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Effect of *Athamanta sicula* oil on inhibition of mild steel corrosion in 1M HCl

Y. EL Ouadi[1], A. Bouratoua[2], A. Bouyenzer[1*], Z. Kabouche[2], R. Touzani[1], H. EL Msellem[1], B. Hammouti[1] and A. Chetouani[1,3]

[1]Laboratoire de Chimie Appliquée et environnement (LCAE-URAC18), Faculté des Sciences, B.P. 717, Oujda, Morocco
[2]Université Constantine 1, Faculté des sciences exactes, Département de chimie
Laboratoire d'Obtention de Substances Thérapeutiques (LOST), Constantine, Algeria
[3]Laboratoire de chimie physique, Centre Régionale des Métiers de l'Education et de Formation "CRMEF", Région de l'Orientale, Oujda, Morocco

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ABSTRACT

The inhibitory effect of Athamanta sicula oil 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. Inhibition was found to increase with increasing concentration of Athamanta sicula oil. The effect of temperature on the corrosion behaviour of mild steel in 1M HCl with addition of Athamanta sicula oil was also studied and thermodynamic parameters were determined and discussed. Values of inhibition efficiency calculated from weight loss, Tafel polarization curves, and EIS are in good agreement. Polarization curves showed that Athamanta sicula oil behave as mixed type inhibitors in Hydrochloric acid 1M. The results obtained showed that oil of Athamanta sicula could serve as an effective inhibitor of the corrosion of mild steel in Hydrochloric acid solution.

Keywords: *corrosion, inhibition, mild steel, oil, Athamanta sicula, electrochemical system, hydrochloric acid.*

INTRODUCTION

The use of inhibitors is one of the most practical methods to secure metals against acid corrosion. Hydrochloric acid is produced in large quantities in Morocco. It is widely used in industries, for example, in the food industry, acid pickling, acid cleaning and acid descaling.

The presence of organic molecules in the corrosive medium retards or stops the attack of metals by adsorbing at the metal–solution interface. The modes of adsorption depend mainly on the chemical structure of the inhibitor, the chemical composition of the solution, the nature of the metal surface and the electrochemical potential of the metal–solution interface. The inhibition generally occurs by the formation of a barrier film on the metal surface leading to the reactivity of the cathodic and/or anodic sites [1–4]. Nitrogen-containing compounds offer more effective inhibitor in different acids [5,6]. Survey literature shows that nitrogenheterocyclic compounds such as pyrazole, triazole, tetrazole [7–15] and pyridine derivatives [16-21] on the corrosion for many metals in acidic solutions offer good protection of metallic materials. Due to the toxicity of certain corrosion inhibitors, recently research on green corrosion inhibitors is net growth [22]. The inhibitors of this class are those who are environmentally friendly and are obtained from of natural products such as plant extracts [23].

Recently, several studies have been conducted on the inhibition corrosion of metals by plant extract [24]; Essential oils [25-27]; or purified compounds [28,29]; Pennyroyal oil [30] ; *Eucalyptus* oil [31] ; jojoba oil [32]; Rosemary oil [33-35] ; *Artemisia* oil [36-38]; lavender oil [39]; Menthol derivatives [27]; eugenol and acetyleugenol [28]; Pulegone [29]; limonene [40]; *Salvia officinalis* oil and extract [41], *Pelargonium* oil and extract [42]. Recently authors used olive oil and argan oil as corrosion inhibitors [43, 44]. All these products are efficient inhibitors for the fight against corrosion of steel in acidic media. In this article, we use the oil of *Athamanta sicula* oil belonging to the genus *Athamanta* (Apiaceae) which comprises about nine species, distributed in southeastern Europe and North-Africa. In Algeria, there is only one species, *Athamanta sicula* (Syn. *Tingara sicula*) [45].

MATERIALS AND METHODS

2.1.1 Plant material

Aerial parts of *athamanta sicula* were collected on May 2012 at Bekira- Constantine (Eastern Algerian). The voucher specimen was identified by Professor Gérard De Bélair (University Badji-Mokhtar, Annaba) and was deposited at the Laboratory of Therapeutic Substances (LOST), University frères Mentouri-Constantine.

2.1.2. Extraction and procedure

Air-dried and powdered aerial parts (2.5 kg) Af *athamanta sicula* were extracted with 80% MeOH. The residue was dissolved in water and extracted with petroleum ether, dichloromethane, ethyl acetate and n-BuOH, successively. The petroleum ether extract was oil content.

2.1.3. GC and GC/MS

GC analysis was performed on a Shimadzu GC17A gas chromatograph equipped with a cross-linked DB5-MS column (40 m × 0.18 mm, film thickness 0.18 µm). The oven temperature was programmed as isothermal at 60°C for 5 min, then raised to 275°C at 5°C/min and held at this temperature for 5 min. Helium was used as the carrier gas at a rate of 1 ml/min. GC/MS was performed using a Shimadzu QP5050 mass selective detector. Operating conditions were the same as for the analytical GC. The MS operating parameters were as follows: ionization potential, 70 ev; ionization current, 2 A ion source temperature, 200ºC; resolution, 1000. scan time, 5 s; scan mass range, 40–400 u; split ratio, 1:10.

Identification of components

The oil components were identified based on their retention indices (determined with reference to a homologous series of normal alkanes), and by comparison of their mass spectral fragmentation patterns with those reported in the literature [46, 47] and for the major components.

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 cm^2 were used. These specimens were degreased ultrasonically with 2-propanol and polished mechanically with different grades of emery paper to obtain very smooth surface.

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 *Athamanta sicula* oil directly to the corrosive solution. Experiments were conducted on several occasions to ensure reproducibility. Concentrations of *Athamanta sicula* oil were 0.5, 1, 2, 3et 5 mL/L.

2.4. Weight loss measurements

The gravimetric method (weight loss, wL) is known to be the most widely used method of monitoring inhibition efficiency [48]. We remind you that the mild steel specimens of dimension 1 x 1 x 0.1 cm were used in these studies. The weight loss measurements were conducted under total immersion using 250 mL capacity beakers containing 100 mL of test solutions, 1M HCl solution containing the inhibitor (oil of *Athamanta sicula)* at different concentrations, for 6 hours, maintained in a thermostated water bath. Immersion is subjected to a temperature of 308 °K to 6 hours. The specimens were weighed before and after the tests using an analytical balance with a precision of 0.1 mg. The specimens were taken out after the 6 hours of immersion, washed, dried and reweighed accurately to determine the weight loss of mild steel. All measurements were performed few times and average values were reported to obtain good reproducibility. The corrosion rate (ρ) in mg cm^{-2} h^{-1} in the absence and presence of *Athamanta sicula* oil was determined using the following equation:

$$\rho = \frac{\Delta W}{A\,t} \qquad (1)$$

where ΔW is the average weight loss of the mild steel specimens, A is the total area of mild steel specimen and t is the immersion time. The percentage inhibition efficiency (IE%) was calculated using the relationship:

$$\text{IE (\%)} = \frac{W0 - Wi}{W0} \text{ x } 100 \qquad (2)$$

where Wo and Wi are the weight loss values in the absence and presence of *Athamanta sicula* oil. 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 1M HCl with and without addition of the inhibitor (oil of *Athamanta sicula*) at different temperatures 313 to 343 °K.

2.5 Electrochemical measurements

The EIS is a method designed to avoid severe deterioration of the exposed surface of the structure studied and was widely used for monitoring the corrosion of a working electrode. This method consists of applying frequencies and low amplitude sinusoidal voltage wave to produce perturbation signals on the working electrode. The corrosion state can be predicted by analyzing the current response of the voltage or the frequencies. In modern practice, the impedance is usually measured with loch-in amplifiers or frequency-response analyzers, which are faster and more convenient than impedance bridges [49, 50]. The electrolysis cell was Pyrex of cylinder closed by cap containing five openings. Three of them were used for the electrodes. The working electrode was mild steel with the surface area of 1 cm^2. Before each experiment, the electrode was polished using emery paper until 1200 grade. After this, the electrode was cleaned ultrasonically with distillate water. A saturated calomel electrode (SCE) was used as a reference. All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of 1 cm^2. The temperature was thermostatically controlled at 308 K°. The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential (Eocp) was obtained. The polarization curve was recorded by polarization from -800 mV to -200 mV under potentiodynamic conditions corresponding to 1mV/s (sweep rate) and under air atmosphere.

The potentiodynamic measurements were carried out using VoltaLab100 electrochemical analyser, which was controlled by a personal computer. AC-impedance studies also were carried out in a three electrode cell assembly. The data were analysed using Voltamaster 4.0 software. The electrochemical impedance spectra (EIS) were aquared in the frequency range 100 kHz to 10 mHz at the free corrosion potential. The charge transfer resistance (Rct) and double layer capacitance (Cdl) were determined from Nyquist plots. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility. All electrochemical studies were carried out with immersion time of 1 hour, with different inhibitory concentrations of Athamanta Sicula Oil, at 308 °K.

RESULTS AND DISCUSSION

3.1. Athamanta sicula oil composition

From the GC-MS analysis, it appears that the oil of *Athamanta sicula* is characterized by the main presence of myristicin (23.43%), alloaromadendrene oxide (4.92%) and germacrene D (4.49%).

3.2. Electrochemical impedance measurements

carried out EIS was on a newly polished steel surface in acidic solution in the absence and presence of inhibitor at an open circuit potential at 308 °K after 30 min of immersion. The locus of the Nyquist plots was regarded as one part of a semicircle. Nyquist plots of steel in inhibited and uninhibited acidic solution containing various concentrations of *Athamanta sicula* oil are shown in Fig. 1. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion [51–53]. It is noteworthy that the best fit of the experimental data was obtained using constant phase elements (CPE) which have frequency dispersion rather than capacitances. Based on the values of the electric lements and parameters obtained in them, capacitances were assessed in accordance with the method described by Hsu and Mansfeld [53]. CPE is a generalized tool, which can reflect exponential distribution of the parameters of the electrochemical reaction related to energetic barrier at charge and mass transfer, as well as impedance behaviour caused by fractal surface structure. On the other hand there are some cases where the CPE is a formal approximation of the system, having very complicated parameter distribution and it is not possible to give some consistent physical interpretation [52]. The dispersion of the capacitive semicircle is explained also by surface heterogeneity due to surface roughness, impurities or dislocations [52–54].

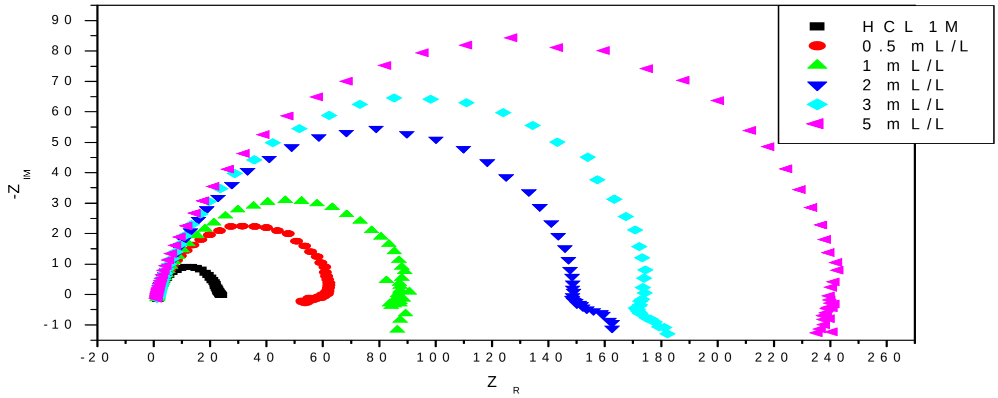

Figure 1. Nyquist plots in absence and presence of different concentrations of Athamanta Sicula Oil in 1M HCl

The charge transfer resistance, R_t values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [55] .To obtain the double layer capacitance (Cdl), the frequency at which the imaginary component of the impedance is maximum (−Zmax) is found and Cdl values are obtained from the equation:

$$C_{dl} = \frac{1}{2\pi f_{\max} R_{ct}} \quad (3)$$

The percentage inhibition efficiency from the charge transfer resistance is calculated by the following relation:

$$E\,(\%) = \frac{R°corr - Rcorr}{R°corr} \times 100 \quad (4)$$

where, R°corr and Rcorr are the charge transfer resistance in presence and in absence of inhibitors, respectively. The impedance parameters derived from these investigations are given in Table 1. It is found that Rt values increase with the increase in *Athamanta sicula* oil concentration indicating an insulated adsorption layer's formation. The double layer capacitance Cdl is expressed in the Helmotz model by:

$$C_{dl} = \frac{\varepsilon_0 \varepsilon}{\delta} S \quad (5)$$

where δ is the thickness of the deposit, S is the surface of the electrode, ε_0 is the permittivity of the air and ε is the medium dielectric constant. The decrease in Cdl values (may be interpreted either by a decrease of local dielectric constant ε [56] or by the thickness of the adsorbate layer of inhibitor at the metal surface [57].

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

Inhibitor concentration	R_{ct} (ohm.cm^2)	f_{max} (Hz)	C_{dl} (µF/cm^2)	E (%)
HCl 1M	21.69	100	73.37	-
0.5 mL/L	62.5	40	63.66	65.29
1 mL/L	90.04	40	44.19	75.91
2 mL/L	151	25	42.16	85.3
3 mL/L	178.6	25	35.64	87.85
5 mL/L	247.9	20	32.1	91.25

From Table 1 , it is clear that the Rct values increased and that the Cdl values decreased with increasing inhibitor concentration. These results indicate a decrease in the active surface area caused by the adsorption of the inhibitors on the mild steel surface, and it suggests that the corrosion process became hindered. The best result for the inhibition efficiency of *Athamanta sicula* oil was obtained at a concentration of 5 mL/L, with efficiency equal to 91.25 %.

3.3/ Polarisation measurements

The polarisation curves of steel in 1M HCl in the absence and presence of *Athamanta sicula* oil at different concentrations at 308 K are presented in Fig. 2. The collected parameters deduced from the polarisation curves such the corrosion potential (Ecorr), corrosion current (Icorr), cathodic Tafel slopes (βc) and percentage inhibition efficiency (EI %) are shown in Table 2. The relation determines the inhibition efficiency (EI %):

$$E(\%) = \frac{I^{\circ}corr - Icorr}{I^{\circ}corr} x100 \qquad (6)$$

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

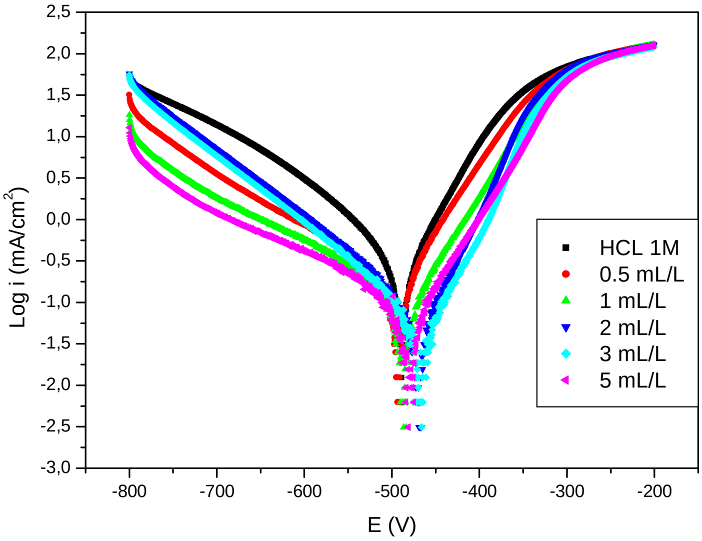

Figure 2. Tafel polarization curves in in 1M HCl with and witout *Athamanta sicula oil* at different concentrations

Generally, the modes of the inhibition effect of inhibitors are classified into three categories [58, 59]: geometric blocking effect of adsorbed inhibitive species, active sites blocking effect by adsorbed inhibitive species, and electro catalytic effect of the inhibitor or its reaction products. It has been discussed in the case of the first mode that inhibition effect comes from the reduction of the reaction area on the surface of the corroding metal, whereas for the other two modes the inhibition effects are due to the changes in the average activation energy barriers of the anodic and cathodic reactions of the corrosion process. The cathodic Tafel slope (βc) show slight changes with the addition of *Athamanta sicula* oil, which suggests that the inhibiting action occurred by simple blocking of the available cathodic sites on the metal surface, which lead to a decrease in the exposed area necessary for hydrogen evolution and lowered the dissolution rate with increasing inhibtor concentration (table 2). The parallel cathodic Tafel plots obtained in Figure 2 indicate that the hydrogen evolution is activation controlled and the reduction mechanism is not affected by the presence of inhibitor [60-62].

Table 2. Electrochemical parameters of mild steel at various concentrations of *Athamanta sicula* oil HCl 1M

Inhibitor concentration	$-E_{Corr}$ (V)	β_C (mV/dec)	I_{Corr} (mA/cm^2)	E (%)
HCl 1M	0.49	-147.7	0.5779	-
0.5 mL/L	0.49	-159.1	0.1738	69.92
1 mL/L	0.48	-203.1	0.1575	72.75
2 mL/L	0.46	-124.4	0.0997	82.74
3 mL/L	0.46	-126.3	0.0861	85.1
5 mL/L	0.48	-154.1	0.0478	91.73

3.4. Effect of temperature

Temperature has a great effect on the corrosion phenomenon. Generally the corrosion rate increases with the rise of the temperature. For this purpose, we made weight loss experiments in the range of temperature 313–343 K°, in the absence and presence of various concentrations of *Athamanta sicula* oil after 1 h of immersion at optimum concentration (5 mL/L). The corresponding data are shown in Table 3.From the weight loss results, the corrosion rate (CR), the inhibition efficiency (E%) of inhibitors and degree of surface coverage (Θ) were calculated using equations 7,8 and 9 [63]:

$$CR = \left(\frac{\Delta W}{Sxt}\right) \qquad (7)$$

$$E(\%) = \quad (1 - \frac{W_{corr}}{W^{o}_{corr}})x100 \qquad (8)$$

$$\theta = \quad (1 - \frac{W_{corr}}{W^{o}_{corr}}) \qquad (9)$$

Where W_{corr} and W^{o}_{corr} are the weight losses for mild steel in the presence and absence of the inhibitor in HCl 1M solution and Θ is the degree of surface coverage of the inhibitors. ΔW is the difference of weight loss for mild steel with and without inhibitors, S is the exposure area of the metallic specimens and t is the immersion time of the metal in corrosive solution.

The fractional surface coverage (Θ) can be easily determined from the weight loss measurements by the ratio E(%) /100, where E(%) is inhibition efficiency and calculated using equation 8. The data obtained suggest that *Athamanta sicula* oil get adsorbed on the steel surface at all temperatures studied and corrosion rates increased in absence and presence of inhibitor with increase in temperature in 1M HCl solutions. In acidic media, corrosion of metal is generally accompanied with evolution of H_2 gas; rise in temperature usually accelerates the corrosion reactions which results in higher dissolution rate of the metal.

Table 3. Corrosion parameters for mild steel in 1M HCl in absence and presence of optimum concentration of the inhibitor studied (oil of *Athamanta sicula*) at different temperatures

Temperature (°K)	Inhibitor	CR (mg/cm^2.h)	E (%)
313	HCl 1M	1.2996	-
	ZKAB1	0.21	83.84
323	HCl 1M	1.828	-
	ZKAB1	0.385	78.94
333	HCl 1M	3.635	-
	ZKAB1	1.083	70.21
343	HCl 1M	6.3363	-
	ZKAB1	2.2716	64.15

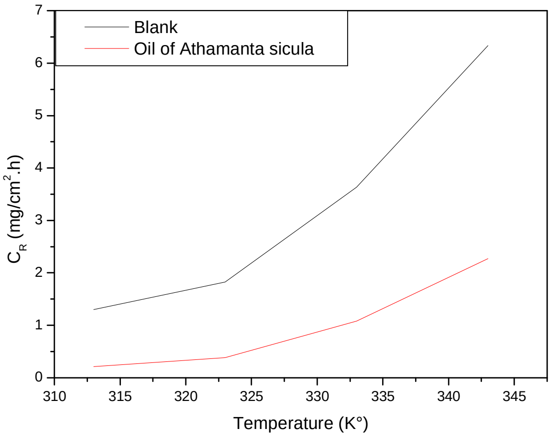

Figure 3. Variation of CR in 1M HCl on steel surface without and with of optimum concentration of *Athamanta sicula* oil at different temperatures

From the Table 3, it is clear that corrosion rate increased with increasing temperature both in uninhibited and inhibited solutions while the inhibition efficiency of *Athamanta sicula* oil decreased with temperature. A decrease in inhibition efficiencies with the increase temperature in presence of Athamanta Sicula Oil might be due to weakening of physical adsorption. In order to calculate activation parameters for the corrosion process, Arrhenius equation. (10) and transition state equation (11) were used [64]:

$$CR = \quad A\exp(\frac{-E_a}{RxT}) \qquad (10)$$

$$CR = \frac{RxT}{Nxh}\exp(\frac{-\Delta S_a}{R})\exp(\frac{-\Delta H_a}{RxT}) \qquad (11)$$

where CR is the corrosion rate, R the gas constant, T the absolute temperature, A the pre-exponential factor, h the Plank's constant and N is Avogrado's number, Ea the activation energy for corrosion process , ΔHa the enthalpy of activation and ΔSa the entropy of activation. The apparent activation energy (Ea) at optimum concentration of *Athamanta sicula* oil was determined by linear regression between Ln(CR) and 1/T (Fig. 4) and the result is shown in Table 4. Inspection of Table 4 showed that the value of Ea determined in 1M HCl containing *Athamanta sicula* oil is higher (78.99 J/mol) than that for uninhibited solution (20.97 J/ mol). The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage. The increase in activation energy could be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with increase in temperature. As adsorption decreases more desorption of inhibitor occur because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of steel comes in contact with aggressive environment, resulting increased corrosion rates with increase in temperature [65, 66]

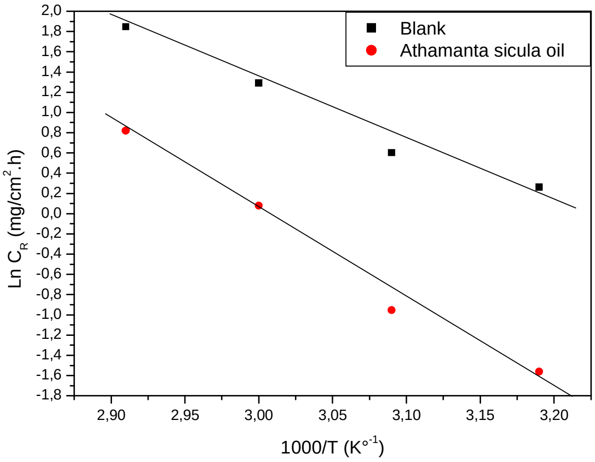

Figure 4. Arrhenius plots of ln CR vs. 1/T for mild steel in 1M HCl in the absence and the presence of *Athamanta sicula* oil at optimum concentration (5 mL/L)

Table4. Parameter thermodynamics for the mild steel dissolution in 1M HCl in the absence and the presence of 5 mL/L extract of *Athamanta sicula* oil

Inhibitor	**Ea (J/mol)**	**ΔHa (KJ/mol)**	**ΔSa (J/mol.K)**
1M HCl	20.97	45.58	-98.3
Athamanta Sicula Oil	72.92	70.14	-35.16

Fig.5, showed a plot of Ln (CR/T) versus 1/T. The straight lines are obtained with a slope (ΔHa/R) and an intercept of (Ln R/Nh +ΔSa /R) from which the values of the values of ΔHa and ΔSa are calculated for Athamanta Sicula Oil of analyzed and are given in Table 4. Inspection of these data revealed that the thermodynamic parameter (ΔHa) for dissolution reaction of steel in 1M HCl in the presence of inhibitors are higher (70.14 kJ/mol) than that of in the absence of inhibitors (45.58 kJ/ mol). The positive sign of ΔHa 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 entropy (ΔSa) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactant to the activated complex.

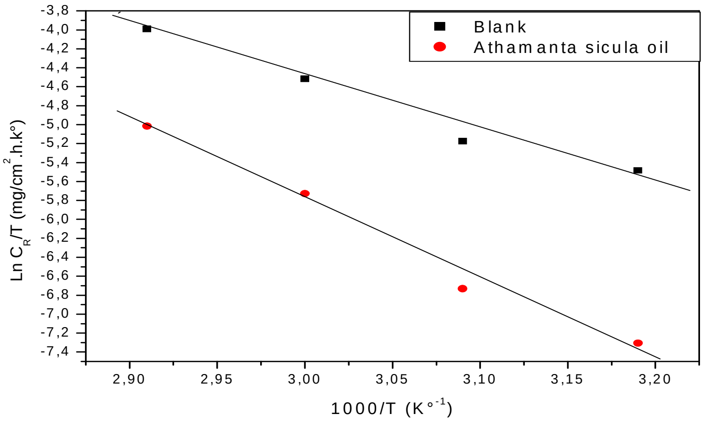

Figure 5. Arrhenius plots of ln CR/T vs. 1/T for steel in 1M HCl in the absence and the presence of 5 mL/L *Athamanta sicula* oil

CONCLUSION

We can deduced that:

- Tafel polarization measurements indicates that *Athamanta sicula* oil act essentially as a mixed type inhibitor.
- The increase in the charge transfer resistance and decrease in double layer capacitance values, with the increase in the inhibitor concentration, showed that *Athamanta sicula* oil formed protective layers on the mild steel surface, covering areas where HCl solution degrades and corrodes rapidly.
- Inhibition efficiency increases with increase in the concentration of *Athamanta sicula* oil but decreases with rise in temperature.
- The corrosion process was inhibited by adsorption of the organic matter on the mild steel surface, obtaining the formation of the film on the metal/acid solution interface, decreasing the degradation of the material.
- Results obtained through weight loss measurements and electrochemical tests demonstrated that *Athamanta sicula* oil act as efficient corrosion inhibitors of the mild steel in 1 M HCl solution.

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