Chapter 3

Thermodynamic modeling and new experimental CO_2 solubility into aqueous EAE and AEEA blend, heat of absorption, cyclic absorption capacity and desorption study for post-combustion CO_2 capture

ABSTRACT

In the present study, carbon dioxide (CO_2) solubility into aqueous blend of 2-(ethylamino) ethanol (EAE) and aminoehtylethanolamine (AEEA) was measured. The performance of CO_2 capture by this amine blend was investigated in terms of CO_2 solubility, heat of absorption, cyclic CO_2 solubility, and initial rate of change of CO_2 solubility. CO_2 absorption study was carried out using bubble column reactor in the temperature range of 298.15 to 323.15 K, 8.11 to 20.27 kPa CO_2 partial pressure, 0.10 to 0.30 weight fraction of AEEA in EAE and AEEA blend, and 10 to 30 wt. % total concentration of blend solution. Desorption experiments were performed at 393.15 K. Maximum CO_2 solubility was 1.033 mol CO_2/mol amine at 298.15 K, 20.27 kPa, 0.30 weight fraction of AEEA in the blend, and 10 weight % of EAE and AEEA solution. A semi-empirical Kent-Eisenberg thermodynamic model and an empirical model were developed to correlate equilibrium CO_2 solubility in the studied range of operating conditions with 2.56 % and 0.45 %

average absolute deviation, respectively. At 313.15 K, 15.20 kPa CO_2 partial pressure and total concentration of 30 wt. % of EAE and AEEA blend, the equilibrium CO_2 solubility was resulted as 0.748 mol CO_2/mol amine and cyclic solubility of 0.503 mol CO_2/mol amine was achieved. Heat of CO_2 absorption was measured based on Gibbs Helmholtz equation and found as -72.2 kJ/mol for 30 wt. % aqueous EAE and AEEA blend. Results of absorption capacity of EAE and AEEA solution and monoethanolamine (MEA) were compared at same operating conditions. This blend had higher CO_2 solubility, lesser heat of absorption, more cyclic capacity and faster rate of change of initial CO_2 solubility than MEA.

3.1 INTRODUCTION

Greenhouse gases present in environment are main sources of global warming. Carbon dioxide (CO_2) is a greenhouse gas and contributed major impact on global warming and climate change. CO_2 gas emitted in environment due to fossil fuel combustion in the coal fired power plant and other industries (cement industry, Iron and steel industry, petrochemical industry, etc.). According to the report of the International Energy Agency, the energy demand of the world will continue to increase more than 30 % up to 2040. Major fraction of energy will be provided by fossil fuels in the upcoming future (IEA, 2017). Therefore, CO_2 capture from flue gases is still an important research area.

Pre-combustion CO_2 capture, post-combustion CO_2 capture and oxy-fuel combustion are mainly 3 technologies to reduce CO_2 emission from fossil fuel combustion. Post combustion CO_2 capture is one of the most effective and developed method to control CO_2 emission and its unit can be retrofitted easily in existing power plants (MacDowell et al., 2010). Adsorption, absorption, membrane separation technique, cryogenic, etc. are several techniques used for separation of gases. However, major difficulties in CO_2 capture from coal fired power plant flue gas streams are low CO_2 concentration (10–15% CO_2) in the gas stream with low flue gas pressure (almost 1 atm) and very large flow rate of flue gas with large concentration of N_2 (Mondal et al., 2015). Absorption technique is most matured and applicable for low pressure (at atmospheric pressure) post combustion CO_2 capture (Rochelle, 2009). Aqueous solutions of conventional alkanolamines e.g. monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) are very often used in chemical absorption-desorption process. 30 wt.% MEA is particularly applied for CO_2 capture from flue gas (low CO_2 partial pressure of 10 to 15 kPa CO_2) at 40 ^oC and as a consequence has become the benchmark amine for post-combustion CO_2 capture (Bui et al., 2018).

Sterically hindered amines e.g 2-(amino)methylpropanolamine (AMP),2-(methylamino)ethanol (MAE), 2-(ethylamino)ethanol (EAE), 2-(isopropylamino)ethanol (IPAE), 2-(butylamino)ethanol (BAE) etc. (Tontiwachwuthikul et al., 1991; Haider et al., 2011; Hawang et al., 2017), and polyamines e.g. piperazine (PZ), ethylinediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), triethylenepentamine (TEPA), etc. are also used for CO_2 capture (Rochelle et al., 2011; Zhou et al., 2010; Gao et al., 2017C; Schäffer et al., 2012; Aronu et al., 2009). Primary (MEA) and secondary (DEA) amine has shown high heat of absorption and faster reaction kinetics. Tertiary amines have high CO_2 loading and low heat of absorption but slow reaction kinetics is its drawback. Aqueous (MEA) attracted a wide range of research and considered benchmark amine for CO_2 capture because of its good absorption capacity and fast kinetics. However, MEA has high heat of absorption and low cyclic capacity so it required large energy penalty for absorbent regeneration (Jou et al., 1995; Jakobsen et al., 2005; Idem et al., 2006). Sterically hindered amines formed unstable carbamate due to hindrance of amino group and showed high CO_2 loading, and lower heat of reaction. Polyamines have been studied recently because of its higher CO_2 loading capacity (mol CO_2/mol amine) and faster kinetics. However, higher heat of regeneration of absorbent is major drawback of polyamines also.

Excellent reviews on the latest advances and developments in post-combustion CO_2 capture using amine solvents has been published in literature (Liang et al., 2015; Liang et al., 2016). From those reviews, it can be found out that there is no single solvent which has all favorable property for CO_2 capture by absorption-desorption process. To minimize demerits and to utilize advantages of individual amines, recently, several amine blends have been investigated for CO_2 capture (Hamidi et al., 2018; Tong et al., 2013; Shokouhi et al., 2015; Gao et al., 2017B; Knuutila et al., 2017; El Hadri et al., 2017; Conway et al., 2014; Sutar et al., 2013; Muchan et al., 2017A; Muchan et al., 2017B; Nwaoha et al., 2017; Wai et al., 2018). Despite it, several developments in solvent to achieve high CO_2 solubility, high recycle capacity, high mass transfer rate, fast reaction kinetics, low heat of CO_2 absorption, low regeneration cost, less corrosive, less viscous, less degradable, etc. for economical CO_2 capture operation are still needed.

EAE is a hindered secondary amine and has higher CO_2 loading with lower heat of absorption because it produces unstable carbamate (Hwang et al., 2017; El Hadri et al., 2017). Moreover, EAE can be produced using renewable resources of agriculture waste biomass (Vaidya and Kenig, 2007). Aminoethylethanolamine (AEEA) is an alkanoldiamine and has high CO_2 loading (mol CO_2/mol amine), faster reaction kinetics but its high heat of absorption (Ma’mun et al., 2007A; Ma’mun et al., 2007B) makes it not very useful as a single absorbent for CO_2 capture. In the literature AEEA has been used as an activator in the amine blends to improve solvent performance for CO_2 capture (Bajpai and Mondal, 2013; Moosavi et al., 2017; Kumar and Mondal, 2018).

In this chapter, an aqueous blend of EAE and AEEA was investigated for post-combustion CO_2 capture. Equilibrium CO_2 solubility (mol CO_2/mol amine) was studied at atmospheric pressure with varying temperature from 298.15 K to 323.15 K. Partial pressure of CO_2 gas was varied in the range of 8.11 kPa to 20.27 kPa that was related to the condition of flue gas of coal fired thermal power plant. Total concentration of blend was in the range of 10 wt. % to 30 wt. % and amount of AEEA in the blend was varied from 0.10 to 0.30 weight fraction of amine (EAE and AEEA). A semi-empirical model based on the Kent-Eisenberg model and an empirical model was developed to predict CO_2 solubility (mol CO_2/mol amine) data in the range of studied operating conditions. Desorption experiment was carried out at 393.15 K temperature and cyclic CO_2 solubility of this blend was calculated. Heat of CO_2 absorption, initial rate of change of CO_2 solubility during absorption as well as during desorption was studied for 30 wt. % of aqueous EAE and AEEA blend, and compared with 30 wt. % MEA solution.

3.2 EXPERIMENTAL SECTION

3.2.1 Materials

The EAE (98 % purity) was purchased from Sigma Aldrich, St. Louis USA. MEA (98 % purity), AEEA (98 % purity) and hydrochloric acid (HCl, 35-38% purity) was purchased from Sd Fine chemical limited, Mumbai, India. EAE and AEEA were used for making aqueous blend for CO_2 absorption. MEA was used as reference amine for validation of experimental set up and comparison for experimental results. HCl was used for titration of amine samples to measure CO_2 solubility. All chemicals were used without further purification. Description of all chemicals which were used in the experimentation was listed in Table 3.1 CO_2 gas (99.99% purity) and N_2 gas (99.99 % purity) purchased from Linde India Ltd. were used to prepare simulated gas for absorption study. Flow of gases was controlled with Mass flow controllers (ALICAT SCIENTIFIC – Model no. MC-500 SCCM-D, ± (0.4% of Reading + 0.2% of Full Scale)). A portable IR CO_2 gas analyzer (Gasboard-3800P; CO_2 range, 0-100% by volume, full scale accuracy = ±2 %) was used to measure the CO_2 gas concentration (in volume %). Double distilled water (made in our laboratory) was used to prepare aqueous amine solutions.

Table 3.1. Information of used chemicals

Chemical Name	CAS number	Source	Initial purity	Purification method
MEA[a]	141-43-5	sd Fine chemical limited, Mumbai, India	98 %[g]	none
EAE[b]	110-73-6	Sigma Aldrich, St. Louis, USA	≥ 98 %[g]	none
AEEA[c]	111-41-1	sd Fine chemical limited, Mumbai, India	98 %[g]	none
HCl[d]	7647-01-0	sd Fine chemical limited, Mumbai, India	35-38 %[g]	none

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
Water	7732-18-5	Our laboratory	99.9 %[g]	Double distillation

[a]Monoethanolamine, [b]2-(ethylamino)ethanol, [c]aminoehtylethanolamine, [d]Hydrochloric acid, [e]carbon dioxide, [f]nitrogen, [g]mass fraction, and [h]volume fraction.

3.2.2 CO_2 absorption study

All the experiments were done at atmospheric pressure and temperature range 298.15 K to 323.15 K. Absorption of CO_2 into aqueous EAE and AEEA blend was studied using a bubble column reactor of 150 ml volume capacity. Experimental set-up for absorption process was given in Figure 2.1 of Chapter 2**.** Water saturation cell and bubble column were placed inside the water bath with controlled temperature (accuracy of ±1 K). Simulated gas mixture was prepared in gas mixing chamber using controlled flow of CO_2 and N_2 gases. Concentration of CO_2 gas was varied from 8 to 20 volume % of gas mixture (8.11 kPa to 20.27 kPa partial pressure of CO_2) and total flow rate of simulated gas stream was kept constant at 240 ml/min. Initially 120 ml of absorbent was loaded in the bubble column and simulated gas stream of desired CO_2 partial pressure at inlet condition was passed into this through water saturation cell. Bubble formation was started and absorption with chemical reaction was taking place. Concentration of CO_2 in gas stream was measured with CO_2 gas analyzer periodically in time interval of 10 min. CO_2 solubility or CO_2 loading is defined by number of moles of absorbed CO_2 per mol of absorbent. In order to find out CO_2 solubility and initial absorption rate, 1 ml of CO_2 loaded sample was taken at 10 minute time intervals. Saturation of absorbent attained when outlet concentration of

CO_2 reached up-to the inlet concentration of CO_2 and CO_2 solubility attained same value repeatedly three time intervals. CO_2 solubility (mol CO_2/mol amine) was calculated using Chittick Apparatus (Horwitz, 1975). In which 1 mL CO_2 loaded sample was titrated with 1M HCl using methyl orange indicator. Volume of gas liberated during titration was collected in burette and CO_2 solubility was calculated by volumetric method using Eq. (3.1) (Gao et al., 2017B). CO_2 solubility calculation was repeated three times and average values were reported. Final solubility was declared at saturation point.

$$\alpha\ (\text{mol CO}_2/\text{mol amine}) = \frac{V_{CO_2}}{22.4 \times C_{amine} \times V_{CO2\ loaded\ sample}} \times \frac{273.15}{273.15+t} \qquad (3.1)$$

$$\text{Absorption capacity (mol CO}_2\text{/L solution)} = \alpha .\ C_{amine} \qquad (3.2)$$

Where, α is CO_2 solubility, C_{amine}, V_{CO_2}, $V_{CO2\ loaded\ sample}$ and t are concentration of amine (mol/L), volume of CO_2 gas (L) dissolved in amine solution, volume of CO_2 in loaded amine sample (L), and room temperature (^{o}C), respectively.

3.2.3 CO_2 desorption study

The experimental set-up for regeneration of absorbent by desorption of CO_2 was shown in Figure 3.1, almost similar to mentioned in literatures (Muchan et al., 2017 B; Kumar and Mondal, 2020). A three necked round bottom flask of 500 mL volume capacity was used as desorption reactor and immersed into the oil bath. A hot silicon oil bath was used to maintain desorption temperature at 393.15 K. Heat for desorption process was supplied by an electric hot plate (IKA, Germany; C-MAG HS 7, with an accuracy of ±10 K). 60 mL of CO_2 loaded solution, that was obtained after saturation of absorption experiment, was filled in desorption reactor. It was difficult to maintain temperature at 393.15 K accurately. The deviation of the desorption temperature was ±5 K and measured by a thermometer (with ±1 K error) that was kept into the sample in the desorption flask.

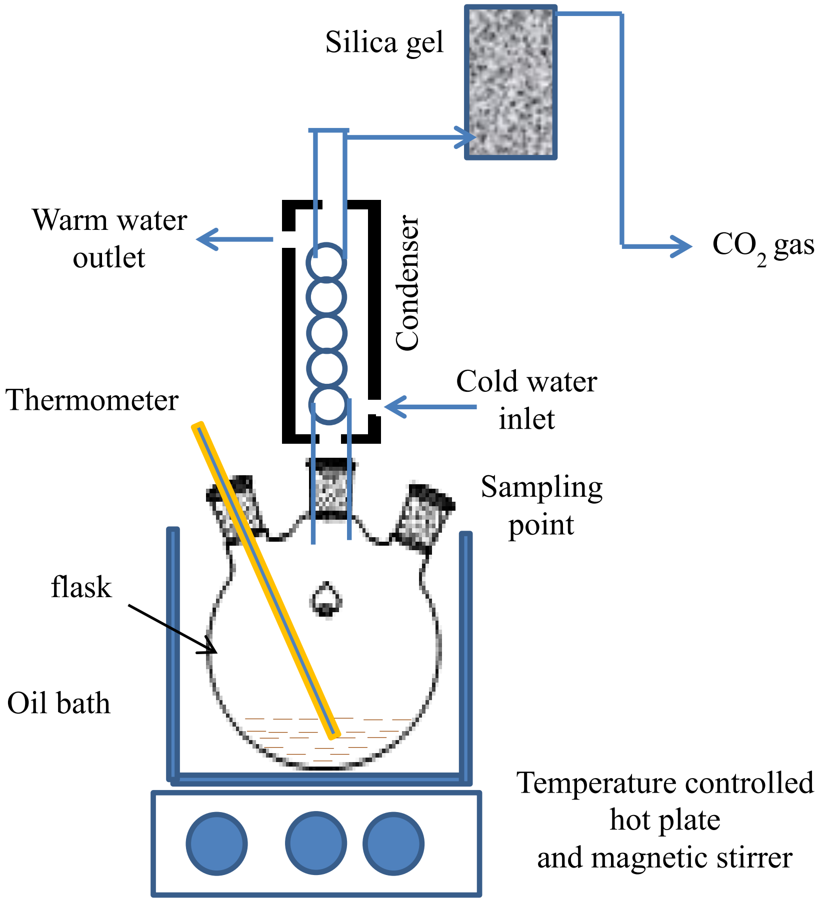

Figure 3.1. Experimental set-up for CO_2 desorption study.

A condenser was connected to the one exit of round bottom flask to prevent the amine loss and water vaporization. Thermal equilibrium between oil in oil bath and CO_2 loaded amine solution in desorption flask was reached in 10-15 min at 393.15 K. After that, CO_2 loading was found out by titration method by Chittik apparatus (Horwitz, 1975) at 10 min time interval. Cyclic CO_2 solubility and cyclic capacity was calculated by Eq. (3.3) and Eq. (3.4), respectively.

$$\Delta\alpha\ (\text{mol } CO_2/\text{mol amine}) = \alpha_{313.15\,K,15.20\,kPa} - \alpha_{393.15\,K,15.20\,kPa} \tag{3.3}$$

$$\text{Cyclic capacity (mol } CO_2/\text{L solution)} = \Delta\alpha . C_{amine} \tag{3.4}$$

3.2.4 Heat of absorption measurement

Heat of absorption of 30 wt. % aqueous EAE and AEEA (21 wt. % EAE + 9 wt. % AEEA) blend was calculated by determining CO_2 solubility of aqueous amine blend at different temperature and CO_2 partial pressure in the range of 298.15 to 323.15 K, and 8.11 to 20.27 kPa, respectively. Heat of absorption was estimated on the basis of Gibbs-Helmholtz equation (Eq. (3.5)) (Kim and Svendsen, 2007).

$$\frac{d(\ln(p_{CO_2}))}{d(\frac{1}{T})} = \frac{\Delta H_{abs}}{R} \tag{3.5}$$

Where, p_{CO_2} , T, and ΔH_{abs} are in kPa, K, and J/mol, respectively. R (J/mol.K) is universal gas constant. ΔH_{abs} was obtained by multiplying R into the slope of the plot between ln(p_{CO_2}) and (1/T). Set of p_{CO_2} and T data was selected at similar CO_2 solubility.

3.3 KENT-EISENBERG MODEL FOR EQUILIBRIUM CO_2 SOLUBILITY INTO AQUEOUS AMINE BLEND

3.3.1 Reaction mechanism

Kent-Eisenberg model (Kent and Eisenberg, 1976) was used to predict equilibrium CO_2 solubility into aqueous EAE and AEEA blend. Kent-Eisenberg model assumed that fugacity and activity coefficients of species formed at the equilibrium are equal to one. This is a very simple thermodynamic model to predict equilibrium CO_2 solubility that's why many researchers used it to calculate equilibrium CO_2 solubility into aqueous amine system (Haider et al., 2011; Mondal and Samanta, 2020; Chung et al., 2010; Tourneax et al., 2008; Aroua and salleh et al., 2004; Kumar et al., 2003; Hsu et al., 2014).

The absorption of CO_2 gas into aqueous EAE and AEEA blend was occurred due to the physical solubility of CO_2 into the H_2O followed by various chemical reactions of CO_2 with aqueous blend system. EAE ($CH_3CH_2NHCH_2CH_2OH$) and AEEA

($OHCH_2CH_2NHCH_2CH_2NH_2$) were denoted by $RNHR'$ and $R'NHR"NH_2$, respectively. Where $R, R', and\ R"$ were used for $–CH_2CH_3$, $–CH_2CH_2OH$, and $–CH_2CH_2–$, respectively. Following set of equilibrium relationship was possible.

Physical solubility of CO_2:

$$CO_2(g) \overset{H_{CO_2}}{\longleftrightarrow} CO_2(l) \tag{3.6}$$

Dissociation of water:

$$2H_2O \overset{K_1}{\leftrightarrow} H_3O^+ + OH^- \tag{3.7}$$

Carbamate formation due to reaction of AEEA with CO_2:

$$R'NHR"NH_2 + CO_2(l) + H_2O \overset{K_2}{\leftrightarrow} R'NHR"NHCOO^- + H_3O^+ \tag{3.8}$$

$$R'NHR"NH_2 + CO_2(l) + H_2O \overset{K_3}{\leftrightarrow} R'NCOO^-R"NH_2 + H_3O^+ \tag{3.9}$$

Dicarbamate formation:

$$R'NHR"NHCOO^- + R'NCOO^-R"NH_2 + 2CO_2(l) +$$

$$2H_2O \overset{K_4}{\leftrightarrow} 2(R'NCOO^-R"NHCOO^-) + 2H_3O^+ \tag{3.10}$$

Hydrolysis of carbamate formed due to EAE:

$$RNCOO^-R' + H_2O \overset{K_5}{\leftrightarrow} RNHR' + HCO_3^- \tag{3.11}$$

Hydrolysis of CO_2:

$$CO_2(l) + 2H_2O \overset{K_6}{\leftrightarrow} H_3O^+ + HCO_3^- \tag{3.12}$$

Dissociation of bicarbonate ion:

$$HCO_3^- + H_2O \overset{K_7}{\leftrightarrow} CO_3^{2-} + H_3O^+ \tag{3.13}$$

Dissociation of protonated amines:

$$[RNHR']H^+ + H_2O \overset{K_8}{\leftrightarrow} RNHR' + H_3O^+ \tag{3.14}$$

$$[R'NHR''NH_2]H^+ + H_2O \overset{K_9}{\leftrightarrow} R'NHR''NH_2 + H_3O^+ \tag{3.15}$$

$$[R'NHR''NH_2]H_2^{++} + H_2O \overset{K_{10}}{\leftrightarrow} [R'NHR''NH_2]H^+ + H_3O^+ \tag{3.16}$$

Dissociation of protonated carbamates:

$$[\, R'NHR''NHCOO^-]H^+ + H_2O \overset{K_{11}}{\leftrightarrow} R'NHR''NHCOO^- + H_3O^+ \tag{3.17}$$

$$[R'NCOO^-R''NH_2]H^+ + H_2O \overset{K_{12}}{\leftrightarrow} R'NCOO^-R''NH_2 + H_3O^+ \tag{3.18}$$

3.3.2 Equilibrium constants

It was assumed that fugacity and activity coefficient of species at equilibrium were unity. Henry law constant for physical solubility and equilibrium constants for all possible equilibrium reactions were described as follows:

$$pCO_2 = H_{CO_2}[CO_2] \tag{3.19}$$

$$K_1 = [H_3O^+][OH^-\ ] \tag{3.20}$$

$$K_2 = \frac{[R'NHR''NH_2COO^-][H_3O^+\ ]}{[R'NHR''NH_2][CO_2]} \tag{3.21}$$

$$K_3 = \frac{[R'NCOO^-R''NH_2][H_3O^+\ ]}{[R'NHR''NH_2][CO_2]} \tag{3.22}$$

$$K_4 = \frac{[R'NCOO^-R''NHCOO^-]^2[H_3O^+]}{[R'NHR''NH_2COO^-][R'NCOO^-R''NH_2][CO_2]^2} \tag{3.23}$$

$$K_5 = \frac{[RNHR'][HCO_3^-]}{[RNCOO^-R']} \tag{3.24}$$

$$K_6 = \frac{[HCO_3^-][H_3O^+]}{[CO_2]} \tag{3.25}$$

$$K_7 = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} \tag{3.26}$$

$$K_8 = \frac{[RNHR'][H_3O^+]}{[[RNHR']H^+]} \tag{3.27}$$

$$K_9 = \frac{[R'NHR''NH_2][H_3O^+]}{[[R'NHR''NH_2]H^+]} \tag{3.28}$$

$$K_{10} = \frac{\left[[R'NHR"NH_2]H^+\right][H_3O^+]}{[[R'NHR"NH_2]H_2^{++}]} \tag{3.29}$$

$$K_{11} = \frac{[R'NHR"NH_2COO^-][H_3O^+]}{[[\ R'NHR"NH_2COO^-]H^+]} \tag{3.30}$$

$$K_{12} = \frac{[R'NCOO^-R"NH_2][H_3O^+]}{[[R'NCOO^-R"NH_2]H^+]} \tag{3.31}$$

3.3.3 Mass balance, charge balance and CO$_2$ balance

It was assumed that amine loss was negligible within the condition used for this study so total amount of amines were conserved into the system and mass balance equation can be written as Eq. (3.32a) and Eq. (3.32b). Total charge was also consumed and a charge balance equation was given in Eq. (3.33).

Equation for mass balance of amines:

Total EAE mass balance:

$$[RNHR']_{total} = [RNHR']_{eqlm} + \left[[RNHR']H^+\right]_{eqlm} + [RNCOO^-R']_{eqlm} \tag{3.32 a}$$

Total AEEA mass balance:

$$[R'NHR"NH_2]_{total} = [R'NHR"NH_2]_{eqlm} + \left[[R'NHR"NH_2]H^+\right]_{eqlm} + \left[[R'NHR"NH_2]H_2^{++}\right]_{eqlm} + [R'NHR"NH_2COO^-]_{eqlm} + [R'NCOO^-R"NH_2]_{eqlm} + [R'NCOO^-R"NHCOO^-]_{eqlm} + \left[[\ R'NHR"NHCOO^-]H^+\right]_{eqlm} + \left[[R'NCOO^-R"NH_2]H^+\right]_{eqlm} \tag{3.32 b}$$

Total charge balance:

$$\left[[RNHR']H^+\right]_{eqlm} + [H_3O^+] + \left[[R'NHR"NH_2]H^+\right]_{eqlm} + 2\left[[R'NHR"NH_2]H_2^{++}\right]_{eqlm} = [HCO_3^-]_{eqlm} + 2[CO_3^{2-}]_{eqlm} + [OH^-] + [RNCOO^-R']_{eqlm} + [R'NHR"NHCOO^-]_{eqlm} + [R'NCOO^-R"NH_2]_{eqlm} + 2[R'NCOO^-R"NHCOO^-]_{eqlm} \tag{3.33}$$

Total CO$_2$ in the liquid phase was balanced by Eq. (3.34)

Total CO_2 balance:

$$\alpha.\left[[RNHR'] + [R'NHR"NH_2]\right]_{total} = [HCO_3^-]_{eqlm} + [CO_3^{2-}]_{eqlm} + [CO_2] + [RNCOO^-R']_{eqlm} + [R'NHR"NHCOO^-]_{eqlm} + [R'NCOO^-R"NH_2]_{eqlm} + [R'NCOO^-R"NHCOO^-]_{eqlm} \quad (3.34)$$

Where α is the CO_2 loading in (mol CO_2/mol amine) and $[\text{species}]_{eqlm}$ denoted concentration of that species in mol/L at the equilibrium.

Equilibrium CO_2 solubility was calculated by following equation:

$$\alpha = \frac{[HCO_3^-]_{eqlm} + [CO_3^{2-}]_{eqlm} + [CO_2] + [RNCOO^-R']_{eqlm} + [R'NHR"NHCOO^-]_{eqlm} + [R'NCOO^-R"NH_2]_{eqlm} + [R'NCOO^-R"NHCOO^-]_{eqlm}}{\left[[RNHR'] + [R'NHR"NH_2]\right]_{total}} \quad (3.35)$$

3.4 RESULTS AND DISCUSSIONS

3.4.1 Experimental set-up validation

Experimental set-up validation for absorption was discussed in the section 2.4.1 of chapter 2. CO_2 loaded MEA solution was used for desorption. Cyclic CO_2 solubility was calculated and compared with Gao et al. (2017 B). Average absolute deviation % for cyclic solubility was found to be 6.30 %.

3.4.2 Equilibrium CO_2 solubility

Effect of different operating parameters (i.e. weight fraction of AEEA (w_{AEEA}) in the blend, total concentration (C_T) of blend, partial pressure of CO_2 (p_{CO_2}) and temperature (T)) on the equilibrium CO_2 solubility of aqueous EAE and AEEA blend was studied. The results were shown in Table 3.2.

Table 3.2. Equilibrium CO_2 solubility data of aqueous EAE and AEEA blend at atmospheric pressure

T (K)	p_{CO_2} (kPa)	w_{AEEA}	C_T (wt %)	α experimental (mol CO_2/mol amine)	α calculated [a] (mol CO_2/mol amine)
298.15	20.27	0.10	10	0.974	0.972
298.15	20.27	0.20	10	1.003	1.002
298.15	20.27	0.30	10	1.033	1.032
298.15	20.27	0.10	20	0.895	0.906
298.15	20.27	0.20	20	0.922	0.935
298.15	20.27	0.30	20	0.954	0.965
298.15	15.20	0.30	10	1.006	1.006
303.15	15.20	0.30	10	0.993	0.993
303.15	15.20	0.30	15	0.966	0.965
303.15	15.20	0.30	20	0.925	0.926
303.15	15.20	0.30	25	0.878	0.877
303.15	15.20	0.30	30	0.820	0.818
313.15	15.20	0.30	10	0.922	0.926
313.15	15.20	0.30	15	0.894	0.897
313.15	15.20	0.30	20	0.855	0.859
313.15	15.20	0.30	25	0.814	0.810
313.15	15.20	0.30	30	0.748	0.751
298.15	8.11	0.30	30	0.782	0.78
303.15	8.11	0.30	30	0.770	0.767
308.15	8.11	0.30	30	0.732	0.740
313.15	8.11	0.30	30	0.698	0.700
318.15	8.11	0.30	30	0.648	0.645
323.15	8.11	0.30	30	0.582	0.577
298.15	12.16	0.30	30	0.811	0.811
303.15	12.16	0.30	30	0.796	0.798
308.15	12.16	0.30	30	0.772	0.772

313.15	12.16	0.30	30	0.731	0.731
318.15	12.16	0.30	30	0.678	0.677
323.15	12.16	0.30	30	0.612	0.608
298.15	15.20	0.30	30	0.831	0.831
308.15	15.20	0.30	30	0.792	0.792
318.15	15.20	0.30	30	0.694	0.697
323.15	15.20	0.30	30	0.629	0.628
298.15	20.27	0.30	30	0.860	0.857
303.15	20.27	0.30	30	0.842	0.845
308.15	20.27	0.30	30	0.821	0.818
313.15	20.27	0.30	30	0.773	0.777
318.15	20.27	0.30	30	0.734	0.723
323.15	20.27	0.30	30	0.663	0.654

[a] calculated by empirical model Eq. 3.40.

In order to study the effect of addition of AEEA in EAE for CO_2 absorption, different proportion of 0.10, 0.20, and 0.30 weight fraction of AEEA in EAE and AEEA amine blend was mixed keeping constant total concentrations of aqueous amine at 10 wt. % and 20 wt. %, at 298.15 K temperature and 20.27 kPa partial pressure of CO_2. From Figure 3.2 it could be seen that CO_2 solubility was increased with increasing AEEA weight fraction from 0.10 to 0.30. This phenomenon was occurred due to high CO_2 loading capacity of AEEA in comparison to EAE.

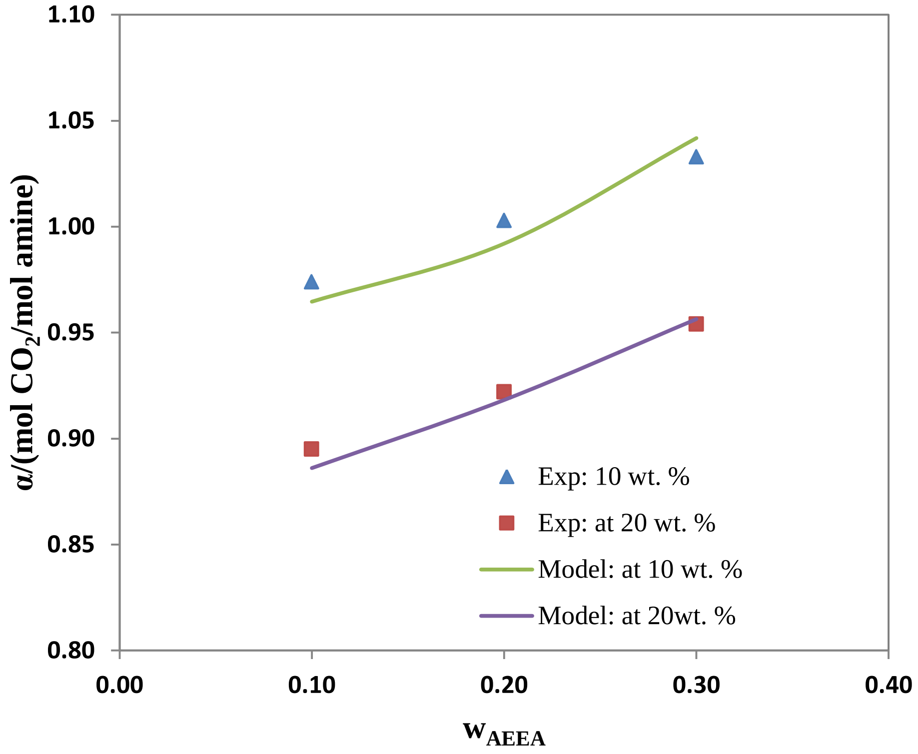

Figure 3.2. Effect of AEEA weight fraction (w_{AEEA}) on the CO_2 solubility at constant 298.15 K temperature and constant 20.27 kPa partial pressure of CO_2 gas for aqueous EAE and AEEA blend: Experimental (Exp.) and model (Eq. 3.35) predicted data.

Total concentration of aqueous amine blend (C_T) was studied in the range of 10 to 30 wt. % of aqueous amine blend in the interval of 5 wt. %. Temperature, partial pressure of CO_2, and weight fraction of AEEA were kept constant at 303.15 K (or 313.15 K), 15.20 kPa, and 0.30, respectively. Variation of CO_2 solubility and absorption capacity with respect to total concentration was shown in Figure 3.3. Increase in amount of amine in mixture results in decrease in CO_2 loading. This might be due to decrease in extent of hydrolysis of carbamate produced by EAE at higher concentration. According to the Le Chatelier's principle, when the amine weight % (concentration) is increased, more amine molecules are available for reaction. Therefore, total amount of CO_2 absorbed in the aqueous blend increased and results in increase in absorption capacity (in the term of mol of CO_2/L solution) of solution. However, the shift of equilibrium could not eliminate the influence brought about by the change in amine blend concentration. So, total amount of CO_2 captured by per mol of amine blend decreased. Similar trend of CO_2 absorption in N-methyl-4-piperindinol (MPDL) solution was reported in literature (Xiao et al., 2017).

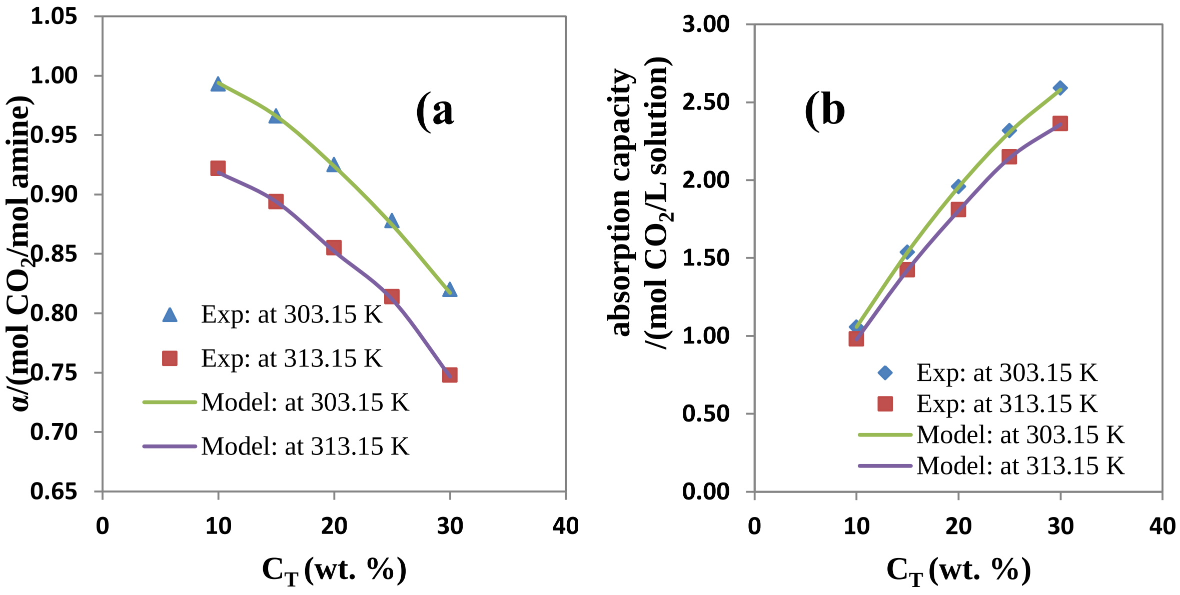

Figure 3.3. Effect of total concentration (C_T) of the aqueous EAE and AEEA blend with 0.30 w_{AEEA} and at 15.20 kPa partial pressure of CO_2 on the CO_2 (a) solubility, and (b) absorption capacity: Experimental (Exp.) and model (Eq. 3.35) predicted data.

Effect of partial pressure of CO_2 (p_{CO_2}) on CO_2 solubility was studied in the range of 8.11 kPa to 20.27 kPa for 30 wt. % concentration of solution and weight fraction of AEEA in the blend was constant at 0.30. From Figure 3.4, it could be shown that increasing partial pressure of CO_2 gas increased the solubility of the gas into the absorbent. This might be due to known fact that physical solubility of the gas is directly proportional to the partial pressure of the gas. Therefore, at higher partial pressure more CO_2 was available in the liquid as dissolved form that's why more amounts of carbamates, dicarbamates, bicarbonate, and carbonate had formed and CO_2 solubility increased by increasing partial pressure.

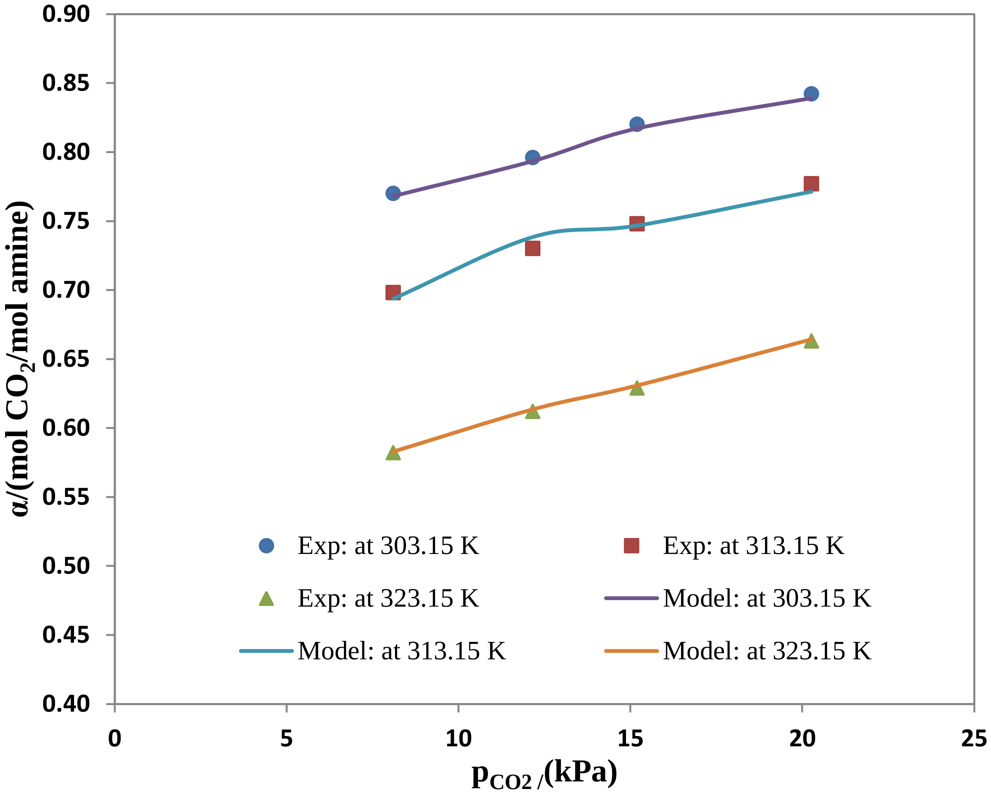

Figure 3.4. Effect of CO_2 partial pressure on the CO_2 solubility for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend: Experimental (Exp.) and model (Eq. 3.35) predicted data.

In order to study the effect of temperature on the CO_2 solubility, experiments were carried out in the range of 298.15 K to 323.15 K. Total concentration of amine blend was kept constant at 30 wt. % with 0.30 weight fraction of AEEA. Increasing temperature affected negatively on the CO_2 loading. That might be due to the reversible exothermic reactions of aqueous amines with CO_2. Therefore, high temperature for CO_2 absorption is not favorable and due to high temperature CO_2 solubility into the aqueous blend decreased. Figure 3.5 depicted the effect of temperature on the CO_2 solubility.

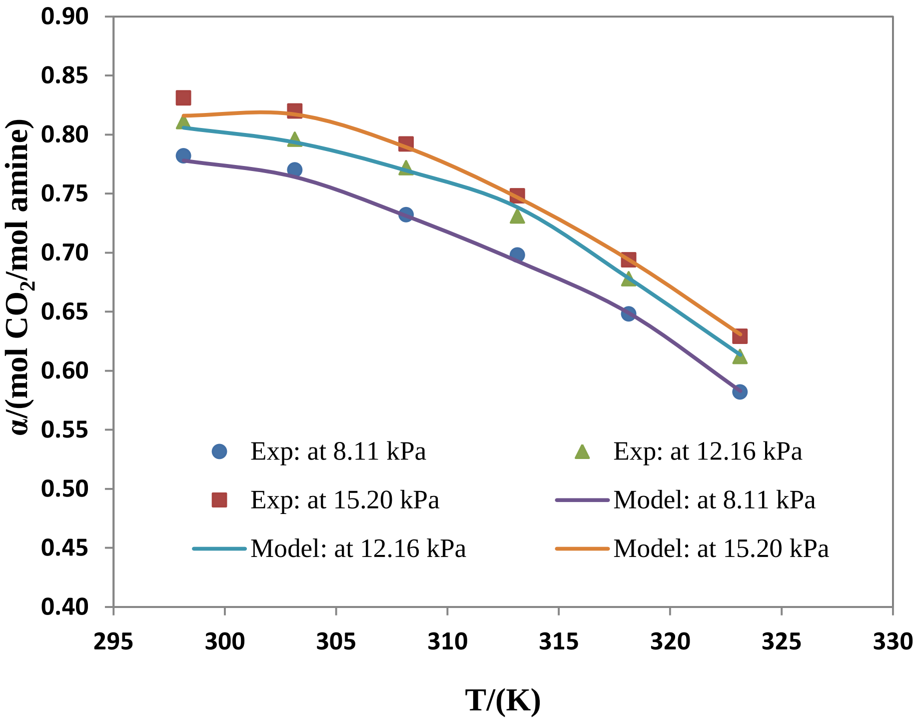

Figure 3.5. Effect of temperature on the CO_2 solubility for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend of constant concentration: Experimental (Exp.) and model (Eq. 3.35) predicted data.

3.4.3 Semi-empirical Kent-Eisenberg thermodynamic model

Experimental equilibrium CO_2 solubility data of aqueous CO_2 with EAE and AEEA blend system were correlated to a semi-empirical model to predict equilibrium CO_2 solubility based on the Kent-Eisenberg model. Henry's law of constant was calculated by Eq. (3.36), given by Hsu et al. (2014).

$$lnH_{CO_2}\left(kPa.\frac{L}{mol}\right) = 20.2669 - \frac{1.38306\times10^4}{T} + \frac{0.06913\times10^8}{T^2} - \frac{0.015589\times10^{11}}{T^3} + \frac{0.012\times10^{13}}{T^4} \tag{3.36}$$

Equilibrium constants K_1, K_6, and K_7 were taken from the literature (Edwards et al., 1978). They defined equilibrium constants in the form of temperature dependency as written by Eq. (3.37):

$$\ln K = a + \frac{b}{T} + c.lnT \tag{3.37}$$

Where, a, b, and c are the coefficient of expression and given in the Table 3.3. T is the temperature in kelvin (K).

Table 3.3. Values of coefficients for temperature dependent equilibrium constants

Parameter	**a**	**b**	**c**	**Temperature validity range (^oC)**	**source**
K_1	140.932	-13445.9	-22.4773	0-225	Edwards et al. (1978)
K_6	235.482	-12092.1	-36.7816	0-225	Edwards et al. (1978)
K_7	220.067	-12431.7	-35.4819	0-225	Edwards et al. (1978)

Kent and Eisenberg (1976) regressed some of equilibrium constant (involved in mainly amines reactions) as function of temperature. In this work, equilibrium constants (K_2, K_3, K_4, K_5, K_8, K_9, K_{10}, K_{11}, and K_{12}) associated with amine species concentration were introduced in the form of exponential function of the temperature, amine (EAE or AEEA) concentration, and partial pressure of CO_2 and given by following Eq. (3.38):

$$\ln K_i = c_1 + \frac{c_2}{T} + c_3 \ln C_{Amine} + \frac{c_4}{C_{Amine}} + c_5 lnp_{CO_2} + \frac{c_6}{p_{CO_2}} \quad \text{(i = 2-5, and 8-12)} \tag{3.38}$$

Where, K_i was equilibrium constant, and c_1 to c_6 are coefficients of Eq. (3.38). Values of c_1 to c_6 were different for different values of K_i , C_{Amine} is the concentration of EAE or AEEA in mol/L. T was the temperature in Kelvin and p_{CO_2} was the partial pressure of CO_2 in kPa. In the equilibrium constant expression where species formed by EAE were associated there EAE initial concentration was used as C_{Amine} and where species formed by AEEA were associated there AEEA initial concentration was used as C_{Amine}.

Objective function (O.F.) = $|\ \alpha_{exp} - \alpha_{calc}\ |$ was minimized using H_{CO_2} , K_1, K_6, K_7, EAE mass balance, AEEA mass balance, total charge balance and for only positive numerical values of species concentration. Equilibrium concentration of formed species were found out by least square method of multiple regression using Microsoft excel solver. The equilibrium constants K_2, K_3, K_4, K_5, K_8, K_9, K_{10}, K_{11}, and K_{12} were calculated by substituting those values of species concentration in Eqs. (3.21-3.24, 3.27-3.31), and regressed in the form of Eq. (3.38). Regressed coefficients of Eq. (3.38) were given in the Table 3.4.

Table 3.4. Regressed coefficients of Eq. (3.38) for estimated reaction equilibrium constants

Parameter	c_1	c_2	c_3	c_4	c_5	c_6
K_2	0.20662	0.19980	1.36339	0.08214	-4.15456	0.85901
K_3	0.47556	0.29765	1.18565	0.07865	-3.65155	0.92355
K_4	0.34985	0.65686	0.97555	0.07865	-9.28613	0.45562
K_5	-2.11802	946.61045	-0.04964	-1.38744	0.37856	3.23808
K_8	-20.56149	-1319.49637	0.43537	0.84106	-0.46521	4.75432
K_9	0.24899	-2.46323	0.23656	0.00786	-11.26782	-6.21235
K_{10}	-5.19691	-1211.03489	-0.04930	-3.01037	0.11439	2.72123
K_{11}	-11.48260	-2111.69646	-0.04867	-6.26037	-0.40489	1.55271
K_{12}	-12.03644	-532.69646	-0.67580	-6.26037	-0.63457	1.34721

There was total 16 possible species into the system at the equilibrium including $[RNHR']_{eqlm}$, $\left[[RNHR']H^{+}\right]_{eqlm}$, $[R'NHR"NH_2]_{eqlm}$, $\left[[R'NHR"NH_2]H^{+}\right]_{eqlm}$, $\left[[R'NHR"NH_2]H_2^{++}\right]_{eqlm}$, $[RNCOO^{-}R']_{eqlm}$, $[R'NHR"NHCOO^{-}]_{eqlm}$, $[CO_2]$, $[R'NCOO^{-}R"NH_2]_{eqlm}$, $[R'NCOO^{-}R"NHCOO^{-}]_{eqlm}$, $[H_3O^{+}]$, $[HCO_3^{-}]_{eqlm}$, $[CO_3^{2-}]_{eqlm}$, $[OH^{-}]$, $\left[[\,R'NHR"NHCOO^{-}]H^{+}\right]_{eqlm}$, and $\left[[R'NCOO^{-}R"NH_2]H^{+}\right]_{eqlm}$.

Equilibrium CO_2 solubility was calculated by solving simultaneously 16 Eqs. of H_{CO_2} , K_1, K_2, K_3, K_4, K_5, K_6, K_7, K_8, K_9, K_{10}, K_{11}, K_{12}, EAE mass balance, AEEA mass balance, and total charge balance. Predicted values of equilibrium CO_2 solubility by Eq. (3.35) were depicted in Figures. (3.2 to 3.5). Average absolute deviation (AAD) % between experimental data and model predicted data was calculated by Eq. (3.39) and reported as 2.56 %.

$$\% \text{ AAD} = \frac{100}{n} \times \sum_{i=1}^{n} \frac{|\alpha exp - \alpha cal|}{\alpha exp} \qquad (3.39)$$

Where, α_{exp}, $\alpha_{cal,}$ and n are experimental CO_2 solubility, calculated CO_2 solubility, and number of data point, respectively.

3.4.4 Empirical model for equilibrium CO_2 solubility into aqueous EAE + AEEA blend

An empirical model was also developed to predict the equilibrium CO_2 solubility into aqueous EAE and AEEA blend. This model was valid in temperature (T) range 298.15 K to 323.15 K (25 to 50 ^{o}C), partial pressure of CO_2 (p_{CO_2}) in the range of 8.11 kPa to 20.27 kPa, weight fraction of AEEA (w_{AEEA}) in the blend was 0.10 to 0.30, and total concentration of aqueous amine blend (C_T) in the range of 10 to 30 wt. % of amine blend. Temperature was used in ^{o}C unit in the model equation. The variation of CO_2 solubility with different operating parameters (t, p_{CO_2} , w_{AEEA} , and C_T) was followed second order polynomial trend line. It was shown in Figure A2 to Figure A5 and given in Appendix-A. It was assumed that CO_2 solubility would follow second order polynomial equation after combining all the operating parameter simultaneously and would be function of t, p_{CO_2} , w_{AEEA} , and C_T . The model equation was presented by following Eq. (3.40):

$$\alpha = c_1 + c_2 t + c_3 t^2 + c_4 p_{CO_2} + c_5 p_{CO_2}^2 + c_6 w_{AEEA} + c_7 w_{AEEA}^2 + c_8 C_T + c_9 C_T^2 \qquad (3.40)$$

Where, c_1 to c_9 are the coefficients of the equation. t, p_{CO_2} , w_{AEEA} and C_T are temperature (^oC), partial pressure of CO_2 (kPa), weight fraction of AEEA, and total concentration of amine blend (weight %), respectively. Coefficients of equation were found out by non-linear multiple regressions using Microsoft excel and listed in Table 3.5.

Table 3.5. Values of coefficients of model (Eq. 3.40) to calculate equilibrium CO_2 solubility of the aqueous EAE and AEEA blend

c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9
0.6669	0.01274	-0.0003	0.01114	-0.0002	0.29819	0.000016	-0.0005	-0.0002

Predicted CO_2 solubility data were best fitted to experimental CO_2 solubility data. Parity plot between experimental and calculated CO_2 solubility was given in Figure 3.6 AAD % for this empirical model was reported as 0.45 %.

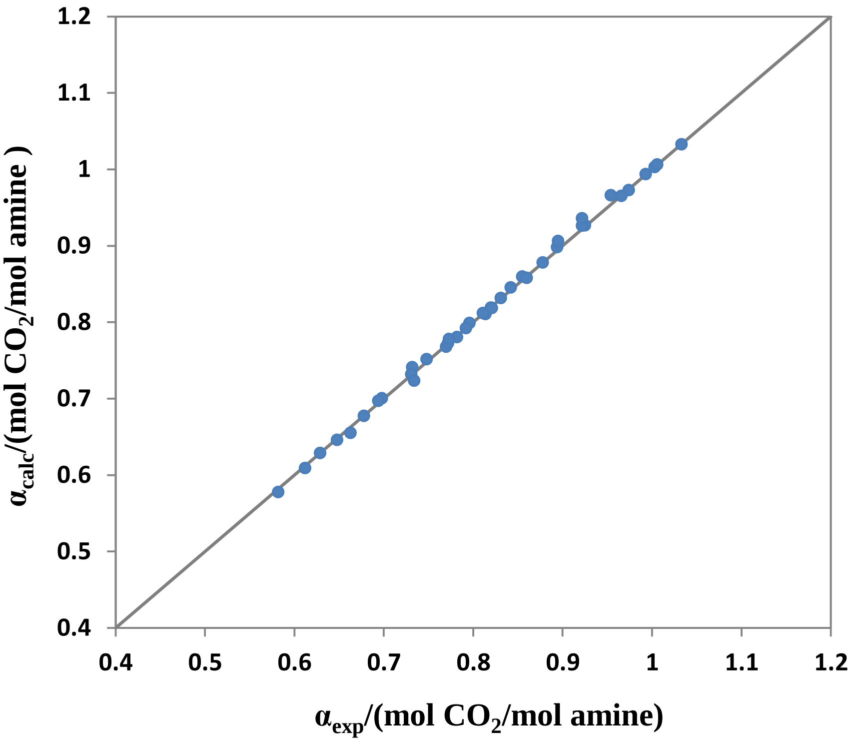

Figure 3.6. Parity plot of experimental and calculated (by Eq. 3.40) CO_2 solubility for the aqueous EAE and AEEA blend.

3.4.5 Heat of CO_2 absorption (ΔH_{abs})

The ΔH_{abs} is the heat generated during CO_2 absorption into the aqueous amine. Higher amount of heat of absorption employed higher heat of regeneration of absorbent. In the present work, experimental CO_2 solubility data of aqueous EAE and AEEA blend given in Table 3.2 was used to determine heat of absorption by Gibbs-Helmholtz equation (Kim and Svendsen, 2007). Figure 3.7 showed, plot of ln(p_{CO_2}) vs. (1/T) for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend, that was plotted using three points of T and p_{CO_2} at similar CO_2 solubility nearly 0.73 (mol CO_2/mol amine) and 0.77 (mol CO_2/mol amine).

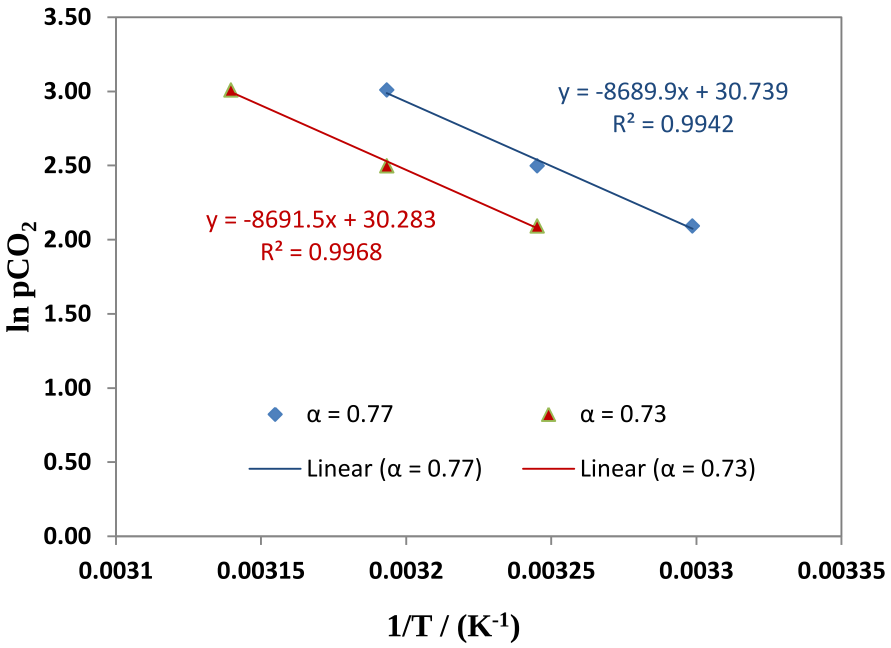

Figure 3.7. Plot of ln(p_{CO_2}) vs. (1/T) for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend.

Slope of the curves of ln(p_{CO_2}) vs. (1/T) were -8689.9 and -8691.5 for CO_2 solubility 0.73 and 0.77 (mol CO_2/mol amine), respectively. ΔH_{abs} was calculated by multiplying R (8.1314 J/mol.K) into the average value of slopes. Heat of CO_2 absorption for aqueous (21wt.% + 9 wt.%) EAE+AEEA blend was -72.2 kJ/mol. Negative values of ΔH_{abs} show that CO_2 absorption into the aqueous EAE and AEEA blend is an exothermic reaction. It is higher than tertiary amines (MDEA; -54.6 kJ/mol) (Xiao et al., 2017), but lower than industrially used benchmark primary amine (MEA; -85.13 kJ/mol) (El Hadri et al., 2017). It could be explained by stability of carbamate and bicarbonate produced by EAE. Heat of formation of carbamate and dicarbamate by AEEA also affect the overall ΔH_{abs} of aqueous EAE+AEEA blend. Because of steric hindrance of ethyl group of EAE, stability of carbamate produced by EAE was reduced and formation of bicarbonate was increased. Bicarbonate formation is an endothermic reaction that's why it consumed some amount of heat that was generated due to the CO_2 absorption and results in lower ΔH_{abs} than MEA. However, carbamate and dicarbamate formation by AEEA was exothermic reaction that increased ΔH_{abs} than MDEA.

3.4.6 CO_2 desorption study

Cyclic CO_2 solubility or cyclic capacity of absorbent is an important factor for selection of absorbent for industrial use purpose to capture CO_2. In order to investigate cyclic capacity of aqueous EAE and AEEA blend, desorption experiment was performed. CO_2 saturated samples at 15.2 kPa of CO_2 partial pressure and 313.15 K temperature of absorption experiment used for desorption study at 393.15 K temperature. Figure 3.7 showed that variation of CO_2 solubility with time for 30 wt. % EAE and AEEA (21 wt. % EAE + 9 wt. % AEEA) solution and 30 wt. % MEA solution. Slope of curve for EAE and AEEA blend was greater than slope of curve of 30 wt. % MEA solution initially. Figure 3.8 depicted cyclic solubility and cyclic capacity of 30 wt. % MEA and aqueous EAE and AEEA blend from 10 to 30 wt. %. The blend of EAE and AEEA had 48.18 % more cyclic capacity than 30 wt. % MEA. It indicates that 30 wt. % EAE and AEEA solution would be required smaller equipment size and smaller absorbent circulation rate in CO_2 capture unit in the plant.

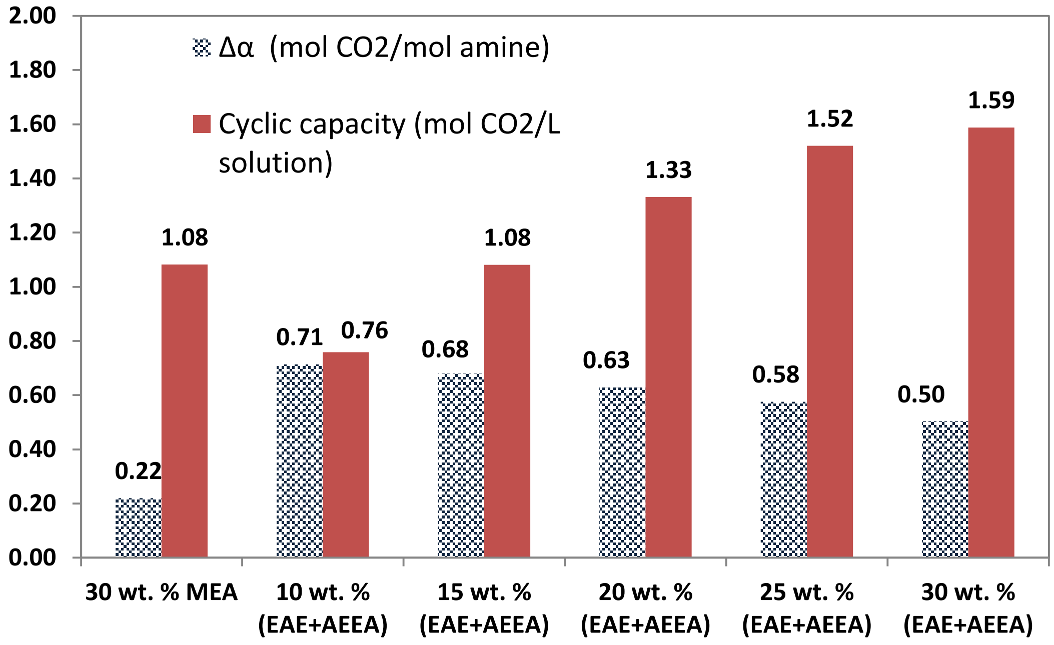

Figure 3.8. Cyclic CO_2 solubility and cyclic absorption capacity of 30 wt.% MEA solution and aqueous EAE and AEEA blend with 0.30 w_{AEEA}.

3.4.7 Rate of change of initial CO_2 solubility

The rate of change of initial CO_2 solubility into the 30 wt. % aqueous EAE and AEEA blend with 0.30 weight fraction of AEEA and 30 wt. % MEA was studied. It was investigated using CO_2 solubility with respect to time data for absorption and desorption. From CO_2 solubility (mol CO_2/mol amine) vs. time (min) graph, shown in Figure 3.9, it could be seen that initially CO_2 solubility varied linearly for absorption as well as desorption of CO_2. Initial variation of CO_2 solubility with respect to time was found by determining slope of the linear portion of curve and mathematically can be written as Eqs. (3.41 and 3.42).

$$Rate\ of\ change\ of\ initial\ CO_2 solubility = \frac{d\alpha}{dt} \tag{3.41}$$

$$\frac{d\alpha}{dt} = (slope\ of\ linear\ portion\ of\ \alpha\ vs.time\ curve) \tag{3.42}$$

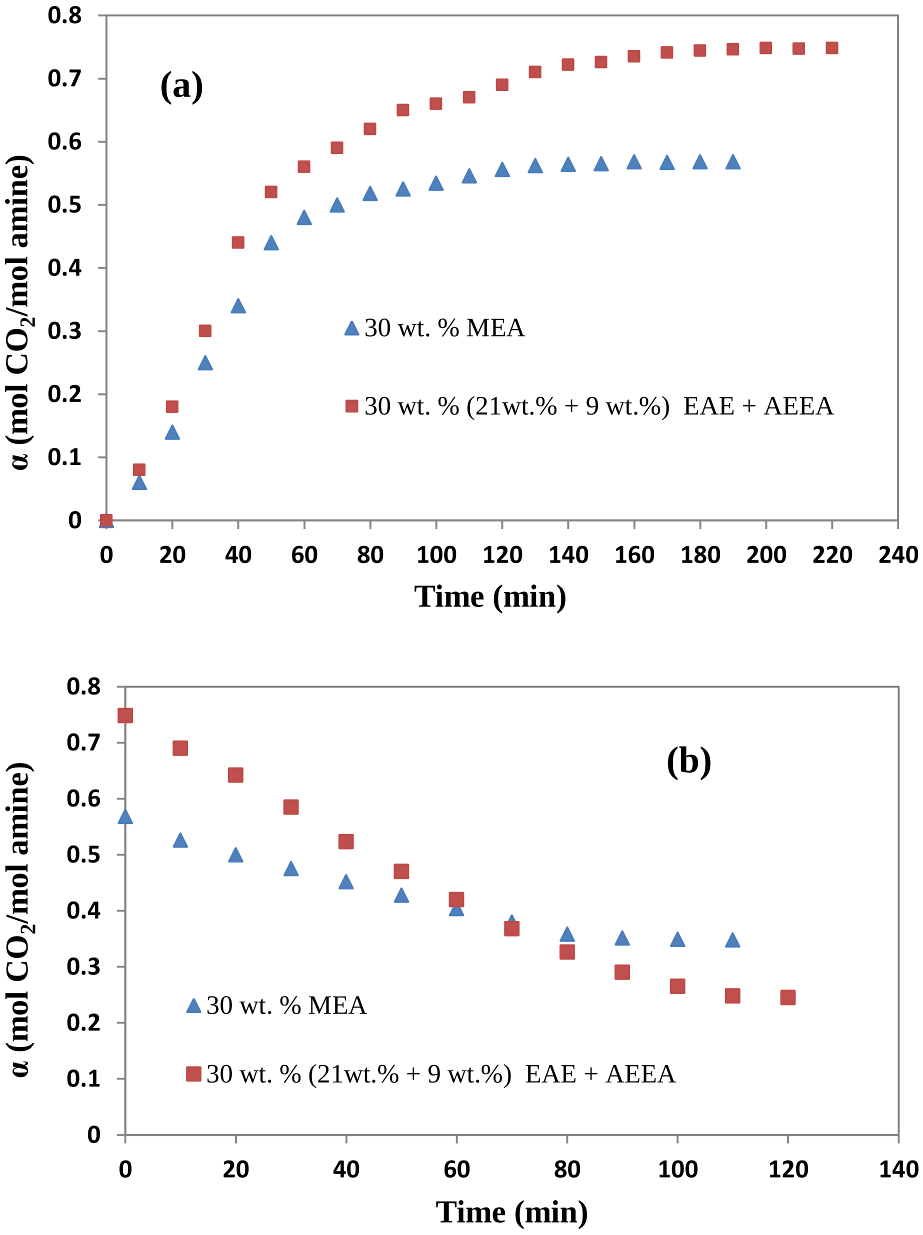

Figure 3.9. CO_2 solubility vs. time plot of 30 wt. % MEA and 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend during (a) CO_2 absorption, and (b) CO_2 desorption.

Slope of linear portion of CO_2 solubility vs. time (t) curve could be seen in Figure A6 of the Appendix-A. Initial change of CO_2 solubility during absorption in 30 weight % (21wt. % + 9 wt. %) aqueous EAE and AEEA was 21.1 % more than in MEA solution. It could be interpreted that faster reaction kinetics of CO_2 and EAE and AEEA blend than MEA. However, this method was not useful to find out actual rate of reaction but relative measurement of consumption of CO_2 into absorbents could be done. Negative slope of linear portion of CO_2 solubility vs. time curve in Figure A7 indicated that initial decrease in CO_2 solubility with respect to time. Dissociation of CO_2 was more rapid in EAE and AEEA blend as compared to MEA. Rate of change of CO_2 solubility during desorption in 30 wt. % aqueous EAE and AEEA was almost double of MEA solution. It might be due to the presence of bicarbonate, carbonate, and secondary carbamate mainly in CO_2 saturated EAE and AEEA solution. Those were less thermally stable than primary carbamate present in CO_2 saturated MEA solution and aqueous EAE and AEEA blend can be regenerated easily than MEA solution.

3.5 CONCLUSIONS

In this research paper, performance of aqueous EAE and AEEA blend was investigated for post-combustion CO_2 capture at atmospheric pressure. Equilibrium CO_2 solubility into the blend of EAE and AEEA solution was found out varying different composition and operating conditions. Highest CO_2 solubility was occurred at 298.15 K, 20.27 kPa CO_2 partial pressure, 0.30 weight fraction of AEEA, and 10 wt. % concentrations of aqueous EAE and AEEA blend. A semi-empirical model, based on the Kent-Eisenberg thermodynamic concept with newly introduced equilibrium constant function and an empirical model were developed to correlate CO_2 solubility (mol CO_2/mol amine) in the range of studied operating conditions. Semi-empirical model and empirical model predicted data were in good agreement with experimental solubility data with 2.56% and 0.45 % AAD, respectively. Result of 30 wt. % EAE and AEEA with 0.30 weight fraction of AEEA solution were compared with 30 weight % MEA solution (benchmark absorbent for CO_2 capture) and concluded as follows:

- At 313.15 K and 15.20 kPa CO_2 partial pressure, 31.69 % more equilibrium CO_2 solubility into EAE and AEEA blend than MEA solution was obtained.
- 15.13 % less heat of CO_2 absorption was found as compared to MEA solution resulting less energy requirement for CO_2 capture.
- Initial rate of change of CO_2 solubility were 21.10 % and 100 % more in EAE and AEEA solution during absorption and desorption of CO_2, respectively.
- Cyclic CO_2 solubility and cyclic capacity of EAE and AEEA solution were much higher than MEA solution.

In overall, it was concluded that EAE and AEEA blend had higher CO_2 solubility, lesser heat of absorption, more cyclic capacity and faster rate of change of initial CO_2 solubility than MEA. Therefore, further research on EAE and AEEA blend related to its physicochemical properties, degradation, corrosion, and kinetics towards reaction with CO_2 should be carried out.

ASSOCIATED CONTENT

Appendix - A

Figure A1 to Figure A7**,** related to this chapter, can be found in the Appendix - A.