefore, operating costs can be substantially reduced by decreasing the regeneration cost. Good agreement between heat of absorption calculated by the Gibbs−Helmholtz equation and experimentally measured heat of absorption for other amine systems has been shown in the literature.[35−39] These results proved the reasonable reliability of the calculation based on the Gibbs−Helmholtz equation. The relationship between the CO_2 partial pressure and the temperature at constant CO_2 equilibrium loading and assuming unity fugacity coefficient in the vapor phase is given by the Gibbs−Helmholtz equation,[33,35−39] which is utilized for calculating the CO_2 absorption enthalpy indirectly

$$\left[\frac{d(\ln(p_{CO_2}))}{d\left(\frac{1}{T}\right)} \right]_{\alpha, CT, w_{1\text{-}5\text{-}DA\text{-}2\text{-}MP}} = \frac{\Delta H_{abs}}{R} \quad (3)$$

where p_{CO_2} is the CO_2 partial pressure (kPa), T is the temperature of amine solution (K), ΔH_{abs} is the CO_2 absorption enthalpy (kJ/mol), and R is the universal gas constant [8.314 J/(mol·K)], and meaning of other notations are the same as those mentioned in this paper. A fitting straight line is plotted in Figure 7 between $\ln p_{CO_2}$ and $1/T$ (at constant
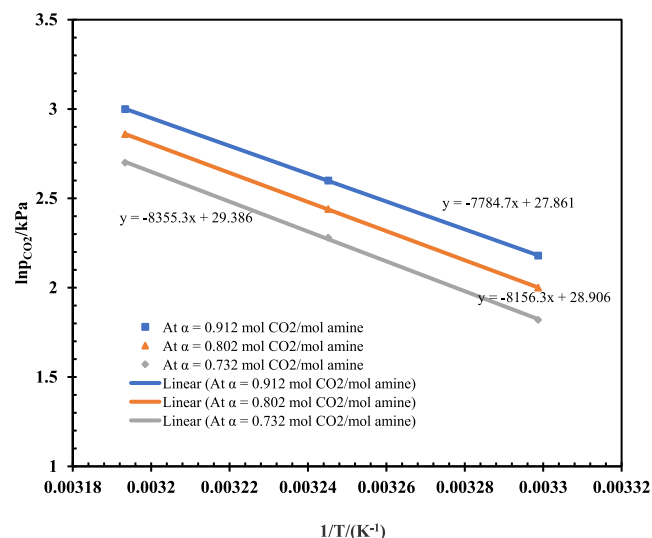
Figure 7. $\ln p_{CO_2}$ vs $1/T$ for estimation of CO_2 absorption enthalpy at different values of α 0.912, 0.802, and 0.732 mol CO_2/mol amine for 30 wt % aqueous 3-DMA-1-P + 1,5-DA-2-MP blend with 0.20 weight fraction of 1,5-DA-2-MP in the amine blend.

α, C_T, and $w_{1,5\text{-}DA\text{-}2\text{-}MP}$) to get the slope, which on multiplying with R value, gave the outcome of the CO_2 absorption enthalpy. ΔH_{abs} was calculated at three different CO_2 loading values and is reported in Table 5. These results showed that

Table 5. Calculated Values of ΔH_{abs} at Different α for 30 wt % Aqueous 3-DMA-1-P + 1,5-DA-2-MP Blend with 0.20 Weight Fraction of 1,5-DA-2-MP in the Amine Blend

α (mol CO_2/mol amine)	ΔH_{abs} (kJ/mol)
0.912	−64.7
0.802	−67.8
0.732	−69.4
overall average	−67.3

there was slight decrease in the ΔH_{abs} value as there was increase in the α value. Hence, the average calculated ΔH_{abs} was approximately −67.3 kJ/mol for the 30 wt % aqueous 3-DMA-1-P + 1,5-DA-2-MP blend with 0.20 weight fraction of 1,5-DA-2-MP in the amine blend. The ΔH_{abs} value for this new aqueous amine blend was appreciably less than that of the industrially used benchmark solvent MEA.

4. CONCLUSIONS

The absorption performance of the 3-DMA-1-P + 1,5-DA-2-MP aqueous blend was experimentally measured to illustrate the effects of the total blend concentration, weight fraction of activator 1,5-DA-2-MP in the blend, partial pressure of CO_2, and temperature of the aqueous amine blend on CO_2 loading. The variation of the activator 1,5-DA-2-MP weight fraction showed that the value of CO_2 loading at equilibrium first increases to maxima and then decreases with increase in $w_{1,5-DA-2-MP}$. The change of the total concentration of the amine blend depicted a maximum rise in the value of α at 10 wt %, which then reduced with the total concentration. The increase in the CO_2 partial pressure from 10.13 to 25.33 kPa illustrated a sharp rise in the value of α up to 20.27 kPa and moderate growth after it in the amine blend. The rise in temperature (293.15−323.15 K) displayed the moderate decline rate up to 313.15 K, and after that, there was steep decline in the rate of the α value. The optimum operating condition for maximum CO_2 absorption capacity α_{max} 0.97 mol CO_2/mol amine was determined as C_T 10 wt %, $w_{1,5-DA-2-MP}$ 0.2, p_{CO_2} 20.27 kPa, and T 313.15 K. Moreover, comparison of the aqueous 3-DMA-1-P + 1,5-DA-2-MP blend with usually utilized 5 M MEA (0.5641) and MEA + MDEA (0.5332 mol CO_2/mol amine) showed better CO_2 loading of the studied amine blend under the same operating condition. In the concurrence of the experimental data, the empirical model for CO_2 loading at equilibrium was established for the studied blend system with an accuracy of 2.7 AARD %. The indirect estimation of the CO_2 absorption enthalpy for this amine blend by the Gibbs−Helmholtz equation concluded to the value of −67.3 kJ/mol and compared to find that it was much lower than the standard MEA value of −84.3 kJ/mol, which revealed the ability of the studied amine blend as a good alternative candidate for CO_2 capture through postcombustion technology. In our next work, the development of the modified Kent−Eisenberg model will be made for solubility calculation of this blend. Desorption performance and reaction kinetics will also be studied for this new blend.

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Notes

The authors declare no competing financial interest.

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