



ISSN: 2230-9926

Available online at <http://www.journalijdr.com>

IJDR

International Journal of
DEVELOPMENT RESEARCH

International Journal of Development Research
Vol. 6, Issue, 02, pp. 6867-6874, February, 2016

Full Length Research Article

THE USE OF ESSENTIAL OIL OF *THYMUS CAPITATUS* ORIGINATING FROM NORTH-EAST MOROCCO, AS ECO-FRIENDLY CORROSION INHIBITORS OF MILD STEEL IN HYDROCHLORIC ACID SOLUTION

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ARTICLE INFO

Article History:

Received 28th November, 2015
Received in revised form
20th December, 2015
Accepted 17th January, 2016
Published online 29th February, 2016

Key Words:

Corrosion Inhibition,
Thymus Capitatus,
Essential oil,
Hydrodistillation,
Electrochemical,
Mild Steel,
Hydrochloric Acid.

ABSTRACT

Thymus Capitatus is a shrub, which is native of the Mediterranean basin. The purpose of this study was to determine the chemical composition and inhibitory effect of essential oil of *Thymus Capitatus* on the corrosion of mild steel in hydrochloric acid (1M). The essential oil of *Thymus Capitatus* has been studied using gas chromatography (GC) and GC-mass spectrometry (GC-MS). 91.2% of the components are detected (32 components) and the major components were, p-Cymene (18.9%), carvacrol (13.4%), acetate of geranyl (12.2%), borneol (10.2%), Camphene (3.9%), α -pinene (2.9%) and trans caryophyllene (2.9%). The inhibitory effect of essential oil of *Thymus Capitatus* 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 698 $\mu\text{A}/\text{cm}^2$ to 290 $\mu\text{A}/\text{cm}^2$ after addition of the inhibitor (essential oil of *Thymus Capitatus*), the charge transfer resistance increases 49 $\text{ohm}\cdot\text{cm}^2$ to 101 $\text{ohm}\cdot\text{cm}^2$ 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.

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INTRODUCTION

The corrosion of metals, including mild steel, is a serious problem in many industries, especially during processes such as the pickling of steel, acid washing and etching (Elmsellem et al., 2016; Elmsellem et al., 2015). Corrosion inhibitors are chemical compounds that in small quantities can retard the degradation of metals in hostile environments. Because these inhibitors represent an economic and effective technique to prevent metal and alloys from being corrupted, inhibitors are widely used in chemical cleaning solutions, industrial water and petrochemical engineering production processes, applied

to the atmosphere and environment and are becoming an indispensable protection measure during industrial production (Xia et al., 2008). These inhibitors are believed to work by influencing the kinetics of the electrochemical reactions that constitute the corrosion process, there by modifying the metal dissolution in acids. The existing data show that most organic inhibitors act by adsorption onto the metal surface (Singha and Quraishi, 2010). 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.

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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, our laboratory adopted a strategy of evaluation of these molecules against corrosion of mild steel in acid media. Many plant extracts have been used as effective corrosion inhibitors of iron or steel in acidic media (El ouadi *et al.*, 2014; El Ouadi, ?; EL Ouadi *et al.*, 2015; Manssouri *et al.*, 2015; El Mounsi *et al.*, 2015; El Ouadi *et al.*, 2015; Znini *et al.*, 2011; Elmsellem *et al.*, 2014; Elmsellem *et al.*, 2015; Elmsellem *et al.*, 2014; Elmsellem *et al.*, 2013; Elmsellem *et al.*, 2015; Elmsellem *et al.*, 2014; Aouniti *et al.*, 2015; Elmsellem *et al.*, 2015). In this paper, electrochemical polarisation, EIS and gravimetric techniques are applied to study the ability of essential oil of *Thymus Capitatus* to inhibit the corrosion of steel in 1M HCl. The effect of temperature is also studied.

Experimental

Inhibitors

Plant material

Thymus Capitatus 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.

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 *Thymus Capitatus* was conducted by hydrodistillation using a Clevenger type apparatus (Figure 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.

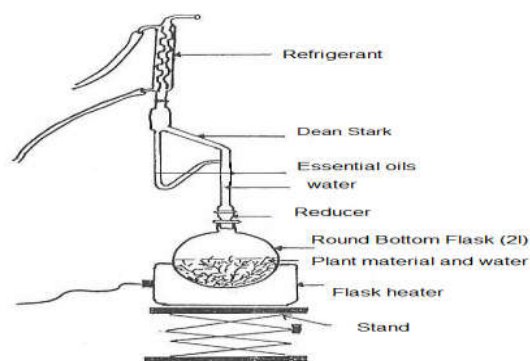


Figure 1. Hydrodistillation by Clevenger apparatus

Essential oil isolation of *Thymus Capitatus*

The dried vegetal material (100 g) were water-distilled (3h) using a Clevenger-type apparatus according to the method recommended by the European Pharmacopoeia (Joulain and König, 1998). The yield of fruits essential oil was 0.5%.

GC analysis

GC analysis were carried out using a Perkin-Elmer Auto-system XL GC apparatus equipped with dual flame ionization detection (FID) system and fused-silica capillary columns (60 m x 0.22 mm I.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.

GC-MS analysis

Samples were also analysed using a Perkin-Elmer Turbo mass detector (quadrupole), coupled to a Perkin-Elmer Auto-system 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 μ L of pure oil.

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 (Hochmuth *et al.*, 2001); ii) computer matching with commercial mass spectral libraries (Adams, 2004) and comparison of mass spectra with those of our own library of authentic compounds or literature data (Hochmuth *et al.*, 2001; Belfilali *et al.*, 2014).

MATERIALS AND METHODS

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 A Rgrade ethanol, acetone and dried at room temperature. MS samples of size 1.0 x 1.0 x 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.

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.

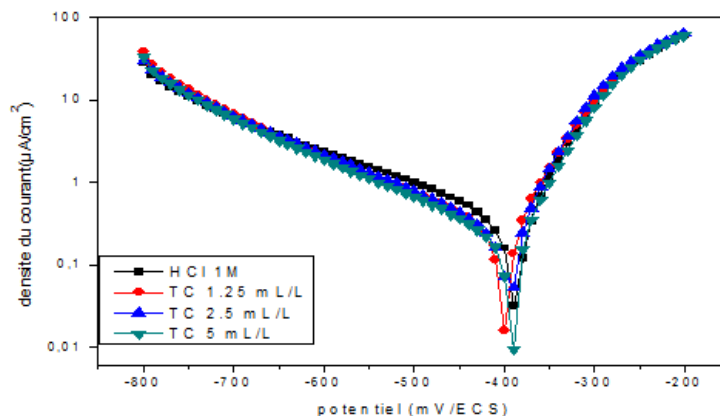


Figure 2. Cathodic and Anodic polarisation curves of mild steel in 1M HCl in the presence of essential oil of *thymus capitatus* at different concentrations

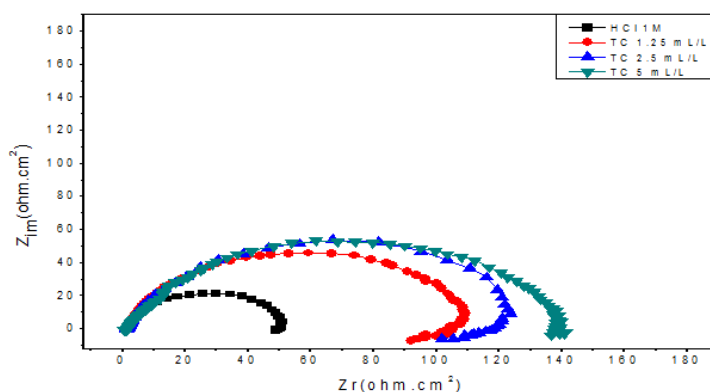


Figure 3. Nyquist plots in absence and presence of different concentrations of *thymus capitatus* oil in HCl 1M

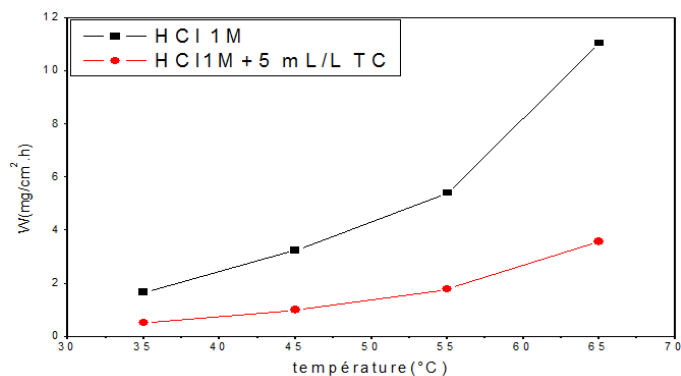


Figure 4. Variation of W in 1M HCl on steel surface without and with optimum concentration of *thymus capitatus* oil at different temperatures

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 *Thymus Capitatus* oil directly to the corrosive solution. Experiments were conducted on several occasions to ensure reproducibility. Concentrations of *Thymus Capitatus* oil were 1.25, 2.5 and 5 mL/L.

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 life time 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 (Chetouani *et al.*, 2006; Kharchouf, 2011). 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 (*Thymus Capitatus* 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 (*Thymus Capitatus* oil) at different temperatures between 313 and 343 K.

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. The electrochemical measurements were performed using a potentiostat PGZ100 piloted by Voltmaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH).

A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The working electrode (WE) in the form of disc was cut from pure iron and was embedded in poly-tetra-fluoro-ethylene (PTFE) to avoid any infiltration of electrolyte then exposing only 1 cm² surface to the aggressive solution. The test solution was thermostatically controlled at 37 °C in air atmosphere without bubbling. All potentials were measured against SCE. The test solution was deaerated for 30 min at E_{corr} in the cell with pure nitrogen. Gas pebbling was maintained through the experiments. Before recording the cathodic polarisation curves, the iron electrode was polarized at -800 mV / SCE for 10 min.

The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from -800 to -200 mV at a scanning rate of 1 mVs⁻¹, which are used for the determination of corrosion current by the extrapolation of anodic and cathodic Tafel lines to a point which gives log i_{corr} and the corresponding corrosion potential (E_{corr}) for each concentration of inhibitors and for the blank solution. The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the restpotential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

RESULTANTS AND DISCUSSION

Essential oil composition

Qualitative and quantitative analyses essential oils were done using GC/MS analyses. The composition of essential oil of *Thymus Capitatus* was shown in the Table 1.

Effect of concentration

Polarization curves

Polarization study has been carried out in order to gain knowledge about the kinetics of the anodic and cathodic

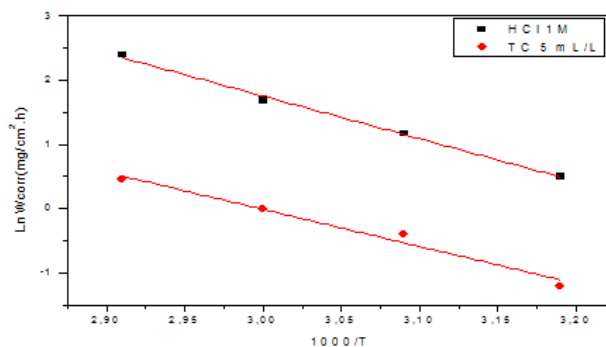


Figure 5. Arrhenius plots of lnW vs. 1000/T for mild steel in 1M HCl in the absence and the presence of oil *thymus capitatus* at optimum concentration (5 mL/L)

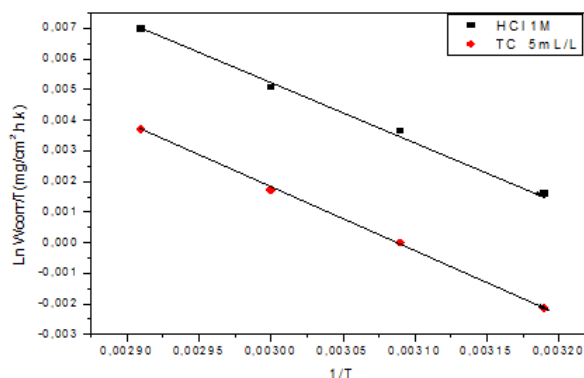


Figure 5'. The variation of Ln W / T vs 1000 / T of the steel in 1M HCl with and without oil of *thymus capitatus* at optimum concentration (5 mL/L)

reactions. Potentiodynamic curves are obtained in the presence and the absence of the studied inhibitor, after pre-polarizing the electrode at its E_{corr} for 30 min, there after pre-polarized at -800 mV for 10 min. After this scan, the potential was swept stepwise from the most cathodic potential to the anodic direction. Potentiodynamic polarisation curves of steel in 1M HCl in the presence and the absence of essential oil of *thymus capitatus* is shown in Figure 2. The corrosion parameters including corrosion current densities (I_{corr}), potential (E_{corr}), cathodic and anodic Tafel slope (β_c and β_a) and inhibition efficiency (EI %) are listed in Table 2. In this case, the inhibition efficiency is defined as follows:

$$EI(\%) = \frac{I_{corr}^{\circ} - I_{corr}}{I_{corr}^{\circ}} \times 100 \quad (1)$$

Where I_{corr}° and I_{corr} are, respectively the uninhibited and inhibited current density respectively. The corrosion current density was calculated from the intersection of cathodic and anodic Tafel lines.

As it can be seen from Table 2, the E_{corr} values were shifted slightly toward the negative in the presence of the inhibitor in comparison to that in its absence and the values of corrosion potential nearly remain constant with the addition of different concentration. These results indicate that essential oil of *thymus capitatus* act as mixed-type inhibitor. According to Ferreira and others (Bartos and Hackerman, 2000; Ferreira *et al.*, 2004), if the displacement in E_{corr} values (i) >85 mV uninhibited system with respect to uninhibited, the inhibitor could be recognized as cathodic or anodic type and (ii) if displacement in E_{corr} is <85 mV, it could be recognized as mixed-type. For studied inhibitor, the maximum displacement range was 12 mV, which indicates that *thymus capitatus* oil is mixed type inhibitor. It is clear from the results that the addition of *thymus capitatus* oil 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

Table 1. Chemical constituents of *Thymus Capitatus* oil (%)

Composés	Ir /lit	Ir /apol	Ir /pol	%
α -Thujene	932	922	1031	0,6
α -pinene	936	930	1029	2,9
Camphene	950	943	1070	3,2
1-octen-3-ol	962	961	1449	1,2
Sabinene	973	965	1125	0,5
β -pinene	978	970	1114	1,2
Myrcene	987	981	1162	1,8
α -terpinene	1013	1010	1181	0,6
p-Cymene	1015	1015	1272	18,9
Limonene	1025	1022	1203	1,1
1,8-Cineole	1024	1022	1208	1,0
γ -terpinene	1051	1050	1247	2,5
trans hydrate de Sabinène	1053	1054	1463	0,8
Linalol	1086	1085	1545	1,5
Camphre	1123	1122	1511	1,2
trans-pinocarveol	1126	1124	1648	0,7
Borneol	1150	1153	1631	10,2
Terpinen-4-ol	1164	1163	1597	0,9
α -Terpineol	1176	1174	1688	0,6
Myrtenol	1178	1180	1781	0,4
1-Methyl-3-methoxy-4-isopropy	1215	1217	1766	1,2
carvacryl methyl ether	1226	1227	1559	1,1
Bornyle acetate	1270	1270	1578	1,2
Thymol	1267	1273	2168	1,5
Carvacrol	1278	1285	2193	13,4
α -terpenyle acetate	1335	1335	1670	2,6
geranyl acetate	1362	1365	1753	12,2
transcaryophyllene	1421	1418	1595	2,9
δ -selinene		1476		0,3
germacrene D-4-ol		1566	2035	0,5
caryophyllene oxide	1578	1570	1965	1,9
α -bisabolol	1659	1669	2200	0,6
				91,2

presence of inhibitors (Elmsellem et al., 2014; Elmsellem et al., 2014). These results demonstrated that the hydrogen evolution reaction was inhibited and that the inhibition efficiency increased with inhibitor concentration. The electrochemical parameter values given in Table 2 reveal that inhibition efficiency increases with an increase of the concentration of inhibitors. We remark that the corrosion current densities were more significantly reduced in the presence of *thymus capitatus* oil. The best efficiency obtained in the presence of the inhibitor studied is 68% at 5mL/L.

Electrochemical impedance spectroscopy measurements

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:

$$E (\%) = \frac{R^{o\text{corr}} - R_{\text{corr}}}{R^{o\text{corr}}} 100 \tag{2}$$

Where, R^ocorr and Rcorr 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. The corrosion behavior of steel in 1M hydrochloric acidic solution, in the absence and presence of *oil thymus capitatus*, is also investigated by the EIS at 308 K after 30 min of immersion. The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies. The double-layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal (-Z_{max}) are found as represented in the equation:

$$C_{dl} = 1 / \omega . R_t \tag{3}$$

$$\omega = 2\pi * f_{\text{max}} \tag{4}$$

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.

Table 2. Electrochemical parameters of steel at various concentrations of thymus capitatus oil in 1M HCl and the corresponding inhibition efficiency

Inhibitor mL /L	-Eco	-E(m'	βa (mV	-βc (I _{corr} (mA/cm	IE%
HCl		389	110	362	0.69	----
1.25		401	64	242	0.29	58
2.5		396	55	227	0.27	61
5		394	56	226	0.22	68

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

Inhibitor(mL/L)	Re (Ω.cm	Rt (Ω.cm ²	F max (Hz)	Cdl (μF.cm'	E _{Rt} %
HCl	1.9	49	63	119	----
1.25	3.2	101	79	19	51.5
2.5	6.5	111	63	22	56
5	1.7	142	14	7	65.5

Table 4. Gravimetric results of mild steel in acid solutions 1M HCl at different concentration of thymus capitatus oil (308 K, 6 h)

Concentration (mL/L)	W (mg/cm ² .h	E%	Θ = E%/100
Blanc	0.50	-	-
1.25	0.26	48	0.48
2.5	0.24	52	0.52
5	0.185	63	0.63

Table 5. Corrosion parameters for mild steel in HCL 1M in absence and presence of optimum concentration of the inhibitor studied (thymus capitatus oil) at different temperatures

T (°K)	W _{HCl} (mg/cm ² .h	W _{inh} (mg/cm ² .h	E(%)
313	1.65	0.51	69
323	3.24	0.98	69
333	5.40	1.77	67
343	11.02	3.55	67

Table 6. Activation parameters Ea, ΔHa and ΔSa for the mild steel dissolution in 1M HCl in the absence and the presence of oil thymus capitatus at optimum concentration (5 mL/L)

Inhibitor	Ea (KJ/mol)	ΔHa (KJ/mol)	ΔSa (J/mol.K)
1M HCL	55.24	157.3	-197.02
Thymus capitatus Oil	48	172.1	-197.01

Nyquist plots for steel in 1M HCl at different concentrations presented in Figure 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 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) (Bentiss *et al.*, 1999; Elachouri *et al.*, 2001). From the impedance data, the charge-transfer resistance (R_t) increases with the inhibitor concentration. Also, the double-layer capacitance (C_{dl}) decreases with increase in the concentration of the inhibitor.

Weight loss corrosion rates and inhibition efficiency

Gravimetric measurements of steel were investigated in 1M HCl in the absence and the presence of various concentrations of oil *thymus capitatus* at 6 h of immersion and 308 K. The following equation was used to determine the inhibition efficiency (E%):

$$E(\%) = \frac{W - W_{inh}}{W} \times 100 \quad (5)$$

Where W and W_{inh} are the corrosion rate of steel in 1M HCl in the absence and the presence of inhibitor, respectively. Table 4 summarizes the gravimetric trends of the steel immersed in aerated molar HCl in the absence and the presence of the inhibitor at various concentrations. It is clear that the corrosion rate decreases with the increase of concentration of *thymus capitatus* oil and in turn the inhibition efficiency (E %) increases to attain 63% at 5mL/L.

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 5. 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 (Figure 4). At elevated temperature, the inhibitory action of inhibitor is slightly increased and become nearly steady (67%). The activation kinetic parameters such as energy (E_a), enthalpy (ΔH_a) and entropy (ΔS_a) may be evaluated from the effect of temperature using Arrhenius law (Eq. (6)) and the alternative formulation of Arrhenius equation (Eq. (7)):

$$W = A \exp\left(\frac{-E_a}{R \times T}\right) \quad (6)$$

$$W = \frac{R \times T}{N \times h} \exp\left(\frac{-\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{R \times T}\right) \quad (7)$$

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. Figures 5, 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 6). Inspection of Table 6 showed that the value of E_a

determined in 1M HCl containing *thymus capitatus* oil (48KJ/mol) is less than that for uninhibited solution (55.24KJ/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 $(\ln R/Nh + \Delta S_a / R)$ from which the values of the values of ΔH_a and ΔS_a are calculated for *oil thymus capitatus* analyzed and are given in Table 6. Inspection of these data revealed that the thermodynamic parameter (ΔH_a) for dissolution reaction of steel in 1M HCl in the presence of *oil thymus capitatus* (172.1 KJ/mol) high than that of in the absence of inhibitor (157.3 KJ/mol). The positive sign of ΔH_a reflect the endothermic nature of the steel dissolution process suggesting that the dissolution of steel is slow in the presence of inhibitor. Negative value of entropies (ΔS_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 reactant to the activated complex.

Conclusion

In this paper, we have studied the corrosion inhibition of *Thymus capitatus* oil for mild steel in 1M HCl solution by gravimetric method and electrochemical techniques. The results obtained are in good agreement and are given as follows:

- The analysis of essential oil isolated from *Thymus capitatus* plant shows that its composition is dominated by p-Cymene, carvacrol, geranyl acetate, borneol (18.9%, 13.4%, 12.2% and 10.2%, respectively).
- *Thymus capitatus* oil act as mixed-type inhibitors without modifying the mechanism of hydrogen evolution.
- The adsorption onto the carbon steel surface was characterized by the decrease in the cathodic and anodic current densities observed in the potentiodynamic polarization curves carried out in the presence of *Thymus capitatus* oil.
- The inhibition efficiency of *Thymus capitatus* oil increases with the increase of inhibition concentration to reach 63% at 5mL/L.
- The data obtained from the three different methods: potentiodynamic polarization, EIS and weight loss have the same tendency.
- The inhibition efficiency of *Thymus capitatus* oil increases slightly with the rise of temperature.
- *Thymus capitatus* oil being natural and environmentally benign products, they can be used as an alternative for toxic chemical inhibitors in acidization and acid pickling of mild steel.

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