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Corrosion Inhibition of Chlorine Substituted Piperidin–4– One On Mild Steel in Sulphuric Acid Medium

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Abstract: ***The inhibitive effect of 3, 5-diethyl 2, 6-diphenyl p-chloro Piperidin-4-one (DEPCPN) on the corrosion of mild steel in 1N H_2SO_4 solution has been studied by weight loss measurement, Potentiodynamic polarization studies and Electrochemical impedance spectroscopy (EIS) techniques. The results of weight loss method reveal that the addition of DEPCPN inhibits the rate of corrosion of mild steel in acid medium. The results of polarization measurements showed that DEPCPN behaves as a mixed type corrosion inhibitor. At constant acid concentration and increasing inhibitor concentration the percentage of inhibition efficiency increases. This is indicated by increase in charge transfer resistance (R_{ct}) and decrease of double layer capacitance (C_{dl}).The adsorption of DEPCPN on mild steel obeys Langmuir's adsorption isotherm.***

Keywords: DEPCPN, Corrosion inhibition, Weight loss, Polarization, Impedance studies

1. Introduction

It is necessary to pay more attention to metallic corrosion than it was done earlier because increased use of metals in all fields of technology and also use of rare and expensive metals whose protection requires special precaution. Various methods are used to protect a metal from corrosion. One such method includes the usage of inhibitors in the corrosive environment. These inhibitors form a film over the surface of the metal and protect the metal from deterioration. Many researchers[1,2,3] also proved the role of inhibitors in prevention of corrosion.

The aim of the present work is to study the corrosion inhibition efficiency of 3, 5-diethyl 2, 6-diphenyl *p*-chloro Piperidin-4-one (DEPCPN) on mild steel in 1N H_2SO_4 solution by Weight loss measurement, Potentiodynamic polarization and Electrochemical impedance spectroscopy (EIS) techniques.

2. Materials and Methods

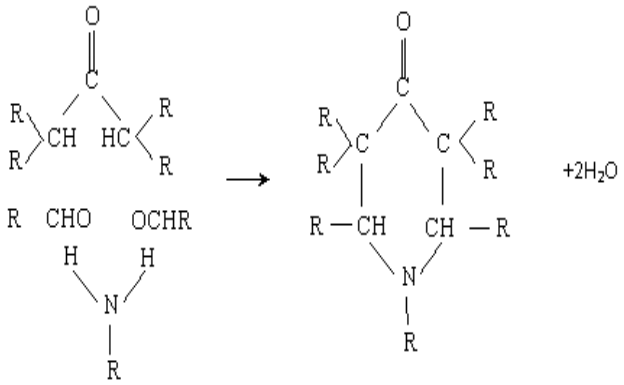
2.1. Preparation of Mild Steel Specimen

Mild steel specimen used for both gravimetric and electrochemical studies has the following composition C - 0.084,Si - 0.12, S -0.021, Mo - 0.008, Mn - 0.037, P - 0.026, Cr - 0.020, Ni - 0.090. Mild steel specimen of size 2.5 X 2cm is employed for the weight loss measurements. A hole of diameter 0.5cm is drilled near the upper edge of the specimen in order to hook it on to the glass rod on immersion. The specimens are polished successively with emery papers 0, 1/0, 2/0, 3/0, 4/0 and 5/0 grades and degreased with Trichloroethylene. Then the specimens are taken out. It is washed well with running water, dried and finally weighed. From the weight loss of specimen in the presence and absence of inhibitor its corrosion efficiency is analyzed.

2.2. Preparation of Inhibitor

3, 5-diethyl 2, 6-diphenyl *p*-Chloro Piperidin-4-one (DEPCPN) inhibitor is synthesized by Mannich reaction[1]. To a solution of dry ammonium acetate (9.8g, 0.125mole) in methanol (30ml) p-chlorobenzaldehyde (29.0g, 0.25mole) and dipropyl ketone (9.0g, 0.125mole) is added. The mixture is just heated to boil and allowed to stand overnight at room temperature. Concentrated HCl (13ml) is then added. The precipitated hydrochloride is then filtered and washed with ethanol-ether (1:5). Recrystallization from ethanol gives the pure hydrochloride 16.0g (40%). Mp is 223 to 228^{0}C (Lit mp 224-226^{0}C).

A suspension of the hydrochloride in acetone is treated with ammonia (1:1) and the free base is precipitated on dilution with excess water. Recrystallization from ethanol gives pure sample mp 96-97^{0}C (Lit mp96-97^{0}C).



2.3 Inhibitor used

3, 5-diethyl 2, 6-diphenyl *p*-chloro Piperidin-4-one (DEPCPN)

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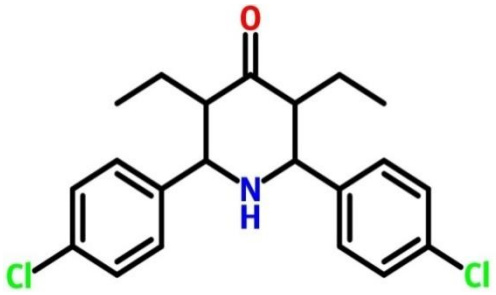
2.4 Structure of Inhibitor



2.5 Weight Loss Measurement

This provides a direct measure for evaluating the corrosion rate of a metal in liquid medium and hence the effectiveness of a specified substance as corrosion inhibitor. This method is carried out on mild steel specimen at room temperature. From this study inhibition efficiency, corrosion rate and surface coverage are calculated. The plot of C/θ Vs C is obtained from this study. The corrosion rate of the iron plates can be evaluated, in principle, from its weight loss or from the volume of hydrogen evolved. Though the later method has the advantage of being able to give continuous results during the course of the experiment, its accuracy is found to be inferior to that of the former method at very low corrosion rates owing to the effects of gas solubility, temperature fluctuation etc., hence data of the former method are taken for evaluation.

2.6. Electrochemical Studies

The corrosion of mild steel and its inhibition by the addition of inhibitor is investigated by both Potentiodynamic polarization and Electrochemical impedance method.

2.6.1. Potentiodynamic polarization studies

The electrochemical measurements are performed in a classical three-electrode cell assembly with mild steel rod (exposed area 0.785cm^2) as working electrode, a platinum electrode and saturated calomel electrode as counter and reference electrodes, which is electrolytically connected to the iron electrode. The measurement of polarization curves are performed with an EG&G instrument, Electrochemical impedance analyzer, model 6310.After the potential of the immersed iron electrode reached its steady value E_{corr} (changing no more than 2 mV/min). The measurement was carried out by sweeping the potential within predetermined limits from negative to positive at a rate of 10mV/sec.

The various corrosion kinetic parameters are obtained from this study on mild steel in the presence and absence of different concentration of the inhibitor.

2.6.2. Electrochemical impedance measurements

Electrochemical impedance measurements are performed using an EG&G instrument, model 6310, PAR–398, frequency response analyzer. In this case the same three electrode assembly used as that in polarization measurement. Alternative current magnitude signal is of 5mV and the frequency range from 100 kHz to 100 MHz.

3. Results and Discussion

Weight loss measurement is a non-electrochemical technique for the determination of corrosion rates (CR) and inhibition efficiency (IE). Table 1 show the % IE and CR for DEPCPN in 1 N H_2SO_4 at room temperature (28˚±1). From the table, it is evident that the concentration of the inhibitor increase, the corrosion rate decrease and the IE increase it is pictorially represent in Figs. 1 and 2. This indicates that the inhibitor molecules get adsorbed on the metal surface and prevent from the further corrosion. However addition of the inhibitors beyond certain concentration namely, 1mM of DEPCPN, the IE decreases indicating desorption of the inhibitor molecule[4].

Adsorption isotherm gives the relation between the coverage of an interface with the adsorbed species and the concentration of the species. Interpretation of the performance of the inhibitor can be enhanced by fitting the data in one of the known adsorption isotherms. An attempt has been carried out to fit various adsorption isotherms and inferred that the Langmuir adsorption model is well obeyed with the experimental data. The plot of C/θ Vs C (Fig. 3) is obtained from this study reveals that the inhibition of corrosion of mild steel by the inhibitor is observed even at very low concentration of 1mM.

Table 1: Inhibition efficiency on mild steel in 1N H_2SO_4 acid by Weight loss measurement at room temperature

Name of the inhibitor	*Inhibitor Concentration (mM)*	*Weight loss(g)*	*Corrosion rate (mmpy)*	*Inhibition Efficiency (%)*	*Surface coverage (θ)*
3,5 -diethyl 2,6- p-chloro diphenyl piperidin-4-one (DEPCPN)	Blank	0.0425	47.3062	-	-
	0.5	0.0238	26.4915	44	0.44
	0.75	0.0221	24.5992	48	0.48
	1	0.0172	19.1451	59.53	0.5953
	2	0.0178	19.813	58.12	0.5812
	3	0.0191	21.26	55.06	0.5506

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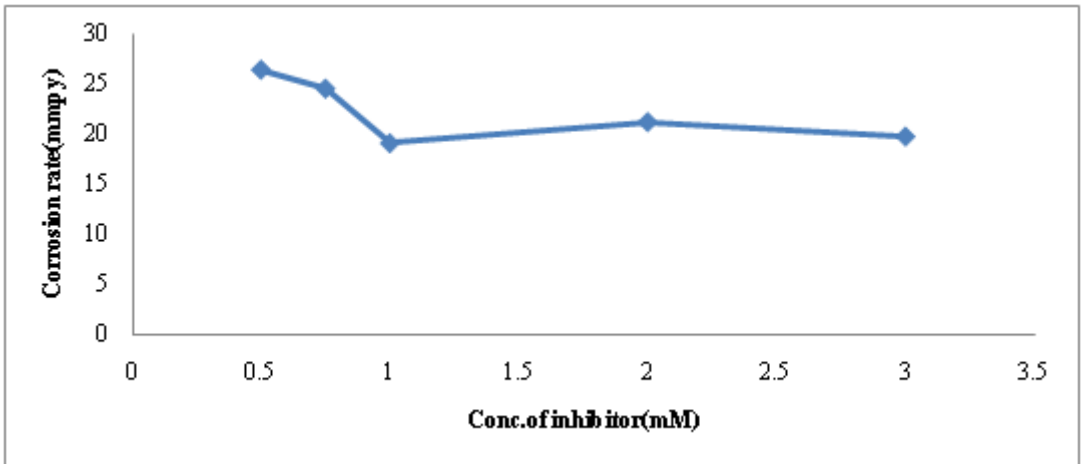

Figure 1: Effect of concentration of inhibitor 3,5-diethyl 2,6-*p*-choloro diphenyl piperidin-4-one (DEPCPN) on corrosion rate

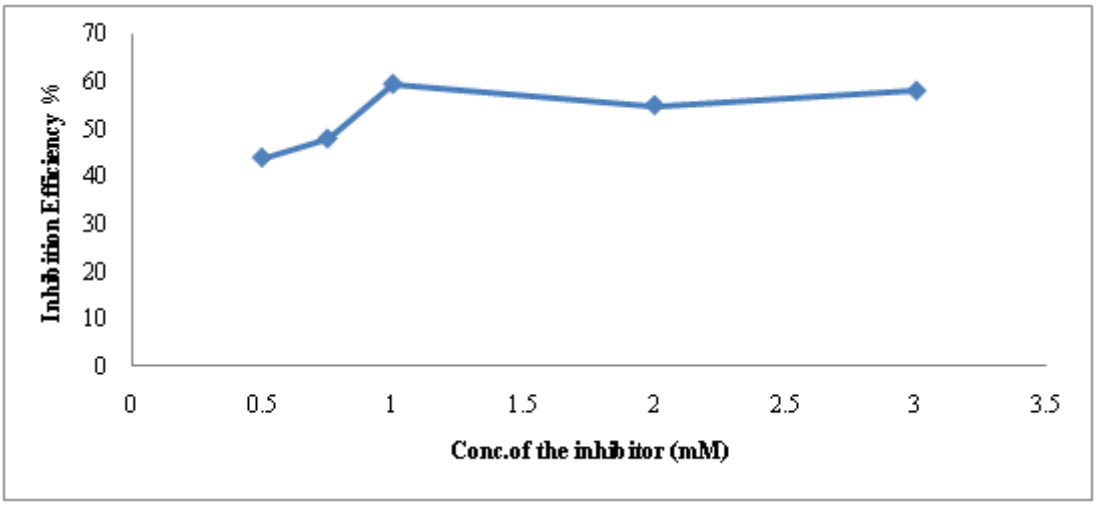

Figure 2: Effect of concentration of inhibitor 3,5-diethyl 2,6-*p*-choloro diphenyl piperidin-4-one (DEPCPN) on inhibition efficiency

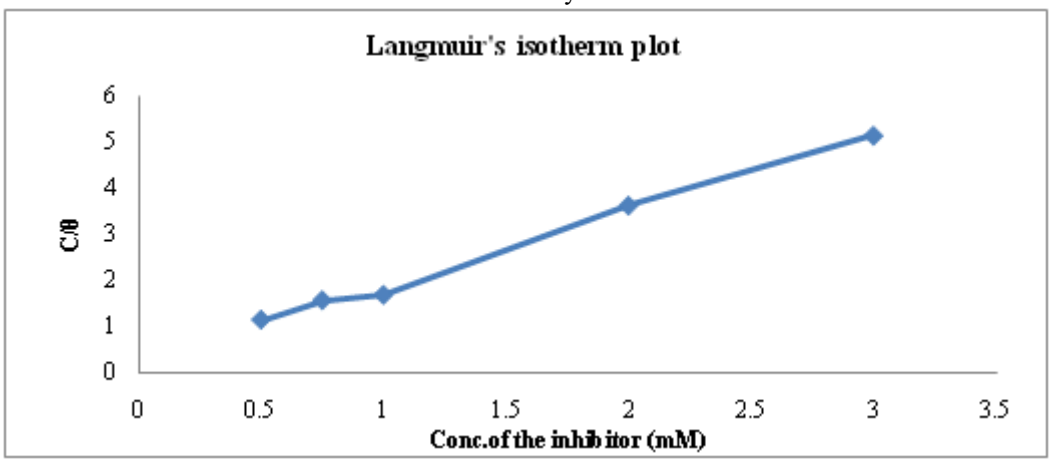

Figure 3: Adsorption isotherm

Fig. 4 represents the potentiodynamic polarization plots for MS in 1N H_2SO_4 in the presence of various concentrations of DEPCPN. The Tafel extrapolation and linear polarization methods are used to obtain the electrochemical parameters. The corrosion parameters viz. corrosion potential (E_{corr}), corrosion current density (I_{corr}), Tafel slopes (ba & bc) are derived from the polarization curves. The values of corrosion current density (I_{corr}) decreased with increase in concentration of DEPCPN. The inhibitor was first adsorbed onto the MS surface and impeded by merely blocking the reaction sites of the metal surface without affecting the anodic and cathodic reaction[5]. The decrease of I_{corr} with the addition of inhibitor indicates the increasing percentage of inhibition efficiency. The inhibition of corrosion by organic molecules present may be caused either by a geometrical blocking effect or by chemical adsorption on active centers of the metal surface. Blocking of active site always does not shift both anodic and cathodic polarization curves, whereas chemisorption on active sites slightly shifts the slopes [6]. By seeing the Tafel slopes, the Tafel constants ba and bc are

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shifted, which reveals that chlorine substituted Piperidone inhibitor is being chemically adsorbed on active sites of the metal surface and behaves as mixed type.

Table 2: Potentiodynamic polarization data of DEPCPN in 1M H_2SO_4 on mild steel surface

Conc. of inhibitor(mM)	*-OCP*	*-E_{corr}(mV)*	*-I_{corr} (mA cm^{-2})*	*-b_a (mV)*	*-b_c (mV)*	*IE(%)*
Blank	0.6077	0.6042	1.08	0.1586	0.2544	-
0.25	0.6292	0.6087	0.8805	0.0779	0.1804	18.47
0.5	0.5949	0.5896	0.5807	0.1518	0.1715	46.23
0.75	0.6104	0.6142	0.3047	0.1199	0.1693	71.79
1	0.6215	0.6255	0.2378	0.1561	0.1651	77.98

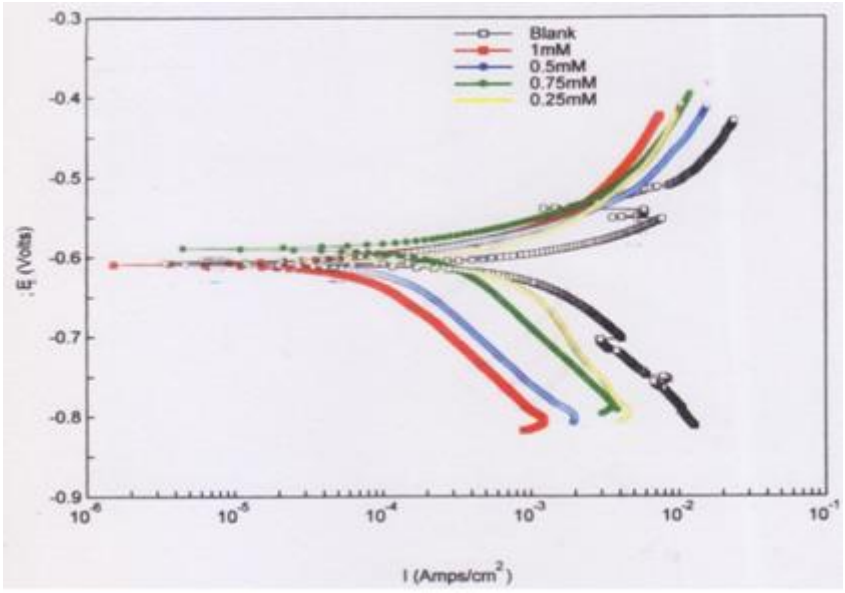

Figure 4: Potentiodynamic Polarization curve of DEPCPN on mild steel surface

The corrosion behaviour of mild steel is investigated by AC impedance measurements at 30±10^{0}C after immersion for 10min. The Nyquist plot for various concentration of the inhibitor is studied and the results are given in Table 3. The impedance parameters like R_{ct}, C_{dl} are noted. Fig. 5 Nyquist impedance spectrum semicircle shape implies the electrode interface under study can conditionally be expressed by a charge transfer resistance, R_{ct}, in parallel with the double layer capacitor C_{dl}. The adsorption of organic molecules on a metal surface usually changes the value of double layer capacity, C_{dl} of the interface. The chemisorbed organic inhibitor molecules on metal surface more or less replace the water molecules within the interface. As a consequence, the double layer capacity decreases with increase in coverage by organic molecules that are the extent of adsorption [7].

The charge transfer resistance (R_{ct}) values for mild steel in uninhibited H_2SO_4 significantly changes after the addition of inhibitor. The value of R_{ct} increases with increase in inhibitor concentration. It also indicates that the corrosion of mild steel is controlled by charge transfer process.

Table 3: Electrochemical Impedance Data for DEPCPN in 1M H_2SO_4 on Mild Steel

Concentration of inhibitor	*R_{ct}(Ohm.cm^2)*	*IE (%)*	*C_{dl} ($F*10^{-5}$)*
Blank	11.64	-	1.8023
0.25	31.61	63.18	1.5774
0.5	43.62	73.31	1.2506
0.75	135.93	91.43	2.0621
1	176.76	93.41	1.1057

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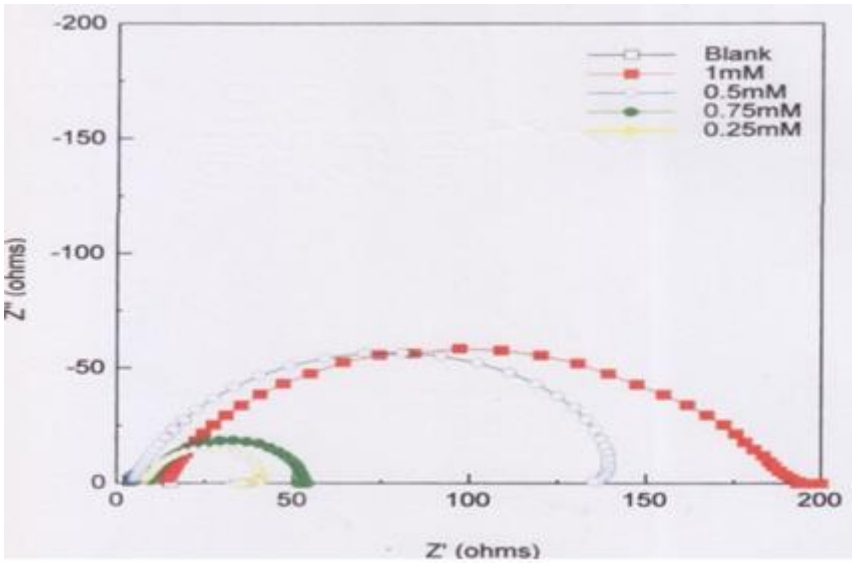

Figure 5: Nyquist plot for DEPCPN in 1M H_2SO_4 on Mild steel surface

The data obtained by electrochemical method and weight loss method shows that the inhibition efficiency of Chlorine substituted piperidone is high even at low concentration of 1mM.

3.1. Mechanism of Inhibition

Analysis of the surface coverage results presented in Tables and for the piperidones reveals that the degree of surface coverage θ increases with increase in inhibitor concentration. This observation suggests that the mechanism of inhibition is basically an adsorption mechanism.

A brief review of literature would through enough light in this direction. It has been stated by Sankarapapavinasam et al[8] that thionones with structural resemblance to piperidones adsorb through the anchoring site „S" atom with a perpendicular orientation to the metal surface [Fig a]. S. Muralidharan et al[9] have suggested that 3-methyl 2,6 diphenyl piperidone adsorbs through perpendicular orientation of piperidone to the mild steel surface [Fig b]. Again Mallika et al[10] have also proposed the similar mechanism for a series of piperidones. On the basis of these above averments in can be concluded for the present work that the piperidones taken for investigation also inhibit corrosion by adsorbing on metal surface in perpendicular orientation using nitrogen as anchoring site. In this mechanism, the nitrogen uses its lone pair of electrons with the vacant d orbital on the Fe – atoms [Fig c].

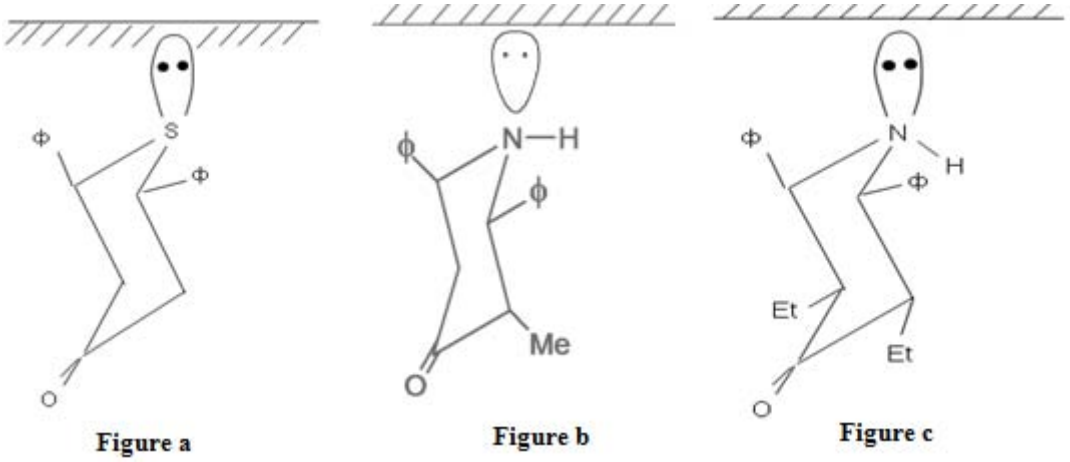

Figure a **Figure b** **Figure c**

3.2. Conclusion

The following conclusions are drawn from the present study

1) The inhibition efficiency of 3, 5-diethyl 2, 6-diphenyl *p*-chloro Piperidin-4-one (DEPCPN) increases with increase in inhibitor concentration and maximum efficiency is observed at 1mM concentration.
2) Temperature has significant effect on corrosion rate and inhibitor efficiency.
3) The adsorption of inhibitor on mild steel surface obeys Langmuir adsorption isotherm.
4) The activation energy E_a increases with increase of temperature.
5) The negative value of ΔG^0_{ads} indicates spontaneous adsorption of the inhibitor on the metal surface.
6) The inhibitor behaves as mixed type inhibitor.

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