

ASPARTIC ACID AS A CORROSION INHIBITOR FOR CARBON STEEL

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Abstract: Carbon steel is one of the most used metal alloys in industrial applications due to its low cost when compared to other metallic materials. However, its use may be limited due to its tendency to corrode. Thus, it is necessary to develop methods that inhibit its degradation. One way to reduce corrosion is through the use of corrosion inhibitors, which are generally organic compounds and can act by adsorption to form protective films. Some organic compounds with heteroatoms such as O, N, S inhibit corrosion by forming a protective film. However, the use of some inhibitors has been limited due to their harmful effect on the environment. For this reason, research has been developed seeking ecologically correct corrosion inhibitors. This work aims to evaluate the inhibitory effect of aspartic acid against the corrosion of carbon steel in different electrolytic media. In the present work, aspartic acid (AA) was used as a corrosion inhibitor in carbon steel. (AA) solutions at concentrations of 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} and 10^{-6} mol L⁻¹ were used as corrosion inhibitors. Diluted solutions of H₂SO₄ under conditions of pH 1.5; 2.1; 2.97 and 4.0 were used as a corrosive agent. The mass loss tests were performed by immersion of carbon steel samples in H₂SO₄ solutions for a period of 168 hours, the mass variation was determined by weighing the samples before and after the immersion time. Additionally, with the mass loss tests, the inhibition efficiency promoted by the inhibitor solutions will be determined. The form of corrosion of carbon steel was determined by evaluating the surface morphology using light microscopy. The inhibition mechanism promoted by aspartic acid was determined by open circuit potential (PCA) assays.

Keywords: Surface treatment, electrochemistry, corrosion inhibitor.

INTRODUCTION

Carbon steel is one of the most used metal alloys in industrial processes due to its mechanical properties. It is a cheap alloy when compared to other alloys, but not very resistant to corrosion. It consists of iron with about 0.05% to 1% carbon, and may contain small amounts, up to 2%, of other elements to improve mechanical properties. (MANNAN, 2012 and KODAMA, 2011, HELLEIS, R, et al, 2022).

Corrosion of metals is defined as the deterioration of this material, by spontaneous processes, chemical and electrochemical reactions in the environment, due to the instability of the material, which can cause damage and even render the metallic part unusable. The metal acts as an anode, giving up electrons, and the corrosive medium acts as a cathode, receiving electrons (GENTIL, 2003). The corrosive process does not cease to occur, however, it is possible to control the corrosion of metals through surface treatments, anodic or cathodic protection and the addition of corrosion inhibitors (SOLTANI et al, 2012; GENTIL, 2003). Limiting corrosion means containing the reaction between the metal and the medium, so that its physical and mechanical properties are not affected during its lifetime (GROSSER, F. N, 2008).

Corrosion inhibition can prevent losses such as loss of strength of materials, product contamination, clogging of pipes, pumps and equipment, loss of heat exchange efficiency in heat exchangers, boilers, cooling towers and distillation towers and high costs. repair and replacement of affected materials and equipment (GREEN and PERRY, 2008).

One of the most interesting methods to delay the corrosive process is the use of inhibitors, which are generally organic compounds and can act by adsorption forming protective films, due to the presence of functional groups containing heteroatoms

such as sulfur, nitrogen and oxygen, which promote corrosion inhibition (ROSSI et al, 2007; SOLTANI et al, 2012; ASSUNÇÃO A. P. et al, 2012; SCENDO M. et al, 2003, SILVA, F. M., 2018). However, the use of some inhibitors has been limited due to their properties being harmful to my environment (HALAMBEK et al., 2010; EL-ETRE, A. Y., 2008, Oliveira, T. M., 2019). Corrosion inhibitors are added to aqueous systems to minimize corrosion of metallic materials. The most commonly used corrosion inhibitors are water-soluble salts such as zinc, phosphates, polyphosphates, phosphonates, nitrates, molybdates, tungstates, silicates, ethanolamines, and fatty amines. The use of inhibitors that are partially or completely biodegradable has been desired (Freeman, M. B. et al, 1995, ROCHA, J. C. 2017).

For this purpose, the use of certain amino acids and certain amino acid homopolymers such as aspartic acid and poly(aspartic acid) as corrosion inhibitors has been reported (KALOTA, D. et al., 1990, CHEN, J., et al, 2019). Aspartic acid (Figure 1) is classified as a non-essential amino acid, which means that under normal physiological conditions, living beings are capable of synthesizing this molecule.

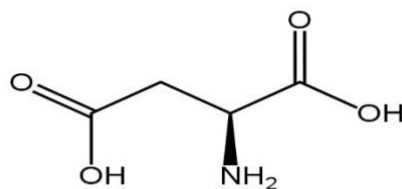


Figure 1. Structural formula of aspartic acid.

The inhibitory action of aspartic acid is related to the presence of two carboxylic acid functional groups, which can promote adsorption on the surface of carbon steel. The protonated and deprotonated forms of the

functional groups influence the adsorption of inhibitor molecules and, as a consequence, determine the characteristics of inhibition. Aspartic acid has its dissociation constants at: pK1 at pH = 2.09; pK2 at pH = 3.87; pK3 at

pH = 9.82 and the isoelectric point PI at pH = 2.97. Figure 2 shows the influence of pH on the formation of deprotonated forms of aspartic acid.

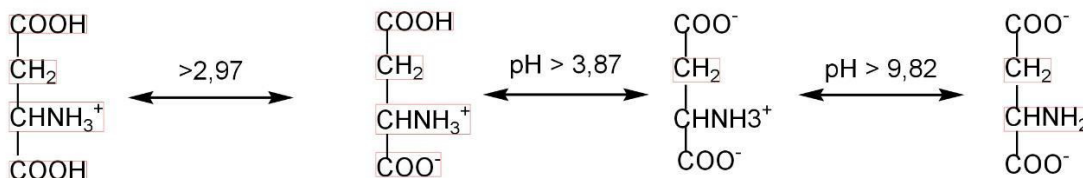


Figure 2. Influence of pH on the formation of deprotonated forms of aspartic acid.

Deprotonation of carboxyls can promote more effective adsorption on the surface of the base metal, as the deprotonated form of the functional group is a stronger ligand. The objective of this work was to evaluate the inhibitory effect of aspartic acid against the corrosion of carbon steel in different electrolytic media.

METHODOLOGY

METALLIC SUBSTRATE

The metallic substrate used was carbon steel SAE 1020 with a square shape and dimensions of 2 x 2 cm. The surface of the plates was sanded with silicon carbide (SiC) sandpaper with a granulometry of 220, 400 and 600 mesh to remove dirt. After sanding, the plates were washed with distilled water and ethanol to remove any impurities and dried with a hot air jet.

ELECTROLYTIC SOLUTIONS

A stock solution of 0.1 molL⁻¹ H₂SO₄ was prepared by diluting with distilled water from 96-98% H₂SO₄ (Synth reagents). Working solutions were prepared from this stock solution, also by dilution with distilled water. The pH values were adjusted to 1.5; 2.1; 2.97

and 4.0. The pH values were adjusted with solid NaOH and using a BEL Engineering PHS3-BW brand pH meter.

ASPARTIC ACID

Aspartic acid solutions were prepared using sulfuric acid solutions as solvent. The concentrations of the aspartic acid solutions were 10⁻², 10⁻³, 10⁻⁴, 10⁻⁵ and 10⁻⁶ mol L⁻¹. The pH of these solutions was adjusted using solid NaOH until pH 1,5; 2,1; 2,97 and 4,0.

MASS LOSS TESTS - CORROSION PENETRATION RATE (TCP)

The mass loss tests were carried out according to the ASTM G31-72 (2004) standard, which standardizes this measure, from which the masses of each sample were determined before and after immersion in the presence and absence of inhibitor solutions for the calculation of the mass difference due to the corrosive process promoted by the medium.

After immersion, the samples were washed with distilled water and dried with a jet of hot air, and then the final weighing was performed using an analytical balance with four decimal places. The mass loss was determined

according to equation (1):

$$W = m_1 - m_2 \quad (1)$$

Being:

m1= mass before immersion (g);

m2= mass after immersion (g);

The speed of the corrosive process was expressed by calculating the corrosion penetration rate (TCP) in millimeters per year (mm/year), using equation (2) (ROCHA, 2013):

$$TCP = \frac{kW}{At\rho} \quad (2)$$

Where k is a constant (87.6), W the mass loss in mg, The exposed area in cm², t the time in hours and ρ the specific mass of the material in g cm⁻³, which for carbon steel this value is of 7.86 g cm⁻³.

MORPHOLOGICAL CHARACTERIZATION

For morphological characterization of the surface of the samples, they were sanded with silicon carbide sandpaper (SiC) with granulometry of 220, 400, 600, 800, 1000, 2000 and 3000 mesh to remove dirt. After sanding, the samples were submitted to polishing with diamond paste with granulometry of 5, 1 and ¼ of μm . After polishing, the pieces were washed with distilled water and ethanol and dried with a hot air jet. Morphological analyzes were performed using a TescanVR Vega3 scanning electron microscope at 500X magnification. Samples were analyzed before and after immersion in the electrolyte.

OPEN CIRCUIT POTENTIAL

Open circuit potential measurements were performed for 2,000 seconds until potential stabilization, and potential values were collected every 5 minutes. An AUTOLAB® potentiostat, model PGSTAT392N, was used to measure the potential.

RESULTS AND DISCUSSION

MASS LOSS TESTS

The carbon steel samples were subjected to immersion tests and the results of mass loss and thickness loss are shown in figure 3.

From the results of mass loss and thickness loss presented in figure 3, it is possible to observe that there was a decrease in mass loss and thickness loss due to the decrease in the concentration of aspartic acid as an inhibitor in the corrosive environment. At all pH values, it is possible to observe that there is a stabilization of mass loss and thickness loss for the aspartic acid concentration of 10⁻³ mol L⁻¹. However, for the value of pH = 4.0 the stability is not well defined, suggesting that in this condition the presence of aspartic acid with the two carbonyls deprotonated the corrosive process happens continuously with the increase of the inhibitor concentration. When comparing the results, it is possible to observe that the increase in pH promotes a decrease in the weight loss of the SAE 1020 carbon steel, this behavior being characteristic of the less corrosive effect promoted in an electrolytic medium with less acidic pH. The AA concentration of 10⁻³ mol L⁻¹ was considered the best condition for the use of aspartic acid, since from this concentration on, the dilution of the solutions did not promote significant mass variations. The results of comparing the mass loss values as a function of pH variation are shown in figure 4.

The results of mass loss as a function of pH (Figure 4) demonstrate that at pH = 1.5 and AA concentration of 10⁻³ mol L⁻¹, the corrosive process is more accentuated and that the presence of the inhibitor promotes a decrease more significant in this condition when compared to the difference in mass loss for the other pH conditions. This result is related to the aggressive effect characteristic of the acidic environment, which is more pronounced. The increase in pH promotes a

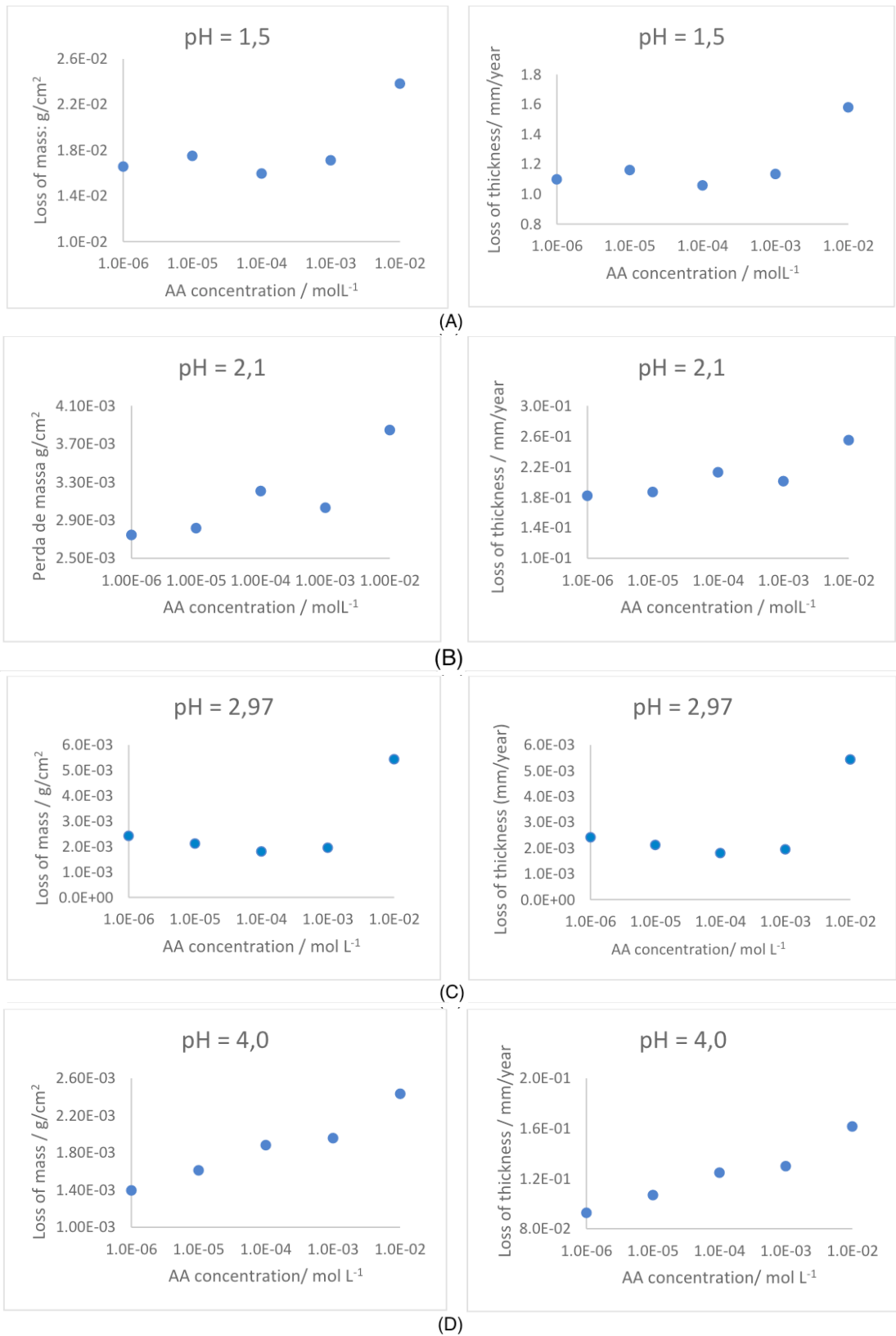


Figure 3. Weight loss and thickness loss tests for SAE 1020 carbon steel immersed in a solution of (A) pH = 1.5; (B) pH = 2.1; (C) pH = 2.97; (D) pH = 4.0.

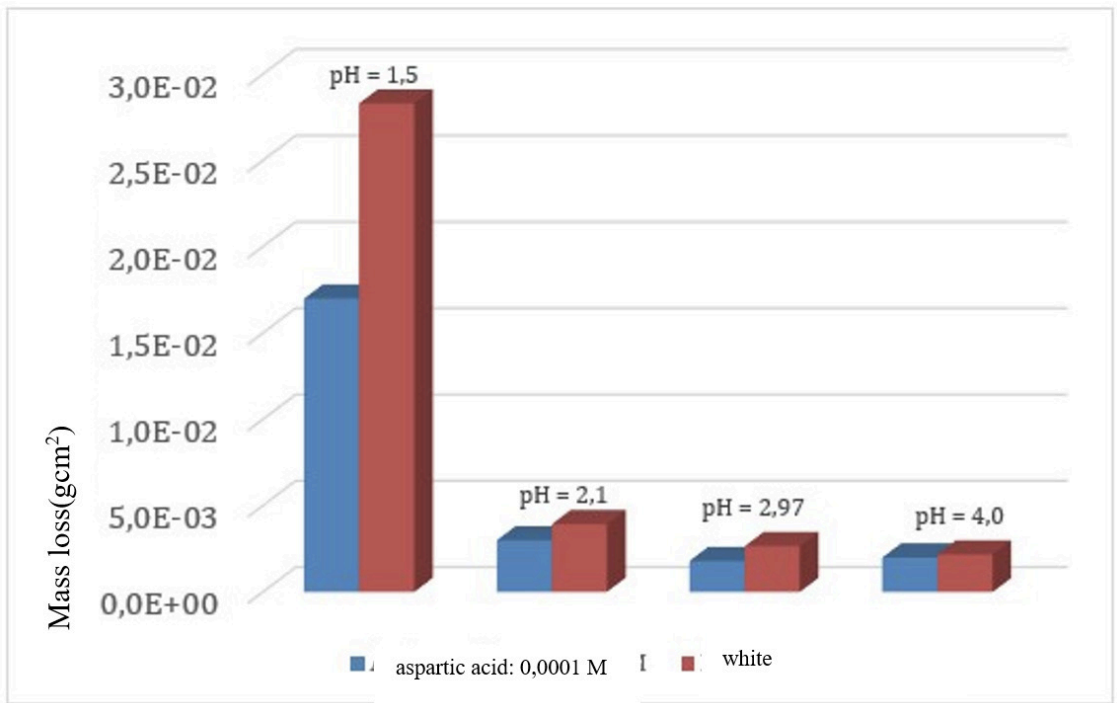


Figure 4. Comparison of mass loss for [AA] = 10⁻³ mol L⁻¹ as a function of pH variation.

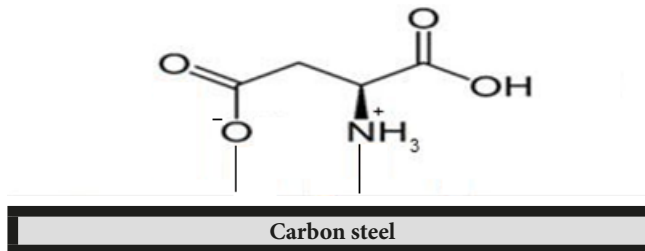
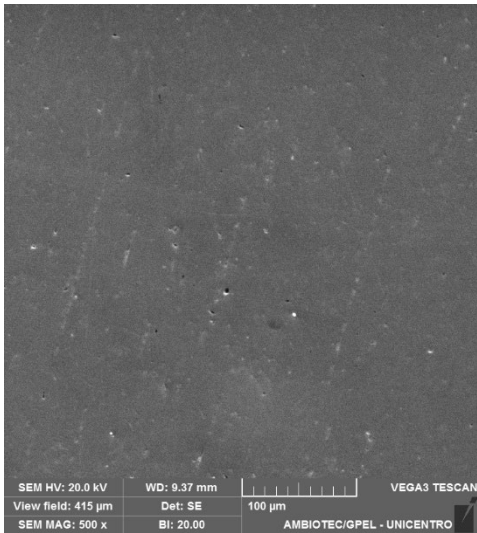
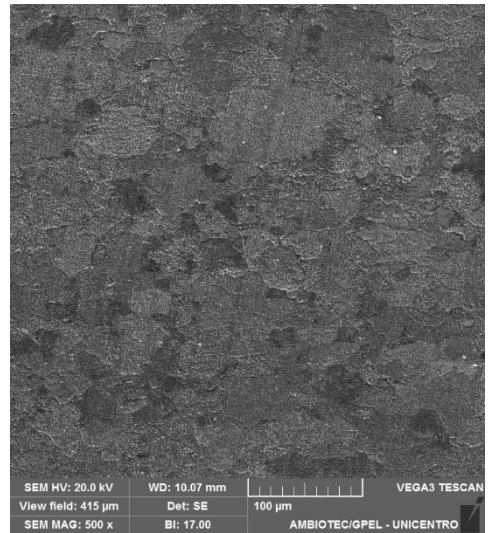


Figure 5. Proposed model for the adsorption of aspartic acid molecules on the surface of carbon steel.

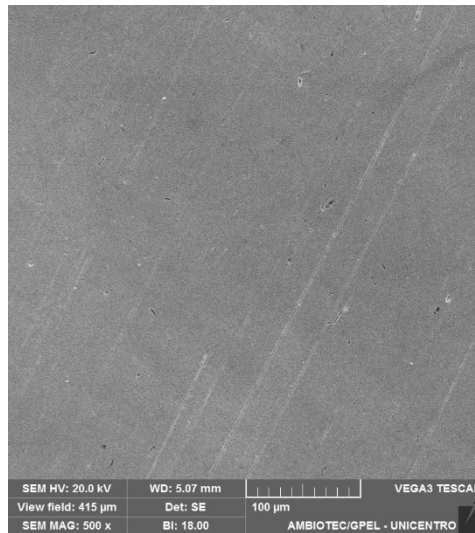
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(A)



(B)



(C)

Figure 6. Scanning Electron Microscopy Images of carbon steel samples (A) not immersed, (B) immersed in a solution of pH = 2.97 and (C) immersed in pH = 2.97 and AA 10^{-3} mol L⁻¹.

Source: the author

change in the corrosive action of the electrolyte and the formation of deprotonated forms of aspartic acid. The increase in the pH value makes the corrosive medium less aggressive and promotes the formation of deprotonated aspartic acid species that can adsorb more effectively on the metal surface. Considering the differences in mass loss, the condition of pH = 2.97 and AA concentration of 10^{-3} mol L⁻¹ was used as a condition for continuing the study.

Figure 5 presents a proposed model for the adsorption of aspartic acid on the surface of carbon steel under pH = 2.97 and AA concentration of 10^{-3} mol L⁻¹.

SCANNING ELECTRON MICROSCOPY (SEM)

The surface morphology of the SAE 1020 carbon steel was evaluated using a scanning electron microscope (SEM) and the images are shown in figure 6.

The analysis of the images in figure 6 allows us to observe the corrosive effect of the electrolytic medium, because from the comparison between Figures 6A and 6B it is possible to verify regions on the metal surface that suffered corrosion in a medium of pH = 2.97 in the absence of acid aspartic. The addition of the inhibitor promoted the corrosion protection of the carbon steel, since the base metal surface did not present corroded regions, as observed in Figures 6B and 6C. These results demonstrate that aspartic acid is acting as a corrosion inhibitor.

OPEN CIRCUIT POTENTIAL

PCA values were obtained by immersion tests performed for samples without and with the inhibitor and the results are shown in figure 7.

The variation of the open circuit potential for the carbon steel sample in the absence of aspartic acid (Figure 7A) demonstrates the

corrosive effect of the pH variation of the electrolytic medium. It is possible to observe that the increase in the pH value tends to shift the open circuit potential to more positive values, suggesting an increase in the corrosion resistance of carbon steel. The shift of the potential to more positive values is related to the formation of a stable oxide on the surface of the base metal, which is favored at higher pH conditions.

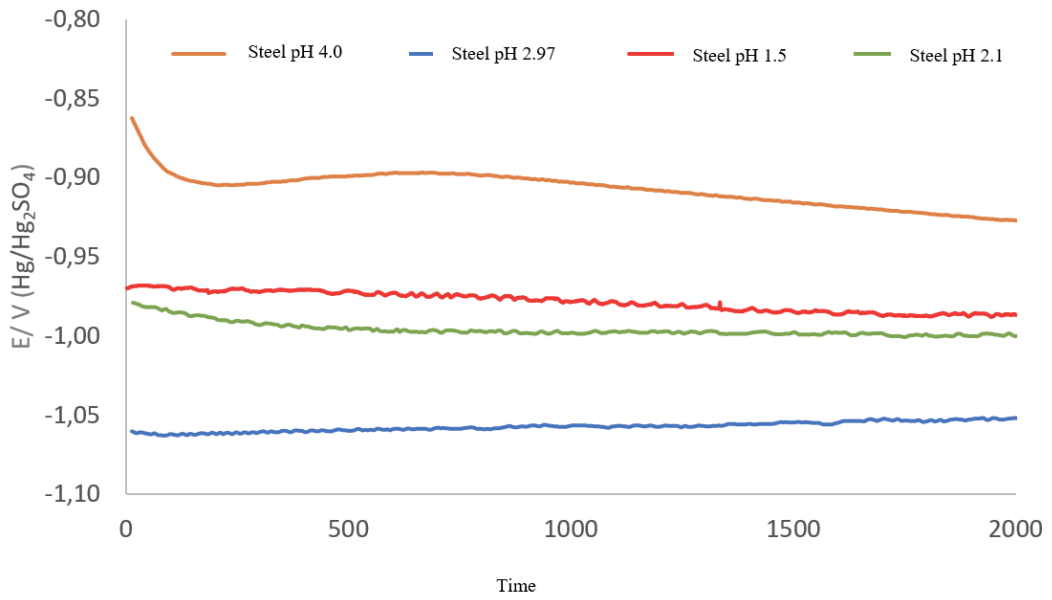
The addition of the inhibitor in the corrosive medium altered the behavior of the variation of the open circuit potential, it can be seen in figure 7B, that there was a displacement of the open circuit potential to more positive values for the samples immersed in the electrolytes of lower pH, suggesting that the inhibitor tends to act more efficiently against corrosion when the pH of aspartic acid is more acidic.

ANODIC POTENTIODYNAMIC POLARIZATION

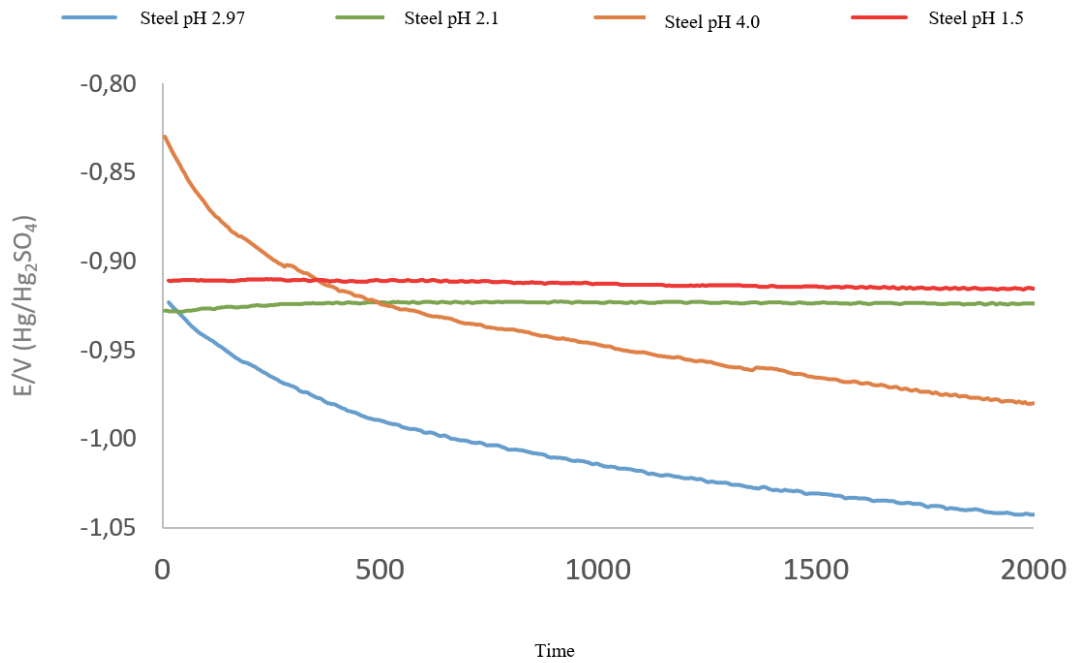
The anodic potentiodynamic polarization results obtained with the pH variation of the electrolytic medium are shown in figure 8.

The analysis of figure 8A demonstrates that there is a difference in the electrochemical response when the electrode is polarized as a function of the pH variation, as higher current density values were obtained for more acidic pH values, indicating a lower corrosion resistance. An active behavior was determined under all pH conditions, evidenced by the high current densities.

The addition of aspartic acid as an inhibitor (Figure 8B) altered the corrosion behavior of carbon steel, as lower current densities were measured for the samples in pH = 2.97 medium, suggesting that in this electrolytic medium the corrosion inhibitor acts in a different way, more efficiently against corrosion of carbon steel. The electrochemical response in the presence of the inhibitor can be attributed to the adsorption of the amino

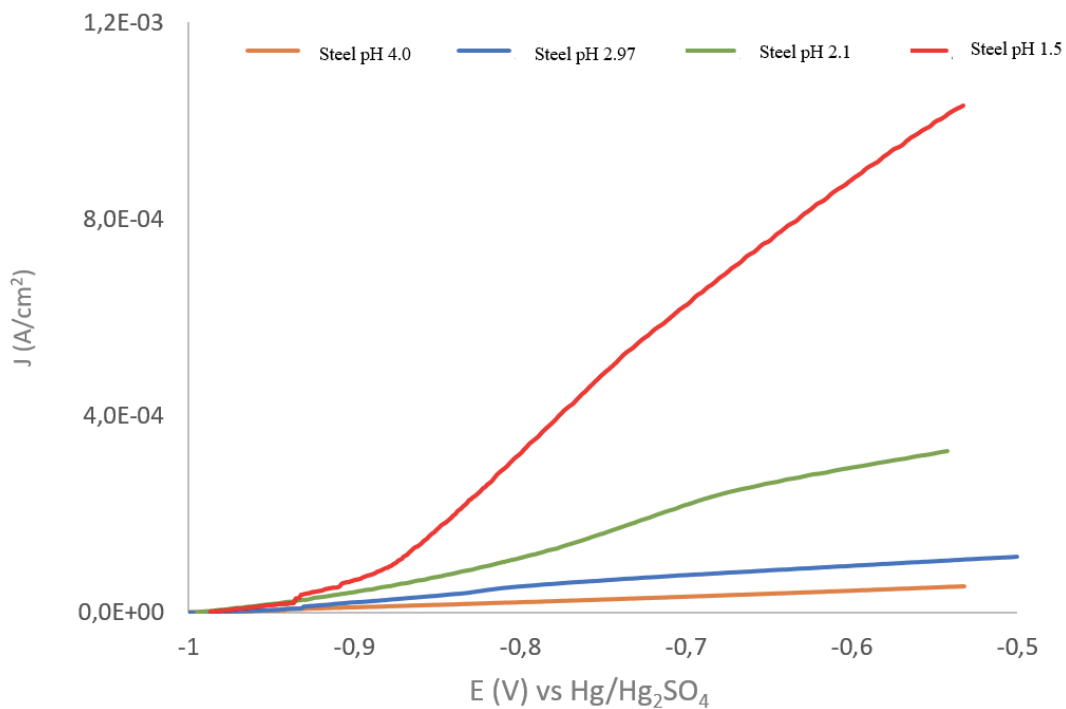


(A)

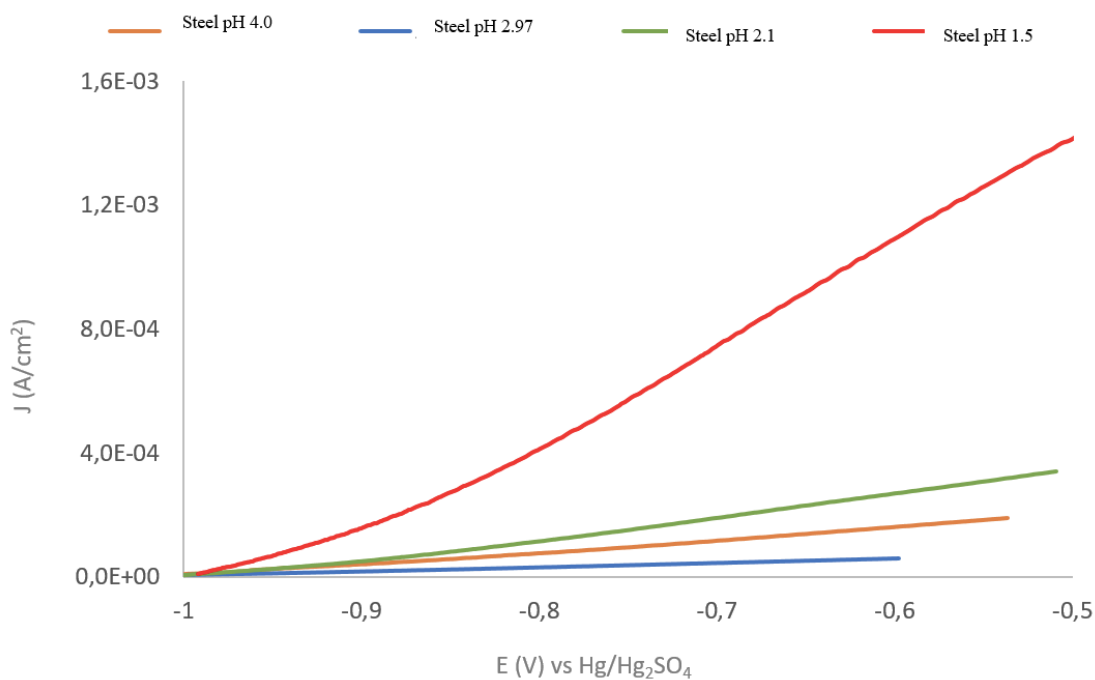


(B)

Figure 7. Open circuit potential curves for samples of SAE 1020 carbon steel in the absence of aspartic acid. (A) Carbon steel, (B) AA 10^{-3} mol L $^{-1}$.



(A)



(B)

Figure 8. Anodic potentiodynamic polarization curves for carbon steel sample in (A) absence of aspartic acid and (B) in the presence of inhibitor.

acid molecule on the surface of the base metal, as suggested in the model presented in Figure 5. The formation of a protective film blocks the surface of the metal, promoting protection against corrosion.

CONCLUSION

- From the results obtained, it is possible to conclude that aspartic acid can be used as a corrosion inhibitor for SAE 1020 carbon steel in H₂SO₄ medium.

- Optical microscopy images suggest a more intense corrosive process for carbon steel in the absence of the inhibitor.
- From the results of efficiency of the inhibition process, it is possible to conclude that aspartic acid was more efficient in protecting carbon steel from corrosion at pH = 2.97 and at the concentration of $1 \times 10^{-3} \text{ mol L}^{-1}$.

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