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Isatin Schiff Base as an Ecofriendly Corrosion Inhibitor for Carbon Steel in 1M HCl

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ABSTRACT

The corrosion inhibition effect of Isatin (1-H-indol-2,3-dione)-p-toluidine (HIPT) Schiff base as an inhibitor on carbon steel in 1M HCl was studied by weight loss, potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) techniques. Weight loss was studied for different immersion time at different concentrations (50-250 ppm) of inhibitor in temperature range 25°C-45°C. The results showed increase in inhibition efficiency, surface coverage but decrease in corrosion rate with the successive increase in the concentration of the inhibitor. HIPT showed maximum inhibition efficiency of 87.94% in 250 ppm concentration. Adsorption of this inhibitor found to obey Langmuir adsorption isotherm. Thermodynamic data indicates the adsorption process to be physical in nature. Polarization data depict inhibitor as mixed type in nature. EIS data revealed the dependence of corrosion process on charge transfer process.

Keywords: Carbon steel, HCl, Inhibitor, Electrochemical impedance

INTRODUCTION

It is commonly noticeable fact that carbon steel is widely used as a constructional material for various industrial applications due to its high mechanical properties and low cost. Several corrosion problems comes into existence by the excessive use of hydrochloric acid in pickling, rescaling and cleaning function on carbon steel surface [1]. Corrosion is an electrochemical process that leads to the flow of electric current in acidic media which results in metal loss. So protection of metal loss of steel metal equipment's used in industries against corrosion is the main concern for the engineers.

Keeping in mind the metal corrosion problem, this created opportunity to work in corrosion field. For many researchers the use of corrosion inhibitor becomes a forefront to protect the metal from corrosion as they have considerable applicability in reducing metallic waste and also in decreasing the threat of material failure [2-5].

The effectiveness of inhibitor depends upon the interaction, adsorption of molecules and ions on metal surface [6]. Organic compounds are found with good corrosion inhibitive properties and reported to act via adsorption on metal surface. The adsorption of inhibitors occurs through the presence of heteroatoms such as nitrogen, oxygen, phosphorus and sulfur. The inhibition efficiency of these heteroatom's have been reported to follow the sequence O<N<S<P [7].

The mode of adsorption generally influenced by some factors such as: The steric factor and aromaticity, availability of π bonds and lone pairs to facilitate the interaction with the vacant d-orbital of metal atom, the presence of functional group such as -CHO, -N=N, R-OH, etc., [8-11]. In earlier studies [12] it has been reported that in heterocyclic nitrogen containing organic compounds, the inhibition efficiency was found to increase with the number of aromatic systems and the availability of electronegative atoms in the molecule.

Now days, the condensation products of aldehydes or ketones with amines i.e., Schiff base have been reported with good inhibitive properties. These are the important class of ligands in co-ordination chemistry [13]. This ability is due to the presence of C=N groups [14,15].

Schiff bases become effective by adsorption on the metal/solution surface and protect it from the hazardous effect of acidic media. It is noted that with increase in inhibition efficiency, the interfacial bonding becomes stronger that's why it is quick desire to elevate corrosion inhibitor. Based on this, some efforts have been directed to predict interactions through theoretical modeling [16-20]. Interactions can be of type, electrostatic attraction between charged metal and charged inhibitor molecule, dipole-type interaction b/w inhibitors and metals and unshared electron pairs π -electron interaction.

The aim of the present work is to investigate the inhibitive properties of isatin Schiff base on carbon steel by gravimetric and electrochemical techniques such as potentiodynamic polarization and impedance measurements in 1M HCl by taking different temperatures and immersion time. Adsorption isotherms were tested to describe the adsorption behaviour of the investigated Schiff base.

EXPERIMENTAL SECTION

Materials and solutions

Carbon steel sheet was taken as test material for corrosion studies. It was supplied in the form of metal sheets with 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). 1.0 M HCl was taken for solution preparation which was prepared by using analytical grade HCl (37%) in distilled water. Stock solution of isatin Schiff base as inhibitor was prepared in the ratio 10:1 in Water: Ethanol mixture by volume to ensure solubility. This stock solution was used for preparing all the required concentration in 1.0 M HCl.

Specimen's preparation

To prepare specimens, carbon steel sheet was cut into rectangular size with dimensions of 3 × 1 cm. These specimens were mechanically polished with emery paper of grades (100, 200, 400, 600 and 1000) to obtain smooth and clean surface. After polishing, specimens were washed with distilled water, degreased with acetone, dried in hot air blower and placed in desiccator.

Weight loss measurement

Weight loss experiment was conducted in wooden air thermostat. Prior to experiment the initial weights of specimens were taken. Then specimens were suspended in 50 ml of acidic solution (with and without inhibitor) in the concentration range of (50, 100, 150, 200, 250 and 300 ppm) at different temperatures for immersion time of 4, 8, 16 and 24 h. All the measurements have been performed in de-aerated acidic solution. After the completion of required time period, specimens were taken out, washed with distilled water, scrubbed with bristle brush, degreased with acetone, dried and again weighed. The difference of weight of specimen (before and after immersion) was taken as weight loss. Average weight loss was taken for triplicate reading.

The inhibition efficiency ($\eta\%$) and surface coverage (θ) were calculated by using the following equations:

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

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

Where, W_i and W_0 stand for the carbon steel coupon in presence and absence of inhibitor respectively. The corrosion rate C_R ($\text{mm} \cdot \text{y}^{-1}$) of carbon steel was calculated using the relation:

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

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].

Electrochemical measurements

Electrochemical measurements were carried out for carbon steel specimens in 1M HCl solution. Experiments were performed in a conventional three electrode cell where platinum acts as Counter Electrode (CE), a Saturated Calomel Electrode (SCE) and carbon steel specimens as a working electrode. Both Impedance and polarization measurements were carried out at open circuit potential using computerized AUTOLAB Salartron Model 1280B potentiostat. Carbon steel specimens were used in rectangular shape having 5 cm long stem with 1 × 1 cm exposed surface area and the rest remained covered with epoxy resins. Before starting the experiment, the working electrodes were abraded with emery papers of (100-1000 mesh grades), washed with double distilled water, degreased with acetone and then dried in air blower. Firstly the working electrode was immersed in test solution for 30 min to attain a stable value of Open Circuit Potential (OCP) at room temperature. All the measurements were performed in 1M HCl solution in the presence and absence of inhibitor in the concentration range (50, 100, 150, 200 and 250 ppm).

Electrochemical impedance 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 represented in the form of Nyquist plots (Z_{real} vs. Z_{img}).

Polarization curves were obtained through instrument for carbon steel specimens in different test solutions with a scan rate of 1 mV/s by changing the electrode potential from -250 to +250 mV (SCE Vs. OCP). Different corrosion kinetic parameters were derived from the Tafel polarization curve.

RESULTS AND DISCUSSION

Weight loss measurements

Effect of inhibitor concentration

Weight loss method has practical importance because of its applicability. A series of weight loss were conducted for different immersion time and temperatures in 1M HCl in absence and in presence of different concentrations of inhibitor solution. Results of weight loss parameters are compiled in Table 1. The table shows values of Surface coverage (θ), Inhibition efficiency (IE%) and Corrosion rate (C_R) calculated using Eqns. 1, 2 and 3 respectively. Increasing trend of inhibition efficiency and decreasing in corrosion rate with concentration in Figures 1 and 2 also support the data i.e., with increase in concentration IE% increases and CR decreases.

Effect of immersion time

In order to judge the firmness of inhibitive layer of studied inhibitor by time period, weight loss measurement were performed in blank and in inhibitive acidic solution with different concentration for immersion time of 4 h, 8 h, 16 h and 24 h at a temperature of 35°C. Increase in inhibition efficiency and decrease of corrosion rate is noticed in Table 1 and confirmed in Figures 1 and 2.

This increase in IE% may be due to the surface coverage of specimen by an inhibitive layer of inhibitor molecules. The surface may be less or complete covered indicates the improvement in the quality of protective film with time [22].

Effect of temperature

The temperature effect on carbon steel surface in presence and in absence of inhibitor in 1M HCl solution was studied at 25°C, 35°C and 45°C for immersion time of 16 h by weight loss measurements. Corresponding data is compiled in Table 2 and graphically represented in Figure 3. Results shows decline in IE% with temperature indicates temperature independence of behaviour of studied inhibitor.

Table 1: Weight loss parameter for carbon steel in 1M HCl in different concentrations of HIPT for different immersion time at temperature of 35°C

Time period	Concentration (ppm)	Initial weight (mg)	Final weight (mg)	Weight loss (mg)	C_R ($\text{mm} \cdot \text{y}^{-1}$)	IE%	Surface coverage (θ)
4 h	0	1.121	1.061	0.060	57.03	-	-
	50	1.117	1.090	0.027	25.66	55.00	0.55
	100	1.107	1.095	0.022	20.9	63.30	0.63
	150	1.110	1.090	0.017	16.15	71.66	0.71
	200	1.114	1.099	0.014	13.30	76.66	0.76
	250	1.128	1.115	0.013	12.35	78.33	0.78
8 h	0	1.102	0.978	0.124	58.93	-	-
	50	1.134	1.083	0.051	24.23	58.89	0.58
	100	1.123	1.081	0.042	19.96	66.12	0.66
	150	1.121	1.088	0.033	15.68	73.38	0.73
	200	1.130	1.104	0.026	12.35	79.03	0.79
	250	1.136	1.115	0.021	9.98	83.06	0.83
16 h	0	1.103	0.849	0.254	60.35	-	-
	50	1.109	1.008	0.101	24.00	60.23	0.60
	100	1.158	1.083	0.075	17.82	70.47	0.70
	150	1.109	1.049	0.060	14.2	76.37	0.76
	200	1.127	1.078	0.049	11.6	80.70	0.80
	250	1.127	1.089	0.038	9.02	85.03	0.85
24 h	0	1.116	0.733	0.390	63.05	-	-
	50	1.125	0.979	0.141	22.33	63.84	0.63
	100	1.108	1.003	0.098	15.5	74.87	0.70
	150	1.099	1.014	0.083	13.1	78.71	0.78
	200	1.102	1.036	0.066	10.4	83.07	0.83
	250	1.127	1.076	0.047	7.44	87.94	0.87

Table 2: Inhibition efficiency and corrosion rate of inhibitor in acidic solution for a time period of 16 h at different temperatures

Concentration (ppm)	Inhibition efficiency (%)								
	298 K			303 K			313 K		
	Weight loss	IE%	C_R	Weight loss	IE%	C_R	Weight loss	IE%	C_R
0	0.092	-	21.8	0.254	-	60.3	0.542	-	128.7
50	0.026	71.7	6.1	0.101	60.2	24.0	0.249	54.0	59.16
100	0.018	80.4	4.2	0.075	70.4	17.8	0.234	56.8	55.60
150	0.009	90.2	2.1	0.060	76.3	14.2	0.217	59.9	51.5
200	0.008	91.3	1.9	0.049	80.7	11.6	0.209	61.4	49.6
250	0.006	93.4	1.4	0.038	85.0	9.0	0.171	68.4	40.6

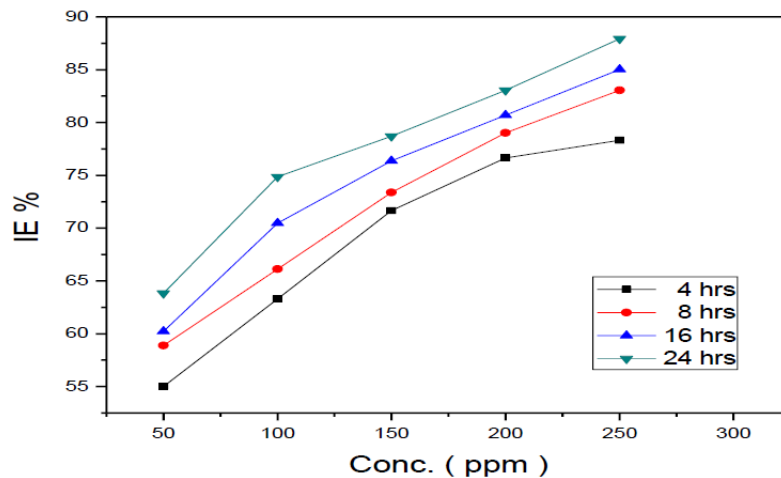


Figure 1: Variation of inhibition efficiency (IE%) with concentrations in absence and presence of inhibitor for different immersion time in 1M HCl at 35°C

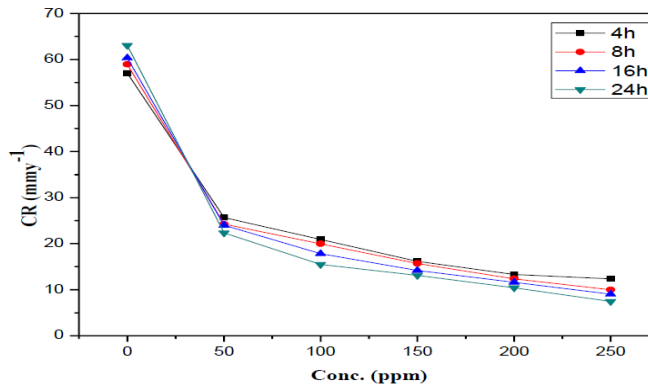


Figure 2: Variation of corrosion rate (C_R) with concentration in absence and presence of inhibitor for different immersion time in 1M HCl at 35°C

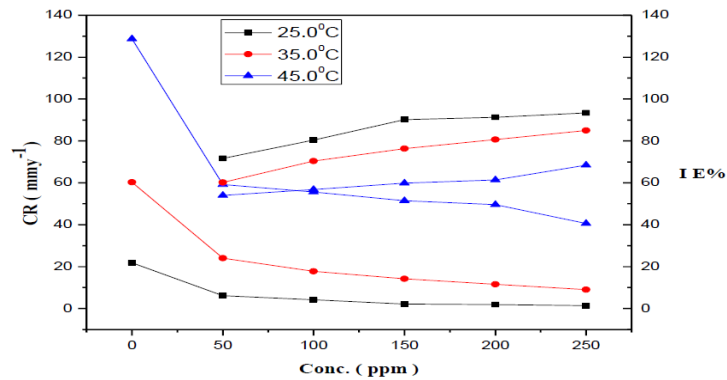


Figure 3: Variation of inhibition efficiency and corrosion rate with concentration in 1M HCl at different temperatures

Electrochemical measurements

Electrochemical impedance measurements studies

The impedance measurements of carbon steel in 1M HCl have been studied in absence and in presence of different concentrations of HIPT as an inhibitor. The spectra in the form of Nyquist and Bode plots are shown in Figures 4-6 respectively. The corresponding experimental data, related to the EIS measurements are presented in Table 3.

Table 3: Electrochemical impedance parameters of carbon steel in 1.0 M HCl solution HIPT inhibitor at room temperature

Concentration of HIPT (ppm)	R_{ct} ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\mu \text{F}/\text{cm}^2$)	Inhibition efficiency ($IE_{EIS} \%$)
0	30.095	238	-
50	78.913	90	61.863
100	91.687	78	67.176
150	132.023	54	77.204
200	133.558	53	77.466
250	189.92	37	84.15

In Nyquist plot semicircles are observed with the center under real axis. It represents one capacitive loop in the spectra at higher frequency zone. This capacitive loop is originated from the time constant of charge transfer resistance and electrical double layer [23-25]. The diameter of the circle increases significantly with the successive addition of inhibitor with concentration. Figure 5 presents the Bode plot for the same impedance data between log Z impedance vs. log frequency at different concentrations of inhibitor. Another bode plot in Figure 6 between phase angle vs. log frequency impedance performance suggest that greater values of phase angles at higher frequency gives indication of more capacitive behaviour [26].

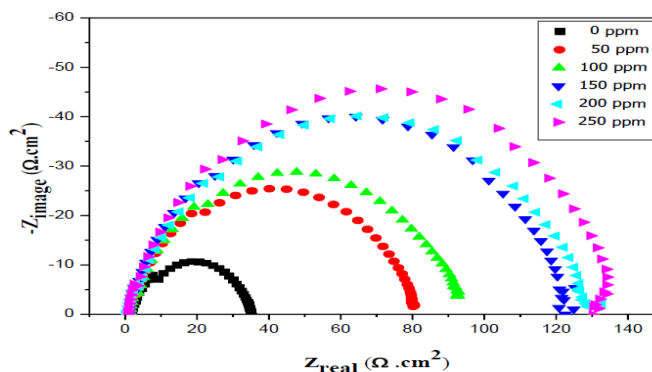


Figure 4: Nyquist plot of carbon steel in 1M HCl in blank and different concentrations of inhibitor

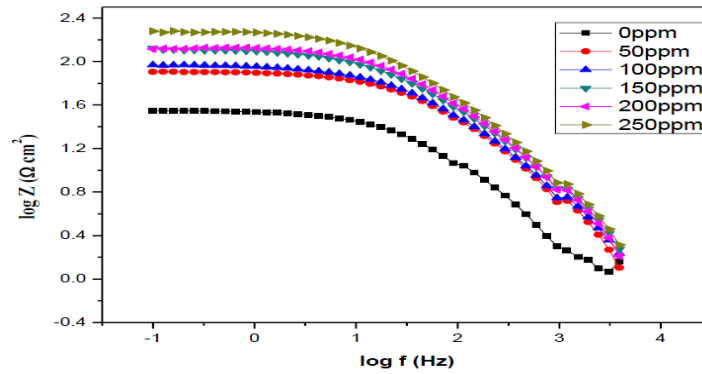


Figure 5: Bode plot of log Z vs. log f in absence and in presence of different concentration of inhibitor in 1M HCl

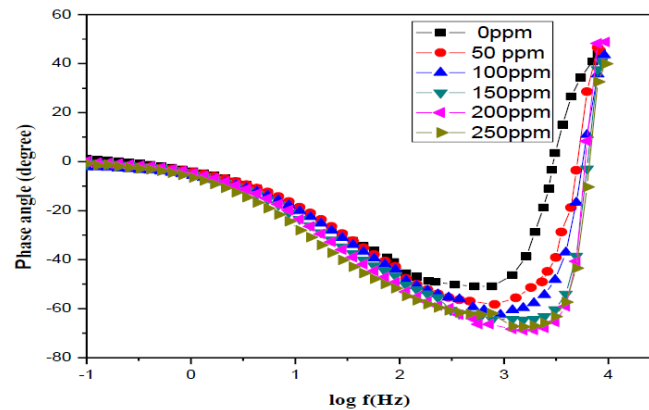


Figure 6: Bode plot of phase angle vs. log f in absence and in presence of different concentration of inhibitor in 1M HCl

The parameters deduced from Nuquist plot analysis are: (1) The resistance of charge transfer R_{ct} . (2) The double layer capacitance, C_{dl} were calculated at the frequency f_{max} at which the imaginary component of the impedance is maximal by the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max}} \times \frac{1}{R_{ct}} \quad (4)$$

Where, f_{max} is frequency and $\pi=3.14$. The surface coverage (θ) and inhibition frequency (IE%) from impedance measurements data can be calculated by using the expressions:

$$IE\% = \left(1 - \frac{R_{ct}^0}{R_{ct}}\right) \quad (5)$$

Where, R_{ct}^0 and R_{ct} are the charge transfer resistance in absence and in presence of different concentrations of inhibitor. The values of R_{ct} , C_{dl} and $IE_{EIS}\%$ for C-steel in 1M HCl, with and without inhibitor under testing are listed in Table 3. The data indicates that there is increase in charge transfer resistance and percentage inhibition efficiency but double layer capacitance values decreases with concentration. The decrease in C_{dl} values could be due to the adsorption of the inhibitor molecules at the metal surface. It has been reported that the adsorption of inhibitor on the metal surface leads to decrease in C_{dl} [27]. Decrease in C_{dl} leads to increase in thickness of electrical double layer [28]. This suggests the adsorption of the inhibitor molecules on the metal/solution interface [29].

Decrease 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 [30].

Polarisation measurements

Potentiodynamic polarization curves for carbon steel in blank and inhibited solution at various concentration of inhibitor in 1M HCl are shown in Figure 7 corrosion kinetic data 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 4.

Table 4: Tafel polarization data of inhibitor for carbon steel in 1M HCl

Inhibitor name	Concentration (ppm)	β_a mV dec ⁻¹	β_c mV dec ⁻¹	$-E_{corr}$ (mV vs SCE)	I_{corr} ($\mu A.cm^{-2}$)	$IE_{pp}\%$
Isatin p-toluidine (HIPT)	0	818	1028	-0.505	43.18	-
	50	763	937	-0.464	18.44	57.29
	100	699	879	-0.500	16.51	61.76
	150	722	856	-0.553	13.32	69.15
	200	826	629	-0.539	10.18	76.42
	250	698	708	-0.524	9.03	79.08

The I_{corr} values in this table decreases from $43.18 \mu A.cm^{-2}$ for blank acid to $9.03 \mu A.cm^{-2}$ at 250 ppm of concentration thereby indicating the adsorption of inhibitor molecules on metal surface and cause inhibition to occur.

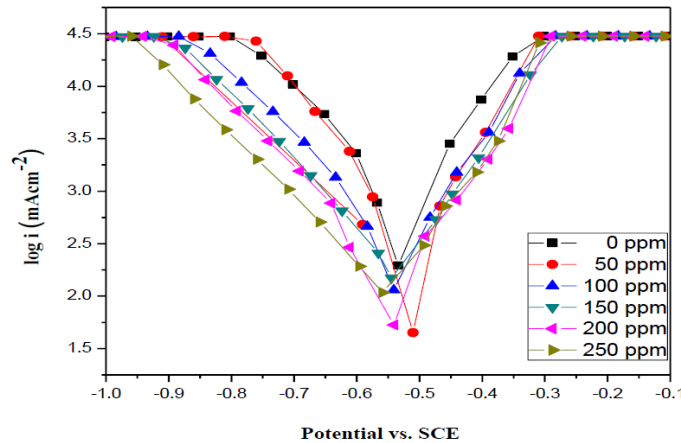


Figure 7: Tafel polarization curve of inhibitor in absence and in presence of inhibitor in 1M HCl

The inhibitor showed maximum inhibition efficiency of 79.08% at 250 ppm. This technique was used to know the kinetics of cathodic and anodic reaction. Increase in concentrations of Schiff base inhibitor affects the anodic and cathodic parts of the curves. The intersection of the linear region by the corrosion potential (E_{corr}) gives the values of (I_{corr}). With the increase in concentration of the inhibitor following observations were recorded in Table 4: Decrease in available surface area for anodic dissolution and hydrogen evolution through the increase in values of (β_a) and (β_c) which describe the inhibitor as mixed type inhibitor. There is change in (E_{corr}) to more negative value and (I_{corr}) also decreases with increase in concentration; it indicates that the inhibitor is an effective mixed type, predominantly cathodic inhibitor. The corrosion current potential was calculated by using the following Equation:

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

Where, b_a , b_c and R_p is the anodic, cathodic Tafel slope and polarization resistance. According to Ferreira and others [31,32], if the change in corrosion potential is greater than 85 mV with respect to blank solution, then the inhibitor is considered to be cathodic or anodic type. Here the displacement in corrosion potential is of (34 mV) indicates it as mixed type inhibitor. The inhibition efficiencies ($IE_{pp}\%$) of the inhibitor was calculated by the following expression:

$$IE_{pp}\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \tag{8}$$

Where, I_{corr} and $I_{corr(inh)}$ are the corrosion current densities of carbon steel without and with inhibitor.

Adsorption isotherm

The Tables 1 and 2 in weight loss measurements indicates the effectiveness of Schiff base in terms of its inhibition efficiency which is found to increase with increase in concentrations. But this can be briefly explained by the study of adsorption of inhibitor molecule on carbon steel surface. Adsorption isotherm provides necessary information about the mode of interaction between the metal/solution interfaces. Two main types of adsorption occurs which gives the information about adsorption process of inhibitor molecules on metal surface: physical adsorption and chemical adsorption. Degree of adsorption depends on chemical structure of inhibitor molecules, composition of inhibitor, composition and surface characteristics of metal, immersion time, temperature and electrochemical potential at metal/solution interface [33].

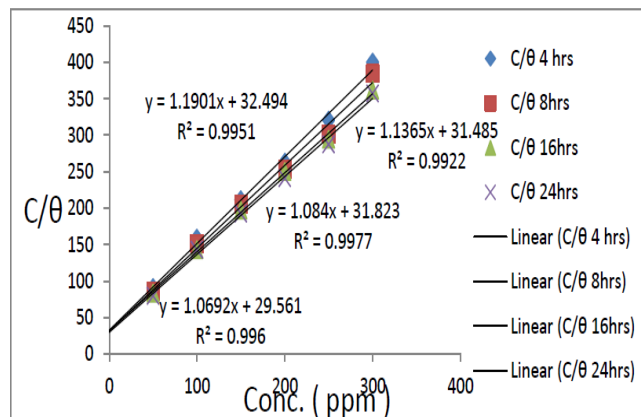


Figure 8: Langmuir adsorption plots for carbon steel in 1M HCl for different immersion time

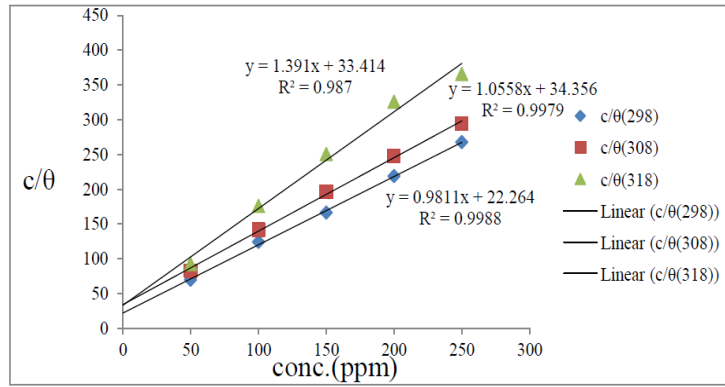


Figure 9: Langmuir adsorption plots for carbon steel in 1M HCl at different temperatures for immersion time of 16 h

Basic information about the mode of interaction can be provided by adsorption isotherm. Surface coverage (θ) values of metals found useful for adsorption isotherm characteristics. Attempts have been made to fit value of (θ) to various isotherms but the best fit is for Langmuir adsorption isotherm (Figure 8). The Langmuir isotherm for monolayer chemisorption is given by Agrawal and Namboodhiri [34].

$$\frac{\theta}{1-\theta} = KC_{inh} \quad (9)$$

On rearrangement it gives,

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \quad (10)$$

Where, θ =Degree of surface coverage, C_{inh} =Inhibitor concentration, K =Equilibrium constant. Figure 9 shows plots of C/θ vs C . From the results it is expected that linear relationship is followed with good correlation coefficient which confirms the validity of the equation. The slope values are less than unity for 298K, 308K and 318K where the values are 0.987, 0.997 and 0.998 respectively. This indicates that Langmuir isotherm is obeyed at three temperatures.

Table 5: Thermodynamic parameters for adsorption of inhibitor on carbon steel surface at different temperatures

Temperature	Log 55.5k	$\Delta G_{ads}^{\circ}/kJ mol^{-1}$
298	4.78	-27.30
308	4.59	-27.11
318	4.60	-28.06

Table 6: Thermodynamic parameters for adsorption of inhibitor on carbon steel surface for different immersion time at 35°C

Inhibitor name	Immersion time	Log 55.5k	$\Delta G_{ads}^{\circ}/kJ mol^{-1}$
298K	4 h	4.62	-26.37
	8 h	4.63	-26.44
	16 h	4.63	-26.42
	24 h	4.66	-26.6

The standard Gibbs free energy of adsorption values obtained using Van'thoff Equation:

$$\text{Van'thoff Equation} = \frac{1}{55.5} \exp\left(\frac{\Delta G_{ads}^{\circ}}{RT}\right) \quad (11)$$

Are listed in Tables 5 and 6 for different temperature and time periods. The adsorption depending upon electrostatic interaction between charged molecules and charged metal surface is regarded as physisorption if the adsorption value of standard free energy is about $-20 kJ.mol^{-1}$ or less negative.

If adsorption value is about $-40 KJ mol^{-1}$ or more negative, it indicates charge sharing or transfer from inhibitor molecules to metal surface, hence chemisorptions [35,36]. Results in Tables 5 and 6, for different immersion time and temperature show values of ΔG in the range of -27.11 to -28.06 for studied temperature and from -26.37 to -26.60 at 308K. These values are specify, Langmuir adsorption behave as physisorption.

CONCLUSION

Studied Schiff base acted as a good inhibitor for carbon steel in 1M HCl solution. Inhibition efficiency was found to increase with concentration and time period but decreases with temperatures. Inhibition efficiency given by EIS measurements is in good agreement with weight loss. It proves inhibitor with good inhibitive properties. Tafel polarization data defines inhibitor as mixed- type cathodic inhibitor. Adsorption process was found to obey Langmuir adsorption isotherm.

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