Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(12):149-156
(http://derpharmachemica.com/archive.html)

Corrosion Inhibition of carbon steel by an Isatin Schiff base in acidic medium

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ABSTRACT

The corrosion inhibition effect of Isatin-Aniline (HIAN) Schiff base for carbon steel in 1M HCl was studied by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and monograph techniques. Weight loss was studied for different immersion time with varying concentrations of inhibitor at 25^{0}C. The results obtained from the calculated data showed increasing in inhibition efficiency and surface coverage but decreasing in corrosion rate with increasing inhibitor concentration. HIAN showed maximum inhibition efficiency of 89.7% at 200ppm concentration. This might be due to the adsorption of inhibitor molecule on the surface of metal. Polarization data depicted that with the addition of inhibitor there is reduction in the anodic dissolution and retardation in the cathodic hydrogen evolution of carbon steel which describes it as a mixed type of inhibitor. EIS data revealed the dependence of corrosion process on charge transfer process. Surface morphology was analyzed by metallurgical microscope All these results showed that HIAN as an effective inhibitor for carbon steel with good IE%.

Keywords: Carbon steel, Inhibitor, HCl, EIS, Metallurgical research micrograph.

INTRODUCTION

Acidic solutions such as HCl and H_2SO_4 are normally used in several industrial processes for acid pickling, acid descaling and acid cleaning which causes corrosion attacks. The corrosion of metals has become a major problem in many industries, installation and municipal services such as water and sewage supplies due to excessive use of acids. This problem not only cause increase in the cost, but quality and the efficiency of the plants and that of the products get also decreased. Among several metals, carbon steel is most commonly used as a constructional material in many industries as it is having low cost with excellent mechanical properties. Corrosion of carbon steel is a fundamental academic and serious industrial problem that has acknowledged considerable attention [1]. Various methods have been employed to protect the metals against corrosion attack but the use of corrosion inhibitors is the best practical method for the protection of metal against corrosion especially in acidic media [2, 3]. The most commonly used inhibitors are organic chemicals which contain oxygen, sulphur or nitrogen etc. These are adsorbed most effectively to form a protective layer on metal surface and the adsorption behaviour of these compounds also depends upon molecular structure and size [4 - 6]. Those inhibitors containing heterocyclic compounds with various substituents attached to them and that contains π-bonds are also found to possess good corrosion inhibitive properties by supplying e^- through π-orbital to metals surface [7–12]. There is a special type of interaction present between functional groups, the metal surface and hetero atoms which plays an important role in inhibition due to the free electron pairs located on the hetero atoms [13-16].

Nowadays, studies on nitrogen-containing organic compounds indicates that they show better behaviour for the steel corrosion in hydrochloric acid than sulfuric acid as there exist a synergism inhibition between chloride ion and nitrogen.

Inspite of this the coordination compounds containing important class of ligands in the form of Schiff bases have extensive applications in different fields [17]. Schiff bases are usually condensation product of primary amines and active carbonyl groups. For different hetero atom containing compounds, the condensation products of Isatin have been reported to have good potential for different metals as inhibitors. This behaviour of Isatin derivative has created new ways related to the applicability of such compounds as corrosion inhibitors for carbon steel in aqueous HCl solutions. It was found in research that the inhibition efficiency of Schiff bases is much greater than that of the corresponding amines and aldehydes due to the presence of an –HC=N– group in the molecules [18]. The present work was designed to study the corrosion inhibition of carbon steel in 1 M HCl solutions by a new Isatin Schiff base as corrosion inhibitors and to observe the relation between molecular structure and their inhibitive action in various conditions by using different techniques: weight loss, electrochemical impedance spectroscopy, polarization and monograph techniques.

MATERIALS AND METHODS

2.1 Experimental

2.1.1 Inhibitor

HIAN stock solution was made in 10:1 ratio water: ethanol mixture by volume. Then this solution was used for making different concentrations of inhibitor for experimental use.

2.1.2 Specimens preparation

Before all measurements, the specimens of carbon steel, with composition (wt %) C = 0.19, Mn = 0.26, Si = 0.01, S = 0.017, P = 0.019, Cu=0.01, Cr=0.05. Mo=0.01 and balance Fe, were abraded successively with emery paper of grades (200, 400, 600 and 1000). After this the specimens were washed with bidistilled water, degreased using acetone and finally dried in hot air blower then placed in desiccator for further experimental purpose.

2.1.3 Preparation of solution

1 M HCl was prepared by diluting HCl of analytical-grade (37 %) with bidistilled water then this solution was used further to make desired concentrations of inhibitor.

2.1.4 Weight loss method

Weight loss experiments were performed in the same way as described in [19, 20]. The measurements were done on rectangular specimens having size 3×1 cm^2. Before starting the experiment, the specimens were weighed and then immersed in (50 mL) acidic solution without and with different concentrations of inhibitor for a time periods of 8 hrs and 24 hrs at 25^0C. After the finishing point of the required time period, the specimens were taken out, washed with bidistilled water, cleaned with acetone dried and weighed again. The weight loss values were taken as the difference between the initial weight of test specimens (before immersion) and final weight (after taking out specimen from solution, on completion of required time period). These values were determined using CA 223 Contech precision digital balance with sensitivity of ±1 mg.

The inhibition efficiency (IE %) and surface coverage (θ) were determined by using following equation;

$$(\theta) = \frac{w_0 - w_{inh}}{w_0} \quad (1)$$

$$(IE_{WL}\%) = \frac{w_0 - w_{inh}}{w_0} \times 100 \quad (2)$$

where w_0 and w_{inh} are the weight loss without and with the presence of inhibited solution for carbon steel specimens respectively.

The corrosion rate CR (mmy^{-1}) was calculated by using the relation:

$$CR = \frac{87.6 \times w}{AtD} \quad (3)$$

Where, w is weight loss of carbon steel in (mg), A the area of the coupon (cm^2), t is the exposure time (h) and D the density of mild steel (g cm^{-3}) [21].

2.2 Electrochemical measurements

Electrochemical measurements were carried out in three-electrode cell with a platinum counter electrode (CE), a saturated calomel electrode (SCE) as the reference electrode and carbon steel rod as working electrode having surface area 1.0 cm × 1.0 cm by using AUTOLAB Salartron Model 1280B potentiostat. These electrodes were immersed in 50 ml solution of 1M HCl with and without the presence of inhibitor. Before every measurement the electrode potential was allowed to stand for 25 min at 25^0C to attain a stable value of open circuit potential (OCP) in the test solution and then the experiment proceed further. These specimens were prepared in same way as described previously in weight loss method. All electrolytic solutions were made from an analytical reagent grade HCl and the desired concentrations were made by using bidistilled water.

Electrochemical impedance spectroscopy measurements (EIS) were performed by using system, having frequency range 10 kHz to 0.01Hz with signal amplitude of 10 mV. Different concentrations of the inhibitor were used to study the impedance parameter such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiencies (IE_{EIS} %). The EIS data were controlled by Z-view software.

Tafel curves were obtained by changing the electrode potential from -250 to +250 mV vs. open circuit potential with a scan rate of 1mV/s. The corrosion kinetic parameters such as anodic tafel slope (b_a), cathodic tafel slope (b_c) corrosion potential E_{corr} and corrosion current $I_{corr,}$ data were recorded from instrument and inhibition efficiencies (IE %) were calculated by using the corrosion data.

2.3 Metallurgical research microscopy

This technique was used to study the corroded surface of carbon steel in blank solution and inhibitive layer on surface of specimens with different concentrations of inhibitor and immersion time in 1M HCl. With the help of this technique, percentage porosity (PP), total object (TO), maximum perimeter and area were calculated.

RESULTS AND DISCUSSION

3.1Weight loss measrement

- **Effect of inhibitor concentrations**

The values obtained from weight loss measurement shows increase in inhibition efficiencies (IE), surface coverage (θ) but decrease in corrosion rate with increase in concentrations and immersion time of inhibitor in 1M HCl at 25^{0}C. The calculated data are listed in Table-1**.** and This behaviour could be attributed due to the strong interaction of the compound with metal and resulted in the adsorption of the inhibitor molecules on metal surface [22]. It may also be due to the presence of lone pair of electron on nitrogen atom which it can donate to metal surface to increase adsorption to enhance inhibition. There is an increase in IE% (max. of 89.7% at 200 ppm but slightly decrease of 86.0% at 250 ppm for 24h of immersion time). Figs. (1, 2) are also showing variation in the corrosion rates and inhibition effeciencies with concentration and immersion time. At high concentration of inhibitor, a coherent and compact film is formed on the steel surface which reduces the chances of attack of chemical on metal.

Table-1 Weight loss data for carbon steel in 1M HCl, with and without the presence of inhibitor at different concentrations for different immersion time at 25℃

Time Interval (h)	Conc.(ppm)	Wt.loss (mg)	Surface coverage(θ)	Corrosion rate (CR) (mmy$^{-1)}$	IE_{WL}%
8h	0	79	-	36.68	-
	100	29	0.639	9.28	63.9%
	150	16	0.797	7.43	79.7%
	200	14	0.822	6.50	82.2%
	250	1	0.873	4.64	87.3%
24h	0	186	-	86.37	-
	100	42	0.774	19.50	77.4%
	150	33	0.827	15.32	82.7%
	200	19	0.897	8.82	89.7%
	250	26	0.860	12.07	86.0%

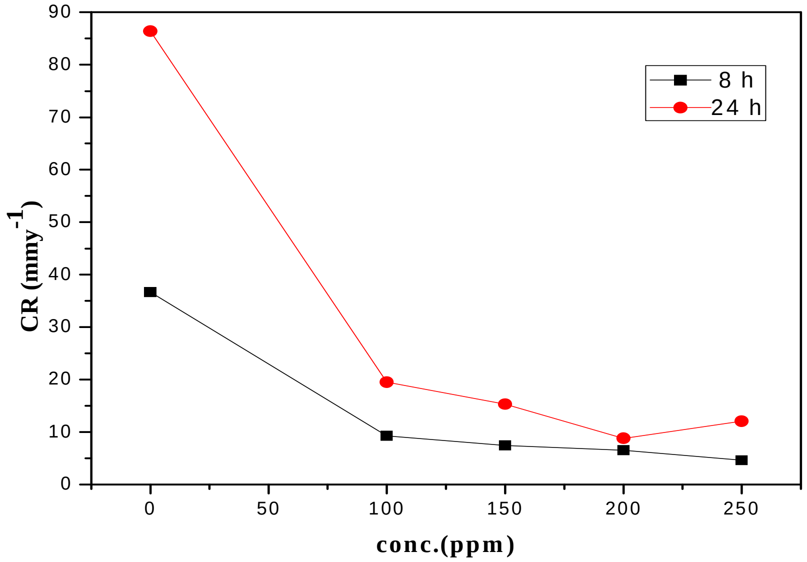


Fig 1: Plot showing effect of concentrations on corrosion rate of inhibitor at immersion time of 8 and 24hrs

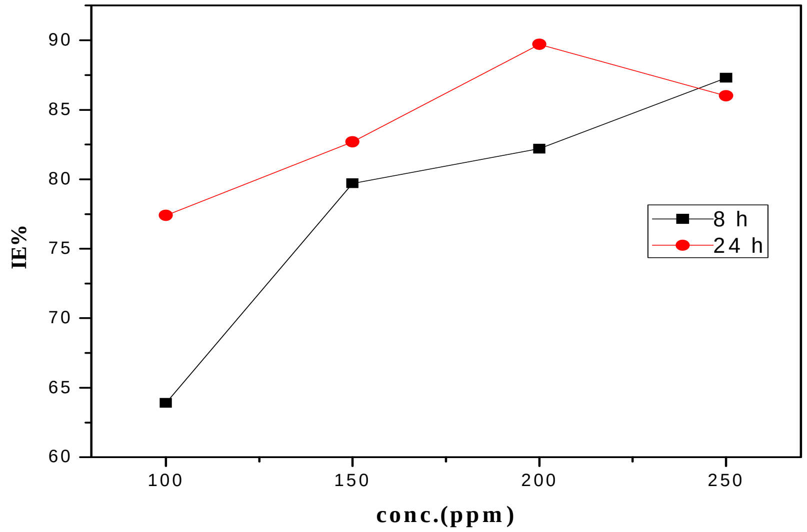


Fig 2: Plot between concentrations and inhibition efficiencies of inhibitors at 25°C different immersion time

3.2 Electrochemical Impedance

EIS measurement helps to explain the corrosion mechanism on the electrode surface. The results obtained by impedance measurements are represented in the form of Nyquist plot i.e Z_{real} part on the X-axis and- Z_{img} part on the Y-axis. The charge transfer resistance values (R_{ct}) were derived from the difference in impedance at lower and higher frequencies [28]. The semicircular curves of Nyquist plot indicates that during dissolution, charge transfer takes place. This shows that corrosion process in 1M HCl solution is controlled by charge transfer process. This is seen from the Fig.3 that with increasing the inhibitor concentrations the shape of curve also increased and it shows that the impedance of carbon steel specimen is significantly changed after the addition of inhibitor. These observations suggest that the inhibitor molecules function by adsorption on the surface of carbon steel. The inhibition efficiency obtained from charge transfer resistance was calculated by using the following expression:

$$IE_{EIS}\% = \frac{R_{ct} - R^{0}{}_{ct}}{R_{ct}} \times 100 \qquad (4)$$

Where, R_{ct} and R^0_{ct} is the charge transfer resistance with and without the different concentrations of inhibitor.

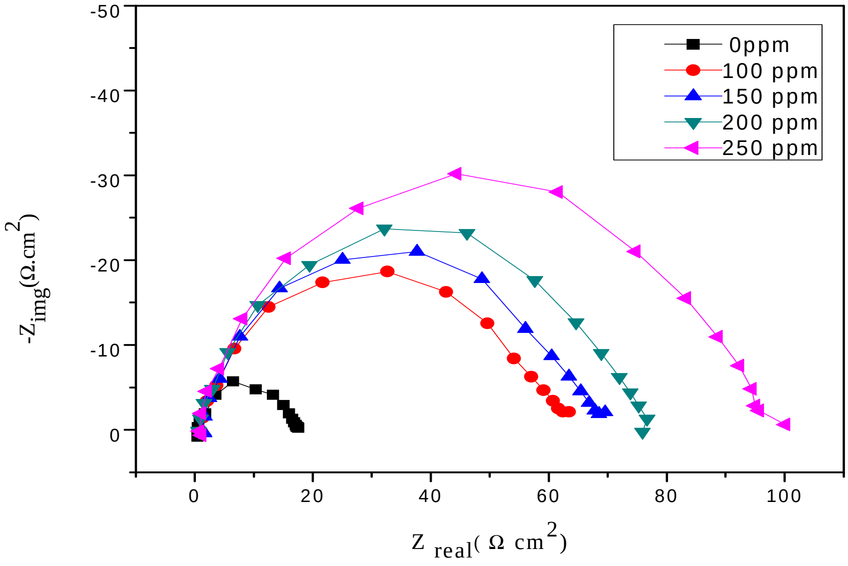


Fig 3: Nyquist impedance diagram for carbon steel samples obtained at 25°C at different concentrations of inhibitor in 1M HCl solution

Results in the Table 2 shows, increase in the values of charge transfer resistance (R_{ct}) with inhibitor concentration but values of double layer capacitance (C_{dl}) decreased with increasing inhibitor concentration. This might be due to increased surface coverage and thickness of electrical double layer which suggest an adsorption of the inhibitor on the surface of carbon steel, as concentration of inhibitor increases. The maximum efficiency was found to be 82.78% in 1M HCl for 250 ppm of inhibitor concentration [29]. The double layer capacitance (C_{dl}) was obtained by applying the following equation:

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

Where, f_{max} is the frequency at maximum imaginary component of impedance and R_{ct} as charge transfer resistances.

Table-2 Electrochemical impedance parameters for carbon steel at different concentrations of inhibitor in 1M HCl at 25℃ obtained by EIS technique

Inhibitor name	Conc. (ppm)	R_{ct} (Ω cm^2)	C_{dl} (μFcm^{-2})	IE_{EIS}%
HIAN (isatin aniline)	0	17.10	313.08	-
	100	64.67	82.73	73.57%
	150	68.62	77.97	75.09%
	200	74.61	71.71	77.09%
	250	99.27	53.90	82.78%

3.3 Potentiodynamic polarization

The effect of HIAN on the cathodic and anodic potentiodynamic polarization curves of carbon steel in 1M HCl is shown in Fig 4. Corrosion kinetic parameters such as corrosion potential E_{corr}, cathodic and anodic tafel slope (b*c* and b*a*) and corrosion current density I_{corr} were obtained by Tafel extrapolation of the cathodic curves to the open circuit corrosion potentials are listed in Table 3. From Fig 4 it was depicted that with the increase in concentration of the inhibitor there is reduction in cathodic and anodic reaction on carbon steel electrode. It clearly shows that with the addition of inhibitor, there is decrease in the anodic dissolution and it also slow down the hydrogen evolution reaction [23].

The corrosion current potential was calculated by using the following equation:

$$I_{corr} = \frac{b_a \times b_c}{2.303(b_a + b_c)} \times \frac{1}{R_p} \qquad (6)$$

Where, b_a , b_c and R_p is the anodic, cathodic tafel slop and polarization resistance.

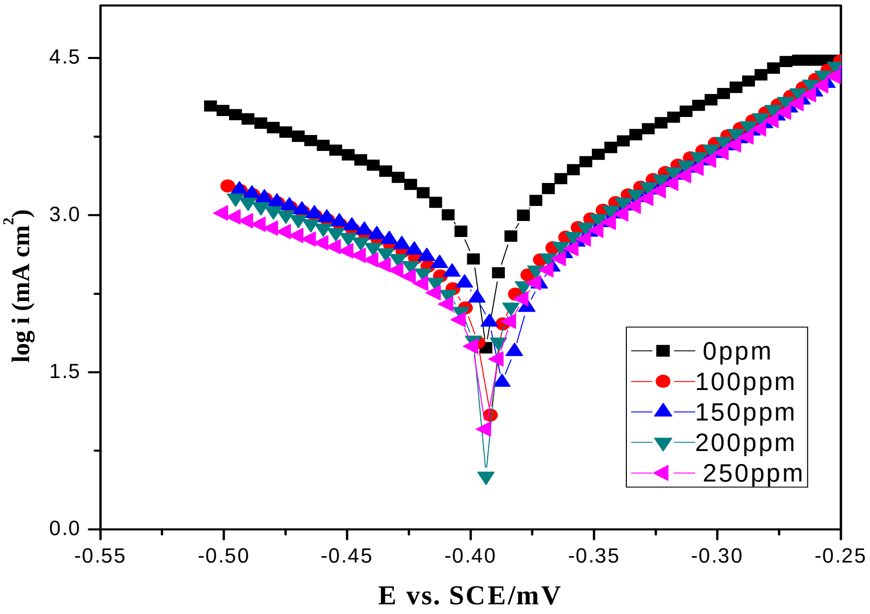


Fig 4: Tafel polarization curves for carbon steel samples obtained at 25°C at different concentration of inhibitor 1.0 M HCl solution

The inhibition efficiencies (IE_p%) of the inhibitor was calculated by the following expression:

$$IE_p\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \quad (7)$$

Where I_{corr} and $I_{corr(inh)}$ are the corrosion current densities of carbon steel without and with inhibitor. Table 3 results show, the decrease in corrosion current density values from 3.36 mA/cm^2 for acid without inhibitor to 1.56 mA/cm^2 for the addition of 250 ppm of HIAN, resulting in 54.76 % of inhibition efficiency. The b_a, b_c and E_{corr}, values do not change significantly with the addition of the inhibitor. This indicates the non-interference of inhibitor in the anodic dissolution or cathodic hydrogen evolution reactions independently suggesting that this inhibitor act as mixed type inhibitor. [24-26].

Table-3 Potentiodynamic polarisation data for carbon steel at different concentrations of inhibitor in 1M HCl solution at 25℃

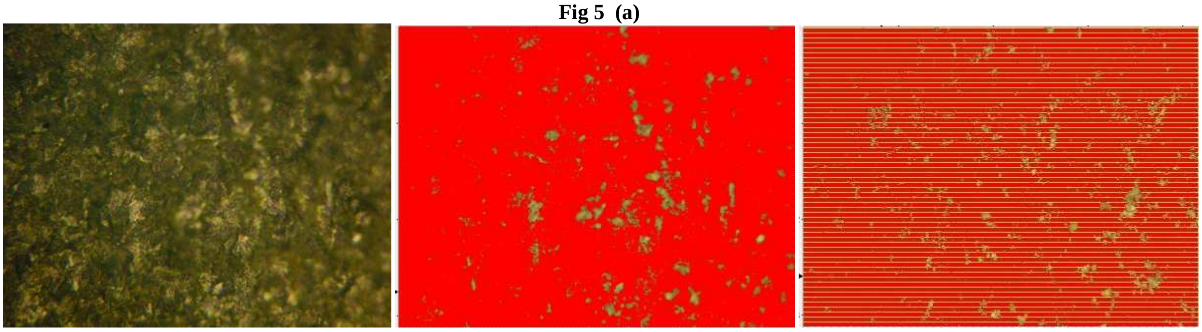
Inhibitor name	Conc. (ppm)	b_c mV dec^{-1}	b_a mV dec^{-1}	$-E_{corr}$ (mV vs. SCE)	I_{corr},(μA cm^{-2})	IE_P%
HIAN (Isatin aniline)	0	617	622	391	3.36	-
	100	597	494	399	2.53	24.17%
	150	416	482	396	1.98	41.07%
	200	320	496	410	1.59	52.67%
	250	387	445	406	1.52	54.76%

In [27] Riggs says (i) $-E_{corr}$ > 85mV then the inhibitor can be considered as anodic or cathodic type inhibitor, if (ii) $-E_{corr}$ < 85mV then the inhibitor will act as mixed type inhibitor. In the present study, maximum displacement in the value of ($-E_{corr}$) recorded is 19 mV which also clarifies it as a mixed type inhibitor.

3.4 Metallurgical Research Microscopy

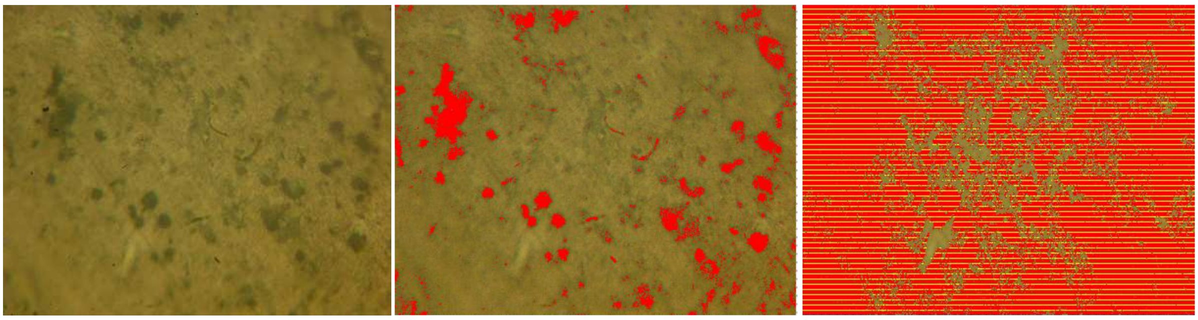
Study of surface morphology was carried out using specimens; obtained by weight loss experiment in 1M HCl and with different concentration of inhibitor for a time period of 24 hrs at 25℃. In Fig 5(a, b, c) the blank specimen is having a no. of cracks and pits can be seen but with increase in concentration the specimen surface becomes more clear and smooth. Table 4 shows a comparative study of porosity and surface morphology. Here pore% and total object gives idea about the roughness of the surface on other side maximum perimeter and maximum area give information about size and depth of pores on carbon steel surface. In Table 4 all the parameters are found to decrease with concentration. For blank specimen in weight loss test 4175.2692 pores cover 828961.218 micron area due to corrosion by which 99.81% surface becomes pores while by addition of inhibitor no. of pores and area decreases and only 1.64% surface remained porous for 250 ppm concentration.

Fig 5 (a)



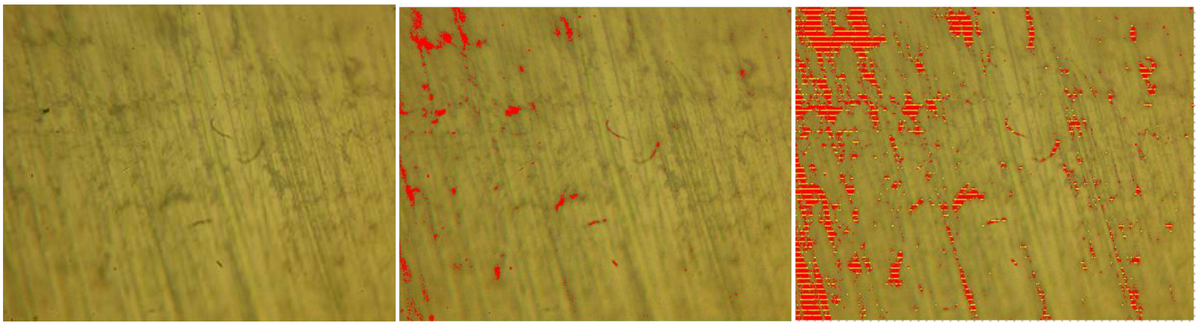
0ppm blank **porosity %** **thickness coating**

(b)



150ppm **porosity%** **thickness coating**

(c)



250ppm **porosity%** **thickness coating**

Fig 5 (a,b,c): Metllurgical surface morphological pictures of carbon steel specimens taken out from test solutions containing different concentration of inhibitor solutions in 24hrs of immersion time

Table-4 Surface morphological studied parameters showing values of coating thickness(CT), total object (TO) and percentage porosity (PP)

Conc.(ppm)	Maximum perimeter (micron)	Maximum area (micron)	Coating thickness Maximum Thickness	Average Thickness	Total object	Pore%
0	4175.269	828961.218	792.105	84.822	925	99.81
150	1210.850	10934.903	286.892	23.437	757	7.34
250	326.663	1301.9391	89.474	8.302	272	1.64

CONCLUSION

Inhibition effect of HIAN was examined by weight loss technique confirms it as a good corrosion inhibitor. It showed regular trends i.e increase in inhibition efficiency and decrease in corrosion rate with increase in concentration and found to exhibit maximum inhibition efficiency of 89.7% at 200 ppm for 24h of immersion time at 25°C. Potentiodynamic polarization technique indicates that the inhibitor acts as mixed type of inhibitor. Polarisation IE results are not in good agreement with weight loss results due to difference in immersion time. EIS technique depicts that charge transfer takes place during corrosion process and adsorption occurred. Metallurgical surface pictures showed decrease in all corrosion parameters and surface becomes more clear and smooth with increase in concentrations.

Acknowledgement
Authors are thankful to the Dept. of Chemistry M.D.U. Rohtak and Dept. of Chemistry C.D.L.U for providing the facilities related to research work.

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