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Inedible Avocado Extract: An Efficient Inhibitor of Carbon Steel Corrosion in Hydrochloric Acid

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The corrosion inhibition of inedible avocado extract (IAE) on the corrosion of carbon steel in molar hydrochloric acid has been evaluated using weight loss method, potentiodynamic polarization measurements and electrochemical impedance spectroscopy. Experimental results obtained revealed that the inhibition efficiency have increased when the concentration of the IAE have increased but decreased with the increase in temperature. Potentiodynamic polarization measurements clearly reveal that the investigated inhibitor is a cathodic inhibitor. The effect of temperature on the corrosion behavior of carbon steel in 1 M HCl without and with addition of 2.00 $g.l^{-1}$ of IAE was studied in the temperature range from 298 to 328 K. Electrochemical impedance data show that the addition of the IAE in the corrosive solution decreases the double layer capacitance and simultaneously increases the charge transfer resistance of the corrosion process, facilitating the formation of an adsorbed layer over the carbon steel surface. The IAE inhibitor adsorbed physically on the carbon steel surface follows the Langmuir adsorption isotherm. The parameters of activation energy was evaluated and discussed.

Keywords: Corrosion, Inhibition, Carbon Steel, HCl, Inedible avocado extract.

1. INTRODUCTION

Acid solution used in industry causes corrosion of iron and its alloy [1-4]. The use of corrosion inhibitors reduces the rate of dissolution of metals and it is considered as the mainly effective technique for the protection of several metals and alloys against such acid attack. Many works have studied the effect of organic compounds containing nitrogen, oxygen and sulphur atoms on the corrosion of steel in acidic media [5-17], the organic inhibitors act by adsorption on the metal surface. Corrosion inhibitors block the active sites and enhance the adsorption process. However, the majority of these compounds are not only expensive but also toxic for environment.

Recently, natural compounds have attracted some attention as ecofriendly inhibitor of corrosion of metal and alloys [18-30]. The inhibition efficiency effect of plant extract can be attributed to adsorption of organic substances on the metals and alloys surface consequently blocking active sites or even forming a protective barrier. Corrosion inhibition of extracts of Verbena, Chamomile, Marrubium Vulgare and Argan on carbon steel in hydrochloric acidic solutions was investigated by Ben Hmamou & al [31-37]. Bammou & al. [38-39] studied the corrosion inhibition of Thymus essential oil and Artemesia on steel in hydrochloric acid and phosphoric acid media. The natural compounds tested have been reported to be excellent inhibitors for metals and alloys in acidic solutions.

In the present work, the behavior of Inedible Avocado Extract (**IAE**) was evaluated at various concentrations as inhibitor of corrosion on carbon steel in 1 M hydrochloric acid solution by using weight loss method, potentiodynamic polarization measurements and electrochemical impedance spectroscopy.

2. EXPERIMENTAL

2.1. Materials preparation and solutions

The material used throughout the experiments was a carbon steel with chemical compositions given in Table 1.

Table 1. Chemical composition of the carbon steel specimens

Element	C	Si	Mn	Cu	S	Fe
Weight%	0.179	0.165	0.439	0.203	0.034	balance

The corrosive solution used 1 M hydrochloric acid was prepared by dilution of an Analytical Grade 37% HCl with double distilled water.

Stock solution of Inedible Avocado Extract (**IAE**) was prepared by stirring cold weighed amounts of the Avogado nuts for 24 h in 1 M HCl solution. The resulting solution was filtered. This extract of this (**IAE**) was used to study the corrosion inhibition properties and to prepare the required concentrations. The solution tests are freshly prepared before each experiment. The concentration range of Inedible Avocado Extract (**IAE**) employed was 0.01 to 2.00 g/l in 1 M hydrochloric acid.

The specimens were embedded in polyester, which had a surface area of 0.32 cm^2 that was in contact with the aggressive media. The working electrode was mechanically polished with emery paper up to 1200 grade, degreased in acetone and rinsed with double distilled water before immersed in the test solution.

2.2. Gravimetric analysis

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat cooling condenser. The steel specimens used have a rectangular form (2 cm×1cm×0.3cm). The duration of tests was 6 h at 298K in 1 M HCl solution contain different concentrations of **IAE**.

The specimens were abraded with a series of emery paper up to 1200 grade and then washed thoroughly with acetone and double distilled water. After weighing precisely, the specimens were immersed in beakers which contained 100 ml acid solutions with different concentrations of **IAE** at a certain temperature remained by a water thermostat. All the aggressive acid solutions were open to air. After 6 h the specimens were taken out, washed, dried, and weighed exactly.

The inhibition efficiencies E_w (%) corrosion in the case of gravimetric analysis method was calculated from the following equation:

$$E_w(\%) = (\frac{W^\circ_{cor} - W_{cor}}{W^\circ_{cor}}).100 \qquad (1)$$

Where W^0_{cor} and W_{cor} are the corrosion rates of carbon steel due to the dissolution in 1 M HCl in the absence and presence of definite concentrations of the **IAE**, respectively.

2.3. Potentiodynamic polarization

Polarization measurements were carried out in a conventional three-electrode electrolytic cell. Saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes respectively. The working electrode is in the form of a disc from carbon steel of the surface 0.32 cm^2. These electrodes are connected to Voltalab PGZ 100 piloted by ordinate associated to "Volta Master 4" software. The scan rate was 1 mV/s started from an initial potential of -800 to -100 mV/SCE. Before recording each curve, a stabilization time of 30 min was allowed, which was proved to be satisfactory to attain a stable value for E_{cor}. All experiments were repeated three times at temperature desired ±1°C. Corrosion current densities were obtained from the polarization curves by linear extrapolation of the Tafel curves. The inhibition efficiency E_p (%) is calculated from the values of the corrosion current densities with the relation:

$$E_p(\%) = (\frac{I^\circ_{cor} - I_{cor}}{I^\circ_{cor}}).100 \qquad (2)$$

where I_{cor} and I°_{cor} were the corrosion current densities with and without inhibitor.

2.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was carried out with a same equipment was used as for the polarization measurements, leaving the frequency response analyzer out of consideration. Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mVs^{-1}. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potential after 30 min of exposure. All potentials were reported versus saturated calomel electrode (SCE). The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility. The inhibition efficiency in the case of electrochemical impedance spectroscopy measurements got from the charge transfer resistance is calculated by:

$$E_{EIS}(\%) = (\frac{R_t^0 - R_t}{R_t^0}).100 \qquad (3)$$

Where R_t and R_t^0 are the transfer resistance in the presence and absence of **IAE** inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1. Weight loss tests

The inhibition efficiency E_W (%) in of carbon steel in molar HCl acid containing various concentrations of **IAE** have been evaluated by weight loss technique after 6 h of immersion time at 298 K. The corrosion rate (W_{cor}) and inhibition efficiency (E_W) obtained by weight loss data are represented in Table 2.

Table 2. Carbon steel weight loss data and inhibition efficiency of **IAE** Extract.

Conc. (g/l)	W_{cor} (mg. $cm^{-2}.h^{-1}$)	E_w (%)
Blank	1.84	--
2.00	1.06	93.22
1.00	1.14	82.68
0.50	1.16	80.76
0.10	1.23	72.88
0.01	1.35	58.14

It can be observed from Table 2 that the corrosion rate values decrease and the inhibitor efficiency values increase with the increase of the **IAE** concentrations. We noted that **IAE** used in this study showed very excellent corrosion inhibitor for carbon steel in 1 M HCl. The best action is attained in the presence of 2.00 g/l **IAE** to reaches 93.22%. This behavior is due to the fact that the adsorption of inhibitor on electrode steel surface increases with the inhibitor concentration.

3.2. Polarization results

Fig. 1 shows the polarization curves obtained for carbon steel electrode in molar hydrochloric acid in the absence and presence of various concentrations of **IAE**. From the polarization curves, corrosion potential (E_{cor}), corrosion current density (I_{cor}) and cathodic Tafel slope (b_c) were determined. The corrosion current density was deduced graphically from the cathode curves by extrapolation the cathodic Tafel segment to the corrosion potential. Tafel behavior characterized by linear regions in the vicinity of the corrosion potential indicates that the hydrogen evolution reaction is activation controlled. Inspection of these curves reveals that the addition of **IAE** has a slight effect in the anodic polarization curves, and a pronounced inhibitive effect on the cathodic part. This indicates that **IAE** can be classified as cathodic type inhibitor and the molecules containing in tested inhibitor are more adsorbed on the cathodic sites resulting in an inhibition of the cathodic reactions.

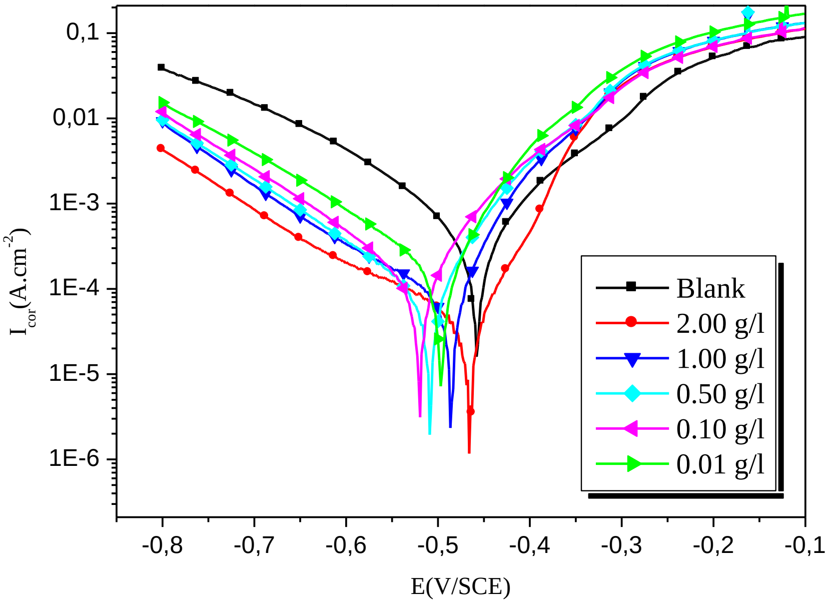

Figure 1. Polarization curves for carbon steel in 1M HCl containing various concentrations of IAE at 298K

Table 3. Electrochemical parameters for carbon steel in 1M HCl at different concentrations of **IAE** at 298K

Conc. (g/l)	I_{cor}(μA/cm^2)	E_{cor} (mV/SCE)	bc (mV/dec)	E_p (%)
Blank	594	-457	-199	
2.00	50	-466	-148	91.58
1.00	90	-485	-147	84.85
0.50	105	-511	-141	82.32
0.10	145	-520	-145	75.59
0.01	230	-498	-150	61.28

The electrochemical data obtained from the polarization curves are presented in Table 3 and indicate that the presence of the **IAE** inhibits the corrosion process by reducing the corrosion current densities to lower values. The cathodic Tafel slope (b_c) for steel in the absence and presence of inhibitor does not change significantly indicating that the **IAE** does not change the mechanism. The free corrosion potential determined after 30 min of immersion does not change in the existence of the inhibitor. The inhibition efficiency calculated from the obtained corrosion current density values increases with increasing of inhibitor concentration. The excellent protection was about 91.58 % at 2.00 g/l.

3.3. Electrochemical impedance spectroscopy measurements

In Fig. 2, impedance measurements of carbon steel at E_{cor} 30 min after the electrode has been immersed in 1 M HCl solution and in absence and the presence of different concentration of **IAE** are plotted in the form of Nyquist plots. The all corresponding impedance diagram is characterized by single deformed capacitive loop, this observation indicates that the corrosion of carbon steel in 1 M HCl solution is mainly controlled by a charge transfer process [40]. The charge transfer resistance values (R_{ct}) were obtained graphically from the Zreal axis corresponding to the capacitive loop diameter. Double layer capacitance (C_{dl}) values can be evaluated using the following relation [41-42]:

$$C_{dl} = \sqrt[n]{Q.R_{ct}^{\,1-n}} \qquad (4)$$

Were Q are the constant phase element (CPE) and n are a coefficient can be used as a measure of surface inhomogeneity. For the ideal electrodes, the CPE are an ideal capacitor when n = 1 and of a CPE the n value are inferior to 1.

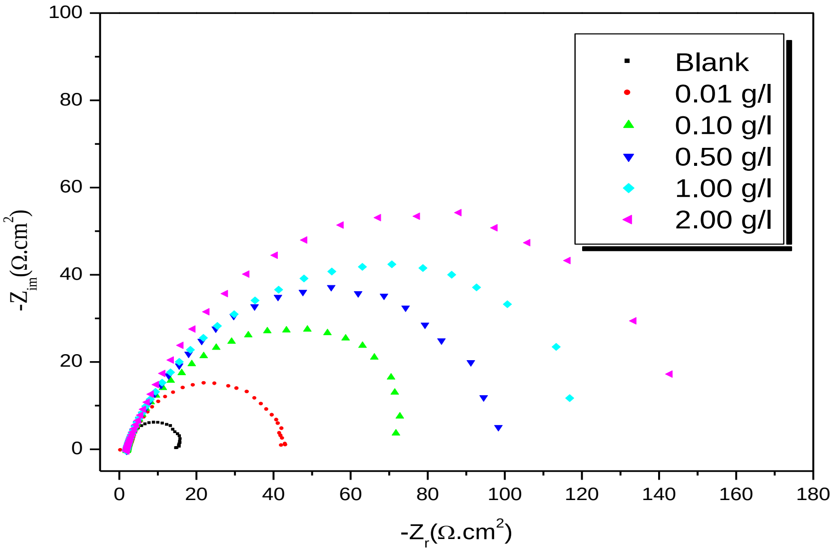

Figure 2. Nyquist plots of carbon steel in 1 M HCl without and with different concentrations of **IAE** at 298K

The electrochemical parameters values derived from the Nyquist plots using Zview software are presented in Table 4. Inhibition efficiency and charge transfer resistance values (R_{ct}) increased with inhibitor concentrations, this suggestion can be attributed to the formation of a protective film on the electrode/solution interface [43-44]. The value of double-layer capacitance (C_{dl}) decreases with addition of **IAE** inhibitor, this decrease is attributed to reduce in the local dielectric constant and/or an increase in the thickness of the formed film by adsorption of inhibitor at the metal surface [45]. Interpretation of this phenomenon is based to the following equation [46]:

$$C_{dl} = \frac{\varepsilon\varepsilon_0}{\delta} S \qquad (5)$$

Where δ is the thickness of the protective film, S is the surface of the used electrode, ε_0 is the permittivity of the air and ε is the dielectric constant of medium.

Table 4. Impedance parameters for corrosion of carbon steel in 1M HCl without and with different concentrations of **IAE** at 298 K.

Conc. (g/l)	R_{ct} ($\Omega.cm^2$)	n	Q ($S^n/\Omega.cm^2$)	C_{dl} ($\mu F.cm^{-2}$)	E_{EIS} (%)
Blank	15	0.86	1.65×10^{-4}	62	--
2.00	145	0.83	0.86×10^{-4}	35	89.66
1.00	119	0.82	1.01×10^{-4}	38	87.39
0.50	96	0.83	1.06×10^{-4}	41	84.38
0.10	71	0.84	1.25×10^{-4}	51	78.87
0.01	37	0.86	1.31×10^{-4}	55	59.46

The different Nyquist representations of impedance were analyzed by fitting the experimental data to a simple equivalent circuit model, Fig. 3.

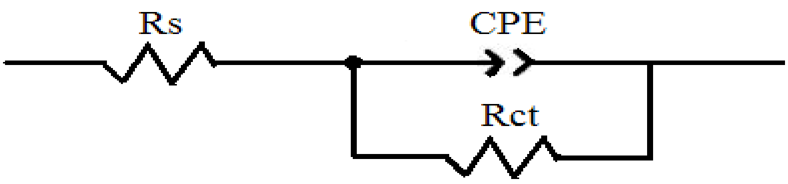

Figure 3. Equivalent electrical circuit corresponding to the corrosion process on the carbon steel in hydrochloric acid.

3.4. Effect of temperature

Temperature has a great influence on the corrosion phenomenon. Generally the corrosion rate increases with increasing the temperature. The effect of temperature on the corrosion behavior of carbon steel in 1M HCl in the absence and presence of 2.00 g/l of **IAE** compounds was investigated by potentiodynamic polarization technique in the temperature range 298 to 328 K (Figs 4 & 5).

The values of associated electrochemical parameters are given in Table 5. From this result, it can be concluded that the value of corrosion current density increases in both case, in the absence and presence of inhibitor, and the value of inhibition efficiency decreases slightly with the increase in the temperature. This phenomenon is due to the desorption of the some molecules from the carbon steel surface by increasing the temperature. In the absence of **IAE** inhibitor, the important elevation of corrosion rate when the electrolyte temperatures increase. After addition of the tested inhibitor in corrosive medium, the dissolution of carbon steel is extensively retarded.

Plots of logarithm of corrosion rate (ln I_{cor}), with the reciprocal of absolute temperature (1/T) for carbon steel in 1M HCl in absence and in the presence of 2.00 g/l **IAE** is shown in Fig. 6. Obtained curve from the Fig. 6 present straight line with slope of E_a/R. Consequently, the activation energy can be evaluated using the flowing equation:

$$LnI_{corr} = \frac{-E_a}{RT} + Lnk \qquad (6)$$

Where E_a is the apparent activation energy; R is the universal gas constant, T the absolute temperature and k the pre-exponential factor.

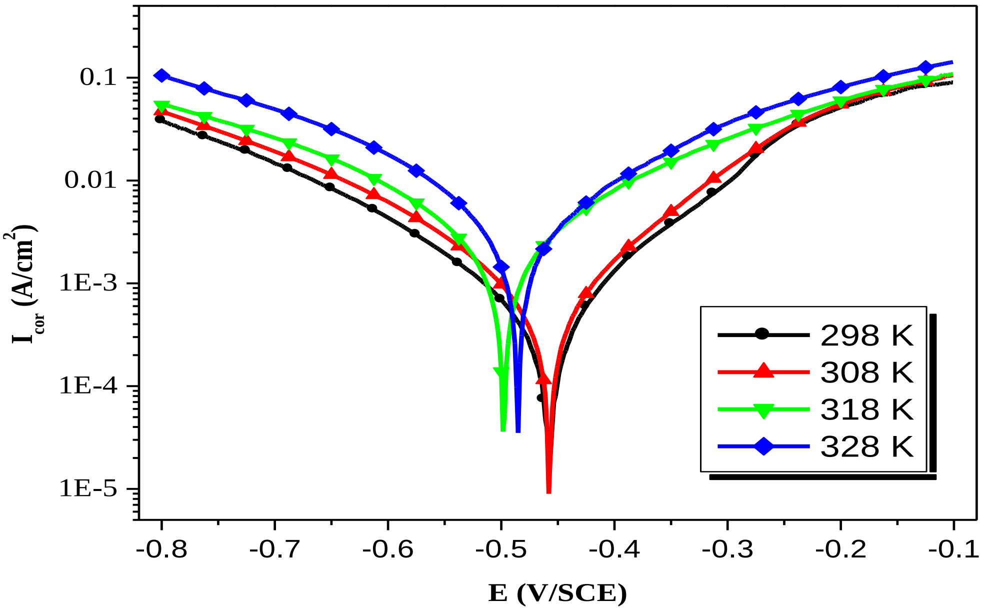

Figure 4. Polarisation curves for carbon steel in 1M HCl at different temperature.

Plot of ln (I_{cor}/ T) vs. 1/ T for carbon steel in 1M HCl in absence and presence of 2.00 g/l **IAE** presented in Fig. 7 give straight line. Thus, ΔH^*_a and ΔS^*_a can be determined by slope and intercept of Fig. 7 using the transition state equation:

$$I_{cor} = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^*}{R}\right)\exp\left(-\frac{\Delta H_a^*}{RT}\right) \qquad (7)$$

Where R is the perfect gas constant, N is the Avogadro's number and h is the Plank's constant.

The value of activation energy E_a, the activation enthalpy ΔH^*_a and the activation entropy ΔS^*_a for the corrosion of carbon steel in 1M HCl were listed in Table 6.

The addition of **IAE** inhibitor affects the values of activation energy E_a. This is can be attributed to the adsorption of inhibitors on carbon steel surface. The adsorption mechanism of **IAE** in 1 M HCl is considered as a physical adsorption phenomenon since the activation energy value of 77.27 kJ mol^{-1}. This is in agreement with works of Ebenso & al [47-48] and Abiiola [49]. The increase in the activation enthalpy ΔH^*_a in presence of the **IAE** implies that the addition of this compound to the acid solution increases the height of the energy barrier of the corrosion reaction. The positive sign of activation entropy ΔS^*_a indicate that an increase in disordering occurs in going from reactants to the electrode/solution interface which is the driving force for the adsorption of **IAE** on the carbon steel surface [50,51].

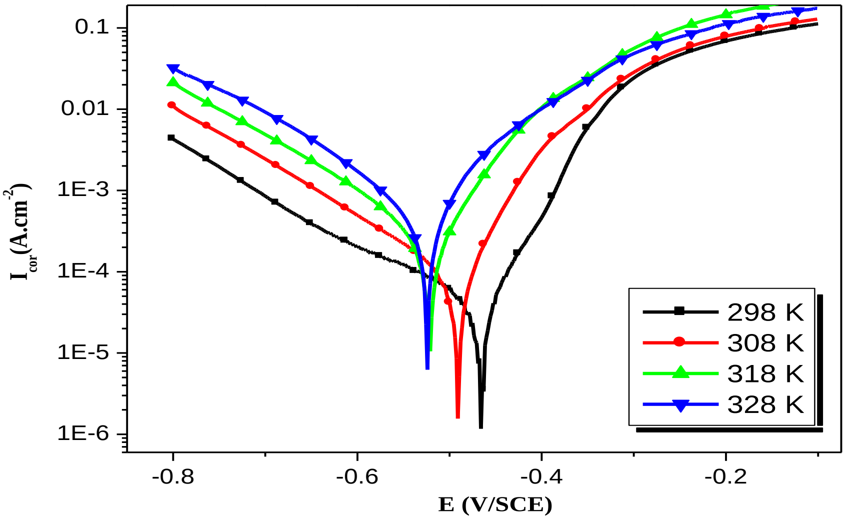

Figure 5. Polarisation curves for carbon steel in 1M HCl + 2.00 g/l **IAE** at different temperature.

Table 5. Electrochemical parameters for corrosion of carbon steel in 1M HCl at different temperature in the absence and presence of 2.00 g/l **IAE**

Concentration	T (K)	E_{cor} (mV/SCE)	I_{cor}(μA/cm^2)	bc (mV/dec)	E_p (%)
Blank	298	-457	594	-199	--
	308	-458	900	-204	--
	318	-500	3360	-214	--
	328	-487	6820	-234	--
2.00 g/l	298	-466	50	-148	91.58
	308	-490	96	-150	89.33
	318	-521	371	-147	88.96
	328	-525	761	-153	88.84

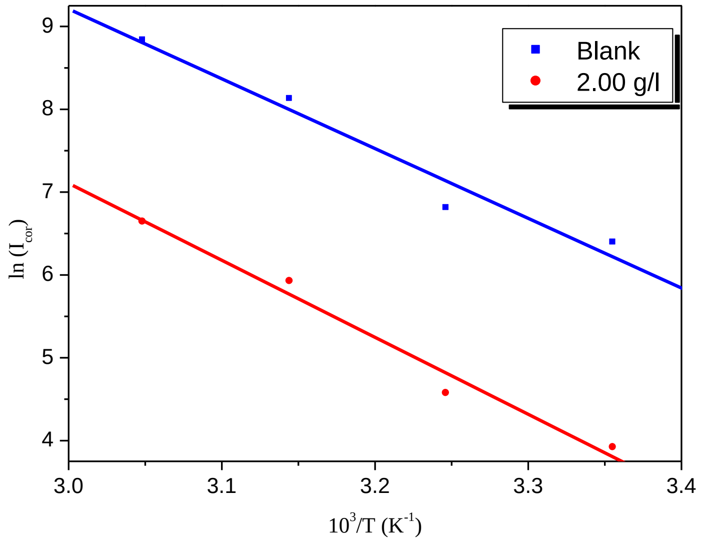

Figure 6. Arrhenius plots of carbon steel in 1 M HCl with and without 2.00 g/l **IAE**.

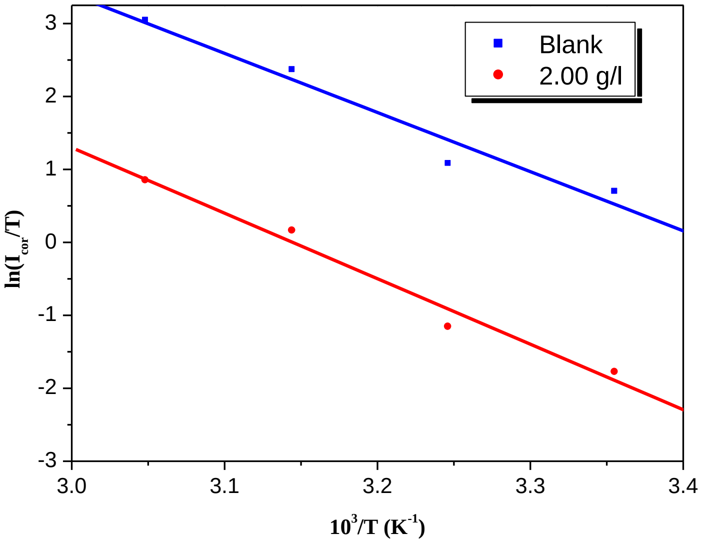

Figure 7. Variation of Ln (Icorr/T) versus $10^3/T$ for bank and 1M HCl + 2.00 g/l of **IAE**.

Table 6. The value of activation parameters for carbon steel in 1M HCl in the absence and presence of 2.00 g/l of **IAE**.

	E_a (kJ.mol^{-1})	ΔH^*_a (kJ.mol^{-1})	ΔS^*_a (J.mol^{-1}.K^{-1})
Blank	70.01	67.41	32.97
2.00 g/l	77.27	74.68	37.28

3.5. Adsorption isotherm

The interaction of **IAE** inhibitor and carbon steel surface in corrosive media is supposed to be related to its adsorption at the metal/solution interface. The surface coverage values ($\theta = \frac{E_p\%}{100}$) for different concentration of **IAE** inhibitor obtained from polarization curve have been used to establish the appropriate isotherm and the adsorption process. The increase in surface coverage with increasing concentration extract can be caused by adsorption of inhibitor on the carbon steel surface. The Plot of C_{inh}/Θ against C_{inh} shows a straight lines with the R value almost unity (0.9998) as shown in Fig. 8, which suggests Langmuir adsorption isotherm for adsorption of the **IAE** inhibitor on the carbon steel surface in 1 M HCl solution according to the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{inh} \qquad (8)$$

Where C_{inh} is the Concentration of **IAE** and k_{ads} is the adsorption equilibrium constant of the adsorption process.

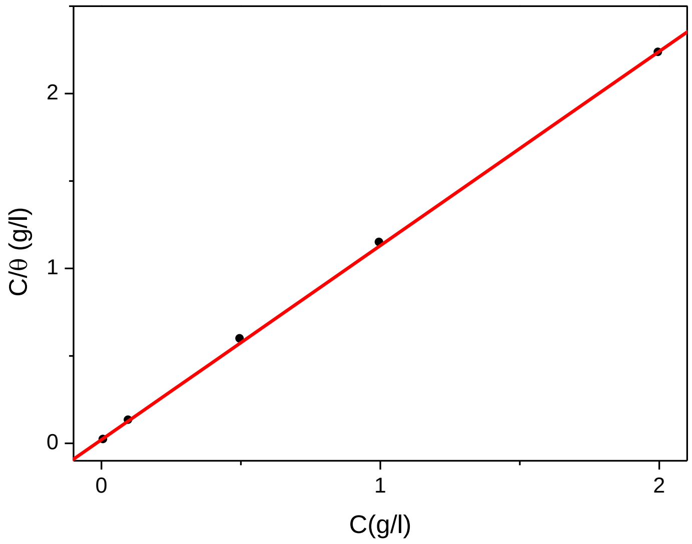

Figure 8. Langmuir isotherm adsorption of **IAE** on the carbon steel electrode in 1M HCl.

4. CONCLUSION

From this research, the following conclusions can be extracted:

- **IAE** considered as a good inhibitor for the corrosion of carbon steel in 1 M HCl solution.
- Inhibition efficiency increases with the inhibitor concentration, this inhibition can be attributed to their adherent adsorption on the metal surface by forming the protective film.
- The inhibition efficiency increases with temperature.

- The EIS results indicate that the double layer capacitances decrease with increasing of inhibitor concentration, this fact may be explained on the basis of adsorption of this inhibitor on the carbon steel surface
- The adsorption of these compounds on the carbon steel surface obeys to the Langmuir adsorption isotherm.

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