



## Evaluation of *Melissa Officinalis* Extract and Oil as Eco-friendly Corrosion Inhibitor for Carbon Steel in Acidic Chloride Solutions

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### ABSTRACT

The extract (E) and oil of *Melissa Officinalis* leaves (EO) have been evaluated as a corrosion inhibitors for carbon steel in 1.0 M HCl solution by means of weight loss measurements, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). Tafel polarization study revealed that extract (E) and oil of *Melissa Officinalis* (EO) act as a mixed type inhibitors. The Nyquist plots showed that with increasing the inhibitors concentrations, the charge-transfer resistance increased and the double-layer capacitance decreased, involving increased inhibition efficiency. The inhibition was found to increase with increasing the concentration of the extract (E) and oil of *Melissa Officinalis* (EO). The values of inhibition efficiency calculated from weight loss, Tafel polarization curves, and EIS were in good agreement. The effect of temperature on the corrosion behaviour of mild steel in 1.0 M HCl with addition of both extract (E) and oil of *Melissa Officinalis* (EO) was also studied and thermodynamic parameters were determined and discussed.

**Keywords:** Corrosion inhibition, Carbon steel, *Melissa Officinalis*, Extract, Oil, Electrochemical techniques.

## INTRODUCTION

The use of chemical inhibitors is one of the most practiced methods for protecting against corrosion, especially in acid media, to prevent metal dissolution and acid consumption<sup>1</sup>. Various organic and non-organic compounds have been studied as inhibitors to protect metals from corrosion. Usually, organic compounds exert a significant influence on metal surface adsorption and therefore can be used as effective corrosion inhibitors. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions containing S, O, or N atoms which are centres for the establishment of the adsorption process<sup>2-11</sup>.

Nevertheless, most of these synthetic organic compounds are not only expensive but also toxic for live beings. Now, the restrictive environmental regulations have made researchers to focus on the need to develop cheap, non-toxic, and environmentally benign natural corrosion inhibitors. These natural organic compounds could be either synthesized or extracted from aromatic herbs, spices, and medicinal plants. Plant extracts are viewed as an incredibly rich source of natural chemical compounds which can be extracted by simple and low-cost procedures and which are biodegradable in nature. The use as corrosion inhibitors of natural compounds extracted from leaves or seeds, for example, have been widely reported by several authors<sup>12-19</sup>.

Recently, Fouda *et al.*<sup>20</sup> used the extract of Melissa as corrosion inhibitor of carbon steel in HCl solutions. The encouraging results incited to examine separately extract and oil of Melissa plant on the corrosion of carbon steel in molar HCl using different techniques including weight loss, potentiodynamic polarization measurements, and electrochemical impedance spectroscopy (EIS). The thermodynamic of activation parameters were also calculated and discussed.

## EXPERIMENTAL

### Inhibitors

#### Plant Material

The aerial part of *Melissa Officinalis* was harvested in January 2013 in the wild in the mountain Assoul located Taza at the Nord-east of Morocco. A

voucher specimen was deposited in the Herbarium of Faculty of Sciences, Oujda, Morocco. The dried plant material was stored in the laboratory at room temperature (298 K) and in the shade before the extraction.

### Hydrodistillation Apparatus and Procedure

Hydrodistillation is an extraction method whose function is to extract the volatile compounds of natural products with water vapour, and is often performed using Clevenger-type apparatus, with 400 mL for 3 hours. The essential oil yields were measured and subsequently dried over anhydrous sodium sulfate and stored at 277 K in the dark before gas chromatographic determination of its composition<sup>18</sup>.

### Characterization and Chemical Composition of Essential Oils

Techniques in chromatography (GC/MS, GC-FTIR, HPLC-DAD) were available for the molecular analysis of organic compounds. The chemical components of *Melissa Officinalis* essential oil were determined by spectral analysis of gas chromatography and gas chromatography coupled to mass spectrometry (GC-MS), which identified six major components. GC analyses were performed using a Perkin-Elmer Autosystem GC apparatus (Waltham, MA, USA) equipped with a single injector and two flame ionization detectors (FID). The apparatus was used for simultaneous sampling with two fused-silica capillary columns (60 m long with i.d. 0.22 mm, film thickness 0.25  $\mu$ m) with different stationary phases: Rtx-1 (polydimethylsiloxane) and Rtx-Wax (polyethylene glycol). The temperature program was for 333-503 K at 275 K/min and then held at isothermal 503 K (30 min.). The carrier gas was helium (1 mL/min). Injector and detector temperatures were held at 553 K. Split injection was conducted with a ratio split of 1:80. Electron ionization mass spectra were acquired with a mass range of 35-350 Da. The injected volume of oil was 0.1  $\mu$ L. For gas chromatography-mass spectrometry, the oils obtained were investigated using a Perkin-Elmer Turbo Mass Quadrupole Detector, directly coupled to a Perkin-Elmer Auto system XL equipped with two fused-silica capillary columns (60 m long with i.d. 0.22 mm, film thickness 0.25  $\mu$ m), with Rtx-1 (polydimethylsiloxane) and Rtx-Wax (polyethylene glycol). Other GC conditions were the same as

described above. Ion source temperature was 423 K and energy ionization 70 eV. Electron ionization mass spectra were acquired with a mass range of 35-350 Da.

The injected volume of oil was 0.1  $\mu\text{L}$ . Identification of the components was based (1) on the comparison of their GC retention indices (RI) on non-polar and polar columns, determined relative to the retention time of a series of n-alkanes with linear interpolation, with those of authentic compounds or literature data<sup>21</sup>, and (2) on computer matching with commercial mass spectral libraries<sup>21,22</sup> and comparison of spectra with those in our personal library. Relative amounts of individual components were calculated on the basis of their GC peak areas on the two capillary Rtx-1 and Rtx-Wax columns, without FID response factor correction.

### Materials

The steel used in this study is a carbon steel with a chemical composition 0.09 wt. % P; 0.38 wt. % Si; 0.01 wt. % Al; 0.05 wt. % Mn; 0.21 wt. % C; 0.05 wt. % S and the remainder iron (Fe).

### Preparation of Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. Inhibitors were dissolved in acid solution at the required concentrations (in mL/L) (volume of inhibitor/volume of blank), and the solution in the absence of inhibitor was taken as blank for comparison purposes. The test solutions were freshly prepared before each experiment by adding essential oil and extract of *Melissa Officinalis* directly to the corrosive solution. The concentrations of essential oils were 0.5, 1, and 2 mL/L; and those of the extract were 2, 4, and 8 mL/L.

### Gravimetric Study

Gravimetric experiments were performed according to the standard methods<sup>23</sup>, the carbon steel specimens (1.0 cm  $\times$  1.0 cm  $\times$  0.1 cm) were abraded with a series of emery papers SiC (120, 600, and 1200 grades) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in a 100 mL beaker containing 250 mL of 1.0 M HCl solution with and without addition of different concentrations of inhibitors. All the aggressive acid

solutions were open to air. After 6 hours of acid immersion, the specimens were taken out, washed, dried, and weighed accurately. In order to get good reproducibility, all measurements were performed few times and average values were reported.

### Electrochemical Measurements

The electrochemical measurements were carried out using Volta lab (Tacussel - Radiometer PGZ 100) potentiostat controlled by Tacussel corrosion analysis software model (Voltmaster 4) at static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode of surface area of 1  $\text{cm}^2$ . The working electrode was carbon steel of the surface 0.32  $\text{cm}^2$ . All potentials given in this study were referred to this reference electrode. The working electrode was immersed in the test solution for 30 minutes to establish a steady state open circuit potential ( $E_{\text{ocp}}$ ). After measuring the  $E_{\text{ocp}}$ , the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 308 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x-axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation:

$$\eta_z \% = \frac{R_{ct}^i - R_{ct}^o}{R_{ct}^i} \times 100 \quad \dots(1)$$

Where,  $R_{ct}^i$  and  $R_{ct}^o$  are the charge transfer resistance in absence and in presence of inhibitor, respectively.

After the ac impedance test, potentiodynamic polarization measurements of carbon steel substrate in inhibited and uninhibited solution were scanned from cathodic to the anodic direction, with a scan

rate of 1 mV.s<sup>-1</sup>. The potentiodynamic data were analysed using the polarization VoltaMaster 4 software. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities ( $I_{\text{corr}}$ ). From the polarization curves obtained, the corrosion current ( $I_{\text{corr}}$ ) was calculated by curve fitting using the equation:

$$I = I_{\text{corr}} \left[ \exp\left(\frac{2.3\Delta E}{\beta_a}\right) - \exp\left(\frac{2.3\Delta E}{\beta_c}\right) \right] \quad \dots(2)$$

The inhibition efficiency was evaluated from the measured  $I_{\text{corr}}$  values using the following relationship:

$$h_{\text{Tafel}}(\%) = \frac{I_{\text{corr}} - I_{\text{corr}(i)}}{I_{\text{corr}}} \times 100 \quad \dots(3)$$

where  $I_{\text{corr}}$  and  $I_{\text{corr}(i)}$  are the corrosion current densities for steel electrode in the uninhibited and inhibited solutions, respectively.

## RESULTS AND DISCUSSION

### Essential oil composition

Qualitative and quantitative analyses of essential oils were carried out using GC/MS analyses. The compositions of essential oils of *Melissa Officinalis* are shown in Table 1.

The most important constituents of essential oils of *Melissa officinalis* are shown in Table 2.

### Gravimetric Measurements

#### Effect of Inhibitor Concentration

The effect of addition of oil and extract of *Melissa Officinalis* tested at different concentrations on the corrosion of carbon steel in 1.0 M HCl solution was also studied by weight loss method at 308 K after 6 h of immersion period. The corrosion rate ( $v$ ) and the inhibition efficiency ( $\eta_{\text{WL}}(\%)$ ) were calculated by the following equations<sup>24</sup>:

$$v = \frac{W}{St} \quad \dots(4)$$

$$\eta_{\text{WL}}(\%) = \frac{v_0 - v}{v_0} \times 100 \quad \dots(5)$$

where  $W$  is the three-experiment average weight loss of the carbon steel,  $S$  is the total surface area of the specimen,  $t$  is the immersion time and  $v_0$  and  $v$  are values of the corrosion rate without and with addition of the inhibitor, respectively.

Table 3 gives the results of the weight loss measurements for the corrosion of carbon steel in 1.0 M HCl solution in the absence and presence of oil and extract of *Melissa Officinalis* at 308 K. Analysis of Table 3 reveals that as the concentration of inhibitors increases, the inhibition efficiency ( $\eta_{\text{WL}}(\%)$ ) increases. This is because more surface area of carbon steel is covered by increasing inhibitors concentration.

#### Effect of Temperature

In order to study the temperature dependence of corrosion rates in uninhibited and inhibited solutions, gravimetric measurements were carried out at the temperatures ranging from 313 K to 343 K in the absence and presence of optimum concentration of inhibitors (2.0 mL/L for EO, and 8.0 mL/L for E). The calculated values of the corrosion rates and inhibition efficiencies within the studied temperature range are shown in Table 4.

Generally, the corrosion rates of carbon steel in acidic solutions increased with the rise in temperature. This is due to a decrease in the overpotential of the hydrogen evolution reaction, resulting in higher dissolution rates of metals. The higher rate of hydrogen gas generation also increasingly agitates the metal corrodent/interface and depending on the nature of the metal-inhibitor interactions, this could also hinder the inhibitor adsorption or perturb already adsorbed inhibitor. On the other hand, for inhibitor species that react with the metal surface, increasing the temperature of the system could augment the interaction between the metal surface and the inhibitor leading to higher surface coverage.

Table 4 showed that the corrosion rate increased with increasing the temperature both in uninhibited and inhibited solutions while the

inhibition efficiency of the essential oil decreased with temperature. On the other hand, the inhibition efficiency of the extract remained almost constant. A decrease in inhibition efficiency with the increase temperature in presence of essential oil might be due to the weakening of physical adsorption, while in case of the extract, the constant value of the inhibition efficiency could be due to chemistry.

Arrhenius and transition state plots were used for determination of  $E_a$  (activation energy),  $\Delta H_a$  (activation enthalpy) and  $\Delta S_a$  (activation entropy) at the studied temperature 313, 323, 333, and 343 K for the carbon steel in the presence and absence of inhibitors (Equation 6):

$$v = Ae^{-E_a/RT} \quad \dots(6)$$

where  $v$  is the corrosion rate,  $A$  is the pre-exponential factor,  $E_a$  ( $\text{J}\cdot\text{mol}^{-1}$ ) is the activation energy, and  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ).

To solve this equation, we take natural logs of both sides (common logs could be used as well):

$$\ln v = \left(\frac{-E_a}{RT}\right) + \ln A \quad \dots(7)$$

The values of  $E_a$  were calculated (Table 5) from the slope (slope =  $-E_a/R$ ) of the straight line of the x-axis ( $\ln v$ ) and y-axis ( $1000/T$ ) of the graph by using of Arrhenius plot for the carbon steel in 1.0 M HCl in the with and without inhibitors (Figure 1).

The transition state equation was used to calculate the  $\Delta H_a$  and  $\Delta S_a$ :

$$v = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right) \quad \dots(8)$$

where  $R$  is the universal gas constant,  $A$  is the Arrhenius pre-exponential factor,  $h$  is Planck's constant,  $N$  is Avogadro's number,  $E_a$  is the activation energy,  $T$  is the absolute temperature in Kelvin,  $\Delta S_a$  is

the entropy of activation, and  $\Delta H_a$  is the enthalpy of activation. To carry out simple calculations, Equation (6) was rearranged to become:

$$\ln\left(\frac{v}{T}\right) = \left(-\frac{\Delta H_a}{RT}\right) + \left[\ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_a}{R}\right)\right] \quad \dots(9)$$

A plot of  $\ln(v/T)$  against  $1000/T$  gives a straight line with the slope equal to  $(\Delta H_a/R)$  and intercept equal to  $[\ln(R/Nh) + (\Delta S_a/R)]$ , as shown in Figure 2. The  $\Delta H_a$  and  $\Delta S_a$  values were calculated and are displayed in Table 5.

From Table 5, the activation energy increases in the presence of the EO, implying that a physical adsorption (electrostatic) process occurred in the initial stage. This phenomenon may be attributed to the change in the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules. It is often interpreted by physical adsorption leading to the formation of an adsorptive film of electrostatic character<sup>25-28</sup>. This conclusion is corroborated by the decrease in inhibition efficiency with increasing temperature (Table 5). According to Szauer and Brand<sup>29</sup>, the increase in activation energy can be attributed to the decrease in the adsorption of the inhibitor on the carbon steel surface with increases in temperature<sup>29</sup>. However, the lower value of  $E_a$  in inhibited solution compared to uninhibited solution can be explained by strong chemisorption bond between the inhibitor and the metal. Some authors reported that electrostatic adsorption proceeds irrespective of the fact that the  $E_a$  value in the presence of inhibitor is lower than that in free solution<sup>30</sup>. In addition, the  $E_a$  values are greater than  $20 \text{ kJ}\cdot\text{mol}^{-1}$  in both the presence and absence of the inhibitor, which indicate that the entire process is controlled by the surface reaction<sup>31</sup>. The positive sign of the enthalpies  $\Delta H_a$  reflects the endothermic nature of the steel dissolution process whereas large negative values of entropies  $\Delta S_a$  imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex<sup>32, 33</sup>.

## Electrochemical Experiments

### Potentiodynamic Polarization Curves

Figures 3(A) and 4(B) represent the potentiodynamic polarisation curves of carbon steel in a 1.0 M HCl solution in the absence and presence of oil and extract of *Melissa Officinalis* at 308 K.

The respective electrochemical parameters (i.e., corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), and the anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) Tafel constants, as shown in Table 6, were derived from Tafel plots.

From the potentiodynamic polarisation curves, it can be seen that the extracts caused a decrease in both anodic and cathodic current densities, which is most likely due to the adsorption of the organic compounds present in the oil and extract of *Melissa Officinalis* at the active sites of the electrode surface. This also slowed both metallic dissolution and hydrogen evolution and consequently slowed down the corrosion process. The two extracts exhibited the same behaviour.

From Table 6, it is also clear that there is a shift toward cathodic region in the values of corrosion potential ( $E_{\text{corr}}$ ). In the literature<sup>34, 35</sup>, it has been reported that if the displacement in  $E_{\text{corr(inh)}}$  is more than 85 mV vs. SCE from  $E_{\text{corr}}$ , the inhibitor can be seen as a cathodic or anodic type; and if displacement in  $E_{\text{corr(inh)}}$  is less than 85 mV vs. SCE, the inhibitor can be seen as mixed type. In our study the maximum displacement in  $E_{\text{corr}}$  value was 40 mV vs. SCE toward cathodic region, which indicates that these investigated oil and extract of *Melissa Officinalis* are mixed type inhibitors. Cao<sup>36</sup> pointed out that the inhibitory action on the metal surface takes place with geometrical blockage of the active site. It can be observed from Table 6 that the  $I_{\text{corr}}$  values decrease considerably in the presence of EO and E and decrease with increasing the inhibitor concentration. Correspondingly,  $\eta_{\text{Tafel}}$  (%) values increase with increasing the inhibitor concentration reaching a maximum value at 2 mL/L for EO and 8 mL/L for E. The cathodic Tafel slope ( $\beta_c$ ) and the anodic Tafel slope ( $\beta_a$ ) of oil and extract of *Melissa Officinalis* changed with inhibitors concentration. This observation suggests that the inhibitors molecules controlled the two reactions and adsorbed on the

metal surface by blocking the active sites on the metal surface, retarding the corrosion reaction.

### Electrochemical Impedance Measurements (EIS)

The electrochemical impedance diagrams for carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of oil and extract of *Melissa Officinalis* are shown in Figures 4(A) and 4(B). Table 7 summarizes impedance data from the EIS experiments carried out both in the absence and presence of oil and extract of *Melissa Officinalis* at various concentrations. The electrochemical impedance diagrams show only one depressed capacitive loop, which is attributed to the one time constant, in the absence and presence of oil and extract of *Melissa Officinalis*, which indicates two significant effects: the charge-transfer resistance significantly increases, and the  $f_{\text{max}}$  decreases, in the presence of both inhibitors, decreasing the capacitance value, which may be caused by reduction in the local dielectric constant and/or by an increase in the thickness of the electrical double-layer.

These results show that the presence of the inhibitors modifies the electric double-layer structure suggesting that the inhibitor molecules act by adsorption at the metal/solution interface. The solution resistance ( $R_s$ ) is identical in the absence and presence of oil and extract of *Melissa Officinalis* and equal to  $1.2 \Omega \cdot \text{cm}^2$ . Deviations from a perfect circular shape indicate frequency dispersion of interfacial impedance. This anomalous phenomenon is attributed in the literature to the non-homogeneity of the electrode surface arising from the surface roughness or interfacial phenomena<sup>37-40</sup>. The charge-transfer resistance ( $R_{ct}$ ) values were calculated from the difference in impedances at lower and higher frequencies. The double-layer capacitance ( $C_{dl}$ ) was calculated from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{\text{max}} R_{ct}} \quad \dots(10)$$

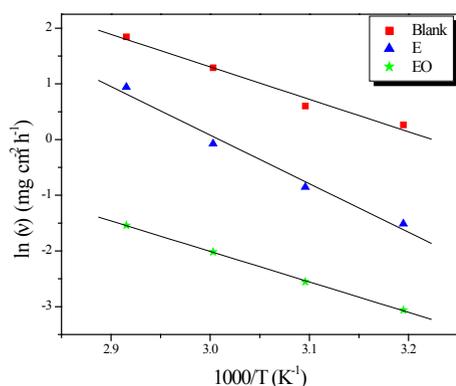
where  $f_{\text{max}}$  is the frequency at which the imaginary component of the impedance is maximal. A  $C_{dl}$  value of  $54.58 \mu\text{F} \cdot \text{cm}^{-2}$  was determined for the carbon steel electrode in 1.0 M HCl.

Data presented in Table 7 show that the value of  $R_{ct}$  increases in presence of oil and extract of *Melissa Officinalis*. The value of  $C_{dl}$  is always smaller in the presence of the inhibitors than in its absence, as a result of the effective adsorption of the inhibitors. It is apparent that a causal relationship exists between adsorption and inhibition. Besides, it is clear from the Table 7 that by increasing the inhibitors concentrations, the  $C_{dl}$  values tend to decrease and the inhibition efficiency increases. This behaviour was the result of an increase in the surface coverage by the inhibitors molecules of oil and extract of *Melissa Officinalis*, which led to an increase in the inhibition efficiency. The decrease in  $C_{dl}$  values may be considered in terms of Helmholtz model<sup>41</sup>:

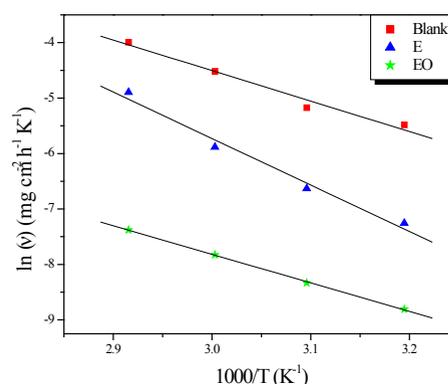
$$C_{dl} = \frac{\epsilon_0 \epsilon S}{\delta} \quad \dots(11)$$

where  $\epsilon$  is the dielectric constant of the medium,  $\epsilon_0$  is the vacuum permittivity,  $S$  is the electrode area, and  $\delta$  is the thickness of the protective layer. In fact, the decrease in  $C_{dl}$  values can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double-layer<sup>42</sup>.

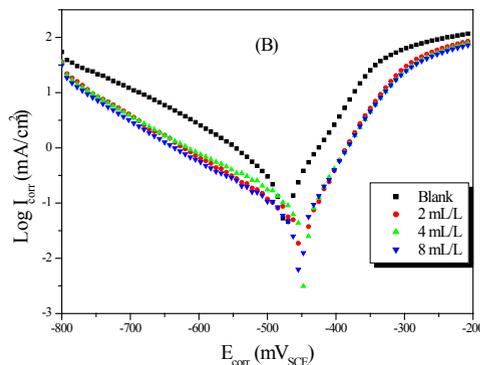
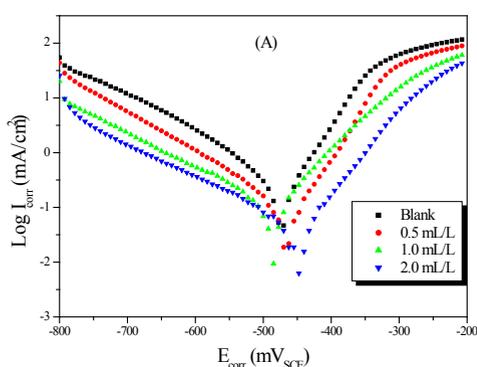
The corrosion rate of carbon steel in 1.0 M HCl solution is controlled by both hydrogen evolution reaction and dissolution reaction of this metal. It is generally accepted that the corrosion inhibition



**Fig. 1:** Arrhenius plots for the corrosion rate of carbon steel in 1.0 M HCl solution in absence and presence of inhibitors



**Fig. 2:** Ln ( $v/T$ ) versus  $1/T$  for the corrosion of carbon steel in 1.0 M HCl in absence and presence of inhibitors

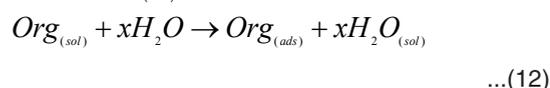


**Fig. 3:** Polarisation curves for carbon steel in 1.0 M HCl in the absence and presence of oil and extract of *Melissa Officinalis* concentrations: Extract oil (A) and extract of *Melissa Officinalis* (B)

**Table 1: Chemical constituents of *Melissa officinalis* essential oil (EO) (%)**

Compounds	Ir l	Ir a	Ir p	%
$\alpha$ -pinene	936	929	1019	0.3
oct-1-en-3-ol	962	961	1440	0.5
Sabinene	973	964	1117	0.4
$\beta$ -pinene	978	969	1107	0.5
Myrcene	987	980	1155	1.1
$\alpha$ -terpinene	1013	1008	1175	0.3
p-Cymene	1015	1011	1263	0.2
Cineole 1,8	1024	1020	1207	0.9
Limonene	1025	1020	1196	0.6
(Z) $\beta$ -Ocimene	1029	1025	1220	0.8
(E) $\beta$ -Ocimene	1041	1035	1234	0.1
$\gamma$ -terpinene	1051	1048	1240	0.7
E-hydrate de sabinene	1053	1056	1457	4.6
P-Mentha-3,8-diene	1059	1059	1259	0.4
terpinolene	1082	1078	1277	0.2
Z-hydrate de sabinene	1082	1083	1536	0.5
1-octen-3-ol acetate	1093	1094	1371	1.8
3-octenyl acetate	1110	1107	1328	0.2
P-Menth-3-en-8-ol		1136	1602	8.8
Menthone	1136	1136	1483	1.0
isomenthone	1146	1140	1457	2.7
Neomenthol	1156	1154	1637	2.4
Terpinen-4-ol	1164	1166	1598	3.5
$\beta$ -Terpineol	1176	1175	1665	0.5
Pulegone	1215	1221	1639	8.8
Z-piperitone oxyde	1230	1235	1717	7.3
Pseudodisphenol	1245	1248		0.2
Isopulegylacetate 1	1263	1258	1631	0.2
Neomenthylacetate	1263	1263	1524	1.9
Thymol	1266	1263	2159	0.3
Bornylacetate	1270	1270	1572	0.3
Diosphenol	1276	1279	1790	1.0
Menthylacetate	1280	1279	1557	1.0
Piperitenone	1318	1313	1900	1.6
Piperitenone oxyde	1335	1341	1939	8.4
E-jasmone	1364	1369	1890	0.2
$\alpha$ -Copaene	1379	1375	1483	0.1
Nepetalactone	1360	1379	1978	1.2
P-Mentha-1,2,3-triol		1395	1880	13.1
$\alpha$ -Gurjunene	1413	1409	1528	0.1
E-Caryophyllene	1421	1420	1591	2.8
Cadina-3,5-diene	1448	1441		0.3
Trans- $\beta$ -farnesene	1446	1448	1661	0.2
$\alpha$ -Humulene	1455	1450	1665	0.3
Cis Muurolo-4(14),5-diene	1462	1458		0.7
Germacrene D	1479	1478	1706	3.4
Bicyclogermacrene	1494	1491	1725	0.4
$\gamma$ -Cadinene	1507	1505	1756	0.1
Calamenene	1517	1509	1817	0.3
$\delta$ -Cadinene	1520	1514	1752	0.1
Spathulenol	1572	1564	2101	0.4
Caryophyllene oxyde	1578	1569	1965	0.5
Viridiflorol	1592	1581	2064	0.3
1,10-di-epi-Cubenol	1615	1603	2040	0.4
$\alpha$ -cadinol	1643	1638	2209	0.4
Total	88.7			

occurs due to the adsorption of organic molecules at the metal/solution interface and the adsorption itself depends on the molecule's chemical composition, the temperature, and the electrochemical potential at the metal/solution interface. In fact, the solvent H<sub>2</sub>O molecules could also adsorb at metal/solution interface<sup>43</sup>. Therefore, the adsorption of organic inhibitor molecules from aqueous solution can be regarded as a substitution adsorption process between the organic compound in the aqueous phase [Org<sub>(sol)</sub>] and water molecules on the metal surface [H<sub>2</sub>O<sub>(ads)</sub>]<sup>44</sup>.



where x is the size ratio, that is, the number of water molecules replaced by one organic inhibitor.

According to the detailed mechanism above, displacement of some adsorbed water molecules might take place on the metal surface by inhibitor

**Table 2: The major components of Melissa officinalis essential oils**

Major components	%
E-hydrate de sabinene	4.6
Z-piperitoneoxyde	7.3
Piperitenoneoxyde	8.4
Pulegone	8.8
P-Menth-3-en-8-ol	8.8
P-Mentha-1,2,3-triol	13.1

**Table 3: Gravimetric results of carbon steel in 1.0 M HCl at various concentrations of oil (EO) and extract (E) of Melissa Officinalis at 308 K**

Medium	Inhibitor (mL.L <sup>-1</sup> )	v (mg.cm <sup>-2</sup> .h <sup>-1</sup> )	η <sub>wL</sub> (%)
Blank	—	0.320	—
EO	0.5	0.103	67.9
	1.0	0.054	83.0
	2.0	0.017	94.7
E	2.0	0.120	62.5
	4.0	0.053	83.5
	8.0	0.033	86.7

species. The increase in efficiency of inhibition of oil and extract of Melissa Officinalis indicates that the inhibitors molecules are adsorbed on the carbon steel surface with higher concentration, leading to greater surface coverage (θ). It has generally been proved that the first step in the adsorption of an organic inhibitor on a metal surface usually involves the replacement of one or more of water molecules adsorbed at the metal surface by the investigated inhibitors molecules<sup>45</sup>.

Adsorption process is usually described by isotherms. The most frequently used isotherms include Langmuir, Temkin, Frumkin, ...<sup>46</sup>. Langmuir isotherm was tested for its fit to the experimental data. Langmuir adsorption isotherm is given by following equation:

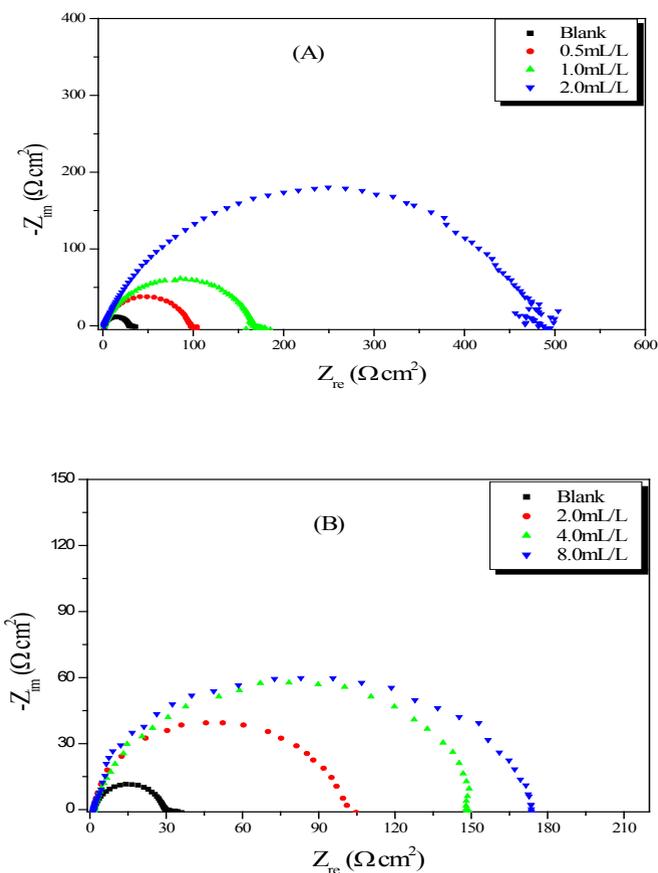
$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

where C<sub>inh</sub> is the inhibitor concentration, and K<sub>ads</sub> the adsorptive equilibrium constant, θ=E%/100 representing the degree of adsorption.

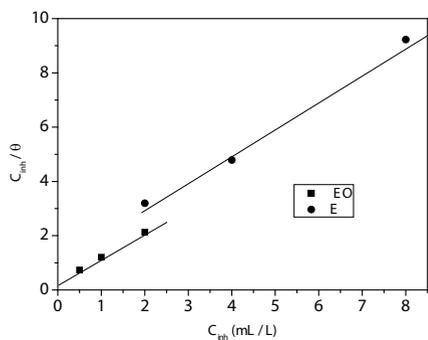
The plot of the (C<sub>inh</sub>/θ) vs C<sub>inh</sub> fitted the gravimetric data follow the Langmuir adsorption isotherm (Figure 5).

**Table 4: Corrosion parameters for carbon steel in 1.0 M HCl in absence and presence of optimum concentration of the inhibitors (2.0 mL/L for EO, and 8.0 mL/L for E) studied at different temperatures**

Temp. (K)	Medium	v (mg.cm <sup>-2</sup> .h <sup>-1</sup> )	θ	η <sub>wL</sub> (%)
313	Blank	1.300	—	—
	EO	0.220	0.83	83.0
	E	0.047	0.96	96.4
323	Blank	1.828	—	—
	EO	0.425	0.76	76.7
	E	0.078	0.95	95.7
333	Blank	3.635	—	—
	EO	0.926	0.74	74.5
	E	0.133	0.96	96.3
343	Blank	6.336	—	—
	EO	2.562	0.59	59.6
	E	0.214	0.96	96.6



**Fig. 4:** Impedance diagrams obtained for carbon steel in 1.0 M HCl in the absence and presence of various oil and extract of *Melissa Officialis* concentrations: Extract oil (A) and extract of *Melissa Officialis* (B)



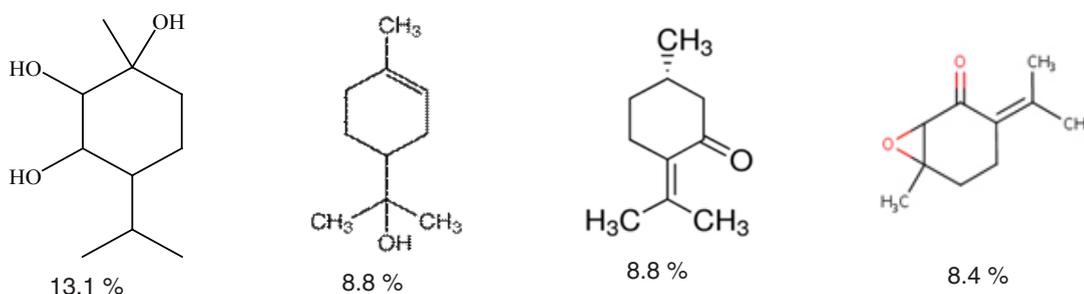
**Fig. 5:** Langmuir adsorption isotherm of EO and E on carbon steel in 1M HCl

**Table 5:** Activation parameters for the carbon steel dissolution in 1.0 M HCl in the absence and the presence of inhibitors at optimum concentration (2.0 mL/L for EO, and 8.0 mL/L for E)

Medium	$E_a$ (KJ/mol)	$\Delta H_a$ (KJ/mol)	$\Delta S_a$ (J/mol.K)
Blank	48.41	45.69	-97.92
EO	72.39	69.67	-36.42
E	45.48	42.76	-134.27

It has been postulated in several works that natural plants (extract or oil) contain infinite components at different contents and the inhibition of corrosion takes place by intermolecular synergistic effect of the various components of inhibitor<sup>47-49</sup>. The

known composition of essential oil facilitates the possibility of action of the various molecules below as the major components having OH group or ketone functions known as active centres of adsorption as shown below.



**Table 6: Electrochemical parameters of carbon steel at various concentrations of Melissa Officinalis oil and extract at 308 K**

Medium	Conc.	$-E_{\text{corr}}$ (mV vs. SCE)	$-b_c$ (mV.dec <sup>-1</sup> )	$b_a$ (mV.dec <sup>-1</sup> )	$I_{\text{corr}}$ ( $\mu\text{A.cm}^{-2}$ )	Tafel (%)
Blank	1.0 M	450	144	67	361.8	—
	0.5 mL/L	490	143	65	135.7	62.5
EO	1.0 mL/L	490	147	72	80.3	77.8
	2.0 mL/L	490	176	71	50.9	85.9
E	2.0 mL/L	470	195	61	119.8	66.9
	4.0 mL/L	470	152	55	76.1	79.0
	8.0 mL/L	480	136	51	45.5	87.4

**Table 7: Corrosion parameters obtained by impedance measurements for carbon steel in 1.0 M HCl at various concentrations of Melissa Officinalis oil and extract**

Medium	Conc.	$R_{\text{ct}}$ ( $\Omega.\text{cm}^2$ )	$f_{\text{max}}$ (Hz)	$C_{\text{dl}}$ ( $\mu\text{F.cm}^{-2}$ )	$h_z$ (%)
Blank	1.0 M	29.0	100	54.9	—
	0.5 mL/L	97.3	40	40.9	70.1
EO	1.0 mL/L	169.8	40	23.4	82.9
	2.0 mL/L	482.9	18	19.4	93.8
E	2.0 mL/L	101.8	30	52.1	71.5
	4.0 mL/L	138.4	25	46.0	79.0
	8.0 mL/L	173.2	20	46.0	83.2

## CONCLUSIONS

Oil and extract of Melissa Officinalis can act as a natural source and eco-friendly corrosion

inhibitor for carbon steel in 1.0 M HCl solutions. Inhibition efficiency increases with the increase of the concentration of the essential oil and extract of Melissa Officinalis. Tafel polarization measurements

show that essential oil and extract of *Melissa officinalis* act essentially as a mixed type inhibitors. The increase in the charge transfer resistance and decrease in the double layer capacitance values, with the increase in the inhibitor concentration, showed that essential oil and extract formed protective

layers on the carbon steel surface, covering areas where HCl solution degrades and corrodes rapidly. The inhibition efficiencies obtained from EIS, Tafel polarization, and weight loss measurements are in reasonable agreement with each other.

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