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Salvia officinalis essential oil and the extract as green corrosion inhibitor of mild steel in hydrochloric acid

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ABSTRACT

Accurate identification of the Essential oil of aerial parts of Salvia Officinalis was obtained by hydrodistillation, was undertaken using GC and GC/MS (gas chromatography- mass spectrometry), followed by principal component analysis (PCA). The oil was predominated by α-Thujone (22.2%). The extract and Essential oil of S. officinalis leaves has been evaluated as a corrosion inhibitor for steel in 1 M HCl solution by means of weight loss measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS). Tafel polarization study revealed that extract of S. officinalis acts as a mixed type inhibitor. Inhibition was found to increase with increasing concentration of the essential oil and extract of S. Officinalis. Values of inhibition efficiency calculated from weight loss, Tafel polarization curves, and EIS are in good agreement. The effect of temperature on the corrosion behaviour of mild steel in 1M HCl with addition of essential oil and extract was also studied and thermodynamic parameters were determined and discussed

Keywords: corrosion inhibition, *Salvia Officinalis,* oil, extract, electrochemical, mild steel, hydrodistillation.

INTRODUCTION

Ever since its first production roughly 4,000 years ago, iron has played a central role in human society due to its excellent mechanical properties and the abundance of its ores. Today, iron is used in much larger quantities than any other metallic material and is indispensable in infrastructure, transportation, and manufacturing. The steel is widely used in many applications such as desalination plants, construction materials, pharmaceutical industry, and thermal power plant, due to their stability, good corrosion resistance, high strength, workability and weld ability [1-10]. Acid solutions are widely used in industry: some of the important fields of application are acid pickling of steel, chemical cleaning and processing, ore production and oil well acidizing. As ordinary acids, HCl and H_2SO_4 are usually used as industrial acids, cleaning and pickling acids. A major drawback is the susceptibility of iron to corrosion. Corrosion of iron and other metals causes enormous economic damage. Millions of dollars are lost each year because of corrosion. Corrosion is the deterioration of essential properties of a material due to reactions with its surroundings. Much of this loss is due to the corrosion of iron and steel although many other metals may corrode as well. Corrosion damage can cause leakage of fluids or gases. Even more dangerous is a loss of strength of the structure induced by corrosion and subsequent failure [9, 11-16].

There are several thousand steel grades published, registered, or standardized worldwide, all of which have different chemical compositions, and special numbering systems have been developed in several countries to classify the huge number of alloys. In addition, all the different possible heat treatments, microstructures, cold forming conditions, shapes, and surface finishes mean that there are an enormous number of options available to the steel user. Fortunately, steels can be classified reasonably well into a few major groups according to their chemical compositions, applications, shapes, and surface conditions. Due to the general aggression of acid solutions, inhibitors are commonly used to retard the corrosive attack on metallic materials. The application of acid corrosion inhibitors in the industry is widely used to prevent or minimize material loss during contact with acid. Corrosion problems have received a considerable amount of attention because of their attack on materials. During past decades, some commercial inhibitors have been synthesized and used successfully to inhibit corrosion of steel in acidic media. However, the major problem associated with most of these inhibitors is that they are not eco-friendly but toxic and expensive. Therefore, the study of new non-toxic corrosion inhibitors is essential to overcome this problem [3-5, 17-26].

It has been observed that the adsorption depends mainly on certain physico-chemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and Π orbital character of donating electrons and also on the electronic structure of the inhibitor. It has been found that certain organic substances containing polar functions with nitrogen, sulphur and/or oxygen atoms in the conjugated system have been reported to exhibit good inhibiting properties of steel in acidic and alkaline environments. The results of parallel studies suggest that the inhibitory behaviour of the compounds subsists in some chemical species or molecules in the inhibiting substances forming a protective layer between the metal surface and the inhibitors. The adsorbate layer formed isolates the metal surface from the aggressive solution thereby reducing the corrosion rate of the metal surface. It has been recognized that the use of organic inhibitors, particularly the naturally occurring organic inhibitors of plant origin, are viable and highly beneficial since they are essentially non-toxic, environmentally benign, readily available, renewable and inexpensive. The research in the field of eco-friendly corrosion inhibitors has been addressed toward the goal of using cheap, effective compounds at low or “zero” environmental impact. Plant extracts are low-cost and biodegradable, and so the study of plant extracts as corrosion inhibitors is an important scientific research field due to both economic and environmental benefits. Up to now, many plant extracts have been used as effective corrosion inhibitors of iron or steel in acidic media [3, 19, 22, 27-31].

Recently, several studies have been carried out on the inhibition of corrosion of metals by plant extract especially essential oils. In this context, our laboratory adopted a strategy of evaluation of this molecules against corrosion of mild steel in acid media, thus, we previously reported that essential oils of Salvia aucheri var. mesatlantica [32], Mentha spicata [33], Warionia saharea [34], Lavandula multifida [35], Pulicaria mauritanica [36], Mentha pulegium [37], Eucalyptus globulus [38], Artemisia herba-alba [39], Cedrus atlantica [40] and Foeniculum vulgaris [41] have been found to be very efficient corrosion inhibitors for mild steel in acid media. In this paper, our choice is focused to essential oil of Asteriscus graveolens (Forssk.) Less. Salvia *officinalis,* use as corrosion inhibitors have been widely reported by several authors, is a shrub of the Lamiaceae family. It is native to the Mediterranean regions. It is most often used in the form of infusion. It is then mainly used against stomach ache and digestion disorders. Recently, several studies have been carried out on the inhibition of corrosion of metals by Salvia *officinalis* [42, 43]. After extraction of essential oil of the aerial part of Salvia *Officinalis* by hydrodistillation using a Clevenger type apparatus and identification of major components for essential oil studied of Salvia *officinalis* essential oil by spectral analysis of gas chromatography and gas chromatography coupled to mass spectrometry (GC-MS), we aim of this study was to study the inhibitive action of essential oils and extracts (Salvia *Officinalis*), on corrosion behaviour of mild steel in 1M HCl by gravimetric method and electrochemical techniques such as potentiodynamic polarisation, linear polarisation and electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL SECTION

2.1. Inhibitors

2.1.1. Plant material

The Lamiaceae family is native to the Mediterranean regions. It is most often used in the form of infusion. It is then mainly used against stomach ache and digestion disorders. It also helps to fight against excess sweat. It is thus often given to postmenopausal women to reduce night sweats. Finally, it would also be effective in relieving inflammation of the upper respiratory tract (nose, mouth and throat) [44-46]. Salvia *officinalis* is not recommended for children, pregnant women, nursing mothers and people with epilepsy. The aerial part of Salvia *Officinalis* was harvested in Mars 2011 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 is stored in the laboratory at room temperature (298 K) and in the shade before the extraction.

2.1.2. Hydrodistillation apparatus and procedure

Often the hydrodistillation was performed by use of Deryng apparatus or Clevenger type apparatus. In this extraction of essential oil of the aerial part of Salvia *Officinalis* was conducted by hydrodistillation using a Clevenger type apparatus fig.1. The essential oil yields were measured. Subsequently, received essential oils were dried over anhydrous sodium sulfate and stored at 277K in the darkoiuy before analysis, until gas chromatographic determination of its composition.

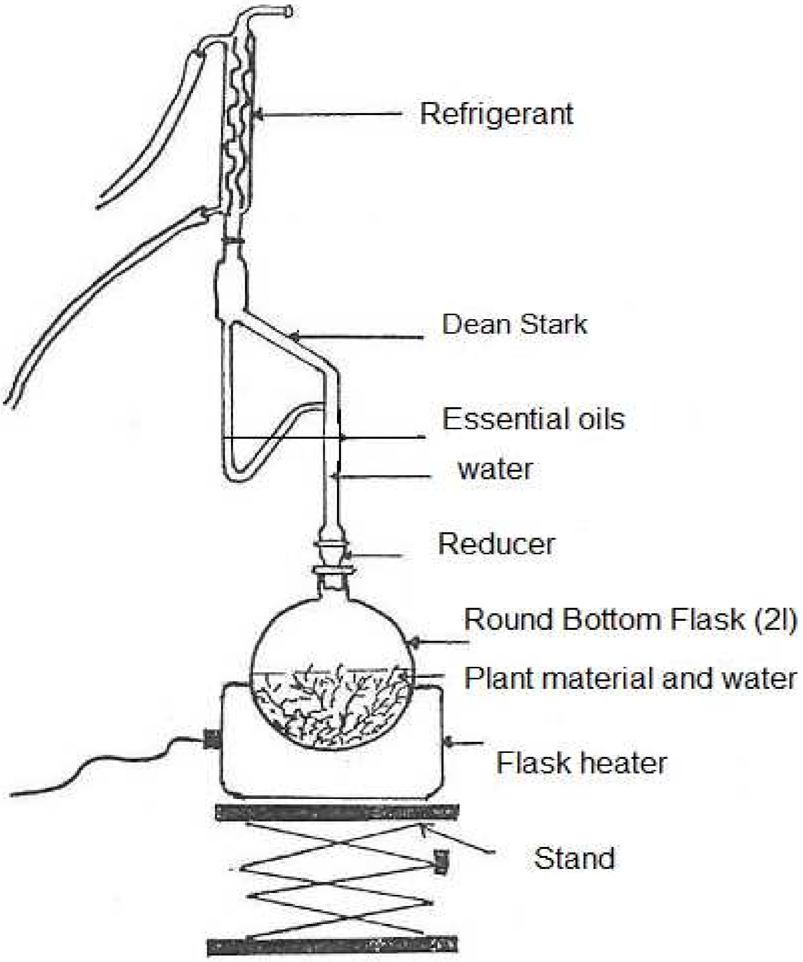

Fig.1. Hydrodistillation by Clevenger apparatus

2.1.3. Characterization and chemical composition of essential oils

Gas chromatography–mass spectrometry (GC-MS) combines the features of gas-liquid chromatography (GC) and mass spectrometry (MS). This makes it possible to identify different substances within a test sample. GC-MS has many uses include drug detection, fire investigation, environmental analysis and explosives investigation. It can also be used to identify unknown samples. GC-MS can also be used in airport security to detect substances in luggage or on human beings. Additionally, GC-MS can identify trace elements in deteriorated materials, even after the sample fell apart so much that other tests cannot work. GC-MS is the best way for forensic experts to identify substances because it is a specific test. A specific test positively identifies the actual presence of a particular substance in a given sample.

The chemical components of Salvia *officinalis* essential oil was determinate by spectral analysis of gas chromatography and gas chromatography coupled to mass spectrometry (GC-MS), being identified six major components for essential oil studied.

GC analyses were performed using a Perkin-Elmer Autosystem GC apparatus (Walhton, MA, USA) equipped with a single injector and two flame ionization detectors (FID). The apparatus was used for simultaneous sampling to two fused-silica capillary columns (60 m · 0.22 mm, film thickness 0.25 lm) with different stationary phases: Rtx-1 (polydimethylsiloxane) and Rtx-Wax (polyethylene glycol). Temperature program: 333–503 K at 275 K/min and then held isothermal 503 K (30 min). Carrier gas: 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. Injected volume: 0.1 lL.

For gas chromatography–mass spectrometry, the oils obtained were investigated using a Perkin-Elmer TurboMass Quadrupole Detector, directly coupled to a Perkin-Elmer Autosystem XL equipped with two fused-silica capillary columns (60 m · 0.22 mm, film thickness 0.25 lm), Rtx-1 (polydimethylsiloxane) and Rtx-Wax (polyethylene glycol). Other GC conditions were the same as described above. Ion source temperature: 423 K; energy ionization: 70 eV; electronionization mass spectra were acquired with a mass range of 35–350 Da. Oil injected volume: 0.1 lL

Identification of the components was based (i) 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 [37] and (ii) on computer matching with commercial mass spectral libraries [37,38] and comparison of spectra with those of 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.

2.2. Solutions and mild steel samples preparation

The 1M solution of HCl was prepared by dilution of quality analysis Merck HCl 37% with distilled water. The test solutions were freshly prepared before each experiment by adding essential oil and extract of Salvia *officinalis* directly to the corrosive solution. Experiments were conducted on several occasions to ensure reproducibility. Concentrations of essential oils were 0.5,1, 2, 4, 8 ml / L, and the extract 8, 10, 12, 14, 16 ml / L.

All studies were carried out using Mild Steel (MS) samples of composition, the steel samples (0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron) were polished with emery paper up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and dried at room temperature. MS samples of size 1.0 x 1.0x 1.0 cm and MS powder were used for weight loss studies. For electrochemical studies, specimens with an exposed area of 1 cm^2 were used. These specimens were degreased ultrasonically with 2-propanol and polished mechanically with different grades of emery paper to obtain very smooth surface.

Contrast to redox reactions of non-metals, it is not necessarily the case that iron oxidation and reduction of the oxidizing agent must occur at the same locality. Spatial separation of oxidative (anodic) and reductive (cathodic) reactions is possible as the metallic matrix allows the free flow of electrons from anodic to cathodic sites. Central to iron corrosion is the high tendency of the metal to give off electrons according to the following anodic reaction [47, 48]:

$$Fe \Leftrightarrow Fe^{2+} + 2e^{-} \qquad E° = -0.47\ V \qquad (1)$$

Where E^o is the revised standard potential (12, 13). Hydrated ferrous ions move into solution only as long as electrons, which cannot enter the aqueous phase, are removed from the surface by a suitable chemical reactant. The most common reactant in iron corrosion is molecular oxygen ($E°$=+0.81 V), and corrosion of iron in toxic environments ultimately leads to the formation of various iron (hydro) oxides (“rust”). In the absence of oxygen, on the other hand, the most common electron acceptors for iron oxidation are protons from dissociated water. Here, the cathodic reaction consisting of proton reduction to molecular hydrogen occurs as follows [49, 50] :

$$2e^{-} + 2H^{+} \Leftrightarrow H_2 \qquad E° = -0.41\ V \qquad (2)$$

Owing to the condition of electroneutrality, the anodic and cathodic half-reactions are stoichiometrically coupled, which in the case of equations 1 and 2 yields the following net reaction:

$$Fe + 2H^{+} \Leftrightarrow Fe^{2+} + H_2 \qquad \Delta G° = -10.6\ kJ/mol \qquad (3)$$

2.3. Weight loss measurements

The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. Although these tests are simple, there is no simple way to extrapolate the results to predict the lifetime of the system under investigation. Moreover, some corrosion processes occur with no significant mass change (e.g. pitting corrosion) making them difficult to detect by gravimetric method [3-10]. The simplest way of measuring the corrosion rate of a metal is to expose the sample to the test medium (e.g. sea water) and measure the loss of weight of the material as a function of time. The gravimetric test is based on the immersion of the steel plates in iron, in 100 ml of a 1M HCl solution containing the inhibitor (essential oil and extract of Salvia *officinalis*) at different concentrations, after be degreased, polished and weighed. Immersion is subjected to a temperature of 308 ° K to 6 hours. Temperature corrosive environment is a factor that can affect the efficacy of inhibiting it. Given the importance of this factor, we performed tests of mass loss of steel in 1 M HCl with and without addition of the inhibitor (essential oil and extracts of Salvia *officinalis*) at different temperatures between 303 and 333 ° K.

2.4. Electrochemical measurements

As mentioned in the previous application notes, most corrosion phenomena are of electrochemical nature and consist of reactions on the surface of the corroding metal. Therefore electrochemical tests methods can be used to characterise corrosion mechanisms and predict corrosion rates.

2.4.1. Potentiodynamic polarization

This potentiostat was connected to a conventional three-electrode cell assembly. 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 working electrode is in the form of a rectangular disk from carbon steel of the surface 0.32 cm2. 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 -100mV/SCE. All experiments were repeated three times at the desired temperature of ±1 _C. Corrosion current densities were obtained from the polarization curves by linear extrapolation of the Tafel curves. Prior to the electrochemical measurement, a stabilization period of 30 minutes was allowed, which was proved to be sufficient to attain a stable value of corrosion potential (Ecorr). Tafel polarization curves were plotted at a polarization scan rate of 0.5 mV/s. Anodic and cathodic curve slopes were extrapolated to corrosion potential, for the determination of the corrosion current densities (Icorr). The Tafel equations predict a straight line for the variation of the logarithm of current density with potential. Therefore, currents are often shown in semi logarithmic plots known as Tafel plots. This type of analysis is referred to as Tafel Slope Analysis. The Tafel slope analysis tool provides a quick estimation of the corrosion rate and the polarization resistance. The corrosion rate is calculated from the estimated corrosion current, I_{corr}, obtained from the intercept of the two linear segment of the Tafel slope.

2.4.2. Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy (EIS) has many advantages in comparison with other electrochemical techniques. During EIS experiments, a small amplitude ac signal is applied to the system being studied. Therefore, it is a non-destructive method for the evaluation of a wide range of materials, including coatings, anodized films and corrosion inhibitors. It can also provide detailed information of the systems under examination; parameters such as corrosion rate, electrochemical mechanisms and reaction kinetics, detection of localized corrosion, can all be determined from these data. Electrochemical impedance spectroscopy (EIS) was carried out with the same equipment used for the polarization measurements, leaving the frequency response analyzer out of consideration. Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mV/s. 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 was 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. All electrochemical studies were carried out with immersion time of 1 hour, with different inhibitory concentrations of essential oil and extract of Salvia *Officinalis*, at 308 K.

RESULTS AND DISCUSSION

3.1. Essential oil composition

Qualitative and quantitative analyses essential oils were done using GC/MS analyses. The composition of essential oils of Salvia offinalis were shown in the Table. 1.

Table 1: chemical constituents of Salvia *Officinalis* oil (%)

Chemical constituents	IL	Ir /apol	Ir /pol	HE% apol
Cis-Salvene	849	853	948	0,3
α-Thujene	932	931	1025	0,7
α-Pinene	936	939	1007	1,7
Camphene	950	952	1046	1,4
Sabinene	973	975	1123	1,3
β-Pinene	978	981	1088	8,2
Myrcene	987	992	1132	2,9
α-Terpinene	1013	1017	1180	0,4
p-Cymene	1015	1021	1236	0,6
Limonene	1025	1030	1201	0,3
1,8-Cineole	1024	1030	1207	18,4
Z–β-Ocimene	1029	1034	1221	0,5
γ-Terpinene	1051	1056	1231	0,8
Terpinolene	1082	1085	1253	0,2
α-Thujone	1089	1098	1409	22,2
β-Thujone	1103	1107	1425	8,4
Camphor	1123	1128	1490	9,4
Trans-Pinocarveol	1126	1128	1620	
Trans Pinocamphone	1139	1143	1490	1,1
Cis Thujol	1149	1155	1532	1,4
Terpinen-4-ol	1164	1167	1575	0,8
Myrtenal	1172	1174	1590	0,2
α-Terpineol	1176	1178	1671	0,3
Myrtenol	1178	1184	1754	0,4
Trans-Caryophyllene	1421	1416	1561	2,6
α-Humulene	1455	1453	1628	3,7
γ-Muurolene	1474	1474	1649	0,1
Caryophyllene oxyde	1578	1567	1926	0,4
Globulol	1589	1581	2036	5,9
Epoxyde d'Humulene 2	1602	1590	1980	0,4
E-Biformene	2017	2033	2601	1,3
TOTAL				96,3

3.2. Electrochemical impedance measurements

Among the different electrochemical techniques that can be used to study corrosion inhibitors, EIS appears as powerful tool for the information that can provide, as for example, double layer capacitance, C_{dl}, and polarization resistance, R_p, values. Changes in these parameters as a function of time or with respect to other variables, allow obtaining important information about the kinetics of the corrosion process being involved [6, 28, 31, 51]. In some cases impedance data obtained at the corrosion potential, E_{corr} have the shape of depressed semicircles with the centre of the semicircle below the real axis. The corrosion behaviour of mild steel in 1M HCl solution, in the absence and presence of essential oil and extract of Salvia *Officinalis*, was investigated by the EIS at 308 K after 1 hour of immersion. The charge-transfer resistance values were obtained from the diameter of the semicircles of the Nyquist diagrams. The inhibition efficiency (E %) of the inhibitor has been found out from the charge transfer resistance values using the following equation:

$$E(\%) = \frac{R^o_{corr} - R_{corr}}{R^o_{corr}} x100 \qquad (4)$$

where, $R°_{corr}$ and R_{corr} are the charge transfer resistance in presence and in absence of inhibitors, respectively. All electrochemical measurements were done in unstirred and non de aerated solutions. The electrochemical impedance plots for mild steel in 1M HCl solution in the absence and presence of various concentrations of aqueous essential oil and extract from Salvia *Officinalis* are shown in Figure 2 and 3. Table 2 and 3 summarizes impedance data from the EIS experiments carried out both in the absence and presence of increasing essential oil and extract concentrations.

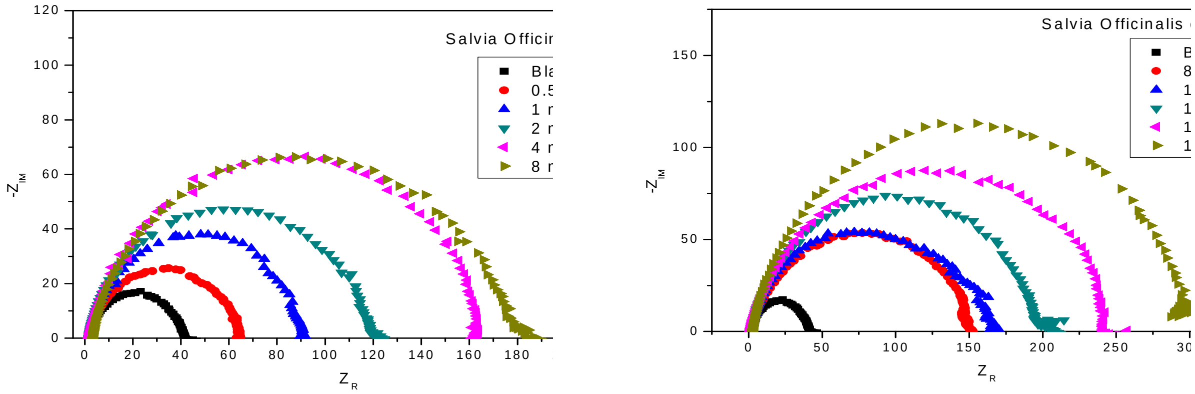

Figure 2 and 3. Nyquist plots in absence and presence of different concentrations of Salvia *Officinalis* oil and extract in 1M HCl respectively

Table 2. Corrosion parameters obtained by impedance measurements for mild steel in 1M HCl at various concentrations of Salvia *officinalis* oil

Inhibitor concentration	R_{ct} (Ohm.cm^2)	f_{max} (Hz)	C_{dl} (mF/cm^2)	E (%)
1M HCl	40.42	2.466	1.59	-
0.5 ml/L	62.10	2.626	0.97	34.91
1 ml/L	88.43	2.409	0.74	54.29
2 ml/L	122.8	2.511	0.51	67.08
4ml/L	160.9	2.197	0.45	74.87
8ml/L	182.3	2.602	0.33	77.82

Table 3. Corrosion parameters obtained by impedance measurements for mild steel in 1M HCl at various concentrations of Salvia *Officinalis* extract

Inhibitor concentration	R_{ct} (Ohm.cm^2)	f_{max} (Hz)	C_{dl} (mF/cm^2)	E (%)
1M HCl	40.42	2.466	1.59	-
8 ml/L	139.6	2.748	0.41	71.04
10 ml/L	164	2.774	0.34	75.35
12 ml/L	210.3	2.473	0.3	80.77
14ml/L	247.1	2.697	0.23	81.6
16ml/L	299.9	2.473	0.21	86.52

The electrochemical impedance diagrams indicate two significant effects in absence and presence of the essential oil and extract of Salvia *Officinalis* : the charge transfer resistance significantly increases, and the f_{max} varies, in the presence of the inhibitors studied, 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. Furthermore, C_{dl} decreases with increase of the concentration of inhibitors. This phenomenon is generally related to the adsorption of organic molecules on the metal surface and then leads to a decrease in the dielectric constant and/or an increase in the thickness of the electrical double layer [8, 52-54]:

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

Where δ is the thickness of the protective layer, S is the electrode area, ε_O the vacuum permittivity and ε is dielectric constant of the medium. For other part, a low capacitance may result if water molecules at the electrode interface are largely replaced by organic inhibitor molecules through adsorption. Its Equivalent Circuit (EC), corresponds to a parallel combination of a capacitance and one resistance, Fig. 4, Constant-Phase Elements (CPE) are widely used in data fitting to allow for depressed semicircles. The capacitor in the (EC) is replaced with a (CPE) for better fit quality. The impedance of a CPE is given by

$$\boldsymbol{Z = Z_0\,(j\omega)^{-1}} \qquad (6)$$

where n can take values between 0 and 1, depending of the circuit element represented. The complex impedance Z(jω) of a depressed semicircle could be expressed as:

$$\boldsymbol{Z = R_S + \frac{R_P}{1+(j\omega C_{dl}R_P)^{-n}}} \qquad (7)$$

The n exponent is a unit less parameter that equals to 1 for an ideal capacitor. In this case, real systems, ideal capacitive behaviour is not observed due to surface roughness, or other effects that causes uneven current distributions on the electrode surface [8, 9, 54-56]. In the case when n=1, the term $\boldsymbol{(j\omega C_{dl}R_P)^{-n}}$ reduces to $\boldsymbol{j\omega C_{dl}R_P}$, where C_{dl} is the interfacial double layer capacitance. This can be interpreted as an indication of the degree of inhomogeneity of the metal surface [38], where n take values slightly higher to 0.5 that corresponds to a severe inhomogeneity, to 1, in which case the electrode surface can be taken as smooth. This degree of inhomogeneity has been associated with the fractal dimension of the surface. Taking into account the degree of depression of the semicircle in the Nyquist diagram, it is possible to determine the fractal dimension of the electrode surface by means of the following equation:

$$\boldsymbol{n = \frac{1}{D_S - 1}} \qquad (8)$$

where D_S is the fractal dimension of the surface, which can take values between 2 for a surface completely smooth, to values less than 3 for a roughness surfaces.

The EIS results of these capacitive loops are simulated by the equivalent circuit exposed in Fig. 3 to purify electric models that could verify or rule out mechanistic models and permit the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system under investigation. The impedance parameters derived from these studies using Z-view software are summarized in Table 3. The values of charge transfer resistance (Rct) that increased with inhibitor concentrations may suggest the formation of a protective film on the electrode/ solution interface [31, 57, 58] .

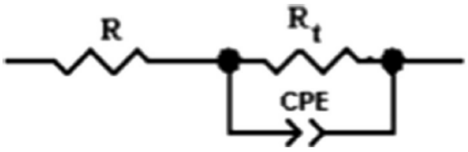

Figure 4: The equivalent circuit of the impedance spectra obtained for of Salvia *Officinalis* extract

The larger inhibitor molecules also reduce the capacitance through the increase in the double layer thickness. 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 [43,44]. 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:

$$C_{dl} = \frac{1}{2\pi f_{\max} R_{ct}} \qquad (9)$$

Where fmax is the maximum frequency at which the imaginary component of the impedance is maximal. From Table 2 and 3, it is clear that the Rct values increased and that the Cdl values decreased with increasing inhibitor concentration.

The elevation values of inhibition efficiency by increasing inhibitor concentration can be attributed to the increase in the number of adsorbed organic molecules against carbon steel surface. The smaller inductive loop obtained at lower frequency present in the graphs can be attributed to the relaxation of adsorbed compounds. These results indicate a decrease in the active surface area caused by the adsorption of the inhibitors on the mild steel surface, and it suggests that the corrosion process became hindered. The best result for the inhibition efficiency of the essential oil of Salvia *officinalis* was obtained at a concentration of 8 ml/L, with efficiency equal to 77.82% and 86.52% for its extract at a concentration of 16ml/L.

3.3. *Tafel polarization curves*

The type of experiment was performed. Immediately upon immersion of the samples in the electrolytes, the open circuit potential (OCP) was monitored for one hours. This was followed by potentiodynamic anodic polarisation measurements. Lastly, in order to investigate whether corrosion products formed on the sample surfaces, the anodic polarisation tests were carried out on the same surface and in the same test solution. All tests were done at room temperature using electrolytes that were not de-aerated during testing. Polarization curves for mild steel in presence and absence of different concentrations of essential oil and extract of Salvia *officinalis* in non aerated solutions are shown in Figure 5 and 6. The extrapolation of Tafel straight line allowed the calculation of the corrosion current density (Icorr). The values of Icorr, the corrosion potential (Ecorr), cathodic Tafel slope (βc), and inhibition efficiency (E %) are given in Table 4 and 5 for essential oil and extract of Salvia *Officinalis* respectively. The (E %) was calculated using the following equation [3-7, 51, 59-61]:

$$E(\%) = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} x100 \qquad (10)$$

where I^{o}_{corr} and I_{corr} are uninhibited and inhibited corrosion current densities, respectively. Under the experimental conditions performed, the cathodic branch represents the hydrogen evolution reaction, while the anodic branch represents the iron dissolution reaction.

Inspection of these results reveal that in presence of inhibitors, the value of corrosion density (Icorr) was decreased. This behaviour reflects its ability to inhibit the corrosion of mild steel in 1M HCl solution. Both the anodic and cathodic current densities were decreased in figure 5 and 6, indicating that essential oil and extract of Salvia *officinalis* suppressed both the anodic and cathodic reactions through adsorption on the mild steel surface. This suggests that the essential oil and extract act as mixed type corrosion inhibitor for mild steel in 1M HCl solution.

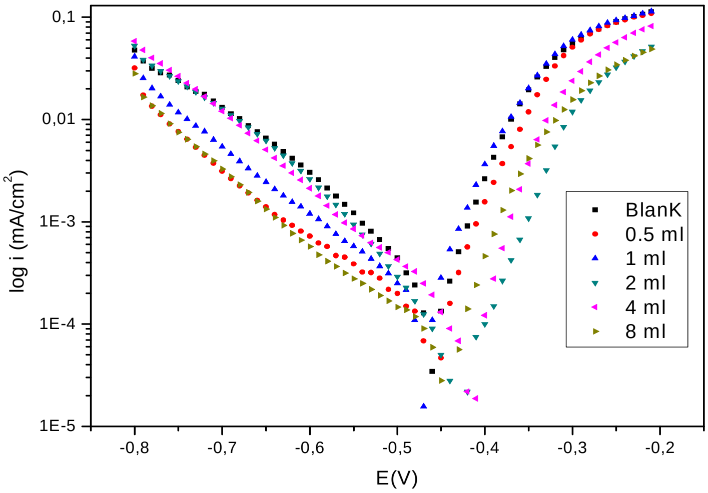

Figure 5. Tafel polarization curves in 1M HCl with and witout Salvia officinlais oil at different concentrations

Table 4. Electrochemical parameters of mild steel at various concentrations of Salvia *Officinalis* oil in 1M HCl

Inhibitor concentration	$-E_{Corr}$ (mV)	β_C (mV/dec)	I_{Corr} (mA/cm^2)	E (%)
1M HCl	459	-147.3	0.3333	-
0.5 ml/L	458.5	-228.1	0.1864	44.07
1 ml/L	471.2	-151.6	0.1596	52.11
2 ml/L	430.6	-114.8	0.0875	73.24
4 ml/L	414.5	-116.4	0.0542	83.73
8 ml/L	441.3	-150.6	0.0498	**85.05**

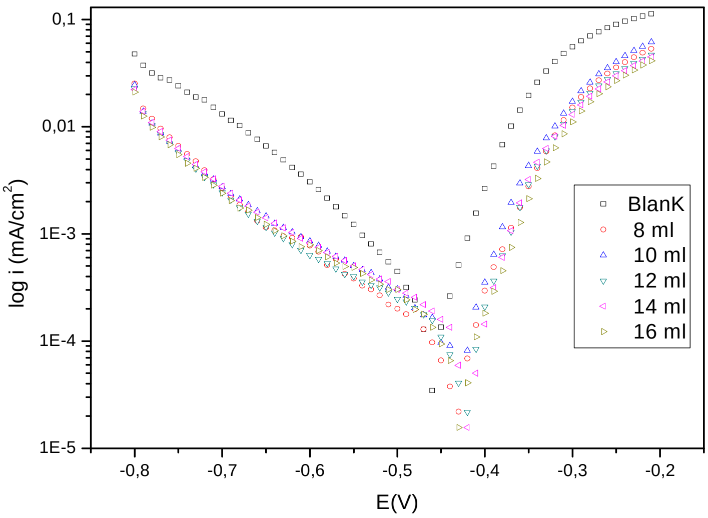

Figure 6. Tafel polarization curves in 1M HCl with and witout Salvia *officinalis* extract at different concentrations

Generally, the modes of the inhibition effect of inhibitors are classified into three categories [32,33]: geometric blocking effect of adsorbed inhibitive species, active sites blocking effect by adsorbed inhibitive species, and electro catalytic effect of the inhibitor or its reaction products. It has been discussed in the case of the first mode that inhibition effect comes from the reduction of the reaction area on the surface of the corroding metal, whereas for the other two modes the inhibition effects are due to the changes in the average activation energy barriers of the anodic and cathodic reactions of the corrosion process. The cathodic Tafel slope (βc) show slight changes with the addition of essential oil and extract, 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 essential oils concentration (table 4 and 5). The parallel cathodic Tafel plots obtained in Figure 3 and 4 indicate that the hydrogen evolution is activation controlled and the reduction mechanism is not affected by the presence of inhibitor [6, 24, 25].

Table 5. Electrochemical parameters of mild steel at various concentrations of Salvia *Officinalis* extract in 1M HCl

Inhibitor concentration	$-E_{Corr}$ (mV)	β_C (mV/dec)	I_{Corr} (mA/cm^2)	E (%)
1M HCl	459	-147.3	0.3333	-
8 ml/L	432.8	-163.4	0.0730	78.09
10 ml/L	429.7	-154	0.0665	80.04
12 ml/L	425.2	-178	0.0634	80.97
14 ml/L	418.2	-164.8	0.0613	82.38
16 ml/L	427.7	-133.7	0.0396	**88.11**

3.4. Weight loss measurements and effect of temperature

For most chemical reactions, the reaction rate increases with increasing temperature. Temperature affects the corrosion rate of metals in electrolytes primary through its effect on factors which control the diffusion rate of oxygen. The corrosion of iron and steel is an example of this because temperature affects the corrosion rate by virtue of its effect on the oxygen solubility and oxygen diffusion coefficient. As temperature increases the diffusion coefficient of oxygen also increases which tends to increase the corrosion rate. However as temperature is increased oxygen solubility in aqueous solutions decreases until at the boiling point all oxygen is removed; this factor tends to decrease the corrosion rate. The net affect of mild steel, is that the corrosion rate approximately doubles for a temperature rise of 30°C up to a maximum temperature at about 80°C, the rate then falls off in an open system because the decrease in oxygen solubility becomes the most important factor. In a closed system, where oxygen cannot escape the corrosion rate continues to increase indefinitely with temperature until all the oxygen is consumed [20, 25, 62].

The corrosion rates of the mild steel in 1 M HCl solutions in the absence and presence of extract of Salvia *Officinalis* were determined at at four temperatures values: 303,313, 323 and 333 K. Fig.7 illustrates the variation of the corrosion rates of the mild steel in 1 M HCl with inhibitor concentration for an exposure time of 1 hour at optimum concentration (8 ml/L for essential oil, 16 ml/L for extract) determined in electrochemical measurements. Figure 7, shows clearly that the leaf extract retards the corrosion rate of the mild steel in the test solutions. The various corrosion parameters obtained are listed in Table 6 for essential oil and extract of Salvia *Officinalis* studied. From the weight loss results, the corrosion rate (C_R), the inhibition efficiency (E%) of inhibitors and degree of surface coverage (Θ) were calculated using equations 5, 6 and 7 [46]:

$$C_R = \left(\frac{\Delta W}{Sxt}\right) \qquad (11)$$

$$E(\%) = \left(1 - \frac{W_{corr}}{W^{o}_{corr}}\right) x100 \qquad (12)$$

$$\theta = \left(1 - \frac{W_{corr}}{W^{o}_{corr}}\right) \qquad (13)$$

Where W_{corr} and W^{o}_{corr} are the weight losses for mild steel in the presence and absence of the inhibitor in HCl solution and Θ is the degree of surface coverage of the inhibitors. ΔW is the difference of weight loss for mild steel with and without inhibitors, S is the exposure area of the metallic specimens and t is the immersion time of the metal in corrosive solution.

Table 6. Corrosion parameters for mild steel in 1 M HCl in absence and presence of optimum concentration of the inhibitors studied at different temperatures

Temperature (K)	Inhibitor	C_R (mg/cm^2.h)	Θ	E (%)
303	1M HCl	0.32	-	-
	Essential oil	0.09	0.7	70
	Extract	0.06	0.81	81
313	1M HCl	0.855	-	-
	Essential oil	0.27	0.67	67
	Extract	0.23	0.73	73
323	1M HCl	1.378	-	-
	Essential oil	0.54	O.61	61
	Extract	0.53	0.62	62
333	1M HCl	2.748	-	-
	Essential oil	1.24	0.51	51
	Extract	1.16	0.58	58

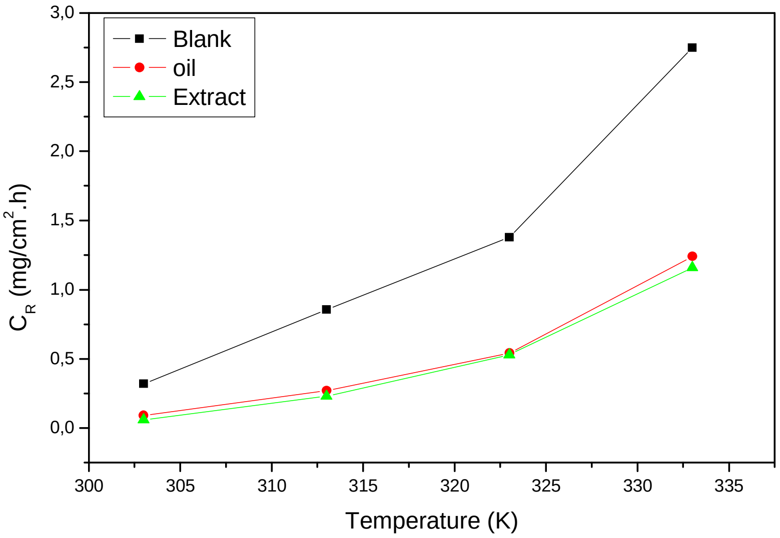

Figure 7. Variation of C_R in 1M HCl on steel surface without and with of optimum concentration of essential oil and extract at different temperatures

The fractional surface coverage (Θ) can be easily determined from the weight loss measurements by the ratio E(%) /100, where E(%) is inhibition efficiency and calculated using equation 6. The data obtained suggest that essential oil and extract get adsorbed on the steel surface at all temperatures studied and corrosion rates increased in absence and presence of inhibitor with increase in temperature in 1M HCl solutions. In acidic media, corrosion of metal is generally accompanied with evolution of H_2 gas; rise in temperature usually accelerates the corrosion reactions which results in higher dissolution rate of the metal.

Inspection of Table 6 showed that corrosion rate increased with increasing temperature both in uninhibited and inhibited solutions while the inhibition efficiency of essential oil and extract decreased with temperature. A decrease in inhibition efficiencies with the increase temperature in presence of essential oil and extract might be due to weakening of physical adsorption. In order to calculate activation parameters for the corrosion process, Arrhenius equation. (8) and transition state equation (9) were used [47]:

$$C_R = \quad A\exp(\frac{-E_a}{RxT}) \tag{14}$$

$$C_R = \quad \frac{RxT}{Nxh}\exp(\frac{-\Delta S_a}{R})\exp(\frac{-\Delta H_a}{RxT}) \tag{15}$$

where C_R is the corrosion rate, R the gas constant, T the absolute temperature, A the pre-exponential factor, h the Plank's constant and N is Avogrado's number, E_a the activation energy for corrosion process , ΔH_a the enthalpy of activation and ΔS_a the entropy of activation. The apparent activation energy (E_a) at optimum concentration of essential oil and extract was determined by linear regression between Ln(C_R) and 1/T (Fig. 8 and 9) and the result is shown in Table 7.

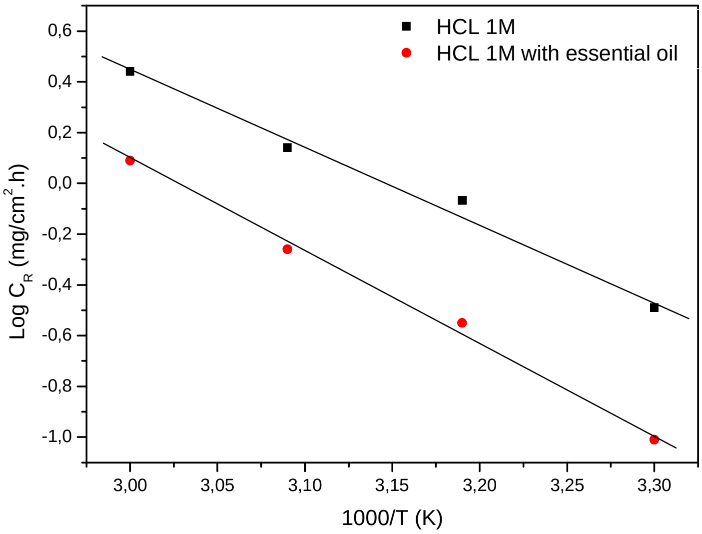

Figure 8. Arrhenius plots of log C_R vs. 1/T for mild steel in 1M HCl in the absence and the presence of essential oil at optimum concentration (8 ml/L)

Table 7: Activation parameters E_a, ΔH_a and ΔS_a for the mild steel dissolution in 1M HCl in the absence and the presence of essential oil and extract at optimum concentration

Inhibitor	**E_a (kJ/mol)**	**ΔH_a (KJ/mol)**	**ΔS_a (J/mol.K)**
1M HCl	24.99	8.73	-26.3
Essential oil	29.9	10	-25.7
Extract	35.16	12.32	-24.6

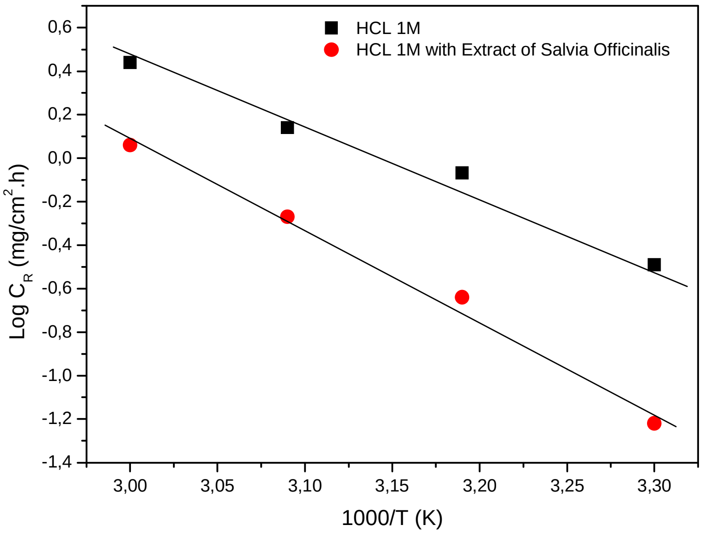

Figure 9: Arrhenius plots of log CR vs. 1/T for mild steel in 1M HCl in the absence and the presence of extract at optimum concentration (16 ml/L)

Inspection of Table 7 showed that the value of E_a determined in 1M HCl containing essential oil and extract of Salvia *Officinalis* are higher (29.9 and 35.16 kJ/mol) than that for uninhibited solution (24.99 kJ/ mol). The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage. The increase in activation energy could be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with increase in temperature. As adsorption decreases more desorption of inhibitor occur because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of steel comes in contact with aggressive environment, resulting increased corrosion rates with increase in temperature [7-9].

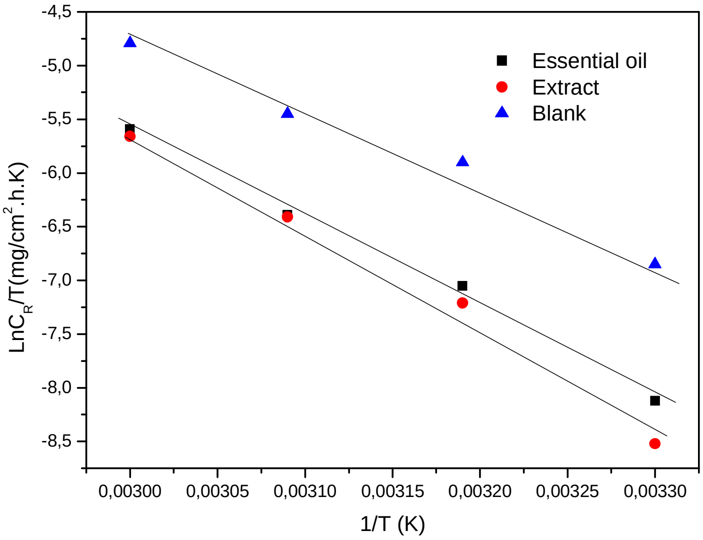

Figure 10. Arrhenius plots of ln C_R/T vs. 1/T for steel in 1M HCl in the absence and the presence of essential oil and extract at optimum concentration (8ml/L for essential oil and 16ml for extract)

Fig.10, showed a plot of Ln (CR/T) versus 1/T. The straight lines are obtained with a slope (ΔHa/R) and an intercept of (Ln R/Nh +ΔSa /R) from which the values of the values of ΔHa and ΔSa are calculated for essential oil and extract of Salvia *Officinalis* analyzed and are given in Table 8. Inspection of these data revealed that the thermodynamic parameter (ΔHa) for dissolution reaction of steel in 1M HCl in the presence of inhibitors are higher (10 and 12.32 kJ/mol for essential oil and extract, respectively) than that of in the absence of inhibitors (8.73 kJ/ mol). The positive sign of ΔHa reflect the endothermic nature of the steel dissolution process suggesting that the dissolution of steel is slow (49) in the presence of inhibitor. Negative value of entropy (ΔSa) 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 reactant to the activated complex.

Corrosion inhibitors function by interfering with either the anodic or cathodic reactions or both. Many of these inhibitors are organic compounds. It is generally assumed that corrosion inhibition performed by adsorption of the additives (ion or neutral polar molecules) to the metal-solution interface. It is known that the potential difference between a metal electrode and the solution is due to a non-uniform distribution of electric charges at the interface. The interaction of ions or neutral molecules at the electrical double layer, changes its properties and structures. The water molecules reabsorbed at the metal surface in contact with the aqueous solution are involved in the successive adsorption processes. The adsorption of an organic substance at the metal solution interface may be written according to the following displacement reaction [63, 64] .

$$Org_{(ads)} + nH_2O \rightarrow org_{(ads)} + nH_2O \quad (16)$$

Where n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. Clearly, the value of n will depend on the cross-section area of the organic molecules with respect to that of the water molecule. Adsorption of organic molecule occurs because the interaction energy between the metal surface and the inhibitor is higher than the interaction energy between the metal surface and the water molecules [5, 65].

The mechanism of action of a corrosion inhibitor depends on the electron density and polarizability of the functional groups present in the molecule. For instance, in the acid essential oil and extract of Salvia *Officinalis* used in this study, some of the constituents may be adsorbed as protonated species and some as (non-protonated) molecular species, with the predominant adsorption mode depending on the prevailing test conditions at any time. It is noteworthy that chloride ions present in the test solutions have the tendency to be specifically adsorbed on metal surfaces, where they facilitate adsorption of protonated inhibitor species by forming intermediate bridges between the metal surfaces and the inhibitor. Such protonated species are often adsorbed at cathodic sites on the metal surface and hence retard the hydrogen evolution reaction, which is probably responsible for the pronounced cathodic inhibiting effect of all inhibitors in the essential oil and extract of Salvia *Officinalis*. In the case of the first mode the inhibition effect comes from the reduction of the reaction area on the surface of the corroding metal, whereas for the other two modes the inhibition effects are due to the changes in the average activation energy barriers of the anodic and cathodic reactions of the corrosion process. Thus, the electrochemical behaviour and the interpretation of the measured electrochemical data will not the same for all the modes. There are many factors affect the inhibition efficiency of the organic compounds in acidic media

CONCLUSION

From the overall experimental results and discussion the following conclusions can be deduced:
1. Tafel polarization measurements show that essential oil and extract act essentially as a mixed type inhibitor.
2. The decrease in the charge transfer resistance and double layer capacitance values, with the increase in the inhibitor concentration, showed that essential oil and extract formed protective layers on the mild steel surface, covering areas where HCl solution degrades and corrodes rapidly.
3. Inhibition efficiency increases with increase in the concentration of the essential oil and extract of Salvia *Officinalis* but decreases with rise in temperature.
4. The corrosion process was inhibited by adsorption of the organic matter on the mild steel surface, obtaining the formation of the film on the metal/acid solution interface, decreasing the degradation of the material.
5. Results obtained through weight loss measurements and electrochemical tests demonstrated that the essential oil and extract of Salvia *Officinalis* act as efficient corrosion inhibitors of the mild steel in 1 M HCl solution..

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