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MODELING POLARIZATION CURVE IN AN AQUEOUS CARBONATED SOLUTION OF PIPERAZINE

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Abstract: A polarization curve model is developed for carbon steel in an aqueous carbonated solution of piperazine (PZ). This model has been used to generate the polarization curve and control the parameters relevant to the corrosion rate of carbon steel in the PZ-CO2-H2O system. Electrochemical experiments are carried out for carbon steel corrosion measurements at 40 °C and different carbon dioxide partial pressure using potentiodynamic polarization technique. The Vapor-liquid Equilibrium and the electrochemical corrosion models are the two main models used in this study. The electrolyte-NRTL equilibrium model was utilized to calculate the chemical species concentration at the carbon steel-solution interface in the PZ-CO2-H2O system. The findings of speciation were then applied to the generation of polarization curves and the prediction of the corrosion rate of the carbon steel surface. The results of the polarization curves modeling were compared to the experimental curves developed in MatLab software 2013a. Comparing experimental and modeled polarization curves and corrosion rate reveals excellent agreement.

Keywords: *CO_2 corrosion; piperazine; modeling; polarization curve; carbon steel.*

1. Introduction

Controlling and cleaning industrial waste gas (CO_2 emission) is one of the essential ways to reduce carbon emissions. Absorption is one strategy for reducing the emission of this greenhouse gas. In chemical industries, the CO_2 absorption process employs an aqueous amine solution such as coal gasification, natural gas sweetening, and ammonia production which is a well-established separation method. It eliminates acidic gases, mostly CO_2, by creating a salt to achieve the required product quality and avoid operational challenges that may arise in subsequent operations.[1].

The corrosion of carbon steel caused by carbon dioxide (CO_2) gas in the petroleum industry is regarded as the most serious operational problems in alkanolamine power plants. In CO_2 capture plants, amine-based solvents including DEA "diethanolamine", MEA "monoethanolamine", MDEA "methyldiethanolamine", and DIPA "diisopropanolamine" are often used to avoid corrosion [2]. The amine system is designed to form soluble salts in amine-based CO_2 capture processes from the reaction of CO_2 gas with

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amine in the absorber and to reverse the process in the regenerator, releasing the acid gas to the regenerator overhead, known as alkanolamine. It produces a water-soluble amine acid gas salt by reacting a a weak acid (CO_2) with weak base (alkanolamine). The presence of carbon dioxide may cause the production of an iron carbonate film during carbon steel corrosions [3].
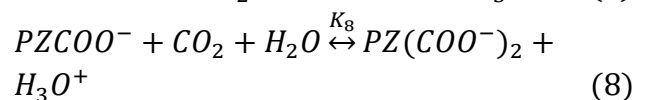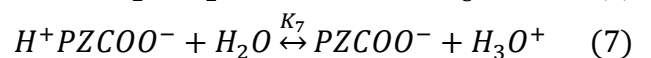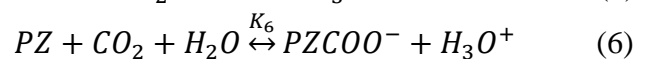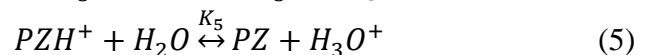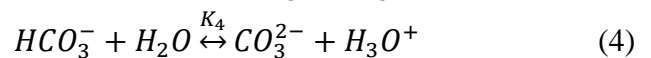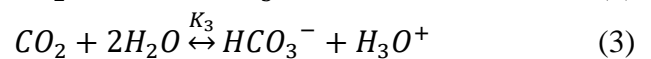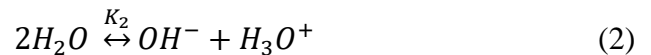
Amine-based solvents have been proven to absorb a substantial amount of CO_2 gas. Because of this, it is the most advanced CO_2 absorption solvent. The AMP, MEA, DGA and MDEA are some of the most regularly utilized amine solvents. These amine solvents have been studied for CO_2 absorption capacity and influence on corrosion rate of carbon steel [2]. Piperazine (PZ) is another amine solvent used for CO_2 absorption, a cyclic chemical compound with two nitrogen atoms in opposing locations. Because it is a cyclic diamine, it could absorb 2 moles of CO_2 for every mole of amine. Also, PZ resists oxidation and thermal degradation [4]. The rate of CO_2 absorption in piperazine has been investigated in many literatures [5, 6]. PZ with CO_2 has a greater rate constant than MEA, according to Bishnoi and Rochelle [7].

PZ has also been proven to be a good activator for increasing CO_2 absorption rate in CO_2 capture solutions such as MEA [8]. The most important resulting of this research is that PZ has been shown to be an efficient activator for removing carbon dioxide from gas streams. Wong et al. [9], who also studied CO_2 absorption by PZ activated AMP and PZ activated MDEA, strongly support this finding. However, very little literature is available on the corrosion of carbon steel in PZ-CO_2-H_2O system.

Instead of time-consuming experiments, the use of a prediction model on CO_2 corrosion behavior was suggested [10]. Several numerical models [11], [12] gave some insight into the fundamental physicochemical processes. However, a more modern model based on mechanistic analyses of CO_2 corrosion processes might be developed to encompass many forms of corrosion by including minor changes in species and accompanying electrochemical reactions [7]. As a result, the primary goal of this study was to generate the polarization curve and control the variables in the carbonated H_2O-PZ-CO_2 system, which plays an important impact in the corrosion process. The current research developed a model at constant temperature and different CO_2 partial pressures. The modeling polarization curve results were compared to experimental polarization curve results under similar conditions.

2. Model Description

The following reactions were considered when CO_2 was dissolved and reacted with an aqueous PZ solution.

$$CO_2(g) \overset{K_1}{\leftrightarrow} CO_2(aq) \tag{1}$$

$$2H_2O \overset{K_2}{\leftrightarrow} OH^- + H_3O^+ \tag{2}$$

$$CO_2 + 2H_2O \overset{K_3}{\leftrightarrow} HCO_3^- + H_3O^+ \tag{3}$$

$$HCO_3^- + H_2O \overset{K_4}{\leftrightarrow} CO_3^{2-} + H_3O^+ \tag{4}$$

$$PZH^+ + H_2O \overset{K_5}{\leftrightarrow} PZ + H_3O^+ \tag{5}$$

$$PZ + CO_2 + H_2O \overset{K_6}{\leftrightarrow} PZCOO^- + H_3O^+ \tag{6}$$

$$H^+PZCOO^- + H_2O \overset{K_7}{\leftrightarrow} PZCOO^- + H_3O^+ \tag{7}$$

$$PZCOO^- + CO_2 + H_2O \overset{K_8}{\leftrightarrow} PZ(COO^-)_2 + H_3O^+ \tag{8}$$

The concentration of species can be obtained by solving the equilibria reactions using known values of the equilibrium constants (k) from the

chemical reactions shown above. The temperature-dependent equilibrium constants were found in the literature [13-17]:

$$H_{CO_2} = \frac{[CO_2]}{P_{CO_2}} \tag{9}$$

$$k_2 = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a_{H_2O}^2} \tag{10}$$

$$k_3 = \frac{a_{HCO_3^-} \cdot a_{H_3O^+}}{a_{CO_2} \cdot a_{H_2O}^2} \tag{11}$$

$$k_4 = \frac{a_{CO_3^{-2}} \cdot a_{H_3O^+}}{a_{HCO_3^-} \cdot a_{H_2O}} \tag{12}$$

$$k_5 = \frac{a_{PZ} \cdot a_{H_3O^+}}{a_{PZH^+} \cdot a_{H_2O}} \tag{13}$$

$$k_6 = \frac{a_{PZCOO^-} \cdot a_{H_3O^+}}{a_{PZ} \cdot a_{CO_2} \cdot a_{H_2O}} \tag{14}$$

$$k_7 = \frac{a_{PZCOO^-} \cdot a_{H_3O^+}}{a_{H^+PZCOO^-} \cdot a_{H_2O}} \tag{15}$$

$$k_8 = \frac{a_{PZ(COO^-)_2} \cdot a_{H_3O^+}}{a_{PZCOO^-} \cdot a_{CO_2} \cdot a_{H_2O}} \tag{16}$$

Where a_i is the activity of species i, P_{CO_2} is the partial equilibrium pressure of carbon dioxide in the gas phase, and H_{CO_2} is Henry's law constant of CO_2 in the solution, obtained from the literature [17].

In order to estimate the total amount of each chemical species present in a solution, the following additional equations must be used for each solution.

Electroneutrality balance:
$$PZH^+ + H_3O^+ = HCO_3^- + OH^- + 2\,CO_3^{-2} + PZCOO^- + 2PZ(COO^-)_2 \tag{17}$$
Mole balance for PZ:
$$PZ + PZCOO^- + PZ(COO^-)_2 + H^+PZCOO^- + PZH^+ = PZ_{Total} \tag{18}$$
Mole balance for CO_2:
$$CO_2 + HCO_3^- + CO_3^{2-} + H^+PZCOO^- + PZCOO^- + PZ(COO^-)_2 = CO_{2\,Total} \tag{19}$$
Total mole fraction:

$$\sum_{i=1}^{i=N} x_i = 1.0 \tag{20}$$

The electrolyte-NRTL model was employed to estimate the activity coefficient for all species in the solution and to explain the non-ideality of the solution[17]:

$$ln\,\gamma_i = \frac{1}{RT}\left[\frac{\partial(n_t G^{ex})}{\partial n_i}\right]_{T,P,n_{j\neq i}} \tag{21}$$
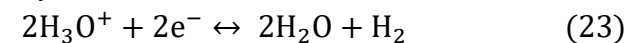
Where:
G^{ex} = excess Gibbs energy, T = system temperature, R = universal gas constant, and n = mole number.

The calculating activity coefficients for every species are taken from the literature [17-19]. Equation 10 to Equation 20 can be solved to compute the concentration of all chemical species in the solution. The corrosion model was developed by analyzing the electrochemical process occurring at the metal surface exposed to an aqueous PZ-CO2 system; the simultaneous electrochemical reactions on the carbon steel surface are described:
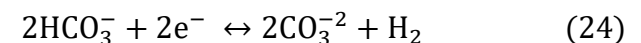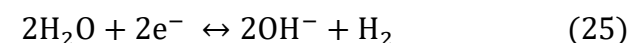
Iron oxidation:
$$Fe \leftrightarrow Fe^{+2} + 2e^- \tag{22}$$
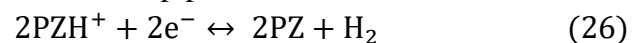Hydronium ion reduction:
$$2H_3O^+ + 2e^- \leftrightarrow 2H_2O + H_2 \tag{23}$$
Bicarbonate ion reduction:
$$2HCO_3^- + 2e^- \leftrightarrow 2CO_3^{-2} + H_2 \tag{24}$$
Water reduction:
$$2H_2O + 2e^- \leftrightarrow 2OH^- + H_2 \tag{25}$$
Protonated piperazine ion reduction:
$$2PZH^+ + 2e^- \leftrightarrow 2PZ + H_2 \tag{26}$$

The rate of the electrochemical reaction depends on the temperature, potential and the concentrations of species reacting at the bulk. Electrochemical rate equations use an

exponential correlation between i and the potential at the carbon steel surface (E):

$$i = i_o \times 10^{\pm \frac{(E - E_{rev.})}{b}} \tag{27}$$

Equation (27) can be written for each electrochemical reaction that occurs throughout the corrosion process. The anodic reaction has a positive sign, while the cathodic reaction has a negative sign. The reversible potential for oxidation and reduction reactions can be calculated using Nernst equation:

$$E_{rev} = E^o + \frac{RT}{nF} \ln\left(\frac{[Products]}{[Reactants]}\right) \tag{28}$$

Where:

E^o = standard potential for the cathodic and anodic reactions, n = number of electrons in the reaction, F = Faraday constant "96500 coulombs/equ". The values for standard electrode potential for oxidation and reduction reactions are given in Table 1.

Table 1. Standard electrode potential for oxidation and reduction reactions at 40 °C.

Reaction	E^o (V)
Fe^{+2} oxidation	-0.4768
H_3O^+ reduction	0.0
HCO_3^- reduction	-0.6347
H_2O reduction	-0.8408
PZH^+ reduction	-0.5823

The electrochemical parameters E_{corr}, i_o, and β for the system considered in the present study were found in the open literature [20-22]. The value of Tafel slop β for oxidation and reduction reactions is:

$$\beta = \frac{2.303\ RT}{n\ \alpha F} \tag{29}$$

Where α is transport constant.

2.1. Implementation the Model

A Matlab program for calculating bulk equilibrium concentration was used. For aqueous solution of CO_2-PZ, eleven variables must be solved in eleven equations. To handle this non-linear algebraic equation system, Newton- Raphson's approach was adopted. Once all chemical species' concentrations were calculated, the mixed potential equation was used. Individual and total cathodic and anodic currents were computed using the model. When the cathodic and anodic currents are balanced, the corrosion potential E_{corr} can be calculated by solving the equation below:

$$i_{Fe/Fe^{+2}} = i_{H_3O^+/H_2} + i_{HCO_3^-/CO_3^{-2}} + i_{H_2O/OH^-} + i_{PZH^+/PZ} \tag{30}$$

The anodic reaction current (i_{Fe}) and the known value of corrosion potential (E_{corr}) were used to compute the corrosion current density (i_{corr}). Faraday's law was then employed to compute the corrosion rate. If the corrosion current density is given in unit A/m^2, the corrosion rate for carbon steel stated in mm/y takes almost the same quantitative.

$$CR = \frac{i_{corr} M_w}{\rho\ nF} \chi = 1.155\ i_{corr} \tag{31}$$

Where,
CR = = rate of corrosion (mm/y),
i_{corr} = corrosion current density in (A/m^2),
Mw = iron molecular weight (kg/mol.),
ρ = metal density (kg/m^3),
n = number of electrons exchanged in the electrochemical reaction, and
χ = unit conversion factor.

2.2. Model Validation

To confirm the performance of the model, the simulated polarization curve and experimental

curve should be compared. The investigations were carried out utilizing an electrochemical approach in a static corrosion cell. The carbon steel specimen has a chemical composition of 0.2% C, 0.51% Mn, 0.013% P, 0.039% S, 0.017% Si, and balanced Fe. Before being exposed, the specimen was polished using silicon carbide sheets of 600 grit, cleaned with acetone, and dried. PZ aqueous solutions with concentrations of 1M were made using 98 percent pure PZ and deionized water. The testing solution was kept at the prescribed temperature and at varying CO_2 partial pressures. Corrosion experiments were performed in a 250 mL glass vessel at 40 °C and atmospheric pressure. Additional information on the experimental setup may be obtained in the literature. [20].

3. Results and Discussion

Validation of the polarization curve generated by the model is required prior to corrosion modeling in order to assure the veracity of the simulation findings to be achieved. The simulated polarization curve obtained from the model was compared to the experimental polarization curve. The simulated polarization curve model predicted the carbon steel corrosion rate in H_2O-CO_2-PZ system at simulation conditions were determined based on the experimental results.

The majority of the generated polarization curves from the model are comparable to the actual polarization curves, as seen in Figure 1 to Figure 4 and Table 2. The generated polarization curves shifted toward smaller corrosion current densities (i_{corr}) at low CO_2 partial pressure and greater corrosion current density (i_{corr}) at high CO_2 partial pressure when compared with experimental polarization curves. It is obvious from the values of

corrosion potential (E_{corr}), the predicted values were close to the experimental values. This deviation may be related to the iron concentration value in the bulk solution, which was obtained as a function of ionic strength and temperature from Sun et al. (2009).
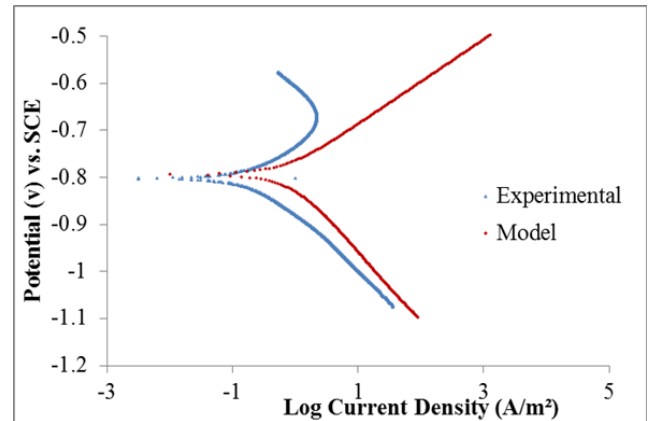

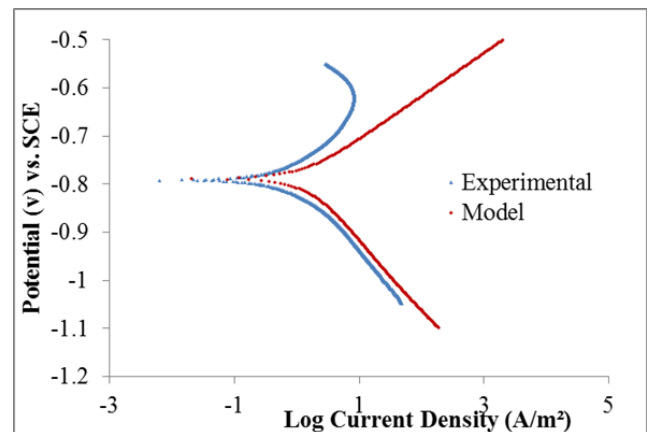**Figure 1.** Polarization curves experimental and model at P_{CO2}=0.96 Kpa and 40 °C.

Figure 2. Polarization curves experimental and model at P_{CO2}=9.58 Kpa and 40 °C.
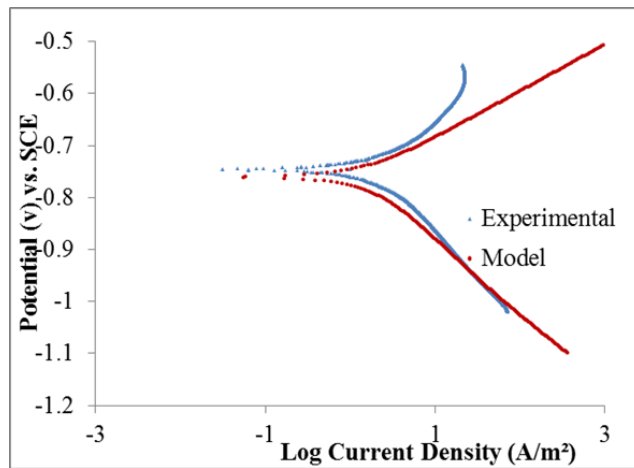
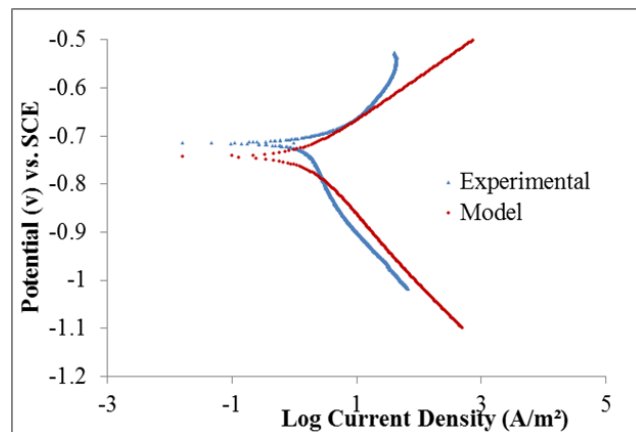**Figure 3.** Polarization curves experimental and model at P_{CO_2}=47.39 Kpa and 40 °C.

Figure 4. Polarization curves experimental and model at P_{CO_2}=47.39 Kpa and 40 °C.

Table 2. Experimental data and modeling for 1 M of PZ system at 40 °C.

P_{CO_2} (kPa)	Experimental Data		Model Data		$^a\delta$	$^b\delta$
	E_{corr} (V)	CR (mm/y)	E_{corr} (V)	CR (mm/y)		
0.96	-0.810	0.212	-0.782	0.187	3.4	11.7
9.53	-0.784	0.795	-0.789	0.615	0.6	22.6
47.72	-0.769	1.033	-0.786	1.175	2.2	13.7
95.61	-0.766	1.314	-0.781	1.473	1.9	12.1

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

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

4. Conclusions

A polarization curve model was developed for corrosion of carbon steel in PZ-CO_2-H_2O system.

Rigorous equilibrium model and mixed potential Theory are the main models used to generate the polarization curves. The model generates the polarization curve based on modeling solution speciation and it is capable to predict the corrosion rate of carbon steel at carbon dioxide partial pressure was in the range of 1 to 100 kPa and selected system temperature 40 °C. Electrochemical experiments are performed to validate the model. The model is shown to be able to identify the main oxidizing agents in the system at 40 °C, investigate the influence of parameters on carbon steel corrosion process and control the conditions leading to corrosion of carbon steel that cannot be studied experimentally. The results from the model are compared with experimental results of electrochemical measurements and good agreement is demonstrated between the modeled polarization curve and the experimental polarization curve.

Acknowledgements

Conflict of interest

The authors declare that they have no conflict of interest.

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