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Investigation of 5-aminosalicylic acid (Mesalazine Drug) as a Corrosion Inhibitor for Carbon Steel in Sulfuric Acid Solution

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The techniques of polarization, electrochemical impedance spectroscopy (EIS) and Fourier transform infrared (FTIR) spectroscopy were employed for investigating the behavior of mesalazine drug (5-aminosalicylic acid) on the corrosion protection of carbon steel in 0.5 M H_2SO_4 solution. The corrosion protection was increased with increasing mesalazine concentration in both acid solutions. As evidenced by polarization data, mesalazine behaves as a mixed-type inhibitor and retards both anodic and cathodic processes. The inhibition efficiency of the drug decreased as the temperature increased up to 55 ^oC. The activation energies for the corrosion of carbon steel in the sulfuric acid solution were increased in the presence of the drug. The thermodynamic parameters for the corrosion process of carbon steel in sulfuric acid medium were calculated from the effect of temperature on the corrosion process. The adsorption of mesalazine on carbon steel in acid solution obeyed the Langmuir adsorption isotherm. The results extracted from the polarization data were in agreement with those obtained from EIS data. FTIR spectroscopy revealed the possible active center sites of mesazaline molecule during adsorption on the steel surface.

Keywords: Mesalazine drug; Potentiodynamic polarization; Electrochemical impedance spectroscopy; Green inhibitor.

1. INTRODUCTION

The compounds which decrease the reaction of the metallic surfaces with the corrosive media are called corrosion inhibitors. Acid solutions that are used in a wide variety of industrial applications require the inhibitors to reduce their aggressivity [1-14]. Sulfuric acid is generally the choice in the steel surface treatment due to its lower cost, minimal fumes and non-corrosive nature of the sulfate ion. However, corrosion inhibitors may cause some negative effects on the environment. Thus, it is important to develop the novel inhibitors obtained from both the natural sources and the non-toxic or low-toxic compounds [1-4]. In this way, many researchers have tried to develop the drugs as corrosion inhibitors

of metallic surfaces [4-12]. The inhibition effect of four antibacterial drugs on the aluminum surface in 2 M HCl solution was investigated by Abdallah [5]. Eddy et al. conducted some researches to develop two penicillins as corrosion inhibitors of carbon steel [6, 7]. The corrosion protection of 304 stainless steel in 1.0 M HCl solution by ampicillin and benzylpenicillin (penicillin G) has been investigated by Fouda et al. [8]. The inhibition effect of amoxicillin on carbon steel in 1 M sulfuric acid was studied by Kumar et al. [9].

In the present paper, the corrosion protection effect of mesalazine drug as a corrosion inhibitor was investigated on the corrosion of carbon steel in 0.5 M H_2SO_4 solution employing techniques of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Fourier transform infrared (FTIR) spectroscopy.

2. MATERIALS AND METHODS

2.1 Materials

The mesalazine drug was purchased from Sigma-Aldrich. The concentrated H_2SO_4 acid solution was obtained from Merck Company. The chemical structure of the mesalazine drug was illustrated in Fig. 1. The surface area of working electrodes (WEs) made of carbon steel was equal to 100 mm^2. The chemical composition of carbon steel was identified as (wt%): Mn (0.73), C (0.15), Si (0.72) and Fe (balance).

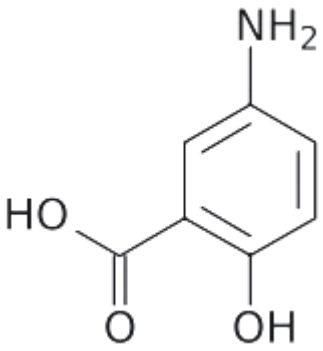

Figure 1. Structure of 5-aminosalicylic acid (mesalazine drug).

2.2 Methods

The inhibition effect of different concentrations of mesalazine drug on carbon steel was investigated in 0.5 M H_2SO_4 solution by potentiodynamic polarization and EIS measurements. After connecting a copper wire to the specimen, it was embedded in a PVC holder using epoxy resin so that the flat surface was the only surface of the working electrode. Each WE was polished using SiC emery papers through 600-2500 grades on the test face, then rinsed with distilled water, degreased with ethanol, and dried with air.

An instrument of potentiostat/galvanostat Autolab 302N (Eco Chemie, Netherlands) supported by a frequency response analyzer FRA-2 and Nova 1.6 software was employed to conduct the potentiodynamic polarization and EIS experiments. The reference electrode and the counter electrode (CE) were a saturated (KCl) Ag/AgCl electrode and a platinum rod with an area of 100 mm^2, respectively. A three-electrode arrangement was employed to conduct the electrochemical measurements. Each sample was immersed for 30 min in the test solution before measurement to obtain stabilized open circuit potential (OCP).

The EIS measurements were performed at OCP over a frequency range of 100 kHz to 10 mHz. The sinusoidal potential perturbation was 5 mV in amplitude. Nova 1.9 software was employed for analyzing the Nyquist plots of the impedance data.

Polarization measurements were potentiodynamically performed at a scan rate of 1 mV/s in the potential range of ±250 mV with respect to OCP. The software of Nova 1.9 was employed for determining polarization parameters.

3. RESULTS AND DISCUSSION

3.1. Polarization measurements

The polarization plots arising from carbon steel soaked in 0.5 M H_2SO_4 solution in the absence and presence of various amounts of mesalazine drug are presented in Fig. 2.

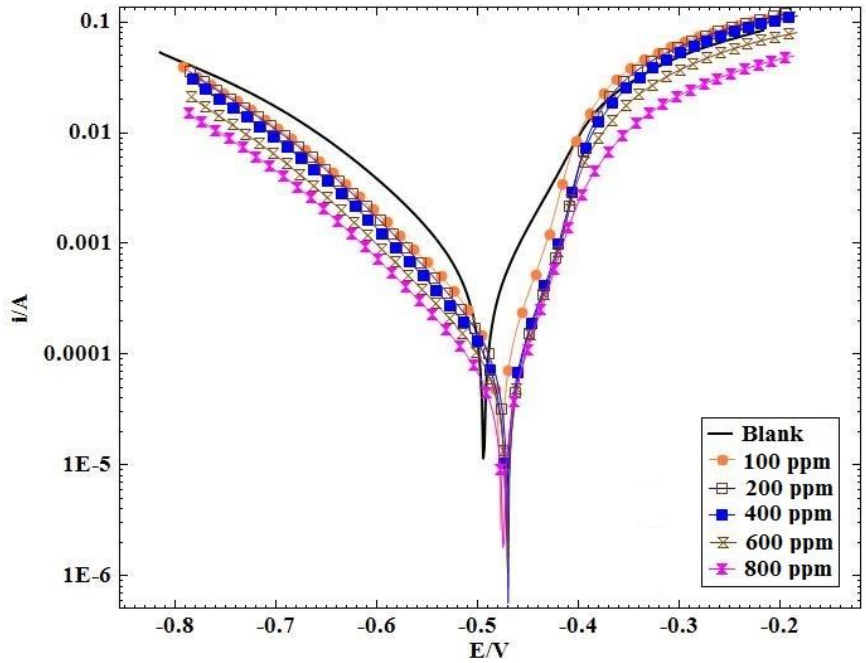

Figure 2. Polarization curves for carbon steel in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of of mesalazine drug at 25°C.

An expected linear Tafel behavior is observed from the cathodic branches of polarization curves shown in Fig. 2. Therefore, the Tafel extrapolation method seems appropriate to evaluate both the cathodic Tafel slope (β_c) and corrosion current density (i_{corr}). In contrast, a typical Tafel behavior was not displayed from the anodic branches of polarization curves. The nonlinearity of the anodic branch may be due to the non-passive surface film formed from the deposition of the corrosion products or the impurities in the steel [15]. Therefore, due to the nonlinearity of the anodic branch, the accurate evaluation of the anodic current density is not possible by the traditional Tafel extrapolation method. However, it has been shown that the anodic current density can be calculated by the sum of the experimental anodic current and the extrapolated cathodic current [16]:

$$i_a = i_a(\text{experimental}) + |i_c| \quad (1)$$

The polarization parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a, β_c) are listed in Table 1. The i_{corr} decreased as the amount of the drug increased. Both the cathodic and the anodic branches of the potentiodynamic polarization curves were affected by the addition of the drug to acid media. Therefore, it is clear that mesalazine can behave as a mixed corrosion inhibitor.

Table 1. Parameters obtained from polarization tests on carbon steel in 0.5 M H_2SO_4 solutions containing different concentrations of mesalazine at 25 ^{0}C.

C /ppm	i_{corr}/μA.cm^{-2}	-E_{corr}/mV	β_a/mV.decade^{-1}	β_c/mV.decade^{-1}	IE_P(%)
0	532	493	74	121	-
100	95	478	42	113	82.1
200	79	470	38	103	85.2
400	71	472	40	118	86.7
600	63	471	39	114	88.2
800	56	475	50	117	89.5

The inhibition efficiency (IE) values listed in Table 1 were obtained from the following equation [17]:

$$IE_P(\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \quad (2)$$

where i_{corr} and i'_{corr} are the current densities of corrosion in the absence and presence of mesalazine, respectively. It is clear that the increase in mesalazine concentration increased the IE value. The IE values showed a considerable increase with the increase in mesalazine concentration; which suggested that the adsorption of mesalazine on the electrode surface retarded effectively the acid corrosion of carbon steel.

It can be seen that a decrease in the corrosion current (i'_{corr}) and a corresponding increase in the inhibition efficiency is accompanied by an increase in the concentration of the drug. The increase in the

IE value is due to the increased surface coverage (θ) by the drug [18]. After obtaining surface coverage values by the equation of θ = IE/100, an attempt was made to test the Langmuir, Frumkin, Temkin and Freundlich isotherms. The Langmuir adsorption isotherm was found to fit well with the experimental data (Fig. 3), which can be expressed as:

$$\theta = \frac{KC}{1+KC} \quad (3)$$

or:

$$\frac{C}{\theta} = C + \frac{1}{K} \quad (4)$$

where C is mesalazine concentration, θ is the surface coverage and K is the equilibrium constant of adsorption. As Fig. 3 shows the plots of C/θ versus C was led to a straight line with a correlation coefficient near 1.0. This confirmed the Langmuir behavior of the adsorption of mesalazine on the carbon steel surface.

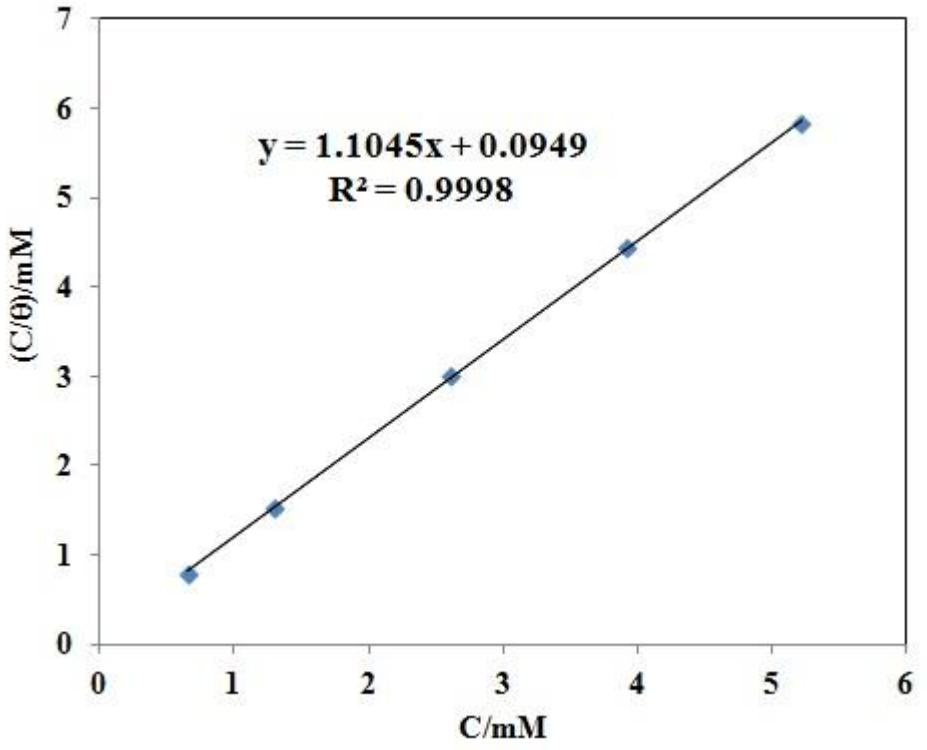

Figure 3. Langmuir adsorption isotherm of the inhibitor in 0.5 M H_2SO_4 solution by using surface coverage values calculated by Tafel polarization results.

3.2 Impedance measurements

Nyquist diagrams for carbon steel in H_2SO_4 solution without mesalazine (i.e. blank) and with various concentrations of mesalazine are presented in Fig. 4. It is clear that the impedance values of carbon steel increased as the amount of mesalazine drug was increased.

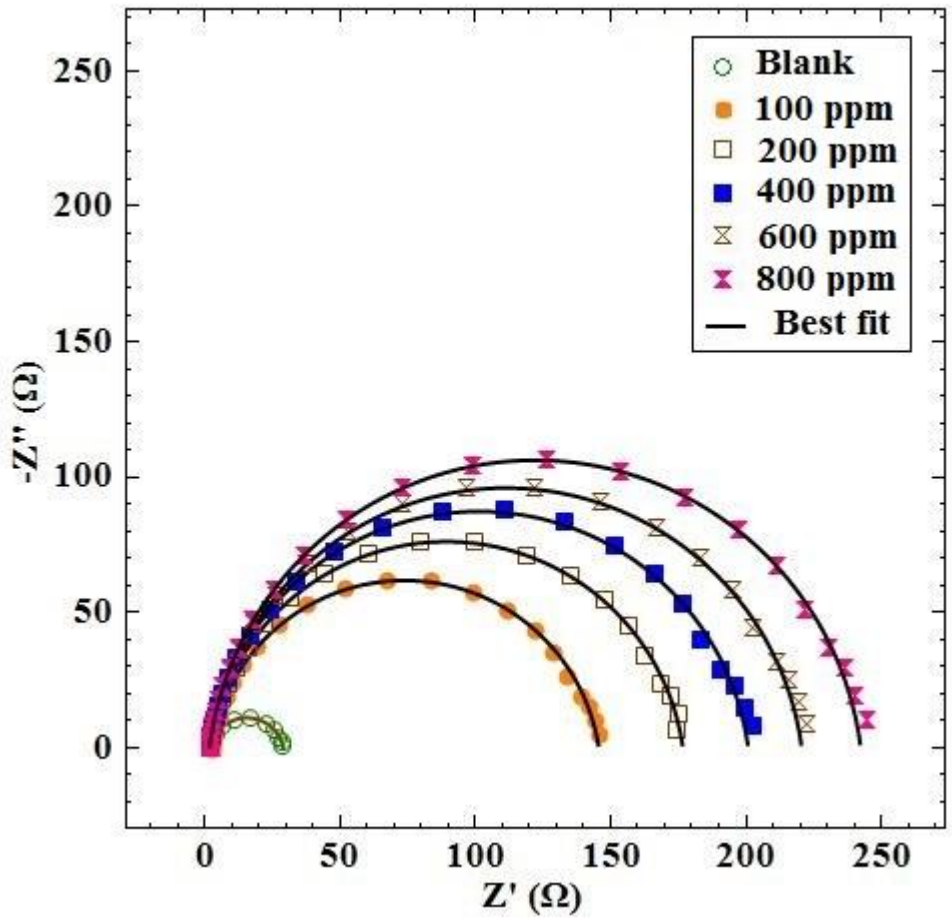

Figure 4. Nyquist plots for carbon steel in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of mesalazine drug at 25°C

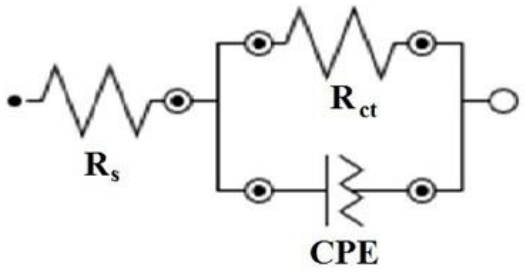

Figure 5. The electrical equivalent circuit used to fit the experimental data.

The impedance data have been fit to an equivalent circuit shown in Fig. 5. The solution resistance and the charge transfer resistance are represented by R_s and R_{ct}, respectively. The impedance of the constant phase element (CPE) is defined as follows [19, 20]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (5)$$

where Y_0 is the CPE constant ($F.cm^{-2}.s^{n-1}$ or $s^n.\Omega^{-1}.cm^{-2}$), j equals $\sqrt{-1}$, ω is the angular frequency and n is the CPE exponent. The following equation was employed to calculate the double layer capacitance, C_{dl}, from the CPE constant, Y_0 [21]:

$$C_{dl} = Y_0(\omega_{max})^{n-1} \quad (6)$$

where ω_{max} is the angular frequency at which the imaginary component of the impedance is maximum. The impedance parameters obtained from EIS measurements in the absence (blank) and the presence of different concentrations of mesalazine are listed in Table 2. As shown in Table 2, the R_{ct} values increased with increasing the concentration of mesalazine drug. On the other hand, the values of C_{dl} decreased when the mesalazine concentration was increased.

Table 2. Impedance parameters and the corresponding inhibition efficiencies for carbon steel in 0.5 M H_2SO_4 solutions containing different amounts of mesalazine at 25 ^{0}C.

C /ppm	$R_s/\Omega.cm^2$	$R_{ct}/\Omega.cm^2$	n	10^6 $Y_0/F.cm^{-2}.s^{n-1}$	$C_{dl}/\mu F.cm^{-2}$	$IE_{EIS}(\%)$
0	1.8	24	0.906	230	134	-
100	1.8	144	0.909	58	37	83.3
200	1.6	175	0.916	46	29	86.3
400	1.5	199	0.920	41	26	87.9
600	1.7	219	0.920	37	22	89.0
800	1.4	241	0.923	35	21	90.0

The following expression was employed for the calculation of inhibition efficiencies in Table 2:

$$IE_{EIS}(\%) = \frac{R_{ct}^{'} - R_{ct}}{R_{ct}^{'}} \times 100 \quad (7)$$

where R_{ct} and $R_{ct}^{'}$ represent the charge transfer resistance of carbon steel in the acidic media without (blank) and with mesalazine drug, respectively. The increase in mesalazine concentration caused to increase the inhibition efficiency. Regarding Tables 1 and 2, a good agreement can be observed between the IE values obtained from the EIS and polarization techniques.

Plots of the data obtained from EIS measurements shown in Fig. 6 proved that the adsorption of mesalazine on the steel surface corresponds with the Langmuir isotherm. Thus, the EIS results are in agreement with the polarization results which confirm the behavior of the Langmuir adsorption isotherm.

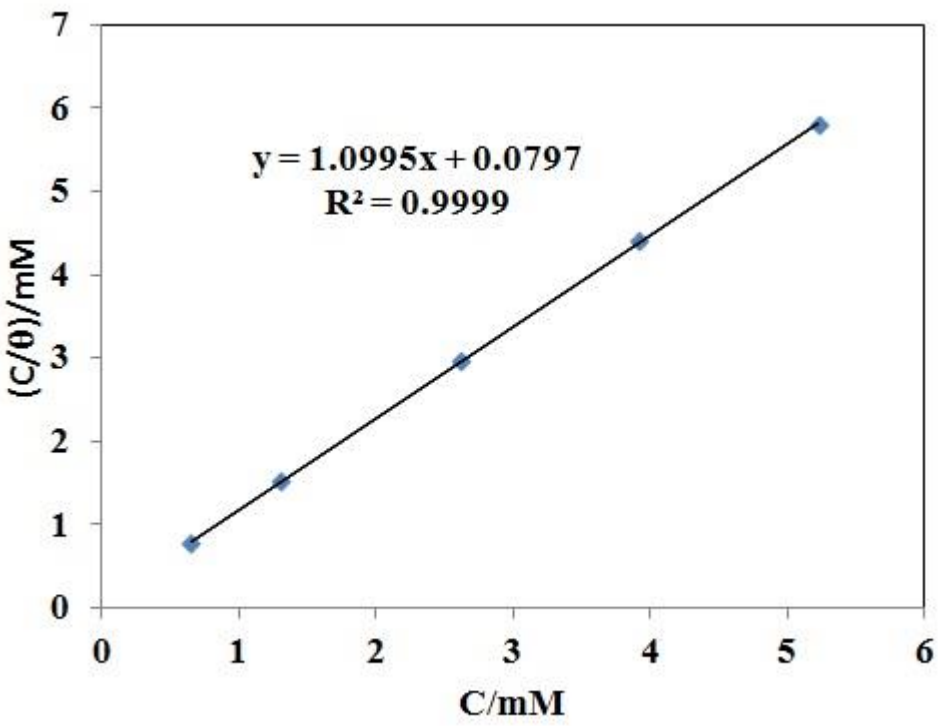

Figure 6. Langmuir adsorption isotherm of the inhibitor in 0.5 M H_2SO_4 solution by using data obtained from EIS results.

3.3 Determination of thermodynamic parameters

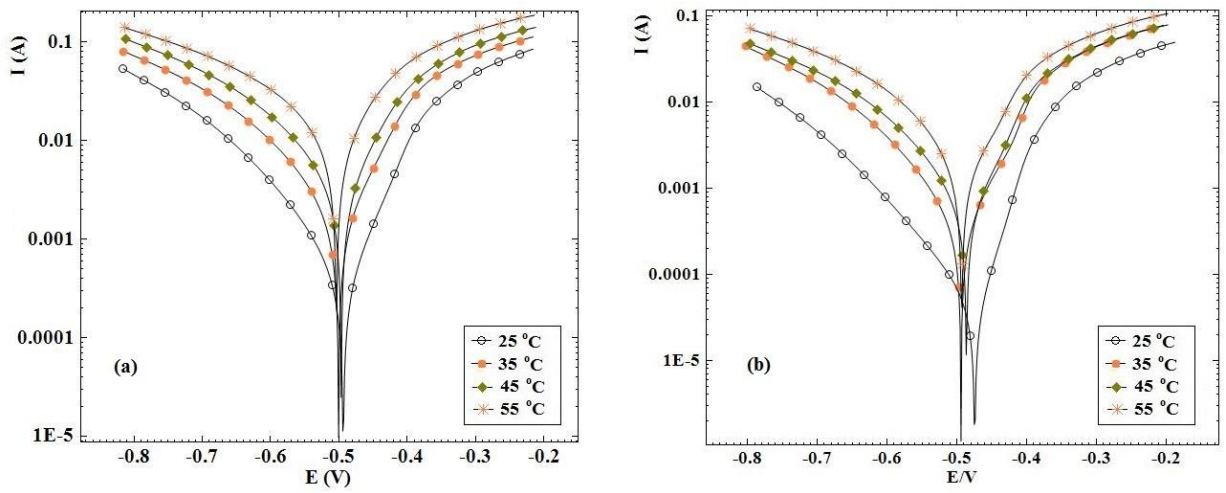

Figure 7. The polarization curves of carbon steel in 0.5 M H_2SO_4 solution at different temperatures (a) without inhibitor and (b) in the presence of 800 ppm of mesalazine.

To investigate the temperature effect and to determine the energy of activation and thermodynamic quantities for carbon steel corrosion in acidic medium, some polarization measurements were done in the temperature range of 25–55 ^{0}C in the absence and presence of an optimum concentration of mesalazine drug (800 ppm). Fig. 7 presents the polarization plots at various temperatures obtained

from H_2SO_4 solutions containing 0 and 800 ppm mesalazine drug. The corrosion parameters arising from Fig. 7 are listed in Table 3.

Table 3. Effect of temperature on the inhibition efficiency of mesalazine drug in 0.5 M H_2SO_4 solutions in the absence and presence of 800 ppm drug obtained by polarization measurements.

T/°C	C/ppm	i_{corr}/μA.cm^{-2}	IE_p%	θ
25	0	532	-	-
	800	56	89.5	0.895
35	0	1209	-	-
	800	152	87.4	0.874
45	0	2558	-	-
	800	378	85.2	0.852
55	0	6161	-	-
	800	1047	83.0	0.830

To demonstrate the validity of the inhibitor at higher temperatures, we were concerned with the variation of inhibition efficiency with the solution temperature. It is apparent from Table 3 that the inhibition efficiency slightly decreases with an increase in temperature from 25 to 55 ^{0}C. The IE% decreases with a rise in temperature from 89.5% to 83.0%. The slight decrease in the inhibition efficiency of the drug with increasing temperature proved the strong bond of the drug adsorption on the steel surface as a piece of evidence for chemisorption of mesalazine drug besides physisorption [22, 23]. These results confirm that mesalazine drug is an excellent inhibitor for corrosion of carbon steel in H_2SO_4 acid solutions in the range of temperature studied.

The Arrhenius equation states the relationship between the corrosion current density, i_{corr} , and the absolute temperature, T. The activation energy of the alloy dissolution reaction, E_a, can be obtained by employing the Arrhenius equation [24, 25]:

$$i_{corr} = A\exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

where A is a constant and R is the gas constant. Activation energies can be calculated from the slope of the Arrhenius plot, which represents the relationship between log i_{corr} and the reciprocal of the absolute temperature (1/T) as shown in Fig. 8. The activation energy values are given in Table 4. The activation energy of carbon steel dissolution in H_2SO_4 solution is 65.7 kJ.mol^{-1}. This value is almost in agreement with that obtained from other research works [23, 24]. It is apparent from Table 4 that the activation energy increased in the presence of mesalazine drug. Generally, the increase in the activation energy can be attributed to the adsorption of the inhibitor on the alloy surface, and thereby a corresponding decrease in the corrosion severity can occur because the lower surface area of the alloy is exposed to the acid solution [26, 27]. Therefore, the increase in E_a proves that the adsorption of mesalazine drug can lead to the formation of a physical barrier on the carbon steel surface reducing the steel reactivity in the electrochemical reactions of corrosion.

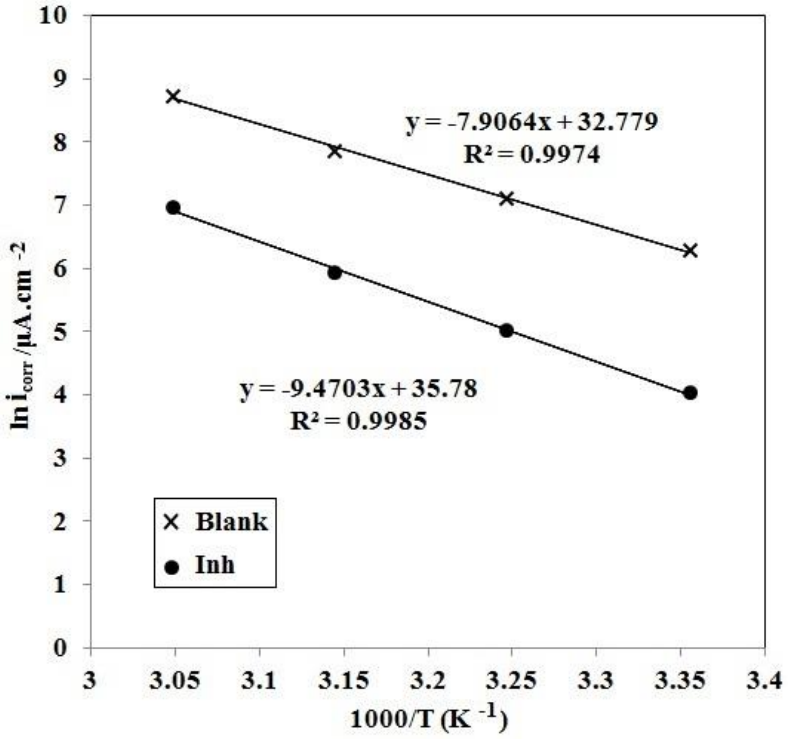

Figure 8. Arrhenius curves of carbon steel in 0.5 M H_2SO_4 solution without inhibitor (Blank) and with 800 ppm inhibitor (Inh).

Table 4. The activation and thermodynamic parameters of adsorption corresponding to polarization data obtained for carbon steel in 0.5 M H_2SO_4 solution in the absence (Blank) and presence of 800 ppm of mesalazine drug (Mes).

Drug	E_a ($kJ.mol^{-1}$)	K_{ads} (M^{-1})	ΔG_{ads} ($kJ.mol^{-1}$)	ΔH_{ads} ($kJ.mol^{-1}$)	ΔS_{ads} ($J.K^{-1}.mol^{-1}$)
Blank	65.7	-	-	-	-
Mes	78.7	10537	-32.9	-15.1	59.7

The equilibrium constant of adsorption, K_{ads}, can be determined from the intercept of the isotherm line shown in Fig. 3. The following equation can be used for determining the free energy of the adsorption of inhibitor on carbon steel surface;

$$\Delta G^{o}_{ads} = -RT\ln(K_{ads}) \quad (9)$$

Table 5 lists the values of K_{ads} and ΔG^{o}_{ads} arising from Langmuir isotherms through polarisation and impedance measurements for mesalazine. A good agreement is observed for ΔG^{o}_{ads} values determined from the polarization and EIS techniques.

Table 5. The values of K_{ads} and ΔG^o_{ads} arising from Langmuir isotherms through polarisation and EIS measurements for the adsorption of mesalazine on the carbon steel in 0.5 M H_2SO_4 solution.

Method	K_{ads} (M^{-1})	ΔG_{ads} ($kJ.mol^{-1}$)
Pol	10537	-32.9
EIS	12547	-33.3

The electrostatic interactions between the drug molecules and the charged steel surface known as physisorption lead to the values of ΔG^o_{ads} around −20 kJ mol^{-1} or less negative; the formation of a coordinate bond of the metal with the drug molecules known as chemisorption shows the values of ΔG^o_{ads} around −40 kJ mol^{-1} or more negative [28]. The calculated ΔG^o_{ads} values in the present work are the intermediate case confirming comprehensive adsorption that is a combination of physical and chemical adsorption.

It is possible to determine the enthalpy of adsorption, ΔH_{ads} , and the entropy of adsorption, ΔS_{ads}, from the plot of ln(θ/(1-θ)) against 1/T according to the following equation[29]:

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln C + \frac{\Delta S^o{}_{ads}}{R} - \frac{\Delta H^o{}_{ads}}{RT} \qquad (10)$$

where T is temperature, θ is surface coverage and C is concentration.

As shown in Fig. 9, the plot of ln(θ/(1-θ)) vs. 1/T at 800 ppm mesalazine shows a straight line with the slope of $-\Delta H^o_{ads}/R$. The obtained values of ΔH^o_{ads} are given in Table 4. The exothermic behavior of mesalazine drug on the carbon steel surface is identified from the negative values of ΔH^o_{ads}.

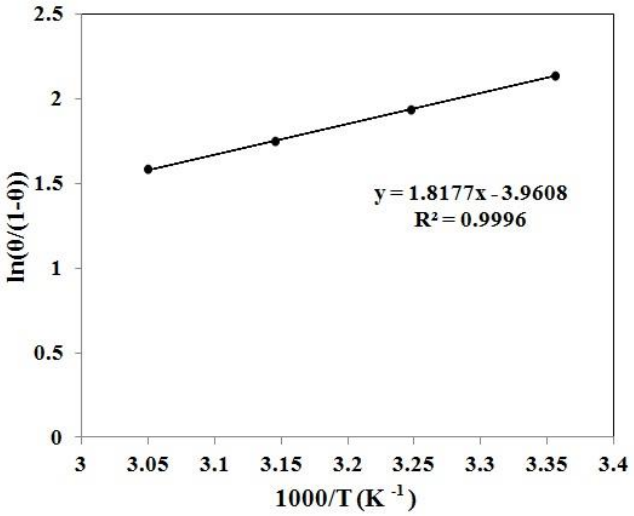

Figure 9. Ln (θ/1–θ) versus 1/T plot of carbon steel in the solution of 0.5 M H_2SO_4 with 800 ppm mesalazine.

The adsorption entropy (ΔS^o_{ads}) can be determined from equation (11):

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \quad (11)$$

The calculated thermodynamic parameters are listed in Table 4. A quasi-substitution process occurs between water molecules adsorbed on the electrode surface and the drug molecules in the aqueous phase [36]. The desorption of water molecules from the electrode surface is required to provide the adsorption of the drug molecules on the steel surface. While the desorption process of water molecules is believed to be endothermic and associated with an increase in entropy, the opposite observes for the drug. It is important to note that the studied thermodynamic quantities can be calculated from the summation of the desorption of water and the adsorption of the drug [37]. Thus, the positive values of ΔS^o_{ads} are attributed to an increase in the solvent entropy [38]. In other words, an increase in disordering is observed from the adsorption of the drug inhibitor on the steel surface [39].

3.4 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectrometry is a useful tool for the determination of bonding type of organic inhibitors adsorbed on the alloy surfaces [30, 31]. The adsorbed layer of the drug molecules can be transferred from the steel surface into KBr powder by rubbing the surface on KBr powder.

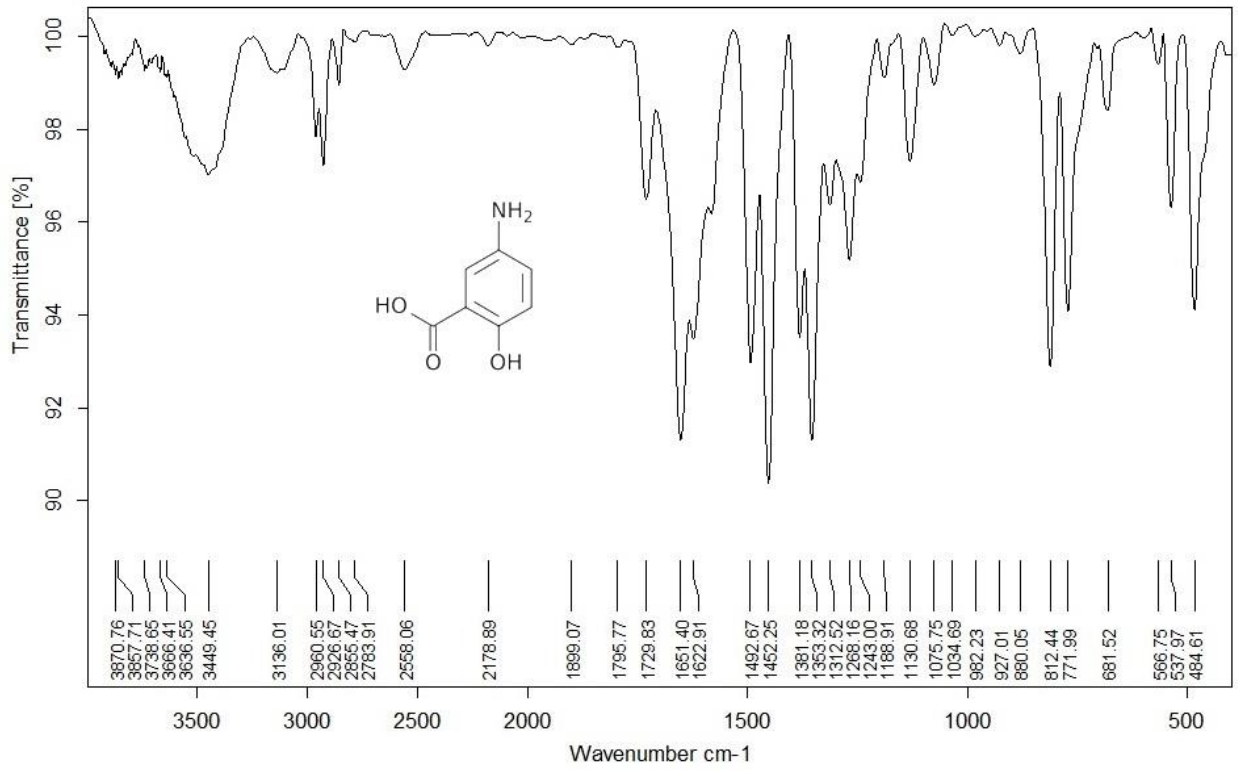

Figure 10. FTIR spectrum of mesalazine drug.

The FTIR spectrum of mesalazine drug and the spectrum of the adsorbed layer formed on carbon steel surface are shown in Figs. 10 and 11, respectively. In order to examine the nature of bonding of

mesalazine adsorbed on the steel surface, FTIR spectra of Figs. 10 and 11 were compared and accordingly, it was found that most of the bands observed in the spectrum of the adsorbed layer (Fig. 11) resemble those appearing in mesalazine spectrum (Fig. 10).

The characteristic peaks of mesalazine spectrum can be assigned to mutual overlapping of N-H and O-H stretching, C=O stretching, N-H bending and C–N stretching [32]. A broad band at 3449 cm^{-1} can be assigned to mutual overlapping of N-H and O-H stretching vibrations. The band at 1651 cm^{-1} can be correlated with C=O stretching vibrations of carbonyl group. An N-H bending vibration was detected by the peak at 1623 cm^{-1}. The absorptions bands at 1623 cm^{-1} and 1353 cm^{-1} were observed due to N-H bending vibration and C-N stretching vibration frequencies, respectively. The aromatic C-H stretching vibrations were detected by the bands near 2900 cm^{-1}. The carbon-carbon stretches in the aromatic ring at 1493 cm^{-1} and 1452 cm^{-1}.

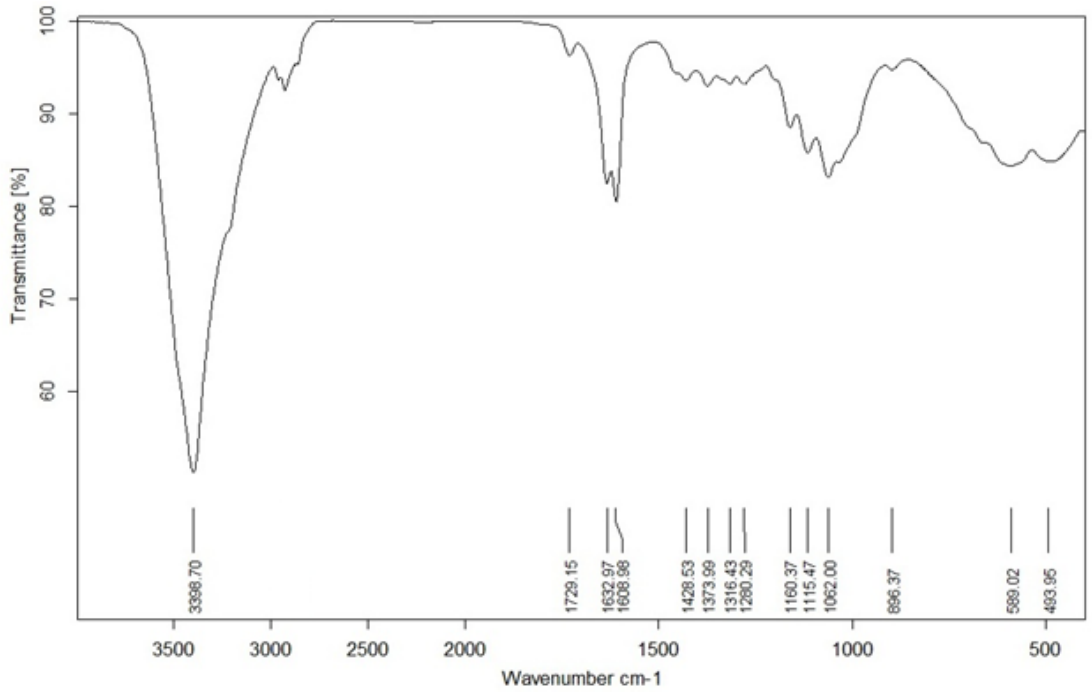

Figure 11. FTIR spectrum of adsorbed layer on carbon steel after 48 h soaking in 0.5 M H_2SO_4 solution containing 800 ppm of mesalazine drug.

The disappearance of the C=O stretching, N-H bending and C–N stretching in the adsorbed drug (Fig 11) may reveal that the oxygen atom of carbonyl group and the nitrogen atom of amino group can act as the active centers in adsorption. Also the disappearance of the carbon-carbon stretching of aromatic ring can confirm the adsorption of drug via aromatic ring on the steel surface. The broad band of O-H stretching at about 3400 cm^{-1} in two spectra (Figs. 10 and 11) indicates that the adsorbed film contains H_2O. Thus, the presence of mesazaline molecules on the steel surface via adsorption was confirmed by these observations.

4. CONCLUSION

The corrosion inhibition of mesalazine drug on the carbon steel in 0.5 M H_2SO_4 solution was studied by techniques of polarization and EIS. It was proved from the polarization data that the Langmuir isotherm can describe the adsorption of the drug on carbon steel surface. The slight decrease in inhibition efficiency with an increase in temperature can be explained in terms of chemical adsorption of the inhibitor molecule on the carbon steel surface. The calculated free energy and enthalpy for the adsorption process proved a combination of physical and chemical adsorption. A reasonable agreement was observed between the values of IE and ΔG^{o}_{ads} obtained from EIS and potentiodynamic polarization measurements. FTIR spectroscopy showed the active sites of mesazaline molecule during adsorption on the alloy surface.

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