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Research Paper

An Electrochemical Investigation on the Effect of Heat-Stable Salts on the Corrosion Resistance of Carbon Steel in MDEA Solution

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Abstract

The purpose of this study is to identify the influence of different concentrations of heat-stable salts (oxalate, acetate, formate, succinate, glycolate) on the carbon steel corrosion in MDEA solution. Natural gas usually contains acidic gases like CO₂ and H₂S along with other sulphur components. These acidic gases have to be scrubbed off from the gas for environmental, operational, and economic reasons. A long-term experiment was conducted to investigate the corrosion behavior of carbon steel in HSS+MDEA solutions and surface analysis techniques (SEM, EDS) were carried out to characterize the morphologies and compositions of the surface layers. To obtain the corrosion behavior of carbon steel in different concentrations of HSS+MDEA solutions the potentiodynamic polarization tests were used. The result showed that the acetate had less corrosion effect and the oxalate had the greatest impact on corrosion of the carbon steel. According to the electrochemical results, these five heat stable salts didn't have a significant corrosion effect on carbon steel till 5000 ppm concentration.

Keywords

MDEA Solution, Carbon Steel, Heat Stable Salts, Polarization Resistance

1. Introduction

Alkanolamines are widely used in natural gas refining processes to separate acid gases such as hydrogen sulfide and carbon dioxide. These two acidic gases are weak acids whose reactions with alkanolamines in the adsorption tower are reversible with increasing temperature in the regeneration tower, but other acids are introduced into the system or formed in the system that is stronger than both hydrogen sulfide and carbon dioxide. Their reactions with alkanolamines are irreversible and cannot regenerate by increasing temperature in regenerator tower and are known as heat-stable acids. The product of the reaction of these acids with amine solvent is called heat-stable salt [1-4].

The heat-stable salts not only reduce the power of amine solvent adsorption to adsorb the acidic gases in the gas stream but also, increase corrosion rate by reducing the pH and increasing the conductivity of the solution [1-4]. These salts are one of the most important amine contaminants.

Studies show that HSS increases the corrosion rate of carbon steel and it depends on the types and concentration of HSS in MEA solution and also implies that HSS doesn't have a significant effect on stainless steel corrosion [3]. In addition, the corrosion rate of carbon steel goes up with increasing of HSS concentration and goes down with increasing of temperature [4].

One of the most important heat-stable acids produced by the chemical and thermal decomposition of amine solvent in the system can be organic acids such as oxalic acid, formic acid, acetic acid, glycolic acid, and succinic acid. The salts of these acids are oxalate, acetate, formate, acetate, and glycolate, succinate, which are known as heat-stable salt anions [5-10].

In the gas refinery, the amount of HSS in the amine is analyzed approximately every six months. Most of the time the results are too high and the problem is that there is less information about the impact of different types and different concentrations of HSS on corrosion of the carbon steel in MDEA solution and also the cost of remedial actions to decrease the amount of HSS in solution are high so it's important to discover mentioned reasons due to almost all gas sweetening equipment are made of carbon steel.

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2. Experimental Procedure

2.1 Materials and Test Solution

Corrosion behavior of different heat stable salts and the effect of their different concentrations on corrosion resistance of the carbon steel in MDEA solution was investigated with the following procedure:

At the First 40% aqueous MDEA solutions were prepared, 99% methyl diethanolamine (MDEA), was used and diluted to 40% using distilled water.

After making 40% MDEA solutions, acetic, formic, oxalic, glycolic, succinic acids were added to prepare heat stable salt solutions. These acids were added to the 40% MDEA solutions at concentrations: 1000, 5000, 10000, 15000, and 20000 ppm.

2.2 Electrochemical Measurements

The specimens were prepared from a carbon steel plate (AISI 1018). The specimens were polished by using emery paper up to Number 1000, washed with alcohol, and finally dried.

Table 1. The Chemical composition of AISI 1018

Element	C	Mn	P	S	Fe
Composition (wt%)	0.18	0.70	0.03	0.04	98.85

The potentiodynamic polarization test was carried out in a standard three-electrode cell in a 500 ml solution. The Ag/AgCl electrode was used as a reference electrode and platinum as a counter electrode. Electrochemical test curves were plotted within ± 500 mV from OCP with a scan rate of 0.01 mV/S. The Electrochemical tests were performed using AUTO LAB type III and corrosion test results were obtained using Nova 2.1 software. To compare the results of electrochemical tests of heat-stable salts in different concentrations, an electrochemical test was performed on pure 40% MDEA with no acids.

To assess the long-term impact of the test solutions on AISI 1018 metal, 5 test specimens were soaked in the 20000 ppm of acids testing solutions which are shown in Table 1 for 100 days.

2.3 Scanning Electron Microscope (SEM)

The scanning electron microscopy (SEM) and the energy dispersive spectroscopy (EDS) technique have been used to characterize the morphologies and compositions of surface layers. The microstructure analysis of the samples corrosion product analysis was conducted using scanning electron microscopy (SEM, Leica Cambridge, Stereoscan S360, UK).

3. Result and discussion

The results of the potentiodynamic test at the different concentrations of acetate in the MDEA solution are shown in Figure 1 and Table 2, from these results the open circuit potential or OCP decreased toward more negative potential which is indicated that in the presence of acetate, corrosion occurred in lower potential. The Tafel slope (β_a) of the system decreases with increasing acetate concentration and the β_a values were rather constant when the concentration changes from 1000 to 15000 ppm. By adding acetic acid to 40% amine solutions, polarization resistance decrease. This result indicated that the formation of acetate heat stable salt increases the corrosion rate of the solution due to increasing the electrical conductivity [6]. Increasing the concentration of acetate salt in the solution up to 20,000 ppm has no significant effect on the corrosion resistance of carbon steel. Also, the corrosion rates up to 20,000 ppm acetate were less than 1 mpy.

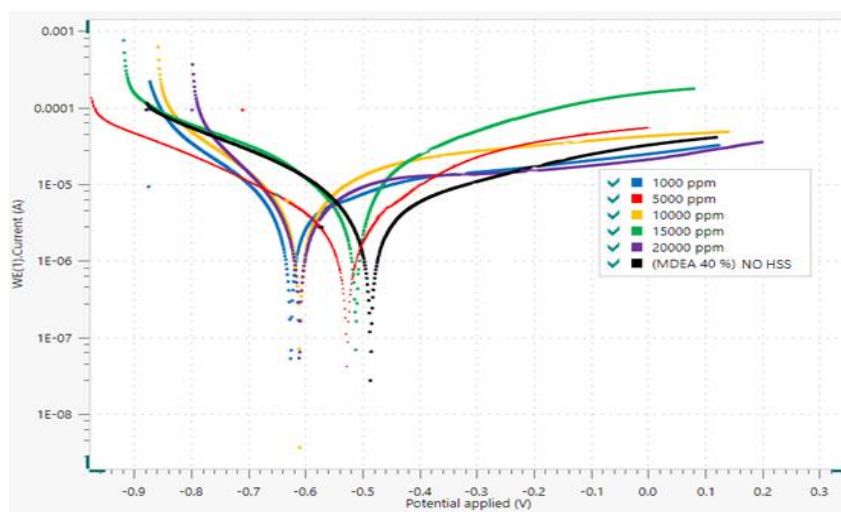


Figure 1. The potentiodynamic curves of Carbon steel in different concentration of acetic acid + 40% MDEA

Table 2. The Electrochemical parameters of Carbon steel 1018 in different concentration of acetic acid + 40% MDEA

Concentration of acetic acid	1000 PPM	5000 PPM	10000 PPM	15000 PPM	20000 PPM	No Acid (40% MDEA)
E_{corr} (V)	-0.62499	-0.51999	-0.60903	-0.51085	-0.60987	-0.48507
i_{corr} (A/cm²)	8.3342E-07	2.0341E-06	1.1802E-06	1.5674E-06	7.4462E-07	8.082E-07
Corrosion rate (mpy)	0.3812	0.930	0.539	0.717	0.340	0.369
Polarization resistance (Ω)	12057	5742.1	10313	8696	12505	15679
B_a (V/dec)	0.056707	0.051637	0.056709	0.05681	0.047655	0.069736
B_c (V/dec)	0.039087	0.056129	0.055413	0.070126	0.038974	0.05017

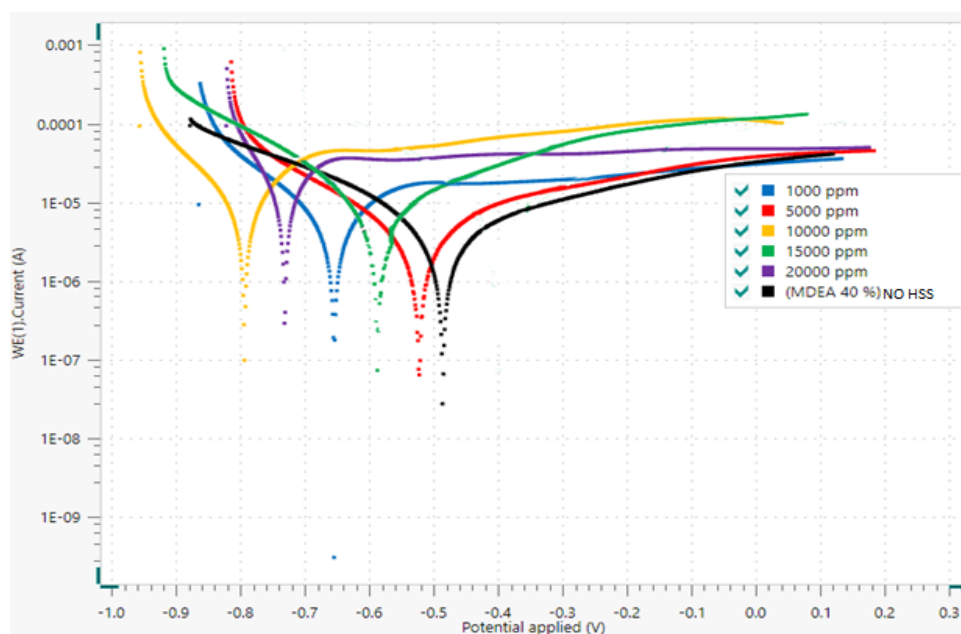


Figure 2. The potentiodynamic curves of Carbon steel in different concentrations of formic acid + 40% MDEA

Figure 2 show the potentiodynamic curves of Carbon steel in different concentration of formic acid in the MDEA solution. As seen in Table 3 the R_p decrease with adding formic acid to the system, also a sharp decrease was observed in the ranges of 10000 and 20000 ppm of formate and the biggest corrosion rate was obtained in these concentrations range. The change of Tafel slope (β_c) relatively remained stable at 0.057 ± 6 (V/dec) which implies a similarity in the reduction of oxidizing agent compared to the acid-free system. The corrosion rates up to approximately 5000 ppm of formate were less than 1 mpy and then corrosion rate increases up to 2.7 mpy in 20000 ppm of formate.

Table 3. The Electrochemical parameters of Carbon steel 1018 in different concentration of formic acid + 40% MDEA

Concentration of formic acid	1000 PPM	5000 PPM	10000 PPM	15000 PPM	20000 PPM	No Acid (40% MDEA)
E_{corr} (V)	-0.65414	-0.52203	-0.79358	-0.59503	-0.73075	-0.48507
i_{corr} (A/cm²)	1.6813E-06	1.3021E-06	3.506E-06	2.4889E-06	6.0266E-06	8.082E-07
Corrosion rate (mpy)	0.769	0.379	1.603	1.138	2.757	0.369
Polarization resistance (Ω)	7711.7	8054.6	3765.6	6598.8	2115.1	15679
B_a (V/dec)	0.059032	0.063674	0.059326	0.094338	0.067707	0.069736
B_c (V/dec)	0.060398	0.059246	0.062345	0.063119	0.051809	0.05017

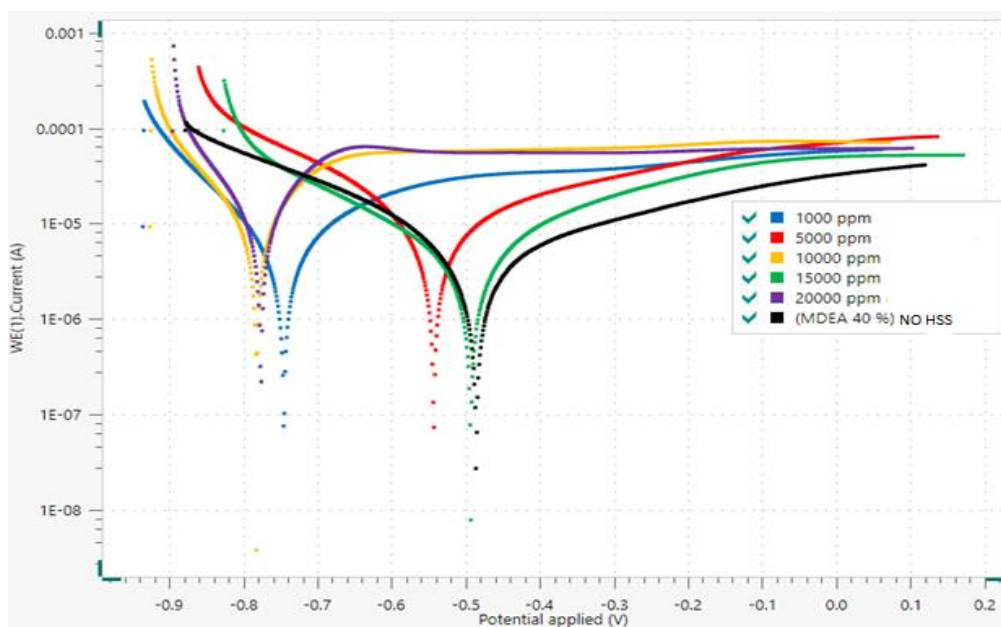


Figure 3. The potentiodynamic curves of Carbon steel in different concentrations of glycolic acid + 40% MDEA

The results of Figure 3 are summarized in Table 4. These results show that the i_{corr} increases linearly by adding glycolic acid to the system and always were greater than that of system with no acid, moreover the polarization resistance decreases by adding glycolic acid, also a significant decrease was observed from 10000 to 20000 ppm. The changes in corrosion rate were similar to the system contains formic acid. The corrosion rates up to approximately 5000 ppm of glycolate were less than 1 mpy and then corrosion rates increase up to 2.65 mpy in 20000 ppm.

Table 4. The electrochemical parameters of Carbon steel 1018 in different concentration of glycolic acid + 40% MDEA

Concentration of glycolic acid	1000 PPM	5000 PPM	10000 PPM	15000 PPM	20000 PPM	No Acid (40% MDEA)
E_{corr} (V)	-0.74494	-0.54237	-0.78187	-0.49235	-0.77604	-0.48507
i_{corr} (A/cm ²)	1.6937E-06	1.96E-06	2.6919E-06	3.0049E-06	5.7982E-06	8.082E-07
Corrosion rate (mpy)	0.774	0.896	1.231	1.459	2.652	0.369
Polarization resistance (Ω)	7899.2	7067.3	3294.5	3035.5	2619.6	15679
Ba (V/dec)	0.068958	0.076137	0.038884	0.0587	0.068866	0.069736
Bc (V/dec)	0.055679	0.05489	0.043006	0.067452	0.071062	0.05017

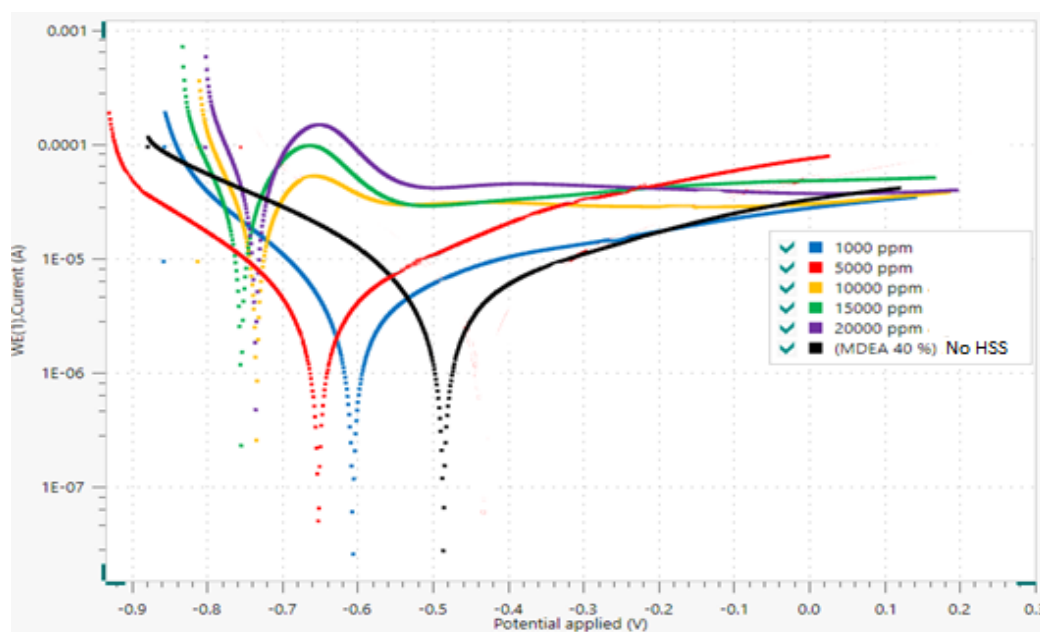


Figure 4. The potentiodynamic curves of Carbon steel in different concentrations of oxalic acid + 40% MDEA

According to Figure 4 and Table 5, the corrosion rate decreased at 10000 ppm of oxalate and increased significantly with increasing concentration. The highest corrosion rate was obtained from the solution contains 2000 ppm of oxalic acid, therefore in all test conditions, the highest corrosion rate was 8.412 mpy.

The polarization resistance concerning the solution without acid (40% MDEA) decreased with increasing oxalic acid concentration, especially from 10000 ppm which means increasing oxalate ion decreasing the corrosion resistance of the metal, as well as increase the corrosion current. Concerning other carboxylic acids, changes in electrochemical properties and corrosion rates are significant.

Table 5. The Electrochemical parameters of Carbon steel 1018 in different concentrations of oxalic acid + 40% MDEA

Concentration of oxalic acid	1000 PPM + 40% MDEA	5000 PPM + 40% MDEA	10000 PPM + 40% MDEA	15000 PPM + 40% MDEA	20000 PPM + 40% MDEA	No Acid (40% MDEA)
E_{corr} (V)	-0.60548	-0.62882	-0.7337	-0.75426	-0.73493	-0.48507
i_{corr} (A/cm²)	8.7877E-07	1.2194E-06	1.0152E-05	1.1717E-05	1.839E-05	8.082E-07
Corrosion rate (mpy)	0.402	0.557	4.644	5.360	8.412	0.369
Polarization resistance (Ω)	15944	13099	1271	1057.6	615.97	15679
B_a (V/dec)	0.082408	0.083417	0.072443	0.0585	0.053678	0.069736
B_c (V/dec)	0.05302	0.065786	0.050362	0.055704	0.05074	0.05017

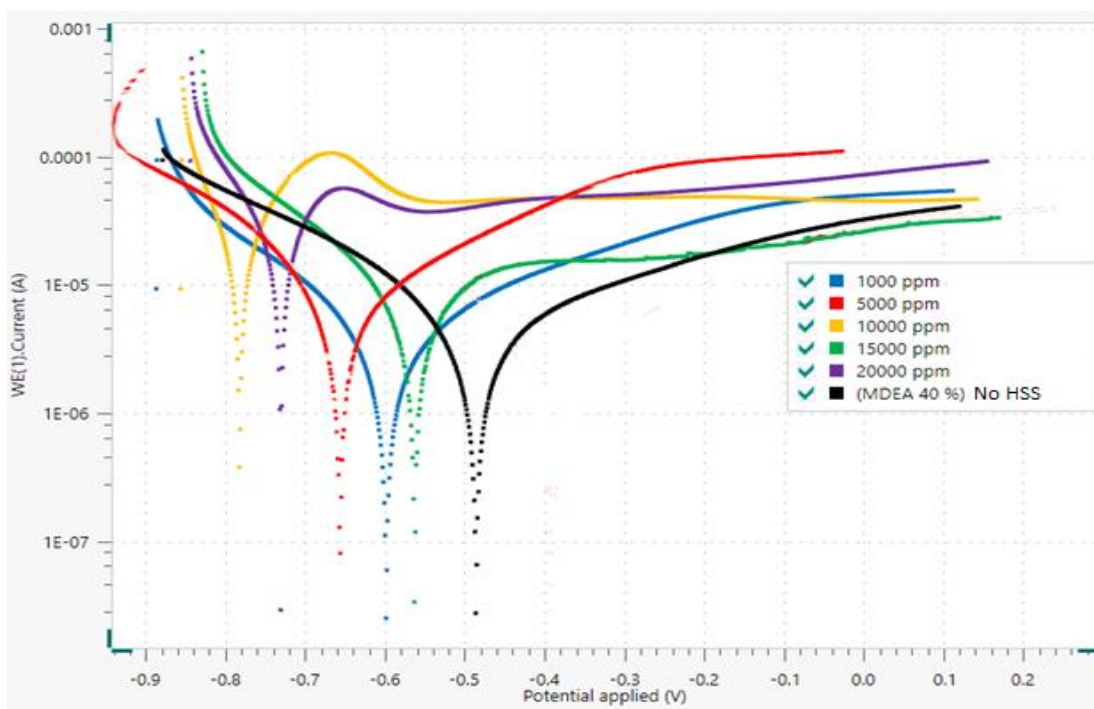


Figure 5. The potentiodynamic curves of Carbon steel in different concentrations of succinic acid + 40% MDEA

According to Figure 5, it is clear that adding succinic acid to the amine solution (40% MDEA) declines the polarization resistance. Table 6 indicates that succinic acid enhances the corrosion rate of the solution which can be due to increased electrical conductivity of the solution. After a concentration of approximately 5000 ppm, a sharp increase in corrosion rate was observed and below this concentration, the corrosion rate was maintained under 1 mpy.

Table 6. The Electrochemical parameters of Carbon steel 1018 in different concentrations of succinic acid + 40% MDEA

Concentration of succinic acid	1000 PPM + 40% MDEA	5000 PPM + 40% MDEA	10000 PPM + 40% MDEA	15000 PPM + 40% MDEA	20000 PPM + 40% MDEA	No Acid (40% MDEA)
E_{corr}, Obs (V)	-0.59783	-0.62921	-0.78181	-0.5622	-0.73031	-0.48507
i_{corr} (A/cm²)	9.2109E-07	5.772E-07	7.1132E-06	8.5769E-06	9.3103E-06	8.082E-07
Corrosion rate (mpy)	0.421	0.264	3.254	3.721	4.259	0.369
Polarization resistance (Ω)	16799	22053	1317.3	1293.8	1232.8	15679
B_a (V/dec)	0.082055	0.065583	0.058002	0.06119	0.042794	0.069736
B_c (V/dec)	0.062969	0.052992	0.048549	0.051773	0.043518	0.05017

The corrosion behavior of all samples can be investigated using SEM results. From SEM results, the maximum corrosion rate is related to the specimen in the oxalate solution therefore this result confirms the results of the electrochemical test which indicated that the highest corrosion rate is related to the solution containing oxalate ion. The corrosion morphology of the samples in solutions containing formate and glycolate, as well as the results of electrochemical experiments, showed that the effect of these two ions on the corrosion resistance of carbon steel was the same.

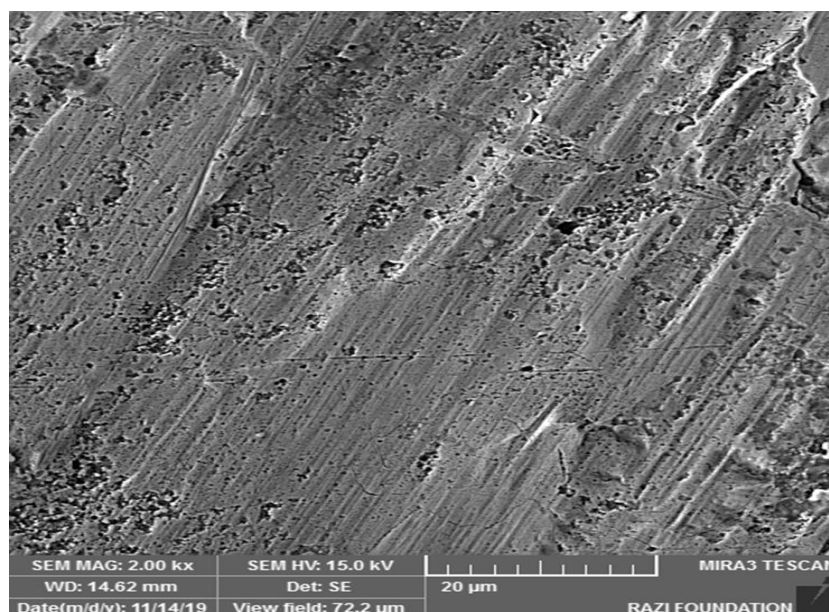


Figure 6. The SEM image of carbon steel 1018 specimen in a solution containing acetic acid

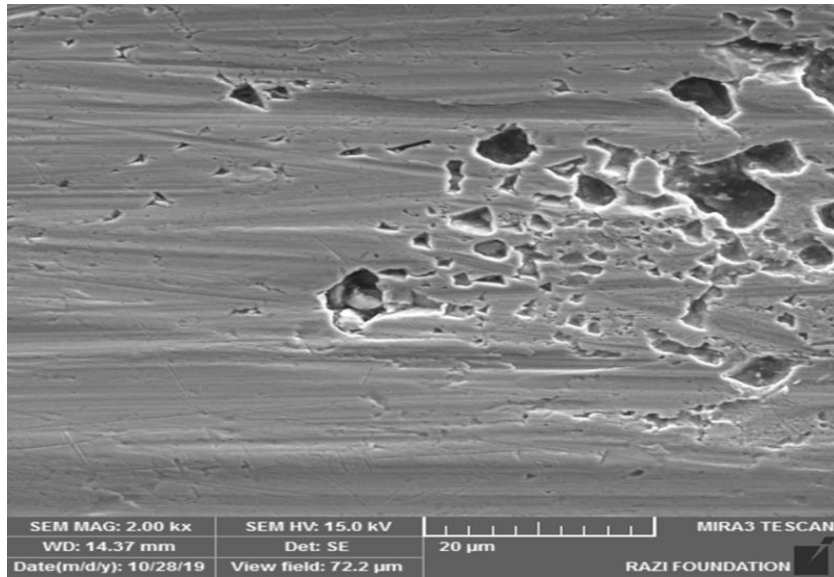


Figure 7. The SEM image of carbon steel 1018 specimen in a solution containing formic acid

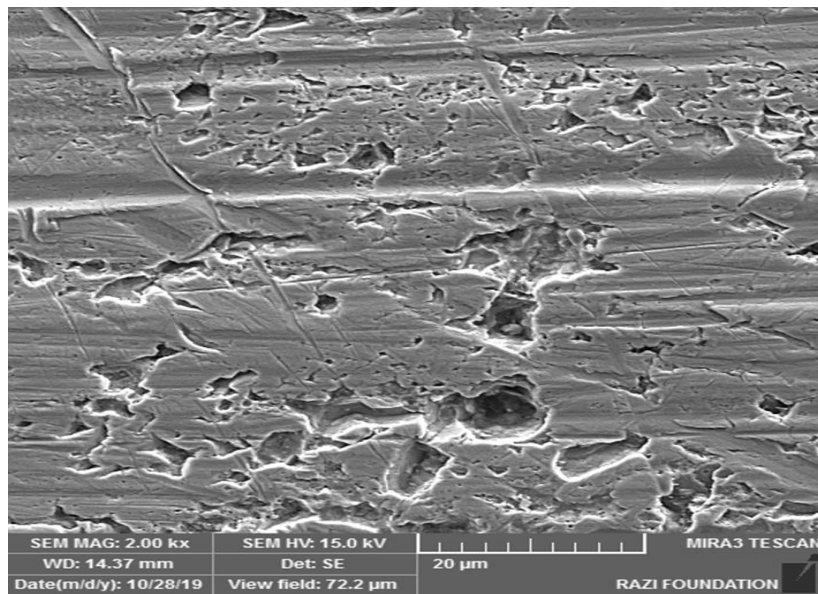


Figure 8. The SEM image of carbon steel 1018 specimen in a solution containing glycolic acid

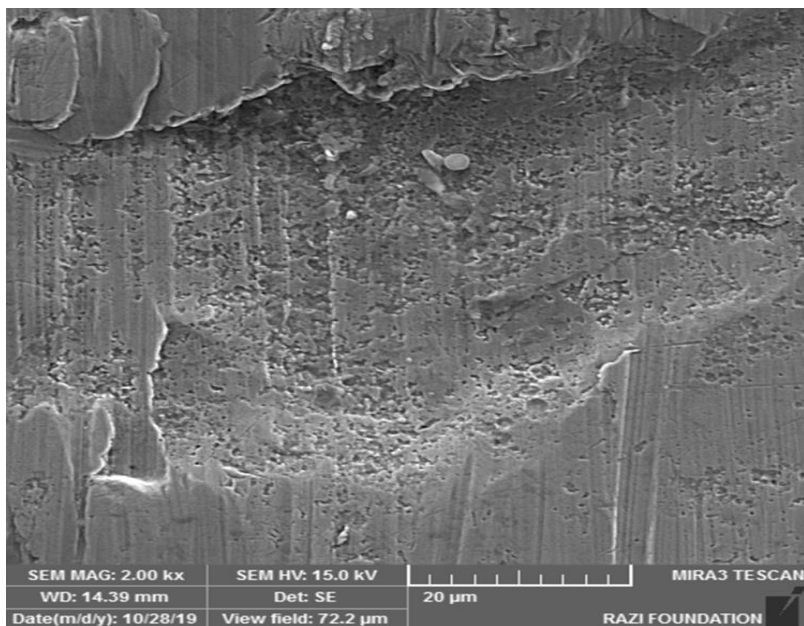


Figure 9. The SEM image of carbon steel 1018 specimen in a solution containing succinic acid

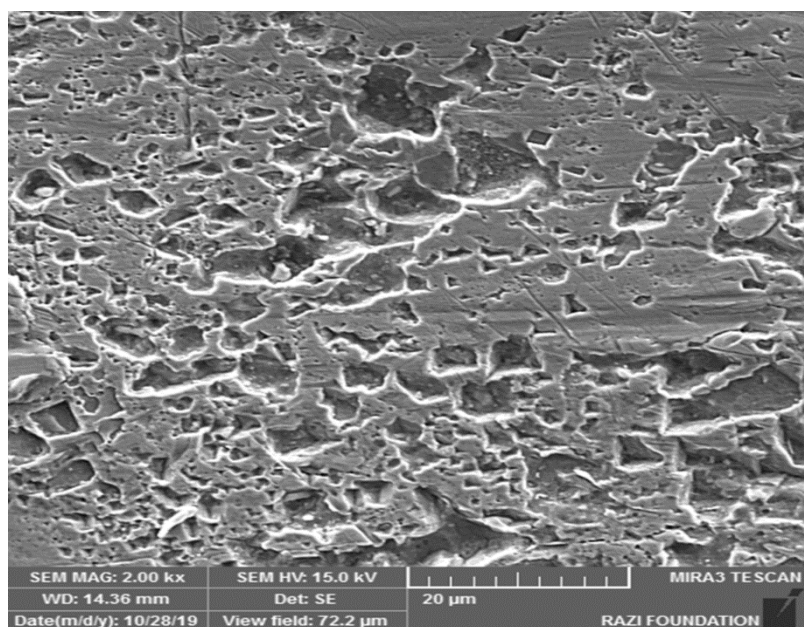


Figure 10. The SEM image of carbon steel 1018 specimen in a solution containing oxalic acid

According to Figure 11 to 15, the amount of oxygen and carbon elements are increased and the iron element is reduced according to the initial chemical composition of the samples shown in Table 2. This result indicated that a formation of FeCO_3 on the carbon steel surface is possible. [4, 6]

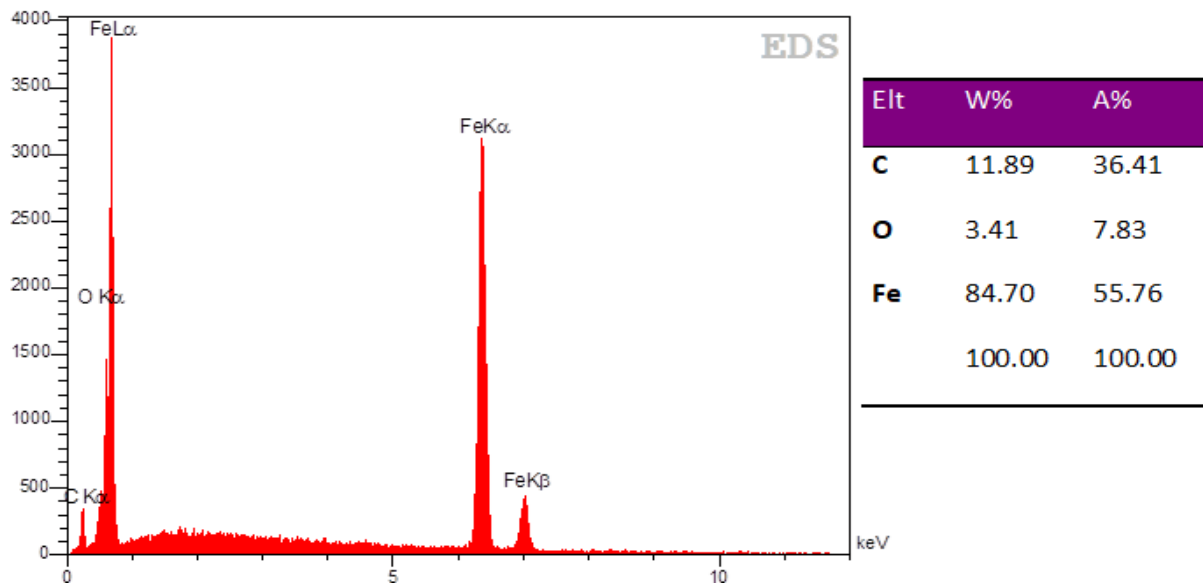


Figure 11. The EDS result of carbon steel 1018 specimen in a solution containing acetic acid

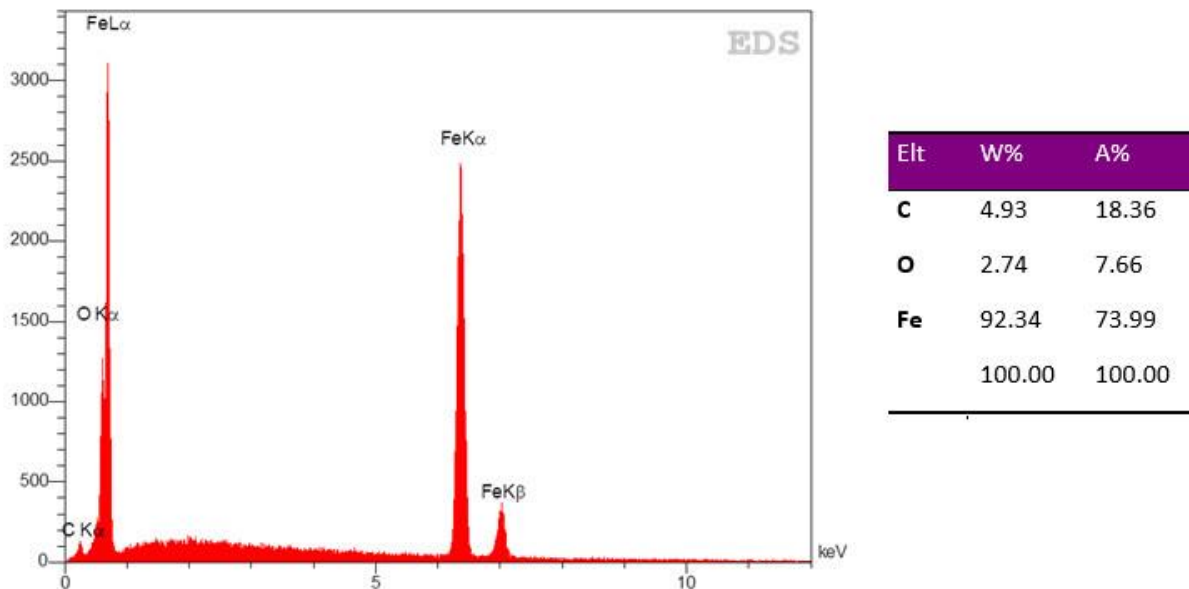


Figure 12. The EDS result of carbon steel 1018 specimen in a solution containing formic acid

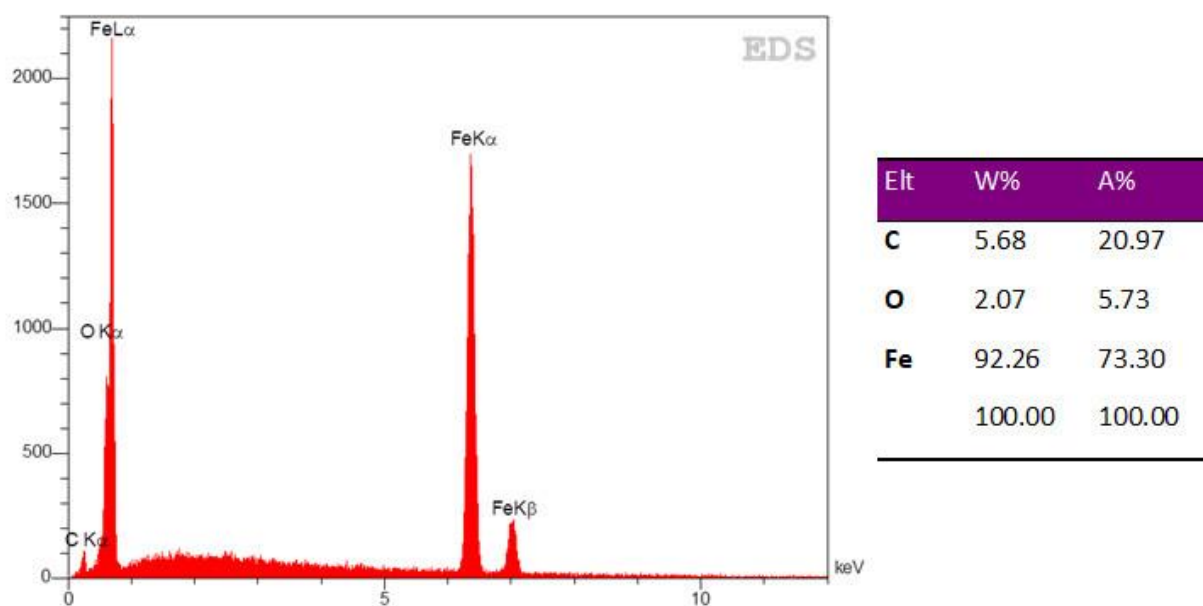


Figure 13. The EDS result of carbon steel 1018 specimen in a solution containing glycolic acid

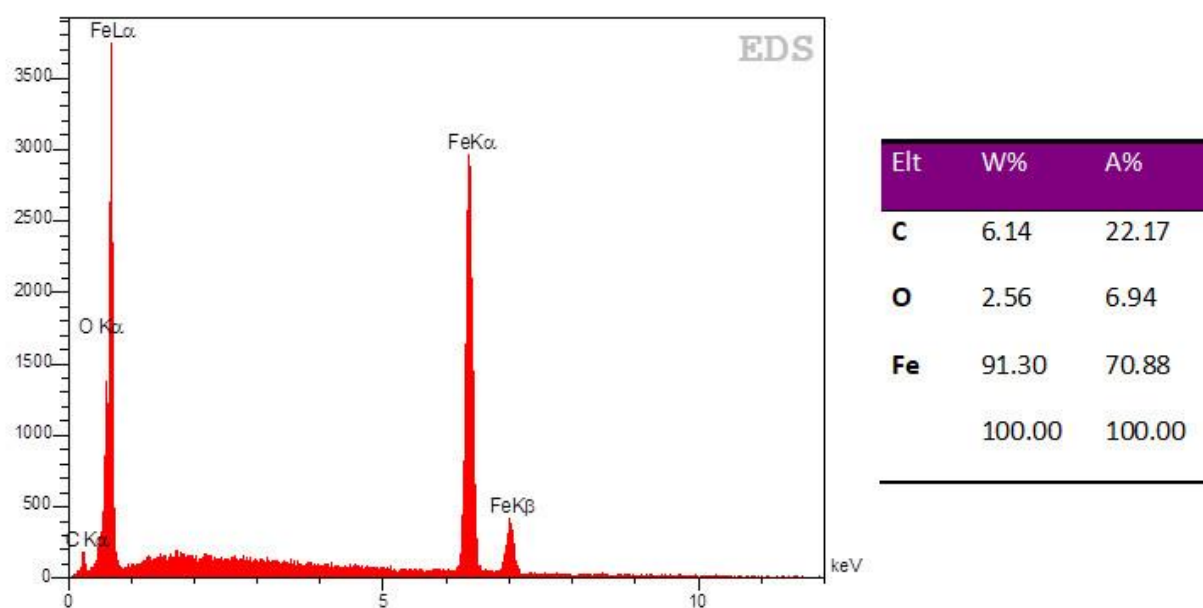


Figure 14. The EDS result of carbon steel 1018 specimen in a solution containing oxalic acid

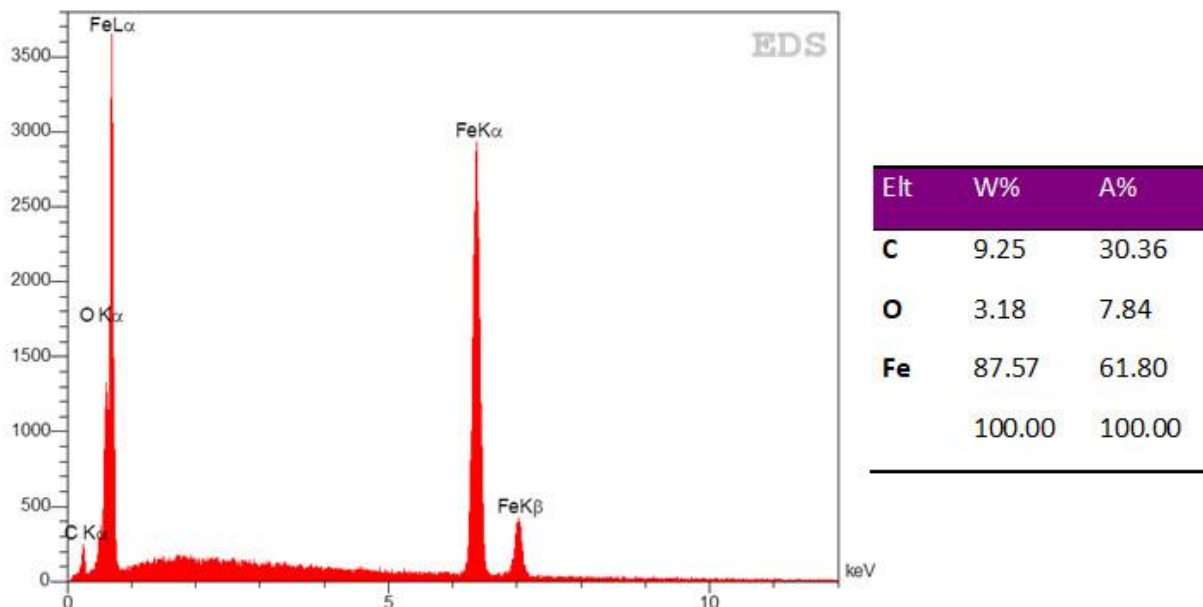


Figure 15. The EDS result of carbon steel 1018 specimen in a solution containing succinic acid

4. Conclusion

- 1- All five tested heat stable salts had no significant effect on the corrosion of carbon steel up to 5000 ppm concentration and their corrosion rates were less than 1 mpy.
- 2- The acetate heat stable salt in MDEA solution had no significant effect on the corrosion rate of carbon steel even at high concentrations, In addition, the effect of different concentrations on the corrosion rate of carbon steel up to 20,000 ppm is less than 1 mpy, which is low according to the NACE classification.
- 3- Oxalate stable salt had the greatest effect on carbon steel corrosion compared to other thermally stable salts. It is clear that from the electrochemical results that after approximately 6000 ppm oxalate concentration, the corrosion rate has increased significantly, although, below this concentration, the corrosion rate is below 1 mpy.
- 4- The SEM results show that most corrosion occurs on a sample that contained oxalate solution.
- 5- The electrochemical and EDS results of the formats and glycols were close to each other, indicating that the corrosion behavior of carbon steel in those solutions was similar.

5. Acknowledgements

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6. Reference

- [1] Kohl, A. and Richard, N. 1997. Gas purification, Gulf Professional Publishing.
- [2] Tanthapanichakoon, A. W. 2006. Electrochemical Investigation on the Effect of Heat-stable Salts on Corrosion in CO₂ Capture Plants Using Aqueous Solution of MEA, Industrial & Engineering Chemistry.

- [3] Khorrami, M. R., Raeissi, K., Shahban, H. and Torkan, M. A. and Saatchi, A. 2008. Corrosion Behavior of Carbon Steel in Carbon Dioxide-Loaded Activated Methyl Diethanol Amine Solution. *Corrosion*. 64 (2):124–130.
- [4] Haws, R. Contaminants in amine gas treating. 2001. CCR Technologies inc.
- [5] Dong, B., Zeng, D., Yu, Z. and Tan, S. 2019. Effects of heat-stable salts on the corrosion behaviours of 20 steel in the MDEA/H₂S/CO₂ environment, *Corrosion Engineering, Science and Technology*. 54(4):339-352.
- [6] Ling H., Liu, S. , Gao, H. and Liang, Z. 2019. Effect of heat-stable salts on absorption/desorption performance of aqueous monoethanolamine (MEA) solution during carbon dioxide capture process. *Separation and Purification Technology*. 212:822-833.
- [7] Durrani, M., Haija, M. and Rangaraj, M. K. 2019. Removal of heat stable salts from aqueous MDEA solution via electrosorption using carbon-based electrodes. *International Journal of Greenhouse Gas Control*. 85:160-173.
- [8] Achazhiyath, A., Alhseinat, E. and Banat, F. 2019. Removal of heat stable salts from industrial lean methyldiethanolamine using magnetic alginate/iron oxide hydrogel composite. *International Journal of Greenhouse Gas Control*. 83:117-127.
- [9] Krajangpit, W., Supap, T., Muchan, P., Saiwan, C., Idemb, R. and Koiwanit, J. 2019. Solvent extraction based reclaiming technique for the removal of heat stable salts (HSS) and neutral degradation products from amines used during the capture of carbon dioxide (CO₂) from industrial flue gases. *Separation and Purification Technology*. 228:44-57.
- [10] Arora, N., Banat, F. and Alhseinat, E. 2019. Capacitive deionization performance of CNTs-Si-Ag based electrodes for the removal of heat stable salts from methyldiethanolamine (MDEA) solution in natural gas sweetening units. *Chemical Engineering Journal*. 356:400-412.