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Chemical Composition and Inhibitory Effect of Essential Oil of *Lavande* (*Lavandula Dentata*) LD on the Corrosion of Mild Steel in Hydrochloric Acid (1M)

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Abstract

Lavande (Lavandula Dentata) LD has been used in a variety of practical applications in medical science, but our objective in the current study was to determine the chemical composition and inhibitory effect of essential oil of LAVANDE (LAVANDULA DENTATA) LD on the corrosion of mild steel in hydrochloric acid (1M). The essential oil of Lavande (Lavandula Dentata) LD has been studied using gas chromatography (GC) and GC-mass spectrometry (GC-MS). 90.5% of the components are detected and the major components were, β-pinene (18.8%), trans-pinocarveol (12.4%), 1,8-cineole (7.8%), α-Pinene (7%), Myrtenol (5.9%), and Myrtenal (4.6%). The inhibitory effect of essential oil of LAVANDE (LAVANDULA DENTATA) LD was estimated on the corrosion of mild steel in 1M in Hydrochloric acid (HCl) using weight loss, Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization curves. The results of the polarization curves show that the corrosion current density decreases 698μA/cm²to 211μA/cm² after addition of the inhibitor (essential oil of LAVANDE), the charge transfer resistance increases 48.87 ohm.cm² to 311.8 ohm.cm² in the electrochemical impedance spectrum after addition of the inhibitor. The inhibition of the compound effect is attributed to the formation of a film on the surface of the steel.

Keywords: Composite, Corrosion inhibition, *Lavandula Dentata* (*LD*), Essential oil, Hydrodistillation, Electrochemical, Mild steel, HCl

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1. Introduction

Considerable efforts are deployed to find suitable compounds to be used as corrosion inhibitors in various corrosive media to stop or delay to the maximum the attack of a metal. Nevertheless, the

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known hazard effects of the most synthetic inhibitors and the need to develop environmentally friendly processes, researches are focused on the use of natural products. Near their environmental and acceptable ecological properties, naturally occurring antioxidants are cheap and readily available and renewable sources of materials [1–10]. These organic compounds are either synthesised or either extracted from aromatic herbs, spices and medicinal plants. These advantages have incited us to draw a large part of program of our laboratory to examine Extracts& Oils of natural substances as corrosion inhibitors. Ginger [11], Henna [12],Thym [13], Jojoba oil [14], Rosemary oil [15,16], Eugenol and acethyleugenol [17], Bgugaine [18,19], Artemisia oil [20,21],purified compounds [22,23], Pennyroyal oil [24], Eucalyptus oil [25], Lavender oil [26], Menthol derivatives [27], Pulegone [28], Limonene [29], Argan oil as corrosion inhibitors [30], essential oil and extract of Salvia Officinalis [31], Pelargonium extract andoil [32], Athamanta sicula oil [33], essential oil of Ammodaucusleucotrichu [34], *Nigella sativa* L extract [35], have been found to be very efficient corrosion inhibitors for iron and steel in acidic media. We cited that all these products are efficient inhibitors for the fight against corrosion of steel in acidic media, we add that jojoba and bgugaine offer an efficiency of 100% for the protection of steel in acidic media [14,19].

In this paper, electrochemical polarisation, EIS and gravimetric techniques are applied to study the ability of essential oil of *LAVANDULA DENTATA* LD to inhibit the corrosion of steel in 1M HCl. The effect of temperature is also studied.

2. Experimental

2.1. Inhibitors

2.1.1. Plant material

The Lamiaceae family is native to the Mediterranean regions. Lavandula dentata was harvested from "bosakour"(national park) located in the area of Al-Hoceima (MOROCCO). The harvest was in May 2010. The flowers, freshly harvested, are dried in the shade in a dry, ventilated place for about 10 days. Become dry, they are collected into clean bags for later use in the extraction of essential oil.

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 Lavandula Dentata 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 277 K in the darkness before analysis, until gas chromatographic determination of its composition.

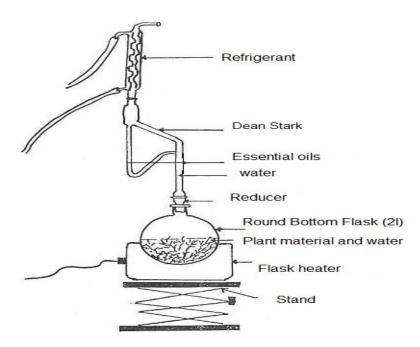


Fig.1. Hydrodistillation by Clevenger apparatus

2.1.3. Essential oil isolation of Lavandula dentata.

The dried vegetal material (100 g) were water-distillated (3h) using a Clevenger-type apparatus according to the method recommended by the European Pharmacopoeia [36]. The yield of fruits essential oil was 1.5%.

2.1.4. GC analysis

GC analysis were carried out using a Perkin-Elmer Autosystem XL GC apparatus equipped with dual flame ionization detection (FID) system and fused-silica capillary columns (60 m x 0.22 mmI.D., film thickness 0.25 μ m), Rtx-1 (polydimethylsiloxane) and Rtx-wax (polyethyleneglycol). The oven temperature was programmed from 60°C to 230°C at 2°C/min and then held isothermally at 230°C for 35 min. Injector and detector temperature was maintained at 280°C. Samples were injected in the split mode (1/50), using helium as carrier gas (1 ml/min); the injection volume was 0.2 μ L of pure oil. Component relative concentrations were calculated based on GC peak areas without using correction factors.

2.1.5. GC-MS analysis

Samples were also analysed using a Perkin-Elmer Turbo mass detector (quadrupole), coupled to a Perkin-Elmer Autosystem XL, equipped with fused-silica capillary columns Rtx-1 and Rtx-Wax. Carrier gas: helium (1 mL/min), ion source temperature: 150°C, oven temperature programmed from

60°C to 230°C at 2°C/min and then held isothermally at 230°C (35 min), injector temperature: 280°C, energy ionization: 70 eV, electron ionization mass spectra were acquired over the mass range 35-350 Da, split: 1/80, injection volume: 0.2 μL of pure oil.

2.1.6. Identification of components

The methodology carried out for identification of individual components was based on: i) comparison of calculated retention indices (RI), on polar and apolar columns, with those of authentic compounds or literature data [37]; ii) computer matching with commercial mass spectral libraries [38] and comparison of mass spectra with those of our own library of authentic compounds or literature data [37,39].

2.2. Materials

Tests were performed on a cold rolled steel (CRS) of the following composition (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 cm² were used. These specimens were degreased ultrasonically with 2-propanol and polished mechanically with different grades of emery paper to obtain very smooth surface.

2.3. Preparation of solutions

The test solutions were prepared by the dilution of analytical grade 37% HCl with distilled water up to the optimum inhibitor concentration. For pH studies, the test solutions were prepared by the dilution of distilled water up to the optimum concentration where it can reach by adjusting the pH using HCl and NaOH. Inhibitor was dissolved in acid solution at required concentrations in (mL/L) 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 *Lavandula dentate* oil directly to the corrosive solution. Experiments were conducted on several occasions to ensure reproducibility. Concentrations of *Lavandula dentata* oilwere 1.25, 2.5 and 5 mL/L.

2.4. 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 [40, 41]. 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 (*Lavandula dentate* oil) 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 (*Lavandula dentata* oil) at different temperatures between 313 and 343 K.

2.5. 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 characterize corrosion mechanisms and predict corrosion rates.

2.5.1. 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 cm^2 . These electrodes are connected to Voltalab PGZ 100 piloted by ordinate associated to "Volta Master 4" software. The scan rate was 1 mV/s started from an initial potential of -800 to -200mV/SCE. All experiments were repeated three times at the desired temperature of $\pm 1^{\circ}$ 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 (E_{corr}). Tafel polarization curves were plotted at a polarization scan rate of 1 mV/s. Anodic and cathodic curve slopes were extrapolated to corrosion potential, for the determination of the corrosion current densities (I_{corr}). 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.

2.5.2. 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. Quasipotentiostatic 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 their reproducibility. All electrochemical studies were carried out with immersion time of 1 hour, with different inhibitory concentrations of Lavandula dentate oil, at 308K.

3. Resultants and discussion

3.1. Essential oil composition

Qualitative and quantitative analyses essential oils were done using GC/MS analyses. The composition of essential oil of *Lavandula Dentata* was shown in the Table. 1. We may observe that the three major compounds are :

$$CH_2$$
 CH_3
 CH_3

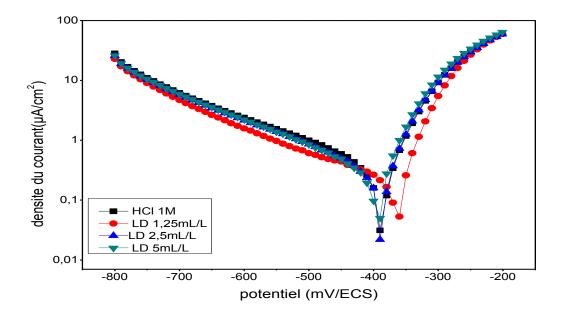
 Table 1: chemical constituents of Lavandula Dentata oil (%)

Composés	Ir /apol	Ir /pol	HE %
Tricyclene	932	1017	0,3
α-Pinene	942	1017	7,0
Camphene	953	1059	1,0
2,4(10) Thujadiene	955	1116	0,7
Oct-1-en-3-ol	971	1433	1,1
Sabinene	973	1113	
β -Pinene	979	1105	18,8
Myrcene	990	1149	
P-Cymene	1015	1253	0,1
Limonene	1023	1203	
1,8-Cineole	1023	1205	7,8
γ-Terpinene	1047	1232	0,4
Linalol oxyde THF E	1056	1426	1,2
Fenchone	1065	1380	0,8
Linalol oxyde THF Z	1069	1453	1,1
Linalol	1082	1528	
α-Thujone	1091	1409	2,1
Fenchol	1097	1570	0,2
β -Thujone	1103	1425	0,3
Campholenal	1101	1468	0,9
Nopinone	1105	1554	3,6
Camphre	1117	1494	2,9
trans-Pinocarvol	1123	1630	12,4
cis-Verbenol	1126	1654	2,2
Pinocarvone	1135	1544	3,0
p-Mentha-1,5-dien-8-ol	1144	1685	
Borneol	1146	1678	1,7
Cryptone	1152	1649	1,3
Terpinen-4-ol	1166	1579	
Myrtenal	1166	1601	4,6
γ-Terpineol	1169	1672	1,0
Hexylbutanoate	1172	1404	
Myrtenol	1178	1764	5,9
trans-Carveol	1202	1799	0,8
Cuminaldehyde	1209	1765	
Carvone	1212	1700	0,5
Peryllaldehyde	1242	1743	
TransPinocarvylacetate	1275	1616	

TOTAL			90,5
α-Bisabolol	1664	2182	0,4
(cis-14-nor)-Muurol-5-en-4-one	1656	2244	1,0
β-Bisabololoxide	1636	2105	0,5
β -Eudesmol	1630	2191	1,1
1-10-diepi-Cubenol	1621	2024	0,2
Globulol	1578	1667	
Caryophylléneoxide	1566	1949	1,0
Calamene	1512	1800	0,8
γ-Cadinene	1507	1731	0,2
β -Bisabolene	1499	1702	0,2
β -Selinene	1482	1690	1,0
α-Humulene	1449		0,1
E- α-Bergamotene	1431	1567	0,2
trans-Caryophyllene	1420	1580	
Z- α-Bergamotene	1413	1544	0,1
Geranyleacetate	1368	1732	
α-Terpinylacetate	1338	1670	

3.2. Polarisation measurements

In order to better understand the inhibition mechanism of this inhibitor, a detailed study on this compound was carried out: On the one hand, cathodic and anodic polarisation curves for steel in 1M HCl in the presence of *Lavandula Dentata* oilat 308 K are shown in Fig. 2.



<u>Figure 2</u>. Tafel polarization curves in in 1M HCL with and without *oil L.Dentata* different concentrations.

It may be noted that the addition of different concentrations of Lavandula Dentata moves the corrosion potential to more anodic values and leads to a reduction of the anode corrosion current densities. It can also be observed a change of the curves; it is a large area of anode passivation.

The inhibitory effect on the concentration of the anodic and cathodic polarization curves appeared only in the anodic branches. The density of the anodic corrosion current decreases with increasing concentration of inhibitor. The adsorption of the components of the essential oil on the metal surface forms a barrier to access of the hydrogen ions. The effectiveness of inhibition increases with the oil content to 70% to 5 mL/L. The inhibition of corrosion is usually explained by adsorption of the inhibitor at the interface solution / metal. For information on molecules that can acta qualitative and quantitative analysis of *oil L.Dentata* was conducted using GC and GC / MS. Components, the relative percentage of each component and the retention values were shown in Table 1. It can be suggested that both β -pinene and 1,8-cineole are the responsible for the inhibition of corrosion process in the acid solution. The extrapolation of the Tafel straight line allows the calculation of the corrosion current density (I_{corr}). The values of (I_{corr}), the corrosion potential (I_{corr}), the cathodic Tafel slopes (I_{corr}), the anodic Tafel slopes (I_{corr}) and the corrosion inhibition efficiency (I_{corr}) for different concentrations of *oil L.Dentata* are given in Table 2.

<u>Table 2</u>. Electrochemical parameters of mild steel at various concentrations of *oil L.Dentata*in HCL 1M.

Inhibitor	-Ecorr (mV/SCE)	$\beta_a (mV)$	- βc (mV)	I _{corr} (mA/cm ²)	IE%
HCl	389	110	362	0.698	
1.25	365	44	295	0.217	69
2.5	389	57	252	0.214	69
5	395	57	243	0.211	70

The inhibition efficiency (EI %) of the inhibitor for the corrosion of steel was calculated by using corrosion current density as follows [42]:

$$EI(\%) = \frac{I^{\circ}corr - Icorr}{I^{\circ}corr} x100$$
 (1)

Where I^ocorr and I_{corr} are the corrosion current density values without and with the inhibitor, respectively.

It is clear from the results that the addition of inhibitor caused a decrease in the current density. The values of the corrosion current (I_{corr}) of steel in the inhibited solution were smaller than this for uninhibited solution. The parallel anodic Tafel plots obtained in Figure 2 indicates that the hydrogen

evolution is activation controlled and the reduction mechanism is not affected by the presence of inhibitors [43-45].

These results demonstrated that the hydrogen evolution reaction was inhibited and that the inhibition efficiency increased with inhibitor concentration.

On the other hand, the inhibiting properties of the tested inhibitor have also been evaluated by the determination of the polarization resistance.

The inhibition efficiency (E%) was defined as follow:

$$E(\%) = \frac{R^{\circ} corr - Rcorr}{R^{\circ} corr} \times 100$$
 (2)

Where, R°_{corr} and R_{corr} are the charge transfer resistance in presence and in absence of inhibitor, respectively.

The corresponding polarization resistance (R_P) values of steel in 1 M HCl in the absence and presence of different concentrations of the inhibitor are given in Table 3.

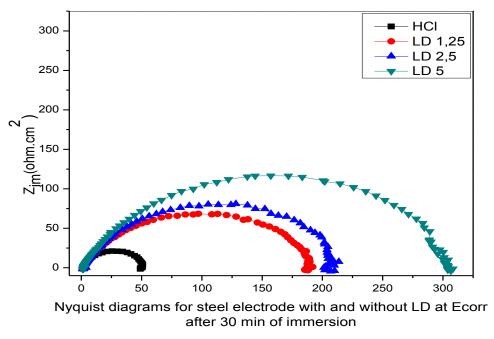


Figure 3. Nyquist plots in absence and presence of different concentrations of *oil L.Dentata* in 1M HCL.

Table 3. Corrosion parameters obtained by impedance measurements for mild steel in 1M HCL at various concentrations of *oil L.Dentata*.

Inhibitor	Ecorr	R _e	R _t	<i>f</i> max	Cdl	E_{Rt}
(mL/L)	(mV/SCE)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	(H_Z)	(µF.cm ²)	(%)
HCl	-500	1.906	48.87	63.29	119.4	

1.25	-436	2.163	190.5	68.311	93.57	74.34
2.5	-440	2.156	218.5	80.98	91.77	77.63
5	-443	2.328	311.8	116.55	80.64	84.32

The corrosion behaviour of steel in 1M hydrochloric acidic solution, in the absence and presence of *oil L.Dentata*, is also investigated by the EIS at 308 K after 30 min of immersion. The charge-transfer resistance (Rt) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. (1978) [46]. The double-layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal (-Zmax) are found as represented in the equation:

$$C_{dl}=1/\omega.Rt$$
 where $\omega = 2\pi * f_{max}$ (3)

Where f_{max} is the frequency, at which the imaginary component of the impedance (Z_{im}) is maximum and R_t is the diameter of the loop. Impedance diagrams are obtained for frequency range 100 kHz to 10 mHz at the open circuit potential for steel in 1M HCl in the presence and absence of inhibitor. Nyquist plots for steel in 1M HCl at different concentrations presented in Fig. 3. 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. As we notice, the impedance diagrams (Fig. 3) show perfect semi-circles whose size increases with the concentration of the inhibitor indicating a charge-transfer process mainly controlling the corrosion of steel. Similar diagrams were described in the literature for the electrode of iron and steel with and without inhibitor in 1M HCl (Bentiss et al., 1999; Elachouri et al., 2001) [47-48]. From the impedance data, the charge-transfer resistance (R_t) increases with the inhibitor concentration (Table 3). Also, the double-layer capacitance (C_{dl}) decreases with increase in the concentration of the inhibitor.

3.3. Effect of temperature

The corrosion rate of steel with temperature was studied in molar HCl both in the absence and presence of inhibitor at a maximal concentration (5 mL/L) in the temperature range 313–343 K using weight loss measurements, the corresponding results are summarized in Table 4.

Table 4. Corrosion parameters for mild steel in HCL 1M in absence and presence of optimum concentration of the inhibitor studied (*oil L.Dentata*) at different temperatures.

T(K)	W° (mg/cm ² h)	W (mg/cm ² h)	E(%)
313	1.65	0.44	73

323	3.24	0.67	79
333	5.40	0.96	82
343	11.02	1.23	89

The corrosion rate is more increased with the rise of temperature for uninhibited acid solution. The presence of inhibitor leads to a decrease in the corrosion rate (fig 4). The inhibitory action of inhibitor is slightly increased at elevated temperature leading to the increase of E%.

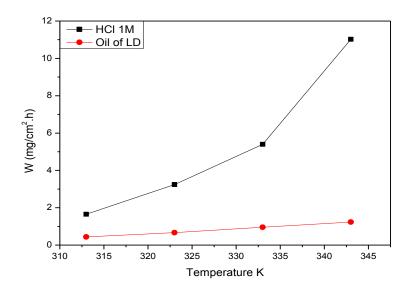


Figure 4. Variation of W in 1M HCl on steel surface without and with of optimum concentration of *oil L.Dentata*at different temperatures.

The activation kinetic parameters such as energy (Ea), enthalpy (ΔH_a) and entropy (ΔS_a) may be evaluated from the effect of temperature using Arrhenius law (Eq. (4)) and the alternative formulation of Arrhenius equation (Eq. (5)) [49]:

$$W = A \exp(\frac{-E_a}{RxT})$$

$$W = \frac{RxT}{Nxh} \exp(\frac{-\Delta S_a}{R}) \exp(\frac{-\Delta H_a}{RxT})$$
(4)

where W 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 Avogadro's number.

Fig. 5 show the plots of ln(W) against 1/T. Straight lines are obtained with a slope of $(-\Delta H^a/R)$ and an intercept of (ln R/Nh+ $\Delta S^a/R$) from which the values of ΔH^a and ΔS^a are calculated (Table 5).

Inspection of Table 5 showed that the value of Ea determined in 1M HCl containing *oil L.Dentata* is less (30.23 J/mol) than that for uninhibited solution (54.6 J/ mol). The decrease in the apparent activation energy may be interpreted as a plot of Ln (CR/T) versus 1/T. The straight lines are obtained with a slope ($\Delta H_a/R$) and an intercept of (Ln R/Nh + ΔSa /R) from which the values of the values of ΔHa and ΔSa are calculated for *oil L.Dentata* analyzed and are given in Table 5. Inspection of these data revealed that the thermodynamic parameter (ΔHa) for dissolution reaction of steel in 1M HCl in the presence of *oil L.Dentata* is less (30.65 kJ/mol) than that of in the absence of inhibitors (55.26 kJ/mol). The positive sign of ΔHa reflect the endothermic nature of the steel dissolution process suggesting that the dissolution of steel is slow [50] in the presence of inhibitor. Negative value of entropies (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.

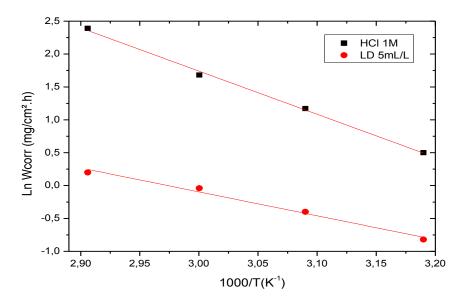


Figure 5. Arrhenius plots of ln CR vs. 1/T for mild steel in 1M HCl in the absence and the presence of *il L.Dentata* at optimum concentration (5 mL/L).

Table5. Activation parameters Ea, Δ Ha and Δ Sa for the mild steel dissolution in 1M HCl in the absence and the presence of *oil L.Dentata*at optimum concentration (5 mL/L).

Inhibitor	Ea (J/mol)	ΔHa (KJ/mol)	$\Delta S_a (J/mol.K)$
1M HCL	54.6	55.26	-17.32
oil L.Dentata	30.23	30.65	- 106.46

IV. Conclusions

- 1. Results obtained through weight loss measurements and electrochemical tests demonstrated that the essential oil of *L.Dentata* act as efficient corrosion inhibitors of the mild steel in 1 M HCl solution.
- 2. The corrosion process was inhibited by adsorption of the organic matter on the mild steel surface.
- 3. Inhibition efficiency increases with increase in the concentration of the essential oil of *L.Dentata*.
- 4. Inhibition efficiency of the essential oil increases with rise in temperature.
- 5. 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 formed protective layers on the mild steel surface, covering areas where HCl solution degrades and corrodes rapidly.
- 6. Tafel polarization measurements show that essential oil of *L.Dentata* act essentially as a mixed type inhibitor (anodic character).
- 7. The physic adsorption of the inhibitor on the surface of the mild steel is mainly credited to the oxygen atoms and instaurations (C=C) present in the essential oil and extract molecules, obtaining the formation of the film on the metal/acid solution interface, decreasing the degradation of the material.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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