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Application of essential oil of thyme vulgaris as green corrosion inhibitor for mild steel in1MHCl

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Abstract

The oil of T. vulgaris, analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) was made. The analyzed oils consist mainly in monoterpene hydrocarbons, with Thymol (41.39%), gamma terpinene (22.25%) and p-cymene (15.59%) being the major constituents, on the corrosion of mild steel in molar hydrochloric acid studied by weight loss measurements, potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) measurements. The results obtained reveal that oil reduces the corrosion rate. The inhibition efficiency increases with the increase of inhibitor concentration. Potentiodynamic polarisation studies clearly reveal that the presence of the naturally inhibitor does not change the mechanism of the hydrogen evolution reaction and acts a mixed inhibitor. The effect of temperature on the corrosion behaviour of mild steel in 1M HCl with and without oil in the temperature range 308-333K, indicates that inhibition efficiency increases with temperature. The associated activation energy has been determined. The adsorption of natural products on the mild steel surface was found obey to Langmuir's adsorption isotherm.

Keywords: mild steel, Thyme. Vulgaris, HCl, Corrosion, Green inhibitor, GC-MS.

1. Introduction

The studies of the inhibition of corrosion of mild steel are multiplied because of the wide use of this material in many operations such as pickling, cleaning, descaling, etc. Hydrochloric acid is often used because of the higher soluble ferrous chloride. To avoid damage and cost, inhibitors are added to secure metal dissolution and acid consumption. This technique is required to remove corrosion scales from the mild steel surface without attainder to the acid attack of the bulk metal [1-3]. The addition of effective inhibitors is the most practical mean of protection. The inhibitors used are expected to be chemically stable to provide high protection under the cited conditions. Furthermore, it's better that inhibitors exhibit no toxicity towards the environments [4-5]. Literature shows the wide applications of naturally substances in many fields because of the diversity of their structures, availability and relatively cost. We have recently focused on the application of natural substances and their oils. Ginger [6], henna [7], jojoba oil [8], rosemary oil [9], bgugaine [10], Murraya koenigi[11], Emblca officianilis [12], Terminalia chebula [13], Sapindus trifolianus[14], and Accacia conicianna[15] was investigated. Corrosion inhibition has also been studied for the essential oils and extracts of lawsonia [16]. Similar results were also shown by Rosmarinous officinalis[17], Annona squamosa [18], Acacia Arabica [19], Carica papaya [20], Azadirachta indica and Vernonia amydalina which were used for mild steel in acid media. Nypafructicans wurmb leaves were studied for the corrosion inhibition of mild steel in HCl media [21,22], The addition of inhibitors is one of the methods used to reduce metal corrosion rate. Such materials usually contain polar functionality with nitrogen, oxygen and / or sulphur in a conjugated system. These functions cause adsorption on the interface of the metal, according to their nature and their charge [4, 9-24]. The efficacy of a compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface which consists of the replacement of water molecule at a corroding interface. In this paper, we aim to test Thyme vulgaris as a non-toxic natural inhibitor for the corrosion of mild steel in molar hydrochloric acid. The study is conducted by gravimetric method and electrochemical techniques such as linear polarization and impedance spectroscopy (EIS). The effect of temperature is made in the range of 308-333 K. Activation energy in the presence and absence of inhibitor is determined.

2. Materials and methods

2.1. Preparing sample and essential oil extraction:

The cultured samples T. vulgaris have been harvested on a farm in Immouzar in Morocco. The biomass thus obtained was subjected to extraction spawning condition for obtaining essential oils. The extraction of plant was performed in the laboratory of the National Institute of Medicinal and Aromatic Plants Taounate, the training technique to water vapour using a Clevenger-type apparatus, fig(1), according to the following protocol. The plant is contacted with distilled water in a flask. The whole is boiled for 2h30 after the appearance of the first drop of distillate at the outlet of the steam condensation tube. The essential oil entrained by the water vapour is then condensed through a condenser and recovered using a syringe. The essential oil recovered were dried over anhydrous sodium sulphate and then stored in sealed glass vials at 4 to 5°C prior to analysis.

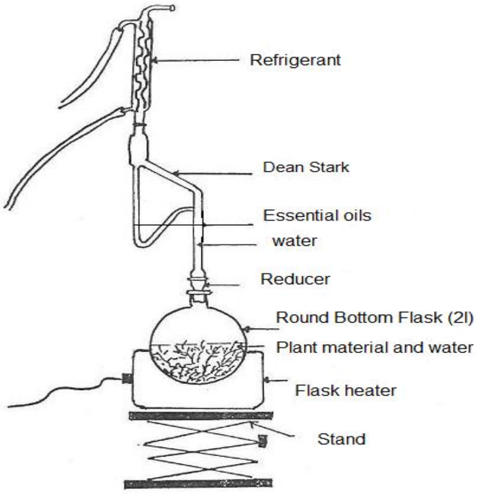

Fig.1: Hydrodistillation of essential oils by Clevenger type apparatus.

The extraction of HE by Hydrodistillation was used to thyme (T.vulgaris), the yield obtained is of the order of 1.40%. The yield of HE, which depends on many factors (growth stage, soil and climate conditions, technique for extracting, etc.) is only 1.40% for thyme. It can be much higher in the same species and is of the order of 3.17% (El Idrissi, 2007). This difference can be explained by the middle of the effect. In this sense, El Idrissi confirmed that HE content thyme exchange with the environment.

2.2. GC and GC-SM analysis:

Gas chromatography (GC) was the techniques used for screening / identification / quantification of many groups of non-polar and/or semi-polar food toxicants (or their GC amenable derivatisation products). The high attainable separation power (potential number of theoretical plates) in combination with a wide range of the detectors employing various detection principles to which it can be coupled makes GC an important tool in the analysis of (ultra)trace levels of toxic food components that may occur in such complex matrices as foods and feeds.

In practice, the methods used for analyses of organic compounds, oil typically consist of basic steps as shown in Fig.2:

(i) Isolation from a representative sample (extraction step);
(ii) Separation from bulk co-extracted matrix components (clean-up step);
(iii) Identification and quantification (determinative step).
(iv) The last step is often optionally followed by confirmation of results (Fig. 2).

Chemical characterization and the determination of extract oil retention indices were performed using a gas chromatograph Varian 3400 type, equipped with a polar capillary column BP - 5 (30m x 0,25mm, film thickness: 0.25 microns), with an FID detector set at a temperature of 250 ° C and fed with a mixture of H_2 / air and an injector set at 250 ° C. The carrier gas used was nitrogen with a flow of 2 ml / min. The column temperature is 40 ° C (isothermal for 5 min) at 200 ° C (isothermal for 5 ° C) at a rate of 4 ° C / min.

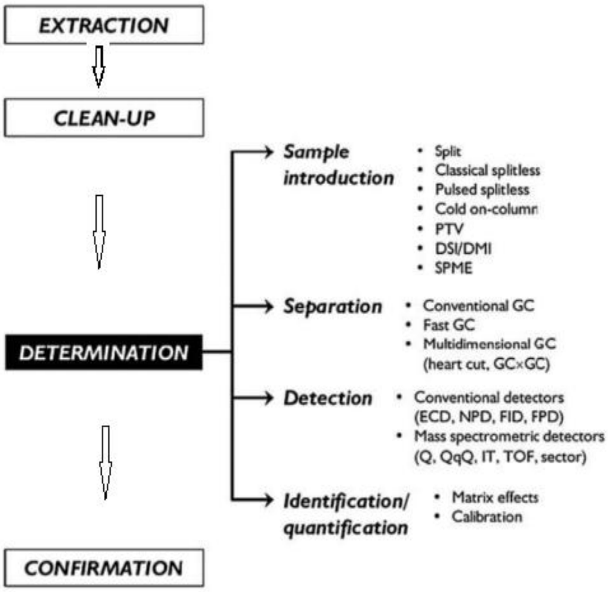

Fig. 2. Basic steps typically involved in GC analysis of oil, alternative approaches applicable in determinative step shown in a greater detail.

The chemical identity of the various components was implemented by gas chromatography coupled with mass spectrometry (GC/MS); allowing a qualitative and quantitative determination of their compounds. The apparatus used is the following Gas chromatograph (Trace GC Ultra) coupled to a mass spectrometer (Polaris Q ion trap MS), ionization was effected by electron impact (70 eV). The database used: NIST MS Search. The table 1 below summarizes the conditions of the injection and the column type and solvent used:

Table1: conditions and database used: NIST MS Search

Solvent	Acetate diethyl ($C_4H_8O_2$)
Column Type	VB-5 (Methylpolysiloxane à 5% phenyl) 30 m * 0.25 mm * 0.25 µm.
Injection volume	1µl
injection Temperature	220°C
Interface temperature	300°C
Injection mode	Split
vector gas	Helium

2.3. Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of green inhibitor employed was 0.1–2 (g/l).

2.4. Weight loss measurements

Coupons were cut into 1.5× 1.5 × 0.05 cm^3 dimensions having composition given in Table 2:

Table 2. The chemical composition of mild steel

%C	%Si	%Mn	%S	%P	%AL	%Fe
0.21	0.38	0.05	0.05	0.09	0.01	99.21

Prior each gravimetric or electrochemical experiment, the surface of the specimens was abraded successively with emery paper. The specimens are then rinsed with acetone and bid stilled water. Weight loss was measured on sheets of mild steel of $2cm^2$ apparent surface area. The samples were polished successively with different emery paper up 1000 grade, washed with distilled water, degreased and dried before being weighed and immersed in 100 ml of the corrosive medium. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The immersion time for the weight loss is 6 h at (308±1) K. In order to get good reproducibility, experiments were carried out in duplicate. The average weight loss was obtained. The corrosion rate (v) is calculated using the following equation:

$$v = \frac{w}{st} \qquad (1)$$

Where: W is the average weight loss, S the total area, and t is immersion time. With the corrosion rate calculated, the inhibition efficiency (Ew) is determined as follows, where W1 and W2 are the weight losses (in g) for mild steel in the absence and the presence of the inhibitor in 1 M HCl solution respectively. The inhibition efficiency of the inhibitor, E%, the degree of surface coverage, θ, and the corrosion rate the mild steel were calculated using the following equations respectively:

$$E\ (\%) = \left(1 - \frac{W_1}{W_2}\right) \times 100 \qquad (2)$$

2.5. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. This potentiostat were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. The working electrode (WE) was in the form of a square cut from mild steel with exposed surface area $1cm^2$. Before measurement, potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from −800 mV to −200 mV at 308 K. The corrosion inhibition efficiency E (%) was evaluated from the measured I_{corr} values obtained from Tafel polarisation method using the relationship, respectively, Where $I°_{corr}$ and I_{corr} are the corrosion current densities without and with the addition of various concentration of the inhibitor.

$$E_I(\%) = (1 - \frac{I_{corr}}{I^0_{corr}}).100 \qquad (3)$$

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Volta lab 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 rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. The charge transfer resistance (Rct) and double layer capacitance (Cdl) were determined from Nyquist plots. Experiments are repeated three times to ensure the reproducibility. All electrochemical studies were carried out with an immersion time of 1 h, with different inhibitory concentrations of essential oil and extract of Pelargonium, at 308 K. The inhibition efficiency (E%) of the inhibitor can be calculated from the charge transfer resistance values using the following equation, where, R_t and $R_{t/inh}$ are the charge transfer resistance in the absence and in presence of inhibitors, respectively:

$$E(\%) = \frac{\left[R_{t/inh} - R_t \right]}{R_{t/inh}} .100 \quad (4)$$

3. Results and discussion

3.1 Characterization and chemical composition of essential oils:

The results of analysis by GC / MS HE extracted from thyme are presented in Table 3. The fig. 3 shows the chromatogram of the HE thyme. The components were identified in the T. vulgaris essential oil, and was dominated by monoterpene hydrocarbons, and the major constituent followed by Thymol (41.39%), gamma terpinene (22.25%) and p-cymene (15.59%). Comparing our results with the literature shows significant qualitative and quantitative differences in the chemical composition. Indeed, our results differ from those obtained by Özcanand al. (2004) who studied the thyme oil composition of a sample of the same species, in which thymol (46.2%), alpha terpinene (14.1%), p-cymene (9 , 9%), the alpha-pinene (3.0%) and carvacrol (2.06%) were found to be the majority. This can be explained by the existence of different chemical races or chemotypes of Thymus vulgaris: thymol, carvacrol, linalool, thuyanol, alpha terpineol, geraniol and paracymene. Extractions with water vapour gave the average yields in HE of the order of 1.40% for T. vulgaris.

Table 3: Composition of T. vulgaris essential oils compounds extraction.

Retention Time (min)	Compounds	Chemical Family	Indicative Value %
5.48	Methyl 2-methylbutanoate	compounds (oxygen)	0.18
11.50	Alpha thujene	Monoterpene hydrocarbon	1.76
11.74	Alpha pinene	Monoterpene hydrocarbon	0.85
12.32	Camphene	Monoterpene hydrocarbon	0.40
13.51	Sabinene	Monoterpene hydrocarbon	0.33
13.81	2-hexen-1-ol 2-ethyl	others (oxygenated)	0.41
14.27	Beta pinene	Monoterpene hydrocarbon	1.63
14.70	Alpha phellandrene	Monoterpene hydrocarbon	0.28
15.24	Alpha terpinene	Monoterpene hydrocarbon	3.25
15.61	p-cymene	Monoterpene hydrocarbon	15.59
17.07	Gamma terpinene	Monoterpene hydrocarbon	22.25
17.30	p-menth-2-en-1-ol	Monoterpene oxygenated	0.65
18.10	terpinolene	Monoterpene hydrocarbon	0.16
18.63	Linalool	Monoterpene oxygenated	1.79
20.16	camphre	Monoterpene oxygenated	0.24
21.04	borneol	Monoterpene oxygenated	0.65
21.48	4-terpinéol	Monoterpene oxygenated	1.15
23.54	Thymol methyl ether	Others (oxygenated)	1.18
23.86	2-isopropyl-4-methylanisole	Others (oxygenated)	0.88
25.80	Thymol	Monoterpene oxygenated	41.39
26.00	Carvacrol	Monoterpene oxygenated	2.06
27.60	Isothymol	Monoterpene oxygenated	0.27
29.81	Caryophyllene	Sesquiterpene hydrocarbon	1.30
31.71	Germacrene D	Sesquiterpene Hydrocarbon	0.40

Regarding the chromatographic analysis of HE by GC/MS, we found that 24 compounds represent 99.05% of HE T.vulgaris with 5 major compounds.

3.2. Weight loss measurements:

Table 4 resumes the corrosion rate obtained in 1M HCl(W^0_{corr}) and at various contents of T. vulgaris essential oils (W_{corr}) determined at 308K after 6h of immersion rate and inhibition efficiencies E_w,, It is clear that the addition of T. vulgaris oil reduces the corrosion rate in HCl solution. The inhibitory effect increases with the increase of inhibitor concentration. E% reaches a maximum of 93.6% at 2 g/l for T. vulgaris essential oil. From weight loss measurement, we can conclude that T. vulgaris essential oil is the excellent inhibitor.

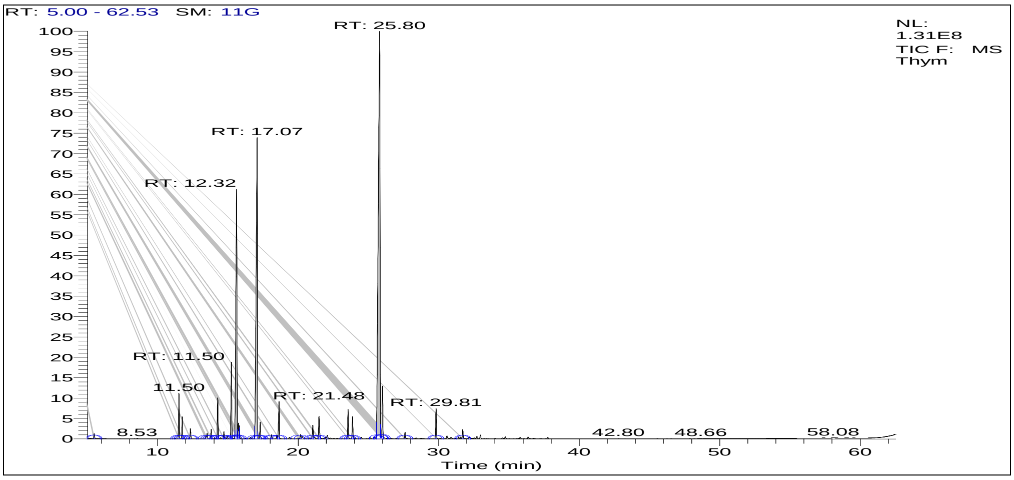

Fig. 3: Chromatogram of T. vulgaris oil

Table 4: Gravimetric results of mild steel in 1M HCl with and without addition the T. vulgaris (T.V)

Inhibitor	C (g/l)	W_{corr} (mg.cm^{-2}.h^{-1})	E_w (%)
Blank	0	0,962	----
T.V	0,25	0.096	90.02
	0.5	0.083	91.3
	1	0.074	92.3
	2	0.061	93.6

3.3. Potentiodynamic polarization curves:

Polarization behaviour of mild steel in 1M HCl in the presence and absence of T. vulgaris essential oils is shown in Fig.4. Table 5 gives values of corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodicTafel slope (β_c) and anodic tafel slope ($\beta_{a)}$. The inhibition efficiency (E_I%) is calculated by the relation (3).

As it is shown in Fig.4 and Table 5, the parallel cathodicTafel curves suggested that the hydrogen evolution was activation-controlled and the reduction mechanism was not affected by the presence of the inhibitor. Thus the presence of naturally T. vulgaris essential oil does not affect the mechanism of this process.

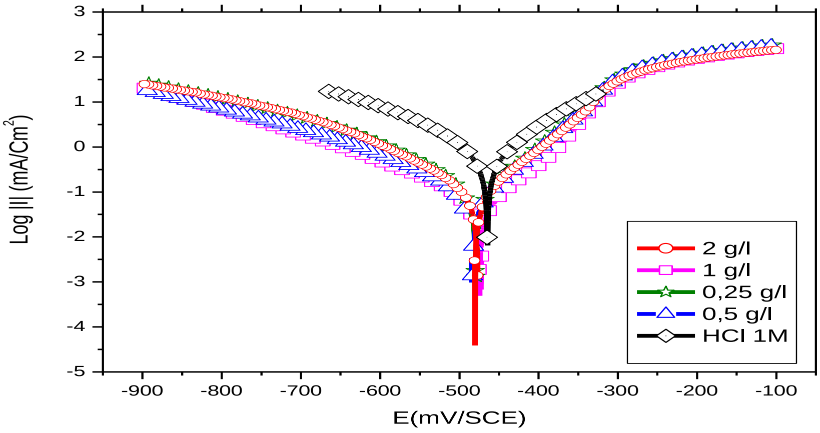

Fig 4: Polarization curve of mild steel in 1M HCl + T. vulgaris at various concentrations at 308k.

The addition of naturally substance causes a decrease of the current density. Values of E_{corr} and cathodicTafel slope (b_c) do not change when the concentration increases. The results demonstrate that the hydrogen reduction is inhibited and that the inhibition efficiency increases with inhibitor concentration to reach a maximum value of 95% at 2 g/l for T. vulgaris essential oil.

The results in Table 5 showed that the inhibition efficiency increased, while the corrosion current density decreased with increasing oil concentrations. This could be explained on the basis of adsorption of oil on the mild mild steel surface and the adsorption process enhanced with increasing inhibitor concentration. In the anodic range, the polarization curves of mild steel in normal HCl with and without T. vulgaris essential oils show that the presence of inhibitor does not change the current vs potential characteristics, From table 5, it is clear from the results that the addition of inhibitor causes a decrease of the current density. The values I_{corr} of mild steel in the inhibited solution are smaller than that for the inhibitor free solution. The values of corrosion potential (E_{corr}) were found to be almost identical at all oil concentrations, indicating that it acts as mixed-type inhibitor [25-26].

Table 5 : Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 1M HCl without and with addition of various concentrations of H.E at 308K

inhibitor	Concentration (g/l)	E_{corr} (mV/SCE)	I_{corr} (µA/Cm)	$-\beta_c$(mV)	β_a(mV)	E_w (%)
T.V	1MHCl	-464	1870,04	207	149	-
	2	-480	81,2	153,5	183	95,7%
	1	-474	123,2	146,8	196	93,5%
	0,5	-484	130,05	152,6	188	93%
	0,25	-479	145,7	145,3	184	92%

3.4. Electrochemical impedance spectroscopy:

EIS is carried out by imposing potential sweeps, potential steps, or current steps, we typically drive the electrode to a condition far from equilibrium, and we observe the response, which is usually a transient signal. Another approach is to perturb the cell with an alternating signal of small magnitude and to observe the way in which the system follows the perturbation at steady state. Many advantages accrue to these techniques [25]. This measurement is equivalent to determining the faradic impedance. EIS is essentially a steady state technique that is capable of accessing relaxation phenomena whose relaxation times vary over orders of magnitudes and permits single averaging within a single experiment to obtain high precision levels. It confirms the conventional polarization techniques for corrosion rate measurements. The technique has been widely used in investigating corrosion inhibition processes [25-26]. It also provides information on both the resistive and capacitive behaviour at interface and makes possible to evaluate the performance of the tested compounds as possible inhibitors against metal corrosion.

The corrosion behaviour of mild steel, in acidic solution in the presence and absence of inhibitor, is investigated by the electrochemical impedance spectroscopy (EIS) at 308 K after 30 min of immersion. Fig. 5 show the EIS diagrams carried out at 308K in acid solution with and without T. vulgaris oil. The impedance parameters derived from these investigations are mentioned in Table 6. 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 equation:

$$C_{dl} = \left(1/_{\omega.R_t} \right) \text{Where } \omega = 2\pi f_{max} \qquad (5)$$

The inhibition efficiency got from the charge transfer resistance is calculated by:

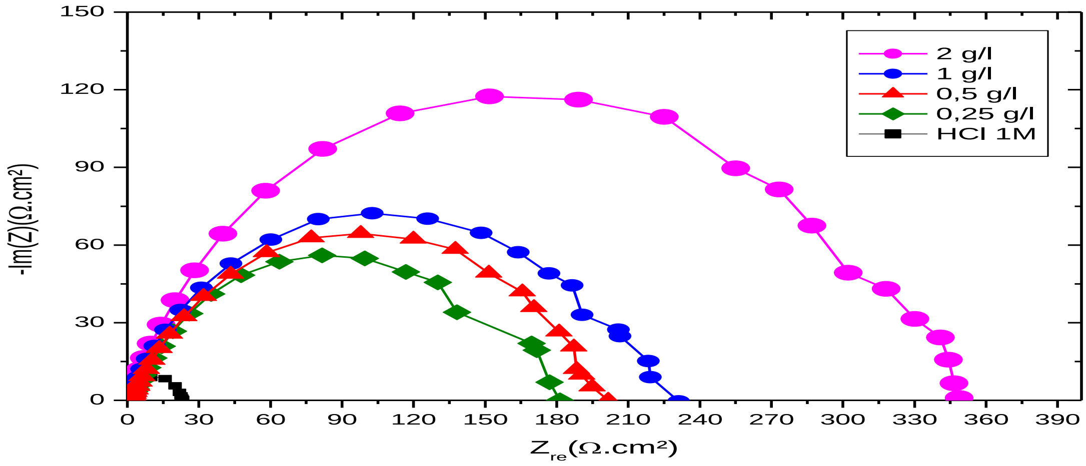

Fig. 5. Nyquist plots of mild steel in 1M HCl containing various concentrations of T. Vulgaris oil at E_{corr}.

Table.6. Impedance parameters for mild Steel in 1M HCl for various concentrations of T vulgaris oils.

Inhibitor	Concentration (g/l)	R_t (Ω.Cm^2)	C_{dl} (µF/cm^2)	E_w (%)
T.V	1MHCl	21,63	149,8	-
	2	348,89	11,03	93 %
	1	232,28	16,23	89 %
	0,5	201,67	17,03	88,4 %
	0,25	181,34	20,1	87 %

Generally, Fig.5 showed that the impedance spectra exhibit one single depressed semicircle, and the diameters of semicircle increases with the inhibitor concentration. The single semicircle can be attributed to the charge transfer that takes place at electrode/solution interface, and the transfer process controls the corrosion reaction of mild steel and the presence of inhibitor does not change the mechanism of dissolution of mild steel [27-30]. When Nyquist plot contains a ‘‘depressed semicircle with the centre under the real axis, such behaviour is characteristic for solid electrodes and often referred to as frequency dispersion has been attributed to roughness and other in homogeneities of the solid surface [25-27]. In these cases the parallel network charge transfer resistance double layer capacitance (R_t/C_{dl}) is usually a poor approximation especially for systems where an efficient inhibitor is present. For the description of a frequency independent phase shift between an applied AC potential and its current response.In fact, the presence of both inhibitors enhances the value of R_t in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of C_{dl} follows the order similar to that obtained for I_{corr} in this study.

The decrease in C_{dl} is due to the adsorption of this compound on the metal surface leading to the formation of film from acidic solution [25,33]. As it can be seen from Table 6, the R_t values increased with the increasing the concentrations of the inhibitors. On the other hand, the values of C_{dl} decreased with an increase in the inhibitors concentration thus with inhibition efficiencies. This situation was the result of an increase the surface coverage by the inhibitor, which led to an increase in the inhibition efficiency. This decrease in the C_{dl} can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, signifying that Oil acts by adsorption at the solution/interface [9-10]. The results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS) with a small variation.

3.5. Effect of temperature:

We have studied the temperature influence on the efficiency of T. Vulgaris oil. For this purpose, we made weight-loss measurements in the range of temperature 308-333K, in the presence and absence of oil at various concentrations during 1h of immersion. The corresponding data are shown in Table 7. We remark that the rise in temperature leads to an increase in corrosive rate with and without inhibitor. We also note the increase in the inhibition efficiency of T. Vulgaris oil with temperature.

Table 7. Effect of temperature on the corrosion rate of mild steel at 2g/l (t=2h)

	HCl	Inhibitor	
T (K)	W_0 (mg/cm².h)	W(mg/cm².h)	E_w(%)
313	1,42	0,084	94,08
323	2,64	0,106	95,98
333	5,14	0.168	96

It's well-known that the rise in temperature leads to an increase in corrosive rate with and without inhibitor. We note the *E*(%) is quietly independent of temperature in the domain studied at high temperature. The fact that the *E*(%) increases with temperature is explained as the likely specific interaction between the iron surface and the inhibitor [30]. The increase of *E*(%) with temperature increase as the change in the nature of the adsorption mode, the inhibitor is being physically adsorbed at lower temperatures, while chemisorptions are favoured as temperature increases. The same phenomenon is explained by others [27-30] as due to increase in the surface coverage by an inhibitor. Thus, at a high degree of coverage, the diffusion through the surface layer containing the inhibitor and corrosion products becomes the rate-determining step of the metal dissolution process.

The corrosion reaction, in 1 M HCl solutions with and without different concentration of Pr-N- Q=S, can be regarded as an Arrhenius type process, the rate of which is given by equation (6) [31].

$$\text{Log (W)} = \frac{-E_a}{RT} + A \qquad (6)$$

Where A is the Arrhenius pre-exponential constant,
E_a is the apparent activation energy of the corrosion process,
R the gas constant (R = 8.314 J.K $^{-1}$.mol^{-1}) and T the absolute temperature.

Figure 7 illustrates the dependence of the corrosion rate in Arrhenius coordinates for mild steel in the corrosive medium with and without addition of Pr-N-Q=S at different temperatures. Straight lines are obtained with a slope of ($-E_a/R$).

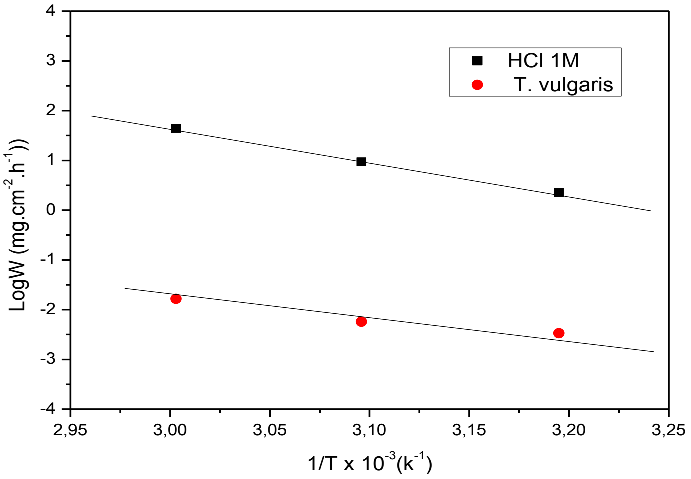

Fig.7. Arrhenius plots of mild steel in 1M HCl with and without 2g/l of T. vulgaris oil.

It is obvious that the activation energy of the inhibited solution in this study increases by increasing the concentration of T. vulgaris. E_a = 58.71kJ/mol and $E_a^{'}$= 47.37 Kj/mol. The addition of inhibitor modified the values of E_a; this modification may be attributed to the change in the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [25-26]. The lower value of the activation energy of the process in an inhibitor's presence when compared to that in its absence is attributed to its chemisorptions, while the opposite is the case with physical adsorption, while unchanged or lower values in inhibited solution suggest charge sharing or transfer from the inhibitor to the metal surface to form coordinate covalent bonds. To establish the adsorption mode of the active constituents, the inhibiting effects of the extract in 1 M HCl were compared. Alternatively, if the active species are adsorbed as molecules which form co-ordinate covalent bonds with the mild steel samples, the almost identical values at higher concentration, particularly at 333 K where the values cited completely coincide 96% implies that chemisorptions of molecular species becomes an important factor at high concentrations. The lower value of the E_a was attributed to a slow rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at the higher temperature. Or it's explained that the decrease in activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from that on the uncovered part on the metal surface to the covered one.

An alternative formulation of the Arrhenius equation is the transition state equation:

$$W = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \qquad (7)$$

h is plank's constant, N is Avogadro's number, and ΔS^* and ΔH^* are the entropy and the enthalpy of activation, respectively. A plot of Log (W_{corr}/T) vs 1/T should give a straight line with a slope of $\Delta H^*/R$ and an intercept of (Log (R/Nh) + $\Delta S^*/R$) as shown in Fig. 8. From this relation the values of ΔH^* and ΔS^* can be calculated (Table8).

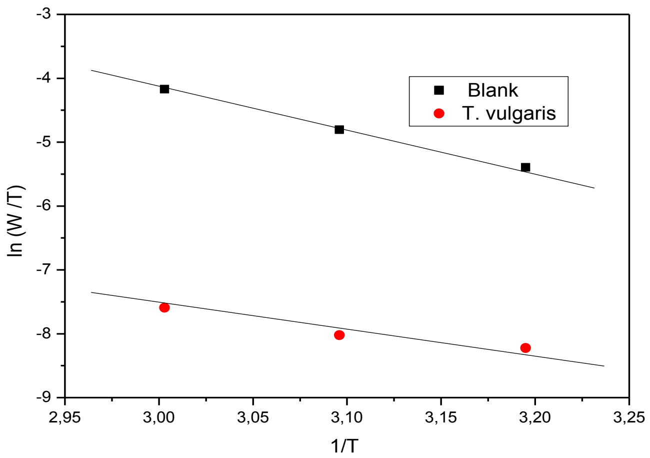

Fig.8: The relation between Log (corrosion rate/T) vs 1/T for mild steel in different additives of Naturally T. vulgaris essential oils.

Table 8: parameter thermodynamic for the dissolution of mild steel in 1M HCl with and without T. vulgaris.

Thermodynamic data	1M HCl	T.V
E_a**(kJ.mol^{-1})**	58.71	47,37
ΔH° **(kJ.mol^{-1})**	55.97	44,92
ΔS° **(kJ.mol^{-1})**	-62.94	-243,02
R	0.99815	0,99951

Inspection of these data, table 8, reveals that the ΔH°a values for dissolution reaction of mild steel in 1M HCl in the presence of T.V are higher than that of in the absence of inhibitors. The positive signs of ΔH° reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow [8, 16, 30] in the presence of inhibitor. One can notice that E_a and ΔH° values vary in the same way. This result permits to verify the known thermodynamic reaction between the Ea and ΔH°a :

$$E_a - \Delta H° = RT \qquad (8)$$

The difference obtained by Equation 8 is around 2.7 kJ/mol indicating that the activation process on the steel surface is done by only monoatomic process [32]:

$$H^+ \rightarrow H \qquad (9)$$

On the other hand, the negative values of entropies imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. Moreover, ΔS°a values are more positive in 1 M HCl solutions containing oil than that obtained in the uninhibited solution. This behaviour can be explained as a result of the replacement process of water molecules during adsorption of T. Vulgaris oil on the mild steel surface [25]. The data show that the thermodynamic parameters (ΔH° and ΔS°) of the dissolution reaction of mild steel in 1M HCl in the presence of the T. vulgaris essential oils are higher than those of the non-inhibited solution. Also, the entropy ΔS° increases negatively with the presence of the inhibitor than the non-inhibited one. This reflects the formation of an ordered stable layer of inhibitor on the mild steel surface. From the previous data, we can say that T. vulgaris essential oils can be used as an effective inhibitor.

Conclusion

T. vulgaris Oil examined acted as an efficient corrosion inhibitor in 1 M HCl. Polarization studies showed that oil was a mixed inhibitor and its inhibition efficiency increased with the inhibitor concentration. Impedance method indicates that oil adsorbs on the mild steel surface with increasing transfer resistance and decreasing of the double-layer capacitance. The inhibitor efficiency determined by electrochemical methods and by gravimetric methods are in good agreement.

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