A comprehensive model is developed for simulating the rate of corrosion of carbon steel in carbonated aqueous activated MDEA (Methyl-di-ethanolamine) solutions. The model includes VLE (Vapor Liquid Equilibrium) and the electrochemical behavior of amine systems. The VLE model is used to predict the speciation of aqueous carbonated MDEA-PZ solutions and their concentrations, activity coefficients, and transport properties. The electrochemical model simulates partial oxidation and reduction processes on the surface of carbon steel. The model was capable to predict the effect of PZ (piperazine) concentration on the carbon steel corrosion rate, for carbonated solutions of MDEA/PZ blends. The model is executed in a Matlab program that simulates the effect of process operating conditions such as solution temperature, CO$_2$ loading, solution pH, total amine concentration, and PZ concentration on carbon steel corrosion rates. Results of speciation and corrosion models are in good agreement with the experimental findings.

**Keywords:** CO$_2$ capture, CO$_2$ corrosion, Methyl-di-ethanolamine, Piperazine, Carbon steel, Polarization curve.

1. **INTRODUCTION**

Amine-based-CO$_2$ absorption process has gained interest as an immediate technological solution for CO$_2$ capture from flue gas streams of coal-fired power plants. The amine scrubbing technology is well established for the sweetening of utility gas streams. On the other hand, yet it suffers from design and operational (solvent volatility, degradation, and corrosivity) problems for post-combustion CO$_2$ capture [1, 2]. Aspect of corrosion is one of the main challenges in post-combustion CCS (carbon capture and storage), which ultimately affects solvent performance efficiency, plant operation and safety. Since corrosion cannot be avoided, it has to be understood in order to select the
material of construction, inhibitors and process parameters. Corrosiveness of amine solutions during CO₂ absorption depends on various parameters such as the type and concentration of amine, CO₂ loading, temperature, and the presence and types of degradation products [3].

A preferred amine system in recent years for the amine scrubbing process is activated methyl-di-ethanolamine. The activated MDEA system is considered a physical absorption system at high CO₂ partial pressure and chemical absorption at low CO₂ partial pressure [4]. Piperazine using as an activator in MDEA is one of the favored subjects of investigation in the recent years [5-7]. Piperazine is an effective promoter in CO₂ absorption using amine scrubbing process [6, 8, 9].

Corrosion studies of some of the blends of PZ on carbon steel has been conducted recently [10, 11]. Corrosion in tin presence of activated MDEA solutions was studied by Zhao et al. [10], showing the same detrimental impact of CO₂ loading and temperature as already observed in MEA (monoethanolamine) or other amine systems. Corrosion product layers of carbon steel were investigated in CO₂-saturated MDEA solutions under 4.5 MPa CO₂ at 100 °C by Guo and Tomoe [12]. Results of Zheng [13] show that the formation of FeCO₃ layer on the surface of carbon steel in carbonated aqueous PZ solutions at high temperature was dense, stable and protective that results a sharp decrease in carbon steel corrosion rate. However, knowledge of the corrosion behavior on carbon steel in activated amine solutions is still not well understood. Choi et al. [14] developed a predictive model for corrosion of carbon steel in CO₂-loaded aqueous methyl-di-ethanolamine systems, based on modeling of thermodynamic equilibria and electrochemical reactions. This model is applicable to uniform corrosion when no protective films are present.

Objective of this work is to develop a mechanistic corrosion rate model of carbon steel in aqueous carbonated solutions of activated methyl-di-ethanolamine under absorber operating conditions. Effect of activator concentration at various temperatures on the corrosion behavior of carbon steel in carbonated solution is investigated.

2. ELECTROCHEMICAL SETUP

2.1 Materials

The specimens were made of carbon steel with a chemical composition of C, 0.20; Mn, 0.51; P, 0.013; S, 0.039; Si, 0.17 and balanced Fe. The specimens were manufactured and supplied by the corrosion meter company (Radiometer France). They were shaped cylindrical, and inserted tight into Teflon. The cylinder base disc was with surface area of 0.196 cm². The specimen was threaded into the rotating electrode, which was connected to the radiometer FCTV101. Carbon steel was chosen as it is generally used in the absorber, lean amine cooler tubes, reflux drum, and regenerator shell. The specimens were ground with 600 grit silicon carbide paper.

Aqueous solutions of activated MDEA were prepared using double distilled water from 99% MDEA reagent, PZ flakes (99% purity), which were purchased from Acros Organics and Merck Millipore respectively. The partial pressure of CO₂ in the flowing gas stream was varied from 1 kPa to 100 kPa by adjusting the flow rates of CO₂ and N₂ of known composition in the reaction gas. The total
pressure of the reactor was monitored using a pressure transducer, temperature ranged from 40 to 80 °C, and total amine concentration was kept 2.0 M. In the mixtures of MDEA/PZ, the piperazine concentration was varied from 0.01 M to 0.1 M.

2.2. Potentiodynamic polarization measurements

The corrosion tests were carried out in a 250 ml cell under atmospheric pressure. The setup consisted of a jacketed cell equipped with the following accessories: (1) three-electrode corrosion cells, platinum wire counter electrodes (auxiliary electrode), a calomel reference electrode, and a working electrode; (2) hot plate equipment with temperature controller; (3) gas (nitrogen and carbon dioxide) supplied on the top of the solution to maintain the CO₂ loading in the solution; (4) Potentiostat /Galvanostat and a radiometer FCTV101; (5) pH meter. The schematic of experimental setup is shown in Figure 1.

![Figure 1. Schematic of the electrochemical experimental setup for corrosion experiment [15].](image)

During each run, a gas mixture of CO₂ and N₂ was bubbled through the cell until gas-liquid equilibrium was attained when a constant pH of solution was observed. Then, potentiodynamic technique was used to run the corrosion tests. In this procedure, before each polarization experiment the carbon steel working electrode surface (specimen) was polished with 600 grit silicon carbide
papers. Then mounted on the specimen holder (rotating working electrode), and immersed into the carbonated activated MDEA solution. The working electrode was subjected to a constant rotation speed of 600 rpm through a radiometer speed control unit.

Potential scanning was effected using a radiometer potentiostat /galvanostat connected to a PC coupled with a control and data acquisition system. The potentiodynamic sweep technique was used to investigate the corrosion mechanism. The sweeps were conducted with a scan rate of 1.8 mV/sec.

The corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) were calculated from the intersection of anodic and cathodic Tafel slopes of the polarization curves using EC-Lab software V10.12, 2011. The corrosion rate (CR) was calculated using the following equation:

$$CR = \frac{3.30 \times 10^{-3} \times i_{corr} \times MW}{\rho}$$

Where CR is the rate of corrosion (mm/yr), $i_{corr}$ is corrosion current density ($\mu$A/cm$^2$), MW is the molar weight of the specimen (g/mol), and $\rho$ is the density of specimen (g/m$^3$).

3. SPECIATION MODEL

3.1 Vapor-liquid equilibrium model

In an open system, due to unlimited supply of gas, there is a constant partial pressure of carbon dioxide gas species on the surface of the amine solution in amine scrubbing process. Vapor-liquid equilibrium of carbon dioxide reaction is described as:

- **R1**: CO$_2$ phase change:
  $$CO_2(g) \rightleftharpoons CO_2(aq)$$

  When carbon dioxide is dissolved in aqueous solution containing PZ and MDEA, aqueous carbon dioxide undergoes a sequence of chemical reactions as follows [16, 17]. Carbonic acid (H$_2$CO$_3$) is not included here as it is in much lower concentration compared to other carbonic species (HCO$_3^-$ and CO$_3^{2-}$). In the follow-up electrochemical work it was confirmed that H$_2$CO$_3$ does not contribute much to the overall corrosion process and could be omitted from the analysis [14].

- **R2**: Dissociation of water:
  $$2H_2O \rightleftharpoons \overset{K_1}{\underset{K_5}{OH}} + H_3O^+$$

- **R3**: Dissociation of CO$_2$:
  $$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

- **R4**: Dissociation of bicarbonate ions:
  $$HCO_3^- + H_2O \overset{K_4}{\underset{K_6}{CO_3^{2-} + H_3O^+}}$$

- **R5**: Dissociation of protonated piperazine:
  $$PZH^+ + H_2O \rightleftharpoons PZ^+ + H_3O^+$$

- **R6**: Formation of piperazine carbamate:
  $$PZ + CO_2 + H_2O \rightleftharpoons PZCOO^- + H_3O^+$$

- **R7**: Dissociation of zwitterion (protonated carbamate):
  $$H^+PZCOO^- + H_2O \rightleftharpoons PZCOO^- + H_3O^+$$

- **R8**: Dissociation of piperazine carbamate:
  $$PZCOO^- + CO_2 + H_2O \rightleftharpoons PZ(COO^-)_2 + H_3O^+$$

- **R9**: Dissociation of protonated methyl-di-ethanolamine:
  $$MDEAH^+ + H_2O \rightleftharpoons MDEA + H_3O^+$$

Where: $K$ is the equilibrium constant of reversible reaction at equilibrium, which were obtained from literature and are given in Table 1 on a mole fraction basis. The $K_i$ of the above reactions is expressed in terms of activity coefficient ($\gamma_i$) and mole fraction chemical species ($x_i$), as given in equation 1 through 8:
In addition, Henry's law can express the physical solubility of CO₂ absorption in amine solution:

\[ P_{CO_2} = H_{CO_2} [CO_2] \]  

Where: \( P_{CO_2} \) is the partial pressure of CO₂, measured during the experiment; \( H_{CO_2} \) is the Henry’s law constant for CO₂, which is a function of temperature as shown in Table 1. To quantify bulk concentration of all chemical species, the additional equations for each solution are listed as in equation 10 through 14:

**Electro neutrality balance:**

\[ MDEAH^+ + PZH^+ + H_2O = HCO_3^- + OH^- + 2 CO_3^{2-} + PZCOO^- + 2PZ(COO^-) \]

**Mole balance for PZ:**

\[ PZ + PZH^+ + PZCOO^- + H^+PZCOO^- + PZ(COO^-)_2 = PZ_{Total} \]

**Mole balance for MDEA:**

\[ MDEA + MDEAH^+ = MDEA_{Total} \]

**Total mole fraction:**

\[ \sum_{i=1}^{N} x_i = 1.0 \]

**Mole balance for CO₂:**

\[ CO_2 + HCO_3^- + CO_3^{2-} + PZCOO^- + H^+PZCOO^- + PZ(COO^-)_2 = CO_2_{Total} \]

### 3.2 Calculation of fugacity coefficients

Under the established phase equilibria, the fugacity of each constituent in the liquid and vapor phase are identical. Under equilibrium conditions, CO₂ molecules distribution takes place between liquid and vapor phases as per equation (15). However, water, PZ, and MDEA distribute themselves according to activity coefficient approach as in equation (16) [18].

\[ \phi_{CO_2}^{\gamma_{CO_2}} P = \gamma_{CO_2} x_{CO_2} H_{CO_2}^{\infty} \exp \left( \frac{\nabla_{CO_2}(P_{H2})}{RT} \right) \]
Where $y_i$ and $x_i$ are concentration of species in vapor and liquid phases, respectively, $v_i^{\infty}$ partial molar volume of CO$_2$ at infinite dilution was calculated by using the Brli–O’Connell method. $P^o$ is the vapor pressure and $\varphi_i^p$ vapor phase fugacity coefficient. The Soave–Redlich-Kwong (SRK) equation of state have been made in use to calculate the vapor phase fugacity coefficients for equations (15) and (16) [19] and the liquid phase activity coefficients are calculated using the e-NRTL (electrolyte – nonrandom two liquid) model.

**Table 1. Temperature dependence of equilibrium constants and Henry’s constant**

<table>
<thead>
<tr>
<th>Component</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>T(K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>132.9</td>
<td>-13446</td>
<td>-22.48</td>
<td>0.0</td>
<td>273-498</td>
<td>[20]</td>
</tr>
<tr>
<td>$K_2$</td>
<td>231.4</td>
<td>-12092</td>
<td>-36.78</td>
<td>0.0</td>
<td>273-498</td>
<td>[20]</td>
</tr>
<tr>
<td>$K_3$</td>
<td>216.0</td>
<td>-12432</td>
<td>-35.48</td>
<td>0.0</td>
<td>273-498</td>
<td>[20]</td>
</tr>
<tr>
<td>$K_4$</td>
<td>-9.6416</td>
<td>-5008.4</td>
<td>0.0</td>
<td>0.0</td>
<td>270-350</td>
<td>[21]</td>
</tr>
<tr>
<td>$K_5$</td>
<td>466.497</td>
<td>1614.5</td>
<td>-97.540</td>
<td>0.2471</td>
<td>273-343</td>
<td>[22]</td>
</tr>
<tr>
<td>$K_6$</td>
<td>6.822</td>
<td>-6066.9</td>
<td>-2.290</td>
<td>0.0036</td>
<td>273-343</td>
<td>[22]</td>
</tr>
<tr>
<td>$K_7$</td>
<td>-11.563</td>
<td>1769.4</td>
<td>-1.467</td>
<td>0.0024</td>
<td>373-343</td>
<td>[22]</td>
</tr>
<tr>
<td>$K_8$</td>
<td>-83.49</td>
<td>-819.7</td>
<td>10.9756</td>
<td>0.0</td>
<td>278-368</td>
<td>[7]</td>
</tr>
</tbody>
</table>

Henry’s constant: $\ln H_{CO_2} = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T$

**3.3 Calculation of activity coefficients**

The e-NRTL equation used in the present study to calculate the excess Gibbs energy is presented in equation (17) [17].

\[
\frac{G^\text{ex}}{RT} = \frac{G^\text{ex,PDH}}{RT} + \frac{G^\text{ex,Born}}{RT} + \frac{G^\text{ex,ic}}{RT} \tag{17}
\]

\[
\frac{G^\text{ex,PDH}}{RT} = -\sum_i x_i \left(\frac{1000}{M_i}\right)^{\frac{1}{2}} \left(\frac{4\pi A \rho I_x}{\rho}\right) \ln \left(1 + \frac{\rho I_x}{\rho} \right) \tag{18}
\]

Where Debye–Hückel parameter ($A_\phi$) and ionic strength of solvent ($I_x$), are given by equations (19) and (20), respectively.

\[
A_\phi = \frac{1}{2} \left(\frac{2\pi N_A d_g}{1000}\right)^{\frac{1}{2}} \left(\frac{e^2}{D kT}\right)^{\frac{3}{2}} \tag{19}
\]

\[
I_x = \frac{1}{2} \sum_i x_i Z_i^2 \tag{20}
\]

The Born correction term for the excess Gibbs energy is presented by equation (21):

\[
\frac{G^\text{ex,Born}}{RT} = \left(\frac{e^2}{2kT}\right) \left(\frac{1}{D} - \frac{1}{D_w}\right) \left(\sum_i x_i Z_i^2 \right) \times 10^{-2} \tag{21}
\]
Mass fraction averages were used to calculate the mixed solvent dielectric constants. The dielectric constants for solvent constituents are presented in Table 2. The e-NRTL expression for the short-range interaction is given as in equation (22):

\[
\frac{G_{\text{ex},c}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm,cm} \tau_m}{\sum_k X_k G_{kc,cm}} - \sum_o X_o \sum_{a'} \left( \frac{x_{a'}^{j}}{\sum_{a''} x_{a''}^{j}} \right) \left( \frac{\sum_j X_j G_{ja,a'c} \tau_{ja,c'}}{\sum_k X_k G_{ka,c'c}} \right)
\]

(22)

Where; j and k are any species, and the quantities of all terms in equation (22) are defined as in equation (23) through (26)

\[
G_{ja,a'c} = \exp \left( -a_{ja,a'c} \tau_{ja,a'c} \right)
\]

(23)

\[
G_{ja,a'c} = \exp \left( -a_{ja,a'c} \tau_{ja,a'c} \right)
\]

(24)

\[
\tau_{cm} = -\frac{\ln G_{cm}}{\alpha_{cm}}
\]

(25)

\[
\tau_{am} = -\frac{\ln G_{am}}{\alpha_{am}}
\]

(26)

Where; c, a, and m represent cations, anions and molecular species, respectively. \(X_i = x_j C_j\) \((C_i = z_j\) for ions and 1 for molecules); \(a_{ij}\) is the non-randomness factor and \(\tau_{ij}\) is the binary energy interaction parameter. The activity coefficients of all species in the solution are calculated from the partial derivative of the excess Gibbs energy with respect to mole number as per equation (27):

\[
\ln \gamma_i = \frac{1}{RT} \left[ \frac{\partial (n_i G^{\text{ex}})}{\partial n_i} \right]_{T,P,n_i} \quad i, j = m, c, a
\]

(27)

<table>
<thead>
<tr>
<th>Species</th>
<th>(a_1)</th>
<th>(b_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>88.36</td>
<td>33030</td>
</tr>
<tr>
<td>PZ</td>
<td>36.76</td>
<td>14836</td>
</tr>
<tr>
<td>MDEA</td>
<td>24.76</td>
<td>8989</td>
</tr>
</tbody>
</table>

\[
D = a_1 + \frac{b_4}{T} \left[ 1 - \frac{1}{273.15} \right] \quad \text{where } T \text{ in (K)}
\]

3.4 Speciation Model parameters

The pure component parameters, such as critical constants, acentric factor, Brelvi–O’Connell parameters, critical compressibility factor used in the Rackett model and the Antoine equation coefficients for the vapor pressure of molecular species were obtained from the literature and are summarized in Tables 3 and 4.
Table 3. Physical properties of pure component for VLE model

<table>
<thead>
<tr>
<th>Properties</th>
<th>CO₂</th>
<th>H₂O</th>
<th>PZ</th>
<th>MDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc (K)</td>
<td>304.20</td>
<td>647.30</td>
<td>638.0</td>
<td>677.79</td>
</tr>
<tr>
<td>Pc (kPa)</td>
<td>7376.0</td>
<td>22048</td>
<td>6870</td>
<td>3876</td>
</tr>
<tr>
<td>Vc (m³/kmol)</td>
<td>0.0939</td>
<td>0.0559</td>
<td>0.3100</td>
<td>0.39</td>
</tr>
<tr>
<td>Acentric factor (ω)</td>
<td>0.2250</td>
<td>0.3440</td>
<td>0.4138</td>
<td>1.24</td>
</tr>
<tr>
<td>Racket Z_RA</td>
<td>0.2736</td>
<td>0.2432</td>
<td>0.2000</td>
<td>0.19</td>
</tr>
<tr>
<td>Brelvi-O’Connell parameter</td>
<td>0.0939</td>
<td>0.0464</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Both α and τ are adjustable parameters of the electrolyte NRTL expression. For the CO₂–amine system, the non-randomness parameter α was fixed at specific values, i.e. 0.2 for both molecule–molecule (α_{m,m}) and water–ion pair (α_{w,ea} or α_{ec,w}) interactions and 0.1 for both amine–ion pair and CO₂–ion pair interactions. The binary energy interaction parameter τ are consistent with those from the work of Austgen et al. [17] and Posey [20]. These binary parameters are categorized into three groups; molecule–molecule pair, molecule–ion pair (or ion pair–molecule) and ion pair–ion pair interactions. Because of their insignificance, the ion pair–ion pair parameters were set to a default value of zero [17]. Water–ion pair and ion pair–water parameters were fixed at default values of 8.0 and - 4.0, respectively. Amine–ion pair and ion pair–amine binary parameters and all CO₂–ion pair and ion pair–CO₂ binary parameters were fixed at values of 15.0 and - 8.0, respectively.

Table 4. Antoine equation coefficients of molecular species

<table>
<thead>
<tr>
<th>Components</th>
<th>CO₂</th>
<th>H₂O</th>
<th>PZ</th>
<th>MDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>72.82912</td>
<td>72.55</td>
<td>70.503</td>
<td>29.137</td>
</tr>
<tr>
<td>B</td>
<td>-3403.28</td>
<td>-7206.7</td>
<td>-791.45</td>
<td>-7588.5</td>
</tr>
<tr>
<td>C</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>D</td>
<td>9.49E-03</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>E</td>
<td>-8.56034</td>
<td>-7.1385</td>
<td>-6.6461</td>
<td>0.0</td>
</tr>
<tr>
<td>F</td>
<td>2.91E-16</td>
<td>4.05E-06</td>
<td>5.21E18</td>
<td>0.0</td>
</tr>
<tr>
<td>G</td>
<td>6.0</td>
<td>2.0</td>
<td>6.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

3.5 Mathematical framework for speciation

A Matlab program based on the above equations was developed for predicting species concentration in the aqueous CO₂–PZ–MDEA systems. Concentrations of all species were unknown and defined as independent variables except the concentrations of CO₂, which were calculated by the equation (9). Consequently, twelve equations (1) – (8), (10) – (13) with twelve unknowns were solved by reducing them to a single seventh order polynomial in terms of hydronium ion concentration.
[H₃O⁺], initial amine concentration and equilibrium constants. The value of [H₃O⁺] is associated with the pH of the solution at equilibrium. There is more than one possible solution for each CO₂ partial pressure. However, only one value of [H₃O⁺] is valid and should lie between 10⁻⁶ mol/l and 10⁻¹² mol/L. This corresponds to values of pH of 6 and 12 respectively. The concentrations of other species then can be calculated. Equations were solved simultaneously using the iteration process of twelve non-linear equations. The obtained outputs are species concentration and activity coefficients for the chemical species.

4. ELECTROCHEMICAL CORROSION MODEL

4.1 Electrochemical reactions on the metal surface

The electrochemical corrosion model describes the electrochemical behavior taking place on steel surface that is exposed to aqueous carbonated solutions of PZ-MDEA. It is assumed that the oxidation reaction is the conversion of Fe to Fe²⁺ while the reduction reactions involve five reactions due to the presence of five reducing agents including H₃O⁺, HCO₃⁻, H₂O, PZH⁺ and MDEAH⁺. The summary of the assumed reactions taking place on surface of the carbon steel are provided by the following reactions:

- Oxidation of iron: Fe ⇔ Fe²⁺ + 2e⁻
- Reduction of hydronium ion: 2H₃O⁺ + 2e⁻ ⇔ 2H₂O + H₂
- Reduction of bicarbonate ion: 2HCO₃⁻ + 2e⁻ ⇔ 2CO₃²⁻ + H₂
- Reduction of water: 2H₂O + 2e⁻ ⇔ 2OH⁻ + H₂
- Reduction of PZH⁺ ion: 2PZH⁺ + 2e⁻ ⇔ 2PZ + H₂
- Reduction of MDEAH⁺ ion: 2MDEAH⁺ + 2e⁻ ⇔ 2MDEA + H₂

4.2 Mathematical model for the electrochemical corrosion process

The dissolution of iron was said to be under charge transfer control because of the unlimited supply of Fe. The relationship between current density and potential was defined as in equation (28) and (29):

\[ i_{\text{Fe/Fe}^{+2}} = i_{\text{o,Fe/Fe}^{+2}} \times 10^{-\frac{E-E_{\text{ref}}}{\beta_a}} \]  \hspace{1cm} (28)

\[ \beta_a = \frac{2.303 \cdot RT}{n \cdot F \cdot \alpha_a} \]  \hspace{1cm} (29)

For the reduction, potential reactants participating in corrosion process are reduction reaction of H₃O⁺, reduction reaction of HCO₃⁻, reduction reaction of H₂O, reduction reaction of PZH⁺ and reduction reaction of MDEAH⁺, in which H₃O⁺, HCO₃⁻, H₂O, PZH⁺, and MDEAH⁺ serve as oxidizing agents. The reduction reactions were assumed to be under mixed potential. For the system of (k) reduction reactions, the general rate equation of the cathodic part is as in equation (30):

\[ i_k = i_{o[k]} \times \left[ \frac{[k]_b}{[k]_b} \times \exp\left(-\frac{n \cdot F \cdot \alpha_a}{RT} \left(E - E_{\text{ref}}\right)\right) \right] \]  \hspace{1cm} (30)
Where: \( i_k \) is the current density of a reduction reaction \( (\text{A/m}^2) \). \( i_o \) is the equilibrium exchange current density of a reaction \( (\text{A/m}^2) \). \([k]\) is the surface concentration of oxidizing agent species \( (\text{mol/l}) \). \([k]_b \) is the bulk concentration of oxidizing agent species \( (\text{mol/l}) \). \( \alpha_c \) is the cathodic symmetry factor. \( n \); is the number of electrons transferred in the reduction reaction. \( F \); is the Faraday’s constant \( (\text{C/mol}) \) and \( E \); is the potential \( (\text{V.vs SCE}) \). Equation (30) takes into account the effect of resistance to charge transfer and mass transfer. The surface concentration of oxidizing agents can be determined from the mass-transfer equation:

\[
i_k = k_m F \left\{ \left[ k \right]_b - \left[ k \right]_s \right\}
\]  

(31)

Where \( k_m \); is the reduction reaction mass-transfer coefficient \( (\text{m/s}) \). Substitution of equation (30) into (31) and solving for \([k]\), yields the final current density vs voltage equation for reduction reactions:

\[
\frac{1}{i_k} = \frac{1}{i_{\text{act}}(k)} + \frac{1}{i_{\text{lim}}(k)}
\]  

(32)

Where \( i_{\text{lim}}(k) \) is the diffusion limiting current density \( (\text{A/m}^2) \) and \( i_{\text{act}}(k) \) is the activation current density in absence of resistance to mass transfer, which is given by equation (33):

\[
i_{\text{act}}(k) = i_o(k) \times 10^\left( \frac{E - E_{\text{rev}}}{\beta_c} \right)
\]  

(33)

Where: \( i_o(k) \); is the exchange current density \( (\text{A/m}^2) \) and \( \beta_c \); is the cathodic Tafel slope \( \text{V/dec} \). The temperature dependence of the cathodic Tafel slope is given as in equation (34):

\[
\beta_c = \frac{2.303 RT}{nF}
\]  

(34)

The reversible potential \( E_{\text{rev}} \) \( (\text{V vs SCE}) \) for species in the solution, which is calculated from the Nernst equation; equation (35):

\[
E_{\text{rev}} = E_T^o + \frac{RT}{nF} \ln \left( \frac{a_{\text{prod.}}}{a_{\text{react.}}} \right)
\]  

(35)

Where: \( E_T^o \) is the standard electrode potential \( (\text{V vs SCE}) \) at any given temperature, \( R \); is the universal gas constant \( (\text{J/mol.K}) \). \( T \); is the absolute temperature \( (\text{K}) \). \( n \); is the number of electrons taking part in the reaction. \( a_{\text{prod.}} \) and \( a_{\text{react.}} \) are the activities of products and reactants, respectively. \( F \); is the Faraday’s constant \( (\text{C/mol}) \). The \( E_T^o \); was determined using equation (36):

\[
\Delta G_r^o = -nFE_T^o
\]  

(36)

Where \( \Delta G_r^o \) is the Gibbs free energy of formation of any compound at any given temperature, which can be calculated using equation (37):

\[
\Delta G_r^o = T \left[ \frac{\Delta G_r^o}{298.15} + \Delta H_r^o \left( \frac{1}{T} - \frac{1}{298.15} \right) \right]
\]  

(37)

Where \( \Delta G_r^o \) and \( \Delta H_r^o \) are standard excess Gibbs energy \( (\text{kJ/mol}) \) of reaction at 298.5 K and standard enthalpy of reaction \( (\text{kJ/mol}) \) at 298.15 respectively and \( T \) is the system temperature \( (\text{K}) \). The values of \( \Delta G_r^o \) and \( \Delta H_r^o \) are given in Table 5.

While the temperature dependence of the exchange current density is given by equation (38):

\[
i_o = i_o^{\text{ref}} \left( \frac{C_{\text{ox}}}{C_{\text{ox},\text{ref}}} \right)^n \exp \left( -\frac{E_o}{K} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right)
\]  

(38)

Where \( E_o \); is the activation energy in \( \text{kJ/mol} \) and \( i_o^{\text{ref}} \) is the reference exchange current density measured at the reference temperature, \( T_{\text{ref}} \); and reference concentration of oxidizing agent, \( C_{\text{ox}} \); is the concentration of oxidizing agent, and \( n \); is the order of reaction.
Table 5. Gibbs free energy and enthalpy of reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation of Fe</td>
<td>84.9</td>
<td>87.9</td>
<td>[23]</td>
</tr>
<tr>
<td>Reduction of $\text{H}_2\text{O}^+$</td>
<td>0.0</td>
<td>0.0</td>
<td>[23]</td>
</tr>
<tr>
<td>Reduction of $\text{HCO}_3^-$</td>
<td>118</td>
<td>29.8</td>
<td>[23]</td>
</tr>
<tr>
<td>Reduction of $\text{H}_2\text{O}$</td>
<td>159.8</td>
<td>111.6</td>
<td>[23]</td>
</tr>
<tr>
<td>Reduction of MDEAH$^+$</td>
<td>98.46</td>
<td>73.8574</td>
<td>[24]</td>
</tr>
<tr>
<td>Reduction of PZH$^+$</td>
<td>111.09</td>
<td>85.78</td>
<td>[25]</td>
</tr>
</tbody>
</table>

The values were extracted from open literature for the reactions [14, 26]. While the protonated piperazine reduction reaction, the exchange current density was assumed to be similar to that of the exchange current density of protonated MDEA. The diffusion-limiting component of the total current density is as given in equation (39):

$$i_{\text{lim}} = \frac{nF\kappa m[K]_b}{D}$$  \hspace{1cm} (39)

$k_m$ is calculated from rotating cylinder correlation of Eisenberg, et al. [27]

$$Sh = \frac{k_m D}{D} = 0.0791 \times Re^{0.7} \times Sc^{0.33}$$  \hspace{1cm} (40)

Where; Sh is Sherwood number, $D$ is diffusion coefficient of species (m$^2$/s), Re; is Reynold number, Sc; is Schmitt number and $d$; is diameter of rotating disc (m). The temperature effect on diffusion coefficient was found from the Stokes-Einstein equation; equation (41):

$$D = D_{\text{ref}} \times \frac{T}{T_{\text{ref}}} \times \frac{\mu_{\text{ref}}}{\mu}$$  \hspace{1cm} (41)

Where; $D_{\text{ref}}$ is the diffusion coefficient of species at a reference temperature ($T_{\text{ref}}$), $\mu_{\text{ref}}$, is the dynamic viscosity of aqueous MDEA-PZ solution at a reference temperature ($T_{\text{ref}}$) and $\mu$; is the viscosity of aqueous MDEA-PZ solution at temperature ($T$). The diffusion coefficients of ionic species are provided in Table 6 and the values of $\mu$ (Ns/m$^2$) can be determined from equation(42) [28]:

$$\mu_{\text{mix}} = \frac{w_1}{w_1 + w_2} \mu_{\text{1, a}} + \frac{w_2}{w_1 + w_2} \mu_{\text{2, a}}$$  \hspace{1cm} (42)

Where $\mu_{\text{mix}}$ is the viscosity of carbonated aqueous MDEA-PZ solution, $\mu_1$ and $\mu_2$ are the viscosities of aqueous MDEA and aqueous PZ at CO$_2$ loading $\alpha$ and $w_1$ the mass fraction of MDEA and PZ. The viscosity of single alkanolamine in (Ns/m$^2$) can be determined from equation (43) [28]:

$$\mu_i = \mu_{\text{H}_2\text{O}} \exp \left( \frac{[(a w_1 + b) T + (c w_1 + d) T^2 + (e w_1 + f) T + g)] [w_1]}{7^2} \right)$$

$$\mu_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}, 20°C} \times \left[ 1 + \frac{(T - 20°C)}{6.09} \right]$$  \hspace{1cm} (44)

Where $\mu_{\text{H}_2\text{O}, 20°C}$ is the viscosity of water at 20 °C (0.001002 Ns/m$^2$) and $T$ is the temperature (°C).
Table 6. Diffusion coefficients of various species in water at 298.15 K

<table>
<thead>
<tr>
<th>Species</th>
<th>Diffusion coefficient (m²/s)</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>2.26E-09</td>
<td>[29]</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1.11E-09</td>
<td>[30]</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>9.31E-09</td>
<td>[30]</td>
</tr>
<tr>
<td>MDEAH⁺</td>
<td>2.35E-10</td>
<td>[31]</td>
</tr>
<tr>
<td>PZH⁺</td>
<td>5.66E-10</td>
<td>[32]</td>
</tr>
</tbody>
</table>

Table 7. Parameters for MDEA and PZ viscosity equation

<table>
<thead>
<tr>
<th>Constant</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA</td>
<td>-0.1944</td>
<td>0.4315</td>
<td>80.684</td>
<td>2889.1</td>
<td>0.0106</td>
<td>0</td>
<td>-0.2141</td>
<td>[28]</td>
</tr>
<tr>
<td>PZ</td>
<td>0.1156</td>
<td>8.444</td>
<td>-9.074</td>
<td>3.224</td>
<td>0.7412</td>
<td>0.0225</td>
<td>-9.074</td>
<td>[33]</td>
</tr>
</tbody>
</table>

4.3 Execution of the corrosion model

The present electrochemical model was executed in Matlab 2013a for simulating the polarization curve of carbon steel in the aqueous MDEA-PZ-CO₂ system. To execute the numerical simulation, solution temperature, amine concentration, CO₂ partial pressure, rotating speed, and electrode diameter were used as inputs. Once all parameters were determined, the model predicted the polarization curve with the individual and total cathodic curves. The intersection of the total cathodic curve with the anodic curve facilitated with the corrosion potential by solving equation (45).

\[
\text{i}_{Fe/Fe^{2+}} = i_{H_2O^+/H_2} + i_{HCO_3^-/CO_3^{2-}} + i_{H_2O/CO_3^{2-}} + i_{PZH^+/PZ} + i_{MDEAH^+/MDEA}
\]

(45)

Corrosion current is calculated from the anodic curve equation (28) at the known corrosion potential. Tafel extrapolation method was applied to determine the corrosion current density, which was used to calculate the corrosion rate by as in equation (46):

\[
CR = \frac{i_{corr} M_w}{\rho n F \chi} = 1.155 \ i_{corr}
\]

(46)

Where, CR is the corrosion rate in mm/yr; \(i_{corr}\) is the corrosion current density in A/m²; \(M_w\) is the molecular weight of iron in kg/mol.; \(\rho\) is the density of metal in kg/m³; \(n\) is the number of electron exchanged in the electrochemical reaction, and \(\chi\) is a unit conversion factor.

5. RESULTS AND DISCUSSION

5.1 Speciation of carbonated MDEA-PZ system

The calculated CO₂ loading of MDEA-PZ solution at different solution temperatures and CO₂ partial pressure is compared with experimental data from literature [5, 7] as shown in Figure 2. Similarly, the comparison of the calculated pH of solution at different CO₂ partial pressures is compared with experimental results [7] as shown in the Figure 3. Derk et al. [7] measured the pH of the aqueous MDEA+PZ solutions as a function of carbon dioxide loading, and their results are
compared with the model prediction as shown in Figure 3. From this Figure, it can be concluded that the model is able to predict the trend in pH fairly well, despite a seemingly constant offset between experimental values and model prediction. However, there seem to be a (consistent) discrepancy between the predicted and measured pH. This might be due to the interaction parameters used in the e-NRTL model to describe the molecular-molecular, molecular-ions, and ions-ions interaction in the solution which were taken from the work of Austgen et al. [17] as a default parameters. Both figures depicted a good agreement in the predicted and experimental results.

**Figure 2.** Comparison between calculated and experimental results of MDEA-PZ at 313.15 K

**Figure 3.** Assessment of experimental and calculated results of pH MDEA-PZ system.
Due to the low concentration of piperazine in MDEA; the PZ species concentrations are low compared to that of MDEA species. Figure 4 represents the predicted species concentration, for the carbonated aqueous solution of 1.8M MDEA+0.1M PZ. It can be observed that a sharp decrease in PZ concentration at low CO₂ loading. This is due to the PZ reaction with CO₂, which is much faster than that of MDEA reaction with CO₂. Furthermore PZ forms carbamates and MDEA does not. Protonated piperazine and piperazine carbamate show a sudden increase till CO₂ loading point of 0.07 (mol CO₂/mol alkalinity), where both species reach to a maximum concentration at this CO₂ loading. The piperazine carbamates further react with CO₂ to give piperazine di-carbamate which appears at CO₂ loading of 0.14 (mol CO₂/mol alkalinity). It reached its maximum concentration at CO₂ loading of 0.6 (mol CO₂/mol alkalinity).

The increase in concentration of the piperazine di-carbamate and that of protonated piperazine carbamate lead to a decrease in the concentration of the protonated piperazine and piperazine carbamate. The behavior of MDEA species in the MDEA-PZ system is similar to that of aqueous carbonated MDEA. MDEA which does not form carbamates reacts with CO₂ only through an acid-base buffer mechanism in which CO₂ is converted primarily to bicarbonate. However, CO₂ must first react with H₂O to produce carbonic acid H₂CO₃, which subsequently dissociate to bicarbonate HCO₃⁻, or it must react directly with OH⁻ to form bicarbonate. It is observed that the concentration of protonated MDEA and bicarbonate do not remain relatively similar through over all CO₂ loading range. The second dissociation constant of CO₂ is not negligible relative to its first dissociation constant, therefore a significant amount of carbonate is formed relative to bicarbonate. Hence, the concentration of bicarbonate is not in general equal to the concentration of protonated MDEA. Figure 4 also shows that at low CO₂ loading the concentration of MDEAH⁺, HCO₃⁻, PZH⁺, and PZCOO⁻ are

Figure 4. Predicted concentration of species in 1.8 M MDEA+ 0.1 M PZ system at 313.15 K
increased with increasing CO$_2$ loading but at high CO$_2$ loading the dominate species are MDEAH$^+$, HCO$_3^-$, PZH$^+$, PZ(COO)$^-$$_2$ and H$^+$PZCOO$^-$. \\

5.2 Carbon steel Corrosion rate in carbonated MDEA-PZ system

The developed corrosion rate model was used to simulate the corrosion process and to predict corrosion rate of carbon steel in aqueous MDEA-PZ systems. The simulation results were compared with experimental corrosion rate data. All comparisons were made using polarization curves and electrode kinetic data, including corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$), and corrosion rate, as shown in Figures 5-8 and Tables 8-11.

Figures 5 and 8 depict that the predicted and experimental polarization curves which are in good agreement. Polarization curves shift in the direction of lower corrosion current density which implies that the predicted corrosion rate values are lower than that obtained from experiments. The deviation of the simulated polarization curves might be due to the value of exchange current density of oxidizing agents which were assumed similar to those of aqueous MDEA system, as reported by Choi et al. [14].

Figures 5-8 and Tables 8-11 also show that the polarization curves produced from the model are closer to the experimental curves. It is evident that the corrosion potential from the model shifted toward lower values compared to the experimental data. The lower corrosion potential predicted from the model resulted from the mixed potential theory used in the model. As mentioned previously, the mixed potential theory is used to calculate the corrosion potential based on the summation of all partial reduction current equal to the oxidation currents.

![Figure 5](image_url)  
**Figure 5.** Comparison of predicted and experimental polarization curves of carbon steel in 1.98 M MDEA+0.01 M PZ; P$_{CO2}$= 47.55 kPa at 313.15 K
Figure 6. Comparison of predicted and experimental polarization curves of carbon steel in 1.9 M MDEA+ 0.05M PZ; $P_{CO2}=95.27$ kPa at 313.15 K

Figure 7. Comparison of predicted and experimental polarization curves of carbon steel in 1.98 M MDEA+0.01 M PZ; $P_{CO2}= 0.83$ kPa at 333.15 K
Figure 8. Comparison of predicted and experimental polarization curves of carbon steel in 1.8 M MDEA+ 0.1 M PZ; P$_{\text{CO}_2}$=55.47 kPa at 353.15 K

Table 8. Comparison of experimental and calculated of carbon steel corrosion data in aqueous 2 M MDEA solution

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$P_{\text{CO}_2}$ (kPa)</th>
<th>Experimental</th>
<th>Model</th>
<th>$\delta^a$</th>
<th>$\delta^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_{\text{corr}}$ (V vs. SCE)</td>
<td>CR (mm/yr)</td>
<td>$E_{\text{corr}}$ (V vs. SCE)</td>
<td>CR (mm/yr)</td>
</tr>
<tr>
<td>313.15</td>
<td>0.96</td>
<td>-0.84</td>
<td>0.22</td>
<td>-0.82</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>9.56</td>
<td>-0.80</td>
<td>0.84</td>
<td>-0.83</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>47.72</td>
<td>-0.80</td>
<td>1.31</td>
<td>-0.82</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>95.61</td>
<td>-0.79</td>
<td>1.76</td>
<td>-0.80</td>
<td>1.72</td>
</tr>
<tr>
<td>333.15</td>
<td>0.83</td>
<td>-0.86</td>
<td>0.46</td>
<td>-0.84</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>8.31</td>
<td>-0.82</td>
<td>1.15</td>
<td>-0.85</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>41.45</td>
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<td>1.75</td>
<td>-0.84</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>82.91</td>
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<td>2.23</td>
<td>-0.84</td>
<td>2.82</td>
</tr>
<tr>
<td>353.15</td>
<td>0.55</td>
<td>-0.86</td>
<td>0.10</td>
<td>-0.84</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>5.55</td>
<td>-0.86</td>
<td>1.19</td>
<td>-0.86</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>27.57</td>
<td>-0.84</td>
<td>1.47</td>
<td>-0.87</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>55.48</td>
<td>-0.85</td>
<td>2.92</td>
<td>-0.86</td>
<td>2.83</td>
</tr>
</tbody>
</table>

$\delta^a = \frac{|E_{\text{corr(Exp)}} - E_{\text{corr(Cal)}}|}{E_{\text{corr(Exp)}}} \times 100$, $\delta_{\text{AAD}} = 2.36\%$

$\delta^b = \frac{|CR_{\text{(Cal)}} - CR_{\text{(Exp)}}|}{CR_{\text{(Exp)}}} \times 100$, $\delta_{\text{AAD}} = 22.59\%$
Table 9. Comparison of experimental and calculated of carbon steel corrosion data in aqueous 1.98 M MDEA +0.01 M PZ solution

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$P_{CO_2}$ (kPa)</th>
<th>Experimental</th>
<th>Model</th>
<th>$\delta^a$</th>
<th>$\delta^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>313.15</td>
<td>0.95</td>
<td>-0.85</td>
<td>0.25</td>
<td>-0.82</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>9.54</td>
<td>-0.80</td>
<td>0.60</td>
<td>-0.83</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>47.55</td>
<td>-0.80</td>
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<td>-0.82</td>
<td>1.36</td>
</tr>
<tr>
<td>95.28</td>
<td>-0.79</td>
<td>1.65</td>
<td>-0.81</td>
<td>1.60</td>
<td>2.73</td>
</tr>
<tr>
<td>0.83</td>
<td>-0.86</td>
<td>0.37</td>
<td>-0.84</td>
<td>0.15</td>
<td>2.19</td>
</tr>
<tr>
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<td>0.73</td>
<td>-0.85</td>
<td>0.74</td>
<td>2.52</td>
</tr>
<tr>
<td>41.20</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>0.31</td>
<td>-0.84</td>
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</tr>
<tr>
<td>5.55</td>
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<td>0.95</td>
<td>-0.86</td>
<td>0.60</td>
<td>0.06</td>
</tr>
<tr>
<td>27.57</td>
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<td>1.66</td>
<td>-0.86</td>
<td>1.70</td>
<td>4.83</td>
</tr>
<tr>
<td>55.31</td>
<td>-0.84</td>
<td>2.35</td>
<td>-0.86</td>
<td>2.56</td>
<td>2.32</td>
</tr>
</tbody>
</table>

$\delta^a = \left| \frac{E_{corr(Cal)} - E_{corr(Exp)}}{E_{corr(Exp)}} \right| \times 100 \%

$\delta^b = \left| \frac{CR_{(Cal)} - CR_{(Exp)}}{CR_{(Exp)}} \right| \times 100 \%

Table 10. Comparison of experimental and calculated of carbon steel corrosion data in aqueous 1.9 M MDEA +0.05 M PZ solution

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$P_{CO_2}$ (kPa)</th>
<th>Experimental</th>
<th>Model</th>
<th>$\delta^a$</th>
<th>$\delta^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>313.15</td>
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<td>-0.84</td>
<td>0.28</td>
<td>-0.82</td>
<td>0.16</td>
</tr>
<tr>
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<td>9.58</td>
<td>-0.81</td>
<td>0.49</td>
<td>-0.83</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>47.55</td>
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<td>1.44</td>
<td>-0.82</td>
<td>1.26</td>
</tr>
<tr>
<td>95.78</td>
<td>-0.79</td>
<td>1.32</td>
<td>-0.80</td>
<td>1.48</td>
<td>1.89</td>
</tr>
<tr>
<td>0.83</td>
<td>-0.85</td>
<td>0.26</td>
<td>-0.84</td>
<td>0.17</td>
<td>1.98</td>
</tr>
<tr>
<td>8.29</td>
<td>-0.84</td>
<td>0.63</td>
<td>-0.85</td>
<td>0.74</td>
<td>0.57</td>
</tr>
<tr>
<td>41.28</td>
<td>-0.81</td>
<td>1.69</td>
<td>-0.84</td>
<td>1.79</td>
<td>4.50</td>
</tr>
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<td>83.24</td>
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<td>-0.84</td>
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<td>1.94</td>
</tr>
<tr>
<td>0.55</td>
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<td>0.18</td>
<td>-0.85</td>
<td>0.14</td>
<td>1.57</td>
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<td>0.64</td>
<td>3.70</td>
</tr>
<tr>
<td>27.49</td>
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<td>1.56</td>
<td>-0.86</td>
<td>1.72</td>
<td>4.37</td>
</tr>
<tr>
<td>55.64</td>
<td>-0.84</td>
<td>2.02</td>
<td>-0.86</td>
<td>2.57</td>
<td>2.21</td>
</tr>
</tbody>
</table>
\[
\delta^a = \left( \frac{E_{corr(\text{cal})} - E_{corr(\text{exp})}}{E_{corr(\text{exp})}} \right) \times 100, \delta_{AAD} = 2.50\% \\
\delta^b = \left( \frac{CR(\text{cal}) - CR(\text{exp})}{CR(\text{exp})} \right) \times 100, \delta_{AAD} = 24.24\%
\]

**Table 11.** Comparison of experimental and calculated of carbon steel corrosion data in aqueous 1.8 M MDEA +0.1 M PZ solution

<table>
<thead>
<tr>
<th>T(K)</th>
<th>(P_{CO_2}) (kPa)</th>
<th>Experimental</th>
<th>Model</th>
<th>(\delta^a)</th>
<th>(\delta^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(E_{corr}) (V)</td>
<td>CR (mmppy)</td>
<td>(E_{corr}) (V)</td>
<td>CR (mmppy)</td>
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<td>-0.79</td>
<td>0.21</td>
<td>-0.81</td>
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<td>-0.86</td>
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</table>

\[
\delta^a = \left( \frac{E_{corr(\text{cal})} - E_{corr(\text{exp})}}{E_{corr(\text{exp})}} \right) \times 100, \delta_{AAD} = 2.26\% \\
\delta^b = \left( \frac{CR(\text{cal}) - CR(\text{exp})}{CR(\text{exp})} \right) \times 100, \delta_{AAD} = 28.75\%
\]

### 5.3 Effect of CO₂ loading and PZ concentration on Corrosion rate

The effect of CO₂ loading is demonstrated by comparing the model with experimental results in aqueous MDEA-PZ solutions. Figures 9 and Figure 10 illustrate that the CO₂ loading has a significant effect on corrosion rate of carbon steel. At high CO₂ loading the solution is more corrosive than that at low CO₂ loading. For instance, the carbon steel corrosion rate in 2M MDEA system increased from 0.22 to 1.76 mm/yr as the CO₂ loading increased from 0.15 to 0.88 (mol of CO₂/mol alkalinity) at 40 °C. Such increase in corrosion rate is due to the increase in dissolved CO₂ to form HCO₃⁻ and MDEAH⁺, which induces more iron dissolution. This is evidenced by greater cathodic current densities in Figure 9. Similar results with respect to HCO₃⁻ concentration effect on carbon steel corrosion rate has investigated by Choi et al. [14] in their work on carbonated aqueous MDEA system’s corrosivity. They concluded that corrosion rate of carbon steel increased with increasing in HCO₃⁻ concentration with a reaction order 2 for iron dissolution reaction under different test conditions. Furthermore, Duan
et al. [34] evaluated the corrosion properties of carbon steel in 50 wt% MDEA systems at 50 °C with different CO₂ partial pressures. They found under the absorber conditions, the addition of CO₂ in MDEA systems significantly increased the corrosion rate and changed behavior from a passive to an active state. They also concluded that the dominant cathodic reactions in aqueous carbonated MDEA system are HCO₃⁻ and MDEAH⁺ reduction reactions.

**Figure 9.** Effect of CO₂ loading on polarization behavior of carbon steel in MDEA-PZ solution with a concentration 1.8M MDEA+0.1M PZ at 80 °C

**Figure 10.** Effect of CO₂ loading on carbon steel corrosion rate in MDEA-PZ aqueous solution at T=313.15 K
However, in MDEA-PZ systems and for a constant total amine concentration with increasing the concentration of PZ appears to nullify the rate as noticed in Figure 10. The effect of PZ concentration on corrosion rate was found to be dependent on the CO₂ loading. As shown in Figure 11, at low CO₂ loading (low CO₂ partial pressure) concentrations of the oxidizing species are very low therefore the effect of temperature is more than the effect of addition of piperazine even it is working as an activator to MDEA to increase the CO₂ loading in the solution and increasing corrosion rate. However, at high CO₂ loading (high CO₂ partial pressure) the addition of piperazine to the MDEA solution will decrease the system ability to absorb CO₂ which means a decrease in oxidizing agent concentration in the solution thereby decreases corrosion rate. This is believed to be due to the concentration of HCO₃⁻ in the systems, at low CO₂ partial pressure the increase in PZ concentration yields higher amount of HCO₃⁻, which in turn dissociate and due to the increasing in CO₂ loading, the increasing in CO₂ loading drives the corrosion process to proceed faster, thus causing increasing in corrosion rate while at high CO₂ partial pressure, the addition of PZ concentration leads to decrease in HCO₃⁻ concentration which in turn decreasing in CO₂ loading and leads to decrease in corrosion rate.

The high corrosion rate in 2 M MDEA, compared to that of MDEA-PZ under the same conditions of (CO₂ loading, solution temperature and PZ concentration) is due to high bicarbonate concentration.

**Figure 11.** Effect of PZ concentration on the carbon steel corrosion rate in MDEA-PZ aqueous solution at three solution temperature
5.4 Effect of temperature on corrosion rate

The effect of solution temperature on corrosion rate was investigated at different CO$_2$ loadings. The increase of solution temperature will result in a decrease of the CO$_2$ loading in aqueous MDEA-PZ systems and thereby decrease the concentration of oxidizing agent in the solution, in which the corrosion process depends on the flow of oxidizing agent at the carbon steel surface. The corrosion results as shown in Figures 12 and 13 show that the solution temperature has a considerable effect on corrosion rate, an increase in solution temperature lead to an increase in corrosion rate. This can be explained by the dependence of reaction kinetics on temperature. It is well established that the reaction rate increases with temperature according to Arrhenius theory. Therefore, the increase in temperature increases rates of metal dissolution and oxidizer reduction, thereby accelerating the corrosion rate.

In the absence of any precipitation and corrosion product layer formation in the carbonated activated MDEA system, temperature accelerates the kinetics of all the process involved in a corroding system: electrochemical reactions, chemical reactions, and transport processes. Hence the final corrosion rate also increases with temperature as indicated in Figures 12 and 13, as is expected. The corrosion rate, which is under charge transfer at initial temperature, become mass transfer limiting current controlled at higher temperatures. The temperature dependence of the carbonated aqueous solutions of MDEA-PZ viscosity at a given CO$_2$ loading and a given concentration of PZ and MDEA, exponentially decreases with increasing temperature. The effect of decreasing viscosity with increases in temperature for aqueous carbonated MDEA-PZ solution can be found in the work by [33]. The increasing in solution temperature led to decrease the viscosity of solution with increase in corrosive species diffusivity according to the Stockes-Einstein equation, decreased pathways for corrosive species to reach the surface of carbon steel, which leads to high carbon steel dissolution.

![Figure 12. Effect of temperature on carbon steel corrosion rate in aqueous MDEA-PZ solutions at low CO$_2$ loading](image)
On the other hand, the corrosion rate decreases with the increase in the PZ concentration with a crossover point (indicated by point C) as shown in Figures 12 and 13. Moreover, by increasing temperature the crossover point shifts toward a higher corrosion rate.

![Figure 13](image)

**Figure 13.** Effect of temperature on corrosion of carbon steel in the MDEA-PZ solutions at high CO₂ loading

![Figure 14](image)

**Figure 14.** Effect of HCO₃⁻ concentration on the carbon steel corrosion rate in aqueous MDEA-PZ solution at three solution temperatures

This crossover point might be because of addition of PZ concentration in the solution. At low CO₂ partial pressure, the addition of PZ concentration to the aqueous MDEA solution increased the CO₂ loading when compared MDEA alone. The addition of PZ to MDEA increases the bicarbonate and protonated amine concentrations which are the main oxidizing agents affecting the corrosion process of carbon steel which led to increase the corrosion rate, whereas at high CO₂ partial pressure
the corrosion rate of carbon steel decreased in the MDEA-PZ system, this is because of the decreasing in the HCO$_3^-$ concentration which is the main oxidizing agents affecting the corrosion process of carbon steel as shown in figure 14. The effect of PZ concentration on CO$_2$ loading in the aqueous carbonated MDEA-PZ solution at high and low CO$_2$ partial pressure can be found in the work by [5].

5.5 Effect of corrosion potential

Figure 15 shows the change of corrosion potential for carbon steel in the carbonated PZ-MDEA system at different PZ concentrations. At low partial pressure of CO$_2$ (< 1 kPa), carbon steel shows active behavior with potential -0.84 V vs SCE and increases to -0.79 V vs SCE at high CO$_2$ partial pressure in 2 M MDEA solution at 313.15 K. However, there is an increase in potential with increase in PZ concentration indicating the corrosion behavior changes from active to the passive by increasing CO$_2$ partial pressure. This can be explained by a decrease in HCO$_3^-$ and MDEAH$^+$ concentration in the MDEA-PZ systems at high CO$_2$ partial pressure and PZ concentration, which they are main oxidizing agents, lead to corrode the carbon steel surface.

![Figure 15](image)

*Figure 15. Variation in corrosion potential for carbon steel as a function of PZ concentration in carbonated MDEA-PZ system at low CO$_2$ partial pressure, 313.15 K*

6. CONCLUSIONS

A comprehensive model was developed for simulating the polarization curves of carbon steel in aqueous carbonated MDEA-PZ systems. The model consists of a thermodynamic model that provides speciation calculations and an electrochemical model that predicts the partial reduction and oxidation processes on the surface of the metal. The model has been validated extensively using thermodynamic and corrosion rate experimental data. Good agreement with experimental results was obtained for most
of the cases. The model adequately represents the effect of PZ concentration, solution temperature and CO₂ loading on the carbon steel corrosion rate in aqueous carbonated solutions of MDEA-PZ. The corrosivity of carbon steel in aqueous carbonated solution of MDEA-PZ was governed mainly by their CO₂ loading such that higher CO₂ loading led to higher corrosion rate. At low CO₂ loading the corrosion rate of carbon steel increased with increasing in solution temperature and PZ concentration whereas, at high CO₂ loading the corrosion rate decreased with increasing solution temperature and PZ concentration.

This model is also used to identify the oxidizing agents responsible for corrosion of carbon steel in aqueous carbonated activated MDEA systems. HCO₃⁻ contributes the most to the changes in corrosion kinetics at higher temperatures and higher CO₂ loading, while H₃O⁺ and H₂O contribute the least at high pH condition. The protonated MDEA and protonated PZ contribute as oxidizing agents based on the concentration of that amine in the solution. Developed models and results of the current study may serve as a prediction tool for designing CO₂ absorption systems at conditions that have not been investigated experimentally.

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References