EQUILIBRIUM SOLUBILITY MEASUREMENT AND MODELING OF CO_2 ABSORPTION IN AQUEOUS BINARY MIXTURE OF 2-(DIETHYLAMINO)ETHANOL AND 1, 6-HEXAMETHYLDIAMINE

ABSTRACT

The CO_2 solubility data are important for the efficient design and operation of CO_2 capture process. The 2-(Diethylamino)ethanol (DEEA) solvent can be manufactured from renewable sources like agricultural products/residue and 1,6-hexamethyldiamine (HMDA) solvents have higher absorption capacity as well as reaction rate with CO_2 than conventional amine-based solvents. The equilibrium solubility of CO_2 into aqueous binary mixture of DEEA and HMDA has been investigated in the temperature range of 303.15-333.15 K and inlet CO_2 partial pressure in the range of 10.133-20.265 kPa. Total concentration of aqueous amine mixtures in the range of 1.0-3.0 kmol/m^3 and mole fraction of HMDA in total amine mixture in the range of 0.05-0.20 were taken in this work. The CO_2 absorption experiment was performed using semi-batch operated laboratory scale bubble column to measure equilibrium solubility of CO_2 in amine mixture and CO_2 absorbed amount in saturated carbonated amine mixture was analyzed by precipitation-titration method using $BaCl_2$. The equilibrium CO_2 solubility in amine mixture was found to be maximum as a value of 0.932 mol CO_2/mol amine, with HMDA mole fraction in total amine of 0.2 at a 1 kmol/m^3 total amine mixture concentration and 303.15 K. A new solubility data of CO_2 in DEEA+HMDA aqueous mixtures in current study was compared with solubility data available in the previous studies conducted by

various researchers. The experimental results were inferred to develop an empirical solubility model to predict the CO_2 equilibrium solubility in DEEA+HMDA aqueous mixture within the specified range of operating conditions. In addition, the heat of absorption of CO_2 in DEEA+HMDA aqueous mixture was estimated by using the Gibbs-Helmholtz equation and it was found to be -68.84 kJ/mol which is lower than benchmark amine MEA. The study shows that, the new absorbent as a mixture of DEEA+HMDA is feasible for CO_2 removal from coal-fired power plant stack gas streams.

5.1 INTRODUCTION

Recently, global warming and climate change are the serious environmental issues due to continuous release of major greenhouse gas CO_2 into the atmosphere. CO_2 is present in the waste gas stream which is released from various process industries like coal-fired thermal power plants, iron and steel plants, cement industries, natural gas treatment plants, chemical and petro-chemical manufacturing units. Among these sources, fossil fuel based coal-fired power plants are responsible for major contribution in anthropogenic emissions of CO_2 worldwide (Adams and Davison, 2007; Zaman and Lee, 2013). So, capture of CO_2 from power plant waste gas streams has become a major challenge for environmentalists in recent year. The removal of CO_2 from power plant flue gas using aqueous amine solutions based on chemical absorption is a preferred CO_2 separation technology due to its cost effectiveness, maturity and handling huge amount of gas streams to a very low CO_2 concentration (Rao and Rubin, 2002). In this technology, various types of conventional alkanolamines like as primary amine monoethanolamine (MEA), secondary amine diethanolamine (DEA) and di-isopropanolamine (DIPA) and tertiary amine N-methyl diethanolamine (MDEA) and triethanolamine (TEA), and sterically-hindered amine 2-amino-2-methyl-1-propanol (AMP), etc. were used for capturing CO_2 from gas stream in gas treating plants as well as fossil fuel based thermal power plants (Kohl and Nielsen, 1997). The cyclic polyamines like piperazine (PZ) and piperazine derivatives 1-(2-aminoethyl)piperazine (AEP), non-cyclic polyamine 1,6-hexamethyldiamine (HMDA), 2-(2-aminoethylamino)ethanol (AEEA) and 1,3-Diamino-2-propanol (DAP), etc. were also tested for CO_2 removal from various gas streams at different operating conditions under lab-scale operation (Bishnoi and Rochelle, 2000; Choi et al., 2016; Mondal et al., 2017; Wilk et al., 2017).

But, novel tertiary amine solvent, particularly DEEA shows better absorption performance than conventional tertiary amine solvent MDEA and it can also be manufactured from renewable sources like agricultural products/residue as well as it shows efficient absorbance performance in CO_2 capture process (Chowdhury et al., 2013; Vaidya and Kenig 2007). Also, polyamine solvents have a good potential for CO_2 capture, because two or more amino groups are present in their chemical structure and also, absorption capacity and higher reaction rate with CO_2 than conventional amine-based solvents (Muchan et al., 2007). Particularly, a polyamine solvent HMDA has a good potential for capturing CO_2 because it possesses high CO_2 absorption capacity and absorption rate (Kim et al., 2015; Mondal et al., 2015). Further, addition of polyamine solvent as an activator with tertiary amine has been proven to exhibit good potential for CO_2 capture.

In past few years, for improving the CO_2 capture performance, a mixture of tertiary amine, particularly DEEA and polyamine has a new research of interest due to advantages of each individual amine solvent. Many researchers investigated the evaluation of CO_2 capture performance parameters in terms of absorption capacity, cyclic capacity, absorption rate, absorption heat, absorption mass transfer co-efficient and reaction rate constant of CO_2, etc. in various aqueous binary amine mixture of DEEA and polyamine such as DEEA+N-Methyl-1,3-diaminopropane (MAPA) (Liebenthal et al., 2013), DEEA+Piperazine (PZ) (Vaidya and Kenig, 2008; Konduru et al., 2010; Fu et al., 2016, Sutar et al., 2013; Gao et al., 2016) DEEA+1, 4-Butanediamine (BDA) (Xu et al., 2013), DEEA+1,6-hexamethyldiamine (HMDA) (Sutar et al., 2013), DEEA+ 2-(2-aminoethylamino)ethanol (AEEA) (Sutar et al., 2013; Gao et al., 2016)**,** DEEA+ Diethylenetetramine (DETA) (Wang et al., 2017; Lee et al., 2017). A little information is available on equilibrium solubility of CO_2 in DEEA+HMDA aqueous mixture but, it requires wide ranges of solubility data at various operating conditions for the efficient design and operation of CO_2 capture process. Also, solubility of CO_2 in amine mixture is prime steps design parameter to determine the absorption capacity and has a significant role in screening of any novel solvents. So, the present work is based on the improvement on CO_2 absorption performance in an aqueous binary mixture of DEEA and HMDA.

In this present research, equilibrium CO_2 solubility in aqueous mixture of DEEA and HMDA was measured using laboratory scale gas-liquid contactor bubble column in the temperature range of 303.15-333.15 K and CO_2 partial pressure range of 10.133-20.265 kPa. Total concentration of aqueous mixture was taken in the range of 1.0-3.0 kmol/m^3 and HMDA mole fraction in total amine mixture was taken in the range of 0.05-0.20. The experimental CO_2 solubility data were compared with literature. Also, an empirical solubility model was developed for predicting the CO_2 solubility in the specified ranges of operating conditions. Furthermore, the CO_2 absorption heat was also evaluated with the help of predicted data on CO_2 solubility.

5.2 EXPERIMENTAL

5.2.1 Chemicals and materials

The reagent grade chemical DEEA and HMDA with mass purity greater than 99% were purchased from Sisco Research Laboratory, Mumbai and Tokyo Chemical Industry Co. Ltd, Japan, respectively. The aqueous binary mixtures of DEEA and HMDA were prepared without any purification using double distilled water in various concentrations as per experimental needs. Simulated CO_2 gas stream consisting of required concentration in the range of (10-20% by volume) was prepared by mixing of two types of gas streams having one cylinder containing 20% CO_2 with balanced N_2 and others cylinder containing pure N_2 with the help of gas mixing chamber. The gas flow meter (0 to 3 LPM) was used to measure volume of gas out from gas cylinder with an accuracy of ±1.0%. The infrared flue gas analyzer (model: Gas Board-3800P; Wuhan Cubic Optoelectronics Co. Ltd., Wuhan, China; with CO_2 measuring range of 0-100% by volume) was used to measured CO_2 in gas phase with an accuracy of ±0.1%. A constant-temperature water bath (model: CE404, Narang Scientific Works Pvt. Ltd., New Delhi) was used for required operating temperature of aqueous mixture of amines (273 K to 473 K) within minute variation of ±0.1 K. Others analytical reagent (AR) grade chemicals NaOH, $BaCl_2.2H_2O$ and HCl were used without any purification for analysis of liquid phase CO_2.

5.2.2 Experimental set-up and procedure

A schematic diagram of experimental set-up for measuring equilibrium CO_2 solubility in aqueous mixture of DEEA and HMDA has been shown in figure 5.1. This experimental set-up described in our previous work (Mondal, 2009) was used for experimentation with some few modifications. The gas-liquid (DEEA-HMDA-CO_2)

system can divide into three parts: simulating gas stream, an absorber, and for gas sampling analyzer. The experimental study on CO_2 solubility in aqueous amine mixture was conducted in laboratory scale borosilicate glass bubble column as an absorber in semi-batch mode. The known amount of aqueous amine mixture loaded in absorber was placed in temperature-controlled water bath and maintained to require working temperature.

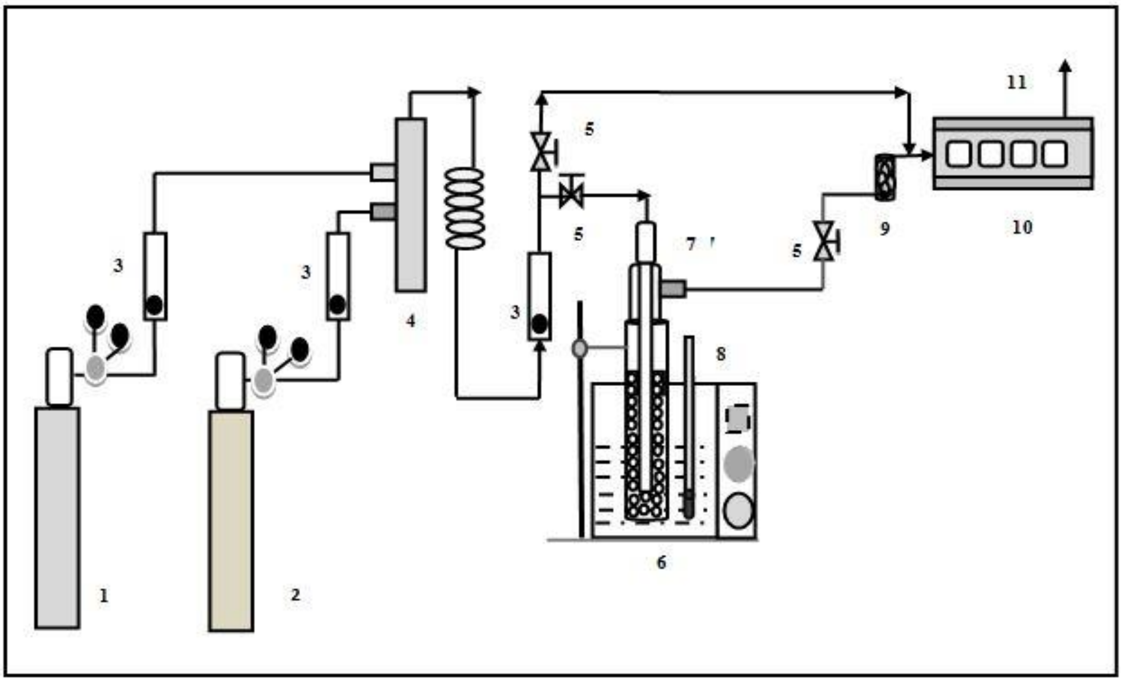

Figure 5.1 Schematic diagram for CO_2 solubility measurement: (1) CO_2 gas cylinder, (2) N_2 gas cylinder, (3) gas flow meter, (4) gas mixing chamber, (5) stainless steel valves, (6) water bath, (7) bubble column, (8) thermometer, (9) moisture absorber column, (10) multi-flue gas analyzer and (11) exhaust

Then, thermometers with sub-divisions of 0.1 K were used to measure both the temperature of water bath and liquid placed inside absorber. After that, N_2 gas was passed slowly through the absorber for approximately 10 min for removing trace gases already present in the column. Then, a fixed composition of CO_2 gas stream through gas flow meter with minimum flow rate was entered into the absorber and maintained continuous flow of CO_2 gas stream with non-interruption of amine mixture to create bubbles during absorption process moving from bottom to the upper surface of liquid. After, a regular interval of time (5 min), the CO_2 outlet gas stream concentration was analyzed by infrared multi-flue gas analyzer and this procedure was continued until the concentration of CO_2 gas stream in inlet and outlet are approximately same to reach gas-liquid equilibrium phase. Then, a saturated CO_2 solution was analyzed by titration method using $BaCl_2$ and HCl as described in details elsewhere (Bajpai and Mondal, 2013). At a given temperature and pressure, three aliquot of CO_2 loaded amine were taken to check the reproducibility and the data were found to be reproducible to within 1%. The temperature was controlled within ±0.1 K from 303.15 to 333.15 K and the partial pressure was monitored for each run with an uncertainty of 0.01 kPa from 10.133 to 20.265 kPa.

5.2.3 Reaction Chemistry of CO_2-DEEA-HMDA system

When CO_2 absorbed in an aqueous mixture of DEEA and HMDA, a set of chemical reactions occur which have been discussed in details in appendix B.2.

5.3 RESULTS AND DISCUSSION

5.3.1 Solubility of CO_2 in DEEA+HMDA aqueous mixture

In the present work, equilibrium solubility of CO_2 in an aqueous binary mixtures of DEEA and HMDA was measured at wide ranges of operating parameters such as total amine concentration (C_T) ranging from 1.0 to 3.0 kmol/m^3, HMDA mole fraction (X) in amine mixture from 0.05 to 0.20, amine mixture temperature (T) from 303.15 to 333.15 K and inlet CO_2 partial pressure (P_{CO2}) in the range of 10.132 to 20.265 kPa. The experimental data obtained at various operating conditions for equilibrium CO_2 solubility in aqueous mixtures are shown in table 5.1, where the equilibrium CO_2 solubility has expressed in term of CO_2 loading as the number of moles of CO_2 absorbed per mole of total amine.

Table 5.1 Experimental CO_2 solubility in aqueous binary mixture of DEEA and HMDA at different operating conditions

	Operating conditions				
S.N.	X	C_T (kmol/m^3)	T (K)	p_{CO2} (kPa)	α_{CO2} (mol CO_2/mol amine)
1	0.05	1	313.15	20.265	0.644
2	0.05	2	313.15	20.265	0.585
3	0.05	3	313.15	20.265	0.547
4	0.1	1	313.15	20.265	0.704
5	0.1	2	313.15	20.265	0.648
6	0.1	3	313.15	20.265	0.602
7	0.15	1	313.15	20.265	0.791
8	0.15	2	313.15	20.265	0.738
9	0.15	3	313.15	20.265	0.692
10	0.2	1	313.15	20.265	0.926
11	0.2	2	313.15	20.265	0.874
12	0.2	3	313.15	20.265	0.841
13	0.2	2	313.15	10.133	0.761
14	0.2	2	313.15	12.666	0.782
15	0.2	2	313.15	15.199	0.801
16	0.2	2	313.15	17.732	0.831
17	0.2	2	313.15	20.265	0.874
18	0.2	2	303.15	20.265	0.932
19	0.2	2	313.15	20.265	0.874
20	0.2	2	323.15	20.265	0.812
21	0.2	2	333.15	20.265	0.771

5.3.1.1 Effect of concentration

Figure 5.2 shows the variation in the CO_2 amount in liquid phase as a function of time for different mole fraction of HMDA in a fixed concentration of total amine mixture for temperature of 20.265 kPa and inlet partial pressure of 313.15K. The effect of HMDA mole fraction on CO_2 solubility was investigated by changing the composition of amine mixture with the help of varying concentration of HMDA as well as DEEA for a fixed total amine concentration of 2 kmol/m^3. For a fixed HMDA mole fraction with a particular concentration of amine mixture, the CO_2 absorbed increases with time and then remains constant which reveals that no more amount of CO_2 is absorbed in this amine mixture and solution becomes completely saturated to achieve gas-liquid equilibrium.

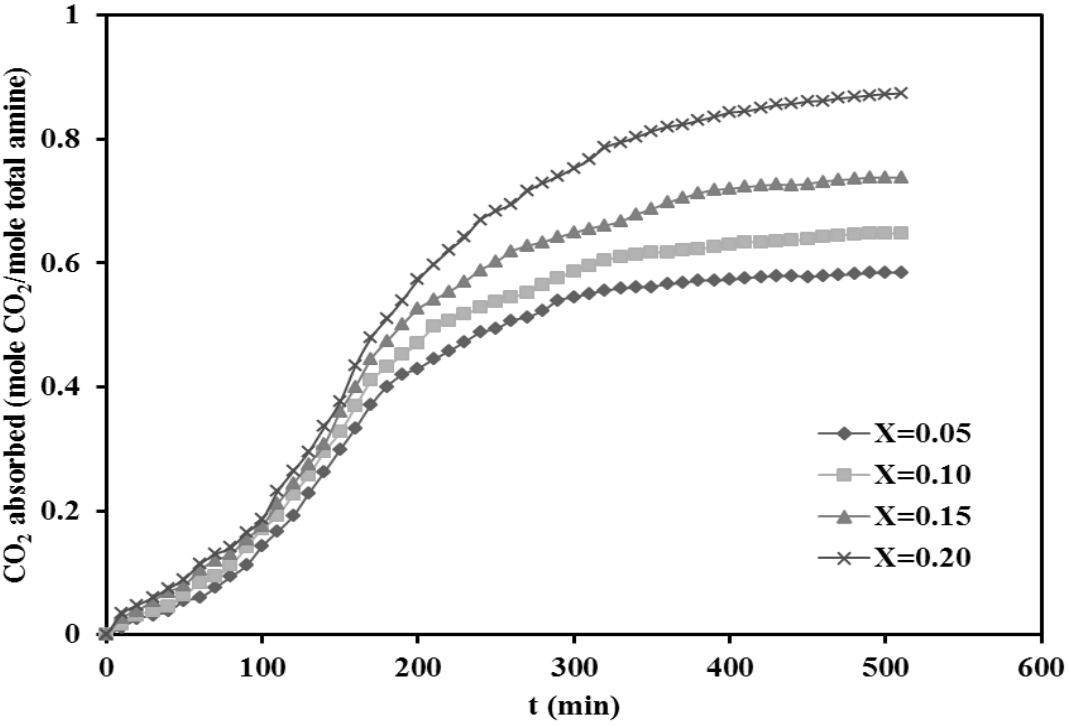

Figure 5.2 CO_2 absorbed against time t with different mole fraction of HMDA in total amine mixture X at temperature T 313.15 K, partial pressure of CO_2 20.265 kPa and total amine concentration C_T 2 kmol/m^3

Figure 5.3 shows the variation of CO_2 solubility with HMDA mole fraction (from 0.05 to 0.20) for different total amine mixture concentration ranging from 1 to 3 kmol/m^3. From figure 5.3, it is observed that, the solubility of CO_2 increases with increasing of HMDA mole fraction in total amine mixture and maximum of equilibrium CO_2 solubility was observed at HMDA mole fraction of 0.2. The CO_2 solubility in amine mixture is enhanced by addition of more amount of HMDA in total amine mixture corresponds to increased CO_2 absorption, because, HMDA possesses two primary amino groups available for reaction with CO_2.

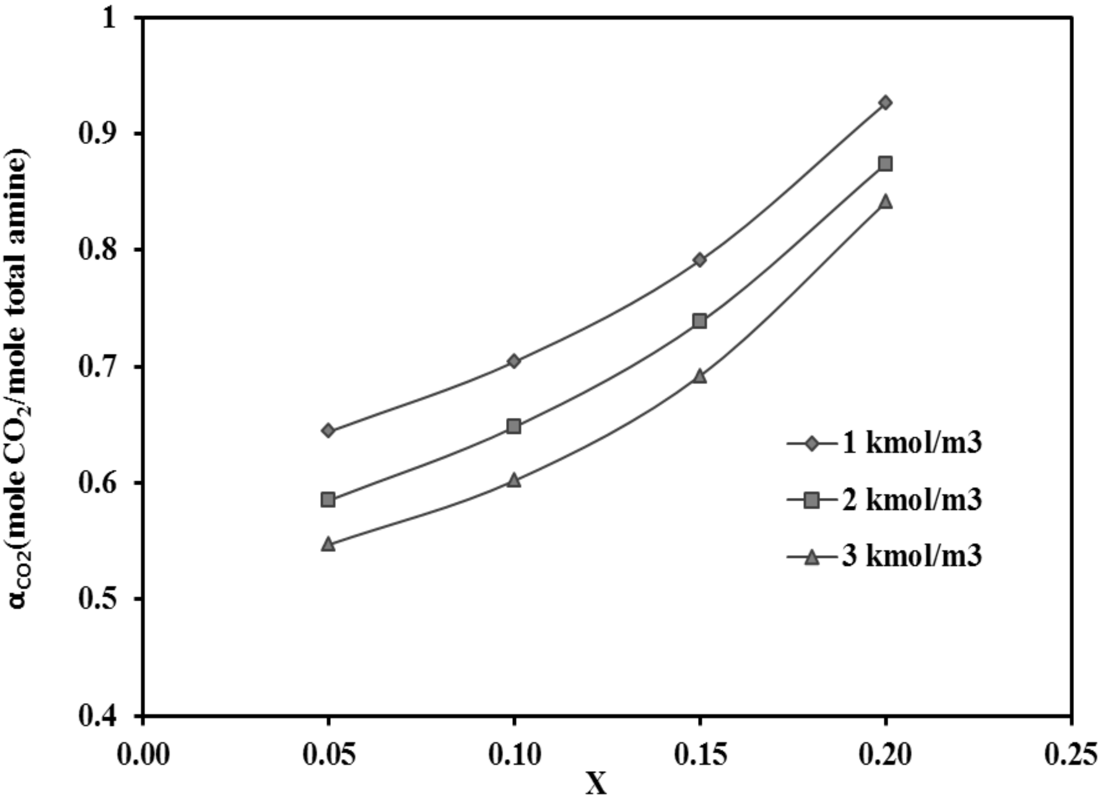

Figure 5.3 CO_2 solubility α_{CO2} against mole fraction of HMDA in total amine mixture X with different total amine concentrations C_T at temperature T 313.15 K and partial pressure of CO_2 20.265 kPa

Figure 5.4 shows the effect of concentration of aqueous mixture of DEEA and HMDA on CO_2 solubility at a temperature of 313.15 K, CO_2 partial pressure of 20.265 kPa, and HMDA mole fraction of 0.2. From figure 5.4 it is observed that there is decrease in CO_2 solubility with increase in amine mixture concentration because at higher concentration a smaller extent of reversion of carbamate to bicarbonate can occur.

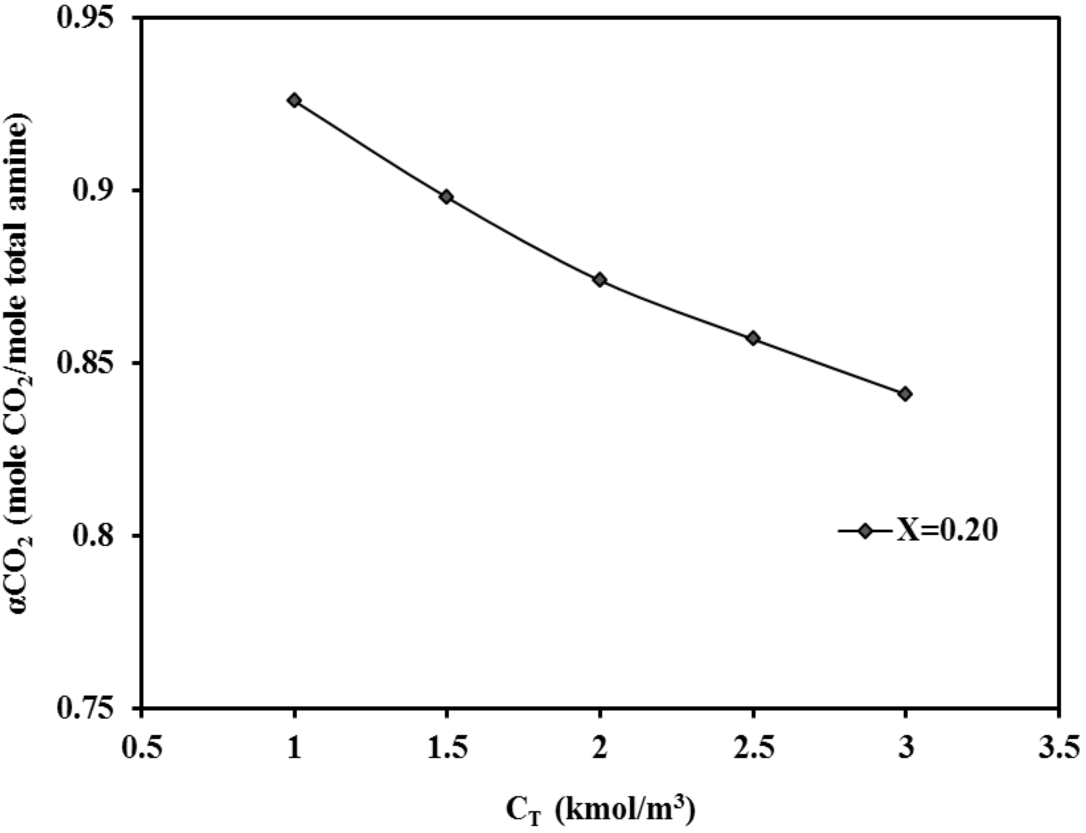

Figure 5.4 CO_2 solubility α_{CO2} against total amine concentrations C_T at temperature T 313.15 K, mole fraction of HMDA in total amine mixture X 0.20 and partial pressure of CO_2 20.265 kPa

5.3.1.2 Effect of CO_2 partial pressure

The inlet partial pressure of CO_2 plays a significant role in CO_2 gas absorption. The influence of CO_2 partial pressure on CO_2 solubility was studied at fixed concentration of amine mixture of 2.0 kmol/m^3 with an HMDA mole fraction of 0.20 temperature 313.15 K and CO_2 partial pressures varies from 10.133 to 20.265 kPa.

As shown in figure 5.5, it is clearly seen that the CO_2 partial pressure incorporates a little result on CO_2 solubility between the variation of 10.199-12.63 kPa and 17.732-20.265 kPa. The CO_2 solubility increases from (0.76 to 0.87) mol of CO_2 per mole of total amine mixture as the CO_2 partial pressure increases from (10.133 to 20.265) kPa.

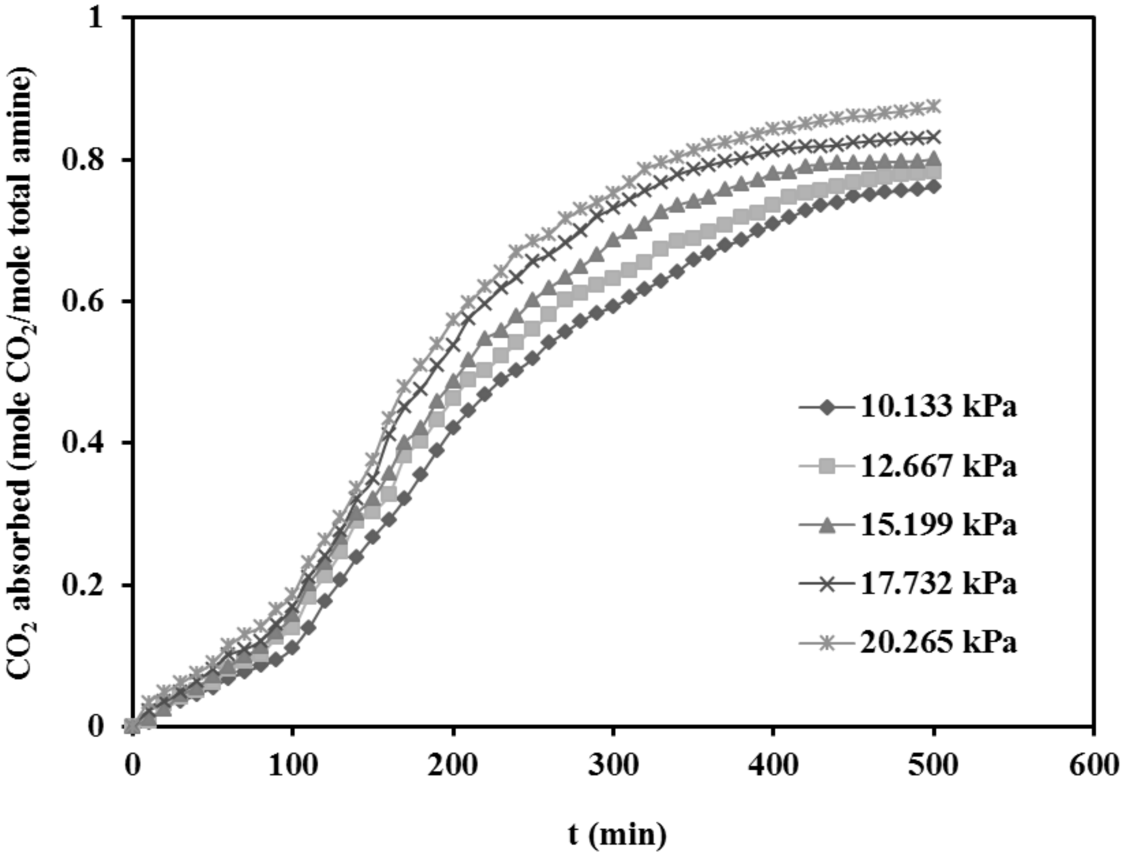

Figure 5.5 CO_2 absorbed against time t with different partial pressure of CO_2 at temperature T 313.15 K, mole fraction of HMDA in total amine and total amine concentration C_T 2 kmol/m^3

Figure 5.6 shows that the equilibrium CO_2 solubility increases with increasing inlet partial pressure of CO_2 in gas stream as a result of gas-phase mass transfer increases due to driving force rise, from the bulk gas phase to the gas-liquid interface.

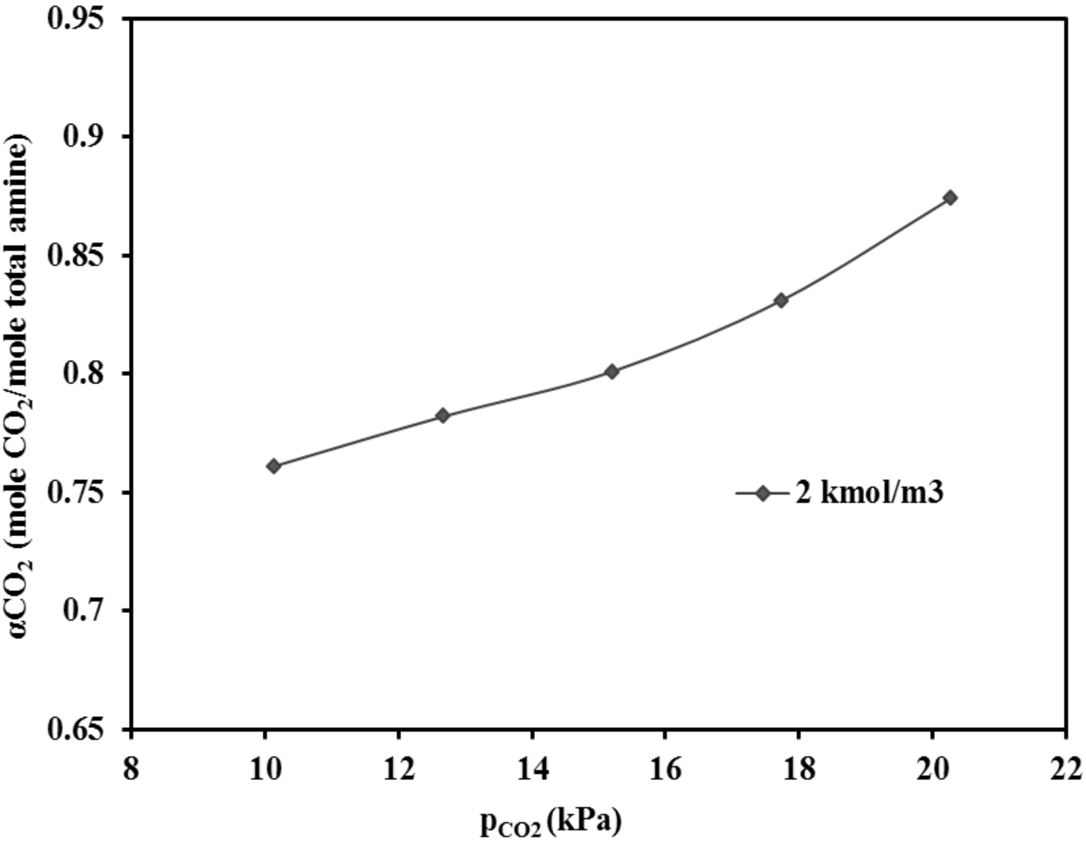

Figure 5.6 CO_2 solubility α_{CO2} against partial pressure of CO_2 at total amine concentration C_T 2 kmol/m^3, temperature T 313.15 K and mole fraction of HMDA in total amine mixture X 0.2

5.3.1.3 Effect of temperature

Figure 5.7 shows the effect of temperature on equilibrium CO_2 solubility in DEEA+HMDA amine mixture over the temperature range (303.15 to 333.15) K. In this regard, CO_2 partial pressure in gas stream, total amine concentration, and HMDA mole fraction within the amine mixture were kept as 20.265 kPa, 2.0 kmol/m^3, and 0.2, respectively. From figure 5.7 and 5.8, the solubility of CO_2 decreases with increasing temperature and it is in agreement with information reported by Kundu and Bandyopadhyay (2006) and Mondal (2009). The reactions between CO_2 and amines in absorption process are reversible in nature and as the temperature is increased then gas-liquid equilibrium is shifted to the reversed direction.

Also, at higher temperatures, desorption of CO_2 takes place, and finally solubility of CO_2 decreases with increasing temperature.

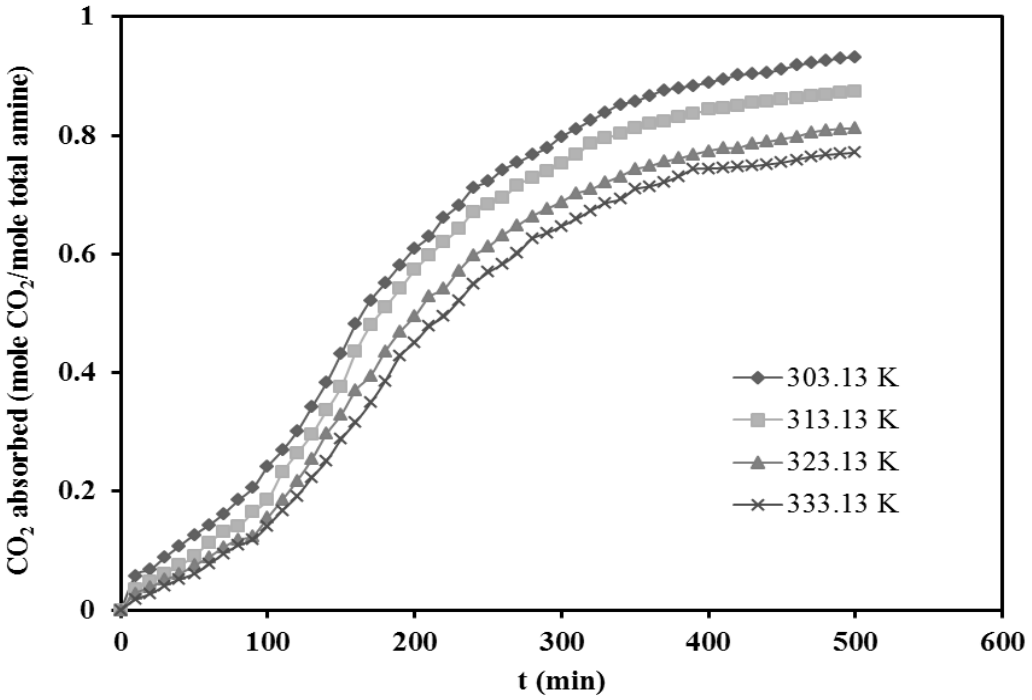

Figure 5.7 CO_2 absorbed against time t with different temperature T at partial pressure of CO_2 20.265 kPa, total amine concentration C_T 2 kmol/m^3 and mole fraction of HMDA in total amine mixture X 0.20

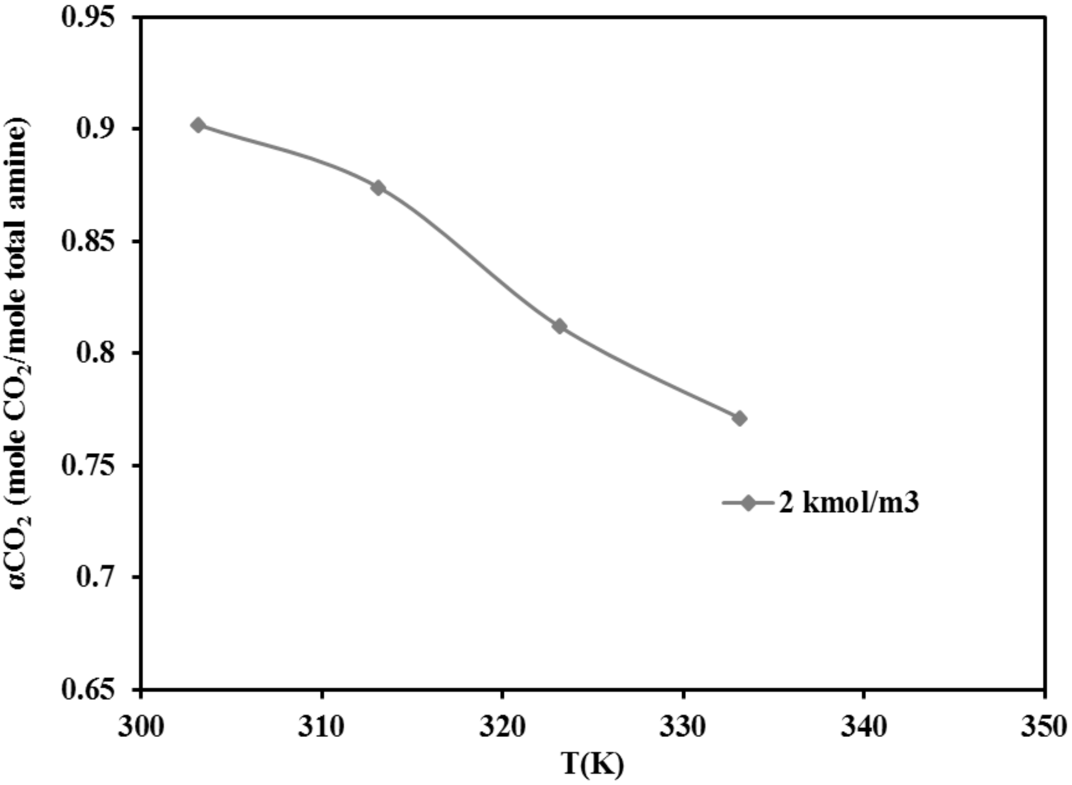

Figure 5.8 CO_2 solubility α_{CO2} against temperature T at total amine concentration C_T 2 kmol/m^3, partial pressure of CO_2 20.265 kPa and mole fraction of HMDA in total amine mixture X 0.20

5.3.1.4 Comparison of the CO_2 solubility in various aqueous mixtures of amines

Maximum CO_2 solubility obtained by different researchers during absorption of CO_2 in various amine mixtures are given in table 5.2. After the comparison, it has been observed that the CO_2 solubility in present amine aqueous mixture DEEA+HMDA more than the CO_2 solubility in previous studied amine mixture.

Table 5.2 Comparison of the solubility of CO_2 in various aqueous mixtures of amines with respect to DEEA+HMDA blend

Amine mixture	Operating conditions			α_{CO2} (mol CO_2/mol amine)	References
	C_T (kmol/m^3)	T (K)	p_{CO2} (kPa)		
DEEA+HMDA	2	303	20.27	0.932	This work
DEEA+HMDA	2	313	20.27	0.874	This work
DEEA+HMDA	2.5	313	20.27	0.857	This work
DEEA+HMDA	2.6	303	4.9	0.844	Sutar et al., 2013
DEEA+PZ	2.5	303	5.80	0.690	Sutar et al., 2013
DEA+AEEA	2	303	20.27	0.740	Bajpai and Mondal, 2013
MDEA+DEA	2	313	20.00	0.696	Kundu and Bandyopadhyay, 2006
DEEA+MEA	2.58	313	20.00	0.531	Luo et al., 2016
MDEA+PZ	2	313	15.20	0.750	Ali and Aroua, 2004
DEEA+MAPA	5+2	313	17.40	0.374	Arshad et al., 2014

5.3.2 Development of CO_2 solubility model

The empirical solubility model was developed to correlate the CO_2 solubility in aqueous amine mixtures of DEEA and HMDA as a function of HMDA mole fraction in total aqueous amine mixtures, concentration of total aqueous amine mixtures, temperature of aqueous amine mixtures and partial pressure of CO_2 at the specified range of operating conditions such as temperature range of 303.15-333.15 K, total amine solution concentration range of 1-3 kmol/m^3, CO_2 partial pressure range of 10.13-20.27 kPa and mole fraction of HMDA in the total aqueous amine mixtures range of 0.05-0.20. The model developed to calculate the CO_2 solubility in the aqueous blend of DEEA and HMDA is expressed by the following equation:

$$\alpha = C_1 + C_2 * X + C_3 * C_T + C_4 * T + C_5 * p_{CO_2} + C_6 * X^2 + C_7 * {C_T}^2 + C_8 * T^2 + C_9 * {p_{CO_2}}^2 \qquad (5.1)$$

Where α is the CO_2 equilibrium solubility in CO_2 solubility in aqueous amine mixtures of DEEA and HMDA (mole of CO_2/mole of total amine), X is the HMDA mole fraction in total aqueous amine mixtures, C_T is the total concentration of aqueous amine mixtures (kmol/m^3), T is the temperature of total aqueous amine mixtures (K), and p_{CO_2} is the CO_2 (kPa) partial pressure. Then the equation 5.1 was solved with the help of MATLAB software to find the value of equation coefficients (C_1 to C_9) by taking different sets of experimental data. The matrix form of equation 5.1 which is used to solve the above equation is given below:

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} & C_{17} & C_{18} & C_{19} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} & C_{27} & C_{28} & C_{29} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} & C_{37} & C_{38} & C_{39} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} & C_{47} & C_{48} & C_{49} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} & C_{57} & C_{58} & C_{59} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} & C_{67} & C_{68} & C_{69} \\ C_{71} & C_{72} & C_{73} & C_{74} & C_{75} & C_{76} & C_{77} & C_{78} & C_{79} \\ C_{81} & C_{82} & C_{83} & C_{84} & C_{85} & C_{86} & C_{87} & C_{88} & C_{89} \\ C_{91} & C_{92} & C_{93} & C_{94} & C_{95} & C_{96} & C_{97} & C_{98} & C_{99} \end{pmatrix} \times \begin{pmatrix} 1 \\ X \\ C_T \\ T \\ p_{CO_2} \\ X^2 \\ {C_T}^2 \\ T^2 \\ {P_{CO_2}}^2 \end{pmatrix} = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \alpha_5 \\ \alpha_6 \\ \alpha_7 \\ \alpha_8 \\ \alpha_9 \end{pmatrix}$$

The above matrix form may also be written as:

$$[C][Z] = [\alpha]$$

or

$$[C] = [Z]^{-1}[\alpha] \qquad (5.2)$$

After solving the equation by taking different sets of value for X, C_T, T, p_{CO_2} and α, the value for the coefficients (C_1 to C_9) was obtained. For each set of coefficients, the CO_2 solubility was calculated by using this empirical solubility model, and the calculated solubility was compared with the corresponding experimental data of CO_2 solubility and percentage deviation was calculated.

The coefficient with the lowest deviation was considered to get the optimum value of CO_2 solubility from this model. The obtained coefficients of equation 5.1 are shown in table 5.3.

Table 5.3 Co-efficient of developed modeling equation for CO_2 solubility in DEEA+HMDA blend

Co-efficient	Value	Unit
C_1	51.07834	mol CO_2 mol amine^{-1}
C_2	5.93000	mol CO_2 mol amine^{-1}
C_3	-0.22550	mol CO_2 mol amine^{-1} m^3 kmol^{-1}
C_4	-0.32082	mol CO_2 mol amine^{-1} K^{-1}
C_5	0.13660	mol CO_2 mol amine^{-1}kPa^{-1}
C_6	-14.73333	mol CO_2 mol amine^{-1}
C_7	0.05450	mol CO_2 mol amine^{-1} m^6 kmol^{-2}
C_8	0.00050	mol CO_2 mol amine^{-1} K^{-2}
C_9	-0.00420	mol CO_2 mol amine^{-1} kPa^{-2}

Finally, the CO_2 solubility in amine blend solution under specified operating conditions was predicted by using the developed empirical solubility model. Then, the predicted values of CO_2 solubility obtained by equation 5.1 were compared with the experimental values and the predicted CO_2 solubility was plotted against the experimental CO_2 solubility as shown in figure 5.9. The accuracy of the developed solubility model has expressed in terms of the absolute relative deviation (ARD) as well as average absolute deviation (AAD). It is defined as follows:

$$ARD = \frac{\left|\alpha_{\exp} - \alpha_{cal}\right|}{\alpha_{\exp}} \times 100\% \qquad (5.3)$$

$$AAD = \frac{1}{N}\sum \left| \frac{\alpha_{\exp} - \alpha_{cal}}{\alpha_{\exp}} \right| \times 100\% \tag{5.4}$$

Where $\alpha_{\exp}$ is the experimental CO_2 solubility and α_{cal} is the calculated/predicted CO_2 solubility and N is the number of data point. The R^2 value from this plot was found to be 0.992. From figure 5.9, it is cleared that the proposed solubility model agrees well which is quite acceptable. So, the developed CO_2 solubility model is reliable for the specified range of operating conditions.

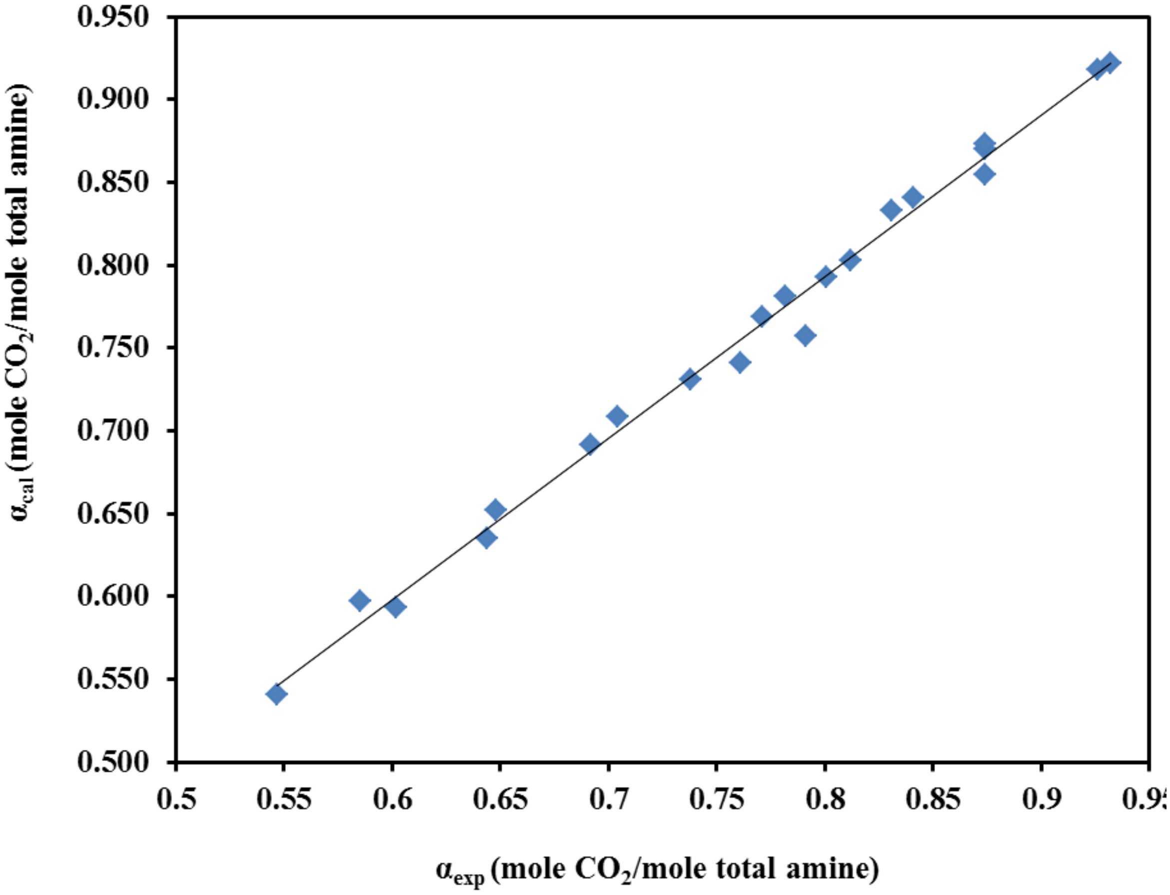

Figure 5.9 Parity plot between predicted (α_{cal}) and experimental CO_2 solubility (α_{CO_2}) for DEEA+HMDA blend

5.3.3 Estimation of heat of absorption of CO_2

The absorption heat of CO_2 (ΔH_{abs}) in aqueous amine solutions has a significant role in the CO_2 capture process because solvent regeneration cost mostly depends upon it. The cost of energy required for the solvent regeneration process accounts for 70-80% of the total operating cost of the CO_2 capture unit (Feng et al., 2010). The operating cost is a prime factor in the CO_2 capture process by using the amine solution which limits the wide application of this amine solvent in the CO_2 capture process. Therefore, to minimize the overall operating cost, regeneration cost needs to be minimized and for that absorption heat of CO_2 is the root cause which needs to be minimized to make the amine-based absorption technology reliable and affordable. The absorption heat can be measured by experimental method by using calorimeter and it can be estimated indirectly by using the Gibbs-Helmholtz equation as shown in equation 5.5.

$$\frac{d\left(\ln p_{CO_2}\right)}{d\left(\frac{1}{T}\right)}=\frac{\Delta H_{abs}}{R} \tag{5.5}$$

Where ΔH_{abs} is the absorption heat of CO_2 in kJ/mol, p_{CO_2} is the partial pressure of CO_2 in kPa, R is the universal gas constant, and T is the temperature in K. The Gibbs-Helmholtz equation was already validated by comparing the results obtained from the equation 5.5 with the experimental results in the work (Lee et al., 1972; Rho et al., 1997; Carson et al., 2000; Kim et al., 2007). It can be observed from their work that the heat of CO_2 absorption calculated from the Gibbs-Helmholtz equation agrees well with the experimental results. Therefore, the Gibbs-Helmholtz equation is appropriate for the estimation of the absorption heat of CO_2 in aqueous amine solution. In this work, the absorption heat of CO_2 in the aqueous amine mixture of DEEA and HMDA was estimated by using equation 5.5. A plot between $\ln p_{CO_2}$ and 1/T at a constant value of CO_2 solubility was drawn by using the predicted solubility data in the specified range of operating conditions and it has shown in figure 5.10. The slope of the plot and universal gas constant were multiplied to obtain the results of CO_2 absorption heat. The absorption heat of CO_2 was calculated to be -67.32, -69.20, and -69.99 kJ/mol for different equilibrium CO_2 solubility of 0.842, 0.824, and 0.803, mol CO_2/mol amine, respectively. Thus, the results show that absorption heat of CO_2 slightly deceases as equilibrium CO_2 solubility increases.

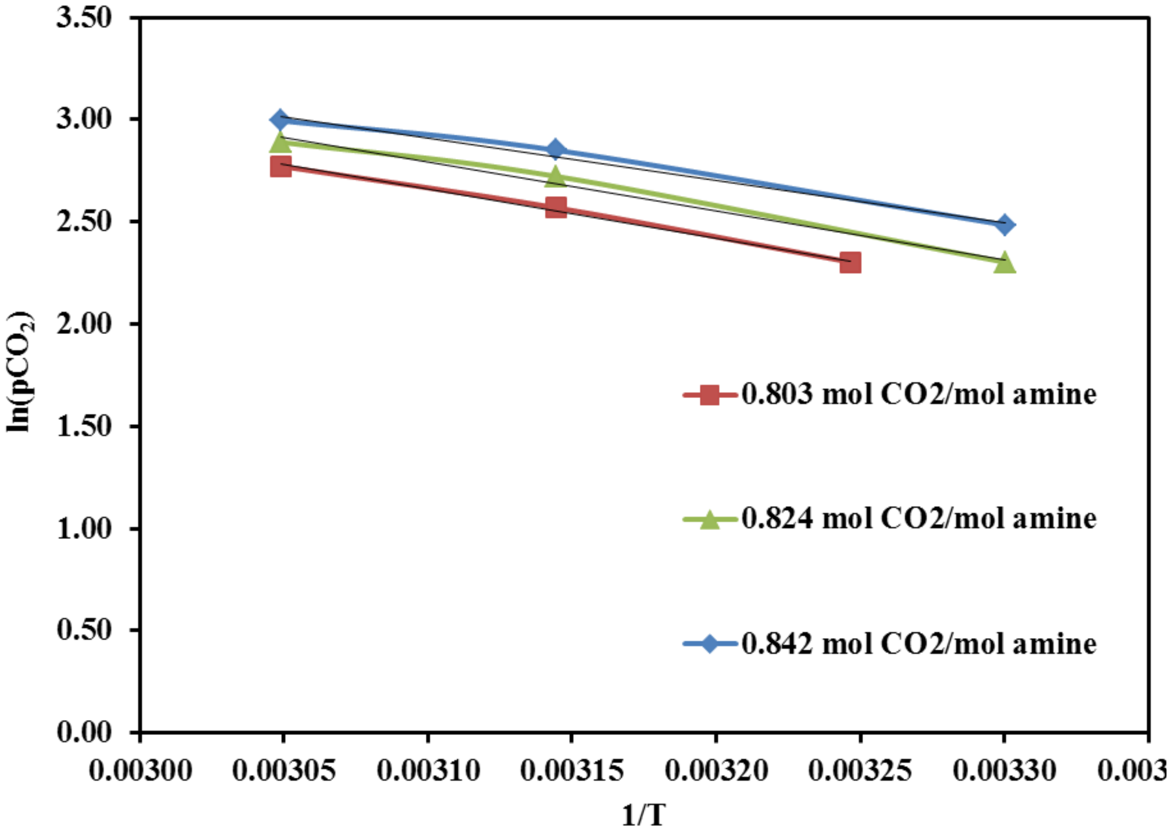

Figure 5.10 Plot between $\ln(p_{CO_2})$ versus 1/T at different equilibrium solubility of CO_2 in DEEA+HMDA solution

Considering all the factors the average absorption heat of CO_2 in aqueous amine mixtures of DEEA and HMDA was calculated to be -68.84 kJ/mol which is lower than that of the benchmark amine MEA (-84.3 kJ/mol) (Kim et al., 2007). However, lower absorption heat of CO_2 is more favourable to energy consumption, but it doesn't represent the total heat cost. Therefore, to compare the total energy requirement of aqueous DEEA+HMDA blend with other amines absorbent, the sensible heat and heat of evaporation can be considered.

Normally, a combination of these three components: the desorption heat (ΔH_{des}), the sensible heat requirement (Q_{sens}), and the heat of water vaporization ($Q_{H_2O_{vap}}$) results into the re-boiler heat duty (Q) in amine regeneration for capture process, as shown in equation 5.6.

$$Q = \Delta H_{des} + Q_{H_2O_{vap}} + Q_{sens} \tag{5.6}$$

However, $Q_{H_2O_{vap}}$ is similar for all amine solvent and Q_{sens} is small as compared to $Q_{H_2O_{vap}}$ as mentioned by Oyenekan (2007). Therefore, the only component that dominates the re-boiler heat duty is the desorption heat of CO_2. The desorption is the reverse process of the absorption. So, the desorption heat of CO_2 has same magnitude as the absorption heat of CO_2 with the opposite sign. Therefore, we can say that the heat of CO_2 desorption of aqueous blend of DEEA and HMDA is 68.84 kJ/mol which is lower than the benchmark absorbent MEA (84.3 kJ/mol). Accordingly, the re-boiler heat duty (Q) for the regeneration of the amine mixture (DEEA+HMDA) is lower than the conventional amine MEA. So, it would be easier to regenerate DEEA+HMDA as compared with MEA. Therefore, CO_2 capture cost can be reduced.

5.4 CONCLUSIONS

In this work, absorbed amount of CO_2 in amine mixtures as a function of time has been presented and it is observed a similar tradition of plots with studied operating parameters such as HMDA mole fraction in total amine, total amine mixture concentration, CO_2 partial pressure, and temperature. At initial stage of experiment, absorption of CO_2 takes place appreciably within 0 to 150 min, and then becomes very slowly to achieve complete dissolution of CO_2 in aqueous amine mixture to form saturated carbonated amine solution. Further, more and more dissolution of CO_2 in the mixture takes place due to the presence of two N groups (-NH2 groups) in HMDA, finally enhanced CO_2 absorption capacity corresponds to higher CO_2 solubility. Maximum equilibrium CO_2 solubility in aqueous amine mixture is observed at 0.2 of HMDA mole fraction in total amine mixture. The total time elapsed to achieve equilibrium is varies from 400 to 600 min depending on concentration of amine mixture and operating parameters. The equilibrium CO_2 solubility in DEEA+HMDA mixture increases with increasing partial pressure of CO_2 but, decreases as temperature rises. Also, the CO_2 solubility in present amine mixture is more than the other previous studied amine mixture of same kind available in literature. An empirical solubility model for CO_2 solubility was developed in the specified range of operating conditions by using experimental solubility data of CO_2. In addition, the absorption heat of CO_2 in an aqueous mixture of DEEA and HMDA was estimated by using the Gibbs-Helmholtz equation and found to be -68.84 kJ/mol which is lower than the MEA (-84.3 kJ/mol) as benchmark amine. So, the present absorbent aqueous mixture of DEEA and HMDA is promising for the removal of CO_2 from coal-fired power plant stack gas stream.