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Study of the Inhibition Effect of Carbendazim Towards Carbon Steel Corrosion in 0.50M HCl Solutions

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The inhibition effect of carbendazim on the corrosion behavior of carbon steel in 0.50M HCl solution was investigated using weight loss, potentiostatic polarization and electrochemical impedance spectroscopy techniques. The inhibition efficiency increased as the concentration of the inhibitor was increased with a maximum achievable inhibition efficiency of almost 90 %. Electrochemical impedance spectroscopy technique was utilized to investigate the effect of temperature on corrosion inhibition and was found to be insignificant and thermodynamic parameters were calculated. The adsorption of the inhibitor on carbon steel surface obeys Langmuir adsorption isotherm.

Keywords: Carbon steel; Carbendazim;corrosion inhibition; adsorption

1. INTRODUCTION

Many different types of industrial activities involve the use of iron and its alloys in acidic media and is a global scientific concern due to the spontaneous deterioration as a result of corrosion. Corrosion has significant economic implications and costs almost 2-4% of the GDP of an industrialized nation. Corrosion control strategies involve considerable scientific and economical importance. Acids are widely used in industrial processes such as. Various industrial processes such as pickling, cleaning, descaling, and oil well acidizing involve the use of acids but these acids also have their disadvantages such as the fast dissolution of metals in acidic conditions. In order to overcome this problem and to diminish the rate of metal dissolution, the common practice is to use certain types of inhibitors [1-2]. Generally, inhibitors suppress the corrosion reactions by: (i) adsorption of ions/molecules on metal surface, (ii) varying the anodic and/or cathodic reaction, and (iii) by decreasing the diffusion rate of reactants to the metal surface [3]. The efficiency of the inhibitor depends on various factors such as corrosivity of the electrolyte solution, concentration, and operation temperature. Corrosion inhibition in acidic media can be achieved by the use of organic compounds that have heteroatom – S, O and/or N due to the higher basicity as reported in literature [4-9]. These heteroatoms act as active centers for adsorption on metal surface [10].

The purpose of the present work is to examine the inhibition effect of carbendazim for carbon steel in acidic environment. Weight loss, potentiostatic polarization and electrochemical impedance spectroscopy (EIS) measurements were used to verify the inhibitory properties of this compound for carbon steel immersed in 0.50 M HCl solution.

2. MATERIALS AND METHODS

2.1 Materials

The inhibitor used in the current work is carbendazim also known as (Methyl 2-benzimidazolecarbamate) the chemical structure of which is shown in Figure 1. Various concentrations of the inhibitor were used. The test solutions used was 0.50 M hydrochloric acid. The compound was used as received without any further modification. The steel panels were cut to dimensions of l = 2.0 cm, b = × 2.0 cm and thickness of 0.08 cm. For the weight loss experiments, the carbon steel panels were abraded with different grades of abraded (sand) paper and subsequently rinsed with distilled water and acetone and allowed to dry prior to experimental tests. The immersion time of the test specimen was 8 hours.

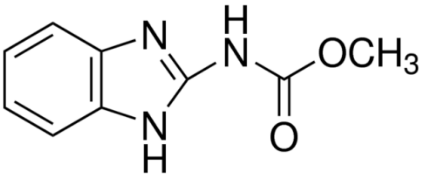

Figure 1. Structure of Carbendazim (Methyl 2-benzimidazolecarbamate)

2.2 Electrochemical tests

The electrochemical tests were conducted using a potentiostatPGstat 302N which was linked to a cell with three electrode thermostats. A saturated calomel electrode (SCE) and a platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was carbon steel that was the same as used for gravimetric measurements. The surface area exposed to the electrolyte is 0.04 cm^2.

Potentiodynamic polarization curves were obtained at a scanning rate of 0.50 mV/s. Before all experiments, the potential was stabilized at free potential for 45 min. The polarization curves are attained in the range of −800 mV to −200 mV at 298 K. Some experiments were conducted at different temperatures (298–328 K) to evaluate the influence of immersion time and temperature on the efficiency of the inhibitor.

The electrochemical impedance spectroscopy (EIS) measurements were conducted with the same potentiostat. The measurements were carried out at rest potentials after 30 min of exposure time at 298 K. The impedance diagrams are given as Nyquist plots. Experiments were repeated at least three times to validate the precision of the experimental data.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization curves

Results of potentiodynamic polarization experiments of different concentrations of carbendazim are given as Tafel plots in Figure 2 with clear shift in anodic-cahodic behaviour. Carbendazim acts as a mixed-type corrosion inhibitor, inhibiting the anodic and cathodic processes of the corrosion reactions by forming a protective film on the metal surface. Some kinetic parameters such as corrosion current density I_{corr}, corrosion potential E_{corr} and cathodic Tafel slopes (b_c) are tabulated in Table1. The inhibition efficiency values (IE_{Icorr}%) were determined using equation 1.

$$IE_{Icorr}(\%) = \frac{(I^0_{corr} - I_{corr})}{I^0_{corr}} x100 \qquad (1)$$

where I_{corr} and $I°_{corr}$ are the values of corrosion current densities of C-steel with and without the inhibitor, respectively.

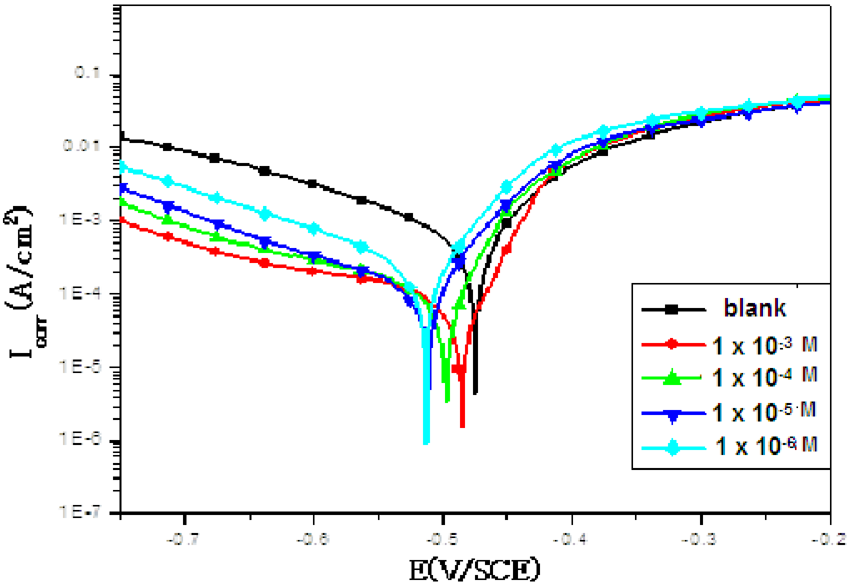

Figure 2. Potentiodynamic polarization curves of C-steel in 0.50M HCl containing different concentration of carbendazim at 298K.

The corrosion current density (I_{corr}) values decrease gradually with the increase of the inhibitor concentration as shown in Table 1. There is a small change in the values of cathodic Tafel slopes, b_c, indicating that, the existence of the additive does not disturb the cathodic slopes (b_c). This shows that adding of carbendazim does not alter the mechanism of the proton discharge reaction. It is also obvious from results in Table 1 that inhibition efficiency values (IE %) increase as the inhibitor concentration increasing.

Table 1. Electrochemical parameters of C-steel at various concentrations of carbendazim in 0.50M HCl and corresponding inhibition efficiency

Inhibitor	Conc. (M)	$-E_{corr}$ (mV/SCE)	I_{corr} (μA cm^{-2})	$-b_c$ (mV dec^{-1})	IE_{Icorr} (%)
Blank	----	347	1723	167	----
carbendazim	1×10^{-6}	381	689	156	60.0
	1×10^{-5}	378	505	177	70.7
	1×10^{-4}	363	348	191	79.8
	1×10^{-3}	355	181	206	89.5

3.2. Electrochemical impedance spectroscopy measurements

Nyquist plots of C-steel in 0.5 M HCl in the absence and presence of various concentrations of inhibitor are shown in Fig. 3. These plots have been obtained after 30 min of soaking in the acidic solutions.

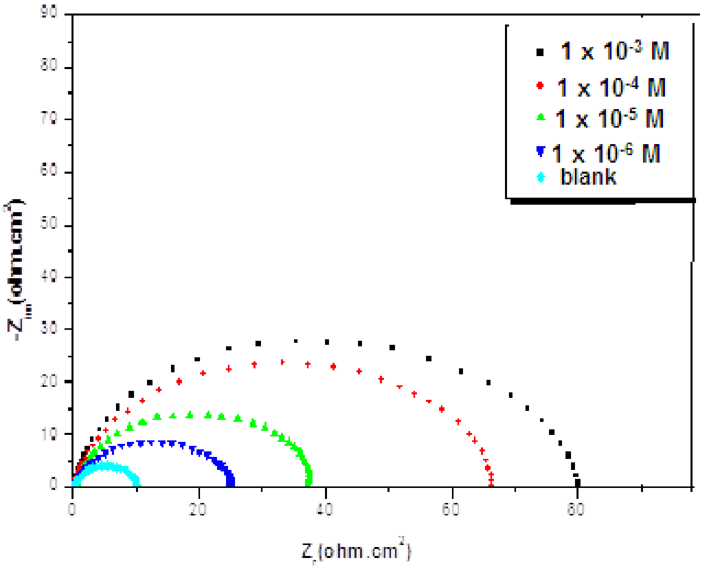

Figure 3. Nyquist diagrams for C-steel electrode with and without carbendazim at E_{corr} after 30 minutes of immersion

Fig. 3 shows that there is a single capacitive loop in all plots. Impedance parameters resulting from the Nyquist plots such as the equivalent circuit diagram and inhibition efficiencies EI_R are presented in Fig. 4 and Table 2.Values of R_t were found by using Eq. 2. [11]:

$$R_t = Z_{re}(\text{low frequency impendace}) - Z_{re}(\text{ high frequency impedence}) \tag{2}$$

Electrochemical double layer capacitance values, C_{dl}, were determined at the frequency f_{max}, at which the imaginary component of the impedance is the highest ($-Z_{max}$) by Eq. 3. [12]:

$$C_{dl} = \frac{1}{2\pi f_{max} R_t} \tag{3}$$

Values of inhibition effectiveness are obtained by Eq. 4:

$$EI_{Rt}\,(\%) = \frac{R_t - R_t^0}{R_t} \times 100 \tag{4}$$

where R_t^0 and R_t are values of charge transfer resistance with and without inhibitor, respectively.

Table 2. Electrochemical Impedance parameters for corrosion of C-steel in acid medium at different inhibitor concentration

Inhibitor	Conc. (M)	R_t (Ω.cm^2)	f_{max} (Hz)	$10^5 C_{dl}$ (μF/cm^2)	EI_{Rt} (%)
Blank	----	13	158	10.0	----
carbendazim	1×10^{-6}	33	63	10.10	60.6
	1×10^{-5}	43	10	4.30	69.8
	1×10^{-4}	64	79	3.05	79.7
	1×10^{-3}	91	63	3.16	90.9

It is clear from the tabulated data in Table 2 that the resistance is increased in the presence of carbendazim compared to that of HCl alone while values of C_{dl} decreased. The decrease in C_{dl} values may be attributed to a decrease in local dielectric constant and/or may be due to an increase in the thickness of the electric double layer [13,14].

Accordingly, from the data obtained, it may be concluded that carbendazim molecules function by adsorption at the metal/solution interface. Similar inhibition mechanism was reported by [15, 16] which stated that the inhibition effectiveness may be due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface hence, decreasing the extent of the metal dissolution reaction.

3.3 Weight loss, corrosion rates and inhibition efficiency

Weight loss method is also used to evaluate the efficiency of carbendazim as corrosion inhibitor. All experiments are carried out at 298 K with an immersion time of 8 hours. Inhibition efficiency EI_w (%) was determined by Eq. 5:

$$EI_W\,(\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \qquad (5)$$

where W'_{corr} and W_{corr} are the corrosion rates of C-steel due to the dissolution in 0.50 M HCl in the presence and absence of carbendazim, respectively.

Table 3. Effect of carbendazim concentration on corrosion rate of C-steel in 0.50 M HCl using weight loss method at 298 K

Inhibitor	Conc. (M)	W_{corr}(mg.cm^{-2}.h^{-1})	E_w(%)
Blank	----	1.93	----
carbendazim	1 x 10^{-6}	0.793	58.9
	1 x 10^{-5}	0.596	69.1
	1 x 10^{-4}	0.374	80.6
	1 x 10^{-3}	0.200	89.6

Data in Table 3 proves that the inhibition efficiency of carbendazim increases with the increasing of it is concentration. It can be observed that the optimum concentration of carbendazim necessary to reach the maximum efficiency is found to be 1 x 10^{-3} M. The results found by weight loss method are in good agreement with those obtained by electrochemical measurements.

3.4. Adsorption and thermodynamic considerations

Usually the adsorption isotherms are used to provide the elementary data about the interaction between the metal surface and molecules i.e. between the adsorbate and adsorbent. The surface coverage values (*θ)*, corresponding to various concentrations of carbendazim at 298K have been used to determine and elucidate the best adsorption isotherm. The adsorption isotherms generally considered are:

Temkin isotherm: $\exp(f.\theta) = K_{ads}.C_{inh}$

Langmuir isotherm: $\frac{\theta}{1-\theta} = K_{ads}.C_{inh}$

Freundluich isotherm: $\theta = K_{ads}.C_{inh}$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process, C_{inh} the inhibitor concentration and f is the factor of energetic inhomogeneity, the surface coverage (θ) is determined by Eq. 6:

$$\theta = \frac{\mathrm{W_{corr}} - \mathrm{W'_{corr}}}{\mathrm{W_{corr}}} \qquad (6)$$

The plot of C_{inh}/θ against C_{inh} gives straight line with a slope value of 1.11 and a correlation coefficient of (R^2> 0.9998) clearly confirms that the adsorption of the carbendazim on the surface of C-steel obeys the Langmuir adsorption isotherm as shown in equation 7.

$$\frac{\mathrm{C}}{\theta} = \frac{1}{\mathrm{K}_{ads}} + \mathrm{C} \qquad (7)$$

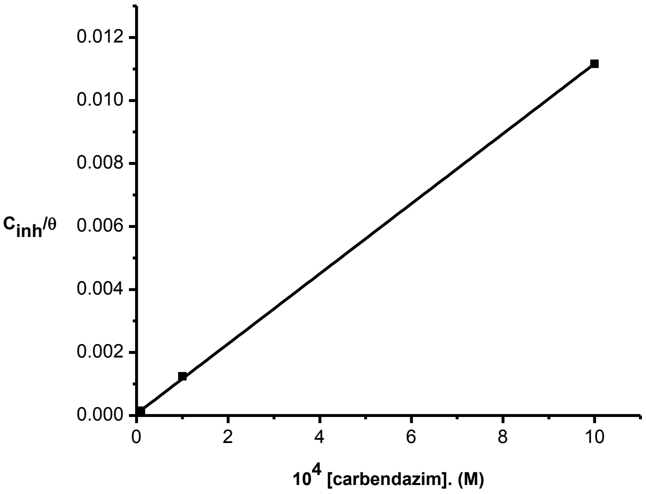

Figure 4. Langmuir adsorption of carbendazim on the C-steel surface in 0.50 M HCl solution

The equilibrium adsorption constant K_{ad} was calculated from the intercept of Fig. 4 as $1.85 \times 10^4 M^{-1}$, indicating a chemical adsorption process as reported by [17].

3.5. Effect of temperature

To investigate the effect of temperature and to calculate some activation parameters of the corrosion process, the impedance measurements at different temperatures in the range of 298-328 K, in the absence and presence of carbendazim at optimal concentration were carried out as presented in Figures 5 and 6. As can be seen from these figures, as the temperature of the experiment increases, the size of the semi-circle in the Nyquist plot decreases indicating a slight decrease in inhibition efficiency. Further details from these plots are highlighted in Table 4.

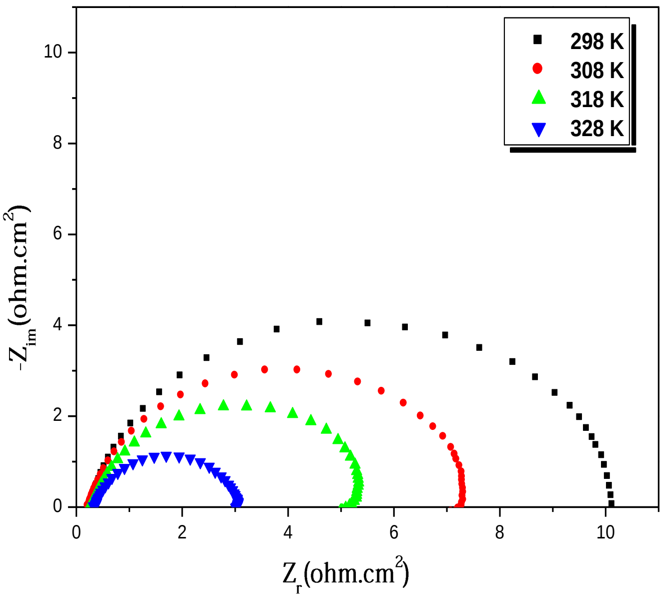

Figure 5. Nyquist diagrams for carbon steel in 0.50 M HCl at different temperatures.

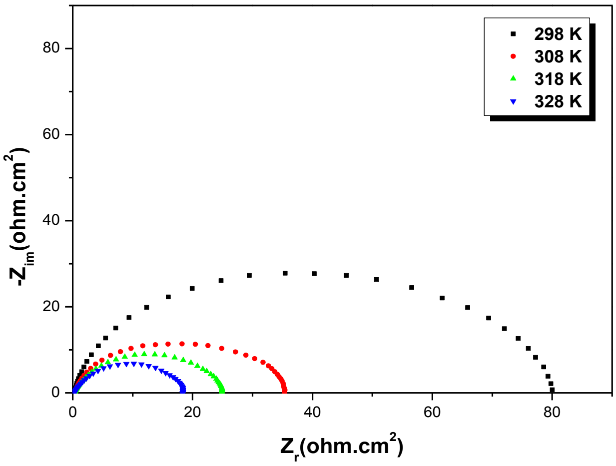

Figure 6. Nyquist diagrams for carbon steel in 0.50 M HCl and 1 x 10^{-3} M of carbendazim at different temperatures.

It is obvious from results tabulated in Table 4 that the values of charge transfer resistance decrease with increasing temperature. This behavior was observed both in inhibited and uninhibited solutions. A slight but persistent decrease in inhibition efficiency of carbendazim was observed over the temperature range studied which further proves that carbendazim can be used as an efficient inhibitor for C-steel.

Table 4. Electrochemical Impedance Spectroscopy (EIS) of carbendazim in 0.50 M HCl on the C-steel at different temperatures

Conc.	Temperature (K)	R_t (Ω.cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	EI_{Rt}(%)
0.50M (Blank)	298	14	163	108	---
	308	10	207	121	---
	318	7	261	129	---
	328	5	667	96	---
10^{-3} M (carbendazim)	298	134	73	43	89.5
	308	84	89	66	88.1
	318	54	114	72	87.3
	328	39	117	91	87.1

Also the charge transfer resistance (Rt) values from Table 4 were utilized to calculate the corrosion current density (I_{corr}) at various temperatures in absence and presence of carbendazim using the following equation [18]:

$$I_{corr} = RT\left(zFR_t\right)^{-1} \qquad (8)$$

where R is the universal gas constant (R = 8.31 J $K^{-1}mol^{-1}$), T is the absolute temperature, z is the valence of iron (z = 2), F is the Faraday constant (F = 96.485 coulomb) and R_t is the charge transfer resistance.

The thermodynamic parameters of the corrosion process of both the inhibited and uninhibited systems can be calculated using equations 9 and 10.

$$\ln \mathrm{Icorr} = -\frac{E_a}{RT} + \ln A \qquad (9)$$

where Icorr is the corrosion current, E_a is the activation energy, T is the absolute temperature, A is the frequency factor and R is the universal gas constant.

$$ln\frac{Icorr}{T} = \frac{-\Delta H}{RT} + ln\frac{kB}{h} + \frac{\Delta S}{R} \qquad (10)$$

where h is Planck's constant, ΔS_a is the entropy of activation, k_B is the Boltzmann constant and ΔH_a is the enthalpy of activation. Plots of ln I_{corr} against 1/T as shown in Fig. 7, and ln (I_{corr}/T) against 1/T, as shown in Fig. 8 exhibit straight line behavior with good correlation coefficients. Values of E_a, ΔH_a and ΔS_a obtained from the slopes of these plots are shown in Table 5.

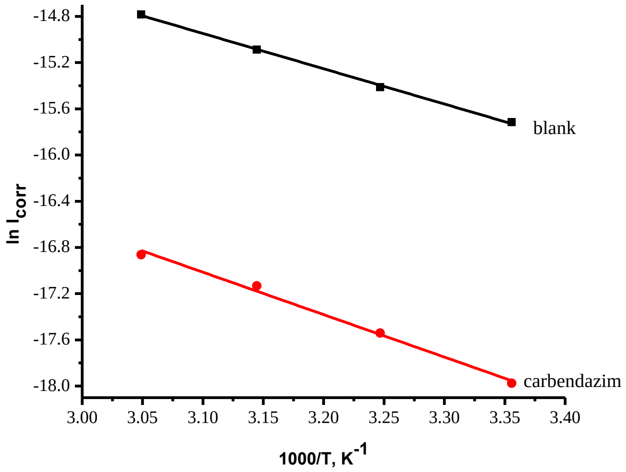

Figure 7. Arrhenius plots of C-steel in 0.50 M HCl with and without 10^{-3}M of carbendazim

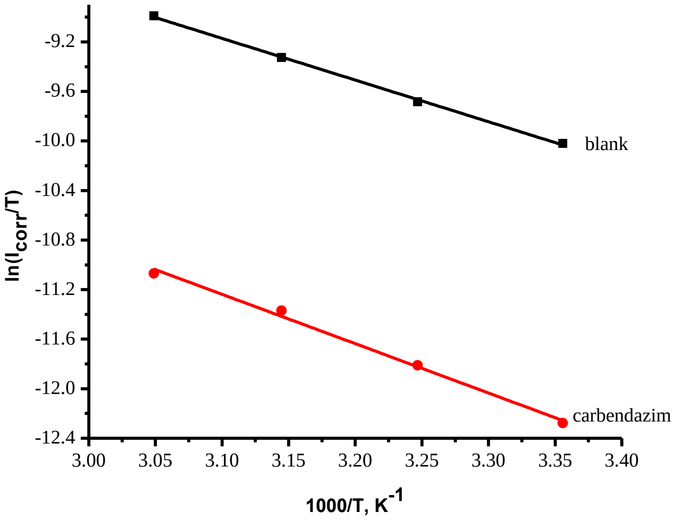

Figure 8. Erying plots of C-steel in 0.50 M HCl with and without 1 x 10^{-3}M of carbendazim at 298K

Table 5. Values of some thermodynamic parameters for C-steel in 0.50 M HCl in the absence and presence of 1 x 10^{-3} M of carbendazim

Inhibitor	E_a(kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J/mol)
Blank	34.57	39.39	-78.35
carbendazim	42.00	31.97	-69.35

These results revealed that the value of E_a increases after addition of the inhibitor confirming that the corrosion process becomes more difficult in the inhibited media. On the other hand, it is clear that values of ΔS_a and ΔH_a for the corrosion process of C-steel in 0.50 M HCl in the presence of inhibitor are lower than those obtained in uninhibited solution. The positive sign of ΔH_a indicates the endothermic nature of the C-steel corrosion process suggesting that the dissolution of C- steel is slow [19] in the presence of carbendazim. Large and negative value of entropies (ΔS_a) implies that the activated complex during the rate determining step denotes an association rather than a dissociation step [20], meaning that a decrease in disordering takes place on going from reactants to the activated complex [21,22].

4. CONCLUSIONS

Carbendazim exhibited good inhibition properties for the corrosion protection of carbon steel in 0.50 M HCl over a wide range of temperatures. The inhibition efficiency of carbendazim increases as its concentration increases up to almost 90% at carbendazim concentration of 10 M. Temperature effect on corrosion rate was found to be insignificant. Data obtained from potentiodynamic polarization study are in good agreement with the weight loss and EIS experiments. Carbendazim acts as a mixed-type corrosion inhibitor, inhibiting the anodic and cathodic processes of the corrosion reactions by forming a protective barrier on the metal surface. Langmuir adsorption isotherm was found to be obeyed. Results of thermodynamic study revealed that the value of E_a increases after addition of the inhibitor confirming that the corrosion process becomes more difficult in the inhibited media.

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