EQUILIBRIUM SOLUBILITY MEASUREMENT AND MODELING OF CO$_2$ ABSORPTION IN AQUEOUS BLEND OF 2-(DIETHYLAMINO)ETHANOL AND ETHYLENEDIAMINE

ABSTRACT

In the present work, the equilibrium CO$_2$ solubility in aqueous blend of 2-(Diethyl amino)ethanol (DEEA) and ethylenediamine (EDA) was performed at atmospheric pressure by using laboratory scale bubbling absorber. The total concentration of amine blend solution in the range of 1.13-4.90 mol/kg and EDA mole fraction in total amine blend in the range of 0.05-0.20 were taken. The experiments for measurement of CO$_2$ solubility were performed at a temperature range of 303.15-333.15 K and CO$_2$ partial pressure range of 10.13-20.27 kPa. The analysis of CO$_2$ in liquid phase was accomplished by direct titration method using HCl solution. The solubility data of CO$_2$ in DEEA+EDA solution of the present study was compared with data available in literatures. The experimental results were implied to develop an empirical solubility model with average absolute deviation of 7.03% to predict the CO$_2$ equilibrium solubility in DEEA+EDA solution within the specified range of operating conditions. In addition, the heat of absorption of CO$_2$ in DEEA+EDA solution was estimated by using the Gibbs-Helmholtz equation and it was found to be -70.50 kJ/mol lower to benchmark amine MEA.

6.1 INTRODUCTION

In recent years, the impact of global warming as well as climate change is a serious environmental issue all over the world. The major issues behind the undesirable climate change and a significant increase in earth surface temperature are emissions of greenhouse gases (GHGs) such as methane, water vapour, carbon dioxide, and nitrous oxide, which have been increasing its concentration into the atmosphere for decades. Among these GHGs, CO_2 is a major contributor having a share of approximately 60% (Metz et al., 2007). Around 78% of CO_2 emission is due to the combustion of fossil fuels for power generation in thermal power plants and transportation (Adams and Davison, 2007). The four industries such as iron and steel, cement production, petroleum refining, and petrochemicals can be considered as the major sources of CO_2 emission. Many studies have been carried out to mitigate the CO_2 emission for minimizing the impact of global warming and to find out a reliable solution. To mitigate the CO_2 emission, basic options are the use of efficient energy, progress of renewable energy and carbon capture and storage (CCS) (Metz et al., 2007). Among these, CCS is the most promising option for the reduction of CO_2 emission. Under the CCS, chemical absorption technology is highly preferred to remove CO_2 from various gas streams emitted from anthropogenic sources because this technology reduces the CO_2 concentration up to a very low quantity. Currently, the absorption process using an amine aqueous solution is widely used in the purification of gases and CO_2 capture process (Tontiwachwuthikul et al., 2011; Rochelle et al., 2009). The commonly used amine absorbents are monoethanolamine (MEA), diethanolamine (DEA), methyl diethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and polyamines (PZ) (Bishnoi and Rochelle, 2000). Several researchers measured the CO_2 capture performance of different tertiary amine such as 2-(Dimethylamino)ethanol (DMEA), 2-(Diethylamino)ethanol (DEEA), 1-dimethylamino-

2-propanol (DMAP-12), 3-dimethylamino-1-propanol (DMAP-31), 4-((2 hydroxyethyl)(ethyl)amino)-2-butanol (HEEAB), 1-(2 Hydroxyethyl)pyrrolidine (1-(2-HE)PRLD), 4-(dipropylamino)-2-butanol (DPAB), 3-diethylamino-1,2-propanediol (DE-1,2-PD), 4-((2-hydroxyethyl)(methyl)amino)-2-butanol (HEMAB) 1-(2-Hydroxyethyl)-piperidine (1-(2-HE)PP), and 4-(dimethylamino)-2-butanol (DMAB) 2-(2-(dimethylamino) ethoxy) ethanol (DMAEOE), 1,2-bis (dimethyl amino) ethane (TEMED), methyl-4-morpholine, pyridine, ethyldiethanolamine (EDEA) and butyldiethanolamine (BDEA) at various operating conditions at lab-scale (Chowdhury et al., 2013; Vaidya and Kenig, 2007; Luo et al., 2016a; Liao et al., 2017; Liu et al., 2019a,b; Ling et al., 2019; Gao et al., 2017). Again, different authors studied the absorption-desorption performance of polyamine such as ethylenediamine (EDA), 1,3-diaminopropane (DAP), N-methylpropane-1,3-diamine (MAPA), 3-Dimethylaminopropylamine (DMAPA), N-methylethylenediamine (MEDA), 2-Dimethylaminoethylamine (DMAEA), diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA) at lab-scale (Arshad et al., 2017; Mannisto et al., 2017; Pawlak & Kruszczak , 2017; Kumar and Mondal, 2018a). Among these, MEA is most widely used in the CO_2 capture process because of its high CO_2 absorption capacity, fast reaction/ absorption rate and low solvent cost (Kohl and Nielsen, 1997). But it requires high energy in the regeneration process which has attracted to the development of an alternative solvent as well as a blended solvent to improve the CO_2 capture performance by compensating the drawbacks of individual solvent. The use of blended solvent as a mixture of tertiary/sterically hindered amine and primary/secondary amine for CO_2 capture was first proposed by Chakravarty et al. (1985). Recently, DEEA has been seen to be another novel tertiary amine absorbent for CO_2 capture because its absorption capacity and absorption rate is more than the conventional tertiary amine

MDEA and it can also be manufactured from agriculture residues (Chowdhury et al., 2013; Vaidya and Kenig, 2007). Also, it required low regeneration cost in comparison to MEA because of its characteristic of a tertiary amine. In order to improve the DEEA absorbent for CO_2 capture, most of the researcher used various types of amine additives as activator or promoter because it has a low absorption rate as a characteristic of a tertiary amine. However, they have more worked on DEEA with different additives such as MEA (Luo et al., 2016a; Liao et al., 2017; Gao et al., 2017), MAPA (Arshad et al., 2017; Mannisto et al., 2017; Pawlak and Kruszczak, 2017), AEEA (Kumar and Mondal, 2018a), HMDA (Kumar and Mondal, 2018b), PZ (Gao et al., 2018; Afkhamipour et al., 2019; Adak and Kundu, 2017) to improve its capture performance with evaluation of solubility, absorption capacity, absorption heat, absorption rate, reaction rate and absorption coefficient, etc. Diamine EDA shows a good absorption performance due to its high absorption capacity, high absorption/reaction rate, and low degradation tendency as well as it can be manufactured from renewable sources like agriculture residue/wastes (Vaidya and Kenig, 2007; Weiland and Trass, 1971; Salvi et al., 2014). A few research data are available on kinetics characteristics of DEEA+EDA blend with CO_2 (Budhwani et al., 2017). But, no more information on CO_2 solubility in an aqueous blend of DEEA and EDA is available at different operating conditions. Therefore, it requires more investigations for CO_2 absorption in DEEA+EDA solution. Because, the experimental CO_2 equilibrium solubility data has a significant role in the development of thermodynamic model, correlations, solvent screening and prime step design parameter for the CO_2 capture process. So, the present work is motivated on the analysis of CO_2 solubility in DEEA+EDA solution at various operating conditions.

In the present work, the solubility of CO_2 in DEEA+EDA solution was measured at different operating conditions such as the total concentration of DEEA+EDA solution
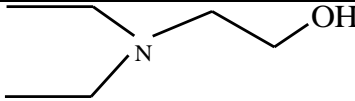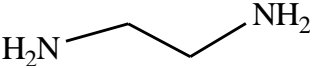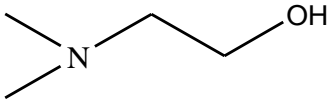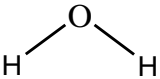
ranging from of 1.13 to 4.90 mol/kg, EDA mole fraction in the amine blend in the range of 0.05-0.20, temperature range of 303.15-333.15 K, and CO_2 partial pressure range of 10.13-20.27 kPa. The CO_2 solubility data of present work were compared with literature. Also, an empirical solubility model was developed for predicting the CO_2 solubility in the range of specified operating conditions. Furthermore, the heat of absorption of CO_2 was also evaluated with the help of predicted data on CO_2 solubility.

6.2 EXPERIMENTAL

6.2.1 Chemicals and materials

The reagent grade chemicals DEEA, EDA and HCl were used in the present work without any further purification. The specifications such as CAS No., structure, purity and supplier of chemicals used in the present work are shown in table 6.1. The aqueous blends of DEEA and EDA with required concentration for the experiments were prepared by using of double distilled water. The total concentration of final prepared amine blend solution was analysed by titrating with HCl solution to check the accuracy of solution concentration. The pH of prepared amine solutions was measured by a digital pH meter (model: Systronics-335, accuracy: ±0.01) after calibration with standard buffer solutions. The simulated gas stream containing CO_2 with required concentration was prepared by using gas mass flow controller (model: Alicat Scientific, accuracy: ±0.6%) and gas mixing chamber. The infrared portable flue gas analyzer (model: Gasboard-3800P, CO_2 range: 0-100 % by volume) was used to measure the gas phase CO_2 concentration with an accuracy of ±0.1%. A water bath was used to sustain required temperature of the aqueous amine blend within a minute variation of ±0.1K.

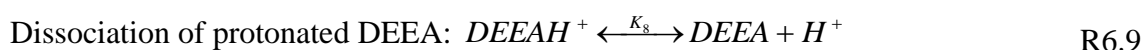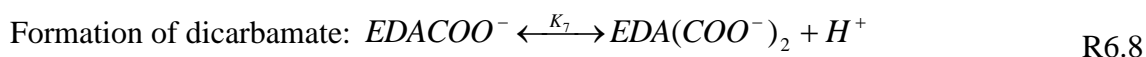**Table 6.1** Specification of chemicals used in the work

Compound	CAS NO.	Structure	Purity	Supplier
2-(Diethylamine)ethanol (DEEA)	100-37-8		0.99 (mass fraction)	Sigma-Aldrich
Ethylenediamine (EDA)	107-15-5		0.99 (mass fraction)	Sigma-Aldrich
Monoethanolamine (MEA)	141-43-5		0.99 (mass fraction)	Sigma-Aldrich
Hydrochloric acid (HCl)	7647-01-0	H-Cl	37 (mass fraction)	Sigma-Aldrich
Carbon dioxide (CO_2)	124-38-9	O=C=O	0.99 (mole fraction)	BOC India Limited
Nitrogen (N_2)	7727-37-9	N≡N	0.99 (mole fraction)	BOC India Limited
Distilled water (H_2O)	7732-18-5		0.99 (mass fraction)	Alpha Chemica

6.2.2 Experimental apparatus and procedure

The equilibrium CO_2 solubility in DEEA+EDA solution was measured with the help of the little-modified apparatus used in the present work as similar to our previous work (Kumar and Mondal, 2018a, b). The whole experimental apparatus can be divided into three sections, including the feed gas stream, absorber, and gas analysis section. The measurement of CO_2 solubility in aqueous amine blend was performed in a laboratory scale bubbling absorber by a continuous flow of the simulated gas streams of CO_2. A known amount of amine solution filled in the absorber was retained in a temperature-controlled water bath to lead the experiment. Then, amine solution and water bath temperature were measured using a thermometer with subdivisions of 0.1 K. Then, N_2 gas at low flow rate was passed into the bubbling absorber for 30 min to remove previous gases present in it. After that, a simulated CO_2 gas stream of fixed concentration was passed into the absorber through the gas flow meter with a flow rate of 0.25 litres per minute without interruption and sustained a constant flow of CO_2 gas streams in amine solution placed inside the absorber. Then, at a fixed interval of time 10 min, the leaving gas stream concentration was measured by gas analyser after absorption and the process was continued till the CO_2 gas concentration in inlet-outlet streams became equal indicating solution achieved saturation point with CO_2. Then, an aliquot of saturated carbonated amine solution was further used to determine the equilibrium CO_2 solubility (loading) by direct titration method using 1M HCl solution and water displacement column (Horwitz, 1980). At the room temperature and pressure, three aliquots of a fixed volume of saturated carbonated amine solution were taken to check the accuracy of the result by averaging the three consecutive analysis of the sample and and the estimated error in the measured solubility is about ±1 %. Then, CO_2 loading was expressed in terms of mole of CO_2 absorbed per mole of total amine blend.

6.2.3 Reaction chemistry of CO₂-DEEA-EDA system

When CO_2 absorbed in aqueous DEEA+EDA solution, the following set of chemical reactions occur in the liquid phase and chemical equilibrium is represented by the equilibrium constants and main reaction mechanisms are also described in details by the authors (Luo et al., 2016b; Wezland and Trass 1971).

Physical solubility: $CO_2(g) \xleftrightarrow{H_{CO2}} CO_2(aq)$ R6.1

Dissociation of water: $H_2O \xleftrightarrow{K_1} H^+ + OH^-$ R6.2

Formation of bicarbonate ion: $CO_2 + H_2O \xleftrightarrow{K_2} HCO_3^- + H^+$ R6.3

Formation of carbonate ion: $HCO_3^- \xleftrightarrow{K_3} CO_3^{2-} + H^+$ R6.4

Dissociation of protonated EDA: $EDAH^+ \xleftrightarrow{K_4} EDA + H^+$ R6.5

Formation of carbamate: $EDA + CO_2 \xleftrightarrow{K_5} EDACOO^- + H^+$ R6.6

Dissociation of carbamate: $EDACOO^- H^+ \xleftrightarrow{K_6} EDACOO^- + H^+$ R6.7

Formation of dicarbamate: $EDACOO^- \xleftrightarrow{K_7} EDA(COO^-)_2 + H^+$ R6.8

Dissociation of protonated DEEA: $DEEAH^+ \xleftrightarrow{K_8} DEEA + H^+$ R6.9

Where, H_{CO_2}, K_1-K_8, R6.1-R6.9 represent the Henry's law constant, equilibrium constants and equations of respective chemical reactions.

6.3 RESULTS AND DISCUSSION

6.3.1 Solubility of CO$_2$ in DEEA+EDA solution

In this work, equilibrium solubility (loading) of CO$_2$ in DEEA+EDA solution was measured at different operating conditions in the semi-batch flow system at atmospheric pressure. The operating conditions such as total amine solution concentration varying from 1.13-4.90 mol/kg, and EDA mole fraction in total amine solution from 0.05-0.20, a temperature range of (303.15-333.15) K and CO$_2$ partial pressure ranges of (10.13-20.27) kPa were selected.

6.3.1.1 Validation of experimental setup and method

Before measuring the CO$_2$ equilibrium solubility in DEEA+EDA solution, the experimental apparatus was validated to confirm the solubility measurement method. This validation was carried out by comparing the equilibrium solubility of CO$_2$ in MEA solution of 4.93 mol/kg at 313.15 K with literature (Aronu et al., 2011; Shen and Li, 1992; Song et al., 1996) data on CO$_2$ solubility as shown in figure 6.1. The average absolute deviation between present obtained data and previous reported data by Song et al., Shen and Li, and Aronu et al. are 0.97 %, 1.16 % and 2.15 %, respectively. From figure 6.1, it can be concluded that the present experimental results and previous results reported by authors are exist with good agreement. Therefore, the present experimental method is reliable for the further measurement of equilibrium CO$_2$ solubility in DEEA+EDA solution.
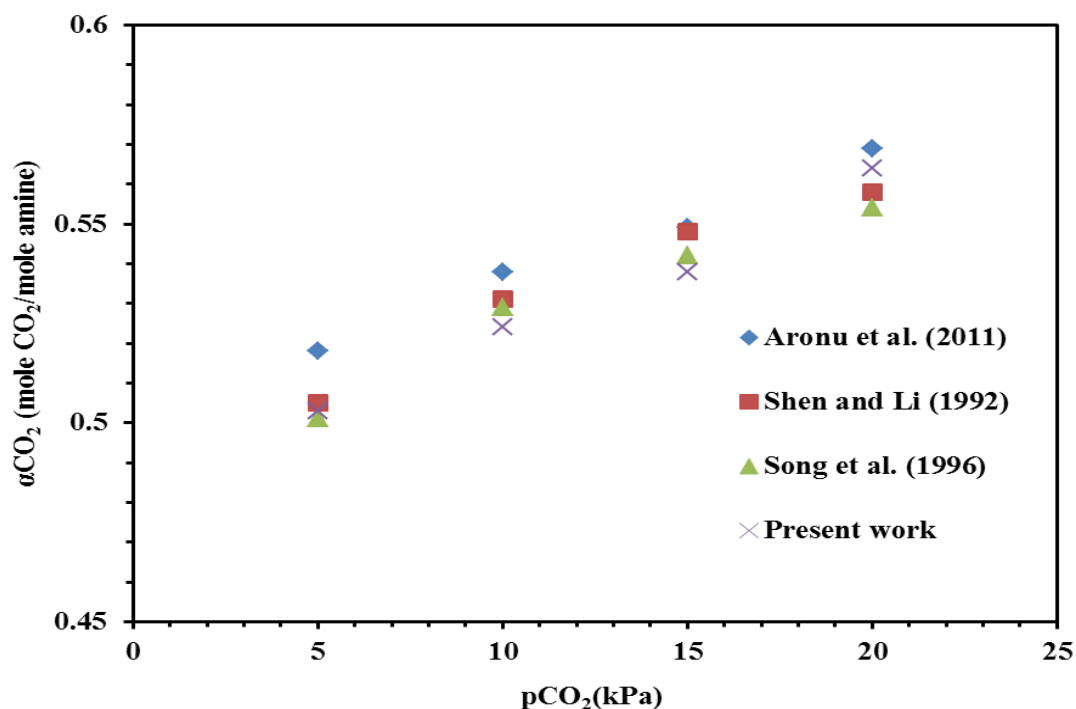
Figure 6.1 Equilibrium solubility of CO_2 in 4.93 mol/kg MEA solution at 313.15 K

6.3.1.2 Effect of concentration

In the present work, the equilibrium CO_2 solubility in DEEA+EDA solution was measured at a temperature of 313.15 K, CO_2 partial pressure of 20.27 kPa for three different compositions of amine blend. The results on the equilibrium CO_2 solubility in DEEA+EDA solution are shown in figure 6.2. From figure 6.2, it can be clearly noticeable that the solubility of CO_2 increases with an increase in the EDA concentration in total amine solution and the maximum CO_2 solubility was observed at an EDA mole fraction of 0.20. This increase of CO_2 solubility in DEEA+EDA solution is due to the occurrence of two primary amino groups in the chemical structure of EDA which provide extra reactive site to promote further CO_2 dissolution in the aqueous amine blend (Singh et al., 2007).

Figure 6.3 shows the effect of total amine blend concentration on the CO_2 solubility at a fixed temperature of 313.15 K, EDA mole fraction of 0.20, and 20.27 kPa of CO_2 partial pressure. From the figure 6.3 it is clear that the CO_2 solubility is going on decreasing with an increase in the concentration of the amine blend because at a higher concentration it restricts the conversion of carbamate to bicarbonate in the gas-liquid reaction. It is also observed that solubility of CO_2 decreased very slightly in the range of concentration from 1.13 to 2.63 mol/kg and then after 2.63 mol/kg concentration it decreased instantaneously.
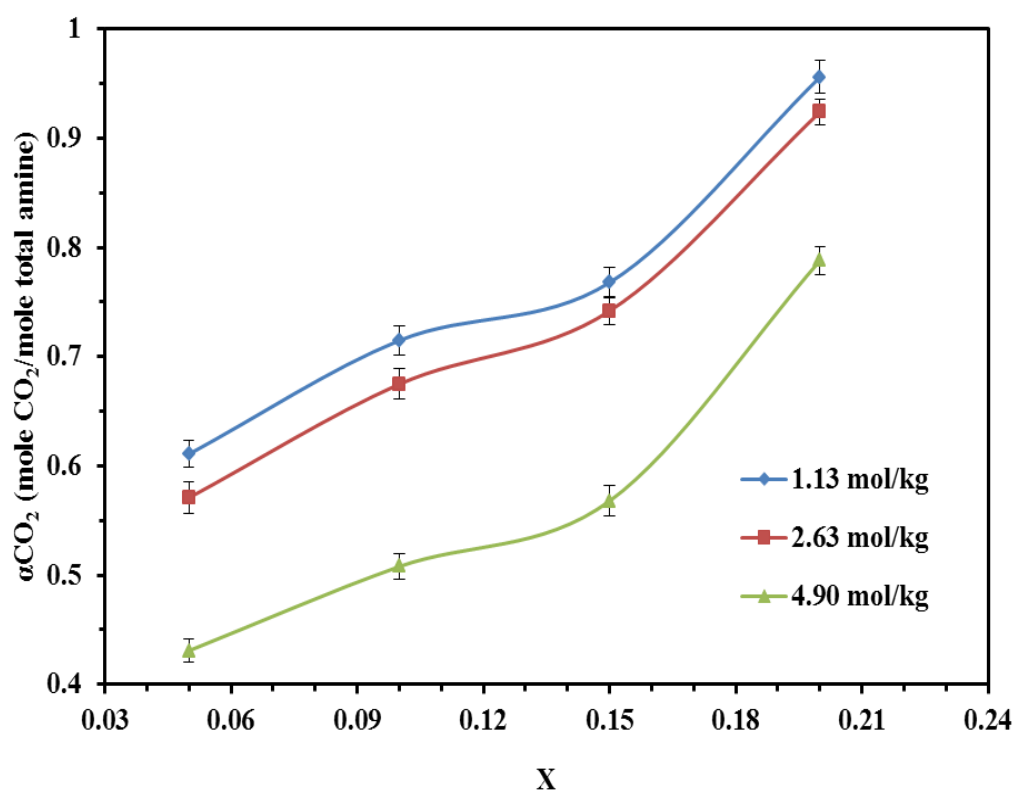

Figure 6.2 Plot of equilibrium solubility of CO_2 versus EDA mole fraction in total amine solution at 313.15 K and 20.27 kPa
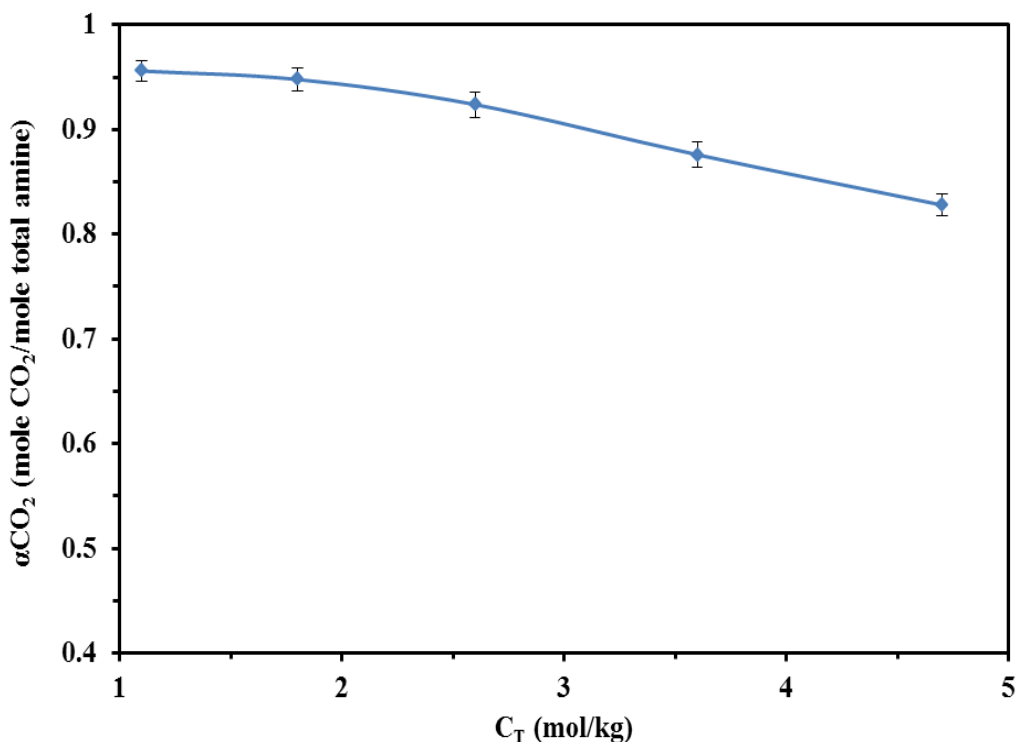
Figure 6.3 Plot of equilibrium solubility of CO_2 versus concentration of total amine solution with 0.20 mole fraction of EDA at 313.15 K and 20.27 kPa

6.3.1.3 Effect of CO_2 partial pressure

The partial pressure of CO_2 gas stream plays a significant role in the gas-liquid equilibrium system. Its influence on the solubility of CO_2 was studied in a fixed amine blend concentration of 2.63 mol/kg with an EDA mole fraction of 0.20 at temperature 313.15 K for CO_2 partial pressure in the range of 10.13-20.27 kPa. From figure 6.4, it is shown that solubility of CO_2 increases with increase in CO_2 partial pressure because the extra molecule of CO_2 transfer from bulk of gas-phase to gas-liquid interface corresponds to a rise in driving force. There is a linear increase in the solubility of CO_2 (0.75-0.8) mol of CO_2 per mole of amine blend as partial pressure of CO_2 increases from (10.13-15.19) kPa and then after 15.19 kPa the solubility of CO_2 increases instantaneously.
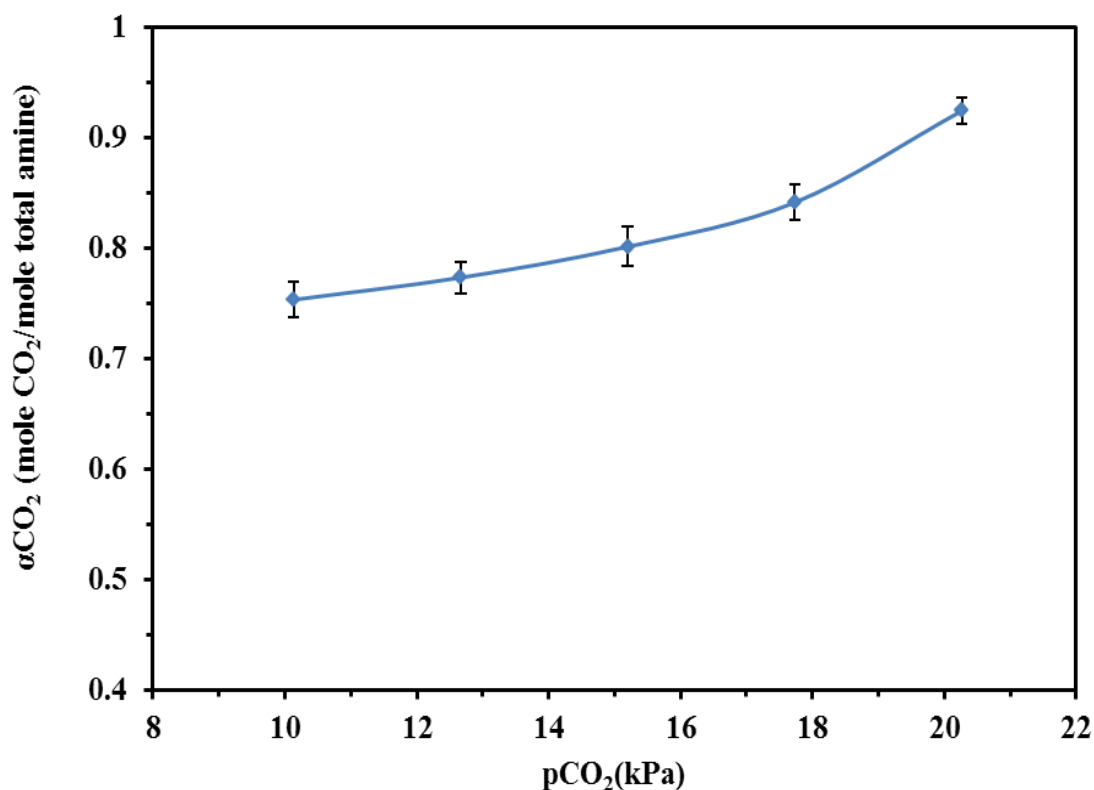
Figure 6.4 Plot of equilibrium solubility of CO_2 versus partial pressure of CO_2 with 2.63 mol/kg concentration of total amine solution and 0.20 mole fraction of EDA at 313.15 K

6.3.1.4 Effect of temperature

The temperature can considerably affect the gas-liquid equilibrium. Figure 6.5 shows the effect of amine blend temperature on solubility of CO_2 in the range of (303.15-333.15) K. In this respect, the total amine blend concentrations, EDA mole fraction in total amine solution, the CO_2 partial pressure were kept fixed at 2.63 mol/kg, 0.20, 20.27 kPa, respectively. The CO_2 solubility decreases with an increase in amine solution temperature and there is little decrease in the CO_2 solubility in the temperature range (303.15-313.15) K. After that, there is a linear decrease in the solubility of CO_2 beyond the temperature of 313.15 K up to 333.15 K. In the absorption process, reversible reactions between CO_2 and amine solution take place and as the temperature goes beyond

a certain value gas-liquid equilibrium shifts in the reverse direction. Also, desorption of CO_2 takes place naturally at higher temperatures and then the CO_2 solubility in amine blend solution typically decreases with increasing temperature. It has also been noticed that there is little decrease in solubility of CO_2 in a lower temperature range of 303.15-313.15 K.
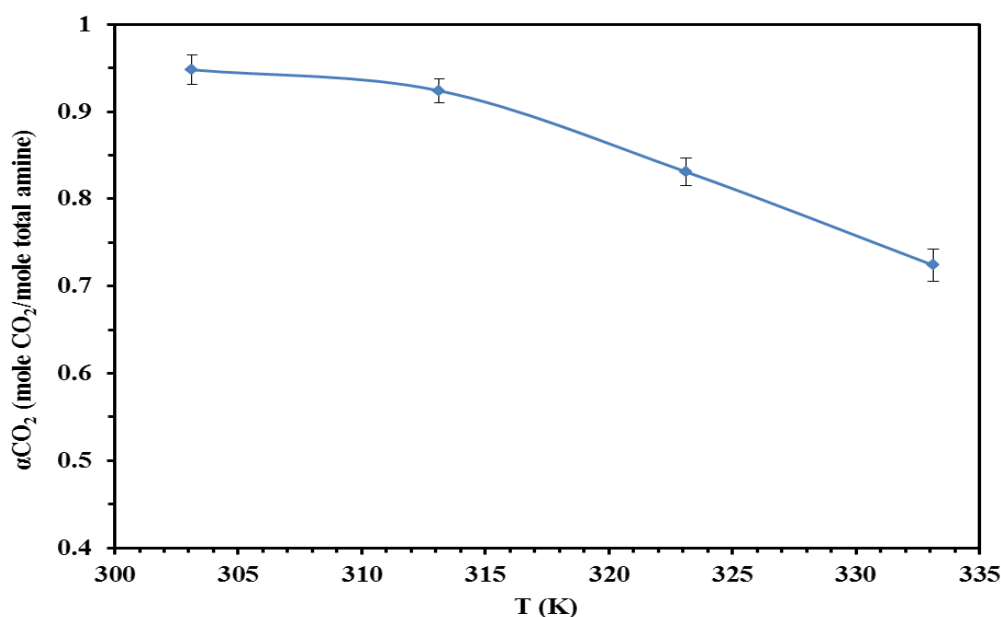
Figure 6.5 Plot of equilibrium solubility of CO_2 versus temperature with 2.63 mol/kg concentration of total amine solution and 0.20 mole fraction of EDA at 20.27 kPa

6.3.1.5 Comparison of CO_2 solubility in different DEEA-based amine blends

The CO_2 solubility in DEEA+EDA solution was compared with previous work performed by numerous authors measured the CO_2 solubility in different amine blend solution and solubility data of each DEEA based blend has shown in table 6.2. After the analysis, it has been noticed that the CO_2 solubility in the present amine blend (DEEA+EDA) solution is higher than the others different DEEA based amine blends presented in table 6.2. DEEA+EDA blend showed the best absorption performance in

term of CO_2 equilibrium solubility among the entire blends because EDA has two primary amino groups in the structure, so it provides extra reactive sites than other diamines (Singh et al., 2007). But, in case of DEEA+PZ blend, PZ has two secondary amine groups in the chemical structure, as known fact that reactivity of primary amine is more than the secondary amine (Rayer et al., 2012). Also, in the case of DEEA+AEEA blend, AEEA contains a primary amine, a secondary amine, and a hydroxyl group in the chemical structure but the hydroxyl group reduces the absorption capacity of AEEA.

Table 6.2 Comparison of CO_2 solubility in different DEEA based aqueous amine blends with respect to DEEA+EDA blend

DEEA+Activator	C_T (mol/kg)	T (K)	P_{CO2} (kPa)	α_{exp} (mol CO_2/mol amine)	Reference
DEEA+EDA	2.63	303	20.27	0.948	Present work
DEEA+EDA	1.13	313	20.27	0.956	Present work
DEEA+MEA	2.6	313	20.00	0.531	Luo et al., 2016a
DEEA+PZ	-	303	5.80	0.691	Sutar et al., 2013
DEEA+PZ	1.12	303	20.20	0.932	Adak and Kundu 2017
DEEA+MAPA	-	313	224.1	0.873	Arshad et al., 2017
DEEA+DETA	-	303	15.20	0.501	Wang et al., 2017

6.3.2 Development of CO_2 solubility model

A empirical solubility model was developed to correlate the CO_2 solubility in DEEA+EDA solution as a function of EDA mole fraction in total amine solution, concentration of total amine solution, temperature of amine solution and partial pressure of CO_2 at the specified range of operating conditions. The different operating conditions such as temperature range of 303.15-333.15 K, total amine solution concentration range of 1.13-4.90 mol/kg, CO_2 partial pressure range of 10.13-20.27 kPa and mole fraction of EDA in the total amine solution range of 0.05-0.20 were taken. The empirical solubility model developed to calculate the CO_2 solubility in the aqueous blend of DEEA and EDA is expressed by the following equation:

$$\alpha = C_1 + C_2 * X + C_3 * C_T + C_4 * T + C_5 * p_{CO_2} + C_6 * X^2 + C_7 * C_T^2 + C_8 * T^2 + C_9 * p_{CO_2}^2 \quad (6.1)$$

Where α is the CO_2 equilibrium solubility in DEEA+EDA solution (mole of CO_2/mole of total amine), X is the EDA mole fraction in total amine solution, C_T is the total concentration of amine solution (mol/kg), T is the temperature of total amine solution (K), and p_{CO_2} is the CO_2 (kPa) partial pressure. Then the equation 6.1 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 6.1 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

$[C] = [Z]^{-1}[\alpha]$ (6.2)

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 6.1 are shown in table 6.3.

Table 6.3 Co-efficient of developed modelling equation for CO_2 solubility in DEEA+EDA blend

Co-efficient	Value	Unit
C_1	26.08621	mol CO_2 mol amine^{-1}
C_2	-0.10364	mol CO_2 mol amine^{-1}
C_3	-0.00170	mol CO_2 mol amine^{-1} m^3 kmol^{-1}
C_4	-0.15649	mol CO_2 mol amine^{-1} K^{-1}
C_5	0.022281	mol CO_2 mol amine^{-1}kPa^{-1}
C_6	14.70079	mol CO_2 mol amine^{-1}
C_7	-0.01150	mol CO_2 mol amine^{-1} m^6 kmol^{-2}
C_8	0.000231	mol CO_2 mol amine^{-1} K^{-2}
C_9	0.000251	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 6.1 were compared with the experimental values which are presented in table 6.4 and the predicted CO_2 solubility was plotted against the experimental CO_2 solubility as shown in figure 6.6.

Table 6.4 Experimental CO_2 solubility (α_{exp}) and calculated CO_2 solubility (α_{cal}) in various compositions of DEEA+EDA, absolute relative deviation (ARD) and average absolute deviation (ARD) in % at different operating conditions of temperature (K) and CO_2 partial pressure (kPa)

Run	X	C_T (mol/kg)	T (K)	p_{CO_2} (kPa)	α_{exp} (mol CO_2/mol amine)	α_{cal} (mol CO_2/mol amine)	ARD (%)
1	0.05	1.15	313.15	20.27	0.621	0.573	7.67
2	0.1	1.14	313.15	20.27	0.680	0.638	6.11
3	0.15	1.14	313.15	20.27	0.780	0.817	4.75
4	0.2	1.13	313.15	20.27	0.956	1.069	11.83
5	0.2	1.83	313.15	20.27	0.948	1.054	11.17
6	0.05	2.70	313.15	20.27	0.571	0.497	12.93
7	0.1	2.67	313.15	20.27	0.675	0.602	10.78
8	0.2	2.63	333.15	20.27	0.724	0.719	0.67
9	0.15	2.65	313.15	20.27	0.742	0.781	5.26
10	0.2	2.63	313.15	10.13	0.753	0.731	2.95
11	0.2	2.63	313.15	12.67	0.773	0.802	3.69
12	0.2	2.63	313.15	15.19	0.801	0.875	9.30
13	0.2	2.63	323.15	20.27	0.831	0.853	2.61
14	0.2	2.63	313.15	17.73	0.841	0.853	1.38
15	0.2	2.63	313.15	20.27	0.924	1.033	11.79
16	0.2	2.63	303.15	20.27	0.948	1.060	11.79
17	0.2	3.56	313.15	20.27	0.856	0.871	1.71
18	0.05	4.90	313.15	20.27	0.431	0.365	15.32
19	0.1	4.82	313.15	20.27	0.473	0.413	12.67
20	0.15	4.75	313.15	20.27	0.590	0.552	6.50
21	0.2	4.67	313.15	20.27	0.788	0.754	4.35
						AAD (%) =	7.03

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:

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

(6.3)

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

(6.4)

Where α_{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 0.976. From figure 6.6, it is cleared that the proposed solubility model agrees well with AAD equal to 7.03 % which is quite acceptable. So, the developed CO_2 solubility model is reliable for the specified range of operating conditions.
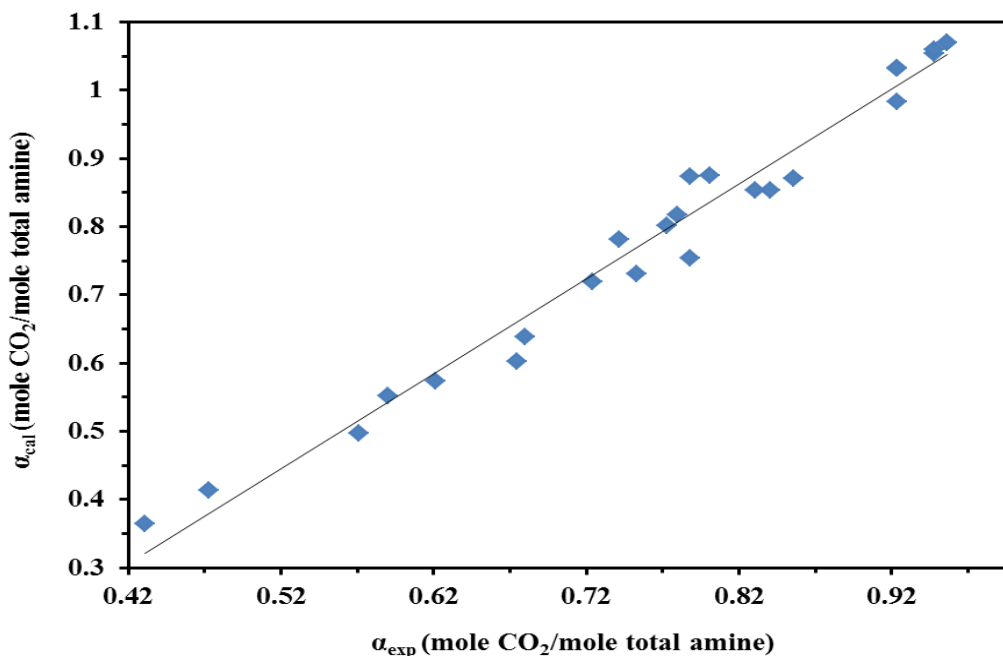

Figure 6.6 Parity plot between calculated (α_{cal}) and experimental CO_2 solubility (α_{exp}) for DEEA+EDA blend

6.3.3 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 6.5.

$$\frac{d\left(\ln p_{CO_2}\right)}{d\left(\dfrac{1}{T}\right)} = \frac{\Delta H_{abs}}{R} \tag{6.5}$$

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 this equation 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 suitable 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 blend of DEEA and EDA was estimated by using

equation 6.5. A plot between $\ln p_{CO_2}$ and 1/T at a constant value of equilibrium CO_2 solubility was drawn by using the predicted solubility data in the specified range of operating conditions and it has shown in figure 6.7. 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 -68.98, -70.03, and -72.49 kJ/mol for different equilibrium CO_2 solubility of 0.921, 0.843, and 0.791 mol CO_2/mol amine, respectively. Thus, the results show that absorption heat of CO_2 slightly deceases as equilibrium CO_2 solubility increases.
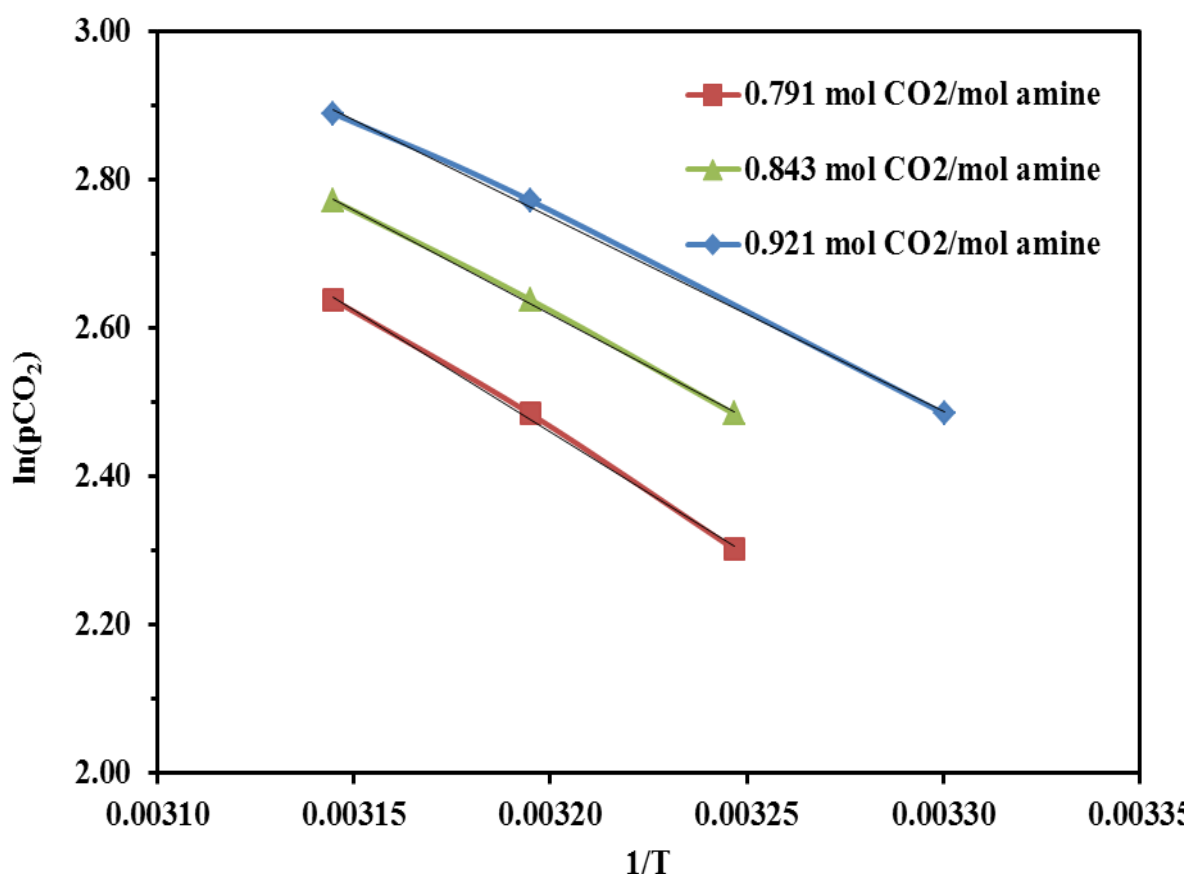

Figure 6.7 Plot between $\ln(p_{CO_2})$ versus 1/T at different equilibrium solubility of CO_2 in

DEEA+EDA solution

Considering all the factors, the average absorption heat of CO_2 in DEEA+EDA solution was calculated to be -70.50 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+EDA blend with other amines absorbent, the sensible heat and heat of evaporation can be considered.

Generally, 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, as shown in equation 6.6.

$$Q = \Delta H_{des} + Q_{H_2O_{vap}} + Q_{sens} \qquad (6.6)$$

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. As it known that, 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 EDA is 70.50 kJ/mol which is lower than the benchmark absorbent MEA (84.3 kJ/mol). Therefore, the re-boiler heat duty (Q) for the regeneration of the amine blend (DEEA+EDA) is lower than the conventional amine MEA. So, it would be easier to regenerate DEEA+EDA compare with MEA. So, the CO_2 capture cost will be reduced.

6.4 CONCLUSIONS

In this work, a good attempt has been done to characterize the potential solvent as an aqueous blend of DEEA and EDA for the CO_2 capture process. The CO_2 solubility in DEEA+EDA solution was measured at various operating conditions of the total concentration of amine solution ranging from 1.13 to 4.90 mol/kg, EDA mole fraction in the amine blend in the range of 0.05-0.20, temperature ranging from 303.15 to 333.15 K, and CO_2 partial pressure range of 10.13-20.27 kPa. After the CO_2 solubility measurement, it is noticed that the highest CO_2 solubility achieved at a 0.20 mole fraction of EDA in 1.13 mol/kg total amine solution. The solubility of CO_2 decreases with increase in temperature of amine solution and increases with increase in CO_2 partial pressure. The present solubility data on CO_2 for DEEA+EDA solution was compared with the previous solubility data on CO_2 for different DEEA based amine blend and it was found that the present amine blend shows highest CO_2 solubility than the previous reported DEEA based amine solution. The empirical solubility model was developed in the specified range of operating conditions by using our experimental results with an average absolute deviation of 7.03%. In addition, the absorption heat of CO_2 in DEEA+EDA solution was estimated with the help of the Gibbs-Helmholtz equation and found to be -70.50 kJ/mol which is lower than that of the benchmark amine MEA (-84.3 kJ/mol). However, DEEA+EDA solution can be considered to be an alternative solvent for post-combustion CO_2 capture.