Chapter 2

Equilibrium CO_2 solubility in the aqueous mixture of MAE and AEEA: Experimental study and development of modified thermodynamic model

ABSTRACT

In the present study, equilibrium solubility of CO_2 was studied in the aqueous blend of 2-(methylamino)ethanol (MAE) and aminoethylethanolamine (AEEA). Total concentration of blend solution, weight fraction of AEEA in aqueous (MAE+AEEA) blend, temperature, and partial pressure of CO_2 was varied from 10 to 30 wt. %, 0.10 to 0.30, 298.15 to 323.15 K, and 8.11 to 20.67 kPa, respectively. Maximum loading 0.944 mol CO_2/mol amine was occurred at 298.15K, 20.27 kPa of CO_2 partial pressure, 10 weight % total concentration with 0.30 weight fraction AEEA. The Kent-Eisenberg thermodynamic model was modified by incorporating newly introduced correction factor (F_k) to predict CO_2 solubility in the aqueous blend of MAE+AEEA. Experimental data and model predicted data was in good agreement with each other. In addition, heat of CO_2 absorption was also calculated for this amine blend and reported as -73.4 kJ/mol.

2.1 INTRODUCTION

In the Intergovernmental panel on climate change (IPCC) fifth assessment report, it is described that human-induced global warming reached approximately 1 ^{o}C above the pre-industrial level in 2017. It may be reached up to 1.5 ^{o}C between 2030 to 2052 if the rate of increase of global warming will not be reduced (IPCC, 2014). The CO_2 gas is a greenhouse gas that contributes over 60 % of global climate change. CO_2 is emitted into the environment mainly due to the fossil fuel combustion in the thermal power plants. There are several techniques for CO_2 capture from a gas stream. Absorption technique is the most mature and efficient technique to remove CO_2 from a gas stream containing CO_2 at low partial pressure. Amine based post-combustion carbon dioxide capture is most suitable and cost-effective for implementing it in the existing power plants (Wang et al., 2017; Liang et al., 2016; Mondal et al., 2015; Rochelle, 2009; Figueroa et al., 2008; Hezrog et al., 2001). Primary amines are shown lower CO_2 loading in comparison to secondary and tertiary amines. However, primary amines have fast reaction kinetics. The heat of regeneration of CO_2 loaded primary amines is very high. Therefore, in recent years many researchers have shown interest in the use of a blend of aqueous amine such as monoethanolamine (MEA)+methyldiethanolamine (MDEA), MEA + aminoethylethanolamine (AEEA), MEA+MDEA+ 4-Dimethylaminopyridine (DMAP), 2-(amino)methylpropanolamine (AMP)+MDEA, MEA+tertiary amines, diethylethanolamine (DEEA)+ 3-(methylamino)propanolamine (MAPA), benzylamine (BZA)+(MEA), AMP+ diethylenetriamine (DETA), N-methyl-2-pyrrolidone (MPDL)+AMP, DEEA+ ethylinediamine (EDA) (Conway et al., 2015; Moosavi et al., 2017; Hamidi et al., 2018; Shokouhi et a., 2015; Gao et al., 2017B; Knuutila and Nannestad, 2017; Conway et al., 2014; Wai et al., 2018; Karlsson et al., 2020; Kumar et al., 2020) for chemical absorption due to aqueous amine blend solvent has shown many advantages over single amine. The use of blended amine can increase the equilibrium CO_2 solubility of tertiary and sterically hindered amines. It can also reduce degradation, corrosion, and energy requirement for regeneration (Sakwattanapong et al., 2005; Bougie and Iliuta, 2012).

2-(methylamino)ethanol (MAE) is a hindered secondary amine and it has a higher CO_2 absorption capacity than ordinary secondary amines as reported in the literature. It is better than primary amine (MEA) in terms of CO_2 loading, cyclic capacity, and heat of absorption (Mimura et al., 1998; Pacheco et al., 2012; Folgueira et al., 2014). Maneenintr et al. (2018) used the MEA+MAE blend for CO_2 removal from flue gas.

Aminoethylethanolamine (AEEA) is an alkanoldiamine. It contains two nitrogen atoms. One is the primary amine and another one is a secondary amine. AEEA has shown higher CO_2 solubility than MEA due to both primary and secondary amines groups present in it. It has also high cyclic capacity and faster second-order reaction rate constant. Because of its advantageous properties, AEEA was also used by researchers as an activator with some secondary and tertiary amines (Kumar and Mondal et al., 2018; Bajpai and Mondal, 2013; Ma’mum et al., 2007A; Ma’mum et al., 2007B).

Thermodynamic models to predict CO_2 solubility in an aqueous amine solution are very useful to design and optimize a CO_2 capture process (Zhang et al., 2011). There are several models used to calculate theoretically CO_2 solubility in which include, the Kent-Eisenberg model, Deshmukh-Mather model, modified Kent-Eisenberg model, Electrolyte NRTL model, etc. Kent-Eisenberg model (Kent and Eisenberg, 1976) assumed that fugacity and activity coefficients of species formed at the equilibrium are equal to one. Deshmukh and

Mather, (1981) used extended Debey-Huckel expression to calculate activity coefficients and developed a rigorous thermodynamic model that used activity coefficients of species to predict CO_2 solubility in aqueous alkanolamine solutions. Hazi-Sulaiman et al. (1998) proposed a modified Kent Eisenberg model to calculate CO_2 solubility in diethanolamine (DEA) and methyldiethanolamine (MDEA). Gabrielsen et al. (2005) proposed a model to correlate partial pressure of carbon dioxide over aqueous solutions of MEA, DEA, and MDEA. They used an approach to combine the Henry's law constant and chemical reaction constant, where only one chemical equilibrium reaction was taken account and ideal gas and ideal liquid properties was assumed. That model is simple for single amine system but may be very rigorous and also would be modified for the amine blend system, especially for amines containing multi-amino groups. Xiao et al. (2017) described a new thermodynamic model using a correction factor for N-methyl-4-piperidinol solution. This model predicted more accurate results than Kent-Eisenberg model. Liu et al. (2017) developed a new Liu-Helei model to predict CO_2 solubility in 1-diethylamino-2 propanol solvent. Xiao et al. (2019) used semi-empirical model and activity coefficient-based model to predict CO_2 solubility in 1-(2-hydoxymethyl)-piperidine solution and reported that activity coefficient model showed better results.

Regeneration cost penalty of CO_2 loaded amines is a drawback of the chemical absorption technique. Total heat of regeneration can be summed as the heat of reaction, heat of vaporization and sensible heat. Higher heat of absorption may because of more regeneration energy and cost (Kim et al., 2014). That's why consideration of heat of reaction of solvent for absorption may be useful in solvent selection.

In the literature, CO_2 solubility data for aqueous blend of MAE+AEEA has not been studied yet. Aim of this chapter was to find out CO_2 loading at various operating conditions for post-combustion CO_2 capture using aqueous MAE+AEEA blend. A new modified Kent-Eisenberg mathematical model was developed to predict the CO_2 loading in aqueous MAE+AEEA. The deviation between experimental data and calculated values was measured. The heat of absorption was calculated using the modified Gibbs – Helmholtz equation as well.

2.2 EXPERIMENTAL SECTION

2.2.1 Materials

The 2-(methylamino) ethanol (MAE) (98 % pure) was purchased from Sigma Aldrich, St. Louis USA. Monoethylethanolamine (MEA) (98%) and aminoehtylethanolamine (AEEA) (98 % pure) were purchased from Sd Fine chemical limited, Mumbai, India. All chemicals were used without further purification. Double distilled water was used to prepare aqueous mixtures. Description of all chemicals which were used in the experimentation are given in Table 2.1. CO_2 gas (99.99% pure) and N_2 gas (99.99 % pure) purchased from Linde India Ltd. were used to prepare simulated gas for absorption study. Throughout the experiments, the volume of samples was measured by micropipette.

Table 2.1. Chemical sample information

Chemical Name	CAS number	Source	Initial purity	Purification method
MEA[a]	141-43-5	sd Fine chemical limited, Mumbai, India	98 %[e]	none
MAE[b]	109-83-1	Sigma Aldrich, St. Louis, USA	≥ 98 %[e]	none

AEEA[c]	111-41-1	sd Fine chemical limited, Mumbai, India	98 %[e]	none
HCl[d]	7647-01-0	sd Fine chemical limited, Mumbai, India	35-38 %e	none
Water	7732-18-5	Our laboratory	99.9 %[e]	Double distillation

[a]Monoethanolamine, [b]2-(methylamino) ethanol, [c]aminoehtylethanolamine. [d]Hydrochloric acid and [e]Mass fraction.

2.2.2 Solution preparation method

To validate our absorption experimental setup and to compare the performance of the new amine blend 30 weight % MEA solution was prepared. The density of liquids was measured using Anton Paar density meter (DMA 35 with 0.001 g/cm^3 accuracy in density). Density data was used to convert volume into the mass. All the aqueous amine solutions were prepared using corresponding amines and double-distilled water. The total concentration (C_T) of aqueous MAE+AEEA blend was varied from 10 wt. % to 30 wt. % at the interval of 5 wt. %. The weight fraction of AEEA (w_{AEEA}) in the MAE+AEEA blend was varied as 0.10, 0.20 and 0.30.

2.2.3 CO_2 absorption experiment

Experimental set up for CO_2 absorption and initial CO_2 loading rate study was shown in Figure 2.1. Simulated gas mixtures containing 8-20 volume % CO_2 and rest N_2 gas were prepared using pure CO_2 and pure N_2 gas in the gas mixing chamber. Mass flow controllers (Alicat Scientific – model no. MC-500 SCCM-D) was used to control the flow of gases.

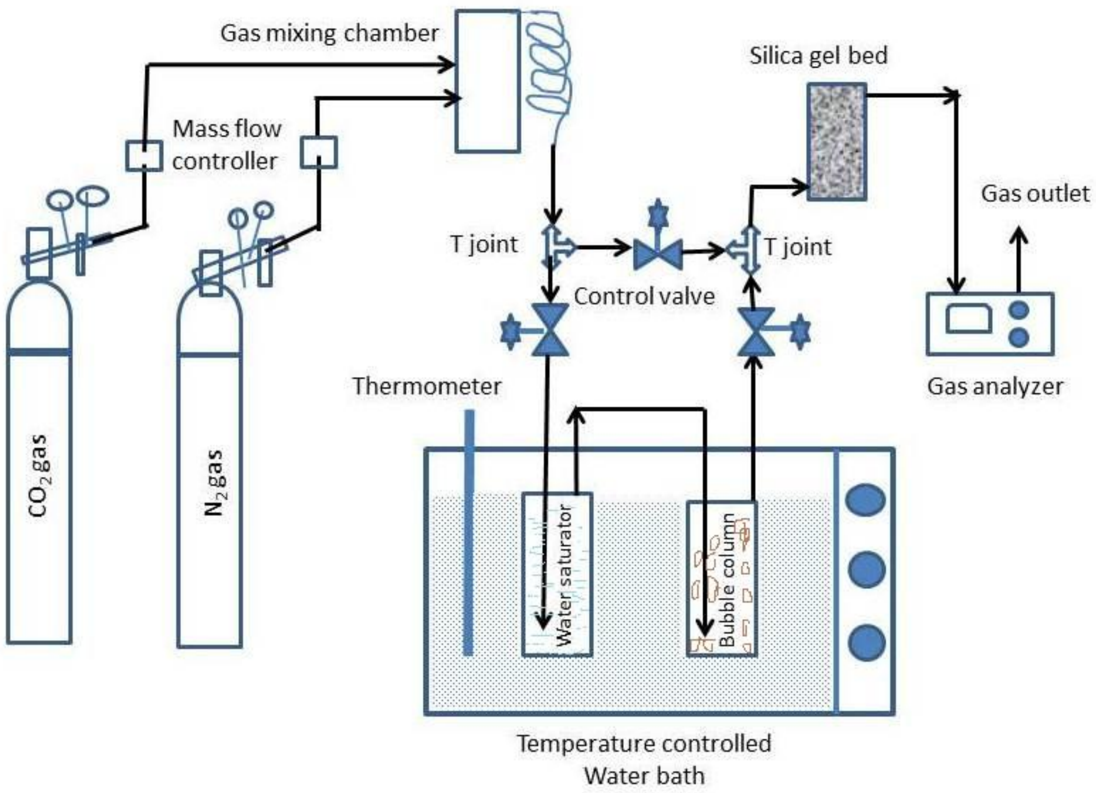


Figure 2.1. Schematic diagram of experimental set up for absorption.

A total flow rate of the mixed gas stream was kept constant at 240 ml/min. The temperature of the reaction medium was maintained at the desired temperature by using a water bath (with temperature accuracy ± 1 K). The CO_2 gas concentration (in volume %) was measured with a portable IR CO_2 gas analyzer (Gasboard-3800P; CO_2 range, 0-100% by volume). The absorption process was taking place in a bubble column of 150 ml volume capacity. Initially, 120 ml of absorbent was filed in the bubble column and the mixed gas stream of desired CO_2 partial pressure at inlet condition was passed into this through water saturator cell. Absorption with chemical reaction process started after first bubble formation. CO_2 concentration at the outlet of bubble column was measured periodically at 10 min time intervals. CO_2 loading was calculated using Chittick Apparatus

(Horwitz, 1975). In which 2 ml CO_2 loaded sample was titrated with 1M HCl using methyl orange indicator. The volume of gas liberated during titration was collected in the burette and loading was calculated by the volumetric method by Eq. (2.1) (Gao et al., 2017B). Absorption capacity of the solution was defined by Eq. (2.2).

$$\alpha\ (\mathrm{mol\ CO_2/mol\ amine}) = \frac{V_{CO_2}}{22.4 \times C_{amine} \times V_{CO2\ loaded\ sample}} \times \frac{273.15}{273.15+t} \qquad (2.1)$$

$$\text{Absorption capacity (mol } CO_2\text{/L solution)} = \alpha .\ C_{amine} \qquad (2.2)$$

Where, α is CO_2 loading, 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 loaded amine sample (L), and room temperature (^oC), respectively. When outlet concentration of CO_2 reached to inlet CO_2 concentration, saturation attended and at that point final value of equilibrium CO_2 loading declared. Loading calculation was repeated three times and average value was reported.

2.3 MODIFIED KENT-EISENBERG MODEL FOR MAE+AEEA+H_2O+CO_2 SYSTEM

2.3.1 Reaction mechanism

The absorption of CO_2 into the MAE+AEEA+H_2O blend was occurred due to the physical solubility of CO_2 into the H_2O followed by various chemical reactions of CO_2 with MAE+AEEA+H_2O system. MEA ($CH_3NHCH_2CH_2OH$) 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 $–CH_3$, $–CH_2CH_2OH$, and $–CH_2CH_2–$, respectively. Following set of equilibrium relationship was possible.

$$CO_2(g) \overset{H_{CO_2}}{\longleftrightarrow} CO_2(l) \qquad (2.3)$$

Dissociation of water:

$$2H_2O \overset{K_1}{\leftrightarrow} H_3O^+ + OH^- \tag{2.4}$$

Carbamate formation:

$$R'NHR"NH_2 + CO_2(l) + H_2O \overset{K_2}{\leftrightarrow} R'NHR"NH_2COO^- + H_3O^+ \tag{2.5}$$

$$R'NHR"NH_2 + CO_2(l) + H_2O \overset{K_3}{\leftrightarrow} R'NCOO^-R"NH_2 + H_3O^+ \tag{2.6}$$

Dicarbamate formation:

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

$$2H_2O \overset{K_4}{\leftrightarrow} 2(R'NCOO^-R"NHCOO^-) + 2H_3O^+ \tag{2.7}$$

Hydrolysis of carbamate formed due to MAE:

$$RNCOO^-R' + H_2O \overset{K_5}{\leftrightarrow} RNHR' + HCO_3^- \tag{2.8}$$

Hydrolysis of CO$_2$:

$$CO_2(l) + 2H_2O \overset{K_6}{\leftrightarrow} H_3O^+ + HCO_3^- \tag{2.9}$$

Dissociation of bicarbonate ion:

$$HCO_3^- + H_2O \overset{K_7}{\leftrightarrow} CO_3^{2-} + H_3O^+ \tag{2.10}$$

Dissociation of protonated amines:

$$[RNHR']H^+ + H_2O \overset{K_8}{\leftrightarrow} RNHR' + H_3O^+ \tag{2.11}$$

$$[R'NHR"NH_2]H^+ + H_2O \overset{K_9}{\leftrightarrow} R'NHR"NH_2 + H_3O^+ \tag{2.12}$$

$$[R'NHR"NH_2]H_2^{++} + H_2O \overset{K_{10}}{\leftrightarrow} [R'NHR"NH_2]H^+ + H_3O^+ \tag{2.13}$$

Dissociation of protonated carbamates:

$$[\,R'NHR"NHCOO^-]H^+ + H_2O \overset{K_{11}}{\leftrightarrow} R'NHR"NHCOO^- + H_3O^+ \tag{2.14}$$

$$[R'NCOO^-R"NH_2]H^+ + H_2O \overset{K_{12}}{\leftrightarrow} R'NCOO^-R"NH_2 + H_3O^+ \tag{2.15}$$

2.3.2 Equilibrium constants

Henry law constant for physical solubility and equilibrium constants for all possible equilibrium reactions were described as follows:

$$pCO_2 = H_{CO_2}[CO_2] \tag{2.16}$$

$$K_1 = [H_3O^+][OH^-] \tag{2.17}$$

$$K_2 = \frac{[R'NHR''NH_2COO^-][H_3O^+]}{[R'NHR''NH_2][CO_2]} \tag{2.18}$$

$$K_3 = \frac{[R'NCOO^-R''NH_2][H_3O^+]}{[R'NHR''NH_2][CO_2]} \tag{2.19}$$

$$K_4 = \frac{[R'NCOO^-R''NHCOO^-]^2[H_3O^+]}{[R'NHR''NH_2COO^-][R'NCOO^-R''NH_2][CO_2]^2} \tag{2.20}$$

$$K_5 = \frac{[RNHR'][HCO_3^-]}{[RNCOO^-R']} \tag{2.21}$$

$$K_6 = \frac{[HCO_3^-][H_3O^+]}{[CO_2]} \tag{2.22}$$

$$K_7 = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} \tag{2.23}$$

$$K_8 = \frac{[RNHR'][H_3O^+]}{[[RNHR']H^+]} \tag{2.24}$$

$$K_9 = \frac{[R'NHR''NH_2][H_3O^+]}{[[R'NHR''NH_2]H^+]} \tag{2.25}$$

$$K_{10} = \frac{[[R'NHR''NH_2]H^+][H_3O^+]}{[[R'NHR''NH_2]H_2^{++}]} \tag{2.26}$$

$$K_{11} = \frac{[R'NHR''NH_2COO^-][H_3O^+]}{[[R'NHR''NH_2COO^-]H^+]} \tag{2.27}$$

$$K_{12} = \frac{[R'NCOO^-R''NH_2][H_3O^+]}{[[R'NCOO^-R''NH_2]H^+]} \tag{2.28}$$

Haider et al. (2011) reported the values of equilibrium constants associated with the reactions of MAE-H_2O-CO_2 system. Ma’mun et al. (2006) studied the solubility of CO_2 in 30 mass % aqueous AEEA solution and proposed equilibrium constant values of reactions of AEEA-H_2O-CO_2 system. Both, Haider et al. (2011) and Ma'mun et al. (2006) proposed mostly equilibrium constants in terms of temperature. Model of Ma'mun et al. (2006) is useful in the temperature range 40 – 120 °C. In the MAE+AEEA+H_2O blend and CO_2 reaction system species interactions would be changed in comparison to individual MAE+H_2O+CO_2 and AEEA+H_2O+CO_2 systems. In order to correct the species concentration at the equilibrium due to different interactions of species formed in the MAE+AEEA+H_2O+CO_2 system and to extend the use of equilibrium constants from 25 to 50 °C. Equilibrium constants for this system could be written as Eq. (2.29):

$$K_i = K_i'.F_{k_i} \text{ (i=2,3,….,12)} \tag{2.29}$$

Where, K_i' is the equilibrium constant of corresponding equilibrium reaction occurred in individual aqueous amines and CO_2 reactions and F_{k_i} is the correction factor proposed in this research paper for blended amines and CO_2 reaction system.

In this research paper it was assumed that Henry's law constant and equilibrium constants K_i' were function of temperature. It can be expressed as follows:

$$\ln H_{CO_2} \, (or \ln \, K_i') = a + \frac{b}{T} + c.\,lnT + d.\,T \tag{2.30}$$

a, b, c, and d, are the coefficients of equation. The H_{CO_2}, K_1' , K_2' , K_3', K_4' , K_6' , K_7' , K_9' , K_{10}' , K_{11}' , and K_{12}' coefficients were taken from published literature and listed in Table 2.2. K_5' was obtained by Eq. (2.31), developed correlation by Haider et al. (2011) for MAE

$$\ln \, K_5' = 1.301 - \frac{4.23}{T} + 0.0025\, pCO_2 + 0.0334\, C + 0.00035\, C^2 \tag{2.31}$$

Where, T, pCO_2, and C are the temperature (K), partial pressure of CO_2 (kPa), and concentration of MAE (mol/l), respectively.

Equilibrium constant (K_8') for dissociation of protonated MAE can be written in the form of pKa value of MAE as follows:

$$pK_a = -\log_{10} K'_8 \qquad (2.32)$$

pKa values for MAE with respect to temperature was taken from Little et al. (1990) K'_8 values fitted in the form of Eq. (2.32). Coefficients of equation were found out and reported in Table 2.2

Table 2.2. Values of coefficients for temperature dependency of Henry's law constant and equilibrium constants

parameter	a	b	c	d	Temperature validity range (^oC)	source
H_{CO_2}	155.1699	-8477.711	-21.95743	0.005780748	0-100	Chen et al. (1979)
K'_1	140.932	-13445.9	-22.4773	0	0-225	Edwards et al. (1978)
K'_2	-32.564	8284.4	0	0	40-120	Ma'mun et al. (2006)
K'_3	-2.506	-3585.2	0	0	40-120	Ma'mun et al. (2006)
K'_4	-22.992	4014.1	0	0	40-120	Ma'mun et al. (2006)
K'_6	235.482	-12092.1	-36.7816	0	0-225	Ma'mun et al. (2006)
K'_7	220.067	-12431.7	-35.4819	0	0-225	Edwards et al. (1978)
K'_8	-39.386	0	0	0.0564	20-60	This work
K'_9	-3.0561	-5865.15	0	0	20-60	Ma'mun et al. (2006)
K'_{10}	0.7568	-5074.99	0	0	20-60	Ma'mun et al. (2006)
K'_{11}	-19.951	-292.57	0	0	40-120	Ma'mun et al. (2006)
K'_{12}	27.08	-16921	0	0	40-120	Ma'mun et al. (2006)

Correction factor F_k was defined as follows equations

$$lnF_{k_i} = c_1 + \frac{c_2}{T} + c_3 \ln C_{AEEA} + \frac{c_4}{C_{AEEA}} + c_5 lnp_{CO_2} + \frac{c_6}{p_{CO_2}} \quad \text{(i = 2,3, and 4)} \qquad (2.33\text{ a})$$

$$lnF_{k_i} = c_1 + \frac{c_2}{T} + c_3 \ln C_{MAE} + \frac{c_4}{C_{MAE}} + c_5 lnp_{CO_2} + \frac{c_6}{p_{CO_2}} \quad \text{(i = 5,6, and 7)} \qquad (2.33\text{ b})$$

$$lnF_{k_i} = c_1 + \frac{c_2}{T} + c_3 \ln C_{MAE} + \frac{c_4}{C_{MAE}} + c_5 C_{MAE} \text{ (i = 8)} \tag{2.33 c}$$

$$lnF_{k_i} = c_1 + \frac{c_2}{T} + c_3 \ln C_{AEEA} + \frac{c_4}{C_{AEEA}} + c_5 C_{AEEA} \text{ (i = 9,10,11, and 12)} \tag{2.33 d}$$

Where, c_1 to c_6 are coefficients of Eq. (2.33 a to 2.33 d). Values of c_1 to c_6 are different for different values of F_{k_i}. C_{AEEA} , and C_{MAE} are concentration in weight % of AEEA and MAE, respectively. T is temperature in Kelvin and p_{CO_2} is partial pressure of CO_2 in kPa.

2.3.3 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 Eqs. (2.34 a and 2.34 b). Total charge was also consumed and a charge balance equation was given in Eq. (2.35).

Equation for mass balance of amines:

Total MAE mass balance:

$$[RNHR']_{total} = [RNHR']_{eqlm} + \left[[RNHR']H^+\right]_{eqlm} + [RNCOO^-R']_{eqlm} \tag{2.34 a}$$

Total AEEA mass balance:

$$[R'NHR"NH_2]_{total} = [R'NHR"NH_2]_{eqlm} + \left[[R'NHR"NH_2]H^+\right]_{eqlm} + \left[[R'NHR"NH_2]H_2^{++}\right]_{eqlm} + [R'NHR"NH_2COO^-]_{eqlm} + [R'NCOO^-R"NH_2]_{eqlm} + [R'NCOO^-R"NHCOO^-]_{eqlm} + \left[[R'NHR"NH_2COO^-]H^+\right]_{eqlm} + \left[[R'NCOO^-R"NH_2]H^+\right]_{eqlm} \tag{2.34 b}$$

Total charge balance:

$$\left[[RNHR']H^+\right]_{eqlm} + [H_3O^+] + \left[[R'NHR"NH_2]H^+\right]_{eqlm} + 2\left[[R'NHR"NH_2]H_2^{++}\right]_{eqlm} = [HCO_3^-]_{eqlm} + 2[CO_3^{2-}]_{eqlm} + [OH^-] + [RNCOO^-R']_{eqlm} + [R'NHR"NH_2COO^-]_{eqlm} + [R'NCOO^-R"NH_2]_{eqlm} + 2[R'NCOO^-R"NHCOO^-]_{eqlm} \qquad (2.35)$$

Total CO$_2$ in the liquid phase was balanced by Eq. (2.36)

Total CO$_2$ balance:

$$\alpha.\left[[RNHR'] + [R'NHR"NH_2]\right]_{total} = [HCO_3^-]_{eqlm} + [CO_3^{2-}]_{eqlm} + [CO_2] + [RNCOO^-R']_{eqlm} + [R'NHR"NH_2COO^-]_{eqlm} + [R'NCOO^-R"NH_2]_{eqlm} + [R'NCOO^-R"NHCOO^-]_{eqlm} \qquad (2.36)$$

Where α is the CO$_2$ loading in (mol CO$_2$/mol amine).

CO$_2$ loading was expressed as follows:

$$\alpha = \frac{\begin{matrix}[HCO_3^-]_{eqlm} + [CO_3^{2-}]_{eqlm} + [CO_2] + \\ [RNCOO^-R']_{eqlm} + [R'NHR"NH_2COO^-]_{eqlm} \\ + [R'NCOO^-R"NH_2]_{eqlm} + [R'NCOO^-R"NHCOO^-]_{eqlm}\end{matrix}}{\left[[RNHR'] + [R'NHR"NH_2]\right]_{total}} \qquad (2.37)$$

2.4 RESULTS AND DISCUSSIONS

2.4.1 Experimental set up and procedure validation

In order to validate the suitability of experimental set up, 30 wt. % MEA was used for CO$_2$ absorption at 313.15 K temperature and at 12.16, 15.20, and 20.27 kPa partial pressure of CO$_2$ gas. Equilibrium solubility was obtained and compared with the results obtained in literature (Gao et al., 2017B; Puxty et al., 2009; Chowdhury et al., 2014). A plot of comparison was given in Figure A1 of Appendix-A. Result obtained by this experimental calculation was in good agreement with literature with 2.55 % average absolute deviation (AAD %).

2.4.2 CO_2 loading

2.4.2.1 Effect of fraction of AEEA in the blend

In order to study the effect of addition of AEEA in MAE for CO_2 absorption different proportion of 0.10, 0.20, and 0.30 weight fraction of AEEA in MAE+AEEA amine blend was mixed keeping constant total concentration of aqueous amine at 10 weight % at 303.15 K and 15.20 kPa partial pressure of CO_2. From Figure 2.2 and Table 2.3 it could be seen that increasing AEEA affects positively on CO_2 loading. This phenomenon is occurred due to the high absorption capacity of AEEA as compared to MAE. In the MAE+AEEA+CO_2+H_2O system maximum fraction of the carbamate ions hydrolyzed to bicarbonate and releasing free amine molecules to absorb more CO_2.

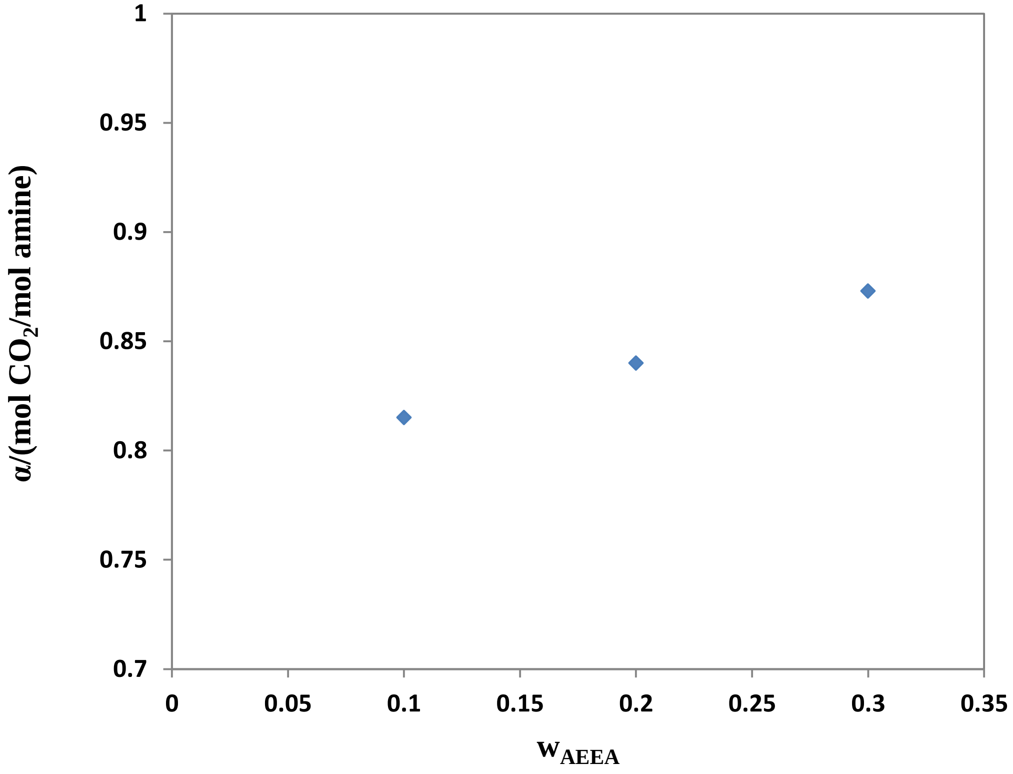


Figure 2.2. Effect of weight fraction of AEEA in the aqueous (MAE+AEEA) blend mixture at T = 303.15 K, p_{CO2} = 15.2 kPa, and C_T = 10 wt. %.

Table 2.3. CO_2 solubility data in aqueous blend of MAE+AEEA with standard uncertainties[a]

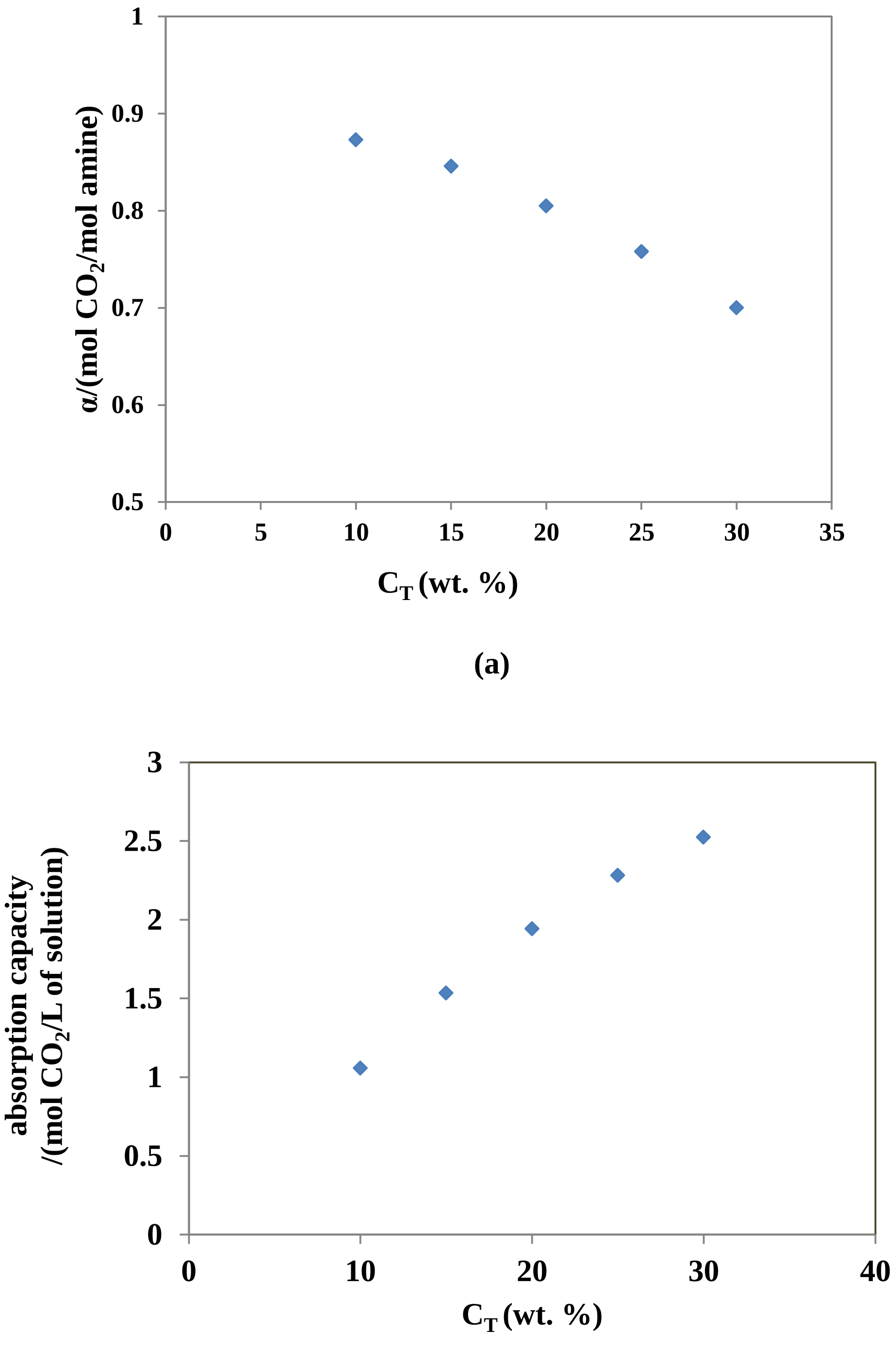
Serial number	T (K)	p_{CO_2} (kPa)	w_{AEEA}	C_T (wt. %)	α_{exp} (mol CO_2.mol amine $^{-1}$)	α_{calc} (mol CO_2.mol amine $^{-1}$)	ARD %
1	303.15	15.20	0.10	10	0.815	0.782	4.05
2	303.15	15.20	0.20	10	0.84	0.812	3.33
3	303.15	15.20	0.30	10	0.873	0.826	5.38
4	303.15	15.20	0.30	15	0.846	0.86	1.65
5	303.15	15.20	0.30	20	0.805	0.824	2.36
6	303.15	15.20	0.30	25	0.758	0.722	4.75
7	303.15	15.20	0.30	30	0.700	0.663	5.29
8	303.15	8.11	0.30	30	0.650	0.626	3.69
9	303.15	12.16	0.30	30	0.676	0.64	5.32
10	303.15	20.27	0.30	30	0.725	0.683	5.79
11	313.15	8.11	0.30	30	0.578	0.542	6.23
12	313.15	12.16	0.30	30	0.610	0.594	2.62
13	313.15	15.20	0.30	30	0.632	0.602	4.74
14	313.15	20.27	0.30	30	0.657	0.636	3.20
15	298.15	15.20	0.30	10	0.886	0.924	4.29
16	308.15	15.20	0.30	10	0.846	0.835	1.30
17	313.15	15.20	0.30	10	0.806	0.812	0.74
18	318.15	15.20	0.30	10	0.752	0.783	4.12
19	323.15	15.20	0.30	10	0.683	0.721	5.56
20	298.15	20.27	0.30	10	0.912	0.944	3.51
21	303.15	20.27	0.30	10	0.900	0.878	2.44
22	308.15	20.27	0.30	10	0.872	0.898	2.98
23	313.15	20.27	0.30	10	0.832	0.875	5.17
24	318.15	20.27	0.30	10	0.777	0.795	2.32

25	323.15	20.27	0.30	10	0.708	0.682	3.67
26	298.15	15.20	0.30	30	0.711	0.677	4.78
27	308.15	15.20	0.30	30	0.672	0.621	7.59
28	318.15	15.20	0.30	30	0.576	0.548	4.86
29	323.15	15.20	0.30	30	0.508	0.536	5.51
30	298.15	20.27	0.30	30	0.737	0.682	7.46
31	308.15	20.27	0.30	30	0.698	0.668	4.30
32	318.15	20.27	0.30	30	0.603	0.582	3.48
33	323.15	20.27	0.30	30	0.534	0.506	5.24
						AAD %	4.17

[a]standard uncertainties u are u(T) = 1 K, u(p_{CO2})= 0.05 kPa, u(w_{AEEA}) = 0.01, u(C_T) = 1, and u(α) =0.005 mol CO_2.mol amine $^{-1}$.

2.4.2.2 Effect of total concentration of amine blend

Total concentration of aqueous blend 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 was kept constant at 303.15 K, 15.20 kPa, and 0.30, respectively. 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 MAE at higher concentration. According to the Le Chatelier’s principle, when the amine weight % (concentration) is increased, more amine molecules are available for reaction. That’s why total amount of CO_2 absorbed in the aqueous blend increased and results in increased absorption capacity (in the term of mol CO_2/L of solution) of the absorbent. 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.



(a)

(b)

Figure 2.3. Effect of total concentration of blend on (a) CO_2 loading, and (b) CO_2 absorption capacity, at T = 303.15 K, p_{CO2} = 15.2 kPa, and w_{AEEA} = 0.30.

Variation of CO_2 loading and absorption capacity with respect to total concentration is depicted in Figure 2.3. Similar trend of CO_2 absorption in N-methyl-4-piperindinol (MPDL) solution was reported in literature by Xiao et al. 2017.

2.4.2.3 Effect of partial pressure of CO_2

Effect of partial pressure of CO_2 was studied in the range of 8.11 to 20.27 kPa for 30 wt. % concentration of amine solution. Temperature was kept constant at 303.15 K and at the 313.15 K, and weight fraction of AEEA in the blend was constant at 0.30. From Figure 2.4, it can be shown that increasing partial pressure of CO_2 gas was favorable for the solubility of the gas into the absorbent.

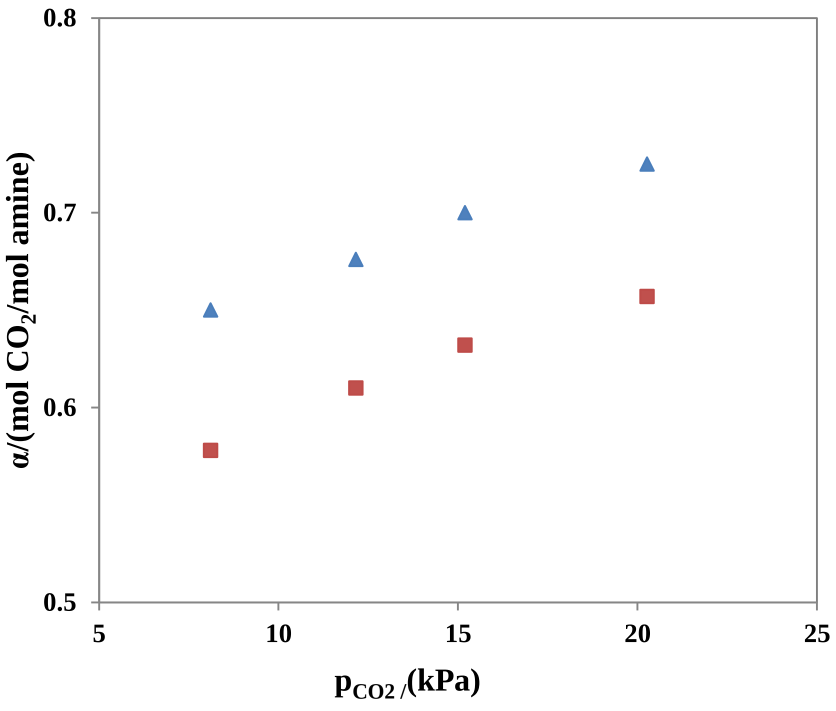
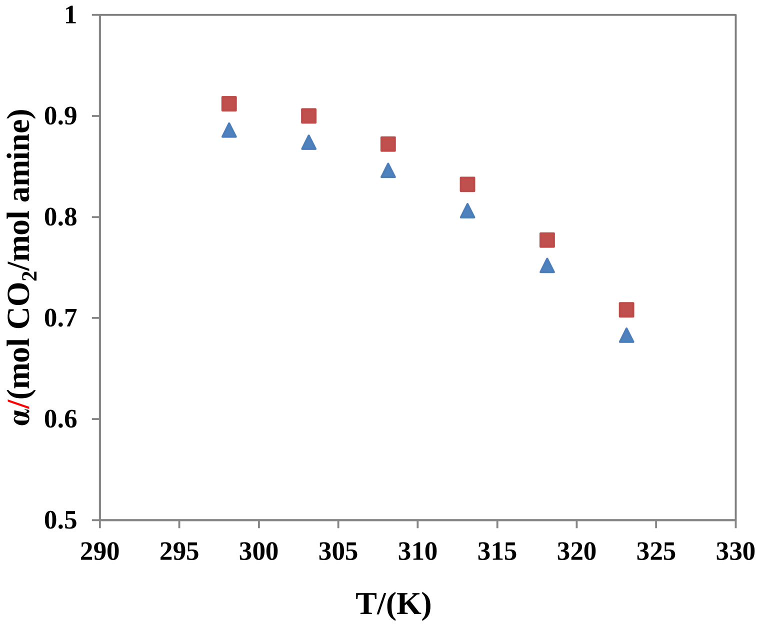


Figure 2.4. Effect of partial pressure of CO_2 on CO_2 loading for T: ▲ 303.15 K; ■ 313.15 K, respectively, C_T = 30 wt.%, and w_{AEEA} = 0.30.

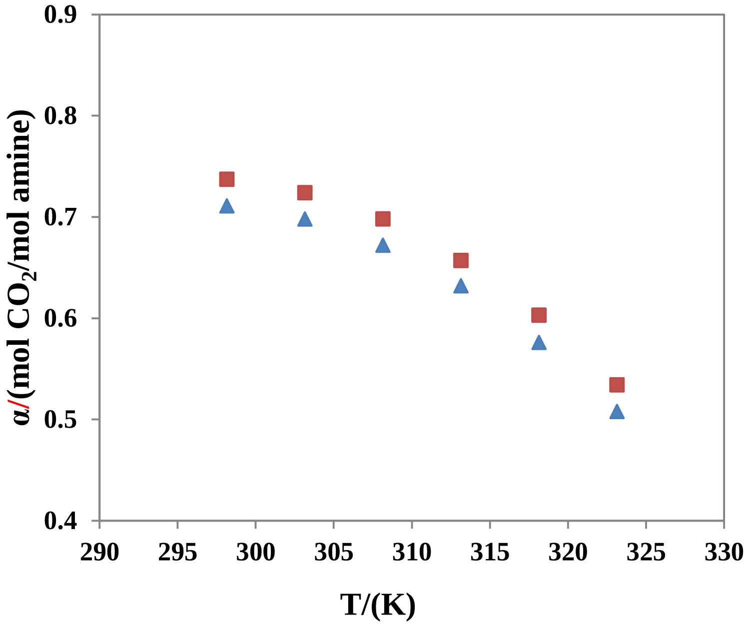
As from the known fact about physical solubility of the gas was directly proportional to the partial pressure of the gas. At higher partial pressure more CO_2 was available in the liquid form that's why more amounts of carbamates, dicarbamates, bicarbonate, and carbonate had formed and CO_2 loading increased by increasing partial pressure.

2.4.2.4 Effect of temperature

In order to study the effect of temperature, experiments were carried out in the range of 298.15 to 323.15 K at 15.2 and 20.27 kPa partial pressure of CO_2. Total concentration of amine blend was kept constant at 10 wt. % and 30 wt. % with 0.30 weight fraction of AEEA. Increasing temperature affected negatively on the CO_2 loading. That might 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 2.5 revealed the effect of temperature on the CO_2 loading.



(a) C_T = 10 wt. %



(b) C_T = 30 wt. %

Figure 2.5. Effect of temperature on CO_2 loading for pCO_2: ▲ 15.2 kPa; ■20.67kPa, respectively, and w_{AEEA} = 0.30 and (a) C_T = 10 wt. %, and (b) C_T = 30 wt. %.

2.4.3 Modified Kent-Eisenberg model with newly introduced correction factor (F_k) for MAE+AEEA+H_2O+CO_2 system

In this paper, a new modified Kent-Eisenberg thermodynamic model with newly introduced correction factor (F_k) for reaction system of aqueous MAE+AEEA blend and CO_2 was developed. This model was assumed to work in the temperature range 298.15 to 323.15 K, partial pressure of CO_2 varied from 8.11 to 20.27 kPa, and total concentration of amine blend from 10 to 30 weight %. Coefficients c_1 to c_6 for Eq. (2.33) were found out by least squares method of non-linear regression using Eqs. (2.16 to 2.36), literature values of coefficient's and experimental data were shown in Table 2.2 and Table 2.3, respectively and summarized in Table 2.4.

Table 2.4. Values of coefficients of correction factor F_k for Equation 2.31

parameter	c_1	c_2	c_3	c_4	c_5	c_6
F_{k_2}	11.28052	-11338.1	-1.30297	-10.1474	3.388565	11.29807
F_{k_3}	-0.11003	1.212198	3.661598	25.74118	-4.90913	-0.11003
F_{k_4}	-14.5219	-0.00725	3.712814	33.6165	-1.94049	-14.5219
F_{k_5}	0.421119	-6.15755	4.291157	21.43172	-5.83461	0.421119
F_{k_6}	3.926334	1.060811	-0.03542	6.82447	-4.03093	3.926335
F_{k_7}	3.499118	0.363044	-4.72461	-29.1387	2.624058	3.499118
F_{k_8}	-0.13229	1.274914	-3.01691	17.85857	0.272216	
F_{k_9}	0.834709	1.260275	-6.95073	9.072631	1.267127	
$F_{k_{10}}$	-8.00051	9.252959	-2.23875	7.139764	1.038107	
$F_{k_{11}}$	-1.66183	0.504874	-3.35866	14.60525	0.845011	
$F_{k_{12}}$	-475.3	34034.13	228.9472	562.5417	-22.1981	

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 $\left[[R'NCOO^-R"NH_2]H^+\right]_{eqlm}$. Including from Eqs. (2.16-2.28), Eq. (2.34a), Eq. (2.34b), and Eq. (2.35) there was 16 equations. Optimize concentrations of species at the equilibrium was found out by solving set of 16 nonlinear equations with 16 variables (species) using “ fsolve ” in MATLAB programming. CO_2 loading was calculated by putting the values of appropriate species concentration in the Eq. (2.37). From Table 2.3, Figure 2.6 and Figure 2.7 it is found that this model makes acceptable prediction of CO_2 loading in the MAE+AEEA+H_2O solution.

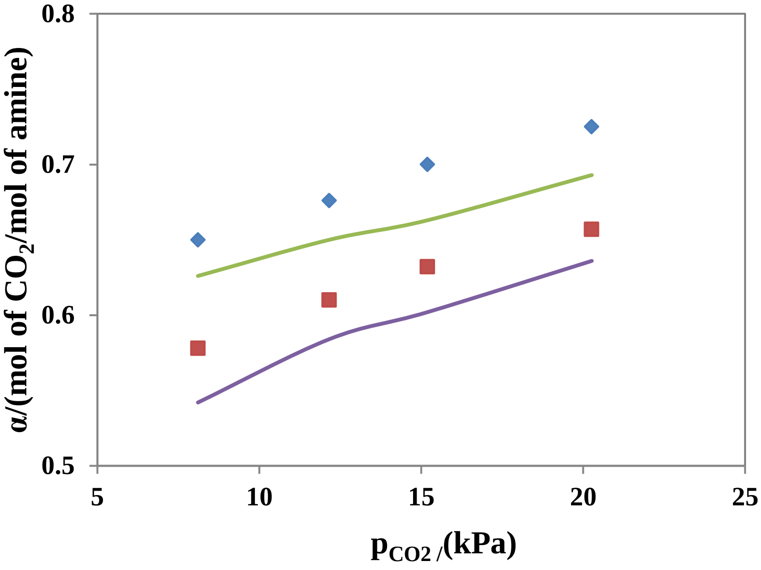


Figure 2.6. Experimental (denoted by symbols) and model predicted (denoted by lines) plot (p_{CO2} vs α) for aqueous MAE + AEEA blend for, T: ▲ 303.15 K; ■ 313.15 K, respectively, C_T = 30 weight %, and w_{AEEA} = 0.30

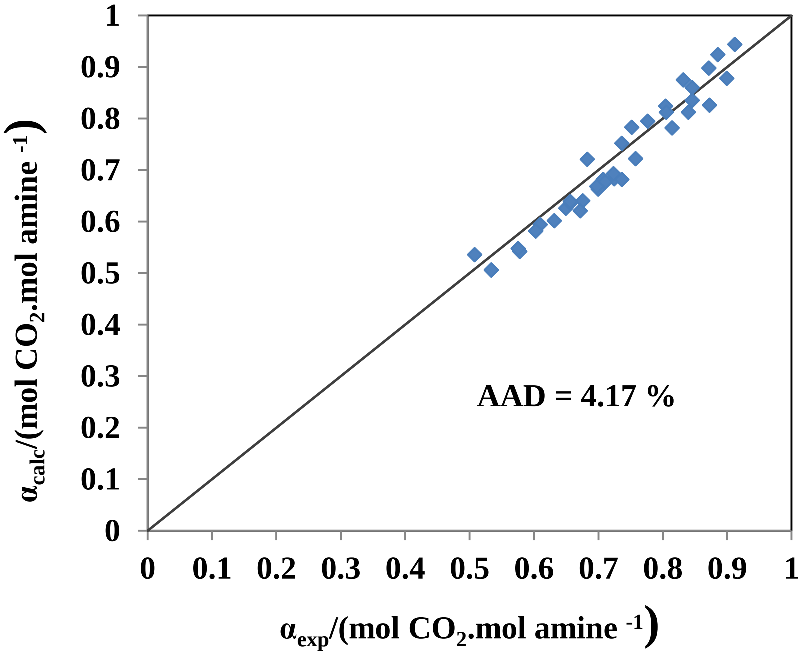


Figure 2.6. Model predicted CO_2 solubility vs. experimental CO_2 solubility data

This model is useful for low solution concentration (10 wt. %) as well as higher concentration (30 wt. %). Absolute relative deviation (ARD) and absolute average deviation between experimental values and calculated values of CO_2 loading were measured by following Eqs. (2.38-2.39) and reported in Table 2.3.

$$\% \text{ ARD} = \frac{|\alpha exp - \alpha cal|}{\alpha exp} \times 100 \tag{2.38}$$

$$\% \text{ AAD} = \frac{100}{n} \times \sum_{i=1}^{n} \frac{|\alpha exp - \alpha cal|}{\alpha exp} \tag{2.39}$$

Where, α_{exp}, α_{calc} ,and n are experimental CO_2 loading, calculated CO_2 loading and number of data point, respectively.

2.4.4 Heat of absorption measurement

Heat of absorption (ΔH_{abs}) was measured using Gibbs – Helmholtz Eq. (2.40).

$$\frac{d(\ln(p_{CO_2}))}{d(\frac{1}{T})} = \frac{\Delta H_{abs}}{R} \tag{2.40}$$

Where, p_{CO_2} , T, and ΔH_{abs} is in kPa, K, and kJ/mol, respectively. R is universal gas constant.

In the literature, this method of calculation of ΔH_{abs} was used by Kim and Svendsen, (2007); Muchan et al. (2017B); Xiao et al. (2017) and Kumar et al. (2020) and reported reasonable values of ΔH_{abs} at constant total pressure and nearly at same CO_2 solubility. Based on the experimental data and model predicted data of CO_2 loading plot of ln(p_{CO_2}) vs. (1/T) was studied at CO_2 loading nearly 0.66 (mol of CO_2/mol of amine) and 0.78 (mol CO_2/mol amine). Slope of the curves of ln(p_{CO_2}) vs. (1/T) were -8689.9 and -8974.4 for CO_2 loading 0.66 and 0.78 (mol CO_2/mol amine), respectively. ΔH_{abs} was found out by multiplying R into the average of slopes. Heat of absorption for MAE+AEEA+H_2O+CO_2

system was -73.4 kJ/mol. It is higher than tertiary amines (MDEA; -54.6 kJ/mol ; MPDL; -49.1 kJ/mol) (Xiao et al., 2017) but lower than industrially used benchmark primary amine (MEA; -85.13 kJ/mol) (El Hadri et al., 2017).

2.5 CONCLUSIONS

Equilibrium CO_2 solubility in the aqueous mixture of MAE+AEEA was studied. Weight fraction of AEEA in the amine mixture varied from 0.10 to 0.30. Highest CO_2 of loading was occurred at 0.30 weight fraction of AEEA. Effect of total concentration of amine blend, partial pressure of CO_2, and temperature on CO_2 solubility was studied by varying different operating conditions. Maximum CO_2 loading 0.944 (mol CO_2/mol amine) was attained at total concentration 10 wt. %, temperature 298.15 K, and CO_2 partial pressure 20.27 kPa. A new modified Kent-Eisenberg thermodynamic model was developed to predict CO_2 solubility in the aqueous MAE+AEEA blend. Absolute average deviation between experimental data and model predicted data was found as 4.17 %. Heat of CO_2 absorption using Gibbs-Helmholtz equation was determined as -73.4 kJ/mol for MAE+AEEA+H_2O+ CO_2 system.