

# Investigate the Corrosion Inhibition of Mild Steel in Sulfuric Acid Solution by Thiosemicarbazide

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## Abstract

Corrosion inhibition of mild steel in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> was investigated in the absence and presence of different concentrations of thiosemicarbazide. The inhibition efficiency of thiosemicarbazide was studied by electrochemical impedance methods, potentiodynamic polarization and scanning electron microscopy at different inhibitor concentrations. Inhibition efficiency, corrosion rate and surface coverage were evaluated at different concentrations of thiosemicarbazide. Electrochemical impedance plots indicated that the presence of the inhibitors increased the charge transfer resistance of the corrosion process, increasing the inhibition efficiency. Polarization curves showed that this compound acted as mixed type inhibitor. The results of the investigation showed that this compound had good inhibiting properties for mild steel corrosion in 0.5 M sulfuric acid. The adsorption isotherm studies showed that Thiosemicarbazide adsorbed chemisorbed and formed a stable surface complex on the mild steel surface. And Langmuir obeyed the adsorption isotherm. Scanning electron microscopy analysis shows that, the surface morphology of the polished mild steel in the presence of thiosemicarbazide as inhibitor is smoother surface as compared with polished mild steel specimen in the absence of inhibitor.

## Keywords

Acidic Medium, Adsorption, Inhibitor Mild Steel and SEM

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## 1. Introduction

The corrosion of materials is one of the main problems facing industrial processes, generating huge financial losses. Metallic industrial structures are often exposed to conditions that facilitate corrosive processes. Acid solutions are used in industries for pickling, acid cleaning and de-scaling of steel components. Acidizing inhibitors are added to protect the base metal from corrosion [1]. The use of organic inhibitors for preventing corrosion is a promising solution [2]. These organic inhibitors are usually adsorbed on the metal surface by the formation of a coordinate covalent bond (chemical adsorption) or the electrostatic interaction between the inhibitor and the metal (physical adsorption) [3]. These compounds were adsorbed, or formed a protective layer/insoluble complex on the metal surface and block the active corrosion sites [4].

Earlier studies have shown that the adsorption mainly depends on the p-electrons or d-electrons and on the heteroatom of the molecule which induces greater adsorption of the inhibitor molecules onto the surface of mild steel. Most of the effective organic compounds bearing heteroatoms with high electron density such as phosphorus, sulfur, nitrogen, oxygen, which are considered as adsorption centers, are effective inhibitors for the corrosion of metals [5]-[8]. In recent years, the efficiency of thiosemicarbazones compounds as organic corrosion inhibitors has been studied in a widely range [9]-[15]. The possibility to form complexes with different metals has also been reported [16]-[18]. The high activity and efficiency of these compounds against corrosion was due to the presence of both nitrogen and sulfur in their structures, generating higher inhibition efficiencies when compared to compounds containing only one of these elements. In addition, sulfur-containing compounds are generally more active than oxygen-containing compounds of similar structure [19] [20].

In this study, the adsorption and the inhibitory efficiency of thiosemicarbazide against the corrosion of mild steel in 0.5 mol/L of  $H_2SO_4$  solutions were investigated. Potentiodynamic polarization, electrochemical impedance techniques and scanning electron microscopy analysis were studied.

## 2. Experimental Technique

### 2.1. Preparation of Inhibitor Solution

The stock solution of 0.1 M inhibitor (thiosemicarbazide) was prepared. The mild steel rod was used as working electrode, which was cut from a cylindrical mild steel rod to a length of about 5 cm with chemical composition are : C (0.16), Si (0.13), Mn (0.7), P (0.019), Cr (0.016), Ni (0.007), Cu (0.077), Mo (0.008), Al (0.016), V (0.003), Ag (0.014) and Fe (remainder). A metallic wire is attached with the specimen then the wire was covered with glass tube which separated the wire from the environment. Then, it fixed in Teflon rods of proper internal diameter by epoxy resin so that only its cross section ( $0.785 \text{ cm}^2$ ) was allowed to contact the test solution. Before the measurements, the surface of mild steel were polished using different grades of silicon carbide paper stating with a coarse one (80) and proceeding into finer grade (2000) and rinsed with deionized water before each experiment, and dried.

### 2.2. Electrochemical Measurements

The assays were performed at room temperature using a three electrode electrochemical cell containing the mild steel rod as working electrode with a  $0.785 \text{ cm}^2$  surface area, a platinum auxiliary electrode and a silver-silver chloride ( $Ag/AgCl$ , 3.0 M KCl) reference electrode. The potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) measurements were performed using (ACM Gill AC) potentiostat/galvanostat under computer control. The working electrode was immersed in test solution for 17 min to establish a steady state open circuit potential ( $E_{ocp}$ ). After measuring the  $E_{ocp}$ , the electrochemical measurements were performed. The EIS experiments were conducted in the frequency range of 10 kHz to 10 mHz. The amplitude was 10 mV. The polarization curves were obtained in the potential ranges from  $-700 \text{ mV}$  to  $-200 \text{ mV}$  with a scan rate at  $30 \text{ mV} \cdot \text{s}^{-1}$ .

### 2.3. Scanning Electron Microscopy

The surface morphology of the formed layers on the mild steel surface after its immersion in the solutions of 0.5 M  $H_2SO_4$  in the absence and in the presence of the inhibitor (0.1 M) was carried out. The specimens were taken out, and dried and the SEM photographs of the surfaces of the specimens were investigated by JSM-6360 LV instrument.

### 3. Results and Discussion

#### 3.1. Electrochemical Impedance Spectroscopy (EIS)

The corrosion behaviour of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, in the absence and presence of thiosemicarbazide, was investigated by the electrochemical impedance spectroscopy measurements (EIS) at different temperature 30°C, 40°C, 50°C and 60°C after an exposure time of 20 min. The Nyquist plots for different inhibitor concentrations at different temperature are shown in **Figure 1**. The electrochemical impedance data from the Nyquist plots are given in **Table 1**.

The Nyquist diagrams show a single semicircle shifted along the real impedance axis ( $Z_{\text{real}}$ ), indicating that the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution is controlled by a charge-transfer process [21]. And the impedance response (diameter of the semicircle) of mild steel in inhibited solution has significantly changed after the addition of thiosemicarbazide in the corrosive media, and the impedance of inhibited substrate increased with increasing thiosemicarbazide concentration.

The charge-transfer resistance values ( $R_{ct}$ ) were obtained from the  $Z_{\text{real}}$ . The higher-frequency intersection corresponds to the solution resistance ( $R_s$ ), and the lower-frequency intersection corresponds to  $R_s + R_{ct}$ . Thus,  $R_{ct}$  values were calculated as the difference between the high-and low-frequency intersection values [22]. The double layer capacitance ( $C_{dl}$ ) and the frequency at which the imaginary component of the impedance is maximal are found as represented in equation [23]:

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

where  $f_{\text{max}}$  is the frequency value at which the imaginary component of the impedance is greatest. And the inhibition efficiency got from the charge transfer resistance is calculated by:

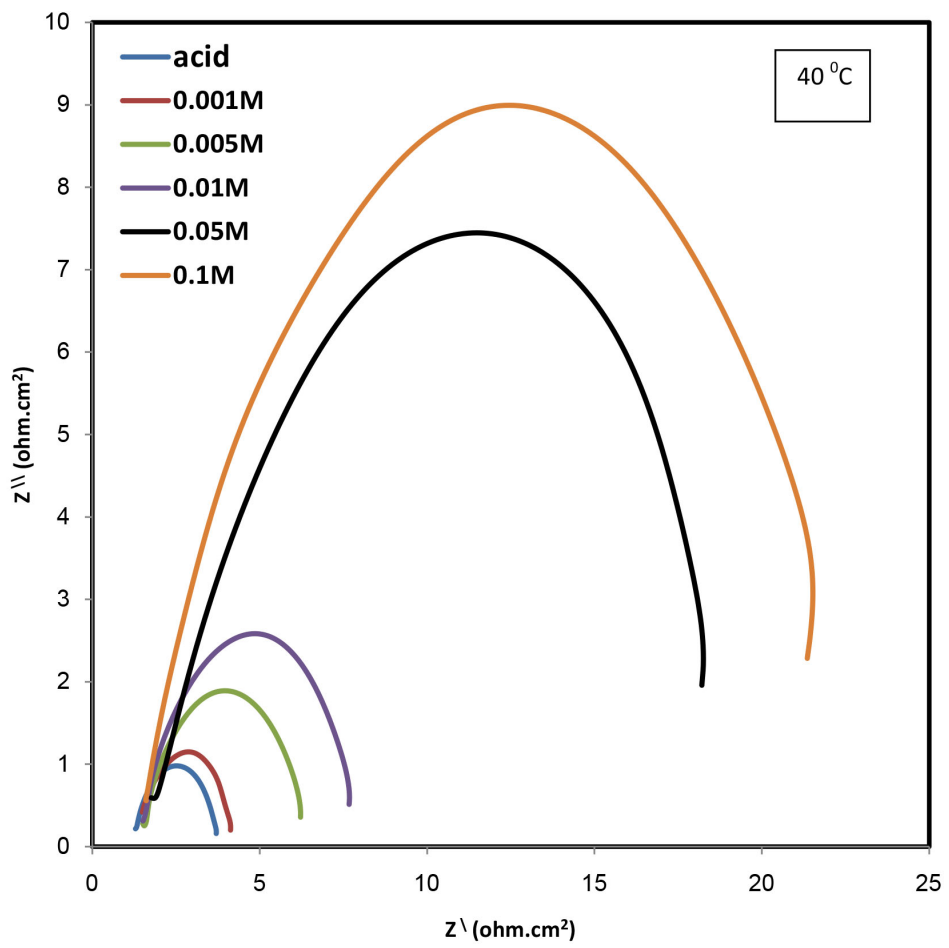
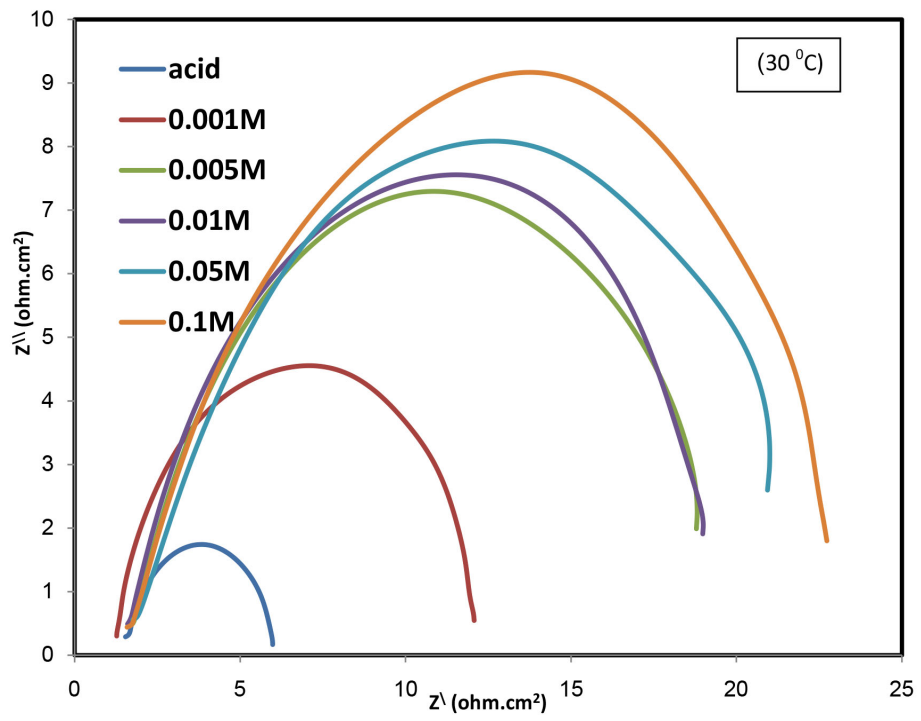
$$\%IE = \left[ 1 - \frac{(1/R_{ct})}{(1/R_{ct})_o} \right] \times 100 \quad (2)$$

where ( $R_{ct}$ ) & ( $R_{ct}$ )<sub>o</sub> are the charge transfer resistances in the absence and presence of the selected concentrations of corrosion inhibitor respectively. In **Figure 3**, the deviation from an ideal semicircle is generally attributed to the frequency dispersion as well as to the inhomogeneities of surface and mass transport resistant [24]. The diameter of the capacitive loop increased in the presence of the inhibitors. **Table 1** showed that, the  $R_{ct}$  values of inhibited substrates are increased with the concentration of inhibitors. The increase in  $R_{ct}$  value can be attributed to the formation of protective film on the metal/solution interface. On the other hand, the values of Capacitances double layer ( $C_{dl}$ ) are decreased with increase in inhibitor concentration which is most probably is due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer, indicating that the inhibitors function by adsorption at the metal surface [25] [26]. Also the effect of temperature on the electrochemical impedance spectroscopy was studied at 30°C, 40°C, 50°C and 60°C. The data in **Table 1** was showed that the impedance increases as the temperature of the solution increase and this leads to an increase in the value of the charge transfer resistance ( $R_{ct}$ ), and this indicate to a reduction in the corrosion rate. This was lead to the increase in the inhibition efficiency from 60.75% to 91.68% for the lowest concentration and from 87.43% to 97.12% for the highest concentration of inhibitor.

#### 3.2. Potentiodynamic Polarization Measurements

The potentiodynamic polarization curves of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with various concentrations of thiosemicarbazide at different temperature 30°C, 40°C, 50°C and 60°C are shown in **Figure 2**. The electrochemical parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current ( $I_{\text{corr}}$ ), anodic and cathodic Tafel slopes (ba and bc) and the inhibition efficiency ( $\eta\%$ ) values at different temperature 30°C, 40°C, 50°C and 60°C are recorded in **Table 2**. The  $\eta\%$  was calculated from polarization measurements according to the relation equation given below;

$$\eta\% = \left( \frac{I_{\text{corr}} - I'_{\text{corr}}}{I_{\text{corr}}} \right) \times 100$$



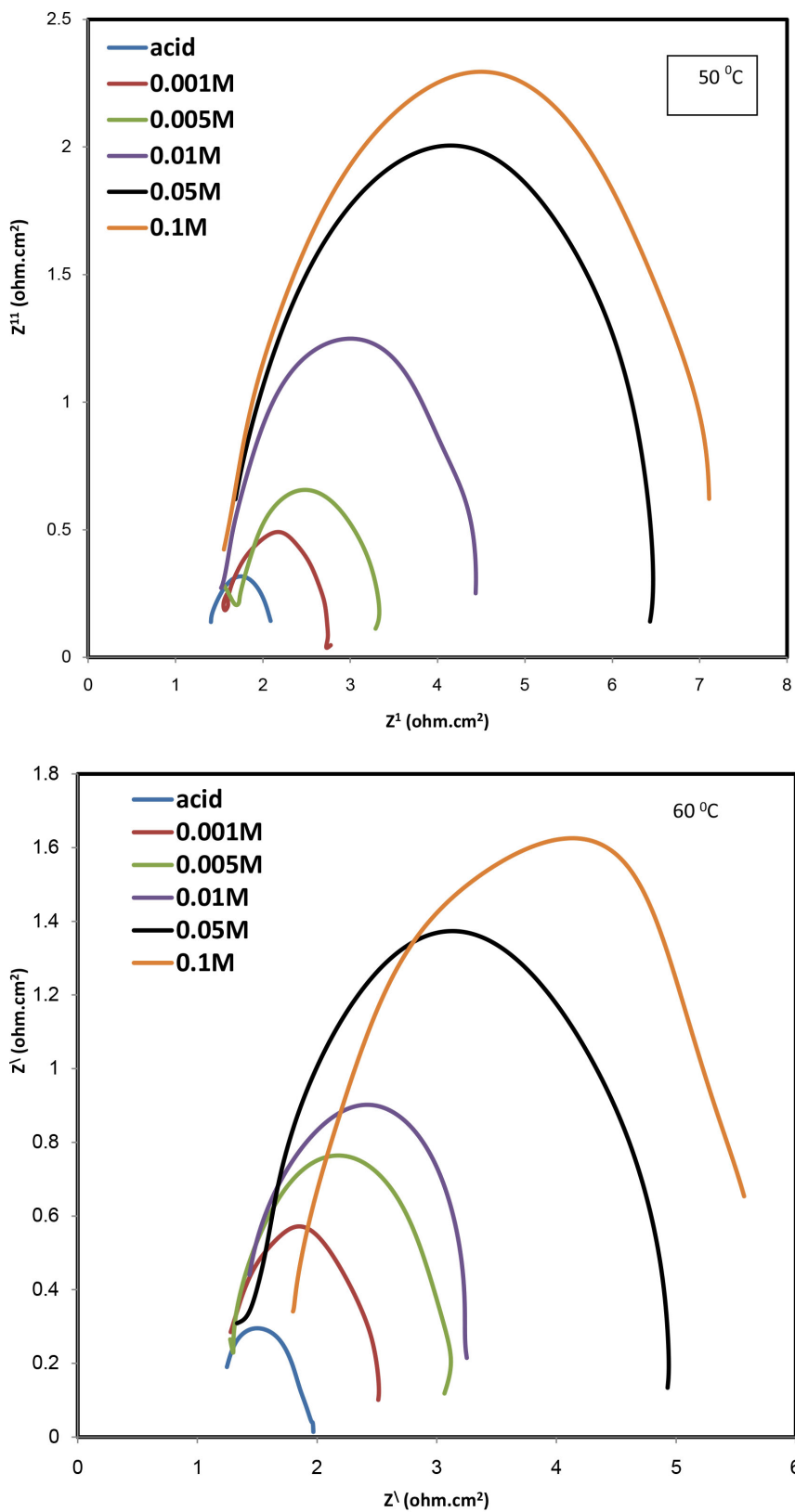


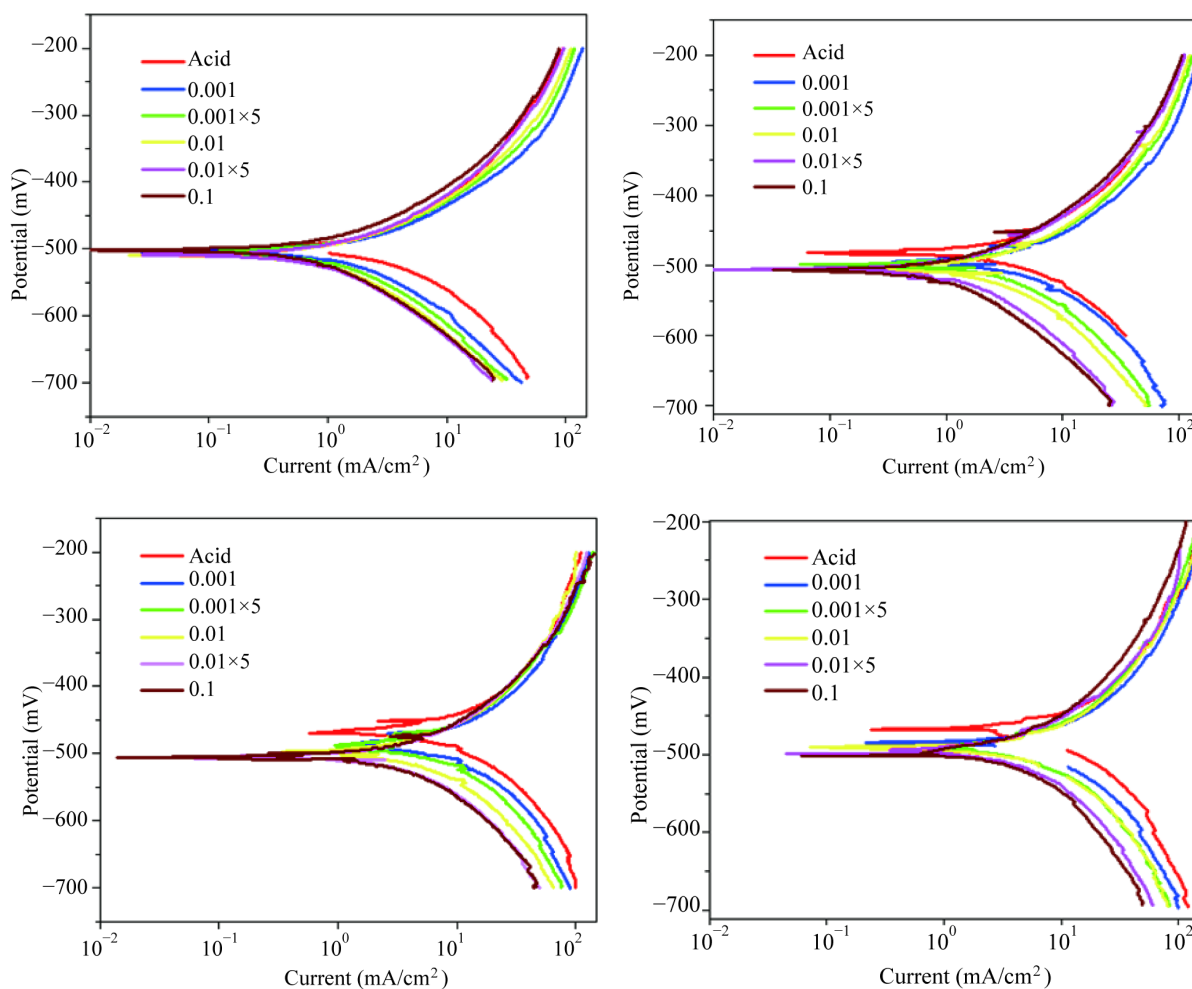
Figure 1. Nyquist diagrams for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of inhibitor at different temperatures 30 °C, 40 °C, 50 °C and 60 °C.

**Table 1.** The impedance data of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of inhibitor at different temperatures 30°C, 40°C, 50°C and 60°C.

Temp.	Conc. (M)	R <sub>ct</sub> (Ohm·Cm <sup>2</sup> )	1/R <sub>ct</sub> (Ohm <sup>-1</sup> ·Cm <sup>2</sup> )	C <sub>dl</sub> (μF·Cm <sup>2</sup> )	% IE
30°C	0.0	4.507	0.2219	627.2	----
	0.001	11.48	0.0871	349.7	60.75
	0.005	18.2	0.0549	310.9	75.26
	0.01	19.27	0.0519	192.5	76.61
	0.05	21.9	0.0474	177.7	78.64
	0.1	35.9	0.0279	124.6	87.43
40°C	0.0	1.001	0.999	853.9	----
	0.001	2.814	0.3553	565.5	64.43
	0.005	4.889	0.2045	422.4	79.53
	0.01	6.404	0.1562	272.1	84.22
	0.05	17.75	0.0563	234.2	94.36
	0.1	21.29	0.047	195.1	95.3
50°C	0.0	0.3011	3.3212	936.4	----
	0.001	1.298	0.7704	647	76.8
	0.005	1.784	0.5605	533	83.08
	0.01	2.989	0.3346	423.1	89.93
	0.05	5.29	0.189	354.6	94.31
	0.1	6.038	0.1656	256.1	95.01
60°C	0.0	0.12	8.3333	1114	----
	0.001	1.442	0.6935	959.7	91.68
	0.005	2.223	0.44498	804.6	94.6
	0.01	2.016	0.496	714.1	94.05
	0.05	3.816	0.262	694	96.86
	0.1	4.192	0.2403	517.3	97.12

where  $I_{corr}$  and  $I'_{corr}$  are corrosion current densities in the absence and presence of the inhibitor, respectively. **Figure 2** shows that the presence of the inhibitor, both anodic and cathodic curves are shifted and the shift depends on the concentration of the inhibitor. The polarization curves for the mild steel in the absence of inhibitor show that the current density in the anodic region increases rapidly indicating extensive dissolution of metal. This led to both the anodic metal dissolution and cathodic hydrogen evolution reactions were inhibited after the addition of thiosemicarbazide to the aggressive medium. **Table 2** shows that there is irregular displacement in the corrosion potential ( $E_{corr}$ ) values for mild steel are varied in irregular shape; this behavior was previously observed in many others studies [27]-[29]. Also, it is clear that the values of  $b_a$  and  $b_c$  are decreased with increase in the concentration of thiosemicarbazide; these results indicate that thiosemicarbazide acts as the mixed type corrosion inhibitor. The inhibitor molecules are first adsorbed on the surface of the mild steel and blocking the available reaction sites [30]. The surface coverage increases as the inhibitor concentrations increase. The presence of defects on the metal surface statements free access to H<sup>+</sup> ions [31] and a significant dissolution of metal carry out, followed by desorption of the inhibitor film from the metal surface [32]. This observed phenomenon is usually described as the corrosion inhibition of the metal with the development of a protective layer of adsorbed species at the metal surface [33].

Also the polarization measurements were taken at different temperatures in the absence and presence of various concentrations (0.001, 0.005, 0.01, 0.05, 0.1 M) of the inhibitor. **Figure 2** shows that the corrosion rate of mild steel rapidly increases with increasing temperature over the range (30°C - 60°C) in presence of the inhibitor. **Table 2** observed that the corrosion rate ( $I_{corr}$ ) of the mild steel in the presence of the inhibitor decreases with increasing its concentration and increases with increasing the temperature, whereas its efficiency increases with

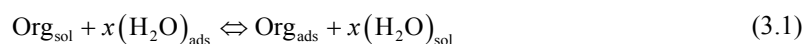


**Figure 2.** Polarization curves of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of inhibitor at different temperatures 30°C, 40°C, 50°C and 60°C.

increasing both its concentration and the temperature. And this was lead to the increase in the inhibition efficiency from 46.72% for the lowest concentration of inhibitor to 73.92% and from 87.41% for the highest concentration of inhibitor to 91.41%. These results are correlated with the data obtained from the impedance measurements.

### 3.3. Adsorption Isotherm and Thermodynamic Consideration

In order to get a better understanding of the electrochemical process on the metal surface, adsorption characteristics were also studied for a corrosive media. This process is closely related to the adsorption of the inhibitor molecules and adsorption is known to depend on the chemical structure. Adsorption isotherms are very important in determining the mechanism of organic electrochemical reactions. The adsorption of organic adsorbate on the surface of metal is regarded as substitutional adsorption process between the organic compound in the aqueous phase (Org.)<sub>aq</sub> and the water molecules adsorbed on the metal surface (H<sub>2</sub>O)<sub>ads</sub> according to following process [34]:



where  $x$  is the number of water molecules replaced by one organic molecule. The adsorption process of inhibitors are influenced by the chemical structures of organic compounds, the nature and surface charge of metal, the distribution of charge in molecule and the type of aggressive media [35]. One of the clearest examples thereof is

**Table 2.** Polarization data of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of inhibitor at different temperatures 30°C, 40°C, 50°C and 60°C.

Temp.	Conc. (M)	E <sub>corr</sub> (mV)	I <sub>corr</sub> (mA/cm <sup>2</sup> )	b <sub>a</sub> (V/decade)	b <sub>c</sub> (V/decade)	η %
30°C	0.0	-503.99	10.567	0.0589	0.1139	—
	0.001	-504.09	5.6301	0.0579	0.1194	46.72
	0.005	-506.89	4.1856	0.057	0.0849	60.39
	0.01	-509.89	3.4243	0.0494	0.0867	69.31
	0.05	-510.05	2.3838	0.0481	0.08513	77.44
	0.1	-511.97	1.33	0.0493	0.1251	87.41
40°C	0.0	-482.44	16.146	0.0521	0.1248	—
	0.001	-497.08	7.3765	0.0536	0.0922	54.31
	0.005	-501.73	5.4658	0.0689	0.0926	66.15
	0.01	-504.82	4.6543	0.065	0.0852	71.17
	0.05	-505.11	3.1598	0.0473	0.0915	80.43
	0.1	-508.71	2.0547	0.0649	0.1461	87.77
50°C	0.0	-468.56	22.513	0.0526	0.124	—
	0.001	-485.46	8.0209	0.0629	0.0947	64.37
	0.005	-495.22	6.4543	0.063	0.1617	71.33
	0.01	-499.52	4.8444	0.054	0.1659	78.48
	0.05	-506.54	4.2806	0.0493	0.1014	80.99
	0.1	-508.02	2.6613	0.0481	0.1144	88.18
60°C	0.0	-456.61	42.347	0.069	0.1417	—
	0.001	-483.52	11.046	0.0473	0.1252	73.92
	0.005	-492.49	8.3707	0.0498	0.1024	73.92
	0.01	-495.58	6.2329	0.0533	0.0996	85.28
	0.05	-497.08	5.6662	0.0631	0.1185	86.62
	0.1	-499.95	3.6366	0.0484	0.1158	91.41

the observation of endothermic adsorption which indisputably identifies chemisorption, as physisorption is an intrinsically exothermic process. The values of  $K$  (Table 3) were studied by fitting different adsorption isotherms, including the kinetic model, Flory-Huggins and Langmuir models. Also the correlation coefficient ( $R^2$ ) was used to choose the isotherm that is the best fit with the experimental data. Good agreement between the two models (kinetic and Flory-Huggins) obtained for all temperatures. The binding constant ' $K$ ' increases as the temperature increases, giving evidence for increasing surface coverage,  $\Theta$ , as the temperature increases. Large values of ' $K$ ' imply improved inhibition efficiency, *i.e.* strong electrical interactions between the double layer existing at the phase boundary and the adsorbate. Both ' $\gamma$ ' and ' $K$ ' are functions of the nature of the inhibitor, the type of the model used, the nature of the aggressive medium, and temperature.

The thermodynamic parameters  $\Delta G^{\circ}_{ads}$ ,  $\Delta H^{\circ}_{ads}$ , and  $\Delta S^{\circ}_{ads}$  & can be obtained from the dependence of the equilibrium constant (obtained from the kinetic model) on temperature by linear the following equation [36]:

$$\ln K = -\Delta H^{\circ}_{ads}/RT + \Delta S^{\circ}_{ads}/R \quad (3)$$

where,  $\Delta H^{\circ}_{ads}$ ,  $\Delta S^{\circ}_{ads}$  and  $\Delta G^{\circ}_{ads}$  are the enthalpy, entropy and Gibbs free energy changes, respectively and  $T$  is the temperature in Kelvin,  $R$  is the gas constant ( $\approx 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). In the system where temperature increase result in higher protection efficiency, a positive  $\Delta H^{\circ}_{ads}$  results. This is interpreted on the basis that stronger surface interaction result at higher temperatures. A plot of  $\ln K$  vs.  $(1/T)$  gives a straight line with a slope of  $(-\Delta H^{\circ}_{ads}/R)$  and intercept of  $(\Delta S^{\circ}_{ads}/R)$ . Value of  $\Delta H^{\circ}_{ads}$  was calculated and was equal to  $110.2 \text{ kJ}\cdot\text{mol}^{-1}$  and the value of  $\Delta S^{\circ}_{ads}$  calculated as  $438 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The  $\Delta G^{\circ}_{ads}$  value is calculated by the use of the following expression [36].



**Table 3.** Curve fitting data of the inhibitor to Langmuir, Flory-Huggind isotherm and kinetic model.

Temperature (°C)	Langmuir		Flory-Huggins			Kinitic model		
	K	R <sup>2</sup>	x	K	R <sup>2</sup>	1/y	K	R <sup>2</sup>
30	73.589	0.88	1.931	1976.97	0.95	1.95	2909.89	0.96
40	208.99	0.98	3.8977	5147.54	0.98	3.66	6627.82	0.99
50	225.72	0.87	2.5766	10055.4	0.97	2.47	13699.5	0.97
60	410	0.87	4.3505	1.3E + 07	0.96	3.95	1.1E + 07	0.98

**Table 4.**  $\Delta G_{ads}$  values for the adsorption of the inhibitor on mild steel surface calculated from the kinetic model at different temperatures.

Temperature (°C)	$\Delta G_{ads}^{\circ}$ (kJ·mole <sup>-1</sup> )
30	-22.51
40	-26.89
50	-31.27
60	-35.65

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \quad (3.16)$$

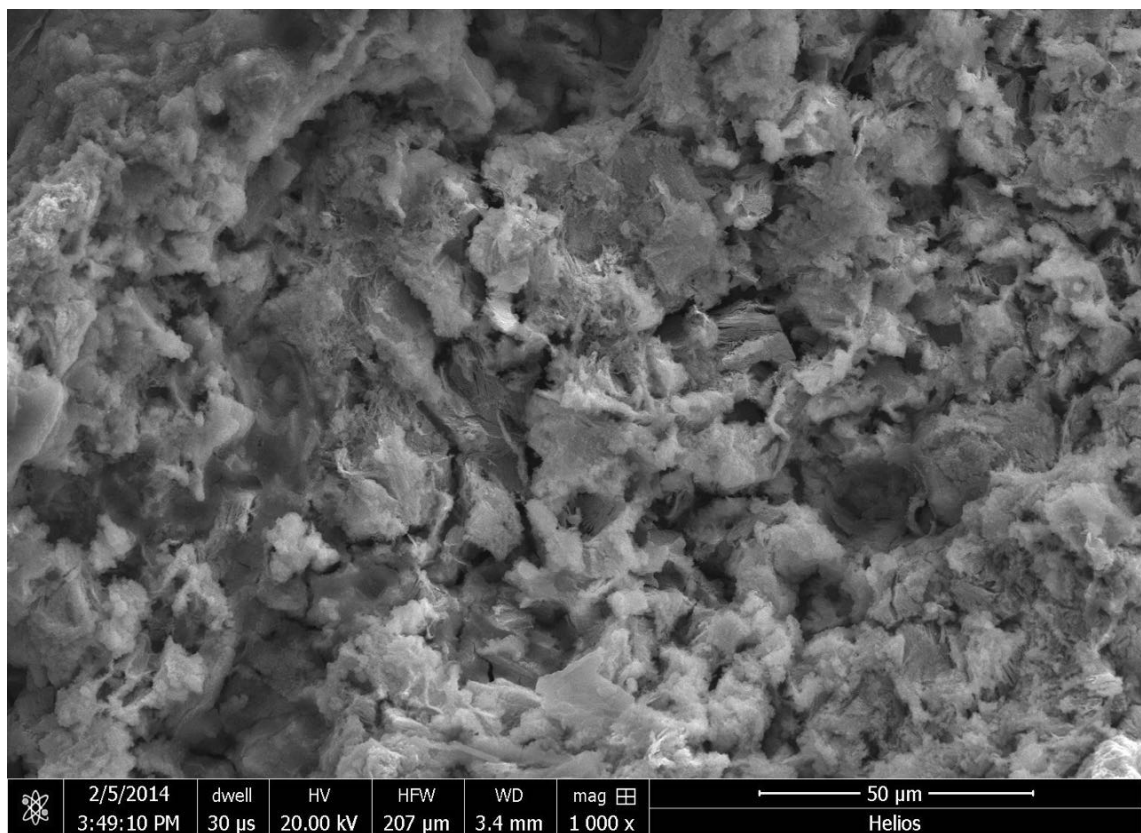
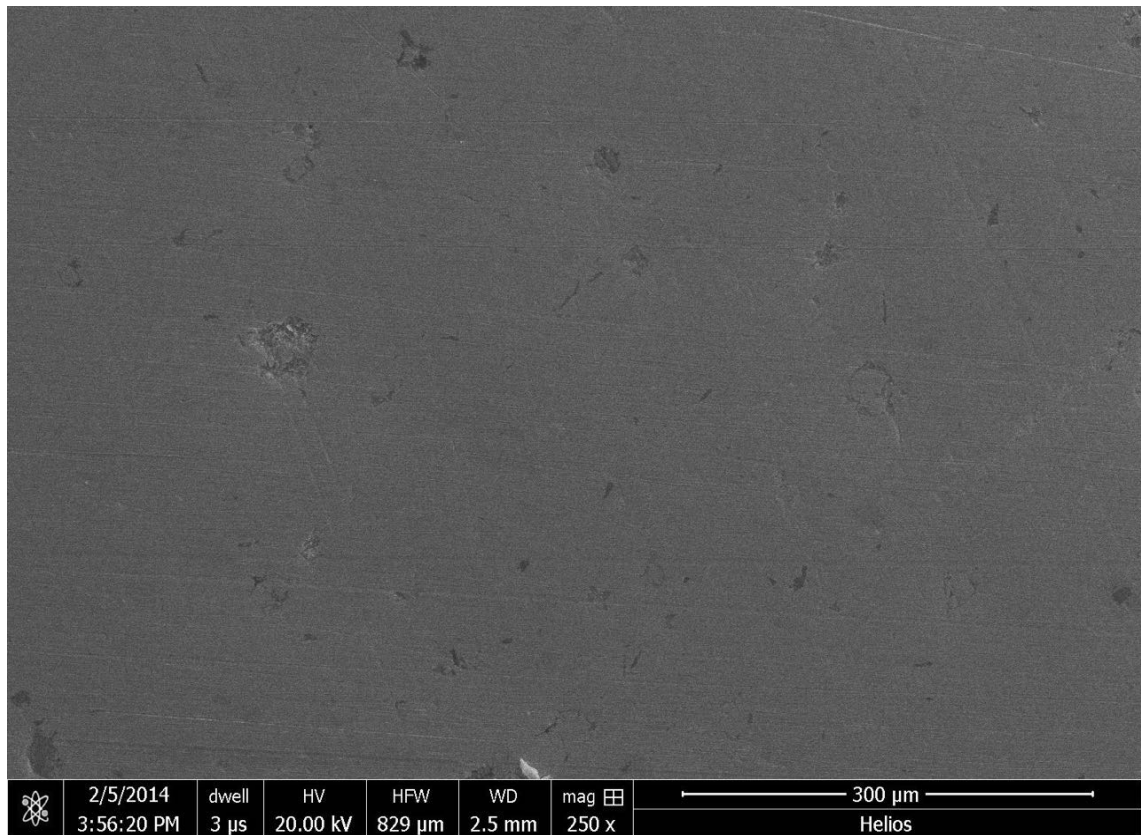
The resulting values of this expression are given in **Table 4** and generally,  $\Delta G_{ads}^{\circ}$  values until  $-20 \text{ kJ}\cdot\text{mol}^{-1}$  are associated with electrostatic interactions between the charged molecules and the charged metal surface (physisorption), whereas those below  $-40 \text{ kJ}\cdot\text{mol}^{-1}$  involve the sharing or transfer of charge from the organic molecules to the metal surface to form a coordinate covalent bond (chemisorption) [37]. The  $\Delta G_{ads}^{\circ}$  values obtained for the inhibitor at the four temperatures are between  $-22.6$  and  $-35.6 \text{ kJ}\cdot\text{mol}^{-1}$ . These values indicate that the adsorption process of the evaluated inhibitor on the mild steel surface may involve complex interactions (both physical and chemical adsorption) [38].

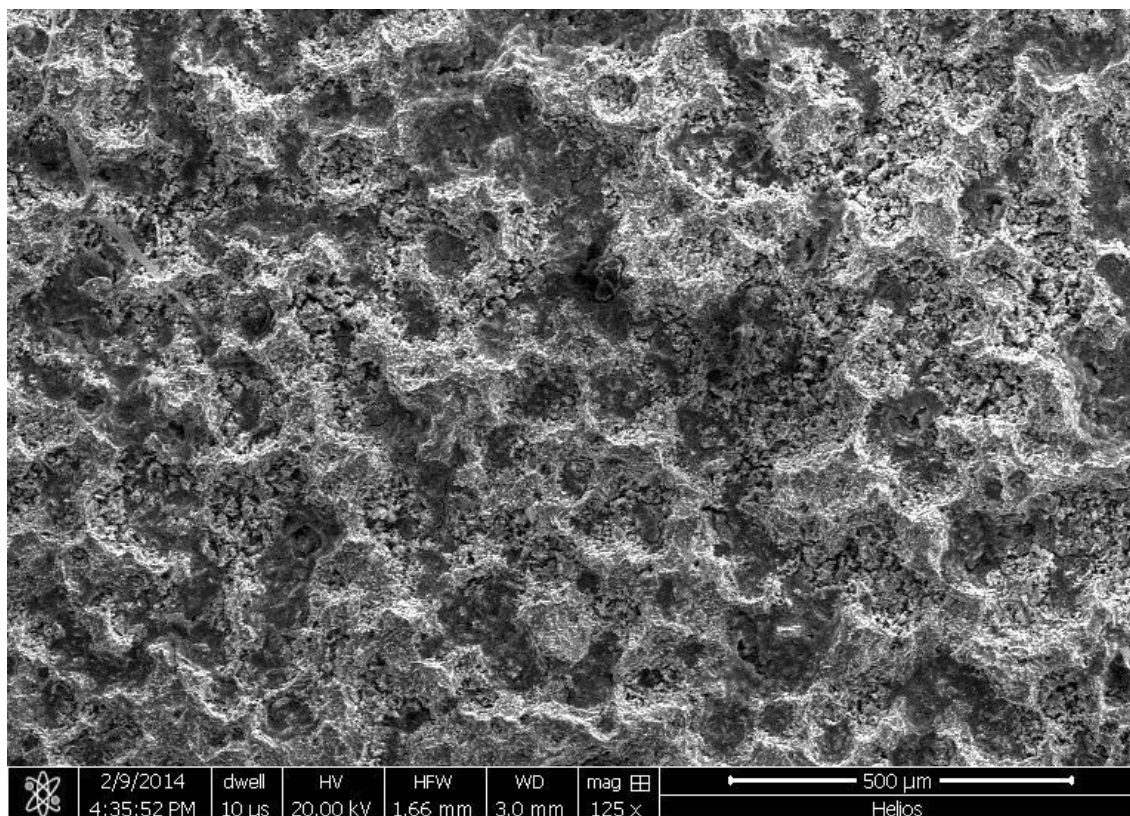
### 3.4. Scanning Electron Microscopy (SEM) Study

Surface morphology of mild steel was studied by scanning electron microscopy after 24 h immersion in 0.5 M  $\text{H}_2\text{SO}_4$  before and after addition of the inhibitor at 30°C. **Figure 3(a)** showed the SEM obtained of polished steel without being exposed to the corrosive environment and it clearer that that the mild steel sample before immersion seems smooth and shows some abrading scratches on the surface while, **Figure 3(b)** showed strongly damaged on mild steel surface due to the formation of corrosion products after immersion in 0.5 M  $\text{H}_2\text{SO}_4$  solution. And shows that an aggressive attack of the corroding medium on the mild steel surface. In contrast, **Figure 3(c)** SEM image of mild steel surface after immersion in 0.5 M  $\text{H}_2\text{SO}_4$  in the presence of 0.1 M of thiosemicarbazide extract the mild steel surface was corroded only negligibly. The result was an enhancement of surface coverage on the mild steel surface such that there was a decrease in contact between the mild steel and the aggressive medium. Thus, a good absorptive protection layer can efficiently inhibit the corrosion of mild steel.

## 4. Conclusions

- 1) The corrosion of MS in 0.5 M  $\text{H}_2\text{SO}_4$  solution can be inhibited by the use of thiosemicarbazide compound.
- 2) As the concentration of thiosemicarbazide increases, the inhibition efficiency of MS increases.
- 3) The electrochemical impedance spectroscopy shows that, the impedance increases as the temperature increases and this leads to an increase in the charge transfer resistance ( $R_{ct}$ ), and this indicates to a reduction in the corrosion rate.
- 4) The polarization data indicate that, the corrosion rate ( $I_{corr}$ ) of the mild steel in the presence of the inhibitor decreases with increasing its concentration and increases with increasing the temperature, whereas its efficiency increases with increasing both its concentration and the temperature.
- 5) The adsorption of thiosemicarbazide molecules on the metal surface from 0.5 mol/L  $\text{H}_2\text{SO}_4$  solution





**Figure 3.** SEM images of mild steel samples: (a) polishing surface (b) after immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution without inhibitor (c) after immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of 0.1 M thiosemicarbazide.

obeyed Langmuir adsorption isotherm model.

6) Surface morphological studied with SEM showed that a film of inhibitor was formed on the electrode surface.

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