

CORROSION INHIBITION OF CARBON STEEL XC70 IN H₂SO₄ SOLUTION BY FERROCENE DERIVATIVE 4-(FERROCENYLMETHYLAMINE) BENZONITRILE

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ABSTRACT:

In this work, we studied the efficiency of corrosion inhibition of carbon steel XC70 in H₂SO₄ 0.5 M solution using ferrocenyl compound prepared in our laboratory, this compound is: 4-(ferrocenylmethylamine)benzonitrile (FC). The inhibitory potential of this compound was determined by electrochemical techniques based on Tafel segments. The results show that the studied compound has an efficiency of inhibition which depends on its concentration the adsorption of these compounds on the surface of the metal is a chemical adsorption. The compound FC had the best ability of inhibition at a concentration of 30 ppm (IE = 75.36%).

Keywords: *Corrosion, carbon steel XC70, Inhibition, ferrocene derivative, Adsorption.*

1. INTRODUCTION

The use of carbon steel has been extensively under different conditions in petroleum industries [1]. Aqueous solutions of acids are among the most corrosive media. Acid solutions are widely used in industries for pickling, acid cleaning of boilers, descaling and oil well acidizing [2], [3], [4], [5] and [6]. Mostly, sulfuric and hydrochloric acids are employed for such purposes [3]. The main problem concerning carbon steel applications is its relatively low corrosion resistance in acidic solutions. Several methods are currently used to prevent corrosion of carbon steel. One such method is the use of an organic inhibitor [2], [7], [8]. and is the most economic option for many oil/gas projects, including in-field flow lines and long, large diameter export lines. Typical corrosion inhibitors used in oil/gas field applications are organic compounds and are employed in small concentrations. Almost all organic molecules used in oil/gas field corrosion inhibitor packages are strongly polar functional compounds, with many being based on nitrogen, such as amines, amides, ferrocene, imidazolines, or quaternary ammonium salts, and include salts of nitrogenous molecules with carboxylic acids, polyoxyalkylated nitrogen containing compounds, nitrogen heterocyclics and compounds containing P, S, and O [9] and [10]. The study of

ferrocene compounds has tremendously increased during the last two decades due to their applications in a variety of areas including catalysis, organic synthesis and the design of new materials. The growing interests of ferrocene derivatives is attributed to their excellent stability towards water and air, have favorable electrochemical properties [11] and are generally non-toxic [12]. Their industrial applications include additives for heating oil to reduce formation of soot, iron-containing fertilizers, UV absorbers and protective coatings for rockets and satellites [13]. It was reported that ferrocene carboxylic acids of the formula Fc-(CH₂)_n-COOH have beneficial properties for potential cancer treatment [14]. For these reasons, we proposed that this basic research is the study of the corrosion inhibition carbon steel XC70 in 0.5M H₂SO₄ solution by

ferrocene derivative. They are soluble in conditions similar to actual conditions of industrial units by the use of electrochemical techniques. Corrosion is an unfortunate given in the oil and gas industry. In this work, tow ferrocene derivatives namely, 4- (ferrocenylmethylamine)benzonitrile (FC), were tested as inhibitors for mild corrosion in H₂SO₄ solutions using polarization resistance (R_p), Tafel .

2. EXPERIMENTAL SECTION

A mild steel sample of the following chemical composition (as percentage) was served as working electrode:

Table 1. Chemical composition of XC70 steel samples.

C	Si	Mn	p	S	Cr	Mo	Ni	Al
0,065	0,245	1,685	0,002	0,001	0,042	0,005	0,026	0,042
Cu	Nb	Ti	V	Fe				
0,010	0,067	0,019	0,014	97,77				

Sulfuric acid solutions H₂SO₄ (0.5 M) were prepared from concentrated solutions and bi-distilled water. Solutions of ferrocene derivative (FC) were prepared by dissolving the required weight in Ethanol.

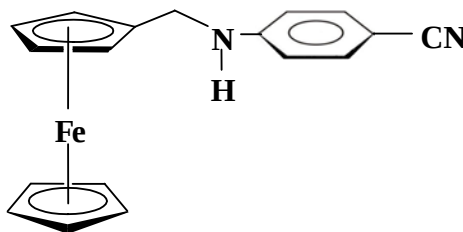


Fig.1 4- (ferrocenylmethylamine)benzonitrile (FC).

For potentiostatic experiments, a cylindrical rod of each sample was embedded in araldite leaving an exposed bottom area of 1.0 cm², and used as working electrode. Each working electrode was polished with different grades of emery papers (400, 600, 800 and 1000 in late 4000), degreased with acetone and rinsed with distilled water fig2.(a) represent the image of the surface of the crude metal and (b) is an image of the surface after polishing before its immersion in the test solution. Potentiostatic polarization studies were carried out using Potentiostat/Galvanostat PGZ-301. Three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode were used. For potentiodynamic experiments, the working electrode was held at the potential of hydrogen evolution for 10 min before the starting of the potential sweep to get rid of any pre-immersion oxide film which may be present on the surface. The electrode was then disconnected from the potentiostat, gently shaken in the solution to release the hydrogen bubbles attached to its surface and left in the test solution until the reach of its steady state potential. Once the electrode acquires its steady state potential it is reconnected to the potentiostat for the polarization experiment procedure. The inhibition efficiency IE was calculated using the following equation:

$$IE\% = \left[\frac{(i_{corr}^0 - i_{corr})}{i_{corr}^0} \right] \times 100 \quad (1)$$

Where i_{corr}^0 and i_{corr} are the corrosion rates in free and inhibited solutions, respectively.

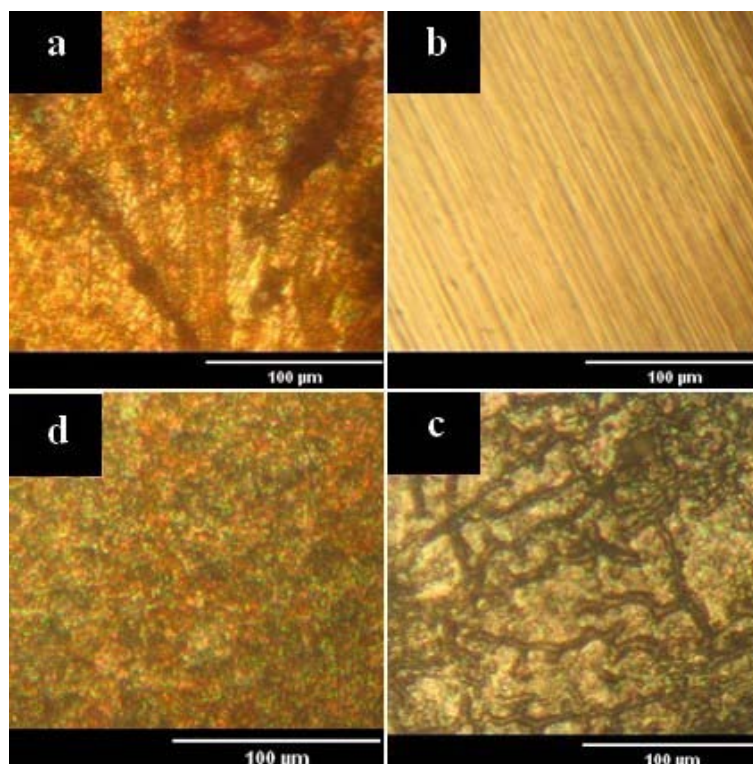


Fig.2 **a)** Micrograph of the surface of the crude steel, **b)** Micrograph of the surface after polishing of the steel, **c)** Micrograph of the surface (reference), **d)** Micrograph of the surface of the steel after immersion XC70.

3. RESULTS

3.1. Effect of inhibitor concentration

Effects of 4- (ferrocenylmethylamine)benzonitrile (FC) were investigated in the concentration range of 10–90 ppm. Fig 3 shows the Tafel polarization readings of carbon steel immersed 0.5M H_2SO_4 at 25 °C with and without FC inhibitor. Electrochemical parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_a and β_b) and corrosion current density (i_{corr}) were extracted by extrapolating the anodic and cathodic branches of Tafel curves at potentials beyond the region of $E_{corr} \pm 95$ mV, using **Volta master 1** program and are listed in Table 1,2. From the results collected in Table 1, 2, it can be seen that by increasing the inhibitor concentration, the corrosion rate is decreased in both the acidic media. Also, it can be observed

Table -1: Inhibition efficiency and surface coverage in the presence of FC in 0.5M H_2SO_4 solutions at 25 °C.

<i>C</i> (ppm)	<i>IE</i> (%)	θ	<i>C</i> / θ
0	53.98	0.5398	0
10	51.86	0.5186	19.2826841
20	64.85	0.6485	30.8404009
30	75.36	0.7536	39.8089172
40	75.38	0.7538	53.0644733
50	77.83	0.7783	64.24258
60	66.69	0.6669	89.968511

70	-	-	
80	71.37	0.7137	112.091915
90	-	-	

Table -2: electrochemical parameters relating to the steel in a medium XC70 0.5M sulfuric acid in the presence of compound FC.

<i>C</i> (ppm)	<i>R_p</i> ohm.cm ²	<i>B_a</i> (mV)	<i>B_c</i> (mV)	<i>i_{corr}</i> (mA/cm ²)	<i>E_{corr}</i> (mV)	<i>V_{corr}</i> (mm/an)	<i>IE</i> (%)
0	23.14	49.2	-82.7	0.4513	-491.6	5.278	53.98
10	38.51	37.6	-66.1	0.2172	-567.7	2.541	51.86
20	49.87	41.4	-73.0	0.1586	-570.4	1.855	64.85
30	63.28	31.8	-62.1	0.1112	-557.5	1.3	75.36
40	68.49	32.4	-65.3	0.1111	-556.0	1.299	75.38
50	48.18	23.8	-37.0	0.1	-540.3	1.17	77.83
60	40.27	25.5	-59.0	0.1503	-484.0	1.758	66.69
80	53.21	30.5	-66.4	0.1292	-480.7	1.511	71.37

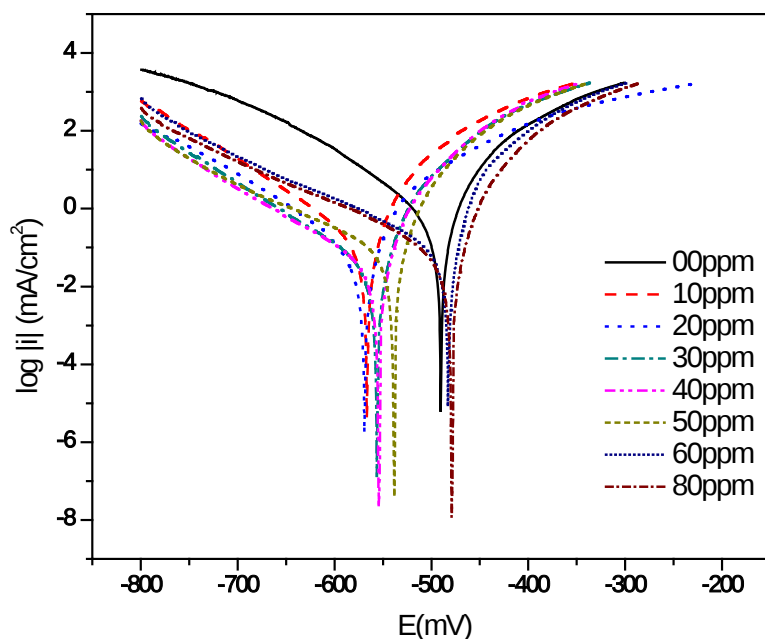


Fig .3 Anodic and cathodic polarization curves for carbon steel in sulfuric acid and with various concentrations of FC at 25 °C

All parameters of the ferrocene derivative obtained from Tafel slope analysis are given in Table 2. The polarization curves of blank carbon steel and inhibitor FC at concentration 80 ppm are plotted in Fig.4-5 shows the effect of FC on the corrosion of mild steel in H₂SO₄ solution. FC increased the current density in the cathodic scan range of potential.

Based on the results obtained it is observed that the addition of the compound FC causes a decrease in the corrosion rate to concentrations 10, 20, 30, 40, respectively 50 ppm (cathode movement), then an increase in the corrosion rate for both concentrations greater than 50 ppm

(displacement anode), while the optimal concentration of the inhibitor is 50 ppm at a rate equal inhibition % 77.84. The corrosion rate over the rise (2.541mm / y) is obtained at a concentration of 10 ppm to 24 while the lowest was 1.17 mm / yr obtained for a concentration of 50 ppm. This value represents a good protection for steel. However, the corrosion rate increases again when the concentration of the inhibitor than 50 ppm, has been attributed to the decrease in the effectiveness of the inhibitor by the excess of the latter. Fig4

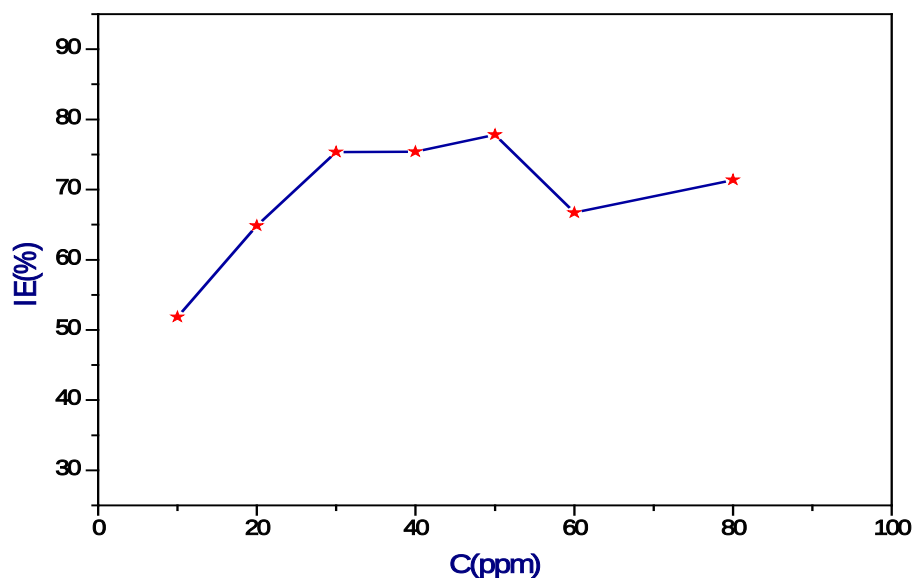


Fig.4 Variation of the inhibition efficiency with the concentration of FC in H_2SO_4 solution at 25 °C.

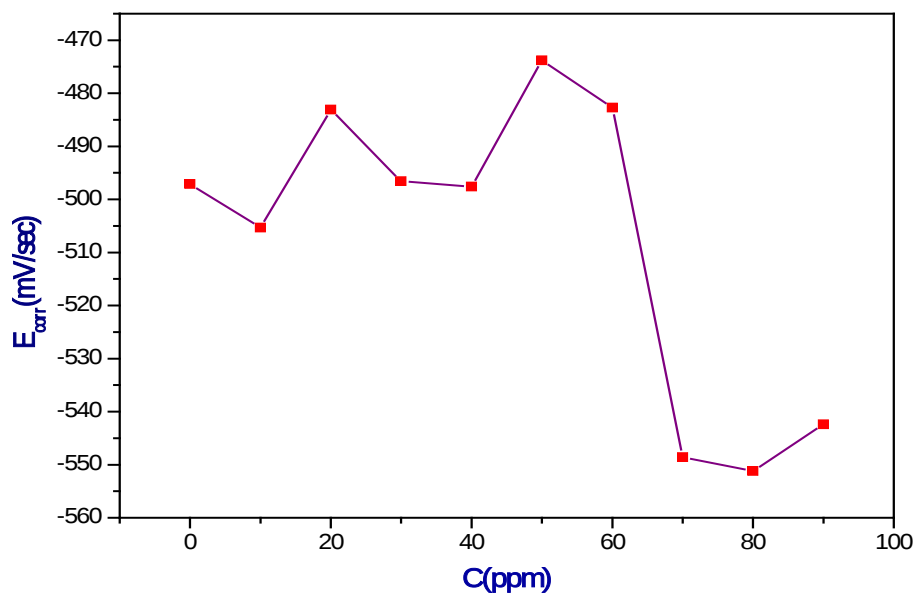
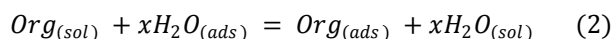


Fig.5 Variation of corrosion potential the concentration of FC in H_2SO_4 solution at 25 °C.

3.2. Adsorption isotherms

Basic information on the interaction between inhibitors and metal surface can be provided using the adsorption isotherms [14].

The adsorption of an organic adsorbate at metal–solution interface can occur as a result of substitutional adsorption process between organic molecules presented in the aqueous solution ($\text{Org}_{(\text{sol})}$), and the water molecules previously adsorbed on the metallic surface ($\text{H}_2\text{O}_{(\text{ads})}$) [15]:



where $\text{Org}_{(\text{sol})}$ and $\text{Org}_{(\text{ads})}$ are the organic species in the bulk solution and adsorbed one on the metallic surface, respectively, $\text{H}_2\text{O}_{(\text{ads})}$ is the water molecule adsorbed on the metallic surface and x is the size ratio representing the number of water molecules replaced by one organic adsorbate. In order to obtain the adsorption isotherm, the degree of surface coverage,

θ for different concentrations of inhibitor in 0.5M H_2SO_4 solutions has been evaluated by the following equation [16]:

$$\theta = \left[\frac{(i_{\text{corr}}^0 - i_{\text{corr}})}{i_{\text{corr}}^0} \right] \quad (3)$$

The θ values are presented in Table 1. According to the Langmuir's isotherm, the surface coverage (θ) is related to inhibitor concentration (C) by the following equation [16]:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (4)$$

Where K_{ads} is the equilibrium constant of the inhibitor adsorption process. As seen from Fig.5, the plot of C/θ versus C yields a straight line with a correlation coefficient more than 0.97, showing that the adsorption of these inhibitor in acid solutions is fitted to Langmuir adsorption isotherm. These results show that the inhibition of carbon steel in H_2SO_4 solutions by ferrocene derivative is an adsorptive process. This isotherm assumes that the adsorbed molecules occupy only one site and there are no interactions between the adsorbed species [7].

The K_{ads} values can be calculated from the intercept lines on the C/θ -axis. This value is also related to the standard free energy of adsorption ΔG_{ads}^0 by the following equation [7, 17]:

$$\Delta G_{\text{ads}}^0 = -RT \ln (55.5K_{\text{ads}}) \quad (5)$$

Where R is the universal gas constant, T the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution.

The values obtained for K_{ads} and ΔG_{ads}^0 were 0.39 and -7618.40 J mol⁻¹, respectively. The negative values of ΔG_{ads}^0 indicate that the adsorption of the inhibitor molecule on the metal surface is a spontaneous process.

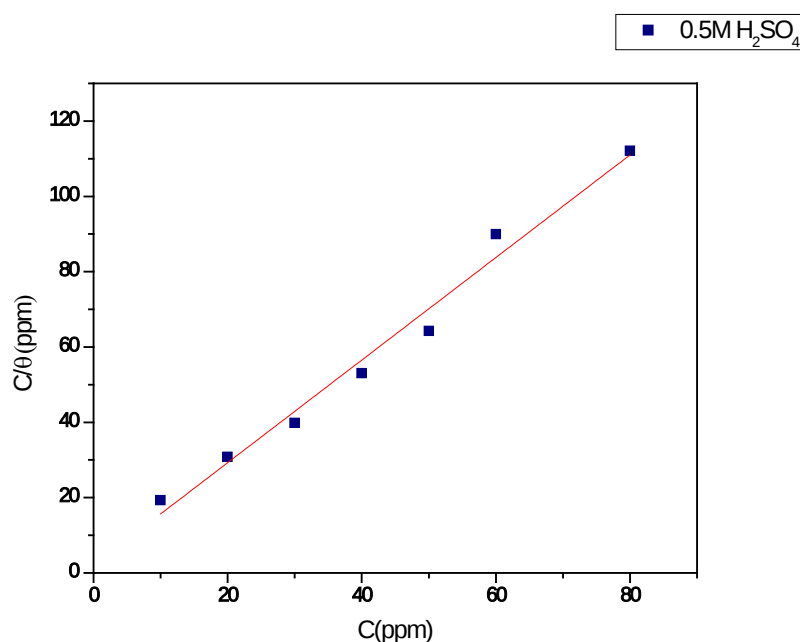


Fig.6 Langmuir adsorption isotherm of FC in 0.5M H₂SO₄ solutions at 25 °C.

4. CONCLUSION

This work takes place in the context of applied research on the aqueous corrosion inhibition by ferrocene compound. For this we studied the inhibitory effect of ferrocene derivative on the corrosion of steel XC70 in an acid medium. The results show that the yield reached 75.36% inhibition for the compound FC concentration of 30 ppm. The layout was Tafel curves to calculate a number of parameters such as corrosion of the coefficients of anodic and cathodic Tafel, the transfer coefficient, the current and the corrosion potential. The plots of corrosion potential depending on the concentration of inhibitors show that the potential in the presence of inhibitors is moved to the most positive values which leads to the conclusion that the compounds studied are anodic inhibitor.

5. REFERENCES

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