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Mass Transfer Modeling of CO_2 Absorption into Blended Aqueous MDEA–PZ Solution

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Highlights

- The rate of CO_2 absorption into methyl diethanolamine-piperazine (MDEA-PZ) solution is investigated.
- The dimensionless parameters of the process are obtained using the Buckingham Pi theorem and considering the effective parameters in mass transfer.
- The CO_2 mass transfer flux in the reactive absorption process depends on the mass transfer parameters of both the liquid and gas phases.
- Based on the dimensionless parameters obtained, a correlation is proposed to calculate the mass transfer flux of acidic gases in the MDEA–PZ solutions.
- The mass transfer flux in the reactive absorption process is modeled based on the four laws of chemical equilibrium, phase equilibrium, mass balance, and charge balance.

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Abstract

In this research, the rate of CO_2 absorption into methyl diethanolamine–piperazine (MDEA–PZ) solution was investigated. To model the mass transfer flux in the reactive absorption processes, the dimensionless parameters of the process were obtained using the Buckingham Pi theorem and considering the effective parameters in mass transfer. The CO_2 mass transfer flux in the reactive absorption process depends on the mass transfer parameters of both the liquid and gas phases. Based on the dimensionless parameters obtained, a correlation is proposed to calculate the mass transfer flux of acidic gases in MDEA–PZ solutions. The mass transfer flux in the reactive absorption process is modeled based on the four laws of chemical equilibrium, phase equilibrium, mass balance, and charge balance. Experimental data from the literature were used to determine the constants of the derived correlation as a function of dimensionless parameters. In the provided correlation, the effects of dimensionless parameters including film parameter, CO_2 loading, ratio of diffusion coefficients in the gas–liquid phase, CO_2 partial to total pressure, and film thickness ratio as well as factors such as temperature, the number of free amines in the solution, the partial pressure of CO_2, on the CO_2 mass transfer flux were investigated. According to the results, the absorption rate decreases with increasing CO_2 loading and film parameter, and the mean absolute deviation is about 3.6%, which indicates the high accuracy of the correlation.

Keywords: CO_2, MDEA–PZ Solution, Buckingham Pi Theorem, Mass Transfer Flux, Loading

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1. Introduction

Energy plays an important role in the economic growth of the world. Greenhouse gas emissions have raised concerns over weather change, and carbon dioxide accounts for about 78.1% of total greenhouse gas emissions (Naami, 2013). The removal of acidic gases is one of the major processes in natural gas purification, oil refining, coal conversion industries, and ammonia production (Ghaemi et al., 2017; Mesbah et al., 2017; Rahmandoost et al., 2014; Esmaili and Ehsani, 2014). Since CO_2 is one of the most important greenhouse gases contributing to global warming, there is a growing interest in removing large amounts of CO_2 from industrial sources (Van Loo et al., 2007). There are different methods for CO_2 capture from gas mixtures such as physical and chemical absorption, adsorption, membrane technologies, and cryogenic separation, and energy waste, removal efficiency, and process cost are the key aspects of the process selection (Khajeh and Ghaemi, 2019; Amiri et al., 2019; Mirzaei and Ghaemi, 2018; Pashaei et al., 2016; Ramazanipour et al., 2019; Taheri et al., 2019). One method to identify the need for gas sweetening is to calculate the partial pressures of acidic gases. At partial pressures above 30 psi and in the presence of water, usually CO_2 corrosion occurs (Krouse et al., 1988). One of the well-known methods for removing CO_2 is the use of aqueous solutions of alkanolamine as a proven and applicable method in many chemical processes such as ammonia production and natural gas processes (Campbell and Maddox, 1970; Ghaemi et al., 2011). Methyl diethanolamine (MDEA) and triethanolamine (TEA) as tertiary amines, which lack a hydrogen atom attached to a nitrogen atom, are weaker than the primary and secondary amines and selectively react with hydrogen sulfide but do not react with carbon dioxide. Tertiary amines can absorb a considerable amount of H_2S when the amine concentration in the solution is low (Pashaei et al., 2017). Many research works have been conducted to improve the defects of single amine systems (Pashaei et al., 2017a, 2017b; Mandal et al., 2001). Blended amines have been used to enhance process performance and optimize the individual properties of the single amines that form the blended amine mixtures (Mirzaei and Ghaemi, 2018; Mandal et al., 2001; Zhang et al., 2001). The choice of the appropriate amine depends on its absorption capacity, kinetics, and recovery capacity. Recently, the use of a mixture of amines has been proposed to combine the benefits of various amines (Bougie and Iliuta, 2011). For example, mixing primary and secondary amines with the tertiary amines, such as the combination of MDEA and monoethanolamine (MEA), reduces the consumption of energy in CO_2 removal technology. MEA reacts with CO_2 more rapidly than MDEA, but MDEA has a higher absorption capacity than MEA. Also, the recovery of MDEA requires less energy compared to MEA. Therefore, MDEA has the advantages of a high CO_2 loading capacity and low-temperature reaction with CO_2 over the primary or secondary amines, which results in the less energy needed for recovery (Heydarifard et al., 2018). Chakravarty et al. offered a mixture of amines that takes the advantage of each amine by adding a small amount of primary amines to tertiary amines and can improve the absorption of CO_2 for a large range without changing its properties (Chakravarty et al., 1985). Blended amines have become important in gas purification processes due to their use in process design. Mandal et al. (2001) studied CO_2 capture in a mixture of MDEA and MEA and a mixture of aminomethyl propanol (AMP) and MEA (Ghaemi, 2020). These mixtures were compared in theory and under experimental conditions (Mandal et al., 2001). Piperazine (PZ) is an organic compound that has two nitrogen atoms, so it can absorb two moles of CO_2 and releases less heat in reaction with CO_2 (Pashaei et al., 2018; Norouzbahari et al., 2015, 2016); PZ is usually added as an activator. PZ reacts with CO_2 more rapidly than MEA and is stable up to a temperature of 150 °C. On the other hand, by varying the concentration of various amines, an optimal absorption system can

be designed for specific applications (Norouzbahari et al., 2015). In this study, MDEA–PZ solution was used to investigate the absorption process of CO_2. Table 1 lists the studies on the absorption processes based on the MDEA–PZ solutions.

These studies experimentally investigated the absorption kinetics and CO_2 solubility in the MDEA–PZ system at different temperatures and loading rates; however, unfortunately, an accurate model or exact equation has not been developed for determining the mass transfer flux of CO_2 to liquid components so far. Thus, it is difficult to calculate the number of trays and lengths of the column in the absorption process. The purpose of this work is to present a general and accurate method with the minimum number of simplifying assumptions for calculating the mass transfer flux of CO_2 to liquid components in an MDEA–PZ solution system. In addition, the effects of different operating conditions on the mass transfer flux of CO_2 to the components of the MDEA–PZ solution are investigated.

Table 1

A review of the studies on the absorption processes using an aqueous solution of MDEA–PZ.

Reference	Concentration ratio (MDEA/PZ)	*T* (K)	Loading
Xu Zhang et al., 2001	50/(3–10) (wt %)	30.3–343	0
Bishnoi and Rochelle, 2004	4/0.6 (mol/L)	313–343	0.01–0.7
Lu et al., 2007	2/0.5 (mol/L)	292–299	0–0.35
Idem et al.,2009	(27, 24, and 21)/(3, 6, and 9) (wt %)	313–333	0.0095–0.33
Aboudheir et al., 2010	(27, 24, and 21)/(3, 6, and 9) (wt %)	313–333	0.0095–0.33
Samanta et al., 2011	(1.89–2.41)/(0.24, 0.6, 0.95) (mol/L)	298–313	0
Sodiq et al., 2014	(0.20–0.9)/(5–41) (mol/L)	298–313	0
Ibrahim et al., 2014	(36-45)/(3-14) (wt %)	333–353	0
Thampson et al., 2014	(7, 5)/(2,5) (mol/L)	293–313	0.2–0.25

2. Theory

2.1. Mass transfer flux

The absorption process of CO_2 is carried out through both physical absorption and absorption via chemical reactions. In physical absorption, the absorbing material is physically transferred to the liquid phase. In this case, the mass transfer flux is obtained from the mass transfer coefficient due to concentration difference. On the other hand, in the chemical absorption, a gas is absorbed by the liquid phase through mass transfer and chemical reaction. Amine-based, carbonate-based, ammonia-based, and ionic liquids are chemical absorption systems (Kierzkowska-Pawlak, 2012). For CO_2 absorption, the chemical absorption process involves the reaction of CO_2 with a chemical solvent and the formation of intermediate compounds bonded weakly through a reversible reaction. This process can be performed in different systems such as bubble columns and fixed-bed columns. In order to express the rate of the overall process, a liquid–gas interface is developed, and mass transfer improves with increasing turbulence in both liquid and gas phases. In the boundary layer, mass transfer occurs through a combination of diffusion and chemical reaction mechanisms. Thus, the rate of the overall process is expressed by both chemical reactions and mass transfer. The enhancement factor (E) of the process is defined as the ratio of the mass transfer coefficient with chemical reaction in the liquid bulk to the mass transfer coefficient without the chemical reaction. In other words, the enhancement factor considers the effect of the chemical reaction on the mass transfer and indicates the increase in the rate of the mass

transfer due to the presence of chemical reaction. Consequently, the mass transfer flux is expressed by Eq. (1) (Edali et al., 2010, Etemad et al., 2015).

$$N_{CO_2} = E \times k_l \left(C^*_{CO_2} - C_{CO_2,b} \right) \tag{1}$$

Table 2 tabulates a list of enhancement factors provided for different chemical systems.

Table 2

Correlations proposed for the enhancement factor of CO_2 reactive absorption processes.

Reference	Reaction type	Enhancement factor
Kierzkowska-Pawlak, 2012	Irreversible second order reaction according to the film theory $A(g) + \upsilon_B B(L) \xrightarrow{k_2} product(L)$	$E_A = 1 + \dfrac{1}{\left[\left(E_{\inf} - 1 \right)^{-1.35} + \left(\dfrac{Ha}{\tan Ha} - 1 \right)^{-1.35} \right]^{1/1.35}}$
Hogendoorn et al., 1997	Irreversible second order reaction according to the surface renewal theory $A(g) + \upsilon_B B(L) \xrightarrow{k_2} product(L)$	$E = -\dfrac{Ha^2}{2\left(E_{\inf} - 1\right)} + \sqrt{\dfrac{Ha^4}{4\left(E_{\inf} - 1\right)^2} + \dfrac{E_{\inf} Ha^2}{\left(E_{\inf} - 1\right)} + 1}$ $E_{\inf} = 1 + \dfrac{D_{BL} C^{\delta}_{BL}}{\upsilon_B D_{AL} C^*_{AL}}$
Hoftyzer et al., 1954	Instantaneous reaction and film theory $A + zB \xrightarrow{k_2} z_p P$	$E = \dfrac{Ha\sqrt{\dfrac{\left(E_i - E\right)}{\left(E_i - 1\right)}}}{\tanh\left[Ha\sqrt{\dfrac{\left(E_i - E\right)}{\left(E_i - 1\right)}} \right]}$, $E_i = 1 + \dfrac{D_{BL}}{D_{AL}} . \dfrac{C_{B\infty}}{z.C_{AI}}$
Last et al., 2002	Irreversible second order and instantaneous reaction	$E = \dfrac{1}{\left(1 - \dfrac{1}{\dfrac{E}{Ha^{3/2}} + \dfrac{1}{E_i^{3/2}}} \right)^{2/3}}$
Wenmakers et al., 2016	Packed-bed column with catalytic particles and instantaneous reaction	$E = \dfrac{1}{2}\sqrt{\pi k\tau}\left[\left(1 + \dfrac{1}{2k\tau} \right) erf\left(\sqrt{k\tau}\right) + \dfrac{\exp(-k\tau)}{\sqrt{\pi k\tau}} \right]$
Hikita, 1964	Pseudo first-order reaction with Higbie's penetration theory	$E = \left(F + \dfrac{\dfrac{\pi}{8}}{F} \right) \times erfc\sqrt{\dfrac{4}{\pi}F^2} + \dfrac{1}{2}\exp\left[-\dfrac{4}{\pi}F^2 \right]$, $\mathrm{F} = \sqrt{M\left(\dfrac{E_a - E}{E_a - 1} \right)}$
Li et al., 2013	Absorption of SO_2 based on surface renewal theory $A + YB \rightarrow \mathrm{Pr}oduct$	$E = 1 + \dfrac{\sqrt{\dfrac{D_{HSO_3^-} K_{HSO_3^-}}{D_{SO_2}}}}{\left(\sqrt{C_{SO2,L}} + \sqrt{C_{SO2}} \right)}$

Reference	Reaction type	Enhancement factor
Alhseinat et al., 2014	Reversible first-order or pseudo first-order reaction based on film theory	$E=\dfrac{\left(Y_1^2-Y_2^2\right)\left(\dfrac{1}{1+K_{13}}\right)}{\left(1-ZY_2^2\right)\dfrac{\tanh\left(Y_1\sqrt{M}\right)}{Y_1\sqrt{M}}-\left(1-ZY_1^2\right)\dfrac{\tanh\left(Y_2\sqrt{M}\right)}{Y_2\sqrt{M}}}+\left(\dfrac{1}{1+K_{13}}-Z\right)\left(Y_1^2-Y_2^2\right),\ M=\dfrac{K_{12}L^2}{D_1}$
Sun et al., 2005	Instantaneous pseudo first-order reaction based on surface renewal	$E=\sqrt{\dfrac{D_{CO_2}}{D_{amine}}}+\dfrac{[amine]}{z[CO_2]_i}\sqrt{\dfrac{D_{amine}}{D_{CO_2}}}$
Awais, 2013	Irreversible pseudo first-order reaction	$E=Ha\left\{1+\dfrac{\pi}{8Ha^2}erf\left[\sqrt{\dfrac{4Ha^2}{\pi}}\right]+\dfrac{1}{2Ha}\exp\left(\dfrac{4Ha^2}{\pi}\right)\right\}$

CO_2 absorption with chemical reaction into a thin falling film is expressed as a combination of chemical reaction and diffusion. As Figure 1 shows, the CO_2 concentration in the gas phase decreases from its value in the gas phase to the concentration at the gas–liquid interface. This concentration of CO_2 is also reduced by the diffusion and chemical reaction to the concentration of CO_2 in the liquid bulk. The mass transfer depends on the resistance in the gas and liquid films, which is expressed by the diffusion coefficient and film thickness of both phases (Koronaki et al., 2015). Most of the mass transfer equations developed for reactive absorption processes are based on enhancement factor, Hata number, and film parameter (Last and Stichlmair, 2002; Ghaemi et al., 2011); these correlations only takes account of the main reaction and are obtained using different simplifications in initial and boundary conditions. Therefore, the correlations based on enhancement factor and Hatta numbers are very simple and have high deviation in the calculation of mass transfer flux. In addition, the correlations are presented for limited operating conditions and are not applicable to a wide range of conditions.

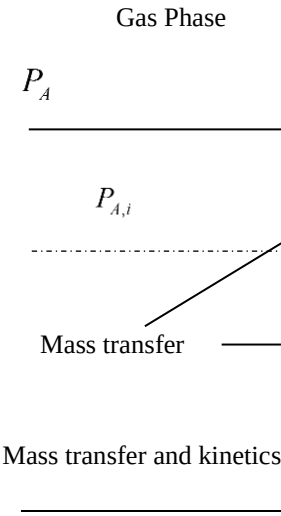

Figure 1

Mass transfer into gas and liquid phase in the film model.

Moreover, they are applicable to absorption processes with a single reaction and a single component. On the other hand, mixed amine systems often include parallel and reversible reactions which make the calculation of enhancement factor impossible. Thus, the application of the enhancement factor may not be accurate enough in the case of complex reaction schemes. Considering the fact that, in absorption processes with blended amines, most of systems are multicomponent and different reactions happen, using simple erroneous relations can lead to an egregious error in the calculation of dimensions and number of units in absorption columns. Therefore, presenting a general, rigorous, and accurate relation for blended solutions with different and varied reactions is necessary. Due to the lack of a general correlation for the calculation of the mass transfer flux of CO_2 into blended amine solutions, in this study, a general and accurate relation is presented to figure out CO_2 mass transfer flux in aqueous mixed amine solutions.

2.2. Chemical absorption process

The process of chemical absorption involves complex mechanisms of both thermodynamic and chemical nature. This process is described as reactive absorption since the reactions and phenomena of the absorbent mass transfer occur simultaneously. An important feature of the absorption process with chemical reaction is the variability of reaction rates from very low (slow reaction) to extremely high (instantaneous reaction). Therefore, modeling this mechanism is challenging and requires several factors to be designed (Zhang et al., 2010). Accurate modeling of thermodynamic properties is essential to simulate and design CO_2 absorption processes in alkanolamine solutions. When CO_2 (acidic gases) dissolves in an aqueous solution forms an electrolyte solution (Pashaei, et al., 2017). Simulation and design of absorption and recovery processes with alkanolamine aqueous solvents need to develop a good understanding of transfer phenomena and accurate thermodynamic models to calculate the driving forces for heat transfer and mass transfer.

2.3. Dimensional analysis of reactive absorption processes

In reactive absorption, the mass transfer flux depends on variables such as:

$$N_A = f\left(k, k_L, D_G, D_L, \delta_G, \delta_L, P_{CO_2}, P_t, C_{CO_2}, C_{Am}\right) \tag{2}$$

Table 3 summarizes all the variables along with their dimensions. The dimensionless parameters are obtained using the Buckingham Pi dimensionless theorem (Etemad et al., 2015).

Table 3

Dependent variables of mass transfer flux with their dimensions.

Parameter	Definition	Dimension	Unit
N_A	Mass transfer flux	$ML^{-2}T^{-1}$	$mol/(m^2.s)$
k	Reaction constant	$L^3M^{-1}T^{-1}$	$m^3/(mol.s)$
k_L	Mass transfer coefficient of liquid phase	LT^{-1}	m/s
D_G	Mass transfer coefficient of gas phase	L^2T^{-1}	m^2/s
D_L	CO_2 diffusion coefficient in liquid	L^2T^{-1}	m^2/s
δ_G	Gas film thickness	L	M
δ_L	Liquid film thickness	L	M
P_{CO_2}	CO_2 partial pressure in gas phase	$ML^{-1}T^{-2}$	Pa

Parameter	Definition	Dimension	Unit
P_t	Total pressure	$ML^{-1}T^{-2}$	Pa
C_{CO_2}	CO_2 concentration	ML^{-3}	mol/m^3
C_{Am}	Blended amine concentration	ML^{-3}	mol/m^3

Table 4

The dimensionless numbers obtained based on Pi Buckingham theorem (Etemad et al., 2015).

No.	Description	Dimensionless number
1	**Enhancement factor: ratio of absorbed amount with chemical reaction to that without chemical reaction**	$E_A = \frac{N_A}{k_L C_{CO_2}}$
2	**Sherwood: ratio of mass transfer with convention mechanism to that with diffusion mechanism**	$sh = \frac{k_L}{\delta_L D_L}$
3	**Film parameter: ratio of the maximum film conversion to the maximum diffusion rate through the film**	$M^2 = \frac{kC_{Am}C_{CO_2}\delta_L}{k_L C_{CO_2}}$
4	**Loading: ratio of CO_2 absorbed amount to amine mole**	$\alpha = \frac{C_{CO_2}}{C_{Am}}$
5	**Ratio of film thickness of gas to liquid**	$\frac{\delta_G}{\delta_L}$
6	**Ratio of CO_2 partial pressure in the gas phase to total pressure**	$\frac{P_{CO_2}}{P_t}$
7	**Ratio of CO_2 diffusion coefficient in the gas phase to that in the liquid phase**	$\frac{D_G}{D_L}$

The film parameter illustrates the influence of the reaction on the mass transfer in the boundary layer at the interface.

$$M^2 = \frac{D_L \sum_{i=1}^{n} r_{i,CO_2}}{k_L^2 [CO_2]^*} \tag{3}$$

Parameter α, also known as the loading parameter, indicates the ratio of the concentration of CO_2 to that of amine. The lower the loading rate is, the greater the mass transfer force is, so the higher the absorption rate becomes.

$$\alpha = \frac{C_{CO_2}}{C_{\text{Amine}}} \tag{4}$$

According to the Buckingham Pi theorem, the mass transfer flux is defined as Equation (5) in terms of dimensionless parameters. It should be noted that this equation is expressed by the assumption of mass transfer with the film model.

$$\frac{N_A}{k_L\left(C^*_{CO_2} - C_{CO_2,b}\right)} = A.(\alpha)^F \left(\frac{D_G}{D_L}\right)^E \left(\frac{\delta_G}{\delta_L}\right)^D \left(\frac{P_{CO_2}}{P_t}\right)^C M^B \tag{5}$$

Coefficients *A*, *B*, *C*, *D*, *E*, and *F* are the final unknowns of the correlation. Equation (5) presents the general correlation of the mass transfer flux in the CO_2 absorption process and is not dependent on the operating conditions and the type of the solvent (Etemad et al., 2015).

2.4. Modeling of electrolyte solution system of MDEA, PZ, CO_2, and H_2O

To design and simulate gas purification plants including mixed amine solutions, the development of velocity-based mass transfer models is important to explain the CO_2 mass transfer flux. In a closed system, at a constant temperature and pressure, the phase equilibrium produces the distribution of molecular components between the vapor and liquid phases, while the chemical reaction in the liquid phase occurs between the acidic gases and alkanolamines to produce the ionic components. The chemical and phase equilibrium are effectively coupled in this system. As a result, the degree of degradation of weak electrolytes in the liquid phase is affected by the partial pressure of the acidic gas in the vapor phase. Hence, the expression of the vapor–liquid equilibrium behavior of acidic gas–alkanolamine–water systems is complicated due to the large number of chemical reactions occurring in this system. Therefore, the expression of phase equilibrium for such systems requires consideration of both phase equilibrium and chemical equilibrium. Vapor–liquid equilibrium (VLE) models play an important role in simulating water–alkanolamine–acidic gas systems. In the liquid and vapor equilibrium of weak electrolyte solutions, the thermodynamic study of these solutions is based on phase equilibrium, chemical equilibrium, mass balance, and charge balance. In these systems, usually the amine vapor pressure is very low, so the presence of amines and ions in the vapor phase is negligible (Ermatchkov and Maurer, 2011).

a. Chemical equilibrium

When CO_2 is absorbed in the MDEA–PZ solution, several chemical reactions are carried out. Based on studies by Bishnoi and Rochelle et al., 2002, for capturing CO_2 in an MDEA–PZ aqueous solution, the following reactions are obtained (Alhseinat et al., 2014).

$$H_2O \xleftrightarrow{K_1} H^+ + OH^- \tag{6}$$

$$CO_2 + H_2O \xleftrightarrow{K_2} HCO_3^- + OH^- \tag{7}$$

$$MDEA + H^+ \xleftrightarrow{K_4} MDEAH^+ \tag{8}$$

$$MDEA + H^+ \xleftrightarrow{K_4} MDEAH^+ \tag{9}$$

$$PIPH_2 + H^+ \xleftrightarrow{K_5} PIPH_3^+ \tag{10}$$

$$PIPH_3^+ + H^+ \xleftrightarrow{K_6} PIPH_4^{2+} \tag{11}$$

$$PIPH_2 + HCO_3^- \xleftrightarrow{K_7} PIPHCOO^- + H_2O \tag{12}$$

$$PIPHCOO^- + HCO_3^- \xleftrightarrow{K_8} PIP(COO^-)_2 + H_2O \tag{13}$$

$$PIPHCOO^- + H^+ \xleftrightarrow{K_9} PIPH_2^+COO^- \tag{14}$$

where $PIPH_2$ stands for piperazine. The equilibrium constants of the proposed reactions are calculated by Equation (15) as function of temperature as listed in Table 5.

$$LnK_r = A + \frac{B}{T} + C.LnT + D.T + \frac{E}{T^2} \tag{15}$$

Table 5

Chemical equilibrium constants of the reactions occurring in the system of MDEA, PZ, CO_2, and H2O (Alhseinat et al., 2014).

Reaction	*A*	*B*	*C*	10^2D	*E*
(6)	140.932	–13445.9	–22.4773	–	–
(7)	–1203.01	68359.6	188.444	–20.6424	**–4.71291** × 10^6
(8)	175.360	–7230.6	–30.6509	1.31478	**–3.72805** × 10^5
(9)	79.474	819.7	–10.9756	–	-
(10)	14.119	3814.4	-	–1.5096	-
(11)	10.118	2192.3	-	–1.7396	-
(12)	–8.635	3616.1	-	-	-
(13)	–3.655	1322.3	-	-	-
(14)	10.026	3493.1	-	-	-

b. Mass balance

The mass balance equations for PZ, MDEA, and CO_2 are as expressed through:

$$m_{PZ,i} = m_{PZ} + m_{PZH} + m_{PZH_2^{2+}} + m_{PZCOO^-} + m_{PZ(COO^-)_2} + m_{PZH^+COO^-} \tag{16}$$

$$m_{MDEA,i} = m_{MDEA} + m_{MDEAH^+} \tag{17}$$

$$\alpha(m_{MDEA,i} + 2m_{PZ,i}) = m_{CO_2} + m_{HCO_3^-} + m_{CO_3^{2-}} + m_{PZCOO^-} + 2m_{PZ(COO^-)_2} + m_{PZH^+COO^-} \tag{18}$$

c. Charge balance

$$m_{H^+} + m_{PZH^+} + 2m_{PZH_2^{2+}} + m_{MDEAH^+} = m_{OH^-} + m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{PZCOO^-} + 2m_{PZ(COO^-)_2} \tag{19}$$

d. Thermodynamic model

To calculate the activity coefficient in this system, the Pitzer model as a comprehensive form of the Debye–Hückel model is used. The first part is dependent on the ionic strength and dielectric constant of the solvent. The second and third parts of the equation express the binary and ternary interactions that are not considered in the Debye–Hückel equation. The binary and ternary interaction parameters are also presented in Table 6 (Alhseinat et al., 2014). The coefficient of activity of the dissolved components in the solution is derived from the excess Gibbs free energy equation, and the activity of water is obtained from the Gibbs–Duhem equation (Bougie and Iliuta, 2010).

$$\ln \gamma_i^{*,m} = -A_Q z_i^2 \left(\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2}\ln(1+1.2\sqrt{I})\right) + 2\sum_{j\neq w} m_j \lambda_{ij}(I) - z_i^2 \sum_{j\neq w}\sum_{k\neq w} m_j m_k \frac{\beta_{jk}^{(1)}}{Ix^2}\left[1-\left(1+x+\frac{x^2}{2}\right)e^{-x}\right] + 3\sum_{j\neq w}\sum_{k\neq w} m_j m_k \tau_{ijk} \quad (20)$$

$$\ln a_w = M_w \left(2A_Q \frac{I^{1.5}}{1+1.2\sqrt{I}} - \sum_{i\neq w}\sum_{j\neq w} m_i m_j \left(\beta_{ij}^{(0)} + \beta_{ij}^{(1)} e^{-x}\right)\right) - M_w \left(2\sum_{i\neq w}\sum_{j\neq w}\sum_{k\neq w} m_i m_j m_k \tau_{ijk} + \sum_{i\neq w} m_i\right) \quad (21)$$

$$A_Q = \frac{1}{3}(2\pi N_A \rho_w)^{1/2}\left(\frac{e^2}{4\pi\varepsilon_0 DkT}\right)^{3/2} \quad (22)$$

$$\lambda_{ij}(I) = \beta_{ij}^{(0)} + \beta_{ij}^{(1)}\left[(2/x^2)(1-(1+x)e^{-x}\right] \quad (23)$$

$$x = 2\sqrt{I} \quad (24)$$

$$I = \frac{1}{2}\sum_i m_i z_i^2 \quad (25)$$

where parameter I represents the ionic strength of the components (mol/kg), and A_Q is Debye–Hückel parameter; m_i and m_j denote the concentration of the components in solution; β_{ij} and τ_{ij} are the binary and ternary interaction parameters respectively as presented in Table 6; Z_i stands for the ionic charge of the components, and T denotes the temperature (K).

Table 6

Binary and ternary interaction parameters for MDEA–PZ solution (Bougie et al., 2009).

Parameter	*A*	*B*
$\beta^{(0)}_{MDEA,MDEA}$	-8.9052×10^{-2}	29.565
$\beta^{(0)}_{PZ,PZ}$	-4.1827×10^{-3}	9.5832
$\tau^{(0)}_{PZ,PZ,PZ}$	-2.7192×10^{-4}	-
$\beta^{(0)}_{CO_2,MDEAH^+}$	-3.9590×10^{-1}	128.39
$\beta^{(0)}_{MDEA,HCO_3^-}$	-3.6344×10^{-1}	166.36
$\beta^{(0)}_{MDEA,CO_3^{2-}}$	1.5252×10^{-1}	-
$\beta^{(0)}_{MDEAH^+,HCO_3^-}$	1.1037×10^{-1}	–25.665
$\beta^{(0)}_{MDEAH^+,CO_3^{2-}}$	-5.0819×10^{-1}	45.2027
$\beta^{(1)}_{MDEAH^+,CO_3^{2-}}$	-4.9169×10^{-1}	-
$\beta^{(1)}_{MDEA,HCO_3^-}$	3.8151×10^{-1}	–106.77
$\beta^{(1)}_{MDEAH^+,HCO_3^-}$	1.9009	–567.29
$\tau_{MDEA,MDEA,HCO_3^-}$	7.5448×10^{-3}	–3.8393

$\tau_{CO_2,MDEAH^+,HCO_3^-}$	7.4943×10^{-3}	–2.6991
$\beta^{(0)}_{PZH^+,PZ(COO^-)_2}$	7.6171×10^{-1}	-
$\beta^{(0)}_{PZH^+,HCO_3^-}$	1.7774	–601.27
$\beta^{(0)}_{PZH^+,PZCOO^-}$	-4.9631×10^{-1}	235.58
$\beta^{(0)}_{PZ,PZCOO^-}$	2.1716×10^{-1}	-
$\beta^{(0)}_{CO_2,PZH^+COO^-}$	-1.5326×10^{-1}	59.234
$\beta^{(0)}_{PZH^+COO^-,PZH^+COO^-}$	1.3693×10^{-2}	–32.0
$\beta^{(1)}_{PZH^+,PZ(COO^-)_2}$	1.4389	-
$\beta^{(1)}_{PZH^+COO^-,PZH^+COO^-}$	−1.8830	807.57
$\beta^{(0)}_{MDEAH^+,PZH^+COO^-}$	1.2337×10^{-1}	–33.586
$\beta^{(0)}_{MDEAH^+,PZ(COO^-)_2}$	5.4347×10^{-1}	-
$\beta^{(0)}_{MDEA,PZCOO^-}$	3.0798×10^{-1}	–40.618
$\beta^{(0)}_{MDEA,PZ(COO^-)_2}$	8.8253×10^{-1}	-
$\beta^{(1)}_{MDEAH^+,PZH^+COO^-}$	2.2281	–654.69
$\tau_{PZH^+COO^-,MDEAH^+,HCO_3^-}$	-1.8801×10^{-2}	6.1786
$\tau_{MDEA,PZ,PZCOO^-}$	5.1208×10^{-2}	–25.619
$\tau_{CO_2,PZH^+COO^-,MDEAH^+}$	2.8842×10^{-2}	–9.6976
$\tau_{MDEA,MDEAH^+,PZCOO^-}$	-6.4467×10^{-3}	-

In calculating the concentration of the components at the interface, we must also add the thermodynamic equilibrium equations to the set of the equations given above. The equilibrium equation for water according to the modified Raoult's law is expressed in:

$$P_w^{sat}\varphi_w^{sat}\exp\left(\frac{V_w(P-P_w^{sat}}{RT}\right)a_w = Py_w\varphi_w \tag{26}$$

The vapor–liquid equilibrium of components MDEA, PZ, and CO_2 based on Henry's law is given by:

$$k_{H,i}\exp\left(\frac{V_i^{\infty}\left(P-P_w^{sat}\right)}{RT}\right)a_i = y_iP_t\varphi_i \tag{27}$$

The Henry's constant of the solubility of MDEA, PZ, and CO_2 in water is defined as:

$$Ln\left(k_{H,i}\right) = A+\frac{B}{T}+C.LnT+D.T \tag{28}$$

Table 7

Henry's constant of the solubility of MDEA, PZ, and CO_2 (Ermatchkov et al., 2011).

Component	*A*	*B*	*C*	*D*
CO_2	192.876	–9624.41	–28.7488	0.0144074
MDEA	137.044	–16747.7	–17.5818	-
PZ	1372.05	–63908.1	–218.487	0.21905

Molar volume of pure water is given by:

$$V_{CO_2,H_2O}^{\infty} = \left(4\times10^{-7}\right)\times T^3 + \left(1.5222\times10^{-4}\right)\times T^2 - 0.165690893\times T + 58.149 \quad (29)$$

Vapor pressure of pure water is expressed in:

$$Ln\left(\frac{P_w^{sat}}{P_t}\right) = \frac{T_C}{T}\left(-7.8595\tau + 1.8441\tau^{1.5} - 11.7866\tau^3 + 22.6807\tau^{3.5} - 15.9619\tau^4 + 1.8012\tau^{7.5}\right) \quad (30)$$

$$\text{where } \tau = 1 - \frac{T}{T_c} \quad (31)$$

where P_c = 22.064 MPa and T_c = 647.096 K.

The fugacity coefficient of carbon dioxide in the gas phase is defined as:

$$\varphi_{CO_2} = \exp\left(\frac{B_{CO_2}\times P}{82.06\times T}\right) \quad (32)$$

$$B_{CO_2}\left(\frac{cm^3}{mol}\right) = 137.6 - 87.7\times\exp\left(\frac{325.7}{T}\right) \quad (33)$$

After calculating the concentration of the components, to calculate dimensionless parameter *M*, it is necessary to figure out the reaction velocity as reads:

$$R_{CO_2} = k_{MDEA,CO_2}C_{MDEA}\left(C_{CO_2}^{*} - C_{CO_2,b}\right) + k_{PZ,CO_2}C_{PZ}\left(C_{CO_2}^{*} - C_{CO_2,b}\right) + k_{OH,CO_2}\left(C_{CO_2}^{*} - C_{CO_2,b}\right) \quad (34)$$

$$\log_{10}\left(\frac{k_{OH^-}^{*}}{m^3kmol^{-1}s^{-1}}\right) = 13.635 - \frac{2895}{T} \quad (35)$$

$$k_{PZ}\left(m^3kmol^{-1}s^{-1}\right) = 2.572\times10^{12}\exp\left(-\frac{5211}{T}\right) \quad (36)$$

$$k_{MDEA}\left(m^3kmol^{-1}s^{-1}\right) = 4.01\times10^{8}\exp\left(-\frac{5400}{T}\right) \quad (37)$$

3. Calculating process variables

3.1. Concentration of CO_2 absorbed in the liquid bulk

The equations derived from the combination of four laws of mass balance, charge balance, chemical equilibrium, and phase equilibrium with the activity coefficient equations using the Pitzer's thermodynamic model are expressed, and the bulk concentration of CO_2 was then calculated using numerical methods. It should be noted that the input variables are temperature, the total concentrations of PZ and MDEA, and loading of CO_2 with respect to amine.

3.2. Concentration of CO_2 absorbed at the interface

Thermodynamic equilibrium must also be considered to obtain the concentration of the components at the interface. The equilibrium equation for water is obtained using the modified Raoult's law (Equation (26)), and the vapor–liquid equilibrium of CO_2 follows the developed Henry's law (Equation (27)).

3.3. Film parameter

The concentration of the components in the liquid bulk and at the interface is calculated. Then, the rate of the reaction is calculated using Equation (34). Afterward, the film parameter can be calculated using the values obtained for the rate of the reaction. Dimensionless parameters are figured out using experimental data under the operating conditions listed in Table 8 (Chen, 2011).

Table 8

Operating conditions for experimental data of CO_2 absorption into MDEA–PZ solution (Chen, 2011).

Concentration (MDEA–PZ)	Loading (mol CO_2/mol amine)	P_{CO2} (Pa)	Total pressure (psig)	Temperature (°C)
5–7/5–2	0.027–0.37	280–65000	20–60	40–100

Finally, the constants of Equation (5) are figured out using the nonlinear regression, and mass transfer flux of CO_2 in the absorption system with MDEA–PZ solution is expressed through Equation (38).

$$N_{CO_2} = 0.2867 k_L (C^*_{CO_2} - C_{CO_2,b}) \alpha^{-0.4089} \left(\frac{P_{CO_2}}{P}\right)^{0.1517} \left(\frac{\delta_G}{\delta_L}\right)^{-2.2614} \left(\frac{D_G}{D_L}\right)^{1.5705} M^{-0.1409} \quad (38)$$

Figure 2 compares the mass transfer flux obtained from Equation (38) with the experimental mass transfer flux and shows an R^2 of 0.951, which indicates that the proposed equation is accurate for calculating the mass transfer flux.

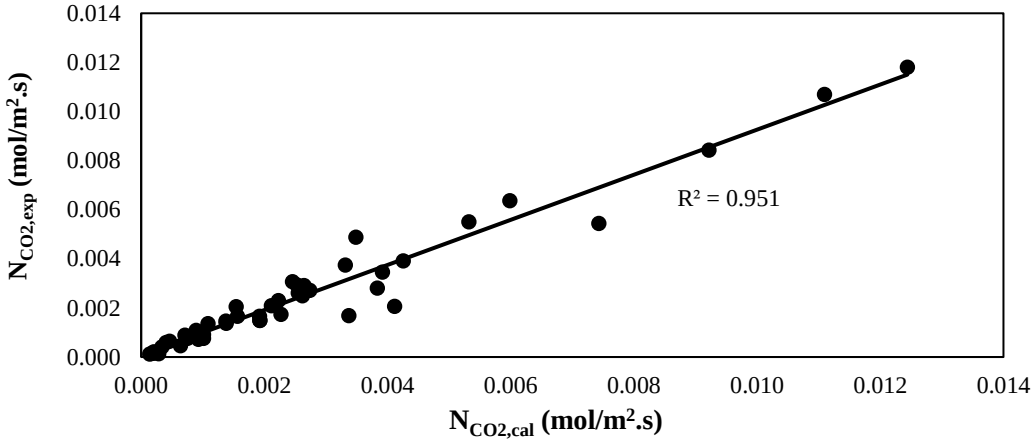

Figure 2

Experimental values of mass transfer flux versus the mass transfer flux derived from Equation (38).

4. Numerical solution

MATLAB software as one of the most powerful engineering software tools is widely used for solving chemical engineering problems due to its flexibility and ease of use; it also has a good environment for programming and simulation. In the present study, MATLAB software was utilized for programming and simulation. It should be noted that the Newton–Raphson method is employed for calculating concentrations and activity coefficient. In the calculations of the concentration and activity coefficients of the components in the liquid bulk and at the interface, the equations of chemical equilibrium, mass balance, charge balance, phase equilibrium along with thermodynamic equations are expressed as a set of nonlinear equations.

$$\begin{aligned} f_1(x_1, x_2, ..., x_n) &= 0 \\ f_2(x_1, x_2, ..., x_n) &= 0 \\ &\text{M} \\ f_n(x_1, x_2, ..., x_n) &= 0 \end{aligned} \tag{39}$$

where $f(x)$'s are the equations and $x_1, x_2, \ldots, x_n$ are the unknown. According to Newton–Raphson method, the final equation will be expresses in:

$$J(x^k) \times t = -f(x^k) \tag{40}$$

where $J(x^k)$ is computable by MATLAB, and t is the step length. The algorithm of this method is shown in Figure (3).

According to this algorithm, an initial guess is needed to solve the equations and thus to calculate the unknowns, i.e. the concentration of the components and activity coefficients. It is important to choose a right guess since if even one of the initial guessed concentrations is incorrect, the answers are complex and unacceptable. Moreover, when the conditions, namely temperature, pressure, partial pressure, loading, and total concentration, change, the initial guesses must usually be varied. It should be noted that in calculating the bulk liquid concentration, input variables are the temperature, the total molality of both amines, and CO_2 loading. In the calculation of the interface concentration, the input variables are temperature, total pressure, the total molality of both amines, and partial pressure of CO_2 in the gas bulk, and the CO_2 loading must be calculated. Finally, by calculating the concentration of the

components in the liquid bulk and at the interface, the rates of the reactions are obtained; thus, parameter *M* and other dimensionless parameters will be figured out. Consequently, using experimental data and nonlinear regression, the mass transfer flux equation is derived.

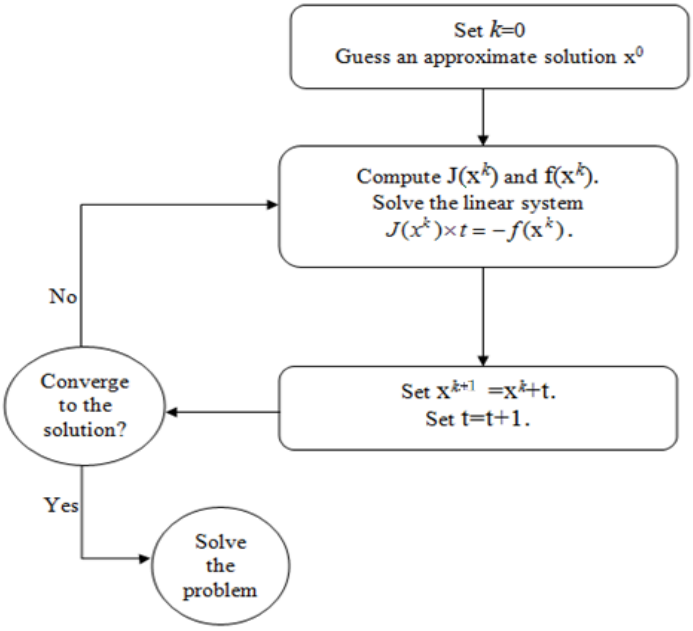

Figure 3

Algorithm for solving the equations of Newton–Raphson method.

5. Results and discussion

In this study, the mass transfer flux of CO_2 was expressed as an equation with a subset of dimensionless parameters, film parameter, loading, gas–liquid diffusion coefficient ratio, gas–liquid film thickness ratio, and the ratio of partial pressure to total pressure using the Buckingham Pi theorem. Then, the MDEA–PZ solution system was modeled, and the equation constants were finally calculated. In the following, some parameters affecting the mass transfer flux of CO_2 have been investigated.

In Figures 4 and 5, the concentration of free amine present in the solution is expressed as a function of different CO_2 loadings. As can be seen, at a constant concentration of solvent, the amount of free amine increases with decreasing the rate of the CO_2 loading. Furthermore, because the amount of CO_2 absorbed increases with raising the CO_2 loading, the mass transfer flux of CO_2 rises. Obviously, as the mass transfer flux of CO_2 increases, more amines react with CO_2, so the amount of free amines in the solution drops.

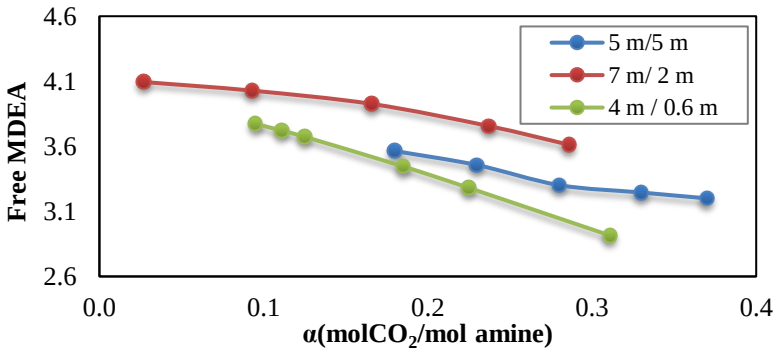

Figure 4

Free MDEA in the solution versus the CO_2 loading at different concentrations.

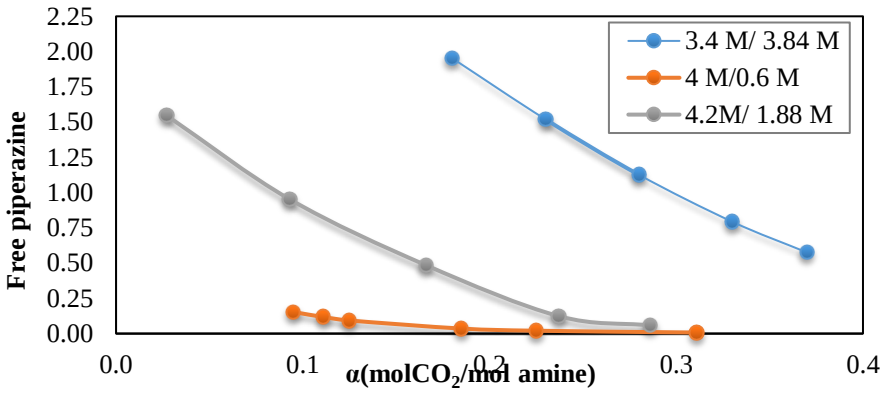

Figure 5

Free piperazine in the solution versus the CO_2 loading at different concentrations.

Figures 6 and 7 delineate the mass transfer flux of CO_2 against different CO_2 loadings at different film parameters. It is obvious that at a lower CO_2 loading (before entering the absorption tower), there is less CO_2 in the solvent; in fact, a fresher solvent creates a larger driving force (concentration difference), so the mass transfer flux of CO_2 increases. Further, the mass transfer flux of CO_2 drops with raising film parameter, and at larger film parameter values, the influence of film parameter on the mass transfer flux of CO_2 decreases.

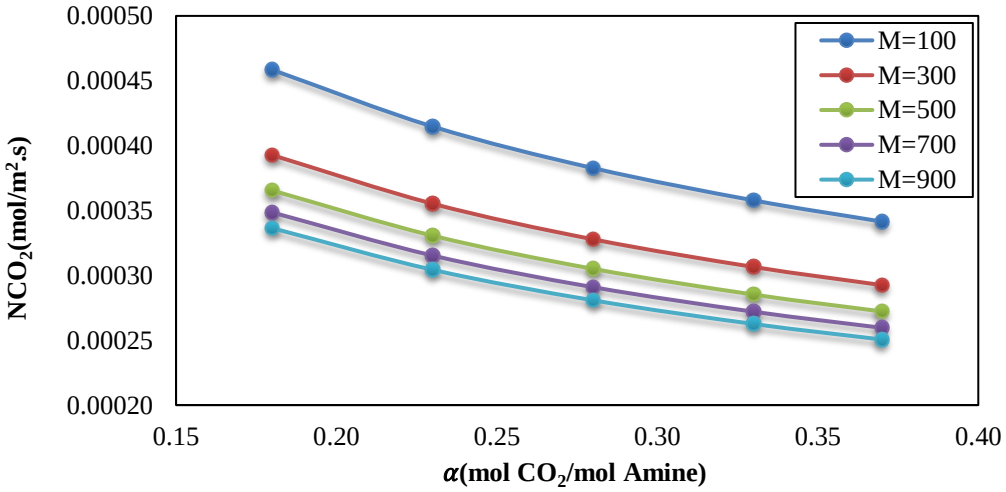

Figure 6

Mass transfer flux of CO_2 against CO_2 loading at different film parameter values.

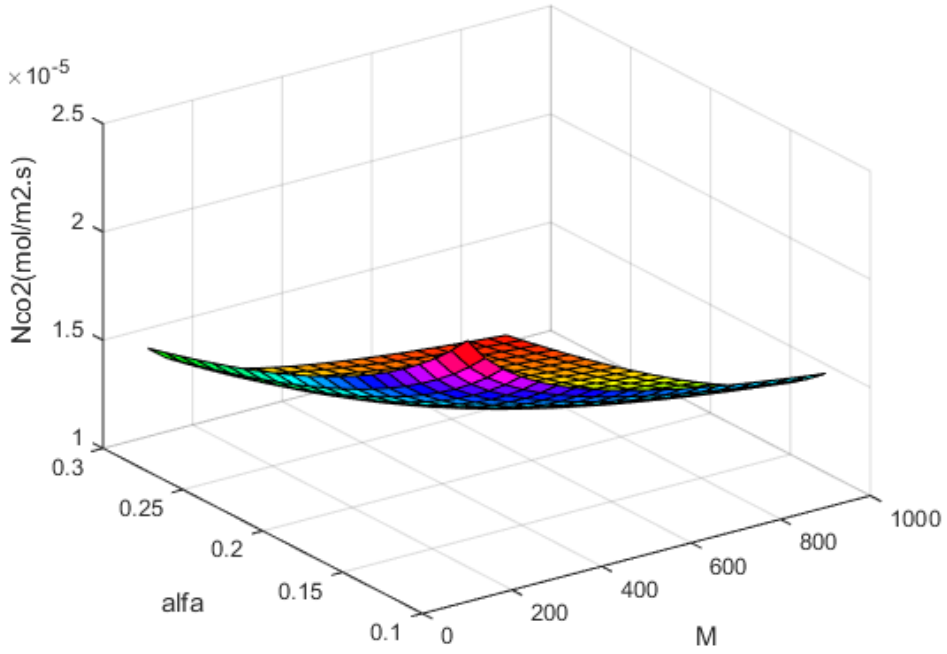

Figure 7

3D plot of the variation of the mass transfer flux of CO_2 against the film parameter and CO_2 loading.

The effect of partial pressure on the mass transfer flux of CO_2 at different CO_2 loadings is presented in Figures 8 and 9. The mass transfer flux of CO_2 rises with increasing partial pressure. In other words, the driving force improves with increasing partial pressure in the gas phase, so the mass transfer flux of CO_2 increases. On the other hand, by increasing the CO_2 loading at a constant pressure, the driving force falls, so the mass transfer flux of CO_2 drops. The changes in the mass transfer flux of CO_2 falls at a high CO_2 loading because the amount of CO_2 present in the solvent rises; thus, the ability of the solvent to absorb CO_2 decreases, thereby reducing the mass transfer flux of CO_2.

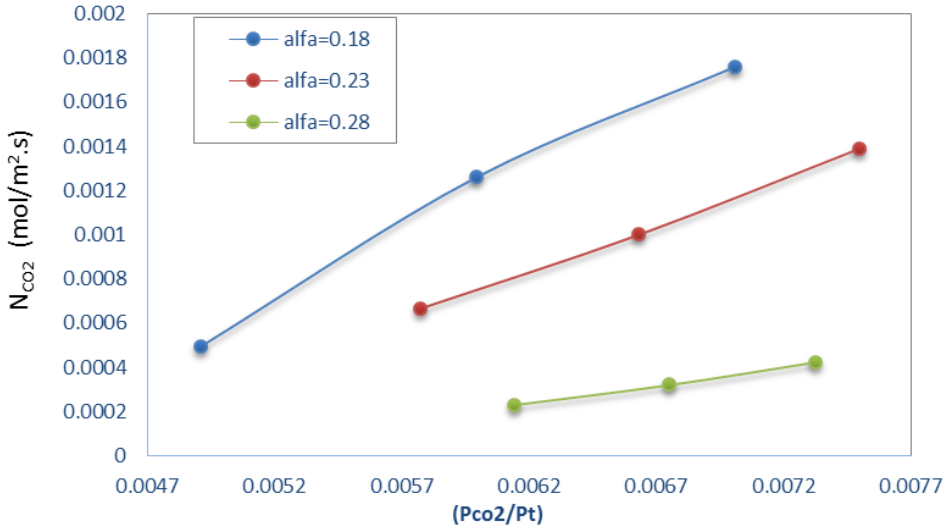

Figure 8

Variation in the mass transfer flux of CO_2 with partial pressure at different CO_2 loadings.

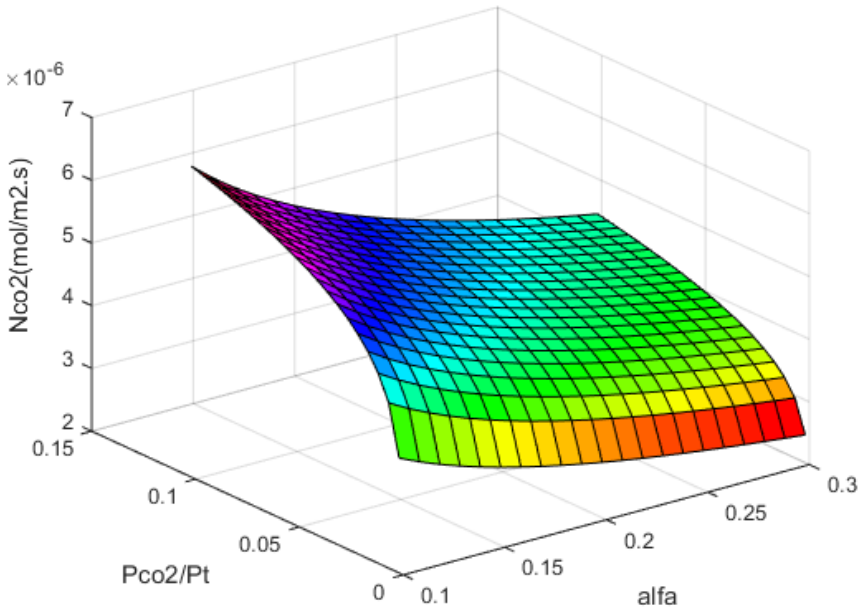

Figure 9

3D plot of the variation in the mass transfer flux of CO_2 with partial pressure at different CO_2 loadings.

Figure 10 illustrates the effect of the temperature and film parameter on the enhancement factor. The slope of the curve decreases with raising the temperature, which indicates that as the temperature rises, the absorption process slows down. In addition, the enhancement factor drops with increasing the temperature, so the mass transfer flux of CO_2 falls; hence, the reduction of the mass transfer flux of CO_2 with temperature demonstrates that the absorption process is obviously exothermic; therefore, the higher the temperature, the lower the mass transfer flux of CO_2.

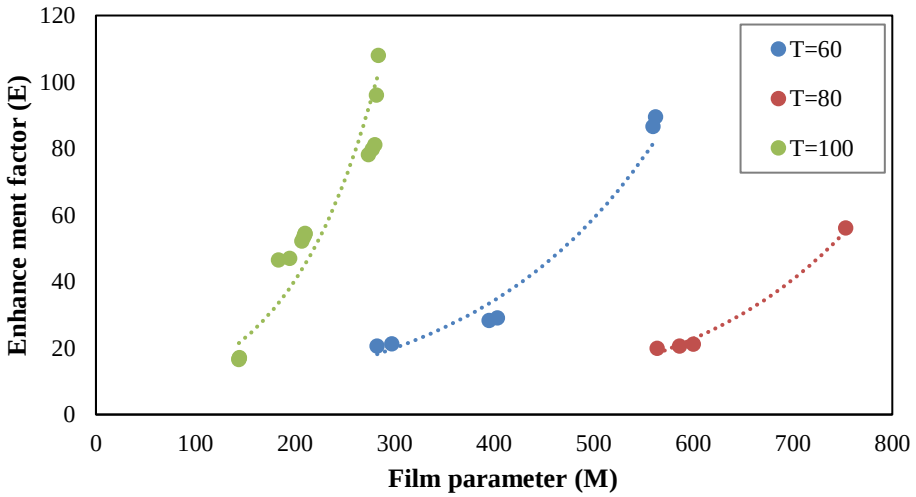

Figure 10

Variation of the enhancement factor with the film parameter at various temperatures.

Figure 11 shows the effect of the film thickness on the mass transfer flux of CO_2 at different temperatures. It is clear that as the film thickness rises, the resistance to mass transfer decreases, so the mass transfer flux of CO_2 declines. Also, as mentioned earlier, the mass transfer flux of CO_2 decreases when the temperature rises.

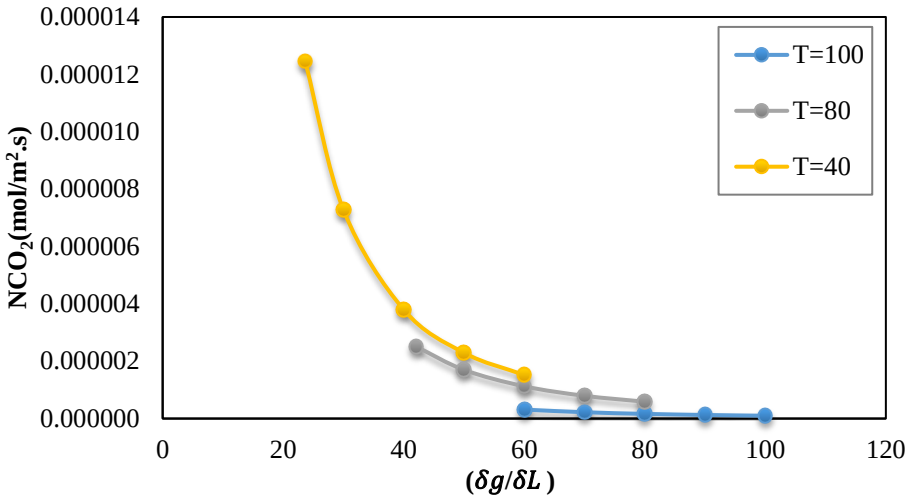

Figure 11

Variation of the mass transfer flux of CO_2 with film thickness at various temperatures.

The absorption rate of CO_2 versus the concentration of free piperazine is investigated in Figure 12 at two different concentrations of the MDEA–PZ solution. According to the figure, the absorption rate of CO_2 strongly depends on the amount of free amines in the solution. Moreover, as the concentration of amine in the solution increases, the amount of free amine in the solution rises.

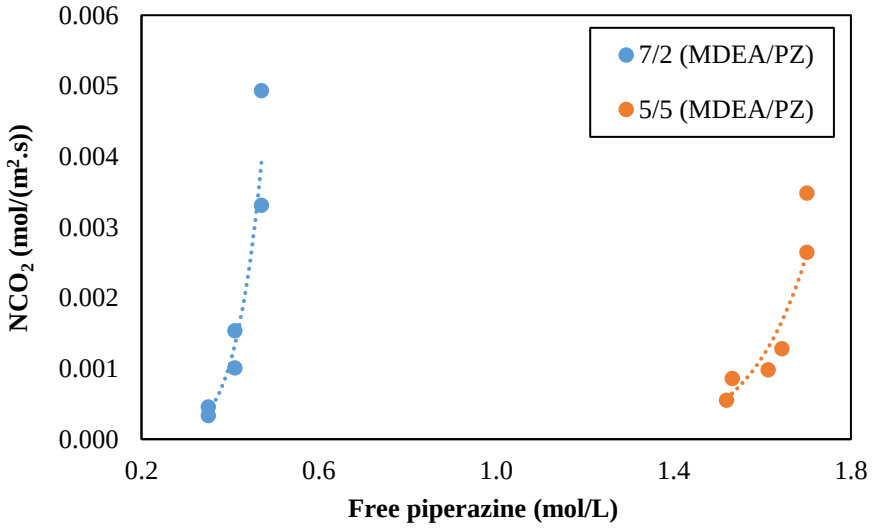

Figure 12

Variation of the mass transfer flux of CO_2 with free piperazine at various total concentration of amine.

Figure 13 depicts the concentration of the ionic components as a function of the CO_2 loading for the solution of 5 mol MDEA and 5 mol PZ in the absorption process. It is obvious that with increasing the CO_2 loading, the amine concentration declines in the solution; in other words, by the chemical reaction in the absorption process, the amine concentration drops and thus the ionic components are formed. It

should be noted that PZH^+ and $PZCOO^-$ are the ionic intermediates that first increase and then decrease with raising the CO_2 loading rate; they are converted to PZH_2^{2+} and $PZ(COO^-)_2$.

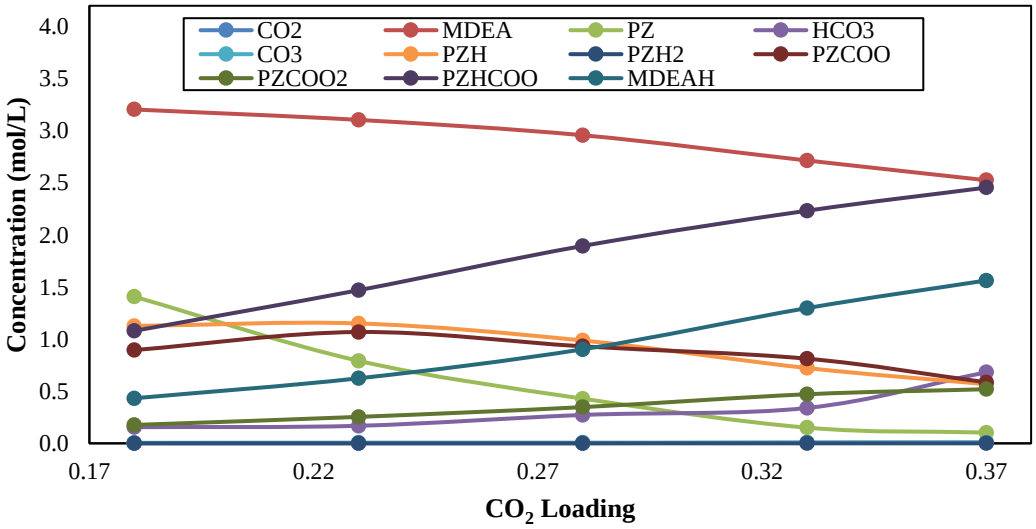

Figure 13

Concentration of the ionic components versus the CO_2 loading.

Table 9 compares the calculated mass transfer flux of CO_2 with the values reported in previous studies. The predicted values show the least deviation from the data reported in the literature, which indicates that the derived equation is highly accurate.

Table 9

Deviation of the derived correlation from the data reported in previous researches.

Author	Deviation
Mandal et al., 2001	5.0
Edali et al., 2010	7.8
Puxty et al., 2011	15.0
Samanta et al., 2002	6.8
Equation (38)	4.8

6. Conclusions

Simulation and design of absorption processes with aqueous solvents of alkanolamines are needed to develop a good understanding of transfer phenomena, and accurate thermodynamic models are required to calculate the driving forces for heat transfer and mass transfer. Since the bulk concentration of all the components is essential for mass transfer analysis, a liquid-balance equilibrium model is considered to estimate the liquid bulk concentration of all the chemical components. In this work, the process of the absorption of CO_2 into an MDEA–PZ aqueous solution was modeled according to the four rules governing chemical equilibrium, phase equilibrium, mass balance, and charge balance. The results were compared with the experimental data in the literature. Moreover, the influences of different operating parameters were also investigated using the proposed model. The CO_2 loading has a negative coefficient that indicates its negative influence on the mass transfer flux of CO_2. Because of the lower initial loading of CO_2, a lower amount of CO_2 is present in the solution; thus, the fresher the solution, the greater its absorption capacity, and the higher the mass transfer flux of CO_2. The mean absolute deviation of the

model is also about 3.6%, which confirms its high accuracy. The model provides a general and accurate method with the least simplifying assumptions for calculating the mass transfer flux of CO_2 in reactive absorption systems. The limitations of this model are considering some simplifications such as the film model and setting a unit value for the Sherwood number. In fact, some amine evaporates and enters the gas phase, while it is assumed herein that there is no amine in the gas phase; thus, considering phase equilibrium equations for the amines along with other equations enhances the accuracy of the model. In future research, it is recommended that other mixed solutions should be used for CO_2 absorption. In the modeling, the partial pressure of the amines should be taken into account as an effective variable in the mass transfer flux correlation. In addition, other mass transfer models such as Higbie's penetration theory and surface renewal theory can be used for the absorption mechanism. Employing high-precision solving methods for calculating the concentration of the components is also suggested.

Nomenclature

$A_Q\,(kg/mol)^{1/2}$	Debye-Huckel parameter
$B_{i,j}\,(cm^3/mol)$	Second virial coefficient between *i, j*
$C_{Am}\,(mol/L)$	Amine concentration
$C_{CO_2}\,(mol/L)$	CO_2 concentration in liquid bulk
$C^*_{CO_2}\,(mol/L)$	CO_2 concentration at interface
$D_g\,(m^2/s)$	Gas phase diffusion coefficient
$D_L\,(m^2/s)$	Liquid phase diffusion coefficient
E	Enhancement factor
Ha	Hata number
$H_{CO_2}\,(Mpa.kg/mol)$	CO_2 Henry's constant
$I\,(mol/kg)$	Ionic strength
$k\,(m^3/mol.s)$	Reaction constant
$k_L^0\,(m/s)$	Liquid phase mass transfer coefficient
K	Chemical equilibrium constant
M	Film parameter
MDEA	Methyl diethanolamine
$M_w\,(kg/mol)$	Water molecular weight
$N_{CO_2}\,(mol/m^2.s)$	CO_2 mass transfer flux
$P_{CO_2}\,(Pa)$	CO_2 partial pressure
$P_t\,(Pa)$	Total pressure
$P_w^{sat}\,(Pa)$	Water saturated vapor pressure
Pz	Piperazine
$r_{CO_2}\,(mol/L.s)$	CO_2 reaction rate
r_i	Volume parameter
q_i	Surface area parameter
Sh	Sherwood Number
TEA	Triethanolamine
$T\,(k)$	Temperature

u_{ij}	Binary interaction of *i*,*j*
y_{CO_2}	CO_2 mole fraction in gas phase
Z	Ion charge
α	Loading
β_{ij}	Binary interaction coefficient
$\delta_g(m)$	Gas film thickness
$\delta_L(m)$	Liquid film thickness
γ_i	Activity coefficient of species *i*
θ_i	Surface fraction of species *i*
λ_{ij}	Second virial coefficient
τ_{ijk}	Tertiary interaction coefficient
ϕ_i	Volume fraction of species *i*

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