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Comparison of the inhibition property of Quinoxaline derivative on mild steel in 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4

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Abstract

Corrosion inhibition of mild steel in 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4 was investigated in the absence and presence of different concentrations of quinoxaline derivative namely 2,3-di(furan-2-yl)quinoxaline(FQ). Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were employed. Impedance measurements showed that the charge transfer resistance increased and double layer capacitance decreased with increase in the inhibitor concentration. Potentiodynamic polarization study showed that the inhibitor acted as mixed-type inhibitors in all the three acids.

1.   Introduction

Mild steel, a structural material of choice due to its versatility, is a very important component of most of the objects and widely used in chemical industries for fabrication of various reaction vessels, tanks, pipes, etc.,. Since mild steel is used under different conditions in chemical and allied industries, it encounters severe attack from acids, due to their aggressive nature, resulting in awful degradation [1-6]. Use of HF-HNO_3 mixture for pickling of metal results in removal of scales and dirt, but the emissions of nitrous gas and formation of nitrate effluents pollute the environment [7]. Therefore, traditional electrolytes consisting of HNO_3 were replaced by environmentally friendly pickling baths consisting of electrolytes such as HCl, H_2SO_4 and H_3PO_4. These acids increase the solubility of the corrosion products and accelerate metal dissolution. In general, HCl and $H_2SO_4$are preferred due to their low costs, in addition low environmental pollution, while H_3PO_4 being mild, is used to remove thin scales present in sophisticated instruments. There is a practice of spent acid recovery techniques to prevent acid pollution. In addition, these are more economical, efficient, trouble free and hence find extensive applications in acidization of oil wells and electroplating industries, for pre and post-operative servicing.

One of the most important applications of hydrochloric acid is its use in the pickling of iron and steel materials to remove rust or iron oxide scale from surface before subsequent processing such as extrusion, rolling galvanizing, etc.,. Sulphuric acid has many applications and it is one of the top products of the chemical industry. Leading uses include lead–acid batteries for cars and other vehicles, ore processing, fertilizer manufacturing, oil refining, waste water processing etc.., Sulphuric acid is used in large quantities by the iron and steel making industry to remove oxidation, rust and scale from rolled sheet and billets prior to sale to the automobile and white goods (appliances) in industry. Phosphoric acid is used in the surface preparation of structural steel to remove mill scale, rust and contaminants, prior to protective surface coating. Phosphoric acid is of particular value in pickling operations where the scale film is thin, or if the film is a hydrate oxide of iron. Phosphoric acid is a major chemical product, which is used especially in the production of fertilizers.

The corrosion of mild steel in any given environment may proceed via, different mechanisms and manifest in various forms. In an attempt to reduce corrosion, some organic compounds called inhibitors are added to the aggressive solution in contact with the metal surface thereby inhibiting corrosion and reducing the corrosion rate of the metal [8]. The experimental work done by us provide valuable information on the corrosion inhibition efficiency of 2,3-di(furan-2-yl)quinoxaline (FQ) [2] in 1M H_2SO_4. To date, however, no study has been performed to investigate the corrosion inhibition efficiency of FQ in different acid medium. The objective of the present paper is to extend our study by comparing the inhibition efficiency of FQwith 3M HCl, 1.5M H_2SO_4 and 1M H_3PO_4 by weight loss and electrochemical methods.

2. Materials and Methods

2.1 Inhibitor
The name and structure of the inhibitor is shown below:

2,3-di(furan-2-yl)quinoxaline(FQ)
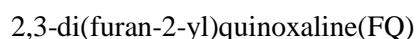
2.2 Preparation of the stock solution
The acid solutions 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4were prepared by dilution of analytical grade acid 96% H_2SO_4, 37% HCl and 86% H_3PO_4 respectively with distilled water. The corrosion inhibition solution was prepared by dissolving the inhibitors in different concentrations in these acid solutions.

2.3 Evaluation of the inhibition efficiency of the studied inhibitors in different acid medium
The inhibition efficiency of the inhibitor in 3M HCl, 1.5M H_2SO_4 and 1M $H_3PO_4$was evaluated by weight loss and electrochemical methods.

2.3.1 Weight loss method
The initial weight of the degreased and dried mild steel plates of size 3 cm × 1 cm × 0.08 cm was taken. The plates were suspended in triplicates into the solution using glass hooks in acid mediumtaken in a 100 ml beaker. Care was taken to ensure the complete immersion of the specimen. After a period of 3 hours the specimens were removed, washed with distilled water, dried and weighed. From the initial and final masses of the plates (i.e., before and after immersion in the solution) the loss in weight was calculated. The experiment was repeated for various inhibitor concentrations in 3M HCl, 1.5M H_2SO_4 and 1M H_3PO_4.

The inhibition efficiency, corrosion rate and surface coverage were calculated from the weight loss results using the formulas:

$$\text{Inhibition Efficiency, (IE\%)} = \frac{(W_b - W_{inh})}{W_b} X 100 \longrightarrow 1$$

WhereW_b= weight loss without inhibitor; W_{inh}= weight loss with inhibitor

$$\text{Corrosion Rate, CR} = \frac{534 X \text{ Weight loss (g)}}{\text{Density (g/cm}^3) X \text{ Area (cm) X Time(h)}} \longrightarrow 2$$

$$\text{Surface Coverage,} \theta = \frac{\%IE}{100} \longrightarrow 3$$

2.3.2 Electrochemical methods

(i) Electrode surface preparation

The mild steel rod with an exposed area of 0.785 cm^2 was polished using 1/0, 2/0, 3/0 and 4/0 emery papers and finally degreased using trichloroethylene and immediately used for the experiments.

(ii) Electrode cell assembly

Electrochemical measurements were carried out in a glass cell with a capacity of 100 ml. A platinum electrode and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. The mild steel (working electrode) was then placed in the test solution (uninhibited and inhibited solutions of three concentrations) for 10-15 minutes before electrochemical measurement.

(iii) Electrochemical study

Electrochemical impedance measurement and potentiodynamic polarization were carried out with IVIUM Compact stat Potentiostat/Galvanostat.

2.3.2.1 Electrochemical impedance spectroscopy method

EIS measurements were carried out at a frequency range of 10 kHz to 0.01Hz with a superimposed sine wave of amplitude 10 mV. From the plot of Z′ vs. Z″ the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated. The inhibition efficiency was calculated using the formula,

$$\text{Inhibition Efficiency}(\%) = \frac{R_{ct\,(inh)} - R_{ct}}{R_{ct\,(inh)}} \times 100 \longrightarrow 4$$

Where R_{ct} and $R_{ct(inh)}$ are the charge transfer resistance obtained in the absence and presence of the inhibitors.

2.3.2.2 Potentiodynamic polarization method

The potentiodynamic polarization measurements were carried out after EIS at a potential range of -200 mV to +200 mV (versus OCP) with a scan rate of 1 mV/sec. The data were collected and analyzed by IVIUM Soft software. The inhibition efficiency was calculated from I_{corr} using the formula,

$$\text{Inhibition Efficiency}(\%) = \frac{I_{corr} - I_{corr\,(inh)}}{I_{corr}} \times 100 \longrightarrow 5$$

Where I_{corr} and $I_{corr(inh)}$ signifies the corrosion current density in the absence and presence of inhibitors.

3. Results

From the inhibition efficiencies obtained from the weight loss experiments for 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4, it is found that the inhibition efficiency increases with increase in inhibitor concentration for all the acids, which is evident from Table 1.

The increase in efficiency of the inhibitor with increase in concentration may be attributed to increase in number of molecules occupied by the inhibitor on the mild steel–acid solution interface. As the number of molecules increases, the corrosion reactions are prevented from occurring over the active sites of the mild steel surface covered by adsorbed inhibitor species, whereas the corrosion takes place on the surface not covered by the inhibitor molecules. The results obtained show that the inhibitors exhibited a higher inhibiting effect on mild steel in the order HCl >H_2SO_4>H_3PO_4. This indicates that the degree of protonation as well as nature of the acid anions influence the corrosion process[9,10].

Nyquist plots obtained in 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4 in the absence and the presence of various concentrations of the studied inhibitor FQ for mild steel at 303 K have been presented in Figures1(a-c). The charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiency values for various

concentrations of the studied inhibitors in 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4 derived from these plots are summarized in Table 2.

Table 1: Inhibition efficiencies for various concentrations of the inhibitor FQ for corrosion of mild steel in acid medium obtained by weight loss measurement at 303 K

Name of the inhibitor	Concentration (mM)	Weight loss (g)	Inhibition efficiency (%)	Surface coverage (θ)	Corrosion rate (g cm^{-2} h^{-1})
1.5M H$_2$SO$_4$	Blank	0.2210	-	-	21.92
	0.5	0.0614	71.43	0.7143	6.09
	1.0	0.0512	76.17	0.7617	5.07
	2.5	0.0496	76.92	0.7692	4.92
	5.0	0.0328	84.74	0.8474	3.25
	7.5	0.0226	89.48	0.8948	2.24
	10.0	0.0107	95.02	0.9502	1.06
3M HCl	Blank	0.2305	-	-	22.84
	0.5	0.0436	81.08	0.8108	4.32
	1.0	0.0319	86.16	0.8616	3.16
	2.5	0.0221	90.41	0.9041	2.19
	5.0	0.0074	96.79	0.9679	0.73
	7.5	0.0059	97.44	0.9744	0.58
	10.0	0.0041	98.22	0.9822	0.41
1M H$_3$PO$_4$	Blank	0.2159	-	-	21.40
	0.5	0.0649	69.94	0.6994	6.43
	1.0	0.0594	72.49	0.7249	5.89
	2.5	0.0481	77.72	0.7772	4.77
	5.0	0.0377	82.54	0.8254	3.74
	7.5	0.0312	85.55	0.8555	3.09
	10.0	0.0148	94.49	0.9449	1.18

Table 2: AC-impedance parameters for corrosion of mild steel in acid medium for selected concentrations of the inhibitor FQ at 303 K

Name of the inhibitor	Concentration (mM)	R_{ct} (ohm cm^2)	C_{dl} (μF cm^{-2})	Inhibition efficiency (%)
1.5M H$_2$SO$_4$	Blank	5.86	31.7	-
	0.5	34.26	30.0	82.89
	5.0	46.32	28.9	87.35
	10.0	54.22	26.0	89.21
3M HCl	Blank	6.26	25.3	-
	0.5	53.75	23.6	88.35
	5.0	69.39	22.4	90.98
	10.0	78.25	20.8	92.01
1M H$_3$PO$_4$	Blank	17.08	36.6	-
	0.5	46.21	27.1	63.04
	5.0	72.64	22.9	76.49
	10.0	75.39	21.6	80.95

It is evident from the plots that the impedance response has been significantly altered after the addition of these inhibitors to the aggressive medium. It is found that the inhibition efficiency values increase with the increase in inhibitor concentration and the double layer capacitance values decrease with the increase in inhibitor concentration. The decrease in C_{dl} values can be attributed to the decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer[11]. These observations suggest that the inhibitors function by adsorption at the metal-solution interface.

Figures 2(a-c) show the potentiodynamic polarization curves for mild steel in 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4 in the absence and presence of the inhibitor FQ. The corrosion current density I_{corr} values have been derived from the extrapolation of the cathodic and anodic Tafel slopes to the corrosion potential (E_{corr}) for all the inhibitor concentrations. It is evident from the polarization curves that all the four inhibitors inhibit both the anodic dissolution of metal and the cathodic evolution of hydrogen.

The various corrosion kinetic parameters b_a, b_c, E_{corr} and I_{corr} values and the inhibition efficiency values derived from the polarization curves for mild steel in 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4 with and without the presence of the inhibitors FQ, PHDQO, TP and PTTA are presented in Table 3. Analysis of the inhibition data reveals that inhibition efficiency increases with increase in inhibitor concentrations. Introduction of the inhibitors to the corrosive medium (HCl and H_2SO_4) shifts the E_{corr} to positive side (nobler side) confirming the greater adsorption of the inhibitors on the anodic sites. On the other hand, when the inhibitors are added to 1M H_3PO_4, E_{corr} is shifted to the negative side. In all the three acids, only a slight shift to positive and negative direction is observed. Further, both b_a and b_c values are altered by the addition of the inhibitors proving that the inhibitors are of mixed type.
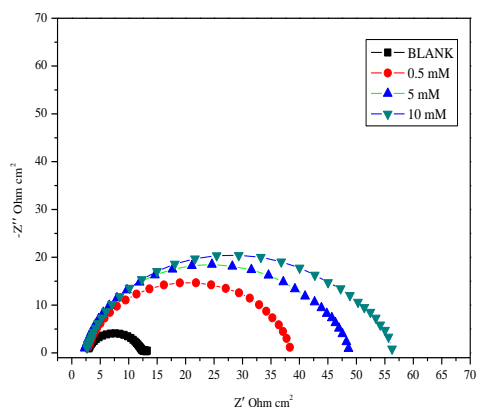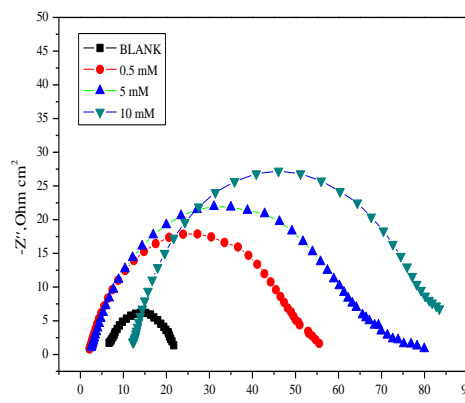

Figure 1a:1.5M H_2SO_4
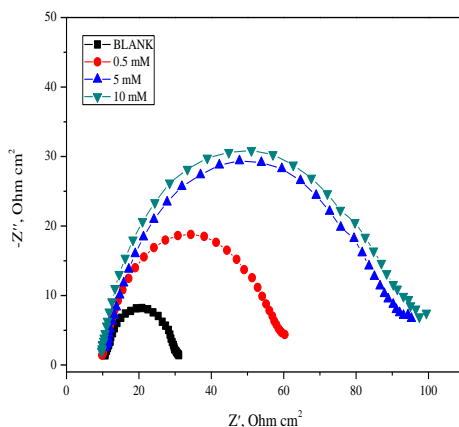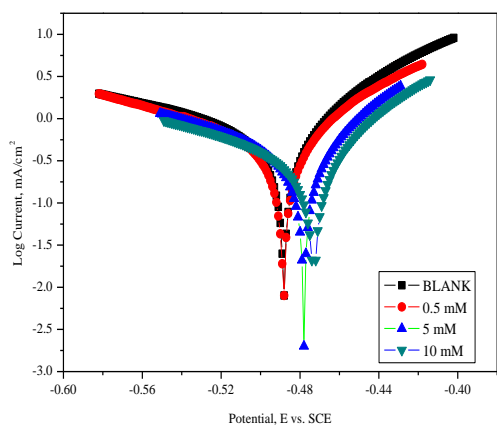
Figure 1b: 3M HCl
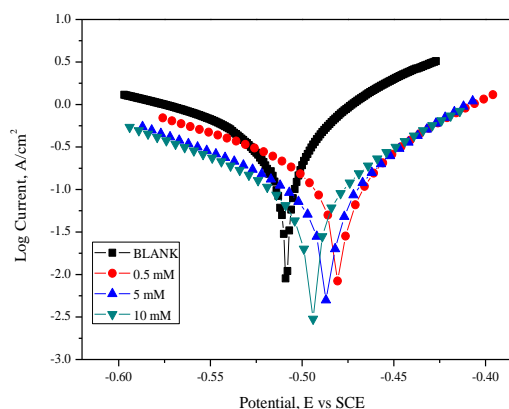
Figure 1c:1M H_3PO_4

Figures 1(a-c): Nyquist diagram for mild steel recorded in acid medium for the selected concentrations of the inhibitor FQ

Table 3: Corrosion parameters for corrosion of mild steel in acid medium with selected concentrations of the inhibitor FQ by potentiodynamic polarization method at 303 K

Name of the inhibitor	Concentration (mM)	Tafel slopes (mV/dec)		$-E_{corr}$ (mV/SCE)	I_{corr} ($\mu A.cm^{-2}$)	Inhibition efficiency (%)
		b_a	b_c			
1.5M H$_2$SO$_4$	Blank	64	149	489.1	675.3	-
	0.5	62	141	486.8	426.3	38.35
	5.0	42	113	473.7	350.3	48.13
	10.0	49	115	473.1	300.2	55.55
3M HCl	Blank	72	126	509.3	395.0	-
	0.5	33	165	476.7	180.4	54.33
	5.0	71	123	482.9	120.2	69.55
	10.0	76	119	496.4	98.2	75.15
1M H$_3$PO$_4$	Blank	86	153	489.6	731.5	-
	0.5	74	179	501.2	462.3	36.80
	5.0	76	189	510.6	451.9	38.22
	10.0	79	201	528.8	410.9	43.84

Figure2a:1.5M H$_2$SO$_4$

Figure 2b:3M HCl
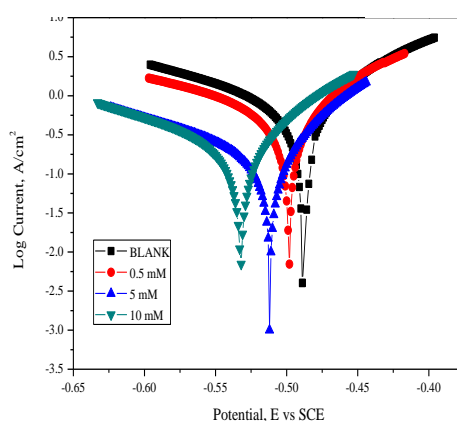
Figure 2c:1M H$_3$PO$_4$

Figures 2 (a-c): Polarization curves for mild steel recorded in acid mediumfor the selected concentrations of the inhibitor FQ

An examination of the inhibition efficiency values derived from all the three techniques employed in this work are presented in the Table4 which reveal that the inhibition efficiency values of the inhibitor FQ in various medium follow the order 3M HCl > 1.5M H_2SO_4 > 1M H_3PO_4.

Table 4: Comparison of inhibition efficiencies for corrosion of mild steel for different concentrations of the inhibitor in 1.5M H_2SO_4, 3M HCl and 1M H_3PO_4 by weight loss method and electrochemical methods

Method	Concentration (mM)	1.5M H_2SO_4	3M HCl	1M H_3PO_4
Weight loss	0.5	71.43	81.08	69.94
	1.0	76.17	86.16	72.49
	2.5	76.92	90.41	77.72
	5.0	84.74	96.79	82.54
	7.5	89.48	97.44	85.55
	10.0	95.02	98.22	94.49
AC-impedance spectroscopy	0.5	82.89	88.35	63.04
	5.0	87.35	90.98	76.49
	10.0	89.21	92.01	80.95
Potentiodynamic polarization	0.5	38.35	54.33	36.80
	5.0	48.13	69.55	38.22
	10.0	55.55	75.15	43.84

From this observation, it may be concluded that the inhibitor is more efficient in hydrochloric acid than in sulphuric acid and phosphoric acid. Comparison of I_{corr} values in the three acid medium reveals that chloride ions themselves have functioned as inhibitor by strongly interacting with the metal surface. The stronger specific reactant adsorption of chloride ions in HCl medium as compared to the SO_4^{2-} ions in sulphuric acid and PO_4^{3-} ions of phosphoric acid medium is also evident from the lower C_{dl} value (25.3 μFcm^{-2}) in HCl in comparison to the higher C_{dl} value (36.8 μFcm^{-2}) in sulphuric acid and (36.6 μFcm^{-2}) in phosphoric acid. This would ultimately mean that while in hydrochloric acid, the chloride ions have worked in co-ordination with the inhibitor molecule through joint adsorption for the corrosion inhibition and hence have played a major role in the process of inhibition. SO_4^{2-} ions of sulphuric acid and PO_4^{3-} ions of phosphoric acid have only played a weaker role compared to Cl^- and the role of inhibitor is important. The inhibition efficiency of the studied inhibitors in 1.5M H_2SO_4 is slightly higher than 1M H_3PO_4. This is because sulphuric acid is diprotic; it has two hydrogen ions to donate. Phosphoric acid is triprotic; it has three hydrogen ions it can donate to a solution. However, this does not determine whether those hydrogen ions will all dissociate in a solution and increase the metal dissolution [11].

According to the authors Damaskin et al[12], Frumkin[13] and Iofa [14], Bentiss et al. [15], Rengamani et al. [16] and Muralidharan et al. [17], the inhibitors exist in either as neutral molecules or in the form of protonated cations. The neutral molecules adsorb on the metal surface due to the sharing of lone pair of electrons on N/ O/ S atoms and the metal surface. The cationic inhibitor molecules electrostatically interact with the negatively charged metal surface through the positive charge on the N/ O/ S atom. Due to smaller degree of hydration, chloride ions are specifically strongly adsorbed and thereby create excess negative charge towards cationic inhibitor molecules in solution, which are strongly adsorbed. However, the SO_4^{2-} and PO_4^{3-} ions with high degree of hydration are weakly adsorbed in general and have little space for organic molecules to adsorb. Hence, higher synergistic inhibition is expected for anion of Cl^- type. For the reason stated above the adsorption is greater from 3M HCl solution than from 1.5M H_2SO_4 and 1M H_3PO_4.

Conclusion

The present study shows that the inhibition efficiency of the inhibitor increases and corrosion rate decreases with increasing concentration of the inhibitor.The inhibition efficiency of the studied inhibitors in various acid medium follow the order HCl > H_2SO_4>H_3PO_4 by weight loss and electrochemical methods.The inhibitor behaved as mixed type inhibitors in1.5M H_2SO_4, 3M HCl and 1M H_3PO_4.

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(2017) ; http://www.jmaterenvironsci.com