



Full Length Article

Elucidating the performance of (N-(3-aminopropyl)-1, 3-propanediamine) activated (1- dimethylamino-2-propanol) as a novel amine formulation for post combustion carbon dioxide capture



Anirban Dey^{a,b}, Sukanta Kumar Dash^b, Bishnupada Mandal^{a,*}

^a Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, India

^b CO₂ Research Group- Department of Chemical Engineering, Pandit Deendayal Petroleum University, Gandhinagar 382007, India

ARTICLE INFO

Keywords:

Carbon dioxide
Equilibrium solubility
APDA
1DMAP
Kent-Eisenberg modeling

ABSTRACT

The exploration of energy-efficient amine solvents for CO₂ removal from flue gas streams has been adopted as a key strategy for the wide implementation of CO₂ capture technology in fossil fuel-based power plants for post-combustion CO₂ capture. The current study entails an insight into the CO₂ absorption performance of a novel aqueous amine blend of N-(3-aminopropyl)-1,3-propanediamine (APDA) and 1-dimethylamino-2-propanol (1DMAP) with special emphasis to the investigation of CO₂ solubility at equilibrium state. In order to investigate the effect of promoter addition, the concentration of APDA has been gradually increased from 0.02 w to 0.10 w in the mixed solvent blend. The generated solubility data are correlated using two different modeling approaches viz., equilibrium based modified form of Kent-Eisenberg (KE) thermodynamic model and feed-forward neural network model. The model prediction is further extended to estimate pH and the overall speciation profile of all the molecular as well as ionic species prevailing in the solvent system. The CO₂ solubility data are also analyzed in view of estimating the heat duty requirement for the absorption process. The heat of absorption of CO₂ in aqueous (APDA + 1DMAP) blend has been calculated using the Gibbs-Helmholtz equation. Along with solubility measurement, important thermophysical properties such as density and viscosity of the aqueous amine solution are also measured and correlated using established Redlich-Kister and Grunberg Nissan models.

1. Introduction

With the advent of the alarming rise in the atmospheric carbon dioxide (CO₂) level owing to the rapid industrialization, there has been an increase in global warming issues across the world. The consumption of coal primarily as an energy source in power plants has led to the emission of CO₂ along with other potentially toxic gases that can seriously impact the overall environmental scenario. In this context, several approaches have been explored in the recent past to capture CO₂ from point sources such as gas treating units, natural gas processing as well as fossil fuel-driven power plants. Among all the suitable techniques, solvent aided chemical absorption process is the most exploited and mature technology studied globally for CO₂ capture applications [1–4]. Although it is a proven technology in the natural gas processing plant, it faces severe technological constraints when applied in thermal power plants. The list includes higher flue gas temperature (~150 °C), lower CO₂ partial pressure which reduces the driving force for overall mass transfer, the presence of other contaminant gases such as SO₂,

NO_x and other particulate matter in the exhaust stream [5]. Another crucial factor is the higher energy consumption of the whole process, which is directly influenced by the higher amount of energy spent in the solvent regeneration process. The conventional solvent employed in gas treating applications such as monoethanolamine (MEA), diethanolamine (DEA) suffers from various drawbacks such as higher solvent degradation rate, lower capacity as well as higher stripping heat duty requirement [3,6,7]. Therefore developing new amine formulations with improved properties such as high CO₂ solubility, faster kinetics, lower energy penalty as well as better resistance to thermal degradation, is the prime objective for meeting the process needs of the wide implementation of absorption led technology in gas treating units [1].

Tertiary amines such as methyldiethanolamine (MDEA) have been employed for decades in the absorption of CO₂ from exhaust gas streams since it is inherited with various desirable traits, significant among them are its higher solvent capacity as well as lower reboiler heat duty requirements [8–10]. However, the slower kinetics induces its limitation of being used as a sole solvent in the aqueous medium.

* Corresponding author.

E-mail address: bpmandal@iitg.ernet.in (B. Mandal).

<https://doi.org/10.1016/j.fuel.2020.118209>

Received 11 March 2020; Received in revised form 29 April 2020; Accepted 24 May 2020

Available online 05 June 2020

0016-2361/ © 2020 Elsevier Ltd. All rights reserved.

Nomenclature			
P_{CO_2}	Equilibrium CO ₂ partial pressure, (kPa)	H_{CO_2}	Henry's Law constant of CO ₂ in the solvent, (kPa.m ³ .kmol ⁻¹)
P_t	Total pressure in the equilibrium cell, (kPa)	S	Error in objective function
P^v	Solution vapour pressure in the equilibrium cell, (kPa)	N	Total set of data points
P_{b1}	Initial buffer cell pressure, (kPa)	m_1	Initial APDA molar concentration, (kmol.m ⁻³)
P_{b2}	Final buffer cell pressure, (kPa)	M_2	Initial 1DMAP molar concentration, (kmol.m ⁻³)
w	Mass fraction	X_i	Input variable
T	Temperature, (K)	Y_i	Output variable
V_b	Volume of buffer cell, (m ³)	ρ_i	Weight coefficient
V_g	Volume of gas phase in the equilibrium cell, (m ³)	b_i	Bias associated with each weight coefficient
R	Universal gas constant, (8.314 J.mole ⁻¹ .K ⁻¹)	ΔH_{abs}	Heat of absorption of CO ₂ in the solvent, (kJ.mol ⁻¹)
$n_{CO_2}^T$	Moles of CO ₂ transferred from buffer cell to equilibrium cell	V^E	Excess Molar volume, (m ³ .kmol ⁻¹)
$n_{CO_2}^g$	Moles of CO ₂ corresponding to gas phase in the equilibrium cell	A^P	Temperature based pair parameter for correlating excess molar volume.
n_{am}	Moles of amine in the solvent mixture	ρ_m	Experimentally measured density of aqueous amine mixture, (kg.m ⁻³)
Z_1	Compressibility factor corresponding to initial buffer cell pressure	x^i	Mole fraction of pure component in the amine mixture
Z_2	Compressibility factor corresponding to final buffer cell pressure	w	Mass fraction of amine
Z_{CO_2}	Compressibility factor corresponding to the equilibrium P _{CO2}	α_{CO_2}	CO ₂ loading in the solvent phase, (mole CO ₂ / mole of amine)
K_i	Reaction Equilibrium constant, (kmol.m ⁻³ basis)	μ_m	Experimentally measured viscosity of aqueous amine mixture, (mPa.s)
		G_{ij}	Temperature based pair parameter for correlating viscosity data.

Recently a new class of tertiary amine, 1-dimethylamino-2-propanol (1DMAP) has drawn considerable attention because of its superior characteristics over its conventional counterpart *N*-methyldiethanolamine (MDEA) [11–13]. The reported result reveals higher kinetics of CO₂ absorption along with good solvent capacity and lower energy penalty. The second-order rate constant of (1DMAP-CO₂) reaction has been found to be 70 m³.kmol⁻¹.s⁻¹ at 313 K as compared to 28 m³.kmol⁻¹.s⁻¹ for MDEA-CO₂ reaction. Also, the heat of CO₂ absorption in 1DMAP solution has been estimated to be 30.5 kJ.mol⁻¹ [11,12]. The lower regeneration energy can be expressed in line with its reaction mechanism. The tertiary amines mostly follow a base-catalyzed hydration mechanism where the amines do not exhibit direct reaction with CO₂ instead in an aqueous medium it promotes the hydrolysis of CO₂ to form bicarbonates as the major reaction species [14]. Although 1DMAP showcases superior kinetics compared to MDEA however it exhibits relatively slower reaction rate when compared against other conventional primary/secondary amines [13]. Due to the prevalence of low reaction rate, the gas treatment operation requires a large number of theoretical stages in the absorption column which in turn increases the tower diameter resulting in higher capital cost of the overall process [11]. To avoid that tertiary amines are often blended with fast-reacting promoters in order to exploit their advantages of substantially higher reaction rate, higher CO₂ loading capacity as well as lower regeneration cost [13,15–18].

Piperazine (PZ), a promising diamine has been rigorously used for decades as a potential rate activator for blending with slow reacting tertiary or sterically hindered amines. However, it faces severe precipitation issues at lower temperature and lean CO₂ loading [19,20]. Hence various other potential polyamines such as hexamethylenediamine (HMDA), 1-(2-aminoethyl) piperazine (AEP), Tetraethylenepentamine (TEPA) has been explored as a promoter for its possible application in gas treating applications [7,21–23]. Recently *N*-(3-aminopropyl)-1,3-propanediamine (APDA) has been proposed as an efficient activator on account of its higher reaction rate and higher equilibrium CO₂ loading [24,25]. The second-order rate constant for APDA-CO₂ reaction has been estimated to be 35775 m³.kmol⁻¹.s⁻¹ which is significantly higher compared to conventional activator Piperazine (PZ) as well as one order higher than monoethanolamine (MEA) [24]. Also, it exhibits higher CO₂ loading of 1.9 (mol of CO₂/mol

of amine) at 185 kPa for 30 wt% aqueous amine solution [25]. Following its desirable traits, (APDA + 1DMAP) can be explored as a novel amine formulation for CO₂ capture from exhaust gas streams. To the best of our knowledge, reliable CO₂ solubility data in aqueous (APDA + 1DMAP) is not available in the open literature. This data is an essential prerequisite for the rational process design of absorber-and-regenerator unit in gas treatment operation. Again, solubility data can be eventually used for calculating the speciation profile as well as minimum recirculation rate for treating the CO₂ loaded rich stream [7,14,26]. Along with precise experimental measurement, the development of reliable modeling approaches is also very much essential for detailed investigation. The experimental results are modeled using an equilibrium based modified form of Kent-Eisenberg (KE) model [27–29]. Also, the thermodynamic framework of the modified Kent-Eisenberg model adopted in the present work relies on the fact that the fugacity coefficients in the gas phase are assumed as 1 (an ideal condition in the gas phase). The activity coefficients corresponding to the entire molecular, as well as ionic species are also considered to be unity in the electrolyte system. This key assumption further makes this model much simpler and it reduces the overall computation time in comparison with other rigorous models such as electrolyte-NRTL, UNIQUAC and Clegg-Pitzer [13,30,31]. In addition to this, the applicability of multilayer based (FFNN) model has been also evaluated to correlate the phase equilibrium data throughout the entire experimental realm. The network architecture is implemented by incorporating the optimized network parameters such as the selection of proper training algorithms, neurons as well as transfer function for each network layer [14,20,25,28].

The prime objective of the present work is to comprehensively study the performance of aqueous (APDA + 1DMAP) system in terms of equilibrium CO₂ solubility and heat of CO₂ absorption. The study involves the generation of reliable phase equilibrium data related to CO₂ absorption in different compositions of aqueous blended amine system over the broad experimental condition of temperature (303.2 to 323.2) K and equilibrium P_{CO2} of (2–200) kPa, respectively. The reaction scheme, as well as the prevalence of important reaction products, is further confirmed with qualitative ¹³C NMR as well as ATR-FTIR analysis. Along with solubility measurement, the study also outlines the measurement of important thermophysical properties such as density

and viscosity of the aqueous amine solution, another important prerequisite data for process design.

2. Experimental

2.1. Materials

The reagent grade chemicals used in the present work viz., 1-di-methylamino-2-propanol (1DMAP), and N-(3-aminopropyl)-1,3-propandiamine having a purity of (> 99%) have been arranged from Sigma Aldrich (USA) and used in the experiment without further refinement. The CO₂ gas having mass fraction purity of (> 99.9%) is acquired from Linde India Ltd. The entire solvent blend used in the present work has been prepared using double-distilled deionized water.

2.2. Equilibrium CO₂ solubility measurements

The equilibrium CO₂ solubility over the entire range of operating conditions was measured using temperature-controlled stirred cell arrangement. The detailed specification of the experimental setup and methodology can be found elsewhere and has been briefly described here [14,20].

The experimental arrangement comprises of equilibrium cell where the reactions between amine solvent and CO₂ gas takes place. The reaction cell was again connected with buffer cell used for storing the gas under the desired conditions of experimental temperature. For accurate pressure and temperature monitoring, both the cells are equipped with pressure transducer and temperature sensors. At the beginning of each experiment, both the cell was allowed to attain the desired thermal equilibrium using circulating temperature-controller attached to the thermostatic bath. Also, to remove any trace impurities, the air molecules existing in both the cell were simultaneously evacuated by implementing the attached vacuum pump. Following the evacuation step, a known amount of amine solvent (50 ml) was allowed to enter the equilibrium cell. Subsequently, the system is evacuated again and it is kept at the experimental state further so that the solvent prevails under its own vapour pressure (P_v). After the vapor pressure measurement, purified CO₂ gas present in the buffer cell was made to enter the equilibrium cell and the pressure corresponding to the buffer cell prior to (P_{b1}) and after the transfer process (P_{b2}) were recorded. The chemical absorption process undergoing inside the equilibrium cell results in the system pressure to get reduced gradually. The decrement in the pressure continues until the system attains equilibrium state, which can be characterized with no net variation in the total pressure indicated at the equilibrium cell for the duration of 1 h. During this instant, the equilibrium CO₂ partial pressure (P_{CO_2}) was estimated using the relation, $P_{CO_2} = (P_i - P_r)$ [27]. The amount of CO₂ absorbed in the solvent phase can be expressed in terms of CO₂ loading or normalized (α_{CO_2}):

$$\alpha_{CO_2} = \frac{n_{CO_2}^T - n_{CO_2}^g}{n_{am}} \quad (1)$$

where n_{am} relates to the total moles of amine introduced into the equilibrium cell, $n_{CO_2}^T$ represents the total amount of reactant gas CO₂ passed into the stirred reactor via buffer cell storage in molar basis and $n_{CO_2}^g$ stands for the total moles of CO₂ prevailing in the gaseous phase of equilibrium cell, which can be estimated as:

$$n_{CO_2}^T = \frac{V_b}{RT} \left(\frac{P_{b1}}{Z_1} - \frac{P_{b2}}{Z_2} \right) \quad (2)$$

$$n_{CO_2}^g = \frac{V_g P_{CO_2}}{RT Z_{CO_2}} \quad (3)$$

In the above equations (2 and 3), Z_1 , Z_2 represents the compressibility factor corresponding to the initial as well as final system pressure existing inside the buffer cell after the transfer of CO₂ gas into equilibrium cell. Whereas, Z_{CO_2} relates to the equilibrium P_{CO_2} which can be

calculated using Peng-Robinson equation of state [26,30]. Although compressibility factor (Z_{CO_2}) is incorporated in Eq. (3) to account for the non-ideality in the gas phase system, their values are ~ 1 . This is due to the fact that the experimental CO₂ partial pressure has been kept low in the equilibrium cell and at the prevailing experimental conditions of temperature and pressure, the vapour phase can be considered to behave ideally having fugacity coefficients nearly unity. The similar methodology can be further continued to generate the solubility data as a function of P_{CO_2} at different conditions of temperature and composition of amine blends. The corresponding standard uncertainty wrt to the generated (α_{CO_2}) has been estimated to be $\pm 5\%$.

2.3. Measurement of thermophysical properties

The key thermophysical properties of the aqueous blended solvent such as density and viscosity were measured at different temperature intervals using Anton Paar supplied digital densitometer (Model: DMA 4500) aided with vibrating oscillating tube and Rolling ball viscometer (Model: Lovis 2000 M/ME). Both the instruments are working on the Peltier mechanism and also acquainted with viscosity correction factor over the complete set of experimental conditions. Before the experimental run, the devices were calibrated with deionized water corresponding to each investigational temperature conditions. The maximum standard uncertainty recorded for each corresponding density as well viscosity measurement has been considered as $\pm 0.05 \text{ kg.m}^{-3}$ and $\pm 0.5\%$ respectively whereas the system temperature was precisely controlled within the range of $\pm 0.02 \text{ K}$.

3. Correlation of CO₂ solubility data at equilibrium state

The equilibrium α_{CO_2} data of aqueous APDA activated 1DMAP blended amine system generated in the present study is correlated via two different approaches, modified Kent-Eisenberg as well as Feed Forward neural network model.

3.1. Modified KE model

The APDA-1DMAP reaction system consists of both chemical and phase equilibria. Amine deprotonation, APDA carbamate formation as well as the formation of bicarbonate species are the major important reactions considered for modeling the current system. As confirmed by Das et al. [24], zwitterion reaction mostly predominates in the APDA-CO₂ system as the polyamine is inherited with two primary and one secondary amine respectively. As a result, it leads to the formation of stable carbamates as the dominant species in the product stream. While in the case of 1DMAP, a tertiary amine, there is no direct reaction with CO₂ instead it leads to the formation of bicarbonate species via hydrolysis reaction of CO₂ gas [11]. As a whole, the general equilibrium reactions considered for the present system can be expressed as:

Physical dissolution of CO₂



Dissociation of water



Formation of bicarbonate ion



Dissociation of bicarbonate ion



Deprotonation of APDA



Carbamate hydrolysis of APDA



Deprotonation of 1DMPH



The important assumption of Kent-Eisenberg (KE) model is based on the fact that the activity coefficients indicative of liquid phase non-ideality and fugacity coefficients relating to gas phase non-ideality are considered as unity since the model neglects the non-ideality pertaining to the liquid phase and gas phase of the amine-CO₂ reaction system [20,28–29]. Hence the equilibrium constants are expressed in terms of concentration of molecular and ionic species. The equilibrium constants can be expressed by Eqs. (4)–(9).

$$K_1 = [H^+][OH^-] \quad (4)$$

$$K_2 = \frac{[HCO_3^-][H^+]}{[CO_2]} \quad (5)$$

$$K_3 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (6)$$

$$K_4 = \frac{[APDA][H^+]}{[APDAH^+]} \quad (7)$$

$$K_5 = \frac{[APDA][HCO_3^-]}{[APDACC\text{O}^-]} \quad (8)$$

$$K_6 = \frac{[DMP][H^+]}{[DMPH^+]} \quad (9)$$

Henry's law can be applied to relate the physically absorbed CO₂ in the blended solvent to the CO₂ partial pressure at equilibrium condition:

$$P_{CO_2} = H_{CO_2}[CO_2] \quad (10)$$

The overall electro neutrality balance corresponding to all the ionic species in the CO₂-amine reaction medium as well as the total amine balance and CO₂ balance equation can be also represented as:

Electroneutrality Balance:

$$[H^+] + [APDAH^+] + [1DMPH^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] - [APDACC\text{O}^-] = 0 \quad (11)$$

APDA Balance:

$$m_1 = [APDA]_t = [APDA] + [APDAH^+] + [APDACC\text{O}^-] \quad (12)$$

1DMPH Balance:

$$m_2 = [1DMPH]_t = [1DMPH] + [1DMPH^+] \quad (13)$$

CO₂ Balance:

$$\alpha_{CO_2} \times (m_1 + m_2) = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [APDACC\text{O}^-] \quad (14)$$

By implementing Eqs. (4)–(13), a polynomial equation as a function of [H⁺] species has been framed which can be again expressed along with different coefficients:

$$L[H^+]^6 + M[H^+]^5 + N[H^+]^4 + O[H^+]^3 + P[H^+]^2 + Q[H^+] + R = 0 \quad (15)$$

Where,

$$\begin{aligned} L &= K_5, \quad M = K_5 \cdot (K_6 + K_4 + m_1 + m_2), \\ N &= K_6 \cdot K_5 \cdot (m_1 + K_4) + K_2 \cdot [CO_2] \cdot (K_4 - K_5) + K_5 \cdot (m_2 \cdot K_4 - K_1), \\ O &= K_2 \cdot K_4 \cdot (K_6 \cdot [CO_2] + m_2 - K_5 \cdot [CO_2] - m_1 \cdot [CO_2]) \\ &\quad - K_5 \cdot (K_2 \cdot K_6 \cdot [CO_2] - K_2 \cdot K_4 \cdot [CO_2]) - K_1 \cdot K_5 \cdot (K_6 + K_4), \\ P &= K_2 \cdot [CO_2] \cdot (-K_4 \cdot K_5 \cdot K_6 - K_2 \cdot K_4 \cdot [CO_2] - 2 \cdot K_3 \cdot K_5 \cdot K_6 - 2 \cdot K_3 \cdot K_4 \cdot K_5 \\ &\quad - K_1 \cdot K_4 - m_1 \cdot K_4 \cdot K_6) - K_1 \cdot K_4 \cdot K_5 \cdot K_6 \\ Q &= K_2 \cdot K_4 \cdot [CO_2] \cdot (-2 \cdot K_3 \cdot K_5 \cdot K_6 - 2 \cdot K_3 \cdot K_2 \cdot [CO_2] - K_1 \cdot K_6 - K_2 \cdot K_6 \cdot [CO_2]) \\ R &= -2 \cdot K_3 \cdot K_2^2 \cdot K_4 \cdot K_6 \cdot [CO_2]^2 \end{aligned}$$

Also, Eq. (14) can be further utilized to derive the expression for estimating the CO₂ loading in the current system.

$$\alpha_{CO_2} = \frac{P_{CO_2}}{H_{CO_2}(m_1 + m_2)} \left[1 + \frac{K_2}{[H^+]} + \frac{K_3 \cdot K_2}{[H^+]^2} + \frac{m_1 \cdot K_2 \cdot K_4}{K_4 \cdot K_5 \cdot [H^+] + K_5 \cdot [H^+]^2 + K_2 \cdot K_4 \cdot [P_{CO_2}/H_{CO_2}]} \right] \quad (16)$$

The concentration of [H⁺] species used in Eq. (16) can be found out by solving Eq. (15) and utilizing the real root of the same under the concentration limit of 10⁻¹² – 10⁻⁶ kmol.m⁻³ (corresponding to pH values in the range of 6 to 12 for the loaded amine solutions).

Kent-Eisenberg in their original work (1976) expresses the equilibrium constant in terms of temperature only [32]. Later, researchers proposed various modifications in the already existing model in order to improve the prediction results of the model [7,10,14,27–29,33–35]. Chakma and Meisen (1987, 1990) stated that in reality the amine-CO₂ reaction system can be considered a non-ideal one [33,34]. The activity coefficients used for defining system non-ideality are composition dependent and hence the equilibrium constants thus derived should also be considered as composition dependent along with the temperature. They have postulated the equilibrium constants of important amine reactions in terms of temperature, acid gas loading, and amine concentration to include all the system non-idealities in the estimation process [33]. Recently, Liu et al. [35] compared various equilibrium based models to correlate the equilibrium CO₂ solubility data in seven novel tertiary amines. Their study reveals the fact that model incorporating a greater number of significant operating parameters can lead to better prediction of CO₂ equilibrium solubility. So taking into consideration the better prediction ability of different modified form of KE model, the important reaction variables such as temperature, equilibrium CO₂ partial pressure, and solvent concentration are considered for the estimation of reaction equilibrium constant in the present work.

In the modified form of Kent-Eisenberg model used in the current study, the equilibrium constant pertaining to already established reaction of R2-R4 and R7 has been taken from literature database and these constants are defined in terms of system temperature:

$$\ln K_i = a_i + b_i/T + c_i \ln T \quad (17)$$

The temperature-dependent accompanied coefficients *a_i*, *b_i* and *c_i*

Table 1
Modified KE model based equilibrium constant parameters and Henrys constant parameter.

$\ln K_1 = \left(87.397 - \frac{8483.95}{T} - 13.833 \ln T \right) (\text{kmol.m}^{-3})$	[14]
$\ln K_2 = \left(\frac{-7261.78}{T} - 22.477 \ln T + 142.58 \right) (\text{kmol.m}^{-3})$	[14]
$\ln K_3 = \left(220.067 - \frac{12431.7}{T} - 35.482 \ln T \right) (\text{kmol.m}^{-3})$	[14]
$K_6 = \left(-7.108 - \frac{-4390}{T} \right) (\text{kmol.m}^{-3})$	[12]
$\ln H_{CO_2} = 20.2669 - \frac{1.38306 \times 10^4}{T} + \frac{0.06913 \times 10^8}{T^2} - \frac{0.015589 \times 10^{11}}{T^3} + \frac{0.012 \times 10^{13}}{T^4} (\text{kPa.m}^3.\text{kmol}^{-1})$	[36]

Table 2
Equilibrium solubility data of CO₂ absorption in aqueous (APDA + 1DMAP) system.

T/K = 303.15 K		T/K = 313.15 K		T/K = 323.15 K	
P _{CO2}	α _{CO2}	P _{CO2}	α _{CO2}	P _{CO2}	α _{CO2}
0.02 w APDA + 0.28 w 1DMAP					
4.826	0.332	4.413	0.289	5.171	0.271
7.998	0.583	7.722	0.506	9.653	0.454
15.100	0.826	19.305	0.678	27.234	0.638
42.541	0.924	48.953	0.822	52.469	0.739
85.150	0.966	94.803	0.888	100.870	0.807
131.966	1.000	137.550	0.905	123.278	0.838
147.341	1.009	159.820	0.922	152.581	0.845
				164.095	0.857
0.04 w APDA + 0.26 w 1DMAP					
3.930	0.305	4.344	0.257	5.998	0.248
7.860	0.542	8.549	0.539	8.687	0.470
16.616	0.803	21.236	0.761	24.270	0.664
48.884	0.937	50.952	0.866	45.919	0.760
87.219	1.001	85.702	0.911	92.321	0.802
126.726	1.028	129.828	0.924	117.694	0.862
152.098	1.058	151.616	0.945	147.755	0.879
		167.267	0.952	156.925	0.899
0.06 w APDA + 0.24 w 1DMAP					
4.344	0.323	5.378	0.234	5.516	0.270
7.653	0.575	9.101	0.552	10.411	0.500
12.617	0.828	20.133	0.759	18.823	0.698
31.509	0.957	56.468	0.887	38.611	0.807
75.084	1.029	105.490	0.950	73.498	0.867
110.937	1.055	134.655	0.967	115.142	0.902
140.929	1.060	156.304	0.974	132.310	0.915
				153.822	0.922
0.08 w APDA + 0.22 w 1DMAP					
3.103	0.334	4.206	0.243	4.757	0.281
6.343	0.588	7.860	0.562	8.205	0.503
14.617	0.788	17.030	0.738	18.271	0.706
34.336	0.971	48.470	0.889	37.025	0.821
73.291	1.044	83.978	0.973	59.157	0.870
108.799	1.071	128.932	0.990	96.458	0.919
133.620	1.093	152.995	1.002	127.898	0.932
		168.301	1.020	149.892	0.940
0.10 w APDA + 0.20 w 1DMAP					
3.861	0.334	4.068	0.295	3.861	0.267
6.274	0.586	7.308	0.535	7.239	0.493
13.996	0.793	14.272	0.742	15.237	0.700
30.957	1.007	40.748	0.903	41.920	0.856
75.842	1.089	88.253	0.996	89.908	0.926
107.007	1.114	129.070	1.033	124.244	0.951
131.483	1.134	147.961	1.054	148.582	0.963

are reported in Table 1. In addition to this, the constants related to the equilibrium reaction of APDA deprotonation (K_4) and hydrolysis of APDA carbamate (K_5) can be estimated by implementing regression analysis in the MATLAB platform. The Henry's constant, H_{CO_2} , used in Eq. (18) which relates the physical solubility of reactant gas into the solvent medium has been also derived from literature source [36].

$$\ln H_{CO_2} = 20.2669 - \frac{1.38306 \times 10^4}{T} + \frac{0.06913 \times 10^8}{T^2} - \frac{0.015589 \times 10^{11}}{T^3} + \frac{0.012 \times 10^{13}}{T^4} \quad (18)$$

3.2. Feed forward ANN model

Artificial neural network model implemented for various applications in separation science domain can be classified dependent on various parameters such as kind of network architecture, learning algorithm as well as the form of input transformation. Out of various ANN models described in the literature, Feed forward multilayer neural network (FFNN) is the most popular choice among researchers since it

can represent effectively the non-linearity between the different variables representing many complex systems [37–40]. This network involves multiple layers including an input layer, one or more hidden layers, and an output layer which are normally linked with a set of neurons, where the information pertaining to the network are processed. In order to improve the prediction accuracy with handling more than one neural interaction, additional hidden layers can be employed. The data pertaining to all the input parameters for a corresponding system are introduced into the input layer. The data are then transferred to the one or more hidden layers via neurons for processing and then it is sent to output layers for the final projection. The output y_i from any given ANN network involving x_i number of input can be estimated by applying a transfer function shown below:

$$y_i = f\left(\sum_{i=1}^n (p_i x_i + b_i)\right) \quad (19)$$

where p_i is the weight coefficient associated with each input variable and b_i is the bias. The utility of a suitable training algorithm is very much essential in smooth network training. Levenberg–Marquardt (LM) backpropagation algorithm has been reported as one of the fastest computation algorithms used for the moderate size of the network and has been used extensively for modeling CO₂ solubility in aqueous amine solvents [28,37]. The prime goal of any training process is basically to reduce the error margin between the experimental input data and model-estimated output data sets. The criteria are again based on some statistical parameters such as MSE (Mean squared error) described as follows:

$$MSE = \frac{1}{N} \sum_{N=1}^N (\alpha_{pred} - \alpha_{exp})^2 \quad (20)$$

In the present work, the networks are developed keeping 70% data for training and 30% for validation and testing, respectively [38,39]. Before the training of the ANN network, the input and output data sets are normalized in the range of 0–1, since all the input and output data are of different units and range.

$$Y_i = \frac{X_i - X_{min}}{X_{max} - X_{min}} \quad (21)$$

where X_{max} and X_{min} represents the maximum and minimum value of input variables X_i used for training and testing procedure. For the optimized training of the network, the involvement of an appropriate number of neurons is very important. A lower value of neurons degrades the performance of the network and eventually restricts the proper training which results in poor accuracy [40]. On the other hand, a higher number of neurons lead to overfitting as the network converges more quickly. The number of neurons for any network can be obtained by the trial and error method by assessing the MSE value. For all the studied amine system, the optimized neurons are figured out by calculating the MSE over the range of neurons 1–20.

4. Results and discussion

4.1. Measurement and correlation of equilibrium CO₂ solubility

The validation of experimental setup as well as experimental methodology adopted in the present study has been presented in detail in our earlier work [14,20]. The composition of mixed ternary system are taken as (0.02w APDA + 0.28w 1DMAP), (0.04w APDA + 0.26w 1DMAP), (0.06w APDA + 0.24w 1DMAP), (0.08w APDA + 0.22w 1DMAP), (0.10w APDA + 0.20w 1DMAP). The equilibrium data generated for the blended amine system are reported in Table 2

4.1.1. Influence of operating conditions on the CO₂ solubility

Several operating variables like reaction temperature, partial pressure of reactant CO₂ gas, and solvent concentration plays a pivotal role

in the determination of equilibrium CO_2 solubility in the solvent system. As an experimental observation, across all temperature and concentration range, the CO_2 solubility exhibited the expected trend of increase with increment in the CO_2 partial pressure. This can be explained based on the fact that a rise in the P_{CO_2} in the equilibrium cell leads to the increase in the number of collisions of individual reactant gas molecules and the solvent stream which in turn increases the net driving force for chemical absorption. This phenomenon eventually results in the enhancement of overall equilibrium solubility [14]. This will continue until the system reached the maximum saturation limit. However, at higher pressure range physical absorption dominates over chemical absorption and hence marginal increment in the α_{CO_2} has been observed in the current study. Also on account of the exothermic reversible nature of CO_2 -amine reaction, the solubility of CO_2 decreases with a rise in system temperature [7,26]. The effect of temperature has been illustrated in Fig. 1. It is evident from the representation that at $P_{\text{CO}_2} = 50$ kPa and $T = 303.2$ K, the aqueous blend of (0.04w APDA + 0.26w 1DMP) recorded the CO_2 loading of 1.06 while it undergoes gradual reduction to 0.89 at temperature $T = 323.2$ K under similar pressure condition. The promotion effect of the addition of APDA can be noticed in the current blended system, since there is a gradual increment in the α_{CO_2} with increase in the activator concentration from 0.02w to 0.10w (Fig. 2). This can be explained in line with the shuttle mechanism which clearly states the fact that the polyamines (inherited with primary or secondary amine group) activated solvent blends show higher CO_2 absorption capacity as well as absorption rate [41]. Also the gradual increase of APDA concentration in the mixed solvent blend results in the inclusion of more number of amine groups, which further enhances the overall CO_2 loading [41].

4.1.2. Modeling of solubility data with modified form of Kent-Eisenberg model

The generated phase equilibrium data obtained for the current amine formulation is correlated using the modified Kent-Eisenberg model. The equilibrium constant (K_4) and (K_5) are estimated as a function of important reaction variables such as P_{CO_2} , amine concentration as well as system temperature. For reducing the error margin among the experimentally generated and modeled solubility data sets, a nonlinear optimization method is implemented for correlating the current system. The objective function corresponding to the same can be expressed as [20,28]:

$$S = \frac{1}{N} \sum_{i=1}^N \left| \frac{\alpha_i^{\text{exp}} - \alpha_i^{\text{est}}}{\alpha_i^{\text{exp}}} \right| \quad (22)$$

where α_i^{exp} and α_i^{est} represent the experimental and estimated normalized CO_2 loading (mol of CO_2 /mol of amine) in aqueous amine system and N represents the total cumulative data entries. Moreover, the above equation can be employed as a constraint equation for estimating the output data. The estimated equilibrium constant as a function of important reaction parameters can be expressed as:

$$\begin{aligned} K_4 &= 1.23 \times 10^{-8} - 4.81 \times 10^{-9}(m_1 \times m_2) - 7.62 \times 10^{-11}(T) + 1.04 \\ &\times 10^{-11}(m_1 \times m_2 \times T) + 1.42 \times 10^{-13}(T^2) + 1.54 \\ &\times 10^{-11}(P_{\text{CO}_2}) + 6.09 \times 10^{-14}(P_{\text{CO}_2}^2) \end{aligned} \quad (23)$$

$$\begin{aligned} K_5 &= 3.084 \times 10^{-2} - 7.807 \times 10^{-1}(m_1 \times m_2) - 7.46 \times 10^{-2}(T) \\ &+ 2.233 \times 10^{-2}(m_1^2 \times m_2^2) - 3.059 \times 10^{-2}(m_1 \times m_2 \times T) \\ &- 7.12 \times 10^{-7}(T^2) - 3.254 \times 10^{-1}(P_{\text{CO}_2}) + 1.231 \times 10^{-2}(P_{\text{CO}_2}^2) \end{aligned} \quad (24)$$

By implementing the above estimated equilibrium constants in Eq. (16), the model estimated α_{CO_2} can be calculated and it is further compared with the generated α_{CO_2} corresponding to the undertaken

blended amine formulation. The (% AAD) for the equilibrium data sets over the entire domain of experimental conditions has been calculated to be 8.35% for the aqueous blended system of (APDA + 1DMP + H_2O) which reflects the good prediction capability of the developed model adopted in the present work.

4.1.3. Estimation of speciation profile, solvent pH and heat of absorption of CO_2 in the solvent

The modified form of KE model established for the current system can be also used to estimate the concentration of all the molecular as well as ionic species prevailing in the reaction system of aqueous (APDA + 1DMP) system. The speciation plot, corresponding to (0.08 w APDA + 0.22 w 1DMP) system at a temperature of 323 K has been represented in Fig. 3. From the speciation plot, it can be observed that the concentration of both the amines viz. APDA and 1DMP decreases gradually upon an increase in CO_2 loading at a fixed temperature and concentration. The reason can be attributed to the fact that the reaction between CO_2 and the aqueous amine molecules leads to the conversion of amine species into intermediate carbamate as well as protonated species. This can be clearly observed from the increasing trend of $[\text{APDAH}^+]$ as well as $[\text{1DMPH}^+]$ in the reaction medium at higher CO_2 loading. Another important reaction product $[\text{HCO}_3^-]$ also gradually increases with the rise in CO_2 loading. It is mostly contributed by the reaction of tertiary amine 1DMP which is present in excess in the solution [14,15,17]. The formation can be explained by the base-catalyzed hydration mechanism which relates the promotion of hydrolysis reaction of CO_2 to form bicarbonate species in a basic medium comprising of tertiary amine. However, the $[\text{CO}_3^{2-}]$ species show higher concentration at lower CO_2 loading condition, which can be again interpreted on account of the existence of strong basic solution facilitated by the excess free amine molecule at low loading leads to the prevalence of more carbonate species [12]. On the other hand reduction in the free amine species at higher loading results in the decrement in the pH of the medium which can further convert $[\text{CO}_3^{2-}]$ to $[\text{HCO}_3^-]$ via reverse reaction of (R4) [12].

The model results can be further analyzed to determine the pH of the blended amine solution with a change in CO_2 loading. The effect of CO_2 loading and solution temperature on the pH of aqueous (0.08w APDA + 0.22w 1DMP) solution can be observed from Fig. 4. It can be clearly inferred from the figure that the estimated trend of pH has been found to be in line with the general trend of pH for the CO_2 loaded aqueous solvent, i.e. pH in the range of 7–12 [7]. The pH corresponding to the activated solvent blend exhibited a decreasing trend upon an

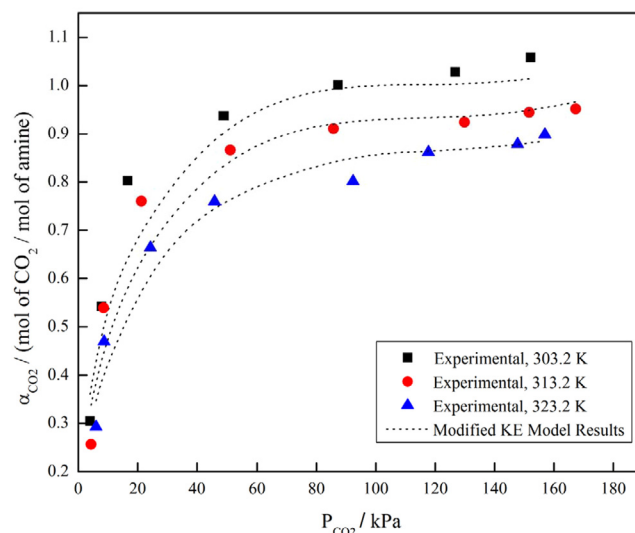


Fig. 1. CO_2 solubility as a function of different experimental temperature corresponding to (0.04 w APDA + 0.26 w 1DMP).

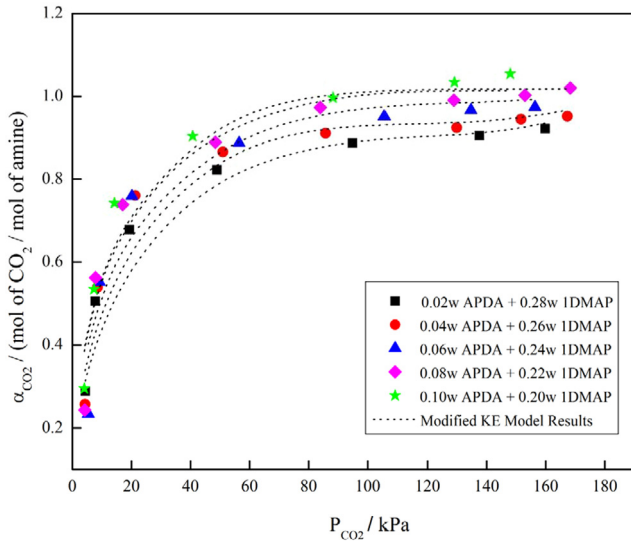


Fig. 2. CO₂ solubility as a function of different composition of solvent blend of (APDA + 1DMAP) system at 313.2 K.

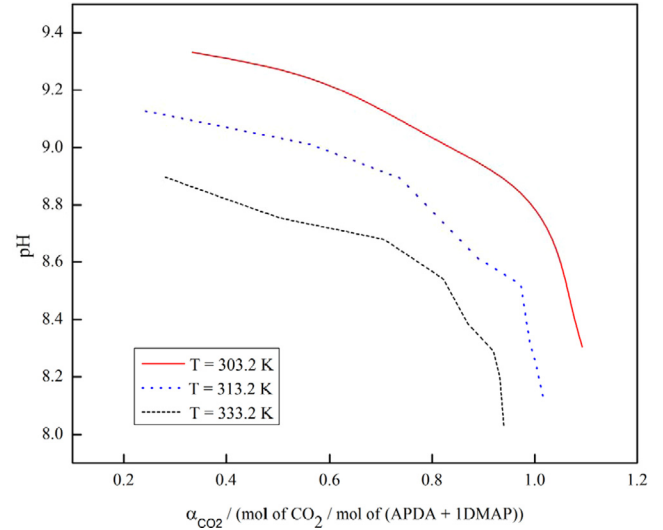


Fig. 4. Modified KE model evaluated solvent pH with change in α_{CO_2} in aqueous (0.08w APDA + 0.22w 1DMAP).

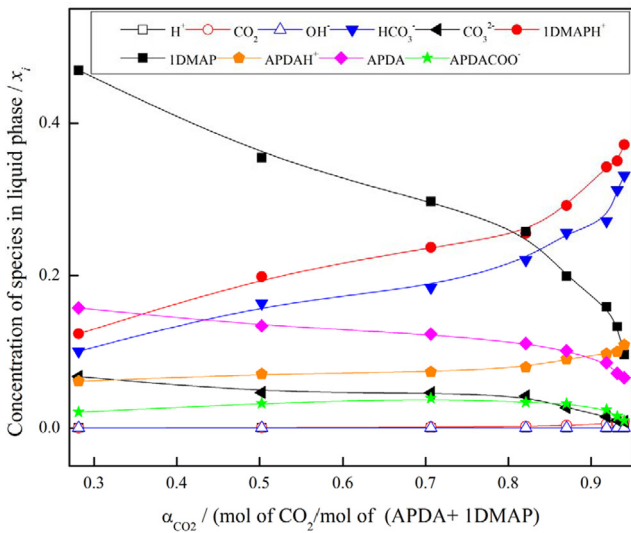


Fig. 3. Modified KE model estimated liquid phase speciation profile as a function of α_{CO_2} in aqueous (0.08w APDA + 0.22w 1DMAP) at $T = 323.2$ K.

increase in the CO₂ loading which can be the result of the incorporation of acidic streams of CO₂ into the amine blend. Also, the increment of solution temperature from 303.2 K to 323.2 K, leads to further enhancement in the ionization of the solution phase which leads to an increase in the concentration of [H⁺]. This phenomenon gives way to the reduction in pH of the CO₂ loaded aqueous amine solution [7].

The reboiler heat duty relates to the largest component of the energy penalty in a PCC plant. The regeneration energy consists of three major components as shown below:

$$Q_{\text{reb}} = Q_{\text{sensible}} + Q_{\text{stripping}} + Q_{\text{desorption}} \quad (25)$$

where, Q_{sensible} is the total amount of sensible heat required to elevate the temperature of the amine solvent, $Q_{\text{stripping}}$ stands for the heat of vaporization required for the formation of steam used in the stripping operation of the regenerator column and $Q_{\text{desorption}}$ is the amount of heat required to strip the CO₂ molecule from the amine solution [12,26]. Out of all these components, the heat of desorption plays an important role in accounting for the total reboiler heat duty. The Heat of absorption (ΔH_{abs}) is a significant factor in evaluating the solvent performance since it directly relates to the heat of desorption of CO₂ from the solvent

phase. Heat of absorption (ΔH_{abs}) can be estimated from Gibbs – Helmholtz equation by evaluating solubility data corresponding to different temperatures at the same CO₂ loading. The equation can be expressed as [26]:

$$\frac{d(\ln P_{\text{CO}_2})}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_{\text{abs}}}{R} \quad (26)$$

where, ΔH_{abs} represent the total of heat of CO₂ absorption (kJ/mol) and R stands for Universal gas constant (kJ/mol.K). The heat of absorption of CO₂ into the aqueous blend of (0.02w APDA + 0.28w 1DMAP) is calculated over the CO₂ loading range of (0.6–0.7) and within the temperature range of (303.2–333.3) K (Fig. 5) [12]. The average estimated ΔH_{abs} for the solvent blend has been found to be about –49 kJ/mol, which is substantially lower than the benchmarked MEA solvent [42]. The lower heat of reaction can be attributed due to the presence of three methyl groups which in turn increases the initial absorption rate and capacity

4.1.4. Modeling of CO₂ solubility data with the ANN model

Along with the implementation of modified KE model the feed-

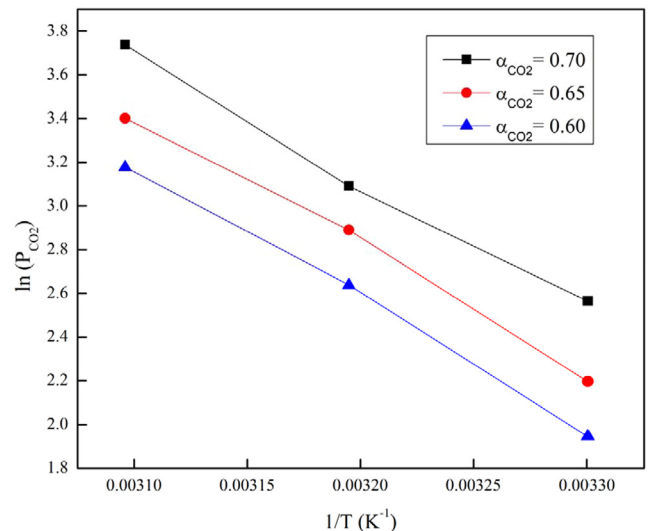


Fig. 5. The Plot of $\ln(P_{\text{CO}_2})$ vs $1/T$ for the assessment of heat of absorption in aqueous (0.02w APDA + 0.28w 1DMAP) solvent.

forward neural network model (FFNN) has also been employed for the current system to estimate the α_{CO_2} over the entire experimental range of pressure and temperature. The optimized network architecture for the aqueous blend of (APDA + 1DMAP) system can be figured out by employing the appropriate number of neurons in the developed network [28]. In view of this, the number of neurons is varied from 1 to 20 and several statistical parameters like (% AAD and MSE) are considered as the base parameters to evaluate the optimized neurons. Following this methodology, the optimized neuron in the present study has been found to be 7 and the network architecture used in the present system is represented in Fig. 6. By implementing the optimized network architecture, the estimated α_{CO_2} value is calculated and the % AAD between the estimated α_{CO_2} and investigational solubility measurement has been found to be 3.18. The suitability as well as the comparison of both the modeling approaches adopted for estimating the CO_2 solubility can be outlined as a cross plot shown in Fig. 7. The lower value of % AAD indicates that the ANN model outperforms the equilibrium based model for predicting CO_2 solubility.

4.1.5. FTIR-ATR and NMR analysis

The possible reaction mechanism, as well as the overall scheme of the CO_2 absorption in the aqueous blended amine solvent, has been further investigated with FTIR spectroscopy (Perkin Elmer Inc. Germany). The analysis has been undertaken within the wave number range of 800 to 2000 cm^{-1} . The FTIR spectra corresponding to the reactant gas unloaded and CO_2 loaded blended amine solvent is presented in Fig. 8. The characteristic intense peak at 1644.11 cm^{-1} and 934.56 cm^{-1} assigned to the N-H peak of the rocking mode of vibration as well as C-NH₂ twisting vibration modes of primary amine group present in the blended amine system [43]. In addition, the peaks corresponding to 1029.38, 1073.78, and 1467.67 cm^{-1} relate to C-N, C-O, and C-H stretching vibration modes. The spectra corresponding to CO_2 loaded solvent at $\alpha_{\text{CO}_2} = 0.80$ clearly confirms the presence of asymmetric stretching of COO^- (carbamate) species at 1480.63 cm^{-1} . Also, the typical stretching band at 1342.89 cm^{-1} indicates the presence of bicarbonate species in the reaction system which again confirms the reaction scheme in line with the tertiary amine 1DMAP as the base solvent.

Along with the IR study, a qualitative ^{13}C NMR investigation has been also used to identify the important reaction products and to support the proposed reaction scheme prevailing in the mixed blend- CO_2 medium. The NMR study has been carried out in a 500 MHz aided NMR spectrophotometer (Ascend, Bruker) using the D_2O solvent (Fig. 9). The peaks originating in the region (164–165 ppm), which corresponds to the low field domain indicates the presence of carbonyl group of carbon present in carbamate species whereas the peak originating at 161 ppm relates to the prevalence of $\text{HCO}_3^- / \text{CO}_3^{2-}$ as the important reaction product [24,44]. The presence of bicarbonate species as the major reaction products confirms the prevalence of base catalyzed hydration mechanism inherited by tertiary amine groups. While the peaks at higher field regions indicate the C signals of various CH_2 groups present in the intermediate carbamate as well as molecular

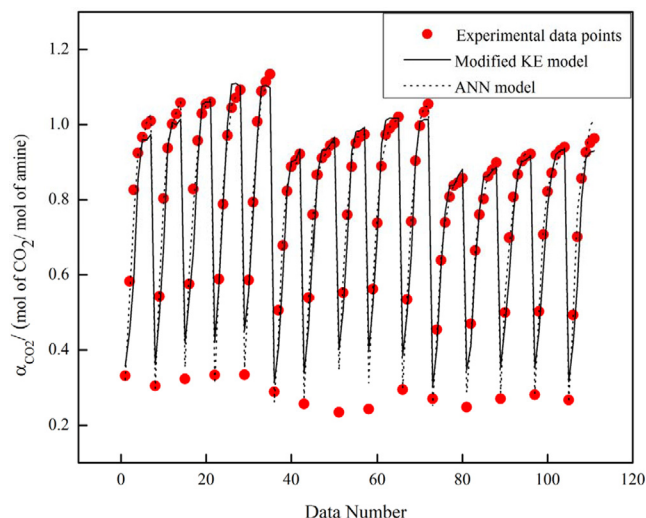


Fig. 7. Comparative cross plot of experimental CO_2 solubility data and different model estimated data of (APDA + 1DMAP + H_2O) system.

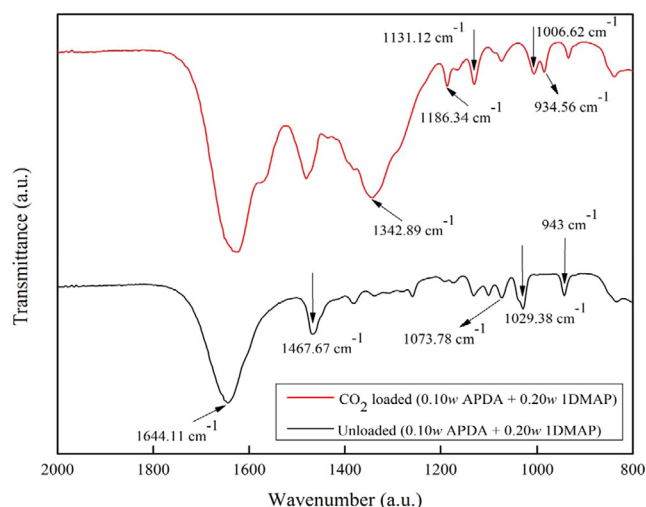


Fig. 8. FTIR-ATR Spectra of unloaded and CO_2 loaded (0.10w APDA + 0.20w 1DMAP) amine solvent.

species [39].

4.1.6. Comparison of solvent performance with conventional solvents

The performance of aqueous (0.04w APDA + 0.26w 1DMAP) system has been compared with various other conventional and recently explored solvent blend in terms of CO_2 solubility in Fig. 10. It can be noticeably inferred from the performance analysis that the CO_2 solubility in the proposed aqueous solvent blend is substantially higher

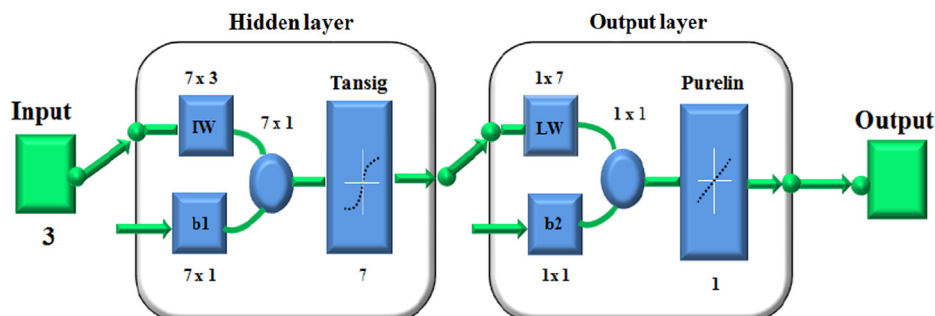


Fig. 6. Optimized ANN architecture used for the prediction of CO_2 solubility in aqueous (APDA + 1DMAP) system.

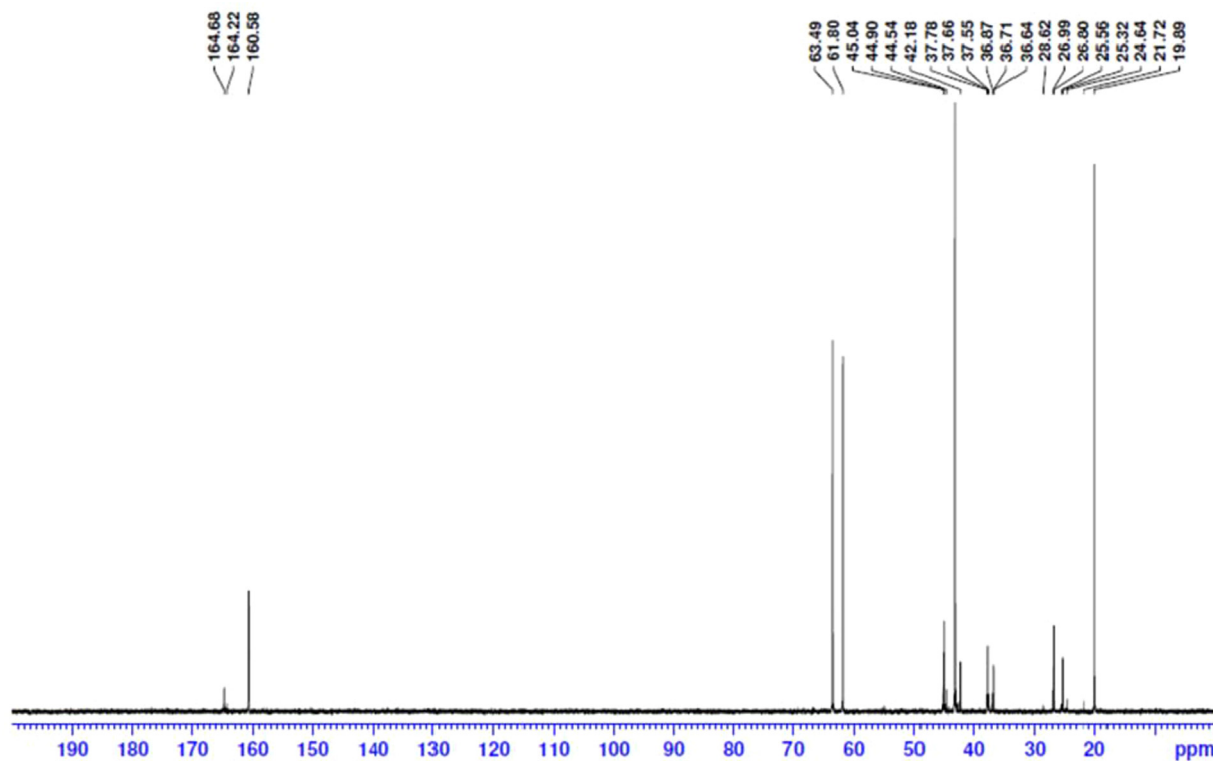


Fig. 9. ^{13}C NMR spectra of CO_2 absorbed aqueous blended (0.10w APDA + 0.20w 1DMAP) amine solvent.

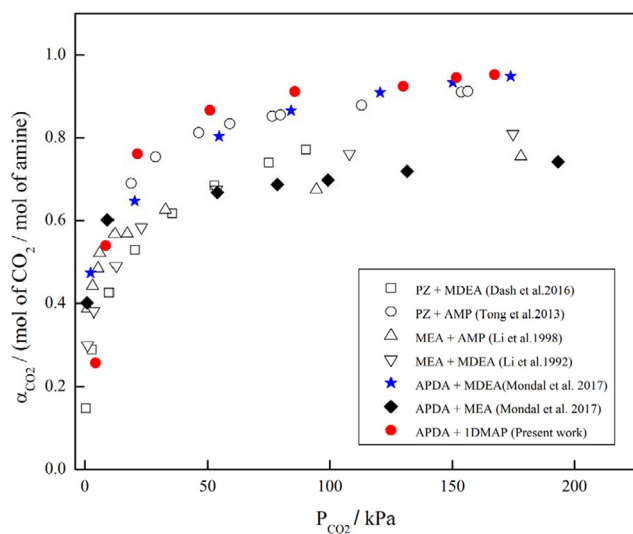


Fig. 10. Comparison of equilibrium CO_2 solubility of aqueous (0.04w APDA + 0.26w 1DMAP) with other conventional solvent blend at 313.2 K.

than the MEA/PZ based system such as (MEA + MDEA), (MDEA + AMP), (PZ + AMP) as well as (PZ + MDEA) at 313 K [29,30,45,46]. Also upon comparison with newly explored solvents such as (APDA + MEA), (APDA + MDEA) [25], it showcases higher solubility, especially at higher CO_2 loading.

4.2. Correlation of thermophysical properties

The thermophysical properties of aqueous (APDA + 1DMAP) system were measured over wide operating conditions of solvent composition and temperature. The experimental data corresponding to density and viscosity measurements have been represented in Figs. 11 and 12. From the experimental results, it can be seen that the density, as

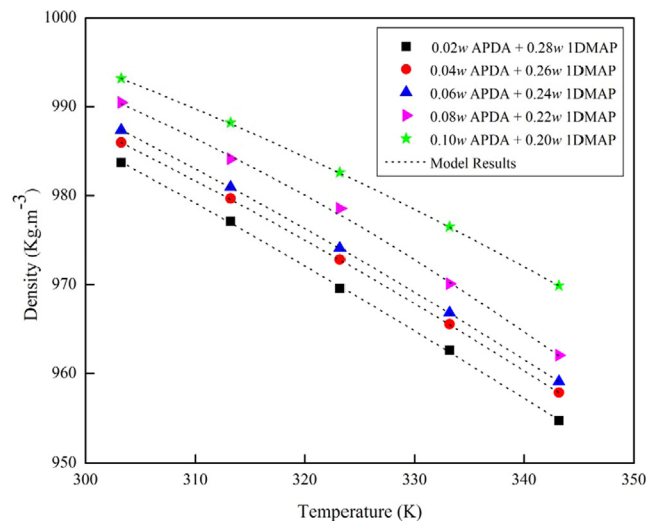


Fig. 11. Density of aqueous blend of (APDA + 1DMAP) as a function of solvent concentration and temperature.

well as viscosity of the aqueous solvent blend, reduces with a rise in the system temperature within the broad domain of (303.2–343.2) K. It can be also observed that at a particular temperature, both the density as well as the viscosity of the mixed amine solution gradually increases upon increasing the concentration of APDA in the blend.

The density measurement recorded in the current study for different temperature and concentration conditions are modeled by implementing a modified form of Redlich-Kister Equation. The R-K equation is dependent on the excess molar volume of the solution as an excess property function. The equation can be expressed as [14,20]:

$$V_{jk}^E = x_j x_k \sum_{p=0}^N A_p (x_j - x_k)^p \quad (27)$$

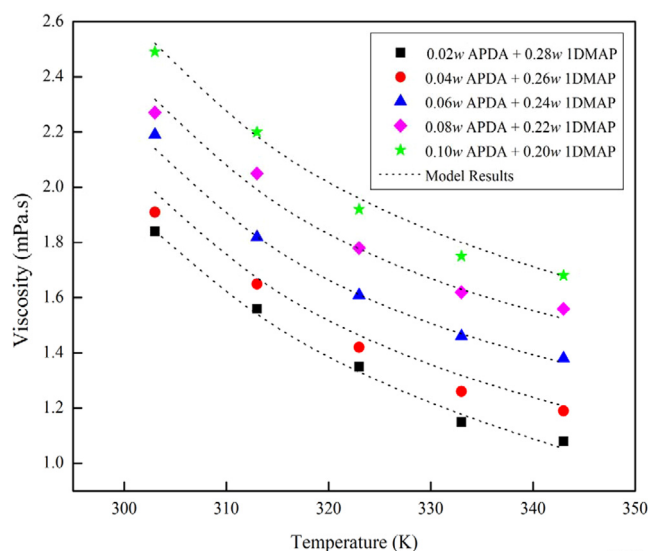


Fig. 12. Viscosity of aqueous blend of (APDA + 1DMP) as a function of solvent concentration and temperature.

Table 3

Binary Redlich-Kister Parameters A_0 , A_1 , A_2 for the excess volume of density of (APDA + 1DMP + H₂O) system.

Parameters		APDA + 1DMP	APDA + H ₂ O	1DMP + H ₂ O
A_0	l	1.413×10^4	-1.675×10^4	7.702×10^3
	m	-89.504	106.102	-48.784
	n	0.141	-0.167	0.077
A_1	l	1.322×10^5	7.803×10^3	-1.634×10^4
	m	-836.603	-49.431	103.538
	n	1.316	0.077	-0.163
A_2	l	1.144×10^6	3.007×10^4	-2.91×10^4
	m	-7.226×10^3	-190.506	184.362
	n	11.345	0.3	-0.290

Table 4

Parameters (G_{12} , G_{23} , and G_{13}) of the Grunberg-Nissan Model for estimating viscosity of (APDA + 1DMP + H₂O) system.

Parameters		APDA + 1DMP + H ₂ O
G_{12}	l	4.369×10^4
	m	-282.741
	n	0.456
G_{23}	l	-98.149
	m	0.597
	n	-8.3×10^{-4}
G_{13}	l	-2.125×10^3
	m	13.637
	n	-2.144×10^{-2}

V^E used in the above equation, stands for the excess molar volume and A_p is the optimized pair parameters which can be estimated as a function of temperature

$$A_p = l + m \cdot (T) + n \cdot (T)^2 \quad (28)$$

Similarly, the viscosity data obtained for the mixed amine system in the current study can be modeled using Grunberg-Nissan Model which can be defined as below [14,20]:

$$\ln \mu_m = \sum x_i \ln \mu_i + \sum \sum x_i x_j G_{ij} \quad (29)$$

In the above equation, the pair parameter G_{ij} can be evaluated as a function of experimental temperature:

$$G_{ij} = l + m \cdot (T) + n \cdot (T)^2 \quad (30)$$

The coefficients of the temperature-dependent parameters can be estimated by regressing the experimentally measured property data sets over the entire range of experimental conditions. The derived coefficients are reported in Tables 3 and 4 and can be further utilized to calculate the model predicted thermophysical properties. The %AAD value for the density and viscosity measurement have been found to be 0.05 and 1.73 which clearly shows that the correlated results are in good agreement with the experimentally measured property data.

5. Conclusions

The phase equilibrium data pertaining to CO₂ absorption in the novel amine formulation of aqueous (APDA + 1DMP) systems were evaluated as a function of important reaction variables. The experimental finding reveals that the CO₂ solubility gradually increases with a rise in the promoter concentration in the mixed blend. The solubility data are well correlated using both modified KE and feed-forward neural network model. The model prediction has been again extended to estimate the speciation profile as well as the pH of the CO₂ loaded solvent as a function of α_{CO_2} . Also, the estimated heat of absorption via Gibbs-Helmholtz equation is substantially lower than the benchmarked MEA solvent. The FTIR-ATR and qualitative ¹³C NMR analysis of the blended solvent system further supports the model estimation and confirms the existence of protonated species, carbamate as well as bicarbonate ions in the reaction medium. Along with solubility study, some of the key thermophysical properties like density and viscosity of the unloaded solvent blends were also measured and well correlated over broad experimental conditions. Finally, a comprehensive comparison with other conventional solvent blends reveals that the understudy solvent blend shows higher CO₂ loading as well as lower heat of absorption. Based on the superior performance showcased by the proposed blend in comparison with other established solvent blend, APDA activated 1DMP system could be a promising candidate for acid gas treating units.

CRedit authorship contribution statement

Anirban Dey: Methodology, Investigation, Validation, Software, Writing - original draft. **Sukanta Kumar Dash:** Supervision. **Bishnupada Mandal:** Supervision, Conceptualization, Writing - review & editing.

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.

References

- [1] Olajire AA. CO₂ capture and separation technologies for end-of-pipe applications-A review. *Energy* 2010;35:2610–28.
- [2] Rao AB, Rubin ESA. A technical, economical, and environmental assessment of amine based CO₂ capture technology for power plant greenhouse gas control. *Environ Sci Technol* 2002;36:4467–75.
- [3] Spigarelli BP, Kawatra SK. Opportunities and challenges in carbon dioxide capture. *J.CO2.Util.* 1 (2013) 69–87.
- [4] Greer T, Bedelbayev A, Igreja JM, Gomes JF, Lie B. A simulation study on the abatement of CO₂ emissions by de-absorption with monoethanolamine. *Environ Technol* 2010;31:107–15.
- [5] Gomes J, Santos S, Bordado J. Choosing amine-based absorbents for CO₂ capture. *Environ Technol* 2015;36:19–25.
- [6] Schaffer A, Brechtel K, Scheffknecht G. Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO₂ capture from flue gases. *Fuel* 2012;101:148–53.
- [7] Mondal BK, Bandyopadhyay SS, Samanta AN. Experimental measurement and Kent-Eisenberg modelling of CO₂ solubility in aqueous mixture of 2-amino-2-methyl-1-propanol and hexamethylenediamine. *Fluid Phase Equilib* 2017;437:118–26.
- [8] A.Hafizia, M.H. Mokaria, R. Khalifeh, M. Farsia, M.R. Rahimpoura, Improving the CO₂ solubility in aqueous mixture of MDEA and different polyamine promoters: The

- effects of primary and secondary functional groups. *J. Mol. Liq.* doi.org/10.1016/j.molliq.2019.111803.
- [9] Hamidi R, Farsi M, Eslamloueyan R. CO₂ solubility in aqueous mixture of MEA, MDEA and DAMP: Absorption capacity, rate and regeneration. *J. Mol. Liq.* 2018;265:711–6.
 - [10] Xiao M, Liu H, Gao H, Liang Z. CO₂ absorption with aqueous tertiary amine solutions: Equilibrium solubility and thermodynamic modeling. *J. Chem. Therm.* 2018;122:170–82.
 - [11] Kadiwala S, Rayner AV, Henni A. Kinetics of carbon dioxide (CO₂) with ethylenediamine, 3-amino-1-propanol in methanol and ethanol, and with 1-dimethylamino-2-propanol and 3-dimethylamino-1-propanol in water using stopped-flow technique. *Chem Eng J* 2012;179:262–71.
 - [12] Liang Y, Liu H, Rongwong W, Liang Z, Idem R, Tontiwachwuthikul P. Solubility, absorption heat and mass transfer studies of CO₂ absorption into aqueous solution of 1-dimethylamino-2-propanol. *Fuel* 2015;144:121–9.
 - [13] Afkhamipour M, Mofarahi M, Rezaei A, Mahmoodi R, Lee CH. Experimental and theoretical investigation of equilibrium absorption performance of CO₂ using a mixed 1-dimethylamino-2-propanol (1DMA2P) and monoethanolamine (MEA) solution. *Fuel* 2019;256. doi.org/10.1016/j.fuel.2019.115877.
 - [14] Dey A, Dash SK, Mandal B. Equilibrium CO₂ solubility and thermophysical properties of aqueous blends of 1-(2-aminoethyl) piperazine and N-methyldiethanolamine. *Fluid Phase Equilib.* 2018;463:91–105.
 - [15] Jaafari L, Jaafari B, Idem R. Screening study for selecting new activators for activating MDEA for natural gas sweetening. *Sep. Purif. Technol.* 2018;199:320–30.
 - [16] AliAbd A, ZakiNaji S. Comparison study of activators performance for MDEA solution of acid gases capturing from natural gas: Simulation-based on a real plant. *Env. Tech. & Innov.* 2020;17. https://doi.org/10.1016/j.eti.2019.100562.
 - [17] Ghaliab L, Ali B, Ashri WM, Mazari S, Saeed IM. Modeling the effect of piperazine on CO₂ loading in MDEA/PZ mixture. *Fluid Phase Equilib.* 2017;434:233–43.
 - [18] Nwaoha C, Tontiwachwuthikul P, Benamor A. CO₂ capture from water-gas shift process plant: Comparative bench-scale pilot plant investigation of MDEA-PZ blend vs novel MDEA activated by 1,5-diamino-2-methylpentane. *Int. Greenh. Gas Control* 2019;82:218–28.
 - [19] Y. Du, Le. Li, O. Namjoshi, K. A. Voice, A. N. Fine, G. T. Rochelle, Aqueous Piperazine/N-(2-Aminoethyl)piperazine for CO₂ Capture. *Energy. Procedia* 37 (2013) 1621–1638.
 - [20] Dey A, Dash SK, Balchandani S, Mandal B. Investigation on the inclusion of 1-(2-aminoethyl)piperazine as a promoter on the equilibrium CO₂ solubility of aqueous 2-amino-2-methyl-1-propanol. *J. Mol. Liq.* 2019. https://doi.org/10.1016/j.molliq.2019.111036.
 - [21] Choi J, Kim Y, Nam S, Yun S, Yoon Y, Lee J. CO₂ absorption characteristics of a piperazine derivative with primary, secondary, and tertiary amino groups. *Kor. J. Chem. Eng.* 2016;33:3222–30.
 - [22] Muchan P, Narku-Tetteh J, Saiwan C, Idem R, Supap T. Effect of number of amine groups in aqueous polyamine solution on carbon dioxide (CO₂) capture activities. *Sep. Purif. Technol.* 2017;184:128–34.
 - [23] Hafizi A, Mokari MH, Khalifeh R, Farsi M, Rahimpour MR. Improving the CO₂ solubility in aqueous mixture of MDEA and different polyamine promoters: The effects of primary and secondary functional groups. *J. Mol. Liq.* 2020;297. https://doi.org/10.1016/j.molliq.2019.111803.
 - [24] Das B, Deogam B, Mandal B. Absorption of CO₂ into novel aqueous bis (3-amino-propyl) amine and enhancement of CO₂ absorption into its blends with N-methyldiethanolamine. *Int. J. Greenh. Gas Control* 2017;60:172–85.
 - [25] Mondal BK, Bandyopadhyay SS, Samanta AN. Equilibrium solubility and enthalpy of CO₂ absorption in aqueous Bis-(3-aminopropyl) amine and its mixture with MEA, MDEA, AMP and K₂CO₃. *Chem Eng Sci* 2017;170:58–67.
 - [26] Dash SK, Samanta AN, Bandyopadhyay SS. (Vapour + liquid) equilibria (VLE) of CO₂ in aqueous solutions of 2-amino-2-methyl-1-propanol: New data and modelling using eNRTL-equation. *J. Chem. Thermodyn.* 2011;43:1278–85.
 - [27] Chang YC, Leron RB, Li MH. Equilibrium solubility of carbon dioxide in aqueous solutions of (diethylenetriamine + piperazine). *J. Chem. Thermodyn.* 2013;64:106–13.
 - [28] Garg S, Shariff AM, Shaikh MS, Lal B, Suleman H, Faiqa N. Experimental data, thermodynamic and neural network modeling of CO₂ solubility in aqueous sodium salt of L-phenylalanine. *J. CO₂ Util.* 2017;19:146–56.
 - [29] Tong D, Maitland GC, Trusler MJP, Fennell PS. Solubility of carbon dioxide in aqueous blends of 2-amino-2-methyl-1-propanol and piperazine. *Chem Eng Sci* 2013;101:851–64.
 - [30] Dash SK, Bandyopadhyay SS. Studies on the effect of addition of piperazine and sulfolane into aqueous solution of N-methyldiethanolamine for CO₂ capture and VLE modelling using eNRTL equation. *Int. J. Greenh. Gas Control* 2016;44:227–37.
 - [31] Kundu M, Bandyopadhyay SS. Solubility of CO₂ in water + diethanolamine + N-methyldiethanolamine. *Fluid Phase Equilib.* 2016;248:158–67.
 - [32] Kent RL, Eisenberg B. Better data for amine treating. *Hydrocarbon Process* 1976;55:87–90.
 - [33] Chakma A, Meisen A. Solubility of CO₂ in Aqueous Methyldiethanolamine and N, N Bis(hydroxyethyl) piperazine Solutions. *Ind Eng Chem Res* 1987;26:2461–6.
 - [34] Chakma A, Meisen A. Improved Kent-Eisenberg model for predicting CO₂ solubilities in aqueous diethanolamine (DEA) solutions. *Gas Sep. Pur.* 1990;4:37–40.
 - [35] Liu H, Chan C, Tontiwachwuthikul P, Idem R. Analysis of CO₂ equilibrium solubility of seven tertiary amine solvents using thermodynamic and ANN models. *Fuel* 2019;249:61–72.
 - [36] Hsu YH, Leron RB, Li MH. Solubility of carbon dioxide in aqueous mixtures of (reline + monoethanolamine) at T = (313.2 to 353.2) K. *J. Chem. Thermodyn.* 2014;72:94–9.
 - [37] Li C, Liu H, Xiao M, Luo X, Gao H, Liang Z. Thermodynamics and ANN models for predication of the equilibrium CO₂ solubility in aqueous 3-dimethylamino-1-propanol solution. *Int. J. Greenh. Gas Control* 2017;63:77–85.
 - [38] Pakzad P, Mofarahi M, Zadpanah A, Afkhamipour M. Experimental data, thermodynamic and neural network modeling of CO₂ absorption capacity for 2-amino-2-methyl-1-propanol (AMP) + Methanol (MeOH) + H₂O system. *J. Nat. Gas Sci. Eng.* 2020;73. https://doi.org/10.1016/j.jngse.2019.103060.
 - [39] Hamzeh ME, Fattahi M, Najibi H, Bruggen B, Mazinani S. Application of artificial neural networks for estimation of solubility of acid gases (H₂S and CO₂) in 32 commonly ionic liquid and amine solutions. *J. Nat. Gas Sci. Eng.* 2015;24:106–14.
 - [40] Norouzbahari S, Shahhosseini S, Ghaemi A. Modeling of CO₂ loading in aqueous solutions of piperazine: Application of an enhanced artificial neural network algorithm. *J. Nat. Gas Sci. Eng.* 2015;24:18–25.
 - [41] Choi SC, Nam SC, Yoon YI, Park KT, Park SJ. Carbon dioxide absorption into aqueous blends of Methyldiethanolamine (MDEA) and alkyl containing multiple amino groups. *Ind Eng Chem Res* 2014;53:14451–61.
 - [42] Abdulkadir A, Rayner AV, Quang DV, Hadri NE, Dindi A, Feron PHM, et al. Heat of absorption and specific heat of carbon dioxide in aqueous solutions of monoethanolamine, 3-piperidinemethanol and their blends. *Energy Procedia* 2014;63:2070–81.
 - [43] Richner G, Puxty G. Assessing the chemical speciation during CO₂ absorption by aqueous amines using in Situ FTIR. *Ind Eng Chem Res* 2012;51:14317–24.
 - [44] Kim YE, Moon SJ, Yoon Y, Jeong SK, Park KT, Bae ST, et al. Heat of absorption and absorption capacity of CO₂ in aqueous solutions of amine containing multiple amino groups. *Sep. Pur. Tech.* 2014;122:112–8.
 - [45] Shen KP, Li MH. Solubility of carbon Dioxide in aqueous mixtures of Monoethanolamine with Methyldiethanolamine. *J. Chem Eng Data* 1992;37:96–100.
 - [46] Li MH, Chang BC. Solubilities of Carbon Dioxide in Water + Monoethanolamine + 2 amino-2-methyl-1-propanol. *J. Chem Eng Data* 1998;39:448–52.