Experimental Investigation of Isatin Schiff base as Corrosion Inhibitor for Carbon Steel in 1MHCl

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ABSTRACT

The inhibition efficiency of Isatin(1-H-indol-2,3-dione) 2-aminothiophenol (H_2IATP) Schiff base as a corrosion inhibitor for carbon steel in 1M HCl solution was investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Weight loss measurements were done by taking different immersion time for various concentrations (50-300ppm) of inhibitor at temperature of 298K. The observed results showed increase in inhibition efficiency (IE %), surface coverage (θ) but decrease in corrosion rate (CR) with increase in the concentrations of the inhibitor. Inhibitor found to exhibit maximum inhibition efficiency of 97.35% at an optimum concentration of 250ppm for 24hrs of immersion time. Langmuir adsorption isotherm was obeyed by the inhibitor. Thermodynamic parameters regulating the adsorption process were calculated and adsorption depicted to be physical in nature. Polarization measurements data confirms the inhibitor as mixed type in nature. EIS data revealed the dependence of corrosion process on charge transfer process.

Keywords : Carbon Steel, HCl, Corrosion Inhibitor, Electrochemical Impedance, Adsorption Isotherm.

I. INTRODUCTION

Acidic solutions are predominantly used in industrial processes to remove unwanted scales and rust. Out of various acids, hydrochloric acids and sulphuric acids are commonly used for regular processes as aggressive solutions due to their special chemical properties. But acidic effect of these acids causes corrosive attacks on metallic materials.

Corrosion is a thermodynamic feasible process and leads to decrease in Gibbs free energy.

So the use of inhibitors is one of the corrective measure and most economical method to protect the useful properties of metals [1-4]. Some organic compounds are found with good inhibitive properties in acidic media [5-11]. Compounds containing nitrogen, sulphur, phosphorous and oxygen have also been reported in literature as proficient inhibitors

[12-14]. But the most effective and efficient inhibitors are those containing π-bonds in addition of lone pairs on heteroatom in their structure which allows the compound to get adsorbed on the metal surface [15-18]. In adsorption process, inhibitor decreases the corrosion rate by formation of barrier film and blocking the active sites on metal surface by displacements of water molecule and finally leads to adsorption of compounds.

Nitrogen containing compounds as corrosion inhibitors, have been studied by many authors as benzimidazole and imidazole derivative [19-29], bipyrazole [30], stilbazole [31] etc. The adsorption of N-heterocyclic inhibitors occurs through nitrogen, unshaired bonds or aromatic rings in the molecular structure. Generally, the number of aromatic ring systems and availability of electronegative atoms in

the molecule found to increase the inhibitors efficiency [32-33].

But the main problem associated with the inhibitors is that, they are toxic and expensive in nature. So it becomes prime concern to study non toxic and eco-friendly corrosion inhibitors having low or zero environmental impacts.

This paper reports the effect of Isatin Schiff base as an eco- friendly corrosion inhibitor on carbon steel surface in 1M HCl solution using different techniques like weight loss, potentiodynamic polarization and electrochemical impedance measurements. Adsorption isotherm was tested to describe adsorption behaviour of inhibitor on metal surface.

II. METHODS AND MATERIAL

Sample and solution preparation

Carbon steel sheets were used for corrosion study as test material. It was supplied in the form of metal sheet plates with following composition(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). Sheets were cut in rectangular form in 3×1 cm dimensions, mechanically polished with different grades emery papers, washed with distilled water, degreased in acetone, dried in hot air blower and finally placed in desiccator. Acidic media was prepared using concentrated HCl of analytical grade 37% and diluted it to 1M HCl solution with double distilled water to make various concentrations of inhibitor.
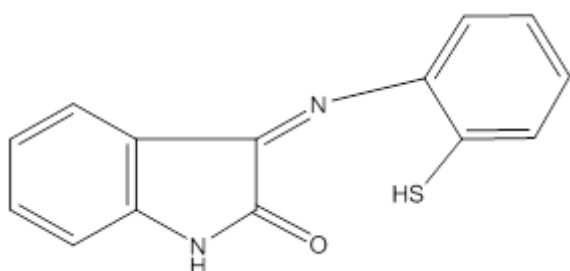
Inhibitor Structure

Figure 1. H_2IATP

Inhibitor solution

Stock solution of inhibitor was prepared in the ratio 10: 1 in water: ethanol mixture by volume; to ensure solubility by using 1M HCl solution.

Weight Loss Measurements

Weight loss measurements were performed in air thermostat as described elsewhere [34]. Before experiment starts; initial weight of samples were taken and the samples then placed in 50mL test solution for 4, 8, 16 and 24hrs of immersion time in blank and various concentrations of inhibitor. Temperature of 298K was controlled thermostatically. After elapsed time, samples were taken out, washed with double distilled water followed by acetone, dried and then again weighed. The weight difference of samples (initially and finally weighed) was taken as weight loss. All the tests were conducted in aerated 1 M HCl solution, performed in triplicate and average values were recorded. From weight loss values; the surface coverage, inhibition efficiency and corrosion rates of inhibitor for carbon steel were calculated by using the following equations:

$$(\theta) = \frac{W_0 - W_i}{W_0} \tag{1}$$

$$(IE\%) = \frac{W_0 - W_i}{W_0} \times 100 \tag{2}$$

where W_i and W_0 stand for the carbon steel coupon in presence and absence of inhibitor respectively.

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

$$(CR) = \frac{87.6 \times \Delta w \times 10^3}{AtD} \tag{3}$$

where Δw is the weight loss of the carbon steel samples (gm), A is area of the sample (cm^2), t is exposure time (h) and D is the density 7.68(g cm^{-2}) [35].

Electrochemical measurements

Electrochemical experiments were performed in conventional three electrode cell assembled as; platinum auxiliary counter electrode (CE), a saturated

AgCl/AgCl$_{sat}$ electrode (SCE); as reference electrode and carbon steel samples; as a working electrode. Rectangular shaped samples were used with 5cm long stem, 1×1cm exposed surface area and remained portion polished with epoxy resins. Firstly samples were abraded with emery papers of (100-1000 mesh grades), washed with double distilled water, degreased with acetone and then dried in hot air. After this, the working electrode was immersed in test solution at its corrosion potential for 30 minutes to attain a stable value of open circuit potential (OCP) at room temperature $25 \pm 2\,^0$C. All measurements were performed in 1M HCl solution in blank and inhibited solutions in the concentration range (50, 100, 150, 200 and 300ppm).

Electrochemical impedance spectroscopy

EIS measurements were carried out in blank and in inhibited test solution of various concentrations at room temperature using computerized AUTOLAB Salartron Model 1280B potentiostat at open circuit potential. Experiments were carried out in frequency range of 10 kHz to 0.01 Hz with signal amplitude of 10 mV at the corrosion potential. The experimental measurements were automatically controlled by Z-view software and impedance figures were presented in the form of Nyquist plots (Z$_{real}$ vs. Z$_{img}$) and Bode plots. Data from Z-view software was used to calculate charge transfer resistance (R$_{ct}$) and double layer capacitance (C$_{dl}$). Inhibition efficiencies were calculated by the equation;

$$IE_{EIS}\% = \left(1 - \frac{R^0_{ct}}{R_{ct}}\right) \qquad (4)$$

Where, R$^0_{ct}$ and R$_{ct}$ are the charge transfer resistance in absence and in presence of different concentrations of inhibitor.

Tafel polarization

Same instrument was used for polarization measurements with a scan rate of 1mV/s. Polarization curves were obtained by changing electrode potential from -250 to + 250mV (SCE vs. OCP). Different corrosion kinetic parameters were derived from the Tafel polarization curve.

Inhibition efficiencies were calculated, using the following equation:

$$IE_{PP}\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \qquad (5)$$

Where, I$_{corr}$ and I$_{corr(inh)}$ are the corrosion current densities for carbon steel in their respective blank and inhibited solution of acid.

III. RESULTS AND DISCUSSION

Weight Loss study
Effect of inhibitor concentration

Weight loss measurement deals with the study of inhibition efficiency and corrosion rates with different concentrations of inhibitor for various time periods at 298K temperature. The calculated values of different weight loss parameters like corrosion rates (CR), inhibition efficiency (IE %) and surface coverage (θ) for immersion period of 4, 8, 16 and 24 hrs at 298 K of temperature are shown in table I.

It is noticed in table1 that corrosion rate (CR) decreases but inhibition efficiency (IE %) and surface coverage (θ) values increases with increase in concentration of inhibitor at fixed temperature. The increase in inhibition efficiency reaches a maximum value of 97.35% at concentration of 250ppm for 24hrs of immersion period. Beyond this concentration the efficiency decreased from 97.35% to 95.36%. It clears that the optimum concentration for maximum inhibition efficiency is 250 ppm.

Corrosion and inhibition efficiency curves in fig.2 (A, B) also support the data listed in the table I. The increase in inhibition efficiency may be due to the adsorption and high bonding ability of inhibitor molecules on carbon steel surface through non-bonding electron pairs on sulphur, oxygen and nitrogen and also through the p-electrons of aromatic ring. Similar fact has been reported [36].
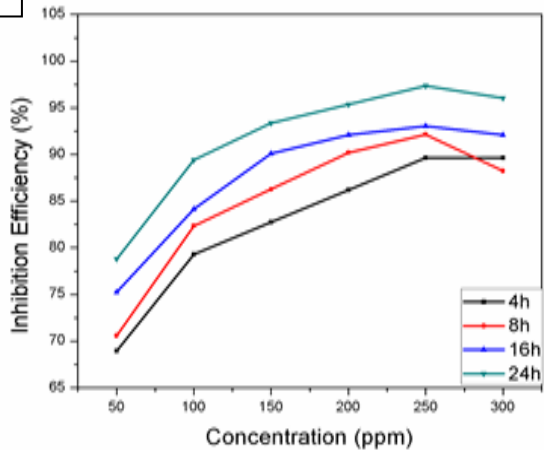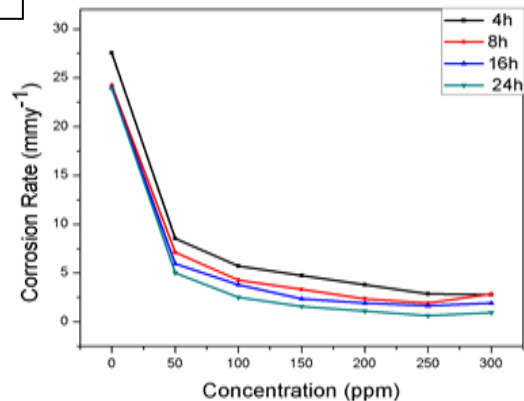
Figure 2. (A) Variation in inhibition efficiency (IE %) and (B) Corrosion rate (CR) of carbon steel in blank and different concentrations of inhibitor, for different immersion time at 298K.

Effect of immersion time

In order to judge the firmness of inhibitive layer on carbon steel surface, the effect of immersion time of test specimen has also been studied from 4hrs to 24 hrs in absence and presence of inhibitor with different concentration in 1M HCl solution at 298 K. Results in the table I reveals that inhibition efficiency increases from 89.65% for 4hrs to 97.35% for 24hrs at 250ppm of concentration. This clears that the surface of metal may be more or less completely covered by the inhibitive layer of inhibitor molecules thereby indicating enhancement in quality of inhibitive film with time [37].

Table 1. Weight loss parameter for carbon steel in 1M HCl solution in different concentrations of H_2IATP for different immersion time at a temperature of 298K.

Time period	Concentration (ppm)	Initial weight (gm)	Final weight (gm)	Weight loss (gm)	Corrosion Rate (C_R) (mmy^{-1})	Inhibition Efficiency(IE%)	Surface coverage (θ)
4h	0	1.090	1.061	0.029	27.56	-	-
	50	1.106	1.097	0.009	08.55	68.96	0.68
	100	1.101	1.095	0.006	05.70	79.31	0.79
	150	1.118	1.113	0.005	04.75	82.75	0.82
	200	1.104	1.100	0.004	03.80	86.20	0.86
	250	1.083	1.080	0.003	02.85	89.65	0.89
	300	1.083	1.079	0.003	02.80	89.65	0.89
8h	0	1.094	1.043	0.051	24.23	-	-
	50	1.109	1.094	0.015	07.12	70.58	0.70
	100	1.095	1.086	0.009	04.27	82.35	0.82
	150	1.108	1.101	0.007	03.32	86.27	0.86
	200	1.076	1.071	0.005	02.37	90.19	0.90
	250	1.106	1.102	0.004	01.90	92.15	0.92

	300	1.067	1.061	0.006	02.85	88.23	0.88
	0	1.086	0.985	0.101	24.00	-	-
	50	1.069	1.044	0.025	05.94	75.24	0.75
	100	1.101	1.085	0.016	03.80	84.15	0.84
16h	150	1.089	1.079	0.010	02.37	90.09	0.90
	200	1.096	1.088	0.008	01.90	92.07	0.92
	250	1.079	1.072	0.007	01.66	93.06	0.93
	300	1.089	1.081	0.008	01.90	92.07	0.92
	0	1.067	0.916	0.151	23.92	-	-
	50	1.084	1.052	0.032	05.0	78.80	0.78
	100	1.077	1.061	0.016	02.53	89.40	0.89
24h	150	1.102	1.092	0.010	01.58	93.37	0.93
	200	1.094	1.087	0.007	01.10	95.36	0.95
	250	1.116	1.112	0.004	0.63	97.35	0.97
	300	1.094	1.088	0.006	0.95	96.02	0.96

Decreasing trend of corrosion rate with time can also be noticed. It may be due to the lacking of sufficient amount of hydrogen ions in acidic solution which is being liberated without replacement, leaving the system with deficiency of major component (hydrogen ions). This decreases the rate of the oxidation of the carbon steel thereby increasing the efficiency of the inhibitor.

Electrochemical impedance spectroscopy

EIS technique is generally used in corrosion research to explain the mechanisms and adsorption process on metal/solution interface [38, 39].

Table 2. Electrochemical impedance parameters of carbon steel in blank and in various concentrations of H_2IATP as an inhibitor at room temperature in 1M HCl solution.

Concentration of H_2IATP (ppm)	R_{ct} ($\Omega.cm^2$)	C_{dl} ($\mu F/cm^2$)	Inhibition efficiency ($IE_{EIS}\%$)
0	15.90	86.96	-
50	45.11	30.65	64.75
100	77.24	17.90	79.41
150	77.80	17.77	79.56
200	95.33	14.50	83.31
250	150.99	9.15	89.46
300	126.02	10.97	87.36

The corresponding data obtained through EIS measurements, performed both in absence and in presence of various concentrations of inhibitor is summarized in table II. The values of R_{ct}, C_{dl} and $IE_{EIS}\%$ for C-steel in 1M HCl solution in absence and in presence of inhibitor shows increase in charge

transfer resistance and percentage inhibition efficiency but decrease in double layer capacitance with increase in concentration. Results in table points towards modified electrical double-layer structure, suggesting the adsorption of Schiff base molecules at the metal/solution interface.

Cdl values were calculated using the equation:

$$C_{dl} = \frac{1}{2\pi f_{max}} \times \frac{1}{R_{ct}} \qquad (6)$$

Where, f_{max} is frequency and $\pi = 3.14$. The inhibition frequency (IE %) from impedance measurements data was calculated by equation (4).

The double layer between the charged metal surface and the solution is considered as an electrical capacitor. This decrease in C_{dl} values happen when the inhibitor molecules (low dielectric constant) replace the adsorbed water molecules (high dielectric constant) on the carbon steel surface. As capacitance is inversely proportional to double layer thickness so decrease in C_{dl} could be attributed to increase in the thickness of electrical double layer on carbon steel surface [40]. On the other hand increase in R_{ct} values suggests the gradual replacement of water molecules from the metal surface by the inhibitor molecules thereby decreasing the number of active sites responsible for corrosion process.

The concentrations effect of Schiff base on impedance behaviour of carbon steel in 1M HCl solution at room temperature were tested and shown by Nyquist, Bode and Phase plot obtained at open circuit potential are represented in figure 3., figure 4. and figure 5. respectively.

It is evident from the plot that impedance response for carbon steel changed from inhibitor free solution to the inhibited solution with increasing concentrations. It is apparent from fig 3. that a depressed semicircle loop is obtained for all impedance spectra at high frequency, which

corresponds to the time constant of the charge transfer and double- layer capacitance [41, 42].

The corrosion of carbon steel is mainly controlled by charge transfer process. Addition of inhibitor does not cause significant change in the shape of Nyquist plot but diameter of the semicircle increases with increase in inhibitors concentration and indicates the formation of protective layer against corrosive attack of solution [43, 44].
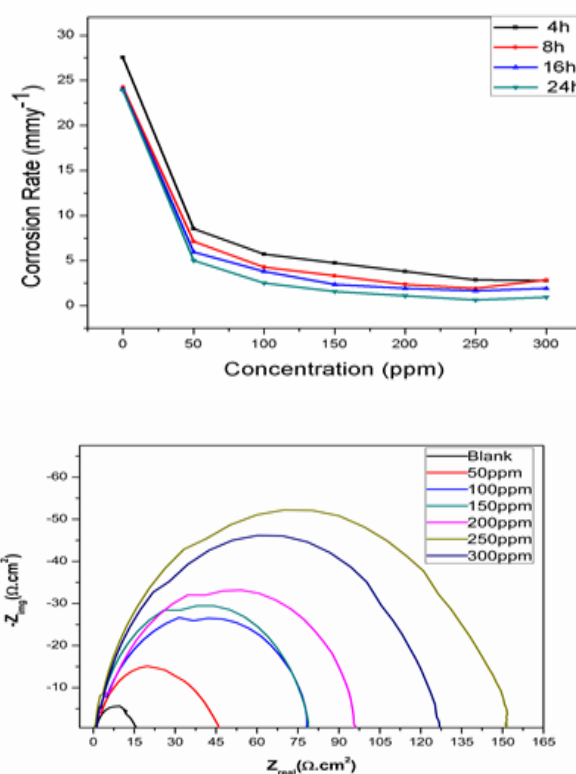

Figure 3. Nyquist plots of carbon steel in blank and in presence of various concentrations of H2IATP as an inhibitor, at room temperature in 1M HCl solution.
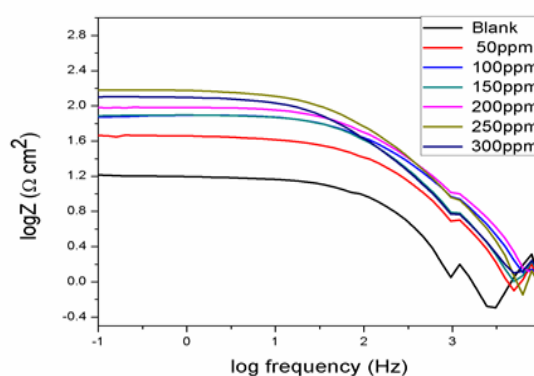
Figure 4. Bode plots of carbon steel in blank and in presence of various concentrations of H2IATP as an inhibitor, at room temperature in 1M HCl solution.
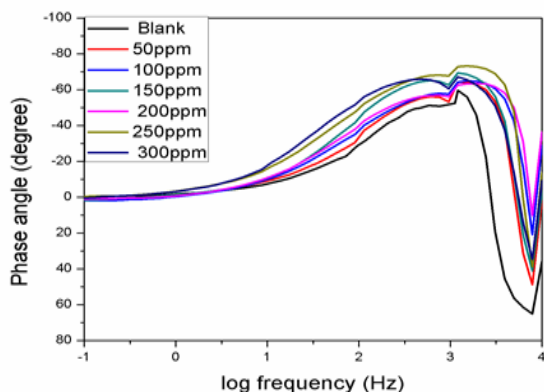

Figure 5. Phase plots of carbon steel between Phase angle vs log frequency (Hz) in blank and in presence of various concentrations of H2IATP as an inhibitor, at room temperature in 1M HCl solution.

Some irregularity in perfect circular shape of semicircle imply frequency dispersion of interfacial impedance, arises due to roughness and heterogeneity of electrode surface [45, 46]. In fig 5, the phase angle shows one time constant for all concentrations of inhibitor. Increase in phase angle suggest improved adsorption property due to surface coverage of carbon steel by Schiff base molecules and formation of high quality protective layer. The increase in impedance at low frequencies in Bode plot depicts the higher protection through the adsorption of inhibitor on metal surface with increase in the concentration of the inhibitor [47].

Potentiodynamic polarization measurements

Potentiodynamic polarization measurements for corrosion of carbon steel in 1M HCl solution in absence and presence of different concentrations of Isatin- 2 aminothiophenol inhibitor were carried out at room temperature. The polarization curves are shown in fig.6 that shows cathodic and anodic behavior of the Schiff base. Various corrosion kinetic parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) are listed in table III that are obtained from the experimental studies.

Table 3. Potentiodynamic polarization kinetic parameters of carbon steel using H2IATP inhibitor in 1MHCl solution at room temperature.

Inhibitor name	Concentration (ppm)	β_a mV dec^{-1}	β_c mV dec^{-1}	$-E_{corr}$ (mV vs SCE)	I_{corr} (μA.cm^{-2})	IE_{pp} %
	0	574	619	-453	4.26	–
Isatin o-	50	513	466	-484	1.83	57.04
aminothiophenol	100	432	528	-479	1.35	68.30
(H2IATP)	150	499	392	-487	1.13	73.47
	200	493	368	-476	0.87	79.57
	250	474	372	-497	0.63	85.21
	300	359	433	-491	0.71	83.33

The results analyzed from table III. illustrated that inhibitor's concentration affect anodic and cathodic current density (i_{corr}) and values goes down on increasing the inhibitor concentration in 1M HCl solution. The I_{corr} values in this table showed decreases from 4.26 μAcm^{-2} to 0.63 μA.cm^{-2} for 250 ppm of inhibitor concentration thereby suggesting that metal surface get covered with a protective layer of inhibitors molecules and prevent corrosion by blocking the active sites [48, 49].

The inhibitor showed maximum inhibition efficiency of 85.21% at 250ppm. The corrosion current potential was calculated by using the following equation:

$$I_{corr} = \frac{b_a \times b_c}{2.303(b_a + b_c)} \times \frac{1}{R_p} \qquad (7)$$

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

Analysis of results suggests that addition of the inhibitor in acidic solution reduces the anodic reaction of metal dissolution and also cathodic reaction i.e. retards the hydrogen evolution reaction [50, 51].
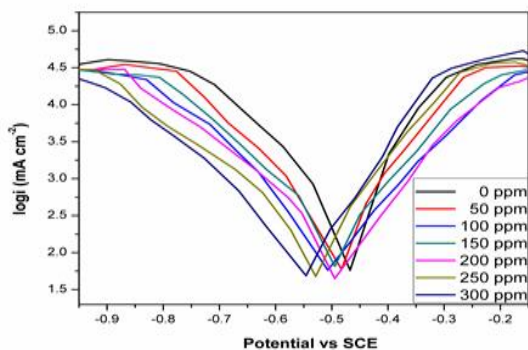

Figure 6. Polarization curves of carbon steel in absence and presence of different concentrations of inhibitor at room temperature.

Change is recorded in (E_{corr}) towards more negative value and (I_{corr}) values also found to decreases with increase in concentration; indicating the inhibitor as an effective mixed type, inhibitor.

If the shift in E_{corr} values is more than 85 mV in the presence of corrosion inhibitor, the compound is considered as anodic type and if an E_{corr} value is lower than 85 mV, the inhibitor is cathodic type [52]. Here the shift in corrosion potential is of (40.00mV) which evaluated the inhibitor as mixed type inhibitor.

Adsorption isotherm

To study the direct relationship of inhibition efficiency and surface coverage (θ) for different concentrations of inhibitor, it is a common practice to fit the rate data in equilibrium adsorption expressions like Langmuir equation. So the interaction of carbon steel surface with various concentrations of H$_2$IATP in 1M HCl solution and different immersion time periods is described by adsorption isotherm. Adsorption on metal surface depends on the chemical composition of the molecule, temperature and electrochemical potential at metal/solution interface. To obtain the adsorption isotherm linear relationship of surface coverage (θ) with inhibitor concentration (C) should be considered. Among the various isotherms the Langmuir isotherm was found to be best graphically fitted adsorption isotherm for studied inhibitor. This equation has also been used for other inhibitor systems [53]

The Langmuir isotherm can be represented as where θ is related to C:

$$\frac{\theta}{1-\theta} = KC_{inh} \qquad (8)$$

on rearrangement it gives,

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (9)$$

Where,
θ = degree of surface coverage, C_{inh} = inhibitor concentration and K_{ads} = equilibrium constant.

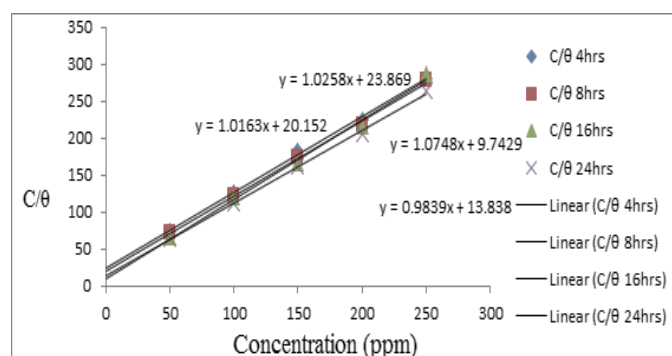The straight line plot of C/θ vs. C is shown in figure 7.

Figure 7. Langmuir adsorption plots for carbon steel in 1M HCl for different immersion time.

Results for 4, 8 and 16 immersion time shows slope line values equal to 1.025, 1.016 and 1.074 respectively. The values are close to unity and this deviation can be understood by considering the type of interaction among adsorbed molecules. Whereas for 24hrs of immersion time, slope line value is equal to 0.983 which somewhat deviate from unity showing interaction and repulsion between adsorbed molecules and indicates that the Langmuir adsorption isotherm is being obeyed. The intercepts of slope line helps in calculating the equilibrium constant which

in turn used to calculate the standard Gibbs free energy by using the equation:

$$\text{Van'th off equation} = \frac{1}{55.5} \exp\left(\frac{\Delta G_{ads}}{RT}\right) \quad (10)$$

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

Table 4. Thermodynamic parameters for adsorption of H_2IATP on carbon steel surface for different immersion time at 298 K.

Inhibitor name	Immersion time	Log 55.5k	ΔG^0_{ads} /kJ mol^{-1}
Isatin o-aminothiophenol (H_2IATP)	4hrs	4.75	-27.13
	8hrs	4.82	-27.55
	16hrs	5.14	-29.35
	24hrs	4.99	-28.48

The calculated values of K_{ads} and ΔG^0_{ads} are listed in table IV. The high values of $K_{ads\,s}$ of the inhibitor show stronger interaction or adsorption of inhibitor molecules on carbon steel surface for different immersion periods in 1M HCl solution. If K_{ads} value (>100 M1), the adsorbed inhibitor layer will be more stable and higher the inhibition efficiency.

The K_{ads} data support H_2IATP as a good corrosion inhibitor for carbon steel in acidic medium.

The negative value of ΔG^0_{ads} obtained through using equation points to the spontaneity of the reaction and stability of the adsorbed inhibitor layer. The ΔG^0_{ads} of about -20 kJmol^{-1} or less negative is regarded as physisorption which depends upon interaction between charged inhibitor molecules and charged metal surface. If the value is around -40 kJ mol^{-1} or more negative then it is associated with chemisorptions which shows charge sharing or

transfer between inhibitor molecules and metal surface through coordinate bond [54]

Here, in the current study the values obtained of ΔG^0_{ads} are in the range between -27.13 kJ mol^{-1} to -29.35 kJ mol^{-1} suggesting the adsorption mechanism to be combination of both physisorption and chemisorptions on the surface of carbon steel. But predominantly physisorption contributes more towards the adsorption process. All negative values of ΔG^0_{ads} implying the adsorption of the inhibitor on the surface of carbon steel in 1M HCl solution as a spontaneous process.

SEM Study

Surface morphology of carbon steel specimens was analyzed by using SEM technique. This technique was chosen in order to support our results. SEM images of carbon steel specimens in 1M HCl and in presence of inhibitor in 250ppm of concentration at temperature of 298K was taken after immersion period of 24h and is shown in Figure 8.
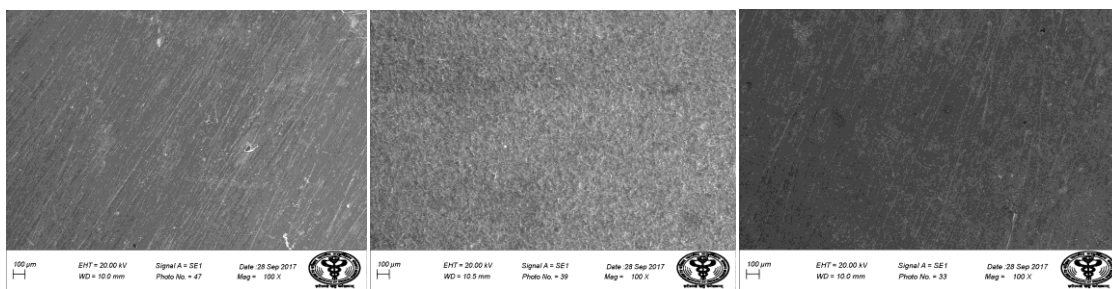
Figure 8. SEM images of carbon steel samples after 24h of immersion period (a) before corrosion (b) in 1M HCl and in (c) with 250ppm of H₂IATP.

It can be seen in Figure 8(a) that the surface is smooth and uniform before corrosion process but in image (b) it gets somewhat damaged showing pits. In (c) rate of corrosion is suppressed and the specimen of carbon steel immersed in inhibitor solution is in better condition than in acidic solution.

IV. CONCLUSION

1. Isatin-2 aminothiophenol performs like a good inhibitor for carbon steel in 1 M HCl solution at 298 K.
2. Weight loss parameters shows increase in inhibition efficiency and decrease in corrosion rates with concentration and immersion times at 298 K.
3. Potentiodynamic curves exhibits depression in anodic and cathodic processes which reveals inhibitor as mixed type.
4. Inhibitor obeys Langmuir adsorption isotherm and thermodynamic parameter shows that inhibitor adsorb through physisorption.
5. SEM study shows that corrosion inhibition is due to adsorption of H₂IATP at carbon steel/ acid solution interface.

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