

Adsorption and thermodynamics study of Ferroin [tris(1,10-phenanthroline iron(II) sulphate complex] as corrosion inhibitor for mild steel in acidic medium.

ABSTRACT

The inhibition effect of Ferroin solution [tris(1,10-phenanthroline iron(II) sulphate complex] as a corrosion inhibitor was analysed against mild steel (MS) corrosion in 0.5M HCl solution using weight loss method, linear polarization, electrochemical impedance spectroscopy, and scanning electron microscopic studies. The weight loss study of MS samples have proved that the reagent used was an efficient corrosion inhibitor. The mixed mode of inhibition was confirmed by electrochemical polarizations and the results of electrochemical impedance spectroscopy have shown the changes in the impedance parameters like R_{ct} and C_{dl} in order to confirm the adsorption phenomenon taking place on the MS surface. The inhibition action of the compound was assumed to occur via adsorption on the steel surface through the active centers present in the inhibitor

KEYWORDS: Ferroin solution; mild steel; linear polarization; EIS; SEM;Corrosion

1. INTRODUCTION

Mild steel is widely applied in buildings, pipelines, bridges, vehicles, storage tanks for industrial water and wastewater systems and even in home appliances due to its low cost and remarkably excellent mechanical properties. The key problem of its application is the dissolution of the metal in acidic solutions that is employed for its acid pickling, industrial acid cleaning, acid descaling and oil well acidizing processes. Corrosion, the dissolution of metal, is a silent toxin for our industries that has attracted numerous researchers. Recently, the inhibition of mild steel corrosion in acid solutions by different types of organic inhibitors has been extensively studied [1-4]. The protection of metal from corrosion using corrosion inhibitors is the basic foundation of this research. The inhibitors are some chemicals that act to protect the metal against corrosion by reacting with the metallic surface, or with the surrounding environment. The use of inhibitors is the most economical and practical methods of reducing corrosive attack on metals [5-7]. And till date it is a continuing effort to discover a corrosion inhibitor that exhibits a greater efficiency of inhibition with its minimum quantity in the acidic medium. The conventional inhibitors used are organic compounds having heteroatoms (N, S, O, P) in their aromatic or long carbon chained structures. Such compounds get adsorbed on the metal surface, thereby blocking its active sites and thus results in inhibiting the corrosion. The adsorption of corrosion inhibitors is mainly due to the physico-chemical characters of the inhibiting molecule like its functional group, steric factors, aromaticity, p orbital character of donating electrons, π electron density at the donor atoms. They mainly have sites that contribute to the formation of a protective layer, via donation of their electron density towards the metal surface [8-10].

The present study aims to investigate inhibitive properties of a reagent Ferroin solution for the corrosion of mild steel.

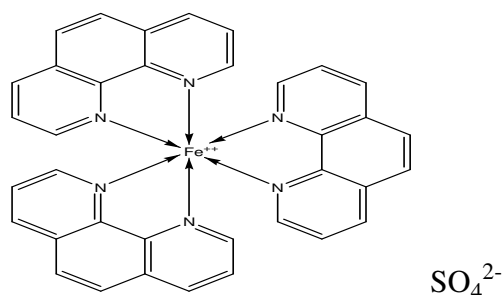
2.EXPERIMENTAL

2.1 Materials:

The aggressive solution 0.5 M HCl was prepared by dilution of analytical grade HCl with double distilled water and all experiments were carried out in unstirred solutions. Before all measurements, the mild steel specimens, having composition (wt %) 0.14C, 0.03Si, 0.032Mn, 0.05S, 0.20P, 0.01Ni, 0.01Cu, 0.01Cr and balanced Fe, were abraded successively with emery papers from 600 to 1200 grade.

The specimen were then washed thoroughly with double distilled water, degreased with acetone and finally dried. After drying, the specimen were placed in desiccator and then used for experiment. The rectangular specimens with dimension $1.0 \times 1.0 \times 0.5$ cm were used in weight loss experiments and surface microscopy, and of size $1.0 \text{ cm} \times 1.0 \text{ cm}$ (exposed) were used for electrochemical measurements.

The inhibitor used is a reagent, Ferroin [tris(1,10-phenanthroline iron(II)sulphate complex] red



Coloured compound in its reduced form with molecular formula $\text{C}_{36}\text{H}_{24}\text{FeN}_6\text{O}_4\text{S}$.

2.2 GRAVIMETRIC ANALYSIS

For the weight loss method, the polished and dried specimens were weighed before and after immersion in 0.5 M HCl for 4 h in the absence and presence of the inhibitor at different temperatures (303K, 313K, 323K and 333K) for each concentration (200ppm, 400ppm, 800ppm and 1000ppm) of the inhibitor. Each experiment was reported in duplicate to calculate the inhibition efficiency of the inhibitor taken.

2.3 POLARISATION MEASUREMENTS

The polarization measurements were performed at the range of temperatures in the absence and presence of various concentrations of the inhibitor as used in weight loss method. For the polarization measurements, a conventional three electrode Pyrex glass cell consisting of a saturated calomel electrode (SCE) as reference electrode, the mild steel specimen as working electrode and a platinum foil as counter electrode were used. All electrodes were dipped in the same test solutions with a Luggin capillary bridge arrangement to minimize resistance polarization. The experiment was carried out using the CHI760C electrochemical analyser and in thermostatic controlled water baths at constant temperature ($\pm 0.5\text{K}$). The anodic and cathodic polarization values were measured under galvanostatic conditions and the corresponding Tafel lines were constructed that provides the data for calculating the corrosion rates and efficiencies of the inhibitors.

2.4 ELECTROCHEMICAL IMPEDENCE SPECTROSCOPY

EIS is a special and reliable laboratory technique, with the applicable software to determine significant parameters like the charge transfer resistance (R_{ct}) rate and double-layer capacitance (C_{dl}) [11]. The AC impedance measurements were carried out in the range of $1.0 - 1.0 \times 10^5$ Hz with the AC signal 5 mV peak-to-peak. The same cell and system as in the polarization method was used. The double-layer capacitance (C_{dl}) and the charge transfer resistance (R_{ct}) were calculated from Nyquist plots.

2.5 SEM STUDIES

SEM studies were performed on the coupons immersed in the acidic medium both in the absence and presence of Ferrioxalate at 1000ppm concentration. The coupons were immersed for 4hr duration at 303K temperature. The coupons were thoroughly polished using range of emery papers, washed and dried in

acetone, similar to weight loss experiment. After the time duration coupons were rubbed to scale off the corroded layer and then, again washed and dried. SEM studies were performed using Model Zeiss Ultra 55 at 500 magnification and 3kV.

3.RESULTS AND DISCUSSION

3.1 GRAVIMETRIC ANALYSIS

The inhibition efficiency of the inhibitor (Table A.1) increases with its increasing concentration in the acidic medium and the decrease in efficiency is observed with the increasing range of temperature.

$$\eta\% = \frac{W - W_{inh}}{W} \times 100 \quad (1)$$

$$CR(mmpy) = \frac{W - W_{inh}}{DAT} \times 87.6 \quad (2)$$

Where, W is the weight loss in blank solution i.e. in absence of inhibitor (g), W_{inh} is the weight loss in presence of the inhibitor (g), D is the density of metal (gcm^{-3}), A is the exposed area of the metal (cm^2) and T is the exposure time in (hr)[12]. Fig. A.1 shows the plot of corrosion rate (mmpy) against inhibitor concentration (ppm) for the corrosion of mild steel in 0.5M HCl in the range of increasing temperatures from 303K to 333 K. The figure showed that the corrosion rate, calculated from eq. 2., decreases as the concentration of the inhibitor increases in addition to the increasing trend of corrosion rate with increasing temperature.

3.2 POLARISATION MEASUREMENTS

To study the effect of Ferroin solution on the polarization behavior of MS and to analyze the inhibition action of reagent on steel corrosion in 0.5 M HCl, polarization curves for different concentrations of inhibitor were plotted. Fig.A.2 and Fig. A.3. presents polarization curves for mild-steel electrode in 0.5 M HCl, in the absence and presence of inhibitor at different concentrations. The electrochemical parameters obtained from polarization measurements are listed in Table 2. From the plot and the table, it is clear that both cathodic and anodic reactions on mild-steel electrode have been inhibited in the presence of the studied compound. Electrochemical corrosion parameters including corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c , β_a), and corrosion current density (I_{corr}), obtained by extrapolation of Tafel lines, are given in Table A.2. The inhibition efficiency (η), was calculated from the following equation. Eq.3, [13]

$$\eta\% = \frac{I_{corr} - I_{corr}^0}{I_{corr}} \times 100 \quad (3)$$

Where, I_{corr} and I_{corr}^0 are the values of corrosion current densities without and with the inhibitor, respectively, which were determined by extrapolation of the cathodic and anodic Tafel curve. The E_{corr} values from the polarization diagrams show that the inhibitor behaves as a mixed type, with small variations in the E_{corr} values of the blank specimens.

3.3 ELECTROCHEMICAL IMPEDENCE SPECTROSCOPY

The corrosion behavior of MS in 0.5 M HCl solution in the absence and presence of the reagent was also investigated using electrochemical impedance spectroscopy (EIS). Nyquist plots of MS in absence and presence of inhibitor solutions in various concentrations of inhibitor are given in Fig. A.4(a) along with equivalent circuit diagram in Fig.A.4(b). It is observed, the impedance response of MS in blank solution significantly changed after addition of inhibitor. The values of inhibition efficiency (η) were calculated by following the equation 4 [15]:

$$\eta\% = \frac{R_{ct}^0 - R_{ct}}{R_{ct}^0} \times 100 \quad (4)$$

Where, R_{ct} and R_{ct}^0 are the charge transfer resistances (cm^2) values in the absence and presence of the inhibitors, respectively. To obtain the values of double-layer capacitance (C_{dl}), the values of frequency at which the maximum imaginary component of the impedance f_{max} were found and were used in the following equation with corresponding R_{ct} values [15]:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (5)$$

Nyquist plots shows depressed semi-circles with the center under the real axis, whose size increased with the increase in concentration of the inhibitor, confirming that the charge transfer processes were mainly controlling the corrosion of MS. Table A.3 reveals that the value of R_{ct} increases prominently with the increase in the inhibitor concentration, while the value of C_{dl} is decreased. This indicates an increase in the surface coverage by adsorption of the inhibitor on the MS, which results in the increase in inhibitor efficiency and the maximum reaches up to 90%. The decrease in the C_{dl} related to the decrease in local dielectric constant or an increase in the thickness of the electrical double layer, suggests that inhibitor molecules function by adsorption at the interface of metal/solution [16] Hence the molecules replace the water molecules gradually by adsorbing at metal/solution interface, leading to the decrease in the extent of dissolution reaction.

It is also significant that the inhibition efficiencies obtained from weight loss measurements are different from electrochemical experiments. This phenomenon attributed to that weight loss experiments give average corrosion rates, whereas the electrochemical experiments give instantaneous corrosion rates [15]. However, the inhibition efficiencies calculated from EIS measurements show the same trend as that obtained from potentiodynamic polarization measurements and weight loss measurements.

3.4 SCANNING ELECTRON MICROSCOPY

The surface morphology of the MS specimens immersed in 0.5M HCl in the presence and absence of the Ferroin solution at 1000ppm concentration were studied by using scanning electron microscopy (SEM). The immersion time of the electrodes for the SEM analysis was 4 hr at 303K temperature. The SEM of the uninhibited sample and the inhibited sample at 500 magnification are given in the Fig.A.5(a) and Fig. A.5(b) respectively. These figures show the surface of MS in the respective mediums.

3.5 ADSORPTION ISOTHERMS

The results show that, the weight loss decreases with the increasing inhibitor concentration and therefore, the inhibition efficiency increases. It can be concluded that this inhibitor acts through adsorption on metal surface and formation of a barrier layer between metal and corrosive media. The adsorption isotherms can provide basic information on the interaction of inhibitor and metal surface. In order to obtain adsorption isotherm, the surface coverage values (θ), for different concentrations (C) of the inhibitor in 0.5M HCl solution have been obtained from electrochemical measurements and tested graphically for fitting of a suitable adsorption isotherm. To confirm the adsorption of inhibitor on metal surface, different adsorption isotherms were studied like Langmuir, Tempkin and Freundlich.

The plot of C/θ versus C (Fig. A.6) [17] yields a straight line with correlation coefficient (R^2) >0.99 , yielding that the adsorption of the reagent obeys the Langmuir adsorption isotherm presented in Eq.6

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (6)$$

where, C is inhibitor concentration, θ is the degree of surface coverage, and K_{ads} is the equilibrium constant for adsorption–desorption process. The value of the equilibrium constant, K_{ads} , was calculated from the reciprocal of the intercept of the isotherm line.

K_{ads} values can be calculated from the intercepts of the straight lines, is related to the standard free energy of adsorption, ΔG_{ads}^0 with following equation 7 and 8[18]:

$$\Delta G_{ads}^0 = -RT \ln 55.5 K_{ads} \quad (7)$$

$$\Delta G_{ads}^0 = -2.303RT(\log 55.5 K_{ads}) \quad (8)$$

ΔG_{ads} was calculated and found $-17.46 \text{ kJmol}^{-1}$. The negative value of ΔG_{ads}^0 indicates spontaneous adsorption of the inhibitor molecules on the MS surface which shows interaction between inhibitor molecules and metal surface. The value of ΔG_{ads}^0 is less than -40 kJmol^{-1} , indicating electrostatic interaction between the charged inhibitor molecules and the charged metal surface, i.e., physical adsorption[19,20]. The negative values indicate the spontaneity of the adsorption process and stability of the adsorbed layer on MS surface.

3.6 EFFECT OF TEMPERATURE

To calculate the activation parameters of the corrosion process and to study the inhibition mechanism due to the temperature, polarization measurements were performed at 303K, 313K, 323K, 333K range of temperatures, in the absence and presence of the inhibitor concentrations the Arrhenius plots were analysed.

The activation energy of the corrosion process could be determined using the Arrhenius equation [21]:

$$I_{corr} = k \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

Where, I_{corr} is corrosion current density, obtained by extrapolation of the Tafel lines of experiments carried out at 303K, 313K, 323K, 333K temperatures. E_a is the activation energy, R is the gas constant, T is the absolute temperature and k is the pre-exponential factor. The values of E_a can be calculated from the slopes of the straight lines in Fig.A.7(a), these values show an increase in the activation energies of the various mediums studied. The E_a value increases from 66.80 kJ/mol to 77.27 kJ/mol, showing the increase in the threshold energy with increasing concentration.

Activation parameters like enthalpy (ΔH°) and entropy (ΔS°) for the dissolution of MS in the acid medium in the absence and presence of various concentrations of Ferroin solution was calculated from the equations. Eq. 10 and eq. 11 [22].

$$\log k = \frac{-\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (10)$$

$$\Delta G_{ads}^\circ = \Delta H_{ads}^\circ - T\Delta S^\circ \quad (11)$$

Where, k represents slope from the langmuir isotherm, R is the universal gas constant, ΔH° is the enthalpy of activation and ΔS° is the entropy of activation. The plot of $\log k$ against $1/T$ Fig.A.7(b), gave straight line with slope $-\Delta H^\circ / 2.303 R$ and intercept $\Delta S^\circ / 2.303 R$ from which ΔH° and ΔS° values were calculated as 10.32 kJ/mol and -9.41 J/mol/K, respectively . Generally, an exothermic process signifies either physisorption or chemisorption or a combination of both. Typically, the enthalpy of physisorption process is lower than that of 40.00 kJ/mol while the enthalpy of chemisorptions process approaches 100 kJ/mol [23]. The entropy of activation (ΔS°) is negative, indicating that a decrease in randomness takes place on going from reactants to the activated complex direction, indicating that a decrease in randomness takes place on going from reactants to the activated complex direction[24]. The apparent activation energy (E_a) and enthalpy (ΔH°) in the acid solution was found to increase and the extent of the increase is proportional to the

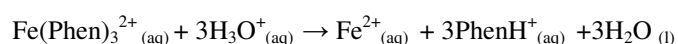
temperature increase, indicating that the energy barrier for the corrosion reaction increases with the temperature.

3.7 MECHANISM of INHIBITION

The above observations and analysis show that the inhibitor is adsorbed on mild steel. Four mechanisms have been suggested for the adsorption of inhibitor at the metal–solution interface [25]. These are:

- (i) electrostatic attraction between charged molecules and charged metal,
- (ii) interaction of unshared electron pairs in the molecule with the metal,
- (iii) interaction of π -electrons with the metal and
- (iv) a combination of all of the above.

Ferroin, a red coloured compound in its reduced form decolourizes in the acidic medium during the static experimental conditions. To explain this observation, it is expected that the Ferroin molecule undergoes dissociation in the acidic solution to give three protonated 1,10-Phenanthroline(Phen) moieties[26] as given in the reaction below:



Moreover, the hydration energy of Fe^{2+} ions [27] present in outer Helmholtz plane (OHP) [25] as well as in bulk and binding energy for Fe^{2+} ions and O^{2-} are comparable [29], as the former ions are bound to water molecules through oxygen in the hydration shell (Fig.8) [28]. So, it may be expected that the cleavage of the primary hydration sheath in outer OHP as well as in bulk may take place because the number of water molecules in the first hydration sheath at the transition state is less than in the ground state, suggesting the dissociative mode of the activation state[30].

Simultaneously, the dissociation of Ferroin also takes place freeing Fe^{2+} ions. So, the possibility to exchange of freed Fe^{2+} ions from their dismantled hydrated sheath with the similar ions coming from the dissociation of Ferroin arises in the acidic solution. The Phen moiety, in turn, bears electron rich sites and a planar geometry. This protonated Phen, Fe^{2+} from MS surface and Cl^- ions from HCl may bind together to form [Fe-Cl-protonated Phen]. These species may get adsorbed on the MS surface and hence hinder the corrosion reaction. Towards higher concentrations, Ferroin gives increased inhibition efficiency, shown in Table A.1, may be attributed to the fact that on shifting from 200ppm to 1000ppm at intervals of 200ppm of the inhibitor, there occurs a gradual enhancement in long range intermolecular interactions of attractive nature[31] and hence improves the extent of adsorption. The higher values of R_{ct} obtained at high concentrations also justify this concept. This phenomenon is more noticeable at lower temperatures.

At higher temperatures, Table A.2 showing gradual decrease in the efficiency, can be explained on the basis of eliminating orientational forces of the inhibitor molecules at elevated temperatures. The inhibitor with electron rich centers, is expected to behave as a polar molecule as well as MS interface containing Fe^{2+} ions, water dipoles, so long range dipole-dipole interaction may occur. Based upon the statistical calculations of dipole–dipole (dd) interactions by Reinganum [32] who proposed that on averaging all the orientations of dipole molecules (for example, inhibiting molecules and free Fe^{2+}) the orientational interaction energy becomes zero.

$$\langle E_{dd} \rangle = 0$$

Where, bracket notation denotes an average over orientations and E is the energy corresponding to the probability of the dipole orientation obtained from Boltzmann factor $\exp^{(-E/RT)}$. Also, without averaging, these orientational forces approach zero at higher temperatures, implies that with increasing temperatures,

orientational forces become negligible, leaving behind the only van der Waals forces. These van der Waals forces at elevated temperatures [32] contributing towards adsorption but to a lesser extent. Hence low efficiency is observed at higher temperatures.

4. CONCLUSION

The inhibition effect of Ferroin solution [tris(1,10-phenanthroline iron(II) sulphate complex] as a corrosion inhibitor was analysed against mild steel (MS) corrosion in 0.5M HCl solution using weight loss method, linear polarization, electrochemical impedance spectroscopy, and scanning electron microscopic studies. The studied compound is a good inhibitor of corrosion.

The inhibition efficiency of the inhibitor increases with increase in its concentration and decreases with the increasing temperature.

Adsorption study showed that the inhibition mechanism obeys Langmuir adsorption isotherm.

The Tafel plots of polarization have shown that the Ferroin solution acted as mixed type inhibitor.

The results of the gravimetric analysis, electrochemical polarizations, and EIS were in very good agreement. Photographs by scanning electron microscopy (SEM) have clearly shown the formation of a protective film on the surface of mild steel.

5. REFERENCES

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Figures.

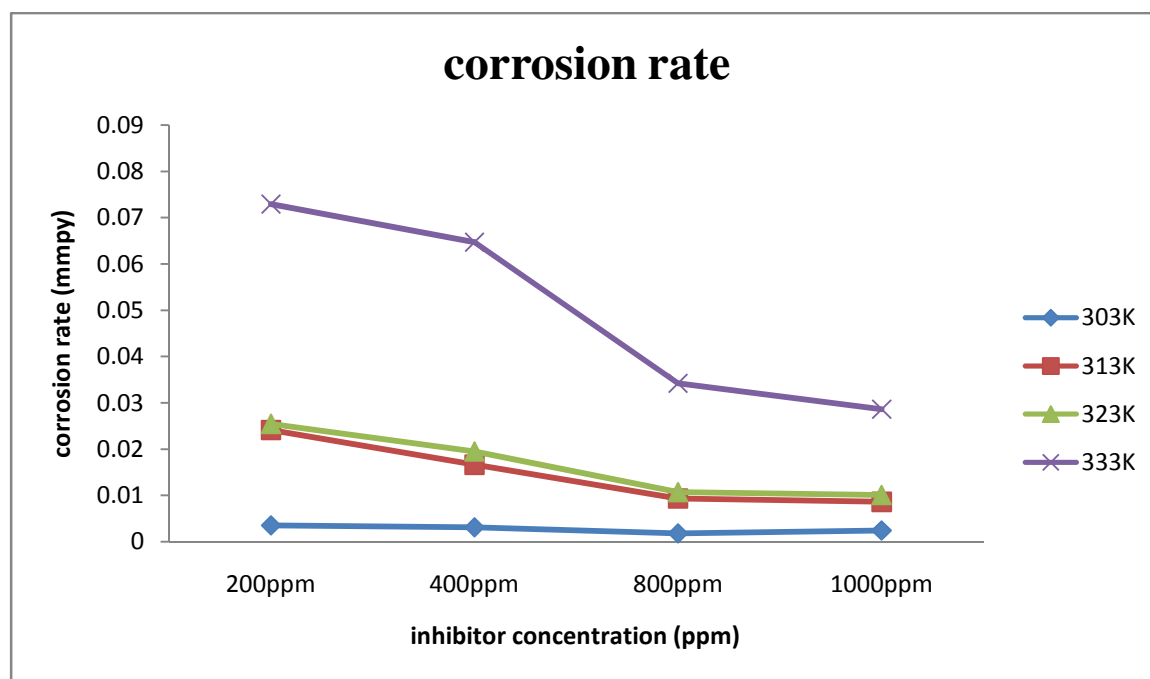


Fig. A.1 . Plot between corrosion rate and inhibitor concentrations (200ppm, 400ppm, 800ppm and 1000ppm) at varying temperatures.

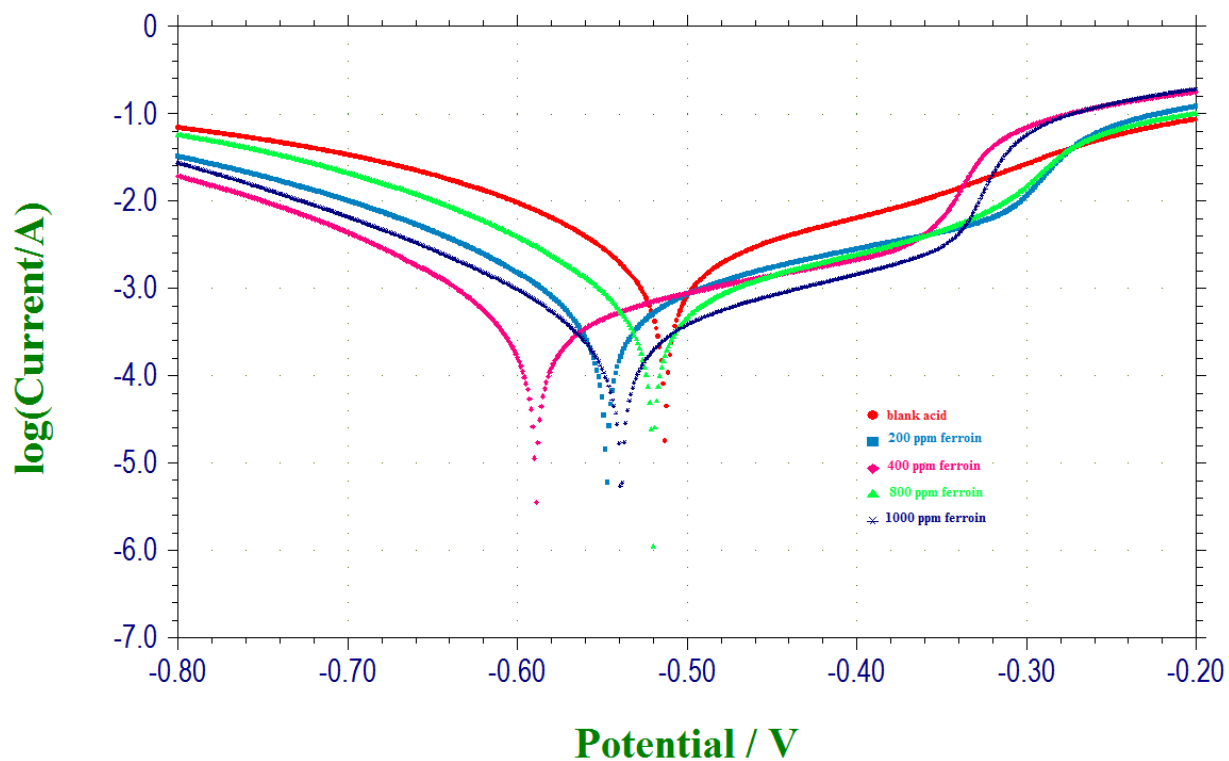


Fig. A.2 Tafel curve at 303 K in absence and presence of Ferriox at 200ppm,400ppm,800ppm and 1000ppm concentrations.

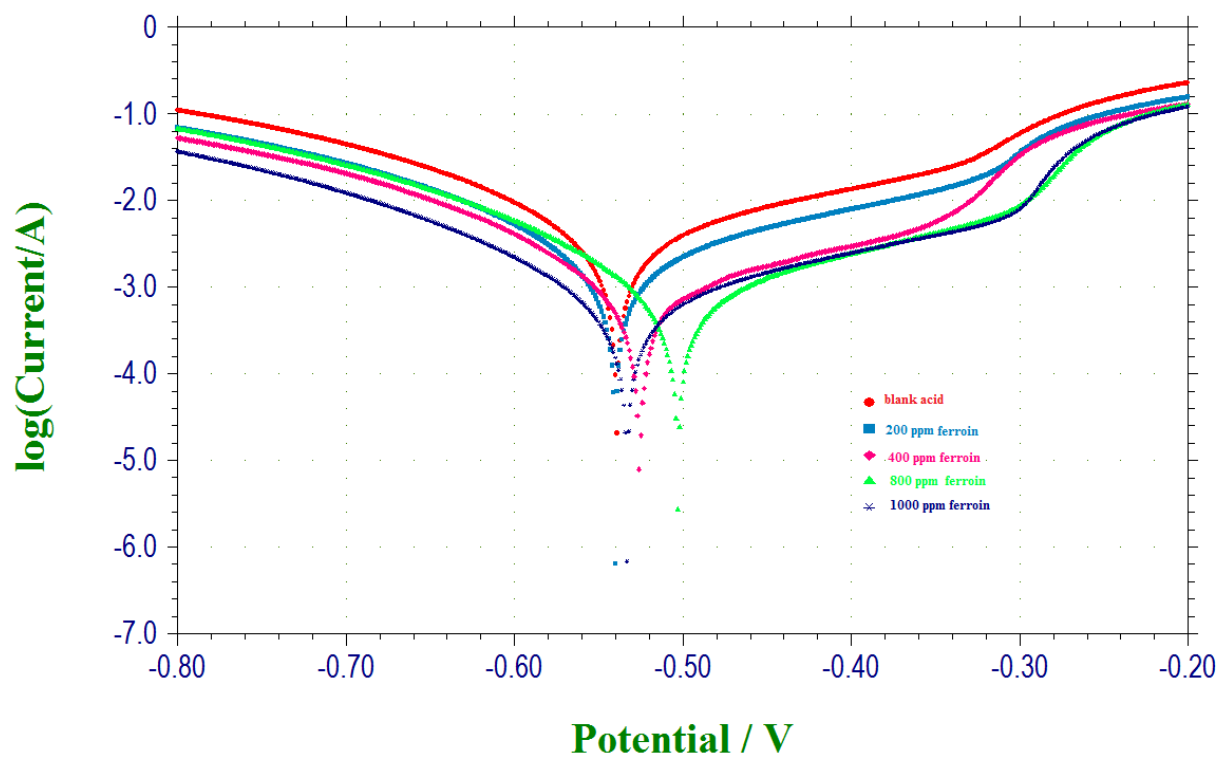


Fig. A. 3 Tafel curve at 313K in absence and presence of Ferrioin at 200ppm,400ppm,800ppm and 1000ppm concentrations.

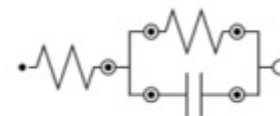
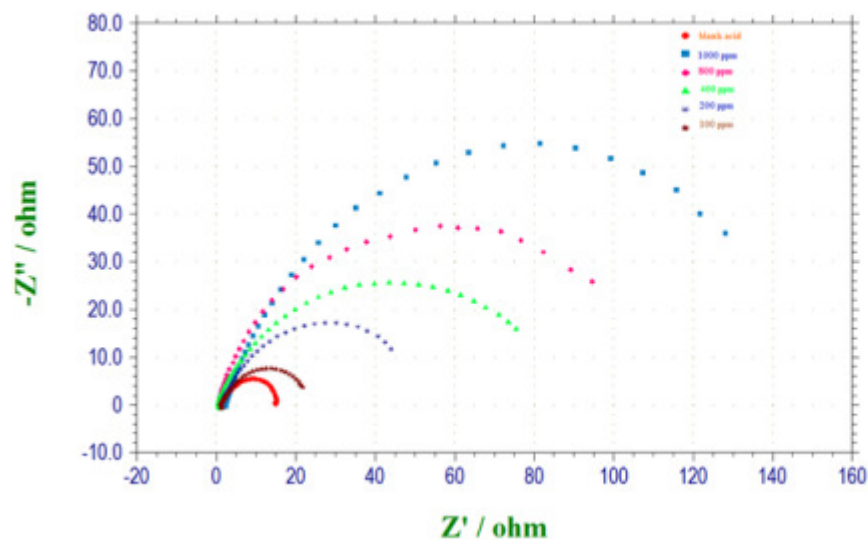


Fig. A.4(a) Nyquist plots in absence and presence of Ferrioin in acidic medium at varying concentration, and (b) Equivalent circuit diagram of EIS study.

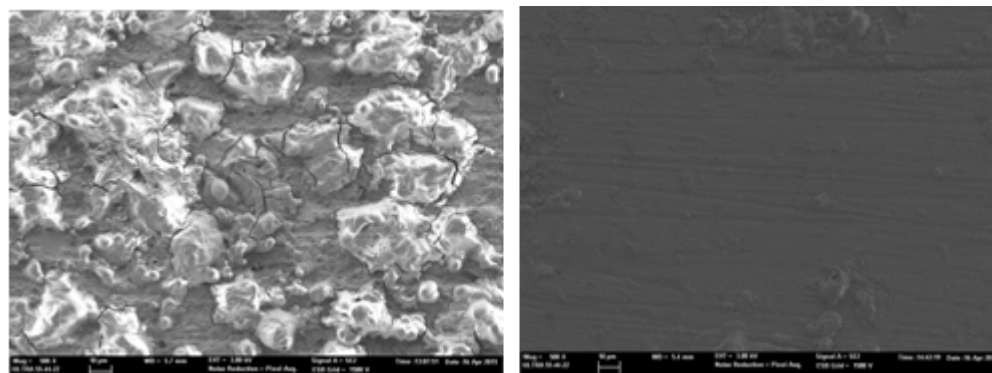


Fig.A.5(a) SEM images of MS surface in acidic medium in the absence of Ferrioin at 303K , and

Fig. A.5(b) SEM images of MS surface in acidic medium in the presence of Ferrioin (1000ppm) at 303K.

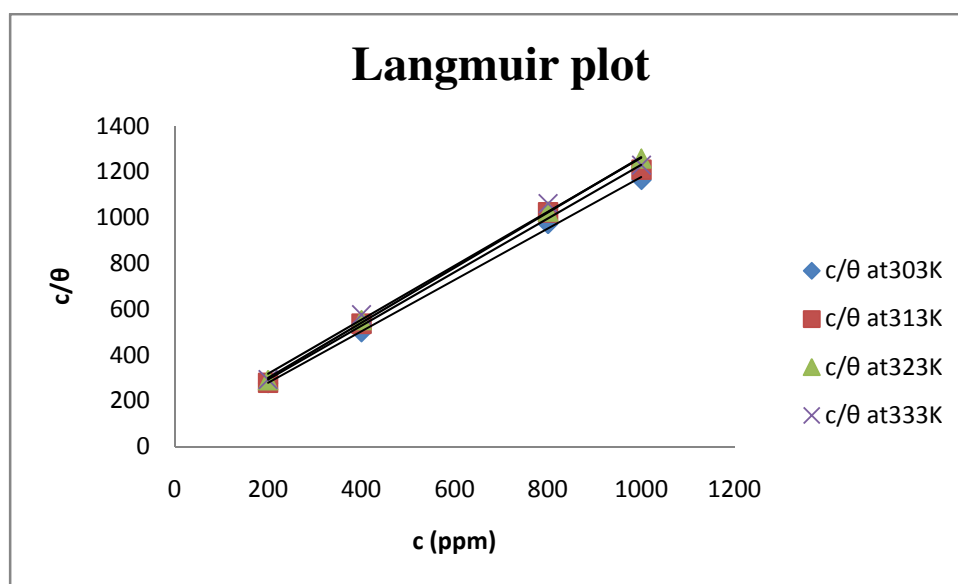


Fig. A.6 Langmuir isotherm for Ferroin solution at range of temperatures (303K, 313K, 323K, 333K).

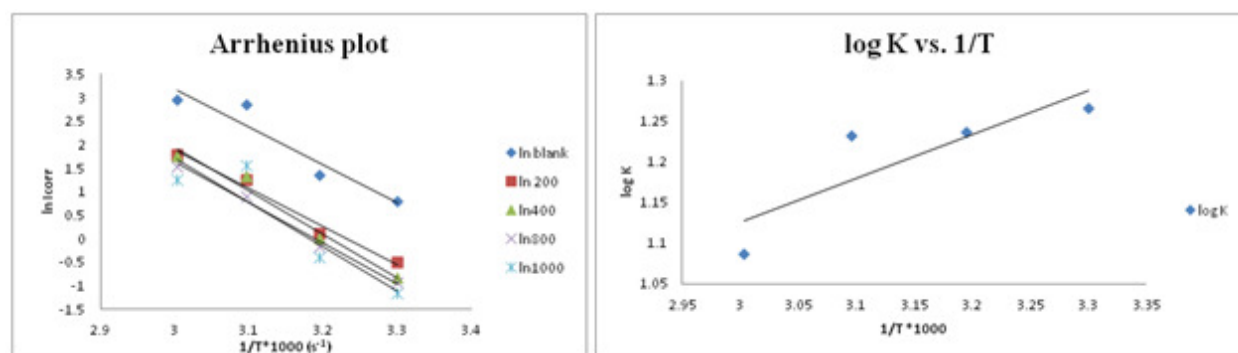


Fig. A.7(a) Arrhenius plot of Ferroin solution at varying concentrations of inhibitor (200ppm, 400ppm, 800ppm, 1000ppm), and Fig. A.7(b) Plot between $\log K$ and $1/T$ for slope (ΔH°) and intercept (ΔS°).

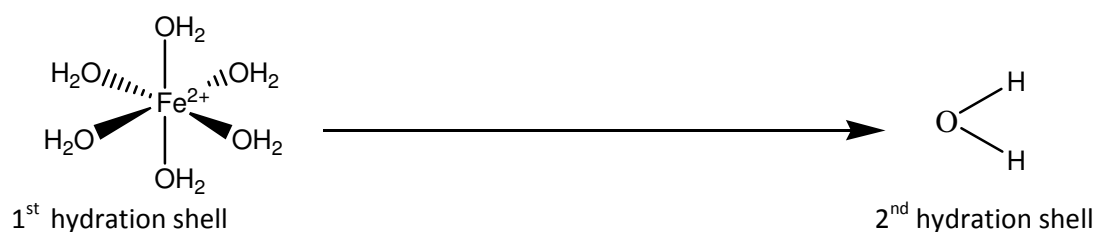


Fig. A.8 Hydration sheath of Fe ion replaced by the inhibitor during adsorption process.

Caption of tables

Temperature (K)	Inhibition efficiency of ferroin solution(%)			
	200ppm	400ppm	800ppm	1000ppm
303	90.33	90.7	92.03	92.56
313	81.9	82.36	83.75	83.74
323	47.51	78.41	78.8	81.23
333	39.9	46.74	74.84	76.42

Table.A.1:Inhibition efficiency of Ferroin at MS surface at 303K, 313K, 323K and 333K.

Temperature (K)	Conc. of inhibitor(ppm)	$E_{corr} \times 1000$ (-mV)	β_a (mV/dec)	β_b (mV/dec)	I_{corr} (mA cm ⁻²)	% η
303	0	513	192.23	131.87	2.218	-
	200	520	198.8	109.22	0.618	72.14
	400	589	220.75	107.61	0.4405	80.14
	800	540	183.18	103.8	0.3928	82.3
	1000	539	189.75	112.84	0.3127	85.9
313	0	539	205.67	131.98	3.95	-
	200	533	220.26	117.75	1.118	71.69
	400	526	206.01	117.72	1.004	74.58
	800	503	195.16	114.71	0.859	78.25
	1000	533	198.02	117.61	0.682	82.73
323	0	543	196.15	205.97	17.41	-
	200	532	178.25	215.36	5.623	69.02
	400	523	142.67	226.44	4.795	72.46
	800	546	141.96	207.25	3.837	77.96
	1000	528	139.87	216.87	3.566	79.52
333	0	517	213.72	170.12	19.08	-
	200	546	208.94	161.1	6.031	68.39
	400	508	213.72	164.09	7.82	73.29
	800	524	231.69	136.27	4.705	75.34
	1000	558	208.24	143.49	3.559	81.34

Table.A.2: Polarisation data at varing concentrations (200ppm,400ppm,800ppm and 1000ppm) and at 303K, 313K, 323Kand 333K) temperatures from Tafel plots showing anodic and cathodic slopes, E_{corr} and I_{corr} values.

Concentration of inhibitor	R_{ct} units	C_{dl} units	I.E(%)
Blank	14.325	435.92	-
100 ppm	25.011	95.84	42.72
200 ppm	56.339	75.53	74.57
400 ppm	103.870	49.92	86.21
800 ppm	114.414	20.95	87.47
1000 ppm	154.610	11.78	90.73

Table.A.3: EIS data showing increase in inhibition efficiency(% η) with variation in charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}).