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Inhibition Effect of *Thymelaea hirsuta* Extract towards Steel Corrosion in HCl Solution.

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The inhibition effect of the *Thymelaea hirsuta* extract (THE) on the corrosion of carbon steel in 1M HCl, solutions was studied by weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The results show that the extract of THE is a good inhibitor in 1M HCl. The adsorption of extract of THE on carbon steel surface obeys Langmuir adsorption isotherm. The effect of temperature on the corrosion behaviour with the addition of extract of THE was studied in the temperature range 298–328 K. The value of inhibition efficiency decreases slightly with the increase in temperature. Changes in impedance parameters (charge transfer resistance, R_t, and double layer capacitance, C_{dl}) were indicative of adsorption of THE on the metal surface, leading to the formation of a protective film. Some thermodynamic functions of dissolution and adsorption processes were also determined and discussed.

Keywords: Carbon steel, Polarisation, EIS, *Thymelaea hirsuta* extract, Acid medium, Corrosion inhibition

1. INTRODUCTION

The use of inhibitors is one of the most practical methods for protecting metals against corrosion, especially in acidic media [1]. 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 is usually used as industrial acid cleaning and pickling acids. Because of the general aggression of acid solutions, inhibitors are commonly used to retard the corrosive attack on metallic materials. The use of chemical inhibitors is one of the most practical methods for the protection against corrosion in acidic media. 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. And so, the study of new non-toxic or low-toxic corrosion inhibitors is essential to overcome this problem. The use of non-toxic inhibitors called green or eco-friendly environmental inhibitors is one of the solutions possible to prevent the corrosion of the material. These advantages have incited us to draw a large part of program of our laboratory to examine natural substances as corrosion inhibitors such as: Argan extract [2-4], Artemisia [5-6], Junipers Extract [7], Horehound (Marrubium vulgare L.) Extract [8] and Chenopodium Ambrorsioides Extract. [9].

Plant extracts are low-cost and biodegradable; the inhibition performance of plant extract is normally ascribed to the presence in their composition of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates, amino acids and proteins as well as hydrolysis products. These organic compounds contain polar functions with N, S, O atoms as well as conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers. However, confronting with the vast varieties of plant, the data regarding the use of plant leaves extract as the corrosion inhibitor are still poor. In the present work, *Thymelaea hirsuta* extract (THE) is chosen to be the corrosion inhibitor. This work is to investigate the corrosion inhibition of *Thymelaea hirsuta* extract (THE) in 1M HCl solutions using weight loss, polarization curves, impedance spectroscopy (EIS). Effects of inhibitor concentration, temperature and acid concentration on the corrosion inhibition were fully investigated and discussed.

2. MATERIALS AND METHODS

2. 1. Materials

The steel used in this study is a carbon steel (C38) (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe).

2.2. Solutions

Thymelaea hirsuta leaves were collected from the area of Tiznit (located in Morocco) at july month 2013. Leaves plant were dried and crushed. Stock solution of the extract was prepared by stirring cold weighed amounts of the THE plant for 48 h in 1.0 M HCl solution (The solution 1.0 M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water). The resulting solution was filtered. This extract was used to study the corrosion inhibition properties and to prepare the required concentrations. The solution tests are freshly prepared before each experiment.

2.3. Weight loss measurements

Coupons were cut into 2x2×0.08 cm^3 dimensions are used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The specimens were washed thoroughly with bidistilled water, degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 80 mL. The immersion time for the weight loss is 6 h at 298 K.

2.4. Polarization measurements

2.4.1 Electrochemical impedance spectroscopy (EIS)

The electrochemical measurements were carried out using Voltalab (PGZ 100) potentiostat and controlled by software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode. The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to a establish steady state open circuit potential (Eocp). After measuring the Eocp, the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 298 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x-axis.

2-4.2 Potentiodynamic polarization

The electrochemical behaviour of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1.0 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -800 mV to -200 mV versus corrosion potential at a scan rate of 1 mV. s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}).

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization curves

The effect of *Thymelaea hirsuta* extract on the corrosion reactions was determined by polarization techniques. The changes observed in the polarization curves after the addition of the inhibitor are usually used as the criteria to classify inhibitors as cathodic, anodic or mixed [10-11].

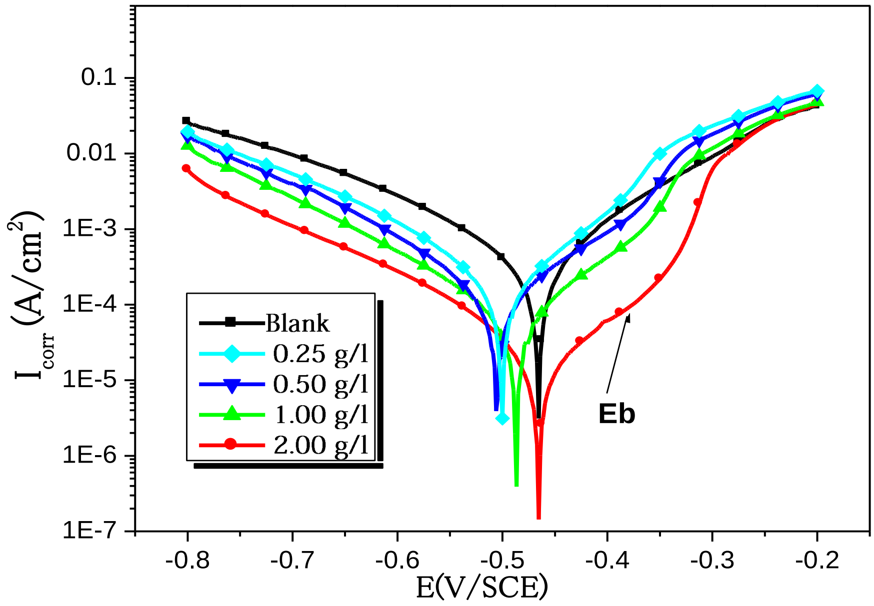

Figure 1. Potentiodynamic polarisation curves of C38 steel in 1M HCl in the presence of different concentrations of *Thymelaea hirsuta* extract.

Table 1. Electrochemical parameters of carbon steel in 1M HCl solution without and with *Thymelaea hirsuta* extract at different concentrations.

Conc. (g/L)	E_{corr} (mV/SCE)	I_{corr} ($\mu A/cm^2$)	$-b_c$ (mV/dec)	E_{Icorr} (%)
Blank	-469	588	168	----
2.00	-468	50	165	91.49
1.00	-490	86	142	85.37
0.50	-508	162	128	72.45
0.25	-503	205	165	65.14

Fig.1 shows the Tafel polarization curves for carbon steel in 1.0 M HCl solution at different concentrations of inhibitor at 298 K. The potentiodynamic parameters such as corrosion potential (E_{corr}), cathodic Tafel slopes (b_c), corrosion current density (I_{corr}) were obtained from Tafel plots and the inhibition efficiency values E(%) were calculated using equation 1.

$$E\ \% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (1)$$

Where I_{corr} and I'_{corr} are uninhibited and inhibited corrosion current densities, respectively.

It can be observed that the addition of *Thymelaea hirsuta* extract (THE) at all the studied concentrations resulted in the significant decrease in the corrosion current density (I_{corr}) and decrease in the corrosion rate. It is also evident that percentage efficiency of the inhibitor increased with increase in the concentration of the inhibitor. There was no remarkable shift in the corrosion potential (E_{corr}) value with respect to the blank. Both anodic and cathodic polarizations are influenced simultaneously, almost to the same extent, which indicate the influence of *Thymelaea hirsuta* extract (THE) on both the anodic and the cathodic reactions; hydrogen evolution and metal dissolution. According to literature report [12], when corrosion potential is more than ± 85 mV with respect to the corrosion potential of the blank, the inhibitor can be considered distinctively as either cathodic or anodic type. However, the maximum displacement in this study is less than ±85 mV.

It is shown from Fig.1 that increasing the *Thymelaea hirsuta* extract (THE) concentration reduces both the cathodic and the anodic currents, and there is no definite trend in the shift of E_{corr} values. Moreover, the recorded polarisation curves in the presence of inhibitor are characterized by the presence of anodic breakdown potential, Eb. The noble shift of E_b and the decrease of the corresponding current densities with increasing the inhibitor concentration reflect the formation of anodic protective film on the electrode surface. [13]. Based on the marked decrease of the cathodic and anodic current densities upon introducing the inhibitor in the aggressive solution, THE can be considered as a mixed-type inhibitor, meaning that the addition of THE reduces the anodic dissolution and also retards the cathodic hydrogen evolution reaction. In addition, the parallel cathodic Tafel curves in Fig.1 show that the hydrogen evolution is activation controlled and the reduction mechanism is not affected by the presence of the inhibitor [14].

The inspection of results in Table1 indicate that Thymelaea hirsuta (THE) inhibits the corrosion process in the studied range of concentrations and E (%) increases with Cinh, reaching its maximum value, 91.49%, at 2g/L. The values of the cathodic Tafel lines, bc, show slight changes with the addition of THE. This result means that the mechanism at the electrode reactions is not changed [15].

3.2. Weight loss measurements and adsorption isotherm

Weight loss measurement were done according to the method described previously [16]. And is a non-electrochemical technique for the determination of corrosion rates and inhibitor efficiency which provides more reliable results than electrochemical techniques because the experimental conditions are approached in a more realistic manner yet the immersions tests are time-consuming [17-18]. Therefore, due to such differences (experimental conditions), the values would obviously differ from the electrochemical values.

All the tests were conducted in aerated 1.0M HCl at 298 K with different concentrations of *Thymelaea hirsuta* extract (THE) extract and the values of the inhibition efficiency and corrosion rate obtained from the weight loss measurements of C-steel for different concentrations of *Thymelaea hirsuta* extract in 1.0M HCl at 298 K after 6h of immersion are given in Table 2. At the end of the tests the specimen were carefully washed in acetone and then weighed. Duplicate experiments were performed in each and the mean value of the weight loss has been reported. The inhibition efficiency (Ew %) and surface coverage (θ) were determined by using the following equations:

$$E_w\ \% = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \qquad (2)$$

$$\theta = 1 - \frac{W'corr}{Wcorr} \qquad (3)$$

where W_{corr} and W'_{corr} are the corrosion rates of C-steel due to the dissolution in 1.0M HCl in the absence and the presence of definite concentration of inhibitor, respectively, and θ is the degree of surface coverage of the inhibitor.

Table 2. Weight loss data of mild steel in 1 M HCl for various concentration of the *Thymelaea hirsuta* extract.

Concen. (M)	**W_{corr} (mg. cm^{-2} . h^{-1})**	**E_w (%)**	θ
Blank	1.001	----	----
2.00g/l	0.092	90.81	0.91
1.00g/l	0.12	88.01	0.88
0.50g/l	0.124	87.61	0.87
0.25g/l	0.154	84.61	0.85

It can be seen from Table 2 that inhibition Thymelaea hirsuta extract (THE) inhibits the corrosion of C-steel and efficiency increases with the increasing inhibitors concentration. Maximum E_w% of Thymelaea hirsuta Endl extract was achieved at 2.00 g/L. These polarization curves tests were in good agreement with the corrosion weight loss and impedance measurements.

The presence of inhibitor leads to decrease the corrosion rate. It is indicated that inhibition efficiency of C-steel increases with the increase of *Thymelaea hirsuta* extract concentration up to 90.81 % at 298 K.

In order to understand the mechanism of corrosion inhibition, the adsorption behaviour of the adsorbate on the carbon steel surface must be known. Two main types of interaction can describe the adsorption of the compounds of *Thymelaea hirsuta* extract (THE): physical adsorption and chemisorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte and the charge and nature of the metal.

The information on the interaction between the inhibitor molecules of THE extract and the metal surface can be provided by adsorption isotherm. The degree of surface coverage (θ) for different concentrations of inhibitor was evaluated from Weight loss measurements. Attempts were made to fit θ values to various isotherms including Frumkin, Temkin and Langmiur. It was found that the data best fit was obtained with the Langmiur isotherm Fig 2. According to this isotherm θ is related to concentration inhibitor [19]

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (4)$$

where K is the adsorption/desorption equilibrium constant, C is the corrosion inhibitor concentration in the solution

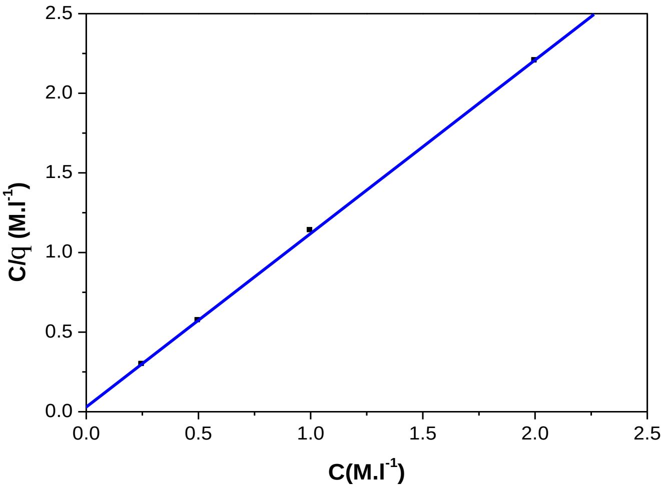

Figure 2. Plots of Langmuir adsorption isotherm of *Thymelaea hirsuta* extract on the steel surface at 298K.

It was found that Fig.2 (plot of $\frac{\theta}{C}$ versus C) gives straight line with slope near to 1, indicating that the adsorption of compound under consideration on C-steel / acidic solution interface obeys Langmiur's adsorption.

3.3. Electrochemical impedance spectroscopy

The corrosion behavior of carbon steel in 1 M HCl solution in the presence of THE was investigated by EIS at 298K after 30 min of immersion. The Nyquist plots for carbon steel obtained at the interface in the presence and absence of THE at different concentrations are given in Fig 3.

As observed, the Nyquist plots contain a depressed semi-circle with the center below the real X-axis, which is size increased by increasing the inhibitor concentrations, indicating that the corrosion is mainly a charge transfer process [20] and the formed inhibitive film was strengthened by the addition of THE.

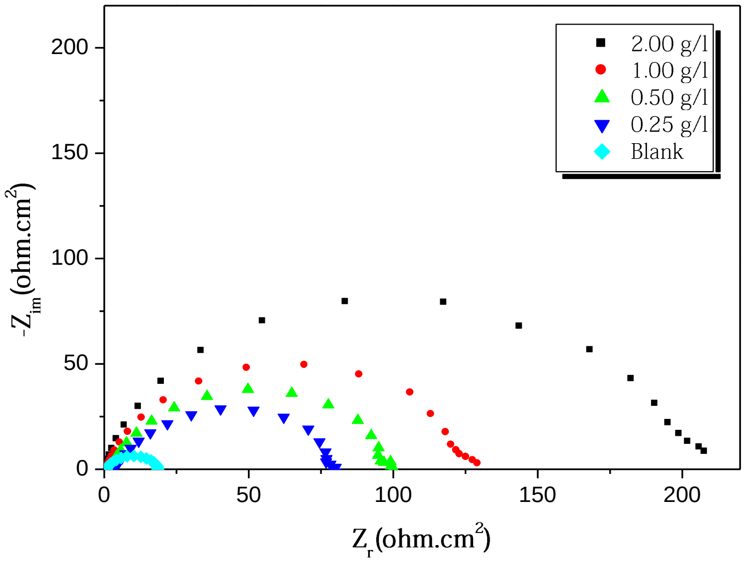

Figure 3. Nyquist plots for carbon steel in 1 M HCl containing different concentrations of *Thymelaea hirsuta* extract.

The depressed semi-circle is the characteristic of solid electrodes and often refers to the frequency dispersion which arises due to the roughness and other inhomogeneities of the surface [21]. It is worth noting that the change in concentration of THE did not alter the style of the impedance curves, suggesting a similar mechanism of the inhibition is involved. The impedance parameters derived from these plots are shown in Table 3.

Table 3. Electrochemical Impedance parameters for corrosion of steel in acid medium at various contents of *Thymelaea hirsuta* extract.

Conc. (g/L)	**R_t (Ω.cm^2)**	f_{max} (Hz)	**C_{dl} (μF/cm^2)**	**E_{Rt} (%)**
Blank	18	40	221	-----
2.00	203	10	78	91.13
1.00	128	10	124	85.94
0.50	102	16	97	82.35
0.25	85	16	117	78.82

Again, the maximum percentage of inhibition efficiency (E_{Rt}%) was achieved at the concentration of 2.00 g/L (91.13%).

This percent inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the equation:

$$E_{Rt}\ \% = \frac{R'_t - R_t}{R'_t} \times 100 \qquad (5)$$

Where R_t and R'_t are the charge transfer resistance values without and with inhibitor, respectively.

4. EFFECT OF TEMPERATURE

The study on the effect of temperature on the corrosion rate and inhibition efficiency facilitates the calculation of kinetic and thermodynamic parameters for the inhibition and the adsorption processes. These parameters are useful in interpreting the type of adsorption by the inhibitor.

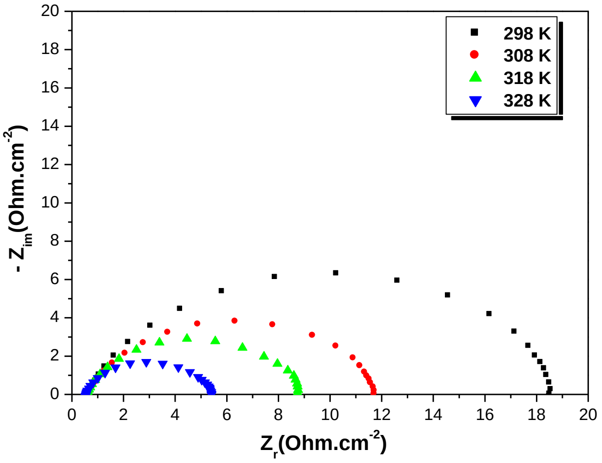

Figure 4. Nyquist diagrams for C38 steel in 1 M HCl at different temperatures.

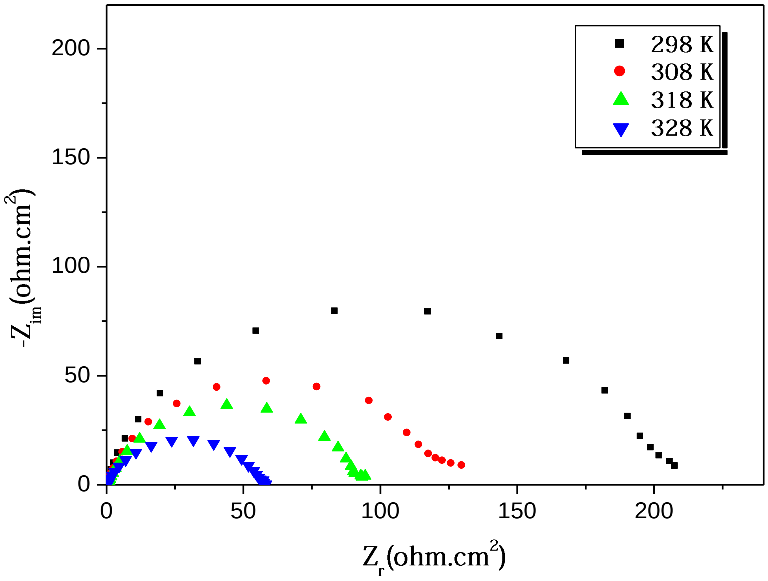

Figure 5. Nyquist diagrams for C38 steel in 1 M HCl + 2.00 g/l of Thymelaea hirsuta at different temperatures.

To investigate the mechanism of inhibition and to calculate the activation energies of the corrosion process, EIS measurement were taken at various temperatures in the absence and the presence of 2.00 g/L of *Thymelaea hirsuta* extract (Fig. 4 and fig.5).

The results reported in Tables 4 showed the R_t (resistance transfer) values decreases with increasing temperature in the absence and the presence of THE.

Table 4. Thermodynamic parameters for the adsorption of *Thymelaea hirsuta* in 1M HCl on the C38 steel at different temperatures.

Inhibitor	Temp (K)	R_{ct} (Ω.cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	E_{Rct} (%)
Blank	298	18	40	221	-
	308	11	63	229	-
	318	8	100	199	-
	328	5	158	201	-
THE	298	203	10	78	91.13
	308	121	10	131	90.91
	318	86	16	116	90.69
	328	52	25	122	90.38

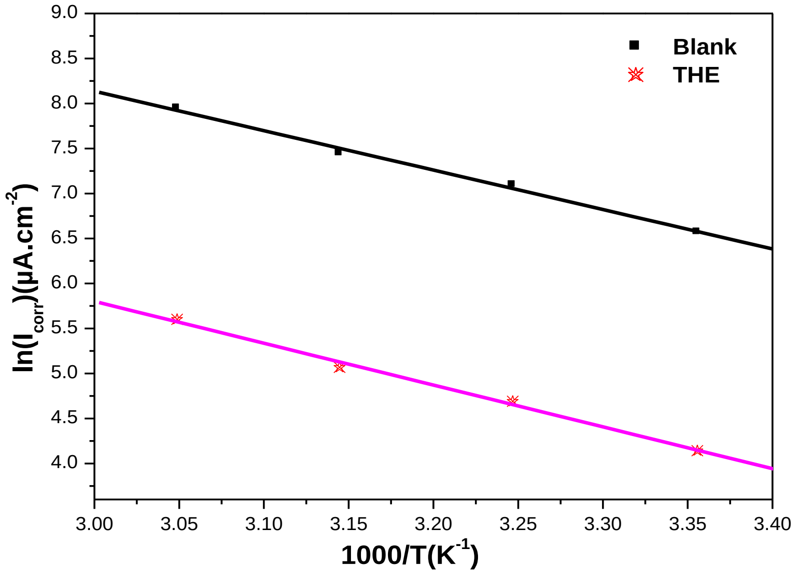

Figure 6. Arrhenius plots of steel in 1 M HCl with and without 2 g/L *Thymelaea hirsuta* extract.

Also inhibition efficiency of THE decreased with increase in temperature. Values of Rct were employed to calculate values of the corrosion current density (Icorr) at various temperatures in absence and presence of THE using the following equation [22]:

$$I_{corr} = RT\left(zFR_t\right)^{-1} \tag{6}$$

where R is the universal gas constant (R = 8.31 J $K^{-1}mol^{-1}$), T is the absolute temperature, z is the valence of iron (z = 2), F is the Faraday constant (F = 96.485 coulomb) and R_t is the charge transfer resistance.

Fig. 6 also shows that the corrosion reaction can be regarded as an Arrhenius-type process (Equation (7)). The activation parameters for the studied system (E_a, ΔH_a^* and ΔS_a^*) were estimated from the Arrhenius equation and transition state equation (Equation (8)) :

$$I_{corr} = A\exp(-\frac{E_a}{RT}) \tag{7}$$

$$I_{corr} = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^*}{R}\right)\exp\left(-\frac{\Delta H_a^*}{RT}\right) \tag{8}$$

where A is Arrhenius factor, E_a is the apparent activation corrosion energy, N is the Avogadro's number, h is the Plank's constant, and ΔH_a^* and ΔS_a^* are the enthalpy and the entropy changes of activation corrosion energies for the transition state complex. R is the perfect gas constant.

The apparent activation energy was determined from the slopes of Ln I_{corr} vs 1/T graph depicted in Fig.6.

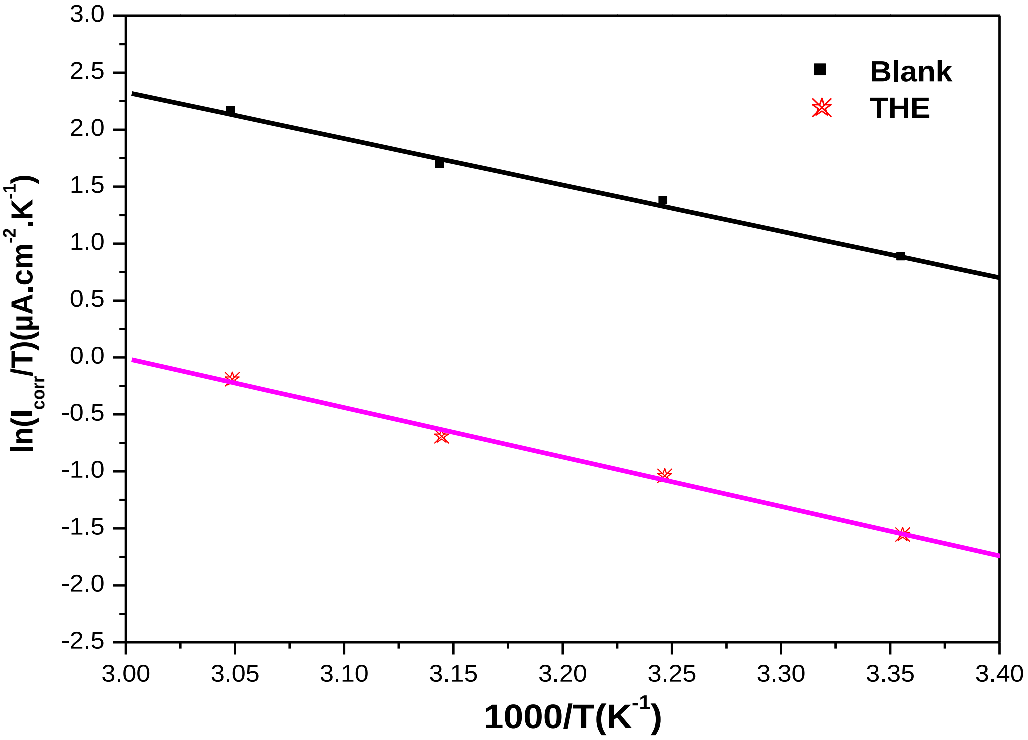

Figure 7. Relation between Ln (I_{corr}/T) and 1000/T at different temperatures.

A plot of ln (I_{corr} /T) against 1/T (Fig.7) gave a straight line with slope (ΔH_a^* /R) and intercept (ln(R/N A h) + (ΔS_a^* /R)), from which the values of ΔH_a^* and ΔS_a^* were calculated and listed in Table 5.

Table 5. Activation parameters for the corrosion of C-steel in 1.0 M HCl containing different concentrations of inhibitor *Thymelaea hirsuta* extract.

Inhibitor	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J/mol)
Blank	36.39	33.80	-76.69
THE	38.61	36.01	-89.74

The increase in activation energy (E_a) of inhibited solutions compared to the blank suggests that inhibitor is physically adsorbed on the corroding metal surface, while either unchanged or lower energy of activation in the presence of inhibitor suggest chemisorption [23]. As reported in Table 5. E_a values increased greatly after the addition of the inhibitor. Hence corrosion inhibition of *Thymelaea hirsuta* (THE) is primarily occurring through physical adsorption. The positive signs of ΔH_a^* reflected the endothermic nature of the C-steel dissolution process. The value of ΔS_a^* is lower for inhibited solution than that for the uninhibited solution. Large negative values of entropies show that the activated complex in the rate determining step is an association rather than dissociation step meaning that a decrease in disordering takes place on going from reactants to the activated complex [24-25].

5. CONCLUSION

It can be concluded as follows:

- *Thymelaea hirsuta* extract act as good mild steel corrosion inhibitors in 1M HCl. All electrochemical tests are in good agreement with the maximum percentage of inhibition efficiency obtained at the concentration of 2.00 g/L of THE.
- Potentiodynamic polarization measurements demonstrate that *Thymelaea hirsuta* extract act as mixed-type inhibitor.
- The values of apparent activation energy increases with the increase in the inhibitor concentration.
- Enthalpy of activation reflects the endothermic nature of C-steel dissolution process.
- The adsorption of organic molecules on the mild steel surface obeys The Langmuir adsorption isotherm.

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