Gazi University Journal of Science
GU J Sci
25(4):835-842 (2012)

ORIGINAL ARTICLE

New Synthesized Schiff base as Inhibitor of Mild Steel Corrosion in Acid Medium

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Received:13.07.2011 Revised:04.05.2012 Accepted: 07.06.2012

ABSTRACT

The inhibition effect of a new synthesized Schiff base, namely 4-nitro-2-methoxy phenyl- N-salicylidine on the corrosion of mild steel in 0.5M HCl acid have been investigated at room temperature using electrochemical impedance spectroscopy(EIS), Tafel polarization and weight loss measurements. It was concluded that the inhibition efficiencies increased with increase in the concentrations of the Schiff base. The inhibition efficiencies obtained from all methods employed are in good agreement with each other. Tafel polarization studies showed that the Schiff base was mixed type inhibitor. The adsorption of this compound on a mild steel surface from 0.5M HCl acid obeyed the Langmuir adsorption isotherm and the thermodynamic calculations revealed that the adsorption of inhibitors was of physical nature.

Key Words: Corrosion Inhibition, Mild Steel, Electrochemical Methods

1. INTRODUCTION

Acid solutions are widely used in industry the most important areas of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing [1,2]. Inhibitors are usually used in these processes to control the corrosion of the metal. Organic compounds containing polar functions with oxygen, nitrogen, or sulfur have been widely studied as inhibitors for the acid corrosion of steel. Some Schiff base compounds have recently been reported as effective corrosion inhibitors for mild steel[3-5] and other metals[6-8]. These substances generally become effective by adsorption on metal surface. The efficient adsorption is the result of either the π-electron of the aromatic system and multiple bonds, or the presence of electronegative atoms (O or N) in the inhibitors molecular structure [9]. Availability of π electron due to the presence of multiple bonds or aromatic rings in the inhibitor molecule would facilitate electron interact with d-orbital of iron [10,11]. The aim of this paper is to study the inhibiting action of a new of new synthesized Schiff base containing nitrogen\ sulfur and aromatic rings. The electrochemical behavior of mild steel in 0.5M HCl in the absence and presence of inhibitor has been studied by potentiodynamic polarization, electrochemical impedance spectroscopy and gravimetric methods.

2. EXPERIMENTAL

Mild steel (0.09% P, 0.38% Si, 0.35% Mn, 0.21% C, 0.05% S and balance Fe) was used for this investigation. Steel samples were polished with different emery papers up to 1200 grade, washed thoroughly with bi-distilled water degreased and dried with acetone. The aggressive solution (0.5M HCl) was prepared by dilution of

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[♠]Corresponding author, e-mail: f-baghaei@mail.uk.ac.ir analytical grade 37% HCl with double-distilled water. Samples were weighted before and after exposure to 0.5M HCl containing various inhibitor concentrations. The solution volume was 100 cm^3. The mild steel specimen used has a rectangular form (2cm×1.5 cm ×0.05 cm). The immersion time was 24h at 298 K.

The polarization studies were carried out on steel disc ($1cm^2$). A saturated calomel electrode SCE and a platinum electrode are used as reference and auxiliary electrode, respectively. The current-voltage characteristics are recorded with a potentiostat/galvanostat EG&G type Princeton Applied Research Model 263A.Tafel current potential curves were recorded from -250 mV to +250 mV vs E_{ocp} at scan rate of 1mV/sce. The electrochemical impedance spectroscopy (EIS) measurements were carried out with a frequency response analyzer (Princeton Applied research Model 1020) and the same equipment was used for the Tafel polarization measurements. The electrochemical impedance and polarization curves carried out on steel disc at the open circuit potential (E_{ocp}) after 30 min immersion in 0.5M HCl acid solution. After determination of steady-state current at E_{corr}, sine wave voltages (10 mV) peak to peak, at frequencies between 100 kHz and 100 mHz were superimposed on the rest potential. The impedance diagrams are given in the Nyquist representation. The Schiff bases of 4-nitro-2-methoxy phenyl- N-salicylidine was synthesized using standard methods and it was recrystallized twice from absolute ethanol and finally dried in air [12]. This Schiff base was used as inhibitor and was added in 0.5M HCl from 50 ppm to 250 ppm. The structure this Schiff base is shown in Figure 1.

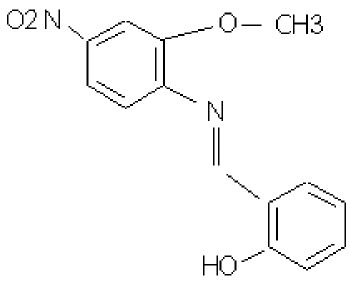

Figure 1. Molecular structure of investigated Schiff base

3. RESULTS AND DISCUSSION

3.1. Gravimetric Measurements

The effect of addition of Schiff base at different concentrations on the corrosion of mild steel in 0.5M HCl was studied by weight loss at 298 K after 24h of immersion period. The inhibition efficiency η_w (%) was determined by the following relation:

$$\eta_w(\%) = [1 - \frac{W_i}{W_0}] \times 100 \quad (1)$$

W_0 and W_i are the mean values of twice weight loss of samples after immersion in solution without and with inhibitor respectively. The results of weight loss measurements are shown in Table 1.

Table 1. Inhibition efficiency of Schiff base for mild steel in 0.5M HCl obtained from weight loss measurements

C_{inh} (ppm)	50	100	150	200	250
η (%)	84.6	87.4	89.5	93.3	95.1

The results obtained show that the mild steel corrosion rate decreases with increasing inhibitor concentration. Then η_w (%) increases with increasing inhibitor concentration. At the highest concentration of 250 ppm has a highest inhibition efficiency of about 95%. This result indicates that Schiff base could act as good inhibitor of mild steel in 0.5M HCl.

3.2. Electrochemical Impedance Spectroscopy

The corrosion behavior of mild steel in 0.5M HCl acid in the presence of Schiff base was investigated by electrochemical impedance spectroscopy (EIS) after 30 min of immersion at corrosion potential. Nyquist plots of mild steel in inhibited and uninhibited in acidic solutions containing various concentrations of Schiff base are shown in Figure 2. These plots having the shape of semicircle indicated the activation-controlled nature of the reactions with single charge transfer process. Also such behavior characteristics for solid electrodes and often referred to as frequency dispersion have been attributed to different physical phenomena such as roughness and in homogeneities of solid surfaces during corrosion [2], impurities, dislocation, grain boundaries, factuality, distribution of active sites, adsorption of inhibitors and formation of porous layers. Similar diagrams were described elsewhere [13] for mild steel electrode in the absence and presence of organic inhibitors in HCl.

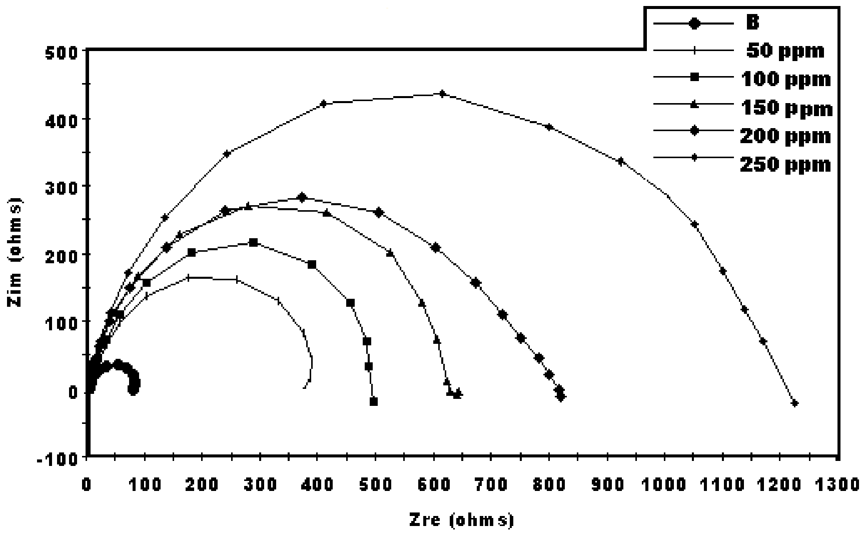

Figure 2. Nyquist plots for mild steel in 0.5 M HCl containing different concentrations of Schiff base.

The results obtained from electrochemical impedance spectroscopy (EIS) method can be interpreted in terms of the equivalent circuit of the electrical double layer shown in Figure 3 which has been used previously to model the iron/acid interface [14]. The constant phase element (CPE) has a non-integer power dependence on the frequency and is used to compensate the non homogeneity in a system. Its impedance is described by the expression:

$$Z_{CPE} = \frac{1}{Y(j\omega)^n} \qquad (2)$$

where Y is a proportional factor, j equals $\sqrt{-1}$, ω is $2\pi f$, n is the phase shift [15]. For $n=0$, Z_{CPE} represents a resistance with $R = Y^{-1}$, for $n = 1$ a capacitance with $C = Y$, for $n = 0.5$a Warburg element and for $n = -1$ an inductive with $L = Y-1$ [16]. Often a CPE is used in a model in place of a capacitor to compensate for non-homogeneity in the system. For example, a rough or porous surface can cause a double-layer capacitance to appear as a CPE with an n value between 0.9 and 1[17].

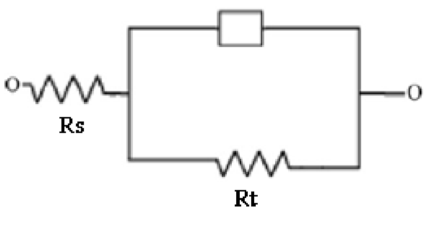

Figure 3. The equivalent circuit model employed in analysis of electrochemical impedance data.

In this equivalent circuit (Figure 3), R_s is the solution resistance between the working and reference electrode, R_t is the charge transfer resistance corresponding to the corrosion reaction at metal/electrolyte interface and CPE is the constant phase element. CPE is substituted for the respective capacitor of C_{dl} in order to fit better the depressed semicircles [18].

To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum $(-z''_{max})$ is found and C_{dl} values are obtained from the equation [19].

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl} R_t} \qquad (3)$$

Where C_{dl} is the double layer capacitance, The charge transfer resistance (R_t) is obtained from the diameter of the semicircle in Nyquist representation. Inhibition efficiency (η_z) of the inhibitor is calculated through the following relationship:

$$\eta_z(\%) = [1 - \frac{R_{t_0}}{R_t}] \times 100 \qquad (4)$$

R_{to} and R_t are charge transfer resistance value with and without inhibitor, respectively.

It is found (Table 2) that, as the Schiff base concentration increases, the R_t values increase, but the C_{dl} values tend to decrease. The decrease in C_{dl} values is interpreted by the adsorption of Schiff base on the metal surface. It is apparent from Nyquist diagrams that the charge-transfer resistance value of mild steel in uninhibited 0.5M HCl solution changes significantly after the addition of the inhibitor.

Table 2. Electrochemical impedance parameters of mild steel 0.5M HCl and in the presence of different concentrations of Schiff base

C (ppm)	R_t (Ωcm^2)	C_{dl}(μFcm^{-2})	η_z(%)
Blank	75	559	-
50	361	297	79.2
100	478	286	84.3
150	640	283	88.2
200	816	233	90.8
250	1221	141	93.9

As the inhibitor concentration increased, R_t values increased (Table 2) which related to lower corrosion rate at higher inhibitors concentration. Figure 4 is shown the plots of mild steel in 0.5M HCl solution, with the addition in the 50 ppm Schiff base from 30 to 150 min.

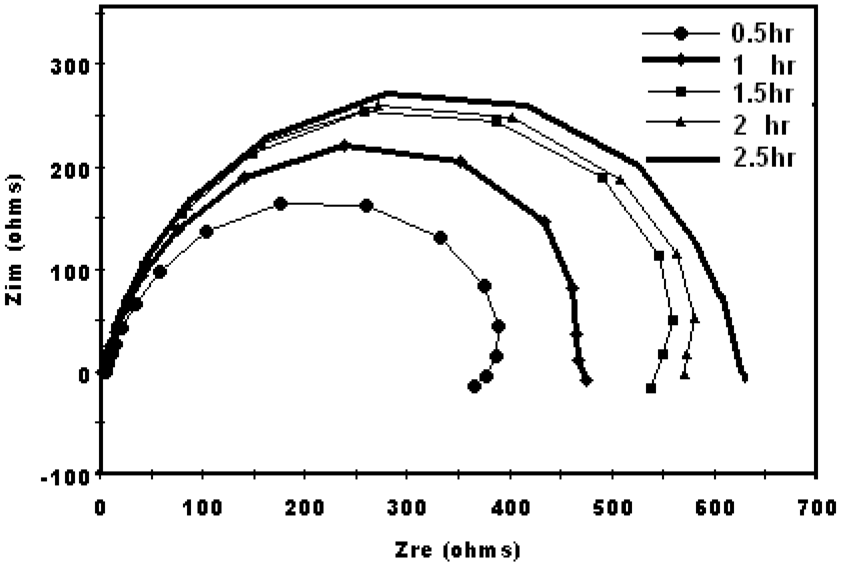

Figure 4. Nyquist plots for mild steel in 0.5M HCl containing 50 ppm Schiff base vs. time.

Figure 5 gives the relation the R_t and C_{dl} with immersion time, R_t of mild steel in 0.5M HCl solution with 50 ppm Schiff base increased with immersion time (to 150 min), while that C_{dl} decreased. Therefore it was also recognized from the results of EIS that the molecules of Schiff base are absorbed on surface of mild steel and formed a film to inhibitor corrosion of the mild steel [20].

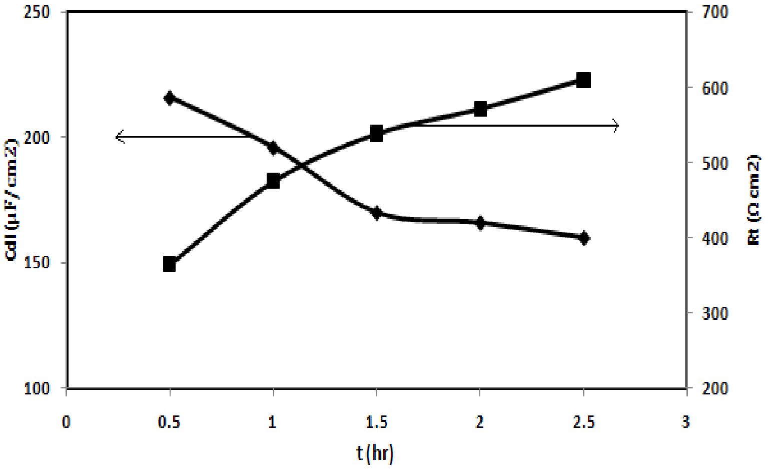

Figure 5. Relationships between R_t and C_{dl} with immersion time for mild steel in 0.5M HCl with 50ppm Schiff base.

3.3. Polarization Measurements

The Tafel polarization curves of mild steel in 0.5M HCl at various concentrations of Schiff base are shown in Figure 6. Table 3 gives values of corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c) and anodic Tafel slope (b_a) for Schiff base. For electrochemical measurements, the inhibition efficiency is calculated by using corrosion current density as follows:

$$\eta_p(\%) = \left[1 - \frac{I_i}{I_0}\right] \times 100 \qquad (5)$$

I_0 and I_i are the corrosion current density value with and without inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

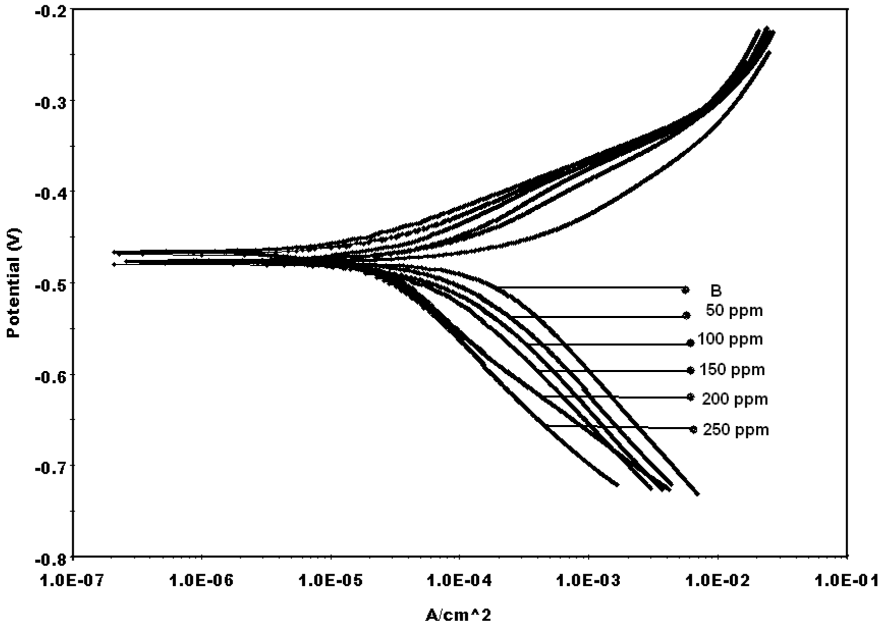

Figure 6. Tafel polarization curves of steel in 0.5M HCl and the presence of different concentrations of Schiff base

Table 3. Tafel polarization parameters of mild steel 0.5M HCl and in the presence of different concentrations of Schiff base.

C (ppm)	E_{corr}(mV)	I_{corr}(μA/cm^2)	b_c(mV/ decade)	b_a(mV/ decade)	η_p(%)
Blank	- 477	263	150	81	-
50	- 475	47	110	70	82.2
100	- 477	38	95	76	85.5
150	- 475	30	116	80	88.6
200	- 469	21	131	72	92.1
250	- 466	14	128	73	94.6

The addition of Schiff base leads to a decrease in both the cathodic and anodic current densities. This result indicates that the tested Schiff base acts as a mixed inhibitor. Nevertheless, corrosion potential shifted to more positive values for inhibitor which show they acted more anodic. On the other hand the changes in potential values (E_{corr}) are not large enough to consider the action of inhibitor only anodic and the Schiff base diminish the iron dissolution by adsorption on anodic sites more than hydrogen evolution as cathodic reaction.

In the presence of Schiff base inhibition efficiency increases with inhibitor concentration to attain a maximum value of 94.6% at 250 ppm. This result indicates that Schiff base could act as good inhibitor of mild steel in 0.5M HCl.

3.4. Adsorption Isotherm

It is general assumption that the adsorption of the organic inhibitors at the metal/surface interface is the first step in the mechanism of the inhibitor action. Organic molecules may adsorbed on the metal surface in four types:

(a) electrostatic interaction between a negatively charged surface, which is provided with specifically adsorbed anions (Cl^-) on iron and the positive charge of the inhibitor, (b) interaction of unshared electron pairs in the molecule with the metal, (c) interaction of π-electron with metal and (d) a combination of the (a–c) types. Efficient adsorption is the result of either π-electron of the benzene system or the electronegative O and N (hetro-atom) atoms [9]. The essential effect of this Schiff base as corrosion inhibitor is due to the presence of free electron pairs in the nitrogen atoms and oxygen atom on OH, π-electrons on the aromatic rings, molecular size, mode of interaction with the metal surface and the formation of metallic complexes [21,22].

The unshared and π-electrons interact with d-orbital of Fe provide a protective film. The inhibitive properties of such compounds depend on the electron densities around the active center, the higher the electron density at the active center, the more effect is the inhibitor.

This Schiff-base has six hetro-atoms (five nitrogen and one oxygen atom on OH group) on this molecule would have the possibility to transfer their unshared electrons to iron bulk and be absorbed .

Two main types of interaction can describe the adsorption of the organic compounds: physical adsorption and chemisorptions. These are influenced by the electronic structure of the metal, the type of electrolyte and the chemical structure of the inhibitor. In order to elucidate the character of adsorption of this Schiff-base, an adsorption isotherm describing the process was determined using the data of Table 3. The surface coverage θ of the metal surface by the adsorbed inhibitor was calculated [21] assuming no change in the mechanism of both the anodic and the cathodic reactions using the equation:

$$\theta = 1 - \frac{I_i}{I_0} \qquad (6)$$

where I_i and I_0 are the corrosion rates in the presence and absence of the inhibitor. Attempts were made to fit these θ values to various isotherms including Frumkin, Langmuir, Temkin and Freundlich. By far the best fit was obtained with the Langmuir isotherm. According to this isotherm, θ is related to the inhibitor concentration C via:

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

where K designates the adsorption equilibrium constant. This equation is the ideal equation that should be applied to the ideal case of the physical and chemical adsorption on a smooth surface with no interaction between adsorbed molecules. It was found that a plot of C/θ vs C gives straight lines with nearly unit slopes showing that the adsorption of Schiff base in 0.5M HCl on the mild steel surface obeys the Langmuir adsorption isotherm (Figure 7).

In this case, the line had a slope of 1.0136 and the correlation coefficient (R^2) was 0.9985. The deviation of the slope from unity is often interpreted as a sign that the adsorbing species occupy more or less a typical adsorption site at the metal/solution interface [23-25].

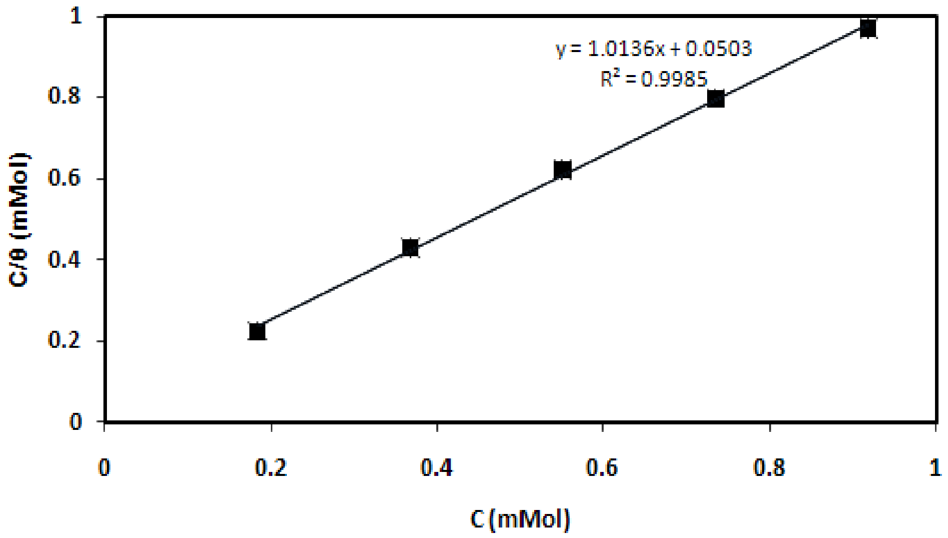

Figure 7. Langmuir adsorption plot for mild steel in 0.5M HCl containing the Schiff base

Free energy of adsorption (ΔG_{ads}) calculated using the following equation.

$$\Delta G_{ads} = -RT\ln(K_{ads}) \qquad (8)$$

Where R universal gas constant, K_{ads} adsorption constant and T absolute temperature. The value for the free energy of adsorption ΔG^0_{ads} can be calculated. For Schiff base, ΔG^0_{ads}= -24.522 KJmol^{-1} is found. The value of the free energy of adsorption around -20 KJmol^{-1}, suggests well the physical adsorption.

The value found for the Schiff base on mild steel thus clearly indicates that the adsorption is of the physical–probably electrostatic–nature, and that no covalent bond between inhibitor molecules and metal surface is established. Adsorption of the inhibitor explains this phenomenon, as solvent molecules (with high dielectric constant) within the electrical double layer become replaced with molecules with less pronounced dielectric properties.

The negative value of ΔG^0_{ads} indicate spontaneous adsorption of inhibitor molecule on the metal surface and more negative value of ΔG^0_{ads} reflects the increasing adsorption capability [26-29].

4. CONCLUSION

The data obtained from the Tafel polarization, EIS techniques and weight loss measurement confirm that the Schiff base is effective corrosion inhibitor for mild steel in 0.5M HCl acid. Electrochemical studies and weight loss measurements have been given similar results. (Relatively good agreement was found between the inhibition efficiencies obtained from electrochemical measurements (EIS and polarization) and weight loss results. The inhibition efficiency values of Schiff base are as a function of Schiff base concentrations, using Tafel polarization , impedance and weight loss results). According to the Tafel polarization studies indicate that the Schiff base is of mixed anodic–cathodic type.

The performance of organic adsorbent-type inhibitor is evaluated by adsorption isotherm. In this study the Langmuir adsorption isotherm provides a formal description of the adsorption behavior of the inhibitor on mild steel.

The values for the thermodynamic parameters for the inhibitor metal interactions clearly indicate that for the Schiff base, the adsorption is of physical nature.

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