



Thermodynamic modeling and new experimental CO₂ solubility into aqueous EAE and AEEA blend, heat of absorption, cyclic absorption capacity and desorption study for post-combustion CO₂ capture

Diwakar Pandey, Monoj Kumar Mondal^{*}

Department of Chemical Engineering and Technology, Indian Institute of Technology, (Banaras Hindu University), Varanasi 221005, Uttar Pradesh, India

ARTICLE INFO

Keywords:

2-(ethylamino)ethanol
Aminoethylethanolamine
CO₂ solubility
Kent-Eisenberg model
Heat of absorption
Cyclic capacity

ABSTRACT

In the present study, carbon dioxide (CO₂) solubility into aqueous blend of 2-(ethylamino) ethanol (EAE) and aminoethylethanolamine (AEEA) was measured. The performance of CO₂ capture by this amine blend was investigated in terms of CO₂ solubility, heat of absorption, cyclic CO₂ solubility, and initial rate of change of CO₂ solubility. CO₂ 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 CO₂ partial pressure, 0.10 to 0.30 wt 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 CO₂ solubility was 1.033 mol CO₂/mol amine at 298.15 K, 20.27 kPa, 0.30 wt fraction of AEEA in the blend, and 10 wt% of EAE and AEEA solution. A semi-empirical Kent-Eisenberg thermodynamic model and an empirical model were developed to calculate equilibrium CO₂ 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 CO₂ partial pressure and total concentration of 30 wt% of EAE and AEEA blend, the equilibrium CO₂ solubility was resulted as 0.748 mol CO₂/mol amine and cyclic solubility of 0.503 mol CO₂/mol amine was achieved. Heat of CO₂ absorption was measured based on Gibbs Helmholtz equation and found as −72.25 kJ/mol for 30 wt% aqueous EAE and AEEA blend. Results of absorption capacity of EAE and AEEA solution and monoethylethanolamine (MEA) were compared at same operating conditions. This blend had higher CO₂ solubility, lesser heat of absorption, more cyclic capacity and faster rate of change of initial CO₂ solubility than MEA.

1. Introduction

Greenhouse gases present in environment are main sources of global warming. Carbon dioxide (CO₂) is a greenhouse gas and contributed major impact on global warming and climate change. CO₂ 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 [1]. Therefore, CO₂ capture from flue gases is still an important research area.

Pre-combustion CO₂ capture, post-combustion CO₂ capture and oxy-fuel combustion are mainly 3 technologies to reduce CO₂ emission from fossil fuel combustion. Post combustion CO₂ capture is one of the most effective and developed method to control CO₂ emission and it's unit can

be retrofitted easily in existing power plants [2]. Adsorption, absorption, membrane separation technique, cryogenic, etc. are several techniques used for separation of gases. However, major difficulties in CO₂ capture from coal fired power plant flue gas streams are low CO₂ concentration (10–15% CO₂) in the gas stream with low flue gas pressure (almost 1 atm) and very large flow rate of flue gas with large concentration of N₂ [3]. Absorption technique is most matured and applicable for low pressure (at atmospheric pressure) post combustion CO₂ capture [4]. Aqueous solutions of conventional alkanolamines e.g. monoethanolamine (MEA), diethanolamines (DEA) and methyldiethanolamine (MDEA) are very often used in chemical absorption–desorption process. 30 wt% MEA is particularly applied for CO₂ capture from flue gas (low CO₂ partial pressure of 10 to 15 kPa CO₂) at 40 °C and as a consequence has become the benchmark amine for CO₂ capture from electricity generation [5].

Sterically hindered amines e.g. 2-(amino)methylpropanolamine

^{*} Corresponding author.

E-mail address: mkmondal13@yahoo.com (M. Kumar Mondal).

<https://doi.org/10.1016/j.cej.2020.128334>

Received 20 September 2020; Received in revised form 9 December 2020; Accepted 24 December 2020

Available online 1 January 2021

1385-8947/© 2021 Elsevier B.V. All rights reserved.

(AMP), 2-(methylamino)ethanol (MAE), 2-(ethylamino)ethanol (EAE), 2-(isopropylamino)ethanol (IPAE), 2-(butylamino)ethanol (BAE) etc. [6–8], and polyamines e.g. piperazine (PZ), ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), triethylene-pentamine (TEPA), etc. are also used for CO₂ capture [9–13]. Primary (MEA) and secondary (DEA) amine has shown high heat of absorption and faster reaction kinetics. Tertiary amines have high CO₂ 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 CO₂ 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 [14–16]. Sterically hindered amines formed unstable carbamate due to hindrance of amino group and showed high CO₂ loading, and lower heat of reaction. Polyamines have been studied recently because of its higher CO₂ loading capacity (mol CO₂/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 CO₂ capture using amine solvents has been published in literature [17,18]. From those reviews, it can be found out that there is no single solvent which has all favorable property for CO₂ capture by absorption-desorption process. To minimize demerits and to utilize advantages of individual amines, recently, several amine blends have been investigated for CO₂ capture [19–30]. Despite it, several developments in solvent to achieve high CO₂ solubility, high recycle capacity, high mass transfer rate, fast reaction kinetics, low heat of CO₂ absorption, low regeneration cost, less corrosive, less viscous, less degradable, etc. for economical CO₂ capture operation are still needed.

EAE is a hindered secondary amine and has higher CO₂ loading with lower heat of absorption because it produces unstable carbamate [7,23]. Moreover, EAE can be produced using renewable resources of agriculture waste biomass [31]. Aminoethylethanolamine (AEEA) is an alkanoldiamine and has been shown high CO₂ loading (mol CO₂/mol amine), faster reaction kinetics but its high heat of absorption [32,33] makes it not very useful as a single absorbent for CO₂ capture. In the literature AEEA has been used as an activator in the amine blends to improve solvent performance for CO₂ capture [34–36].

In this paper, an aqueous blend of EAE and AEEA was investigated for post-combustion CO₂ capture. Equilibrium CO₂ solubility (mol CO₂/mol amine) was studied at atmospheric pressure with varying temperature from 298.15 K to 323.15 K. Partial pressure of CO₂ 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 wt fraction of amine (EAE and AEEA). A semi-empirical model based on the Kent-Eisenberg model and an empirical model was developed to predict CO₂ solubility (mol CO₂/mol amine) data in the range of studied operating conditions. Desorption experiment was carried out at 393.15 K temperature and cyclic CO₂ solubility of this blend was calculated. Heat of CO₂ absorption, initial rate of change of CO₂ 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.

2. Experimental section

2.1. Materials

The EAE (98% purity) was purchased from Sigma Aldrich, St. Louice 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 CO₂ 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 CO₂ solubility. All chemicals were

used without further purification. Description of all chemicals which were used in the experimentation was listed in Table 1. CO₂ gas (99.99% purity) and N₂ 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, \pm (0.4% of Reading + 0.2% of Full Scale)). A portable IR CO₂ gas analyzer (Gasboard-3800P; CO₂ range, 0–100% by volume, full scale accuracy = \pm 2%) was used to measure the CO₂ gas concentration (in volume %). Double distilled water (made in our laboratory) was used to prepare aqueous amine solutions.

2.2. CO₂ absorption study

All the experiments were done at atmospheric pressure and temperature range 298.15 K to 323.15 K. Absorption of CO₂ 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 shown in Fig. 1 with little modifications in experimental set-up used elsewhere [34,35]. Water saturation cell and bubble column were placed inside the water bath with controlled temperature (accuracy of \pm 1 K). Simulated gas mixture was prepared in gas mixing chamber using controlled flow of CO₂ and N₂ gases. Concentration of CO₂ gas was varied from 8 to 20 vol% of gas mixture (8.11 kPa to 20.27 kPa partial pressure of CO₂) 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 CO₂ 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 CO₂ in gas stream was measured with CO₂ gas analyzer periodically in time interval of 10 min. CO₂ solubility or CO₂ loading is defined by number of moles of absorbed CO₂ per mol of absorbent. In order to find out CO₂ solubility and initial absorption rate, 1 ml of CO₂ loaded sample was taken at 10 min time intervals. Saturation of absorbent attained when outlet concentration of CO₂ reached up to the inlet concentration of CO₂ and CO₂ solubility attained same value repeatedly three time intervals. CO₂ solubility (mol CO₂/mol amine) was calculated using Chittick Apparatus [38]. In which 1 ml CO₂ loaded sample was titrated with 1 M HCl using methyl orange indicator. Volume of gas liberated during titration was collected in burette and CO₂ solubility was calculated by volumetric method using Eq. (1) [22]. CO₂ solubility calculation was repeated three times and average values were reported. Final solubility was declared at saturation point.

Table 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% ^g	none
EAE ^b	110-73-6	Sigma Aldrich, St. Louice, USA	\geq 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 gas	124-38-9	Linde India Ltd.	99.99% ^h	none
N ₂ gas	7727-37-9	Linde India Ltd.	99.99% ^h	none
Water	7732-18-5	Our laboratory	99.99% ^g	Double distillation

^aMonoethanolamine, ^b2-(ethylamino)ethanol, ^caminoethylethanolamine, ^dHydrochloric acid, ^ecarbon dioxide, ^fnitrogen, ^gmass fraction, and ^hvolume fraction.

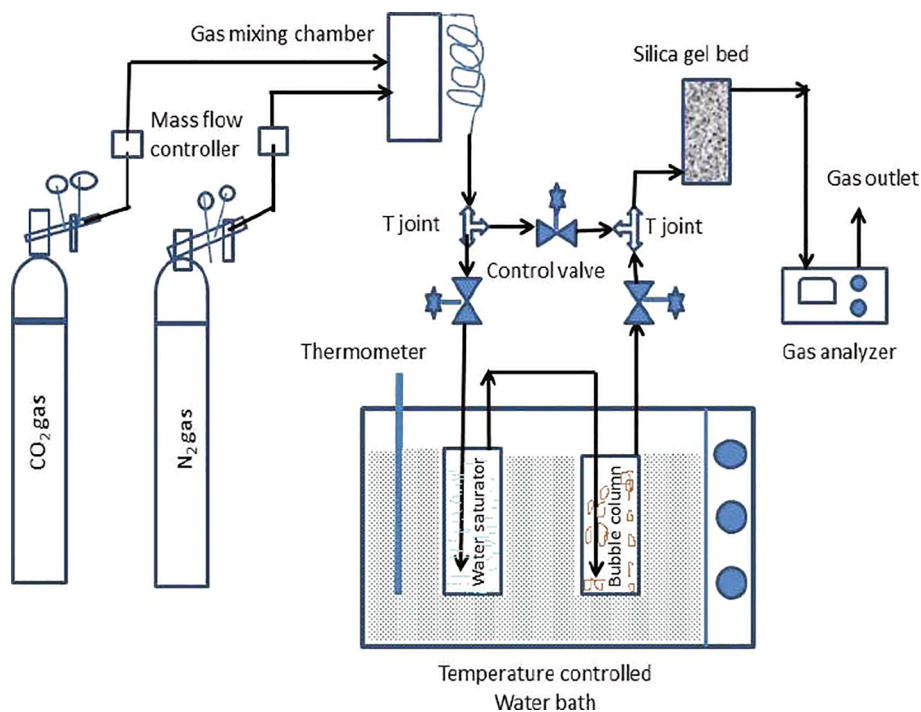


Fig. 1. Experimental set-up for CO₂ gas absorption study.

$$\alpha(\text{mol CO}_2/\text{mol amine}) = \frac{V_{\text{CO}_2}}{22.4 \times C_{\text{amine}} \times V_{\text{CO}_2\text{loaded sample}}} \times \frac{273.15}{273.15 + t} \quad (1)$$

$$\text{Absorption capacity}(\text{mol CO}_2/\text{L solution}) = \alpha \cdot C_{\text{amine}} \quad (2)$$

where, α is CO₂ solubility, C_{amine} , V_{CO_2} , $V_{\text{CO}_2\text{loaded sample}}$ and t are concentration of amine (mol/L), volume of CO₂ gas (L) dissolved in amine solution, volume of CO₂ in loaded amine sample (L), and room temperature (°C), respectively.

2.3. CO₂ desorption study

The experimental set-up for regeneration of absorbent by desorption of CO₂ was shown in Fig. 2, almost similar to mentioned in literatures [28,37]. 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 CO₂ 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. 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 CO₂ loaded amine solution in desorption flask was reached in 10–15 min at 393.15 K. After that, CO₂ loading was found out by titration method by Chittik apparatus [38] at 10 min time interval. Cyclic CO₂ solubility and cyclic capacity was calculated by Eq. (3) and Eq. (4), respectively.

$$\Delta\alpha(\text{mol CO}_2/\text{mol amine}) = \alpha_{313.15\text{K}, 15.20\text{kPa}} - \alpha_{393.15\text{K}, 15.20\text{kPa}} \quad (3)$$

$$\text{Cyclic capacity}(\text{mol CO}_2/\text{L solution}) = \Delta\alpha \cdot C_{\text{amine}} \quad (4)$$

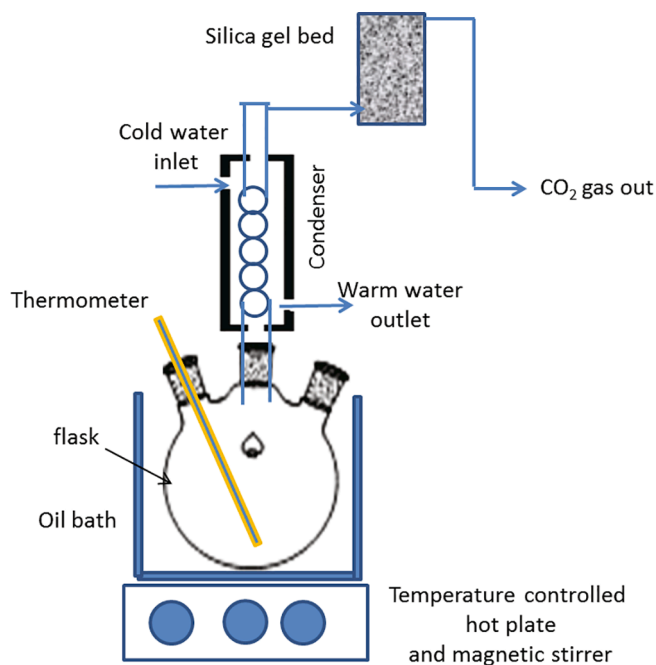


Fig. 2. Experimental set-up for CO₂ desorption study.

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 CO₂ solubility of aqueous amine blend at different temperature and CO₂ 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. (5)) [39].

$$\frac{d(\ln(p_{CO_2}))}{d(\frac{1}{T})} = \frac{\Delta H_{abs}}{R} \quad (5)$$

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. Kent-Eisenberg model for equilibrium CO_2 solubility into aqueous blend

3.1. Reaction mechanism

Kent-Eisenberg model [39] was used to predict equilibrium CO_2 solubility into aqueous EAE and AEEA blend. Kent-Eisenberg model [41] 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 [7,42–47].

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 :



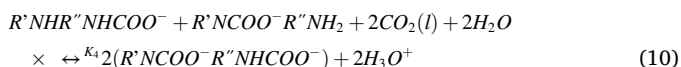
Dissociation of water:



Carbamate formation due to reaction of AEEA with CO_2 :



Dicarbamate formation:



Hydrolysis of carbamate formed due to EAE:



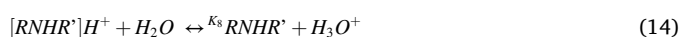
Hydrolysis of CO_2 :



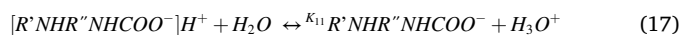
Dissociation of bicarbonate ion:



Dissociation of protonated amines:



Dissociation of protonated carbamates:



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:

$$p_{CO_2} = H_{CO_2}[CO_2] \quad (19)$$

$$K_1 = [H_3O^+][OH^-] \quad (20)$$

$$K_2 = \frac{[R'NHR''NH_2COO^-][H_3O^+]}{[R'NHR''NH_2][CO_2]} \quad (21)$$

$$K_3 = \frac{[R'NCOO^-R''NH_2][H_3O^+]}{[R'NHR''NH_2][CO_2]} \quad (22)$$

$$K_4 = \frac{[R'NCOO^-R''NHCOO^-]^2[H_3O^+]}{[R'NHR''NH_2COO^-][R'NCOO^-R''NH_2][CO_2]^2} \quad (23)$$

$$K_5 = \frac{[RNHR']HCO_3^-}{[RNCOO^-R']} \quad (24)$$

$$K_6 = \frac{[HCO_3^-][H_3O^+]}{[CO_2]} \quad (25)$$

$$K_7 = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} \quad (26)$$

$$K_8 = \frac{[RNHR']H^+}{[RNHR']H^+} \quad (27)$$

$$K_9 = \frac{[R'NHR''NH_2]H^+}{[R'NHR''NH_2]H^+} \quad (28)$$

$$K_{10} = \frac{[R'NHR''NH_2]H^+}{[R'NHR''NH_2]H_2^{++}} \quad (29)$$

$$K_{11} = \frac{[R'NHR''NH_2COO^-][H_3O^+]}{[R'NHR''NH_2COO^-]H^+} \quad (30)$$

$$K_{12} = \frac{[R'NCOO^-R''NH_2][H_3O^+]}{[R'NCOO^-R''NH_2]H^+} \quad (31)$$

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. (32a) and Eq. (32b). Total charge was also conserved and a charge balance equation was given in Eq. (33).

Equation for mass balance of amines:

Total EAE mass balance:

$$[RNHR']_{total} = [RNHR']_{eqm} + [[RNHR']H^+]_{eqm} + [RNCOO^-R']_{eqm} \quad (32 a)$$

Total AEEA mass balance:

$$\begin{aligned} R'NHR''NH_2]_{total} = & [R'NHR''NH_2]_{eqm} + [[R'NHR''NH_2]H^+]_{eqm} + [[R'NHR''NH_2]H_2^{++}]_{eqm} + [R'NHR''NH_2COO^-]_{eqm} + [R'NCOO^-R''NH_2]_{eqm} \\ & + [R'NCOO^-R''NHCOO^-]_{eqm} + [[R'NHR''NHCOO^-]H^+]_{eqm} + [[R'NCOO^-R''NH_2]H^+]_{eqm} \end{aligned} \quad (32 b)$$

Total charge balance:

$$\begin{aligned} [RNHR']H^+]_{eqm} + [H_3O^+] + [[R'NHR''NH_2]H^+]_{eqm} + 2[[R'NHR''NH_2]H_2^{++}]_{eqm} = & [HCO_3^-]_{eqm} + 2[CO_3^{2-}]_{eqm} + [OH^-] + [RNCOO^-R']_{eqm} \\ & + [R'NHR''NHCOO^-]_{eqm} + [R'NCOO^-R''NH_2]_{eqm} + 2[R'NCOO^-R''NHCOO^-]_{eqm} \end{aligned} \quad (33)$$

Total CO₂ in the liquid phase was balanced by Eq. (34)

Total CO₂ balance:

$$\begin{aligned} \alpha \cdot [[RNHR'] + [R'NHR''NH_2]]_{total} = & [HCO_3^-]_{eqm} + [CO_3^{2-}]_{eqm} + [CO_2] + [RNCOO^-R']_{eqm} + [R'NHR''NHCOO^-]_{eqm} + [R'NCOO^-R''NH_2]_{eqm} \\ & + [R'NCOO^-R''NHCOO^-]_{eqm} \end{aligned} \quad (34)$$

Where α is the CO₂ loading in (mol CO₂/mol amine) and [species]_{eqm} denoted concentration of that species in mol/L at the equilibrium.

Equilibrium CO₂ solubility was calculated by following equation:

$$\alpha = \frac{[HCO_3^-]_{eqm} + [CO_3^{2-}]_{eqm} + [CO_2] + [RNCOO^-R']_{eqm} + [R'NHR''NHCOO^-]_{eqm} + [R'NCOO^-R''NH_2]_{eqm} + [R'NCOO^-R''NHCOO^-]_{eqm}}{[[RNHR'] + [R'NHR''NH_2]]_{total}} \quad (35)$$

4. Results and discussion

4.1. Experimental set-up validation

In order to validate the suitability of experimental set up, 30 wt% MEA was used for CO₂ absorption at 313.15 K temperature and at 12.16, 15.20, and 20.27 kPa partial pressure of CO₂ gas. Equilibrium solubility was obtained 0.568 (mol CO₂/mol amine) and compared with the results obtained in literature [22,48,49]. A plot of comparison was given in Fig S1 of supporting information. CO₂ loaded MEA solution was used for desorption. Cyclic CO₂ solubility was calculated and compared with [22]. Average absolute deviation for CO₂ solubility and cyclic solubility were found to be 2.55% and 6.30%, respectively.

4.2. Equilibrium CO₂ 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 CO₂ (p_{CO2}) and temperature (T)) on the equilibrium CO₂ solubility of

aqueous EAE and AEEA blend was studied. The results were shown in Table 2. In order to study the effect of addition of AEEA in EAE for CO₂ absorption, different proportion of 0.10, 0.20, and 0.30 wt 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 CO₂. From Fig. 3 it could

be seen that CO₂ solubility was increased with increasing AEEA weight fraction from 0.10 to 0.30. This phenomenon was occurred due to high

CO₂ loading capacity of AEEA in comparison to EAE.

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%.

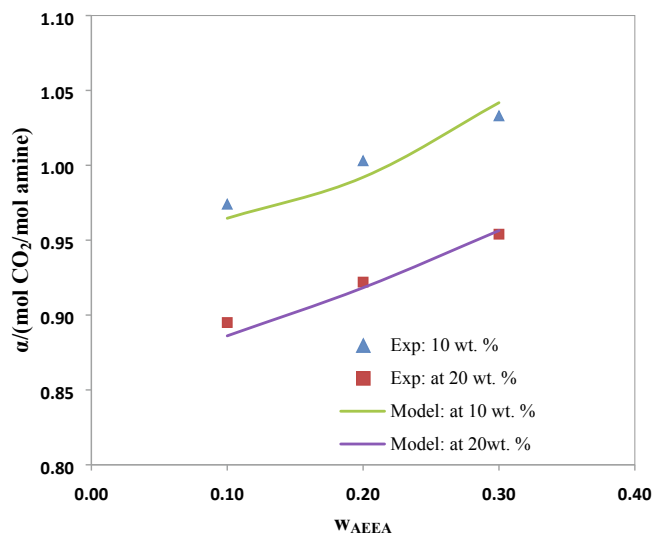
Temperature, partial pressure of CO₂, and weight fraction of AEEA were kept constant at 303.15 K (or 313.15 K), 15.20 kPa, and 0.30, respectively. Variation of CO₂ solubility and absorption capacity with respect to total concentration was shown in Fig. 4. Increase in amount of amine in mixture results in decrease in CO₂ 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. That's why total amount of CO₂ absorbed in the aqueous blend increased and results in increase in absorption capacity (in the term of mol of CO₂/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 CO₂ captured by per mol of amine blend decreased. Similar trend of CO₂ absorption in N-methyl-4-piperindinol (MPDL) solution was reported in literature [40].

Effect of partial pressure of CO₂ (p_{CO2}) on CO₂ 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 Fig. 5, it could be shown that increasing partial pressure of CO₂ 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 CO₂ was available in the liquid as dissolved form that's why more amounts of carbamates, dicarbamates, bicarbonate, and carbonate had formed and CO₂ solubility increased by increasing partial pressure.

In order to study the effect of temperature on the CO₂ 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 wt

Table 2Equilibrium CO₂ solubility data of aqueous EAE and AEEA blend at atmospheric pressure.

T (K)	p _{CO2} (kPa)	w _{AEEA}	C _T (wt %)	α _{experimental} (mol CO ₂ /mol amine)	α _{calculated} (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

^acalculated by empirical model Eq. (40).**Fig. 3.** Effect of AEEA weight fraction (w_{AEEA}) on the CO₂ solubility at constant 298.15 K temperature and constant 20.27 kPa partial pressure of CO₂ gas for aqueous EAE and AEEA blend: Experimental (Exp.) and model (Eq. (35)) predicted data.

fraction of AEEA. Increasing temperature affected negatively on the CO₂ loading. That might be due to the reversible exothermic reactions of aqueous amines with CO₂. Therefore, high temperature for CO₂ absorption is not favorable and due to high temperature CO₂ solubility into the aqueous blend decreased. Fig. 6 depicted the effect of temperature on the CO₂ solubility.

4.3. Semi-empirical Kent-Eisenberg thermodynamic model

Experimental equilibrium CO₂ solubility data of aqueous CO₂ with EAE and AEEA blend system were correlated to a semi-empirical model to predict equilibrium CO₂ solubility based on the Kent-Eisenberg model. Henry's law of constant was calculated by Eq. (36), given by Hsu et al. [47].

$$\ln H_{CO_2} \left(kPa \cdot \frac{L}{mol} \right) = 20.2669 - \frac{1.38306 \times 10^4}{T} + \frac{0.06913 \times 10^8}{T^2} - \frac{0.015589 \times 10^{11}}{T^3} + \frac{0.012 \times 10^{13}}{T^4} \quad (36)$$

Equilibrium constants K₁, K₆, and K₇ were taken from the literature [50]. They defined equilibrium constants in the form of temperature dependency as written by Eq. (37):

$$\ln K = a + \frac{b}{T} + c \cdot \ln T \quad (37)$$

Where, a, b, and c are the coefficient of expression and given in the Table 3. T is the temperature in kelvin (K).

Kent and Eisenberg [41] regressed some of equilibrium constant (involved in mainly amines reactions) as function of temperature. In this work, equilibrium constants (K₂, K₃, K₄, K₅, K₈, K₉, K₁₀, K₁₁, and K₁₂) 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 CO₂ and given by following Eq. (38):

$$\ln K_i = c_1 + \frac{c_2}{T} + c_3 \ln C_{Amine} + \frac{c_4}{C_{Amine}} + c_5 \ln p_{CO_2} + \frac{c_6}{p_{CO_2}} \quad (i = 2 - 5, \text{ and } 8 - 12) \quad (38)$$

Where, K_i is equilibrium constant, and c₁ to c₆ are coefficients of Eq. (38). C_{Amine} is the concentration of EAE or AEEA in mol/L. T is the temperature in Kelvin and p_{CO₂} is the partial pressure of CO₂ 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.) = |α_{exp} - α_{calc}| was minimized using H_{CO₂}, K₁, K₆, K₇, 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 multiple regression using Microsoft excel solver. The equilibrium constants K₂, K₃, K₄, K₅, K₈, K₉, K₁₀, K₁₁, and K₁₂ were calculated by substituting those values of species concentration in Eqs. (21)–(24), (27)–(31), and regressed in the form of Eq. (38). Regressed coefficients of Eq. (38) were given in the Table 4.

There was total 16 possible species into the system at the equilibrium including [RNHR']_{eqm}, [[RNHR']H⁺]_{eqm}, [R'NHR''NH₂]_{eqm}, [[R'NHR''NH₂]H⁺]_{eqm}, [[R'NHR''NH₂]H₂⁺]_{eqm}, [R'NCOO-R']_{eqm}, [R'NHR''NHCOO]_{eqm}, [CO₂], [R'NCOO-R''NH₂]_{eqm}, [R'NCOO-R''NHCOO]_{eqm}, [H₃O⁺], [HCO₃⁻]_{eqm}, [CO₃²⁻]_{eqm}, [OH⁻], [[R'NHR''NHCOO]⁻H⁺]_{eqm}, and [[R'NCOO-R''NH₂]H⁺]_{eqm}.

Equilibrium CO₂ solubility was calculated by solving simultaneously 16 Eqs. of H_{CO₂}, K₁, K₂, K₃, K₄, K₅, K₆, K₇, K₈, K₉, K₁₀, K₁₁, K₁₂, EAE mass balance, AEEA mass balance, and total charge balance. Predicted values of equilibrium CO₂ solubility by Eq. (35) were depicted in Figs. 3–6. Average absolute deviation (AAD) % between experimental data and

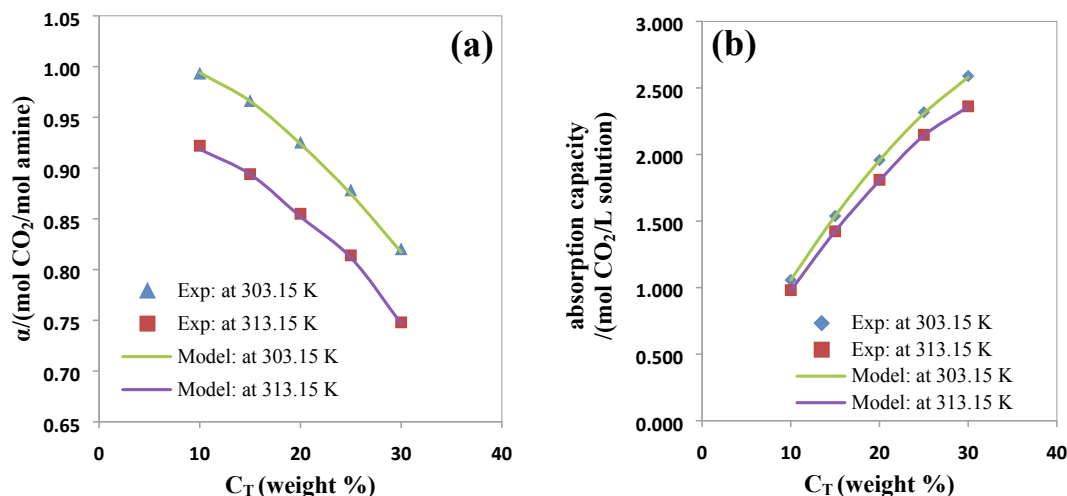


Fig. 4. Effect of total concentration (C_T) of the aqueous EAE and AEEA blend with 0.30 w_{AEEA} and at 15.20 kPa partial pressure of CO₂ on the CO₂ (a) solubility, and (b) absorption capacity: Experimental (Exp.) and model (Eq. (35)) predicted data.

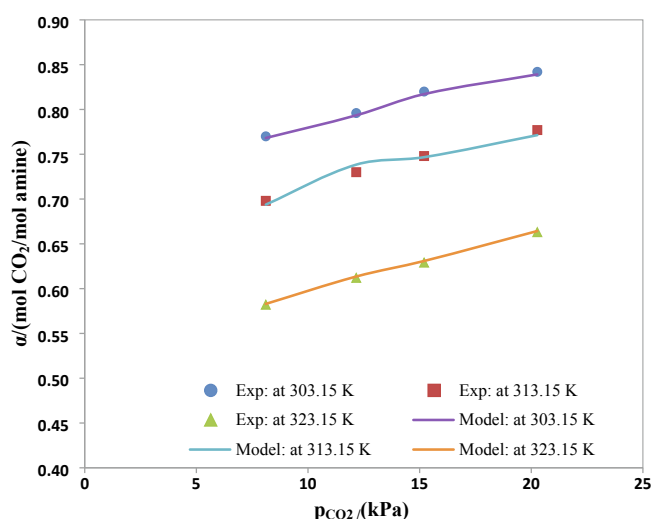


Fig. 5. Effect of CO₂ partial pressure on the CO₂ solubility for the 30 wt% (21 wt% + 9 wt%) aqueous EAE and AEEA blend: Experimental (Exp.) and model (Eq. (35)) predicted data.

model predicted data was calculated by Eq. (39) and reported as 2.56%.

$$\%AAD = \frac{100}{n} \times \sum_{i=1}^n \frac{|\alpha_{exp} - \alpha_{cal}|}{\alpha_{exp}} \quad (39)$$

where, α_{exp} , α_{cal} , and n are experimental CO₂ solubility, calculated CO₂ solubility, and number of data point, respectively.

4.4. Empirical model for equilibrium CO₂ solubility into aqueous EAE and AEEA blend

An empirical model was also developed to predict the equilibrium CO₂ 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 °C), partial pressure of CO₂ (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 °C unit in the model equation. The variation of CO₂ 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 Fig. S2 to Fig. S5 and given in supporting information. It

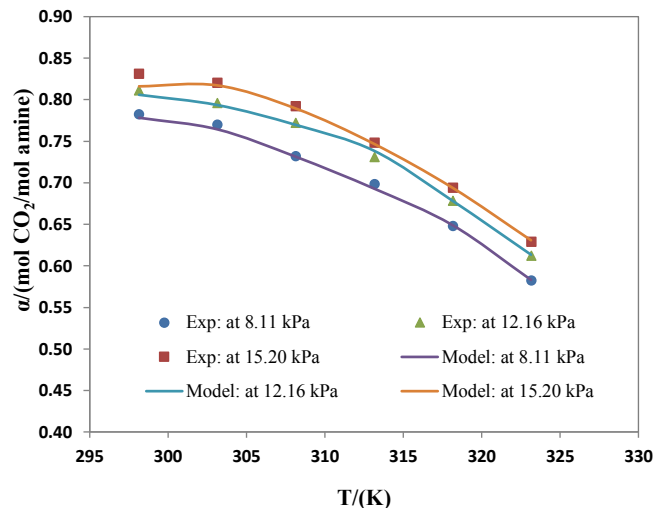


Fig. 6. Effect of temperature on the CO₂ solubility for the 30 wt% (21 wt% + 9 wt%) aqueous EAE and AEEA blend of constant concentration: Experimental (Exp.) and model (Eq. (35)) predicted data.

was assumed that CO₂ 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. (40):

$$\alpha = c_1 + c_2 t + c_3 t^2 + c_4 p_{CO_2} + c_5 p_{CO_2}^2 + c_6 w_{AEEA} + c_7 w_{AEEA}^2 + c_8 C_T + c_9 C_T^2 \quad (40)$$

Where, c_1 to c_9 are the coefficients of the equation. t , p_{CO_2} , w_{AEEA} and C_T are temperature (°C), partial pressure of CO₂ (kPa), weight fraction of

Table 3

Values of coefficients for temperature dependent equilibrium constants.

Parameter	a	b	c	Temperature validity range (°C)	source
K_1	140.932	-13445.9	-22.4773	0–225	Edwards et al. [50]
K_6	235.482	-12092.1	-36.7816	0–225	Edwards et al. [50]
K_7	220.067	-12431.7	-35.4819	0–225	Edwards et al. [50]

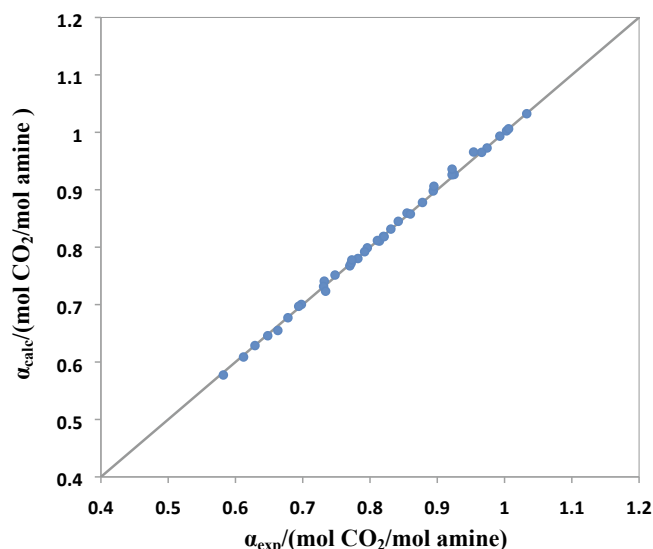
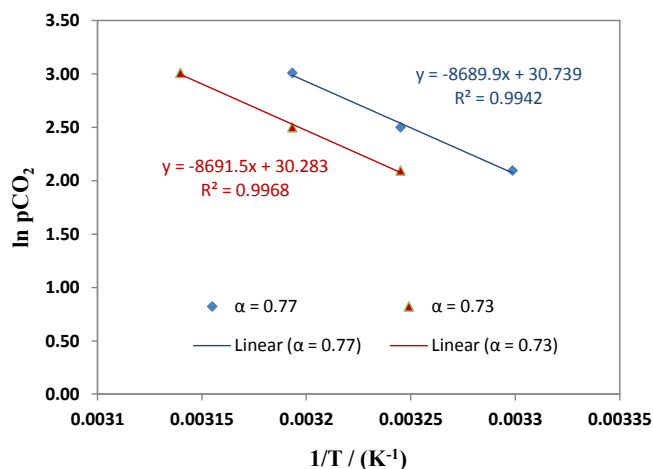
Table 4

Regressed coefficients of Eq. (38) for estimated reaction equilibrium constants.

Parameter	c_1	c_2	c_3	c_4	c_5	c_6
K_2	0.206621	0.199805	1.363386	0.082141	-4.154564	0.859012
K_3	0.475563	0.297655	1.185646	0.078655	-3.651552	0.923556
K_4	0.349855	0.656867	0.975556	0.078655	-9.286135	0.455621
K_5	-2.118026	946.610456	-0.049643	-1.387437	0.378564	3.238086
K_8	-20.561489	-1319.496376	0.435377	0.841057	-0.465212	4.754323
K_9	0.248999	-2.463233	0.236565	0.007866	-11.267815	-6.212356
K_{10}	-5.196909	-1211.034896	-0.049307	-3.010367	0.114387	2.721228
K_{11}	-11.482604	-2111.696465	-0.048676	-6.260371	-0.404893	1.552714
K_{12}	-12.036449	-532.696465	-0.675803	-6.260371	-0.634569	1.347207

Table 5Values of coefficients of model (Eq. (40)) to calculate equilibrium CO₂ 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

**Fig. 7.** Parity plot of experimental and calculated (by Eq. (40)) CO₂ solubility for the aqueous EAE and AEEA blend.**Fig. 8.** Plot of $\ln(p_{CO_2})$ vs. $(1/T)$ for the 30 wt% (21 wt% + 9 wt%) aqueous EAE and AEEA blend.

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 5. Predicted CO₂ solubility data were best fitted to experimental CO₂ solubility data. Parity plot between experimental and calculated CO₂ solubility was given in Fig. 7. AAD % for this empirical model was reported as 0.45%.

4.5. Heat of CO₂ absorption (ΔH_{abs})

The ΔH_{abs} is the heat generated during CO₂ absorption into the aqueous amine. Higher amount of heat of absorption employed higher heat of regeneration of absorbent. In the present work, experimental CO₂ solubility data of aqueous EAE and AEEA blend given in Table 2 was used to determine heat of absorption by Gibbs-Helmholtz equation [39]. Fig. 8 exhibited graph of $\ln(p_{CO_2})$ vs. $(1/T)$ for the 30 wt% (21 wt% + 9 wt%) aqueous EAE and AEEA blend which was plotted using three points of T and p_{CO_2} at similar CO₂ solubility nearly 0.73 (mol CO₂/mol amine) and 0.77 (mol CO₂/mol amine). Slope of the curves of $\ln(p_{CO_2})$ vs. $(1/T)$ were -8689.9 and -8691.5 for CO₂ solubility 0.73 and 0.77 (mol CO₂/mol amine), respectively. ΔH_{abs} was calculated by multiplying R (8.1314 J/mol.K) into the average value of slopes. Heat of CO₂ absorption for aqueous (21 wt% + 9 wt%) EAE + AEEA blend was -72.25 kJ/mol. Negative values of ΔH_{abs} show that CO₂ absorption into the aqueous EAE and AEEA blend is an exothermic reaction. It is higher than tertiary amines (MDEA; -54.6 kJ/mol) [40], but lower than industrially used benchmark primary amine (MEA; -85.13 kJ/mol) [24]. 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 CO₂ 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.

4.6. CO₂ desorption study

Cyclic CO₂ solubility or cyclic capacity of absorbent is an important factor for selection of absorbent for industrial use purpose to capture CO₂. In order to investigate cyclic capacity of aqueous EAE and AEEA blend, desorption experiment was performed. CO₂ saturated samples at 15.2 kPa of CO₂ partial pressure and 313.15 K temperature of absorption experiment used for desorption study at 393.15 K temperature. Fig. 8 showed that variation of CO₂ solubility with time for 30 wt% EAE and AEEA (21 wt% EAE + 9 wt% AEEA) solution and 30 wt% MEA solution.

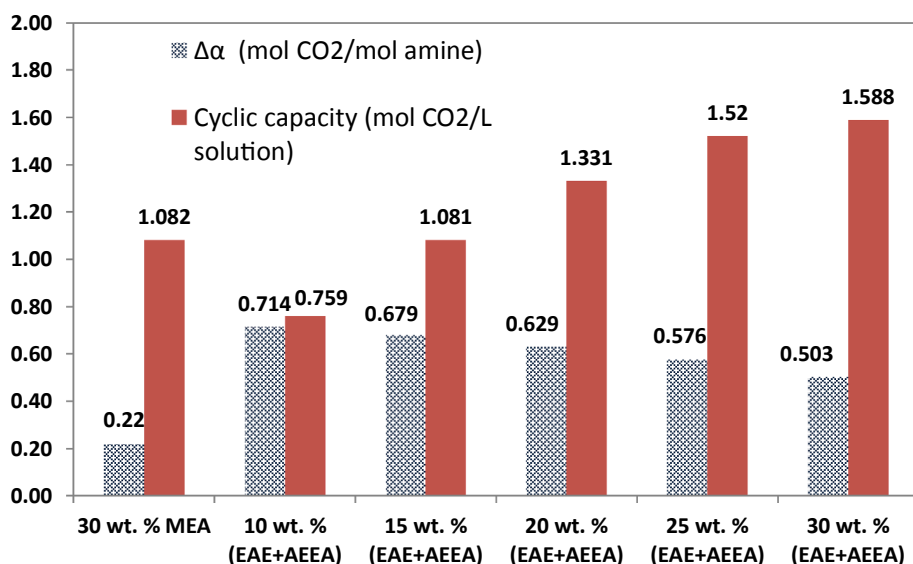


Fig. 9. Cyclic CO₂ solubility and cyclic absorption capacity of 30 wt MEA solution and aqueous EAE and AEEA blend with 0.30 w_{AEEA}.

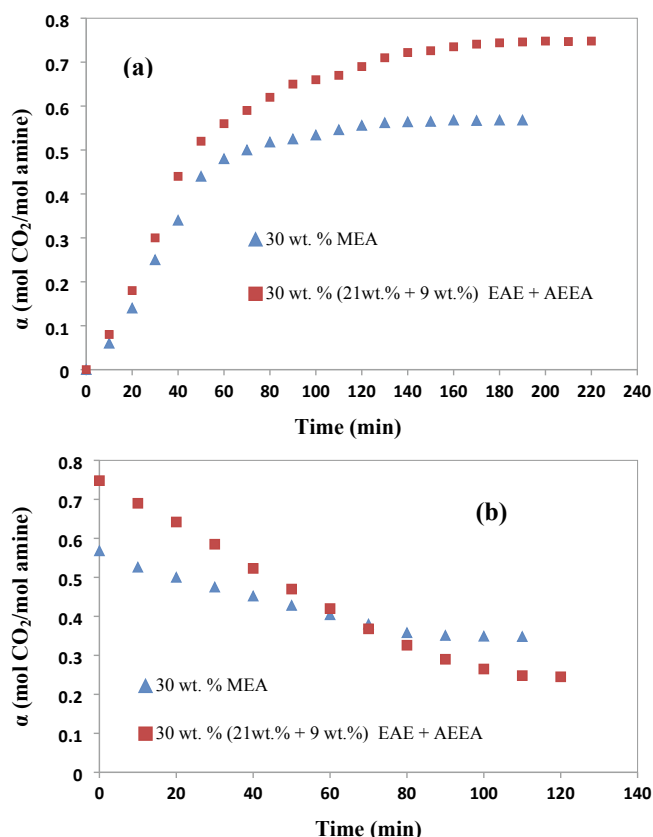


Fig. 10. CO₂ solubility vs. time plot of 30 wt% MEA and 30 wt% (21 wt% + 9 wt%) aqueous EAE and AEEA blend during (a) CO₂ absorption, and (b) CO₂ desorption.

Slope of curve for EAE and AEEA blend was greater than slope of curve of 30 wt% MEA solution initially. Fig. 9 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 CO₂ capture unit in the plant.

4.7. Rate of change of initial CO₂ solubility

The rate of change of initial CO₂ solubility into the 30 wt% aqueous EAE and AEEA blend with 0.30 wt fraction of AEEA and 30 wt% MEA was studied. It was investigated using CO₂ solubility with respect to time data for absorption and desorption. From CO₂ solubility (mol CO₂/mol amine) vs. time (min) graph, shown in Fig. 10, it could be seen that initially CO₂ solubility varied linearly for absorption as well as desorption of CO₂. Initial variation of CO₂ solubility with respect to time was found by determining slope of the linear portion of curve and mathematically can be written as Eqs. (41) and (42).

$$\text{Rate of change of initial CO}_2 \text{ solubility} = \frac{d\alpha}{dt} \quad (41)$$

$$\frac{d\alpha}{dt} = (\text{slope of linear portion of } \alpha \text{ vs. time curve}) \quad (42)$$

Slope of linear portion of CO₂ solubility vs. time (t) curve could be seen in Fig. S6 in supporting information file. Initial change of CO₂ solubility during absorption in 30 wt% (21 wt% + 9 wt%) aqueous EAE and AEEA was 21.1% more than in MEA solution. It could be interpreted that faster reaction kinetics of CO₂ 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 CO₂ into absorbents could be done. Negative slope of linear portion of CO₂ solubility vs. time curve in Fig. S7 indicated that initial decrease in CO₂ solubility with respect to time. Dissociation of CO₂ was more rapid in EAE and AEEA blend as compared to MEA. Rate of change of CO₂ 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 CO₂ saturated EAE and AEEA solution. Those were less thermally stable than primary carbamate present in CO₂ saturated MEA solution and aqueous EAE and AEEA blend can be regenerated easily than MEA solution.

5. Conclusions

In this research paper, performance of aqueous EAE and AEEA blend was investigated for post-combustion CO₂ capture at atmospheric pressure. Equilibrium CO₂ solubility into the blend of EAE and AEEA solution was found out varying different composition and operating conditions. Highest CO₂ solubility was occurred at 298.15 K, 20.27 kPa CO₂ partial pressure, 0.30 wt 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 predict CO₂ solubility (mol CO₂/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 wt fraction of AEEA solution were compared with 30 wt% MEA solution (benchmark absorbent for CO₂ capture) and concluded as follows:

- At 313.15 K and 15.20 kPa CO₂ partial pressure, 31.69% more equilibrium CO₂ solubility into EAE and AEEA blend than MEA solution was obtained.
- 15.13% less heat of CO₂ absorption was found as compared to MEA solution resulting less energy requirement for CO₂ capture.
- Initial rate of change of CO₂ solubility were 21.10% and 100% more in EAE and AEEA solution during absorption and desorption of CO₂, respectively.
- Cyclic CO₂ 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 CO₂ solubility, lesser heat of absorption, more cyclic capacity and faster rate of change of initial CO₂ solubility than MEA. Therefore, further research on EAE and AEEA blend would be carried out and it would be used for CO₂ capture in industries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors acknowledge the support and financial assistance provided by the Indian Institute of Technology (Banaras Hindu University) Varanasi and Ministry of human resource development, Government of India to carry out the present work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2020.128334>.

References

- [1] G.E. Iea, Two Million and Counting, International Energy Agency, Outlook (2017).
- [2] N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C.K. Williams, N. Shah, P. Fennell, An overview of CO₂ capture technologies, *Energy Environ. Sci.* 3 (11) (2010) 1645–1669.
- [3] B.K. Mondal, S.S. Bandyopadhyay, A.N. Samanta, Vapor–liquid equilibrium measurement and ENRTL modeling of CO₂ absorption in aqueous hexamethylenediamine, *Fluid Phase Equilib.* 402 (2015) 102–112.
- [4] G.T. Rochelle, Amine Scrubbing for CO₂ Capture, *Science* 325 (2009) 1652–1654.
- [5] M. Bui, C.S. Adjiman, A. Bardow, E.J. Anthony, A. Boston, S. Brown, P.S. Fennell, S. Fuss, A. Galindo, L.A. Hackett, J.P. Hallett, Carbon capture and storage (CCS): the way forward, *Energy Environ. Sci.* 11 (5) (2018) 1062–1176.
- [6] P. Tontiwachwuthikul, A. Meisen, C.J. Lim, Solubility of carbon dioxide in 2-amino-2-methyl-1-propanol solutions, *J. Chem. Eng. Data* 36 (1991) 130–133.
- [7] H.A. Haider, R. Yusoff, M.K. Aroua, Equilibrium solubility of carbon dioxide in 2 (methylamino) ethanol, *Fluid Phase Equilib.* 303 (2011) 162–167.
- [8] S.J. Hwang, J. Kim, H. Kim, K.S. Lee, Solubility of carbon dioxide in aqueous solutions of three secondary amines: 2-(butylamino) ethanol, 2-(isopropylamino) ethanol, and 2-(ethylamino) ethanol secondary alkanolamine solutions, *J. Chem. Eng. Data* 62 (2017) 2428–2435.
- [9] G. Rochelle, E. Chen, S. Freeman, D. Van Wagener, Q. Xu, A.K. Voice, Aqueous piperazine as the new standard for CO₂ capture technology, *Chem. Eng. J.* 171 (2011) 725–733.
- [10] S. Zhou, X. Chen, T. Nguyen, A.K. Voice, G.T. Rochelle, Aqueous ethylenediamine for CO₂ capture, *Chem. Sus. Chem.* 3 (2010) 913–918.
- [11] J. Gao, J. Yin, F. Zhu, X. Chen, M. Tong, W. Kang, Y. Zhou, J. Lu, Post-combustion CO₂ capture using diethylenetriamine (DETA) solvent in a pilot-plant test bed compared to monoethanolamine (MEA) solvent, *Env. Prog. Sus. Energy* 36 (2017) 1131–1138.
- [12] A. Schäffer, K. Brechtel, G. Scheffknecht, Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO₂ capture from flue gases, *Fuel* 101 (2012) 148–153.
- [13] U.E. Aronu, H.F. Svendsen, K.A. Hoff, O. Juliussen, Solvent selection for carbon dioxide absorption, *Energy Procedia* 1 (2009) 1051–1057.
- [14] F.Y. Jou, A.E. Mather, F.D. Otto, The solubility of CO₂ in a 30 mass percent monoethanolamine solution, *Can. J. Chem. Eng.* 73 (1995) 140–147.
- [15] J.P. Jakobsen, J. Krane, H.F. Svendsen, Liquid-phase composition determination in CO₂–H₂O–alkanolamine systems: An NMR study, *Ind. Eng. Chem. Res.* 44 (2005) 9894–9903.
- [16] R. Idem, M. Wilson, P. Tontiwachwuthikul, A. Chakma, A. Veawab, A. Aroonwilas, D. Gelowitz, Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the boundary dam CO₂ capture demonstration plant, *Ind. Eng. Chem. Res.* 45 (2006) 2414–2420.
- [17] Z.H. Liang, W. Rongwong, H. Liu, K. Fu, H. Gao, F. Cao, R. Zhang, T. Sema, A. Henni, K. Sumon, D. Nath, Recent progress and new developments in post-combustion carbon-capture technology with amine-based solvents, *Int. J. Greenh. Gas Cont.* 40 (2015) 26–54.
- [18] Z. Liang, K. Fu, R. Idem, P. Tontiwachwuthikul, Review on current advances, future challenges and consideration issues for post-combustion CO₂ capture using amine-based absorbents, *Chin. J. Chem. Eng.* 24 (2016) 278–288.
- [19] R. Hamidi, M. Farsi, R. Eslamloueyan, CO₂ solubility in aqueous mixture of MEA, MDEA and DAMP: Absorption capacity, rate and regeneration, *J. Mol. Liq.* 265 (2018) 711–716.
- [20] D. Tong, G.C. Maitland, M.J. Trusler, P.S. Fennell, Solubility of carbon dioxide in aqueous blends of 2-amino-2-methyl-1-propanol and piperazine, *Chem. Eng. Sci.* 101 (2013) 851–864.
- [21] M. Shokouhi, A.T. Zoghi, M. Vahidi, B. Moshtari, Solubility of carbon dioxide in aqueous blends of 2-amino-2-methyl-1-propanol and N-methyldiethanolamine, *J. Chem. Eng. Data* 60 (2015) 1250–1258.
- [22] H. Gao, Z. Wu, H. Liu, X. Luo, Z. Liang, Experimental studies on the effect of tertiary amine promoters in aqueous monoethanolamine (MEA) solutions on the absorption/stripping performances in post-combustion CO₂ capture, *Energy & Fuels* 31 (2017) 13883–13891.
- [23] H.K. Knuutila, Å. Nannestad, Effect of the concentration of MAPA on the heat of absorption of CO₂ and on the cyclic capacity in DEEA-MAPA blends, *Int. J. Greenh. Gas Cont.* 61 (2017) 94–103.
- [24] H.N. El, D.V. Quang, E.L. Goetheer, M.R. Zahra, Aqueous amine solution characterization for post-combustion CO₂ capture process, *Appl. Energy* 185 (2017) 1433–1449.
- [25] W. Conway, Y. Beyad, P. Feron, G. Richner, G. Puxty, CO₂ absorption into aqueous amine blends containing benzylamine (BZA), monoethanolamine (MEA), and sterically hindered/tertiary amines, *Energy Procedia* 63 (2014) 1835–1841.
- [26] P.N. Sutar, P.D. Vaidya, E.Y. Kenig, Activated DEEA solutions for CO₂ capture—A study of equilibrium and kinetic characteristics, *Chem. Eng. Sci.* 100 (2013) 234–241.
- [27] P. Muchan, J. Narku-Tetteh, C. Saiwan, R. Idem, T. Supap, Effect of number of amine groups in aqueous polyamine solution on carbon dioxide (CO₂) capture activities, *Sep. Purif. Technol.* 184 (2017) 128–134.
- [28] P. Muchan, C. Saiwan, J. Narku-Tetteh, R. Idem, T. Supap, P. Tontiwachwuthikul, Screening tests of aqueous alkanolamine solutions based on primary, secondary, and tertiary structure for blended aqueous amine solution selection in post combustion CO₂ capture, *Chem. Eng. Sci.* 170 (2017) 574–582.
- [29] C. Nwaoha, R. Idem, T. Supap, C. Saiwan, P. Tontiwachwuthikul, W. Rongwong, M. J. Al-Marri, A. Benamor, Heat duty, heat of absorption, sensible heat and heat of vaporization of 2-Amino-2-Methyl-1-Propanol (AMP), Piperazine (PZ) and Monoethanolamine (MEA) tri-solvent blend for carbon dioxide (CO₂) capture, *Chem. Eng. Sci.* 170 (2017) 26–35.
- [30] S.K. Wai, C. Nwaoha, C. Saiwan, R. Idem, T. Supap, Absorption heat, solubility, absorption and desorption rates, cyclic capacity, heat duty, and absorption kinetic modeling of AMP–DETA blend for post-combustion CO₂ capture, *Sep. Pur. Tech.* 194 (2018) 89–95.
- [31] P.D. Vaidya, E.Y. Kenig, Absorption of CO₂ into aqueous blends of alkanolamines prepared from renewable resources, *Chem. Eng. Sci.* 62 (24) (2007) 7344–7350.
- [32] S. Ma'mun, H.F. Svendsen, K.A. Hoff, O. Juliussen, Selection of New Absorbents for Carbon Dioxide Capture, *Energy Convers. Manage.* 48 (2007) 251–258.
- [33] S. Mamun, V.Y. Dindore, H.F. Svendsen, Kinetics of the reaction of carbon dioxide with aqueous solutions of 2-((2-aminoethyl) amino) ethanol, *Ind. Eng. Chem. Res.* 46 (2007) 385–394.
- [34] A. Bajpai, M.K. Mondal, Equilibrium Solubility of CO₂ in Aqueous Mixtures of DEA and AEEA, *J. Chem. Eng. Data* 58 (2013) 1490–1495.
- [35] S. Kumar, M.K. Mondal, Equilibrium solubility of CO₂ in aqueous blend of 2-(diethylamine) ethanol and 2-(2-aminoethylamine) ethanol, *J. Chem. Eng. Data* 63 (2018) 1163–1169.
- [36] M. Moosavi, C.J. Sisco, A.A. Rostami, F.M. Vargas, Thermodynamic properties and CO₂ solubility of monoethanolamine + diethylenetriamine/ aminoethylethanolamine mixtures: Experimental measurements and thermodynamic modeling, *Fluid Phase Equilib.* 449 (2017) 175–185.

- [37] S. Kumar, M.K. Mondal, Selection of efficient absorbent for CO₂ capture from gases containing low CO₂, *Korean J. Chem. Eng.* 37 (2) (2020) 231–239.
- [38] W. Horwitz, Association of official analytical chemists (AOAC) methods, George Banta Company, Menasha, WI, 1975.
- [39] I. Kim, H.F. Svendsen, Heat of absorption of carbon dioxide (CO₂) in monoethanolamine (MEA) and 2-(aminoethyl) ethanolamine (AEEA) solutions, *Ind. Eng. Chem. Res.* 46 (2007) 5803–5809.
- [40] M. Xiao, D. Cui, H. Liu, P. Tontiwachwuthikul, Z. Liang, A new model for correlation and prediction of equilibrium CO₂ solubility in N-methyl-4-piperidinol solvent, *AIChE J.* 63 (2017) 3395–3403.
- [41] R.L. Kent, B. Eisenberg, Better data for amine treating, *Hydrocarbon Process* 55 (1976) 87–90.
- [42] B.K. Mondal, A.N. Samanta, Equilibrium solubility and kinetics of CO₂ absorption in hexamethylenediamine activated aqueous sodium glycinate solvent, *Chem. Eng. J.* 386 (2020), 121462.
- [43] P.Y. Chung, A.N. Soriano, R.B. Leron, M.H. Li, Equilibrium solubility of carbon dioxide in the amine solvent system of (triethanolamine + piperazine + water), *J. Chem. Thermodyn.* 42 (2010) 802–807.
- [44] D. Le Tourneaux, I. Iliuta, M.C. Iliuta, S. Fradette, F. Larachi, Solubility of carbon dioxide in aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol, *Fluid Phase Equilibria* 268 (2008) 121–129.
- [45] M.K. Aroua, R. Mohd Salleh, Solubility of CO₂ in Aqueous Piperazine and its Modeling using the Kent-Eisenberg Approach, *Chem. Eng. Technol.* 27 (1) (2004) 65–70.
- [46] P. Kumar, J. Hogendoorn, S.J. Timmer, P.H.M. Feron, G.F. Versteeg, Equilibrium solubility of CO₂ in aqueous potassium taurate solutions: Part 2: Experimental VLE data and model, *Ind. Eng. Chem. Res.* 42 (12) (2003) 2841–2852.
- [47] Y.-H. Hsu, R.B. Leron, M.-H. Li, Solubility of carbon dioxide in aqueous mixtures of (reline+monoethanolamine) at T = (313.2 to 353.2)K, *J. Chem. Thermodyn.* 72 (2014) 94–99.
- [48] G. Puxty, R. Rowland, A. Allport, Q. Yang, M. Bown, R. Burns, M. Maeder, M. Attalla, Carbon dioxide post-combustion capture: a novel screening study of the carbon dioxide absorption performance of 76 amines, *Env. Sci. Technol.* 43 (16) (2009) 6427–6433.
- [49] F.A. Chowdhury, H. Yamada, Y. Matsuzaki, K. Goto, T. Higashii, M. Onoda, Development of novel synthetic amine absorbents for CO₂ capture, *Energy Procedia* 63 (2014) 572–579.
- [50] T.J. Edwards, G. Maurer, J. Newman, J.M. Prausnitz, Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes, *AIChE J.* 24 (1978) 966–976.