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Corrosion Mechanism of Carbon steel in MDEA-Based CO$_2$ Capture Plants

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ABSTRACT

In the present study, the corrosion properties of carbon steel were evaluated in 50 wt.% Methyldiethanolamine (MDEA) solutions, related to the carbon dioxide (CO$_2$) capture process in fossil fuel-fired power plants. Tests were conducted under an absorber (50°C) condition with different combinations of CO$_2$, oxygen (O$_2$) and heat stable salts (HSS): bicine, formate and sulfate. Corrosion behavior of carbon steel was monitored using electrochemical methods (linear polarization resistance and cyclic polarization). Under the absorber conditions, the addition of CO$_2$ in the MDEA systems significantly increased the corrosion rate and changed the corrosion behavior from a passive to an active state. In addition, the presence of O$_2$ and HSSs in the MDEA/CO$_2$ systems promoted the corrosion process by accelerating both the anodic and cathodic reactions for the corrosion of carbon steel.

Key words: MDEA, CO$_2$ capture, carbon steel, carbon capture and storage

INTRODUCTION

Alkanolamine solutions are commonly used to remove acid gas contaminants, such as carbon dioxide (CO$_2$) and hydrogen sulfide (H$_2$S), from various process gas streams in the oil & gas industry, the steel industry, syngas plants, chemical plants, and many others.[1] Recently this technology is considered for capturing CO$_2$ from the flue gas stream as a part of carbon capture and storage (CCS) process.

The CO_2 absorption process using aqueous amine solutions has been affected by corrosion related problems in the past.[2-6] Many studies have been done on corrosion associated with removing acidic gases, usually CO_2 and H_2S, from natural and refinery gas streams. However there are significant differences with exhaust gas applications, including oxygen-rich environment and contaminants from products of combustion (nitrogen oxides (NO_x), sulfur oxide (SO_x), particulates, etc.). These specific conditions involving flue gas can introduce more complicated corrosion problems in alkanolamine systems. Thus, to carry out a proper study of carbon steel corrosion during the CO_2 capture process coming from power plant flue gases, the effect of all possible components present in the system must be considered in terms of identifying the corrosion behavior as well as the corrosion mechanism at different operating conditions.

Although there are extensive research data available on corrosion and corrosion inhibition in MEA systems,[7-9] minimal information has been reported in the literature concerning the electrochemical behavior and corrosion mechanisms of carbon steel in CO_2-loaded MDEA solutions.

In our previous work, the short-term and long-term corrosion behavior of carbon steel in MDEA / water (H_2O) / CO_2 / O_2 / HSSs mixtures was investigated under the absorber condition.[10] Furthermore, a predictive model was developed for corrosion of carbon steel in CO_2-loaded aqueous MDEA systems based on modeling of solution speciation and key electrochemical reactions.[11]

The objective of the present study was to evaluate corrosion mechanism of carbon steel in MDEA / H_2O / CO_2 / O_2 / HSSs mixtures, which represents the absorber condition. By comparing effects of all oxidizing agents in the MDEA / H_2O / CO_2 system, an attempt was made to understand general corrosion mechanism of carbon steel in the system. In addition, effect of individual HSS (bicine, formate and sulfate) on the corrosion behavior of carbon steel were investigated in the MDEA / H_2O / CO_2 / O_2 system by short-term corrosion experiments.

EXPERIMENTAL PROCEDURE

The specimens were made of carbon steel (ASTM[(1)] A36) with a chemical composition of 0.23% C, 0.79% Mn, 0.02% P, 0.03% S, 0.29% Cu, 0.20% Si, and balance Fe. The specimens were ground with 600-grit silicon carbide (SiC) paper, cleaned with isopropyl alcohol (C_3H_8O) in an ultrasonic bath, and dried prior to exposure. Corrosion tests were carried out in a 2-L glass cell at 50°C under atmospheric pressure. Further details of the experimental setup can be found elsewhere.[10,11]

Effects of CO_2 and MDEA

When carbon steel is exposed to the MDEA / H_2O / CO_2 system, the electrochemical reactions occurring simultaneously at the steel surface are dissolution of iron and reduction of the various "oxidizing agents":[11]

- Anodic (oxidation) reaction
$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

- Cathodic (reduction) reactions:
$$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2 \tag{2}$$
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{3}$$
$$2H_2CO_3 + 2e^- \rightarrow 2HCO_3^- + H_2 \tag{4}$$
$$2HCO_3^- + 2e^- \rightarrow 2CO_3^{2-} + H_2 \tag{5}$$
$$2MDEAH^+ + 2e^- \rightarrow 2MDEA + H_2 \tag{6}$$

[(1)] American Society for Testing Materials (ASTM) International, 100 Barr Harbor Dr., West Conshohocken, PA 19428.

H_3O^+, H_2O, H_2CO_3, HCO_3^- and $MDEAH^+$ are the potential oxidizing agents in the $MDEA/CO_2/H_2O$ system. Since the system is alkaline (close to pH 9), it can be shown that the contribution of H_3O^+ reduction (reaction (2)) is quite small due to the very low concentration in solution, when compared to other species.

In order to evaluate the effect of individual oxidizing agent on the corrosion behavior of carbon steel in MDEA / H_2O / CO_2 system, 6 different solutions were prepared as shown in Table 1. Solution 1 was prepared by adjusting pH of DI water with dilute NaOH solution to 9.1 in which H_2O is the only oxidizing agent. Solution 2 was prepared by adjusting pH of 0.5 M $NaHCO_3$ solution with Na_2CO_3 crystal to 9.1 and purged by N_2 in order to have HCO_3^- and H_2O as oxidizing agents. Solution 3 was prepared by purging N_2 and CO_2 mixtures (P_{CO2}= 0.008 MPa) into solution 2 to add H_2CO_3 in the solution. Solutions 4 and 5 were prepared by adjusting pH of 50 wt. % MDEA solution with H_2SO_4 and HCl to 9.1, respectively. Solution 6 was prepared by purging N_2 and CO_2 mixtures (P_{CO2}= 0.012 MPa) into 50 wt. % MDEA solution which contains all possible oxidizing agents (H_2O, HCO_3^-, H_2CO_3 and $MDEAH^+$). The concentrations of HCO_3^-, H_2CO_3 and $MDEAH^+$ in solutions 2 to 5 were the same as in the solution 6.

Table 1
Test Solutions for Evaluating the Effect of Oxidizing Agents in MDEA / H_2O / CO_2 Systems

No.	Solutions	Oxidizing agent	pH
1	$NaOH/H_2O$	H_2O	9.1
2	$NaHCO_3^-/NaCO_3^{2-}/H_2O$	H_2O, HCO_3^-	9.1
3	$NaHCO_3^-/NaCO_3^{2-}/H_2O/CO_2$	H_2O, HCO_3^-, H_2CO_3	9.1
4	$MDEA/H_2O/H_2SO_4$	H_2O, $MDEAH^+$	9.1
5	$MDEA/H_2O/HCl$	H_2O, $MDEAH^+$	9.1
6	$MDEA/H_2O/CO_2$	H_2O, HCO_3^-, H_2CO_3, $MDEAH^+$	9.1

Corrosion behavior of carbon steel in each solution was evaluated by linear polarization resistance (LPR) and potentiodynamic measurements. LPR measurements were performed in a range of ±10 mV with respect to the corrosion potential, and a scan rate of 0.166 mV/s. The potentiodynamic scans were carried out after the completion of the LPR measurements, in the following manner: the scan was first conducted in the cathodic (more negative) direction from the open-circuit potential (OCP) with a scan rate of 0.166 mV/s. The OCP was then allowed to return close to its previous value, which happened in about 20 minutes. Then the scan was conducted in the anodic (more positive) direction from OCP with the same scan rate of 0.166 mV/s.

Effect of heat stable salts (HSSs)

Table 2 and Figure 1 demonstrate the test conditions and procedure. The test conditions were selected in order to investigate the effect of individual HSS on the corrosion of carbon steel in an aqueous MDEA solution. The HSSs were made up by the dissolution of their acid forms in an aqueous MDEA solution. The corrosion rate was measured using LPR and electrochemical impedance spectroscopy (EIS) measurements. LPR measurements were performed within ±10 mV with respect to the corrosion potential with a scan rate of 0.166 mV/s. EIS measurements were conducted in the frequency range between 10 kHz and 10 mHz. Sinusoidal voltage of ±10 mV was supplied at the corrosion potential. The cyclic potentiodynamic polarization tests were carried out after conducting LPR and EIS measurements. The specimen was scanned potentiodynamically at a rate of 0.166 mV/s to a potential corresponding to a current density of 10 A/m^2. At this point, the scan direction was reversed. The downscan was continued until the initial corrosion potential.

Table 2
Test Conditions for Evaluating O$_2$ and Individual HSS Effects

Test condition #	Corrosion system
1	CS / 50 wt.% MDEA / 12% CO$_2$ / 6% O$_2$
2	CS / 50 wt.% MDEA / 12% CO$_2$ / 6% O$_2$ / 10000 ppm Bicine
3	CS / 50 wt.% MDEA / 12% CO$_2$ / 6% O$_2$ / 2818 ppm Formic acid
4	CS / 50 wt.% MDEA / 12% CO$_2$ / 6% O$_2$ / 3002 ppm Sulfuric acid
5	CS / 50 wt.% MDEA / 12% CO$_2$ / 6% O$_2$ / 10000 ppm Bicine + 2818 ppm Formic acid + 3002 ppm Sulfuric acid

* CS: carbon steel (A36)
**P$_{CO2}$= 0.012 MPa, P$_{O2}$= 0.006 MPa

Prepare solution / add gas → Insert steel coupon

| Measure pH	OCP measurement	LPR measurement	EIS measurement	Cyclic polarization tests	→ Time
~ 6 hours	~ 2 hours	~ 10 minutes	~ 30 minutes	~ 6 hours	
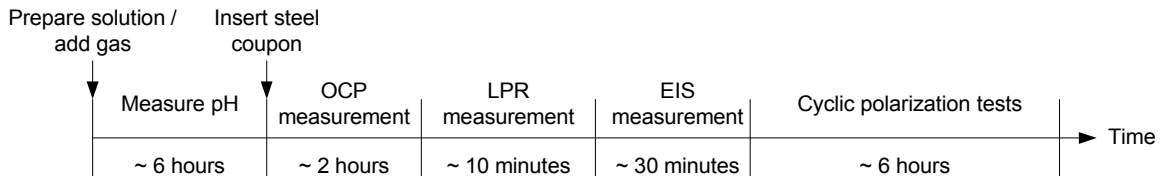
Figure 1: Experimental procedure for evaluating individual HSSs effect on the corrosion of carbon steel in the absorber environments.

RESULTS

Effect of CO$_2$ and MDEA

Figure 2 illustrates the OCP and corrosion rate of carbon steel in different test solutions. The corrosion rates of carbon steel in solution 2 (H$_2$O, HCO$_3^-$), 4 (H$_2$O, MDEAH$^+$) and 5 (H$_2$O, MDEAH$^+$) showed low values with noble potentials, indicating spontaneous passivation of carbon steel. However, it showed high corrosion rates in solution 1 (H$_2$O), 3 (H$_2$O, HCO$_3^-$, H$_2$CO$_3$) and 6 (H$_2$O, HCO$_3^-$, H$_2$CO$_3$, MDEAH$^+$) with low potential values, indicating active dissolution of carbon steel.
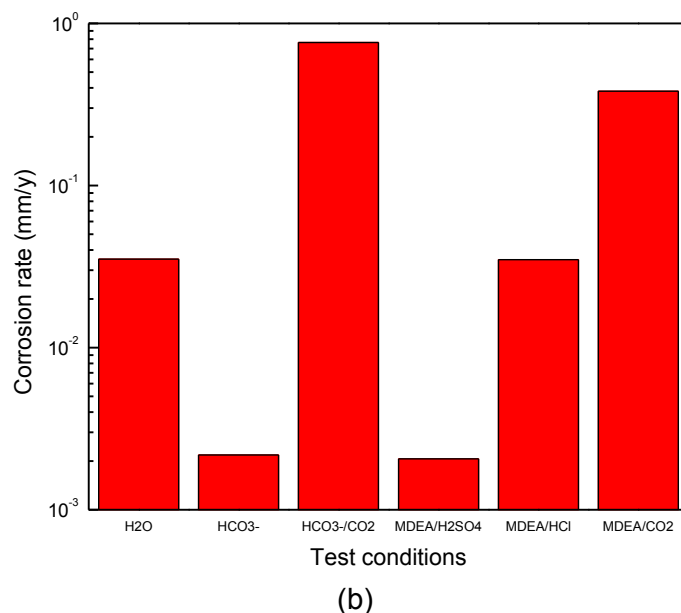

(a)

(b)
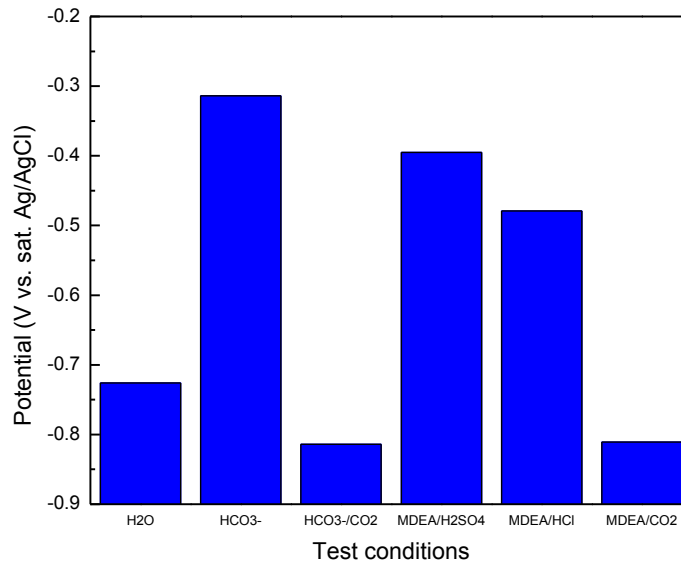
Figure 2: Effect of oxidizing agents on the corrosion properties of carbon steel in different solutions: (a) OCP, (b) Corrosion rate.

It is interesting to note that carbon steel showed different corrosion behavior in solution 2 and solution 3 where the difference is only the presence of small concentration of H_2CO_3. This can be explained by the dissolution of initial surface layer, $Fe(OH)_2$ in the presence of H_2CO_3;
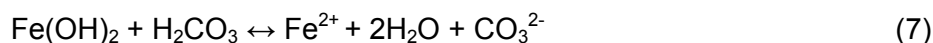
$$Fe(OH)_2 + H_2CO_3 \leftrightarrow Fe^{2+} + 2H_2O + CO_3^{2-} \tag{7}$$

Figure 3 shows polarization curves of carbon steel in solution 1 (H_2O), solution 2 (H_2O, HCO_3^-) and solution 3 (H_2O, HCO_3^-, H_2CO_3). The cathodic polarization curve in solution 1 is mainly due to the water reduction, which showed lower current density compared with those in solution 2 and solution 3. This indicates that the contribution of H_2O as an oxidizing agent is low for this high pH condition. For the cathodic curves in solution 2 and solution 3, there is little difference in the current densities which implies that the contribution of H_2CO_3 is negligible and HCO_3^- reduction reaction is the dominant cathodic reaction.

Figure 4 shows the change of OCP for carbon steel in a 50 wt.% MDEA system at 50°C with different CO_2 partial pressures. With low partial pressures of CO_2 (~ 0.0017 MPa), carbon steel shows passive behavior with noble potential values. However, there is an abrupt drop in potential around 0.002 MPa indicating that the corrosion behavior changes from passive to active. This can be explained by the increase of H_2CO_3 concentration in the MDEA solution which can dissolve the passive film on the steel surface.
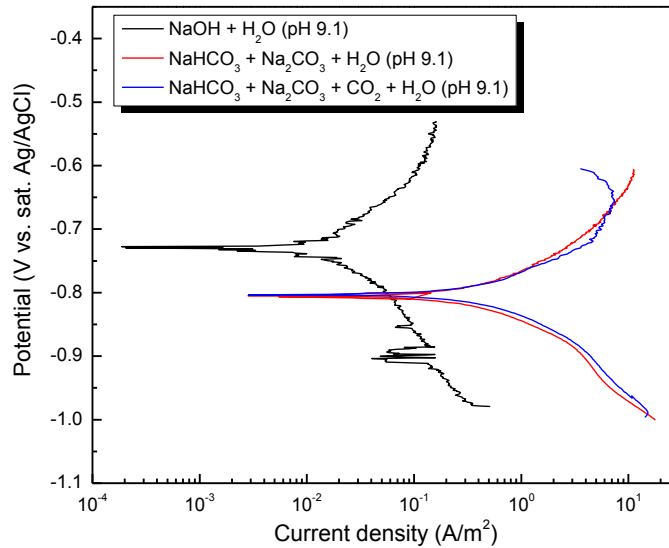
Figure 3: Polarization curves of carbon steel in solution 1 (H_2O), solution 2 (H_2O, HCO_3^-) and solution 3 (H_2O, HCO_3^-, H_2CO_3).
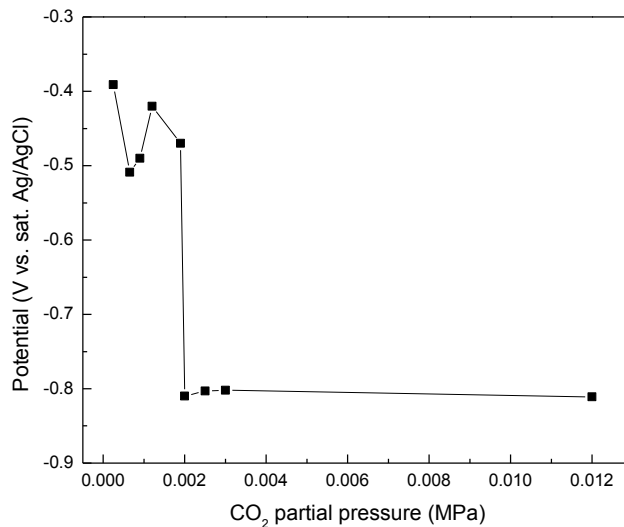

Figure 4: Variation of OCP for carbon steel as a function of CO_2 partial pressure in MDEA / H_2O / CO_2 system.

Figure 5 shows the polarization curves of carbon steel in solution 4 (H_2O, $MDEAH^+$), solution 5 (H_2O, $MDEAH^+$) and solution 6 (H_2O, HCO_3^-, H_2CO_3, $MDEAH^+$). The cathodic polarization curves showed similar current densities for all three tests which proves that the dominant cathodic reaction in solution 5 and 6 are $MDEAH^+$ reduction and $MDEAH^+$ acts as a dominant oxidizing agent in solution 6.

Based on the above observation, it can be concluded that the dominant cathodic reactions in the MDEA / H_2O / CO_2 system are HCO_3^- reduction and $MDEAH^+$ reduction reactions.

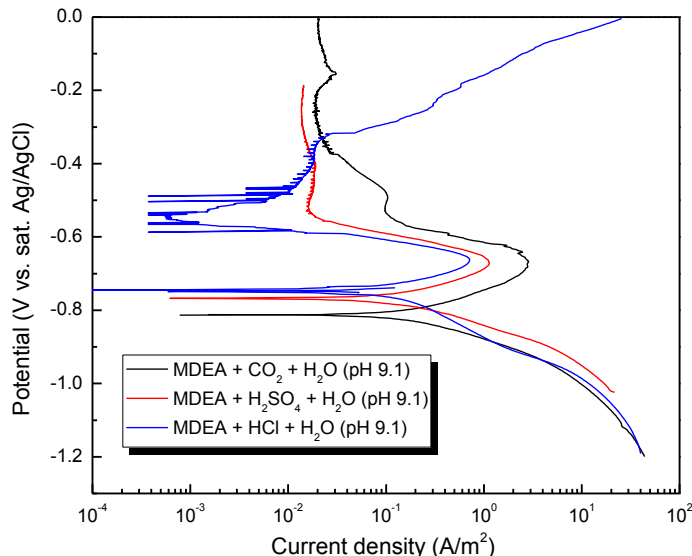**Figure 5: Polarization curves of carbon steel in solution 4 (H₂O, MDEAH⁺), solution 5 (H₂O, MDEAH⁺) and solution 6 (H₂O, HCO₃⁻, H₂CO₃, MDEAH⁺).**

Effect of HSSs

The results of OCP and LPR / EIS measurements for 50 wt.% MDEA / 12% CO_2 / 6% O_2 with different HSSs are described in Figure 6 and Figure 7, respectively. For all conditions, the OCP measured in an active potential region and the addition of bicine decreased the OCP toward more active direction which is similar to the OCP of combined HSSs condition (HSSs in Figure 6). The corrosion rates obtained from LPR and EIS were averaged for each condition. The addition of bicine increased the corrosion rates of carbon steel significantly in the MDEA system but the corrosion rate slightly increased when formate and sulfate were added in the system. This indicates that between bicine, formate and sulfate, bicine is the most corrosive HSS for carbon steel in the MDEA system and it is also the cause of the increase of the corrosion rate for the combined HSSs condition.
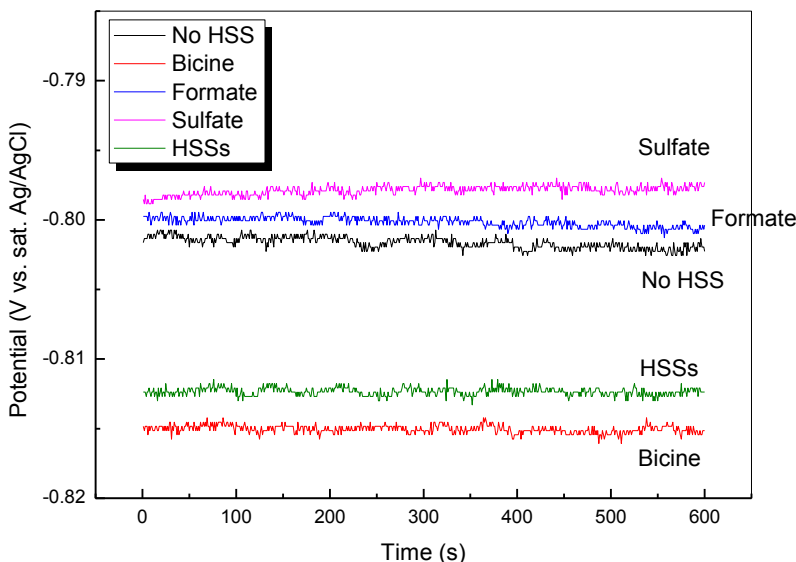

Figure 6: Variations of OCP for carbon steel in the MDEA/CO₂/O₂ condition with different HSSs.
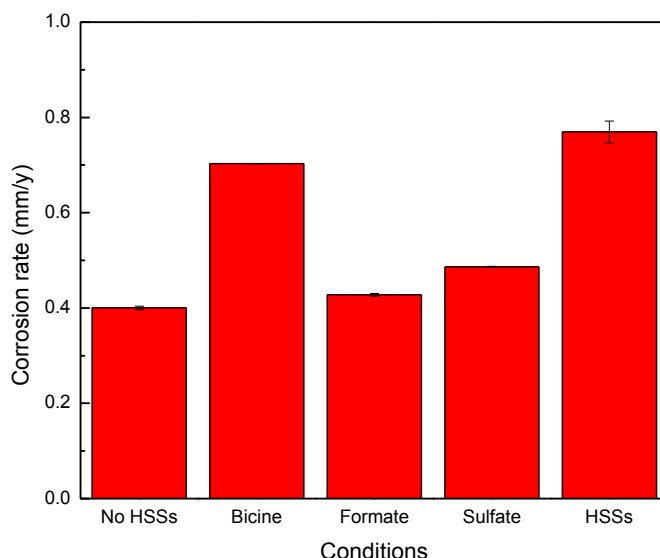
Figure 7: Corrosion rate of carbon steel with different HSSs in the MDEA system.

Figure 8 represents the result of pH measurements in the MDEA system with different HSSs. The solution pH values were slightly decreased by adding HSSs in the MDEA system.
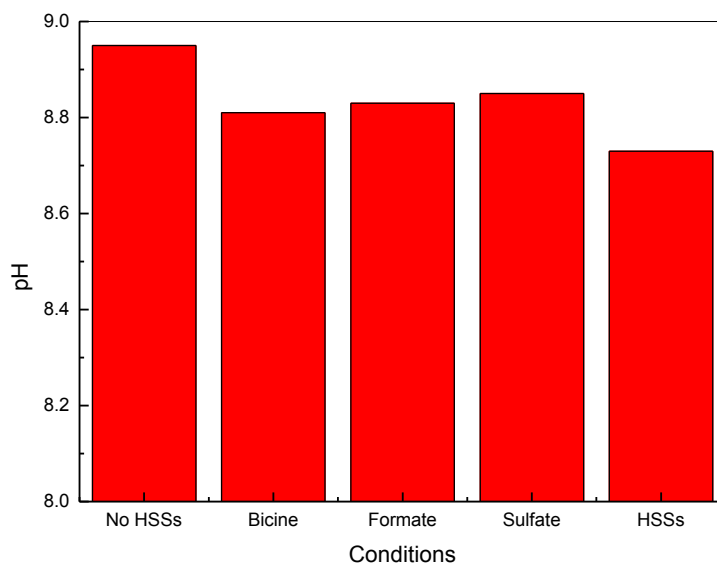

Figure 8: Solution pH with different HSSs in the MDEA system.

Figure 9 through Figure 11 illustrate the cyclic polarization curves for carbon steel in the MDEA system with different HSSs. There is no significant difference between the cathodic polarization curves with different HSSs. Furthermore, the presence of HSSs did not induce pitting attack for all conditions. However, as shown in Figure 9, the addition of bicine slightly increased current density in the active region of the anodic polarization curve (-0.6 V ~ -0.8 V). This implies that the mechanism of iron dissolution in the presence of bicine might have altered due to the iron chelating effect[12] or slight decrease in pH.

As shown in Figure 10 and Figure 11, the polarization curve shows more than one stable corrosion potential, achieved by adding formate and sulfate, indicating unstable passivation.[13] However, those HSSs do not affect corrosion rate in the active state.
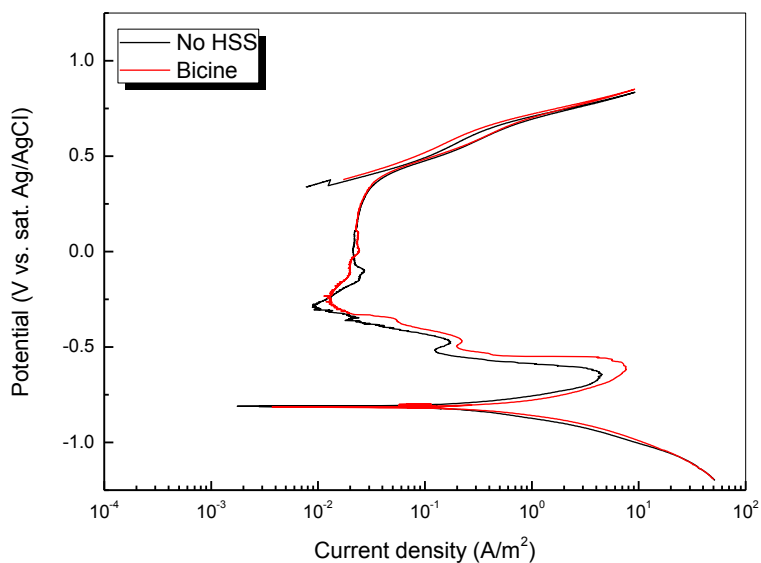

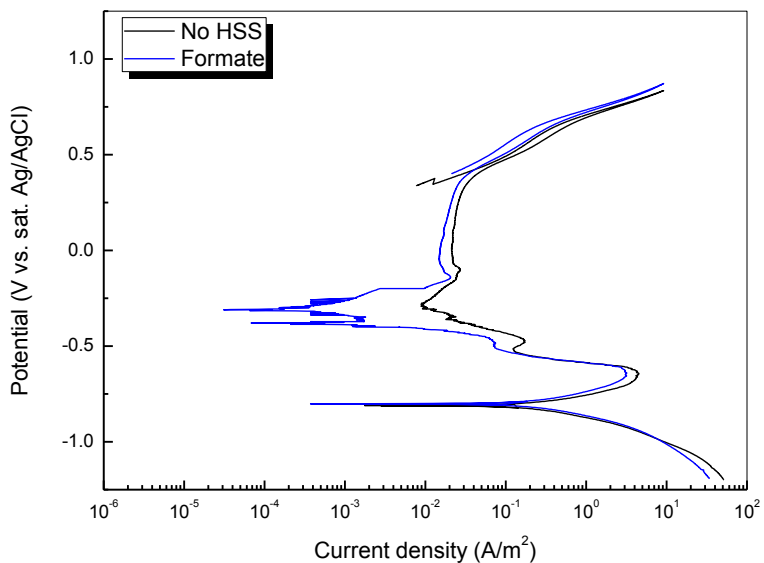**Figure 9: Cyclic polarization curves of carbon steel in the MDEA system with/without bicine.**

Figure 10: Cyclic polarization curves of carbon steel in the MDEA system with/without formate.
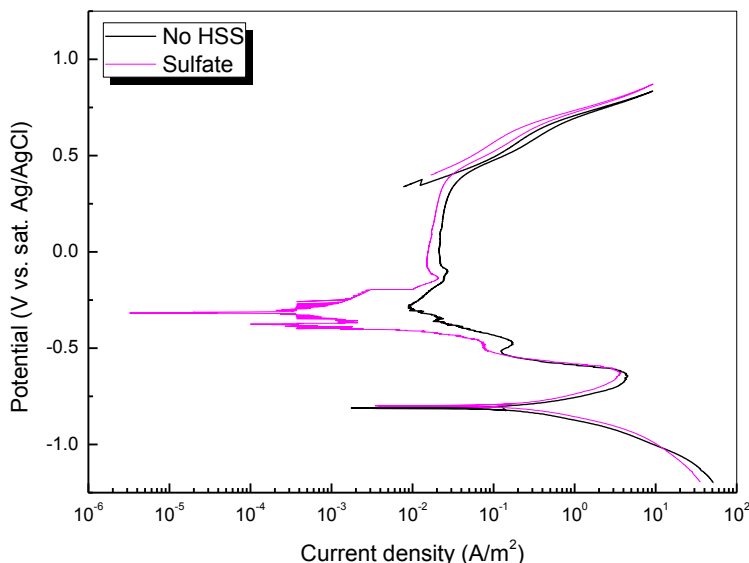
Figure 11: Cyclic polarization curves of carbon steel in the MDEA system with/without sulfate.

CONCLUSIONS

- The addition of carbon dioxide (CO_2) in the Methyldiethanolamine (MDEA) systems significantly increased the corrosion rates and changed the corrosion behavior from passive to active state.
- In the active state, both bicarbonate (HCO_3^-) and protonated methyldiethanolamine ($MDEAH^+$) are the main oxidizing agents in the system.
- From the different heat stable salts (HSS), bicine was the largest contributor to the increase in the corrosion rate, at least in the short-term corrosion experiments. Bicine affects the anodic reaction most likely acting as a chelator due to its high affinity toward iron or by decreasing pH of solution.
- Formate and sulfate did not change the corrosion behavior of carbon steel in the active state, whereas they made the passive film unstable in the passive state.

ACKNOWLEDGEMENTS

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