Steel Corrosion Inhibition by Acid Garlic Essential Oil as a Green Corrosion Inhibitor and Sorption Behavior

L. Afia¹, O. Benali², R. Salghi¹,*, Eno. E. Ebenso³,*, S. Jodeh⁴, M. Zougagh⁵, B. Hammouti⁶

¹ Equipe de Génie de l’Environnement et Biotechnologie, ENSA, Université Ibn Zohr, BP: 1136 Agadir, Maroc.
² Département de Biologie, Faculté des sciences, Université Dr. Tahar Moulay – Saïda- Algérie.
³ Material Science Innovation & Modelling (MaSIM) Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
⁴ Department of Chemistry, An-Najah national University, P. O. Box 7, Nablus, Palestine.
⁵ Regional Institute for Applied Chemistry Research, IRICA, Av. Camilo Jose Cela 10, E- 403004, Ciudad Real, Spain & Albacete Science and Technology Park, E-02006, Albacete, Spain
⁶ LCAE-URAC18, Faculté des Sciences, Université Mohammed 1er, Oujda, Maroc.
*E-mail: r.salghi@uiz.ac.ma, Eno.Ebenso@nwu.ac.za

Received: 19 September 2014 / Accepted: 19 October 2014 / Published: 28 October 2014

The aim of this work was to investigate the inhibition effect of acid garlic essential oil (GO oil) as an inhibitor on the corrosion of carbon steel in a 1M HCl solution at different temperatures by weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods. The GO oil acts as an effective corrosion inhibitor for carbon steel in a hydrochloric acid medium. The inhibition process is attributed to the formation of an adsorbed film of inhibitor on the metal surface which protects the metal against corrosion. The result indicates that the inhibition efficiency (%) increases as with the concentration of the inhibitor. The (%IE of GO oil depends on its concentration, and attains approximately 95.8% for 2.5 g/L at 298K. The effect of temperature on the corrosion behavior of carbon steel in 1 M HCl, with the addition of essential oil was also studied. The adsorption of the essential oil on the carbon steel surface obeyed the Langmuir adsorption isotherm. Values of inhibition efficiency calculated from weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy are in good agreement. Polarization curves showed that GO oil behaves as a mixed-type inhibitor. The activation energy as well as other thermodynamic parameters for the inhibition process was calculated and discussed. The results obtained showed that the acid garlic essential oil could serve as an effective inhibitor of the corrosion of carbon steel in hydrochloric acid solutions.

Keywords: acid garlic essential oil, Inhibition, Corrosion, Weight loss, Electrochemical measurement
1. INTRODUCTION

Essential oils are complex volatile compounds produced in different plant parts known to have various functions in plants. The complexity in essential oil is due to terpene hydrocarbons, as well as their oxygenated derivatives such as alcohols, aldehydes, ketones, acids, and esters. Allium sativum (A. sativum) (garlic), belonging to the family Alliaceae, is a plant containing 1%-2% essential oil on a dry basis with a wide variation of chemical composition as a function of genetic diversity, habitat and agronomic treatment of culture. Steam distillation is widely used to extract and condense the volatile organosulphur compounds in garlic, and the final oily product is called garlic oil (GO) [1]. Garlic has a long folklore history as a treatment for colds, coughs and asthma and is reported to strengthen the immune system. It has many medicinal effects such as the lowering of blood cholesterol level [2], antiplatelet aggregation [3], anti-inflammatory activity [4] and inhibition of cholesterol synthesis [5]. Garlic has been long known to have antibacterial [6-8], antifungal [9], anticancer [10,11], antioxidant and antiviral [12] activities.

On the other hand, in most industries whose facilities are constituted by metallic structures, the phenomenon of corrosion is invariably present. This problem originates very important material and economic losses, due to partial or total replacement of equipment and structures, and plant-repairing shutdowns [13]. The use of corrosion inhibitors constitutes one of the most economical ways to mitigate the corrosion rate, protect metal surfaces against corrosion and preserve industrial facilities [14-15]. Large numbers of organic compounds have been studied and analyzed to investigate their potential as corrosion inhibitors [16-17]. Most of these studies revealed that almost all organic molecules containing heteroatoms such as nitrogen, sulphur, phosphorous and oxygen show a significant inhibition efficiency [18-21]. Despite these promising findings about possible corrosion inhibitors, most of these substances are not only expensive but also toxic [22], and non-biodegradable thus causing pollution problems. Hence, these deficiencies have prompted the search for their replacement. The studies of plant extracts as low-cost and eco-friendly corrosion inhibitors are of great interest from an environmental perspective and are attracting a significant level of attention [23-25].

In the present work, the efficiency of acid garlic essential oil (GO oil) as a green inhibitor for the corrosion of carbon steel in a 1 M hydrochloric acid is discussed on the basis of Tafel polarization, electrochemical impedance spectroscopy (EIS) and weight loss data.

2. MATERIALS AND METHODS

2.1. Extraction of garlic essential oil

The green garlic plant (immature garlic) was purchased from a local market in Agadir city. Prior to extraction, the dead auxiliaries were removed. The collected materials were washed in running tap water followed by rinsing in distilled water. In each batch 100 g of garlic was blended with 20 ml of bidistilled water for 2 min. The sample flask was charged with the batch in 100 mL of bidistilled water. The water distillation extraction procedure was carried out for 2h using a Clevenger-type
apparatus recommended by the French Pharmacopoeia [26]. For the condensation of steam the condenser was cooled with cold water. The experimental procedure was repeated several times. So, essential garlic oil sample was collected. The oil was analyzed using a Hewlett-Pac T. kard 5972 MS, fitted with HP 5890 Series II GC and controlled by a G1034C Chemstation. A sample of 1µL was injected under the following conditions: DB-1 fused silica capillary column (20 m x 0.20 mm, film thickness 0.2 µm); carrier gas helium (0.6 mL/min); injector temperature 250 °C; column temperature 50°-250°C at 3°C/min; MS electronic impact 70 eV.

2.2. Weight loss measurements

The carbon steel used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe). Coupons were cut into 2 × 2 × 0.08 cm³ dimensions are used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The specimens were washed thoroughly with bidistilled water, degreased and dried with ethanol. Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume was 80 cm³. The immersion time for the weight loss was 6 h at 298 K.

2.3. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster software. This potentiostat is connected to a cell with three electrode thermostats with double walls (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was the same used for gravimetric measurements. The surface area exposed to the electrolyte was 0.04 cm². Potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5 mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarization curves were obtained from −700 mV to −300 mV at 298 K. The solution test was there after being de-aerated by bubbling nitrogen. Gas bubbling was maintained prior to and throughout the experiments. In order to investigate the effects of temperature and immersion time on the inhibitor performance, some tests were carried out in a temperature range of 298–328 K. The electrochemical impedance spectroscopy (EIS) measurements were carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr after immersion in solution with bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz, they were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hours of exposure at 298 K. The impedance
diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

3. RESULTS AND DISCUSSION

3.1. Chemical composition of the Allium sativum essential oil (GO)

The results of GC/MS analyses of the oil led to the identification of the main components with their percentages (Table 1). Garlic essential oil was particularly rich in monoterpane hydrocarbons. The main component of Allium sativum essential oil has 1(7),5,8-o-menthatriene (20.5 %), di-2-propenyldisulfide (10.7%) and elemicin (9.5 %).

Table 1. Chemical composition (%) of the Allium sativum essential oil

<table>
<thead>
<tr>
<th>Compound</th>
<th>Allium sativum essential oil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(7),5,8-o-Menthatriene</td>
<td>20.5</td>
</tr>
<tr>
<td>Oxygenated monoterpenes</td>
<td>6</td>
</tr>
<tr>
<td>Trans-Limone oxide</td>
<td>4</td>
</tr>
<tr>
<td>elemicin</td>
<td>9.5</td>
</tr>
<tr>
<td>Sesquiterpene hydrocarbons</td>
<td>0.8</td>
</tr>
<tr>
<td>Oxygenated sesquiterpenes</td>
<td>0.9</td>
</tr>
<tr>
<td>di-2-Propenyldisulfide</td>
<td>10.6</td>
</tr>
<tr>
<td>Dimethyl tetrasulphide</td>
<td>4.6</td>
</tr>
<tr>
<td>3,3-Thiobis-1-propene</td>
<td>2.4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>4.1</td>
</tr>
<tr>
<td>Total Esters</td>
<td>0.3</td>
</tr>
<tr>
<td>Total monoterpenes</td>
<td>30.5</td>
</tr>
<tr>
<td>Total sesquiterpenes</td>
<td>1.7</td>
</tr>
<tr>
<td>Total of identified compounds</td>
<td>63.7</td>
</tr>
</tbody>
</table>

3.2. Effect of concentration

3.2.1. Gravimetric measurements

Values of the inhibition efficiency and corrosion rate obtained from the weight loss measurements of carbon steel for different concentrations of GO oil in 1 M HCl at 298 K after 6 hours of immersion are given in table 2.

Inhibition efficiency P (%) was calculated as follows:

\[ P \% = \frac{W_{0\text{\corr}} - W_{\text{\corr}}}{W_{\text{\corr}}} \times 100 \]  

(1)
where $W_{corr 0}$ and $W_{corr}$ are the corrosion rates of carbon steel due to the dissolution in 1 M HCl in the absence and presence of different concentrations of the inhibitor, respectively.

From this table we can see that the inhibition efficiency increases with the increasing inhibitor concentration. From the results one observes that the optimum concentration of the inhibitor required to achieve the efficiency was found to be 2.5 g/L ($P=95\%$).

**Table 2.** Corrosion parameters for carbon steel in a 1M HCl solution in the absence and presence of different *Allium sativum* essential oil concentrations.

<table>
<thead>
<tr>
<th>Conc.(g/L)</th>
<th>$W_{corr}$ (mg. cm$^{-2}$)</th>
<th>$E_w$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.8614</td>
<td>----</td>
</tr>
<tr>
<td>0.5</td>
<td>1.2946</td>
<td>30.5</td>
</tr>
<tr>
<td>1.0</td>
<td>0.8981</td>
<td>51.8</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5139</td>
<td>72.4</td>
</tr>
<tr>
<td>2.0</td>
<td>0.1587</td>
<td>91.5</td>
</tr>
<tr>
<td>2.5</td>
<td>0.0927</td>
<td>95.0</td>
</tr>
</tbody>
</table>

Indeed, Fig. 1 has shown that the corrosion rate values of carbon steel decreases when the inhibitor concentration increases while $E_w$ (%) values of GO oil increases with the increase of the concentration reaching a maximum value. This behavior can be attributed to the increase of the surface covered $\theta$, and that due to the adsorption of phytochemical components of the essential oil onto the carbon steel surface resulting in the blocking of the reaction sites, and protection of this surface from the attack of the corrosion active ions in the acid medium. Consequently, we can conclude that the GO oil is a good corrosion inhibitor for carbon steel in a 1M HCl solution.

**Figure 1.** Variation of corrosion rate ($W_{corr}$) and inhibition efficiency ($E_w$) with GO oil concentration for carbon steel in 1M HCl at 298 K.
3.2.2. Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of carbon steel in a 1M HCl solution, in the absence and presence of GO oil, was also investigated by the electrochemical impedance spectroscopy (EIS) at 298K after 30 min of immersion. Impedance diagrams are obtained for a frequency range 100 KHz –10 mHz at the open circuit potential for carbon steel in 1M HCl in the presence and absence of GO oil. Nyquist plots for carbon steel in 1M HCl at various concentrations of this oil are presented in Fig 2.

The EIS results are simulated by the equivalent circuit shown in Fig. 3 to pure electric models that could verify or rule out mechanistic models and enable the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system under investigation [27]. In the electrical equivalent circuit, Rs is the solution resistance, R_T the charge transfer resistance and C_dl is the double layer capacitance.

![Figure 2. Nyquist diagrams for carbon steel electrode and GO oil at E_{corr} after 30min of immersion.](image)

![Figure 3. The electrochemical equivalent circuit used to fit the impedance spectra.](image)

Table 3 gives values of charge transfer resistance, R_T double-layer capacitance, C_dl , and f_{max} derived from Nyquist plots and inhibition efficiency E_{RT} (\%°).

The values of R_T were given by subtracting the high frequency impedance from the low frequency one as follow :

\[
R_T = Z_{re}^{low} - Z_{re}^{high}
\]  

(2)
The values of electrochemical double layer capacitance, $C_{dl}$, were calculated at the frequency $f_{\text{max}}$, at which the imaginary component of the impedance is maximal ($-Z_{\text{max}}$) by the following equation:

$$C_{dl} = \frac{1}{2\pi f_{\text{max}} R_T}$$

(3)

The percent inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the equation:

$$\text{EI}_{RT} \text{ (%) } = \frac{R_T - R_T^0}{R_T} \times 100$$

(4)

where $R_T^0$ and $R_T$ are the charge transfer resistance values without and with the inhibitor, respectively.

Table 3. Electrochemical Impedance parameters for corrosion of carbon steel in acid medium at various contents of GO oil.

<table>
<thead>
<tr>
<th>Conc.(g/L)</th>
<th>R ($\Omega$.cm$^2$)</th>
<th>$f_{\text{max}}$(Hz)</th>
<th>$C_{dl}$(µF/cm$^2$)</th>
<th>$\text{EI}_{RT}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>74</td>
<td>79</td>
<td>27.24</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>105</td>
<td>68</td>
<td>22.30</td>
<td>29.5</td>
</tr>
<tr>
<td>1.0</td>
<td>148</td>
<td>56</td>
<td>19.21</td>
<td>50.0</td>
</tr>
<tr>
<td>1.5</td>
<td>280</td>
<td>44</td>
<td>12.92</td>
<td>73.6</td>
</tr>
<tr>
<td>2.0</td>
<td>909</td>
<td>20</td>
<td>8.76</td>
<td>91.9</td>
</tr>
<tr>
<td>2.5</td>
<td>1112</td>
<td>18</td>
<td>7.96</td>
<td>93.3</td>
</tr>
</tbody>
</table>

The recorded EIS spectrum for carbon steel in in 1M HCl at 298 (Fig. 2) showed one single depressed capacitive loop. The same trend (one capacitive loop) was also noticed for carbon steel immersed in 1M HCl containing GO oil (0.5–2.5g/L). The diameter of Nyquist plots increased when increasing the concentration of GO oil, indicating strengthening of inhibitive film. Moreover, the single capacitive loop can be attributed to the charge transfer that takes place at electrode/solution interface, and the charge transfer process controls the corrosion reaction of carbon steel and the presence of inhibitor does not change the mechanism of dissolution of carbon steel [28-29]. It is also clear that these impedance diagrams are not perfect semicircles and this difference has been attributed to frequency dispersion [30] and has been attributed to roughness and other inhomogeneities of solid surface [31]. From the impedance data (Table 3), we conclude that the $R_T$ values increase with inhibitor concentrations and consequently the inhibition efficiency increases to 93.3% at a concentration of 2.5g/L. In fact, the presence of GO oil is accompanied by the increase of the value of $R_T$ in an acidic solution confirming a charge transfer process mainly controlling the corrosion of carbon steel. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor (Figure 4). The decrease in $C_{dl}$ is due to the adsorption of the inhibitor on the metal surface leading to the formation of film or a complex from the acidic solution [32]. We also
noted the increase of the value of $R_T$ with the inhibitor concentration leading to an increase in the corrosion inhibition efficiency (Figure 4).

![Figure 4](image_url)

Figure 4. Variation of Double layer capacitance ($C_{dl}$) and inhibition efficiency ($E_{RT}$) with GO oil concentration for carbon steel in 1M HCl at 298 K.

3.2.3. Polarization tests

Potentiodynamic anodic and cathodic polarization plots for carbon steel specimens in a 1 M HCl solution in the absence and presence of different concentrations of GO oil at 298 K are shown in Figure 5. The respective kinetic parameters including corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$), cathodic Tafel slope ($\beta_c$) and inhibition efficiency ($IE_{corr} \%$) are given in Table 4.

The inhibition efficiencies were calculated from $I_{corr}$ values according to following equation:

$$IE_{corr} (\%) = \frac{I_{0corr} - I_{corr}}{I_{0corr}} \times 100 \tag{5}$$

where $I_{0corr}$ and $I_{corr}$ are the corrosion current densities in the absence and the presence of the inhibitor.

![Figure 5](image_url)

Figure 5. Potentiodynamic polarisation curves of carbon steel in 1M HCl in the presence of different concentrations of GO.
Table 4. Electrochemical parameters of carbon steel at various concentrations of GO in 1M HCl and corresponding inhibition efficiency.

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>$E_{\text{corr}}$ (mV/SCE)</th>
<th>$I_{\text{corr}}$ (µA/cm$^2$)</th>
<th>$-b_c$ (mV/dec)</th>
<th>IE$_{\text{corr}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-467</td>
<td>96</td>
<td>108</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>-469</td>
<td>67</td>
<td>148</td>
<td>30.2</td>
</tr>
<tr>
<td>1</td>
<td>-478</td>
<td>47</td>
<td>146</td>
<td>51.0</td>
</tr>
<tr>
<td>1.5</td>
<td>-481</td>
<td>26</td>
<td>133</td>
<td>72.9</td>
</tr>
<tr>
<td>2</td>
<td>-483</td>
<td>8</td>
<td>129</td>
<td>91.7</td>
</tr>
<tr>
<td>2.5</td>
<td>-489</td>
<td>4</td>
<td>120</td>
<td>95.8</td>
</tr>
</tbody>
</table>

Inspection of Fig. 5 shows that the addition of GO oil has an inhibitive effect in the both anodic and cathodic parts of the polarization curves. Thus, addition of this inhibitor reduces the carbon steel dissolution as well as retards the hydrogen evolution reaction. In addition, the parallel cathodic Tafel curves in Fig. 5 show that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of the inhibitor [27]. In the domain anodic (Fig. 5), the polarization curves of carbon steel have shown that the addition of the essential oil decreases the current density. So, it could be concluded that this essential oil acted as a mixed type inhibitor for carbon steel in a 1 M HCl solution. The analyses of the data in Table 4 revealed that the corrosion current density ($I_{\text{corr}}$) decreases considerably with increasing GO oil concentration. The cathodic Tafel slope ($b_c$) didn’t change upon the addition of GO oil, which suggests that the inhibiting action occurred by simple blocking of the available cathodic sites on the metal surface, which lead to a decrease in the exposed area necessary for hydrogen evolution and lowered the dissolution rate with increasing natural oil concentration. The dependence of IE (%) versus the inhibitor concentration of GO oil is also presented in Table 4. The obtained efficiencies indicate that GO oil acts as a good corrosion inhibitor.

3.3. Effect of temperature

Temperature can modify the interaction between the carbon steel electrode and the acidic medium in the absence and the presence of inhibitors. To assess the influence of temperature on corrosion and corrosion inhibition processes, polarization tests were carried out at various temperatures (298–328 K) in the absence and presence of 2.5 g/L GO oil, as shown in Fig. 6a and 6b. Corresponding electrochemical data are given in Table 4.

As seen from Fig.6 (a and b) and Table 4, the corrosion current density increases with increasing temperature, in both uninhibited and inhibited solutions. Inhibition efficiency for GO oil decreases with an increase in temperature and a slight change in their values are observed in the range of temperatures studied. Thus the compounds can be regarded as temperature-independent inhibitors.
**Figure 6a.** Polarisation curves of carbon steel in 1M HCl at different temperatures.

**Figure 6b.** Polarisation curves of carbon steel in 1M HCl in the presence of 2.5 g/L of GO oil at different temperatures.

The nearly constant efficiency of the inhibitors in the temperature range studied can be considered as the slight change in the nature of the adsorption mode: physisorption of the inhibitor is dominant in the temperature range studied, while chemisorption accompanied by physisorption can occur slightly with increasing the temperature.
Table 5. Effect of temperature on the carbon steel corrosion in the absence and presence of 2.5 g/L of GO at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>E_{corr} (mV/SCE)</th>
<th>I_{corr} (µA/cm^2)</th>
<th>-b_c (mV/dec)</th>
<th>E_I (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>-467</td>
<td>87</td>
<td>99</td>
<td>---</td>
</tr>
<tr>
<td>308</td>
<td>-444</td>
<td>157</td>
<td>126</td>
<td>---</td>
</tr>
<tr>
<td>318</td>
<td>-445</td>
<td>305</td>
<td>129</td>
<td>---</td>
</tr>
<tr>
<td>328</td>
<td>-437</td>
<td>399</td>
<td>136</td>
<td>---</td>
</tr>
<tr>
<td>GO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>-489</td>
<td>4</td>
<td>120</td>
<td>95.8</td>
</tr>
<tr>
<td>308</td>
<td>-534</td>
<td>4.4</td>
<td>95</td>
<td>97.2</td>
</tr>
<tr>
<td>318</td>
<td>-514</td>
<td>8.3</td>
<td>86</td>
<td>97.3</td>
</tr>
<tr>
<td>328</td>
<td>-541</td>
<td>16.9</td>
<td>101</td>
<td>95.8</td>
</tr>
</tbody>
</table>

To calculate the activation parameters of the corrosion process, Arrhenius equation (6) was used:

\[
I_{\text{corr}} = A \exp \left( -\frac{E_a}{RT} \right)
\]

Where \( k \) is the pre-exponential factor, \( E_a \) is the apparent activation energy of the corrosion process, \( R \) is the gas constant and \( T \) is the absolute temperature.

Fig. 7 shows Arrhenius plots of the logarithm of the current density vs 1/T for carbon steel in the corrosive medium with and without addition of 2.5 g/L GO oil. Straight lines are obtained with a slope of \(-E_a/R\). Activation energy (E_a) values are deduced from this graph and listed in Table 5.

From Table 5, it is observed that the values of E_a obtained in presence of 2.5 g/L GO oil are higher than that obtained in the inhibitor-free solution.

Figure 7. Arrhenius plots of carbon steel in 1 M HCl with and without 2.5g/L of GO oil
The higher $E_a$ value in the inhibited solution can be correlated with the increased thickness of the double layer, which enhances the activation energy of the corrosion process [33].

The temperature dependence of the inhibiting effect and the comparison of the values of the apparent activation energy of the corrosion process in the absence and presence of the inhibitor can provide further evidence [34-35] concerning the mechanism of the inhibiting action. The decrease of the inhibitor efficiency with temperature rising, which refers to a higher value of $E_a$, when compared to that in acid media without an inhibitor, is explained as an indication for an electrostatic character of the inhibitor’s adsorption. The lower value of $E_a$ in an inhibited solution when compared to an uninhibited one shows that chemisorption bond between the inhibitor and the metal is highly probable [36]. Activation energy, $E_a$ values in the table are higher for inhibited solution than for the uninhibited media, indicating a high inhibitive action of the additives by increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor’s adsorption on the carbon steel surface (physisorption).

Table 6. The values of activation parameters $\Delta H^*$, $\Delta S^*$ and $\Delta G^*$ for carbon steel in 1M HCl in the absence and the presence of 2.5 g/L of GO oil.

<table>
<thead>
<tr>
<th>E_a (kJ/mol)</th>
<th>$\Delta H^*$ (kJ/mole)</th>
<th>$\Delta S^*$ (J/mole K$^{-1}$)</th>
<th>$\Delta G^*$ (kJ/mole at T=298K)</th>
<th>E_a-$\Delta H^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>44.23</td>
<td>41.57</td>
<td>-181.88</td>
<td>54.24</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>39.92</td>
<td>37.33</td>
<td>-109.55</td>
<td>69.97</td>
</tr>
</tbody>
</table>

Thermodynamique parameters, such as enthalpy and entropy of corrosion process, may be evaluated from the effect of temperature. An alternative formulation of Arrhenius equation is (7) [37]:

$$I_{corr} = \frac{RT}{Nh}.\exp\left(\frac{\Delta S^*}{R}\right).\exp\left(-\frac{\Delta H^*}{RT}\right)$$

Where N is the Avogadro’s number, h the Plank’s constant, R is the perfect gas constant, $\Delta S^*$ and $\Delta H^*$ the entropy and enthalpy of activation, respectively.

Fig. 8 shows a plot of $\ln(I_{corr}/T)$ against $1/T$ for GO oil. Straight lines are obtained with a slope of $(-\Delta H^*/R)$ and an intercept of $(\ln R/Nh + \Delta S^*/R)$ from which the values of $\Delta H^*$ and $\Delta S^*$ are calculated respectively and listed in Table 5.

The positive values of $\Delta H^*$ both in the absence and presence of the inhibitor reflect the endothermic nature of the carbon steel dissolution process and it indicates that the dissolution of carbon steel is difficult [38].

From Table 5, it is clear that entropy of activation $\Delta S^*$ decreases more negatively in the uninhibited than inhibited systems imply that the activation complex in the rate determining steps represents association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [39].
3.4. Adsorption isotherm

In order to clarify the nature and the strength of adsorption, the experimental results were fitted to a series of adsorption isotherms, and the best fit was obtained with the use of the Langmuir adsorption isotherm. A straight line was obtained upon plotting $C_{\text{inh}}/\theta$ vs. $C_{\text{inh}}$, which is presented graphically in Fig. 9.

Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best. Therefore, it is concluded that, a monolayer inhibitor film forms on carbon steel surface, and there are no interactions between the adsorbed inhibitor molecules [40-41].
4. CONCLUSIONS

We have studied the inhibiting effect of the acid garlic essential oil (GO oil) in 1M HCl on the carbon steel by using various methods. The results obtained are in good agreement and are given as follows:

- The major constituents of Allium sativum essential oil has 1(7),5,8-o-menthatriene (20.5 %), di-2-propenyldisulfide (10.7%) and elemicin (9.5 %).
- The GO oil provides good inhibition of the corrosion of carbon steel in normal hydrochloric acid medium.
- The inhibition efficiency increases with increased chamomile oil concentration to attain a maximum value of 95.8% at 2.5 g/L.
- The GO oil acts on carbon steel surface in a 1 M HCl solution as a mixed type inhibitor.
- The inhibition efficiency of GO oil is independent of temperature.
- Langmuir isotherm was best fitted with the experimental data obtained at different concentrations.

References

2. Y. Yeh, S. Yeh, Lipids, 29 (1994) 189.
34. E.S. Ivanov, Inhibitors for Metal Corrosion in Acid Media. Metallurgy, Moscow. (1986).

© 2014 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).