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Carbon steel corrosion in HCl in the presence of aqueous extract of *Melissa Officinalis*

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Abstract

The inhibitive action of the aqueous extract of Melissa officinalis toward the corrosion of C-steel in a 2.0 M HCl solution was investigated using weight loss measurements and Tafel polarization curves . It found that the extract acts as good corrosion inhibitor for tested system. The inhibition efficiency increases with increasing extract concentration. The inhibitive action of the extract is discussed with a view to adsorption of its component s onto the steel surface, making a barrier to mass and change transfer. The adsorption of extract components onto the steel surface was found to be a spontaneous process and to follow the Langmuir adsorption isotherm.

1. Introduction

Industrial processes such as prickling and acid cleaning often involve contact between a metal and aggressive solution, requiring the use of an inhibitor [1]. Most effective inhibitors are organic compounds containing electronegative functional groups and π electrons in triple or conjugated double bonds [2-16]. These compounds also have heteroatoms (such as N, O, and S) and aromatic rings in their structure, which are the major adsorption centers [17-29]. In view of this, several inhibitors have been synthesized and used successfully to inhibit corrosion of metals, including carbon steel. However, the major problem associated with most of these inhibitors is that they are not ecofriendly as they contain heavy metals and other toxic compounds [1]. ‘‘Green’’ corrosion inhibitors are biodegradable and do not contain toxic substances [30,31]. Most of the natural products are non-toxic, biodegradable and readily available in plenty.

The present work devotes to investigate the effect of Melissa Officinalis Extracts (M.O) as corrosion inhibitor for carbon steel in 2 M Hcl, using weight loss measurements, potentiodynamic polarization measurements room and in different temperature. The thermodynamic parameters were also calculated and discussed.

2. Experimental

2. 1. Materials and medium

The steel used in this study is carbon steel (L-37) which is used in manufacturing of petroleum pipes lines with a chemical composition (in wt%) of 0.1 % C, 0.4 % Mn, 0.0267 % S, 0.06 % P and the remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use. The acids solution (2.0 M HCl) was prepared by dilution of an analytical reagent grade 37% HCl with double-distilled water.

2. 1. 1. Extract preparation

Fresh leave of Melissa Officinalis were extensively washed under running tape water for removal of dust particles and epiphytic hosts normally found on the surface, followed by washing with sterilized distilled water. They were further air-dried on filter paper at room temperature and then powdered with the help of sterilized pestle and mortar. Dry powder was further extracted by using aqueous solvent.

Air-dried powder of the respective plant part was mixed well in 100 ml sterilized distilled water and kept at room temperature for 24h on an orbital shaker with 150 ppm. The solution was further filtered using muslin cloth; the filtrate was centrifuged at 5000 rpm for 15 min. The supernatant thus obtained was filtered through Whitman’s filter no.1, and then the filtrate was evaporated until decreases. The solid residue was collected and used in preparation of stock solution from which the desired concentration were prepared by dilution. The extract main component has the formulas shown in Fig.1.

Citronellal (39%) citral (33%)

Fig. 1. Major components in ***Melissa officinalis*** extract.

2. 2. Weight loss measurements.

Steel (L37), with 2.0 x 2.0 x 0.04 cm sizes for each, were used for weight loss measurements. Weight loss experiment was carried out as described elsewhere [32]. The corrosion rate (CR) and the percentage protection efficiency IE (%) were calculated according to the following equations:

$$CR = \frac{\Delta m}{St}$$

$$IE(\%) = \frac{CR_{corr} - CR_{corr(inh)}}{CR_{corr}} \times 100 \qquad (1)$$

where Δm (mg) is the mass loss, S (dm^2) is the area, *t* (h) is the immersion period, and CR_{corr} CR_{corr} and $CR_{corr(inh)}$ $CR_{corr(inh)}$ are the corrosion rates of steel in absence and presence of the inhibitors, respectively.

The values of surface coverage for different concentrations at different temperatures were calculated from weight loss measurements and represented in Table1.

$$\theta = IE/100\theta = IE/100 \qquad (2)$$

2. 3. Potentiodynamic polarization.

Potentiodynamic measurements were carried out using three-compartment glass cell and PS remote potentiostat and PS6 software for calculation of electrochemical parameters. Platinum electrode was used as a counter electrode (separated from the cell solution by a sintered glass frit) and saturated calomel electrode SCE (inside a Luggin probe) as a reference electrode.

A cylindrical rod embedded in araldite with an exposed surface area of 0.45 cm^2 was used. The electrode surface was polished with different grades of emery paper, degreased with acetone, and rinsed with distilled water.

The inhibition efficiency IE (%) was calculated from polarization measurements according to the relation given below:

$$IE(\%) = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \qquad (3)$$

where I_{corr} I_{corr} and $I_{corr(inh)}$ $I_{corr(inh)}$ are current densities in free and inhibited acid, respectively. They are determined by extrapolation of the anodic and cathodic Tafel lines.

3. Result and Discussion

3.1. Weight loss Measurements

The effect of addition of the extract compound on the weight loss of steel in 2 M Hcl as a corrosive medium was studied. The values of the corrosion rate (CR) and inhibition efficiency IE (%) obtained from weight loss at different concentration of extract at room temperature (30^{o}C) are presented in Table 1. It has been found that the corrosion rate in both free and inhibited acid solutions decreases with increasing time and extract concentrations.

Table 1: Data of carbon steel corrosion in 2 HCl solution devoid of and containing different concentrations of ***Melissa officinalis*** extract at different exposure times.

Medium	**t, (h)**	**48**	**96**	**144**	**192**	**240**	**288**
Free	**CR**	**0.099**	**0.091**	**0.088**	**0.082**	**0.079**	**0.074**
100	**CR**	**0.08**	**0.06**	**0.051**	**0.037**	**0.035**	**0.03**
	IE%	**19.2**	**34.1**	**42**	**54.9**	**55.7**	**59.5**
200	**CR**	**0.063**	**0.044**	**0.038**	**0.03**	**0.028**	**0.023**
	IE%	**36.4**	**51.6**	**56.8**	**63.4**	**64.6**	**68.9**
300	**CR**	**0.056**	**0.04**	**0.035**	**0.028**	**0.026**	**0.02**
	IE%	**43.4**	**56**	**60.2**	**65.9**	**67.1**	**73**
400	**CR**	**0.049**	**0.038**	**0.032**	**0.026**	**0.024**	**0.015**
	IE%	**50.5**	**58.2**	**63.6**	**68.3**	**69.6**	**79.7**
500	**CR**	**0.043**	**0.033**	**0.029**	**0.022**	**0.019**	**0.009**
	IE%	**56.6**	**63.7**	**67**	**73.2**	**75.9**	**87.8**
1000	**CR**	**0.04**	**0.031**	**0.026**	**0.021**	**0.017**	**0.004**
	IE%	**59.6**	**65.9**	**70.5**	**74.4**	**78.5**	**94.6**

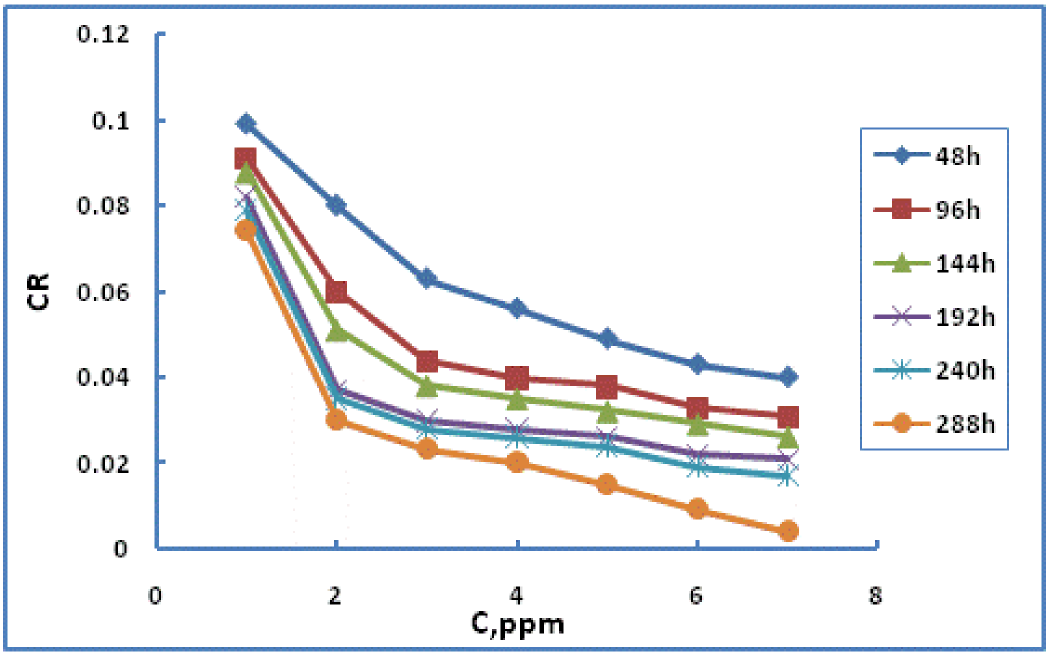

Fig. 2. Relation between extract concentration and corrosion rate.

1. The corrosion rate in both free and inhibited acid solutions decreases with increasing the extract concentrations and times shown in figures 2 and 3.

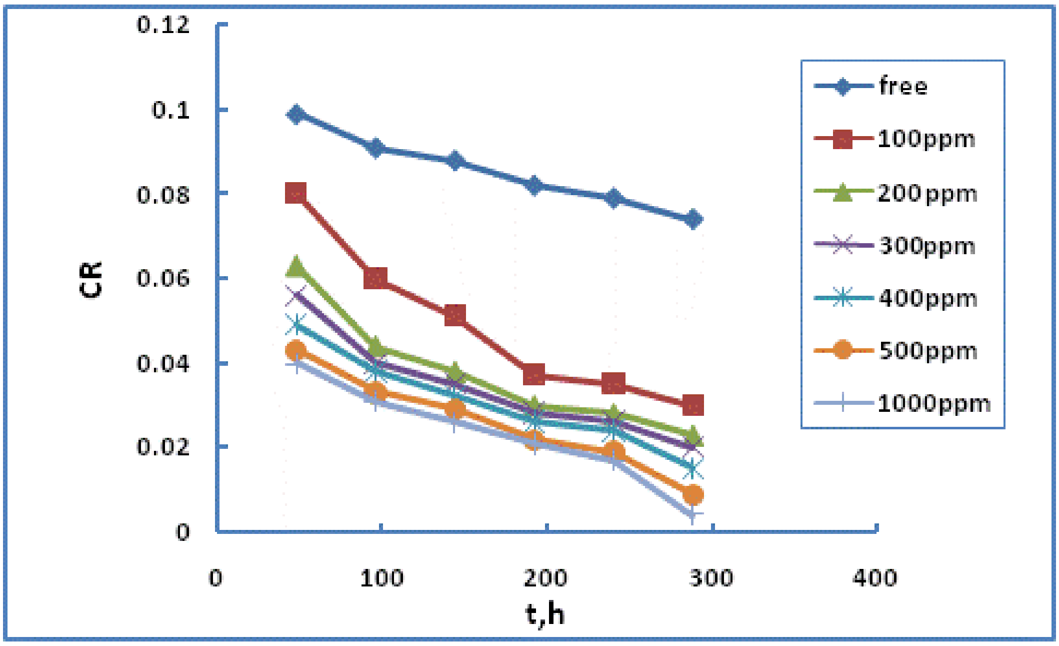

Fig. 3. Relation between exposure time and corrosion rate.

2. The inhibition efficiency of ***Melissa officinalis*** extract increases with increasing its concentration. Fig. 4 represents the relation between inhibition efficiency and extract concentration. Inspection of the figure reveals that inhibition efficiency increases with the increased extract concentration. The relation is nearly linear indicating that all the added molecules in the tested concentration range find their free surface site to adsorb on. Thus, every added single molecule takes directly its part in the inhibitive action.

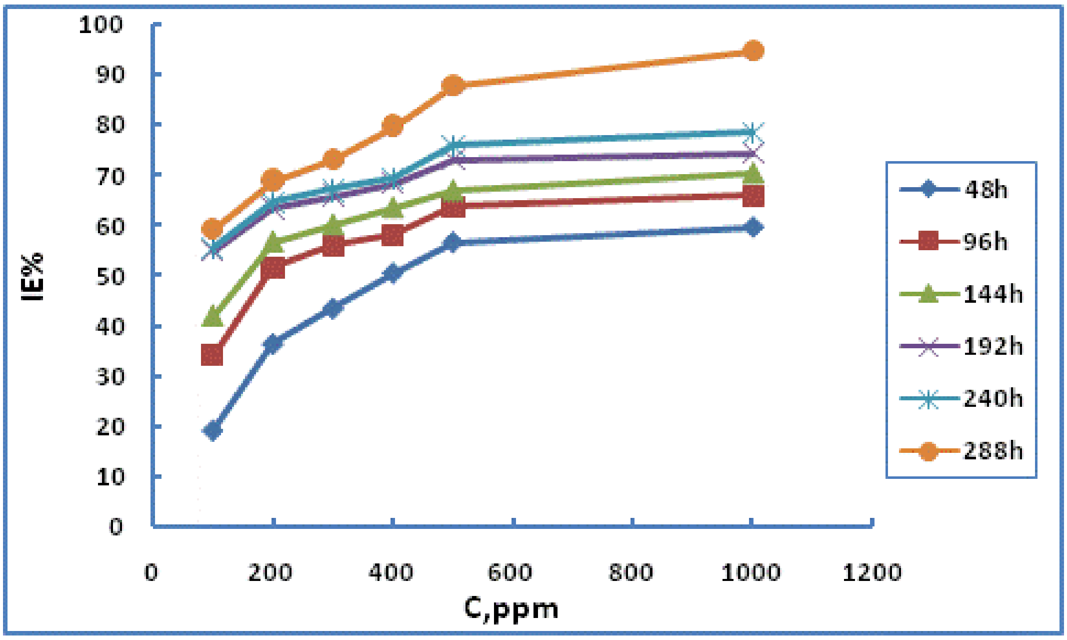

Fig. 4. Relation between extract concentration and inhibition efficiency.

3. The inhibition efficiency increases as the exposure time is increased. The relation between time of exposure and inhibition efficiency is represented in Fig. 5. Inspection of Fig. 5 reveals that the inhibition efficiency increases in linear relation with time of exposure.

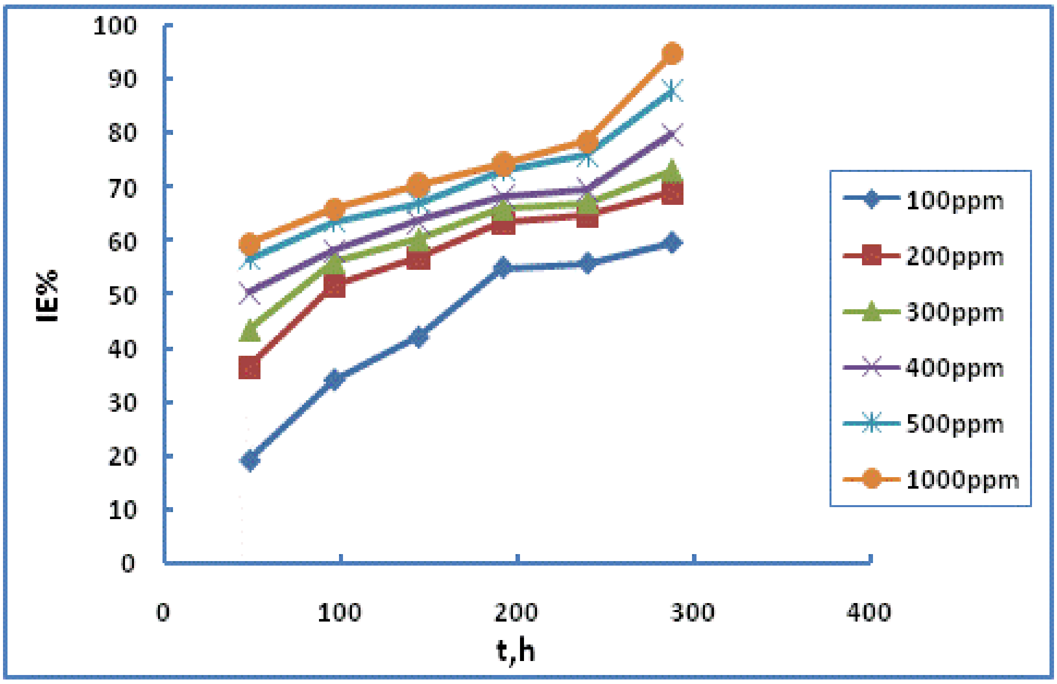

Fig. 5. Relation between exposure time and inhibition efficiency.

3. 2. Polarization studies.

The effect of addition of various concentration of the natural extracted compound on the anodic and cathodic polarization curves of steel in 2 M Hcl solution at 30^0Cis shown at Fig. 6.

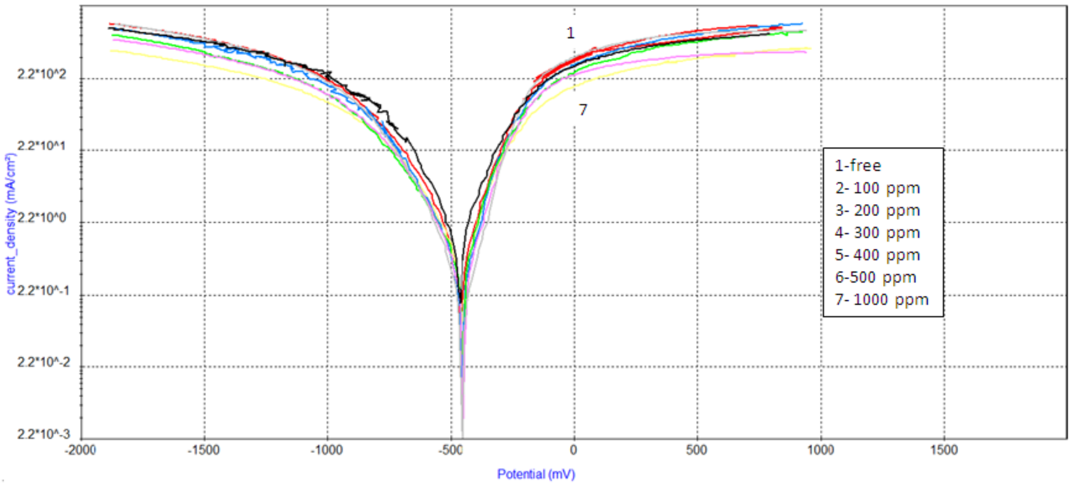

Fig. 6. Polarization curves of carbon steel in 2 M HCl in absence and presence of various concentrations of ***Melissa officinalis*** extract.

Inspection of the data of Table 2 reveals that:

i. The addition of increasing concentrations of ***Melissa officinalis*** extract causes some shift of the corrosion potential value toward more negative direction.

ii. The corrosion current decreases markedly upon addition of ***Melissa officinalis*** extract indicating its inhibition action toward carbon steel corrosion in the acidic medium.

iii. No considerable changes could be recognized for both anodic and cathodicTafel constants upon the addition of the extract. This result indicates that the addition of extract does not affect the mechanism of carbon steel dissolution. Furthermore, these findings suggest that ***Melissa officinalis*** extract acts as mixed type inhibitor. The extract molecules adsorb on both anodic and cathodic sites and thus retard both anodic and cathodic reactions.

iv. The inhibition efficiency increases with increasing extract concentration. Its value increases up to89.8%in presence of 1000 ppm of the extract.

Table 2: Corrosion parameters of carbon steel in 2 M HCl solutions devoid of and containing different concentrations of ***Melissa officinalis*** extract.

Conc., ppm	**- E_{corr}, mV**	**β_a mV/decade**	**- β_c mV/decade**	**I_{corr} mA/cm^2**	***IE%***
Free	**455**	**127**	**140**	**0.608**	**--**
100	**468**	**92**	**135**	**0.263**	**56.7**
200	**455**	**87**	**160**	**0.227**	**62.7**
300	**449**	**83**	**171**	**0.195**	**67.9**
400	**452**	**78**	**136**	**0.143**	**76.5**
500	**453**	**81**	**140**	**0.101**	**83.4**
1000	**455**	**74**	**107**	**0.062**	**89.8**

3. 3. Adsorption isotherm

Basic information about the interaction between the inhibitor molecules and carbon steel surface can be provided by the adsorption isotherm. In the range of studied temperature, the best correlation between the extract concentration and surface coverage was obtained using Langmuir adsorption isotherm that given by [33]:

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

where K_{ads} is the adsorption equilibrium constant of the inhibitor adsorption process and C is the inhibitor concentration.

Table 3: Corrosion parameters of carbon steel in an aqueous solution of 2M HCl in absence and presence of different concentration of inhibitor at different temperature.

C,ppm	**Corrosion rate (*mA/cm^2*) at**					**Inhibition efficiency (%) at**				
	30˚C	**40˚C**	**50˚C**	**60˚C**	**70˚C**	**30˚C**	**40˚C**	**50˚C**	**60˚C**	**70˚C**
100	**0.347**	**1.537**	**2.885**	**4.332**	**5.118**	**42.9**	**26**	**12**	**8**	**6**
200	**0.227**	**0.995**	**1.925**	**3.15**	**29.5**	**62.7**	**52.1**	**41.3**	**33.1**	**29.5**
300	**0.195**	**0.918**	**1.751**	**2.589**	**3.321**	**67.9**	**55.8**	**46.6**	**45**	**39**
400	**0.143**	**0.822**	**1.466**	**2.354**	**3.213**	**76.5**	**60.4**	**55.3**	**50**	**41**
500	**0.101**	**0.447**	**1.302**	**2.256**	**3.153**	**83.4**	**78.5**	**60.3**	**52.1**	**42.1**
1000	**0.062**	**0.407**	**1.131**	**2.077**	**2.777**	**89.8**	**80.4**	**65.5**	**55.9**	**49.1**

The linear regressions between C/θ and C for each temperature over concentration range (100 –500 and 1000ppm) are shown in Fig. 7 and the adsorption parameters are listed in Table 2. The results show very high correlation coefficients and the slopes values are close to one. These finding confirm that the adsorption of the inhibitor molecules in 2M HCl follows Langmuir adsorption isotherm.

The values of K_{ads} were calculated from the intercepts of the straight lines on the C/θ – axis. The K_{ads} was related to the standard free energy of adsorption, ΔG^o_{ads} according to the following equation [34]:

$$K = \frac{1}{55.5} exp \frac{-\Delta G^o_{ads}}{RT} \qquad (5)$$

The value of 55.5 is the molar concentration of water in mol dm^{-3}. The obtained value of ΔG^o_{ads} is listed in Table 4.

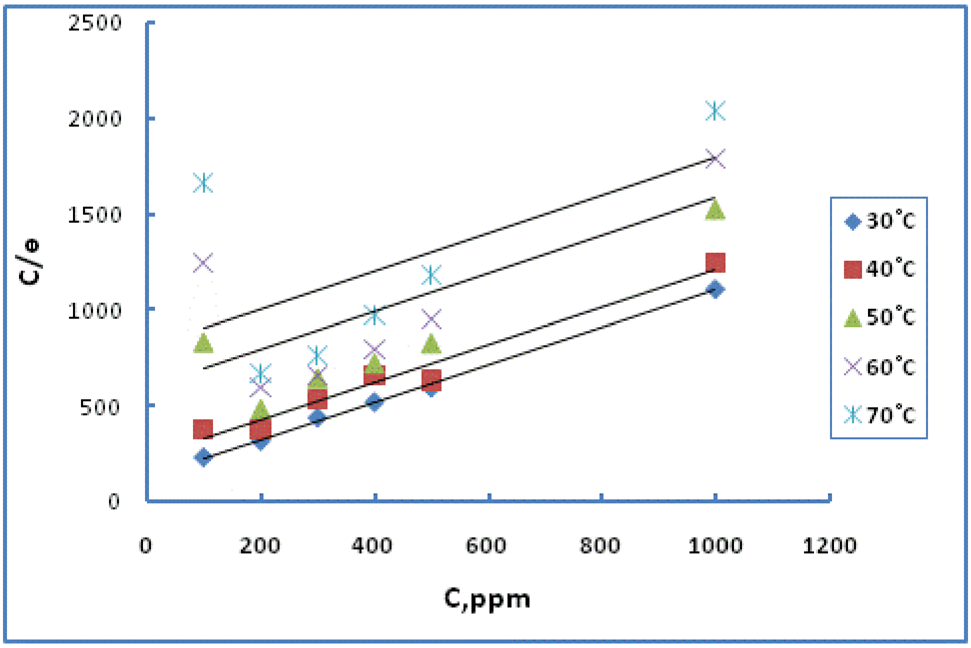

Fig. 7. Langmuir adsorption isotherm drawn using (ppm) concentrations of the different extracts in 2 M HCl solution at different temperature, 30^0C, 40^0C, 50^0C, 60^0C, 70˚C.

Table 4: Thermodynamic adsorption parameters for carbon steel in 2M HCl in the presence of optimum concentrations of *Melissa officinalis extract* at different temperatures.

T(˚C)	**K**	**ΔG^o kJmol^{-1}**	**R^2**
30	**1.025**	**-4.423**	**0.998**
40	**1.017**	**-4.56**	**0.970**
50	**1.010**	**-4.698**	**0.867**
60	**1.006**	**-4.838**	**0.806**
70	**1.004**	**-4.981**	**0.754**

The negative values of ΔG^o_{ads} indicate spontaneous adsorption of the inhibitor molecules on the carbon steel surface while their magnitude suggests the strong interaction between inhibitor molecules and the metal surface [35, 36].

From the result ΔGads values were found to be negative and less than the threshold value of -40KJmol-1 required for chemical adsorption hence the adsorption of ***Melissa officinalis*** extract on the surface of carbon steel is spontaneous and follows physical adsorption mechanism [37- 39].

3.4. Thermodynamic parameters

Thermodynamic parameters are an important tool for further explanation of the corrosion inhibition mechanism. Fig.8 represents the plots of the logarithm of the corrosion rate R_{corr} (mg $cm^{-2}h^{-1}$) of carbon steel vs. 1000/*T* for carbon steel in 0.1M H_2SO_4 in absence and presence of inhibitor. The apparent activation energy (E_a) was calculated by using Arhenuis equation [40]:

$$\log I_{corr} = \log A - \frac{E_a}{2.303\,RT} \qquad (6)$$

where I_{corr} represents the rate of corrosion reaction, *A* is Arrhenius factor and E_a is the apparent activation energy of the corrosion reaction. Plotting of log I_{corr} versus 1/T gave straight lines, as shown in Fig 8. The values of apparent activation energies for corrosion reactions of carbon steel in different media are calculated from the slopes of these lines and represented in Table 5.

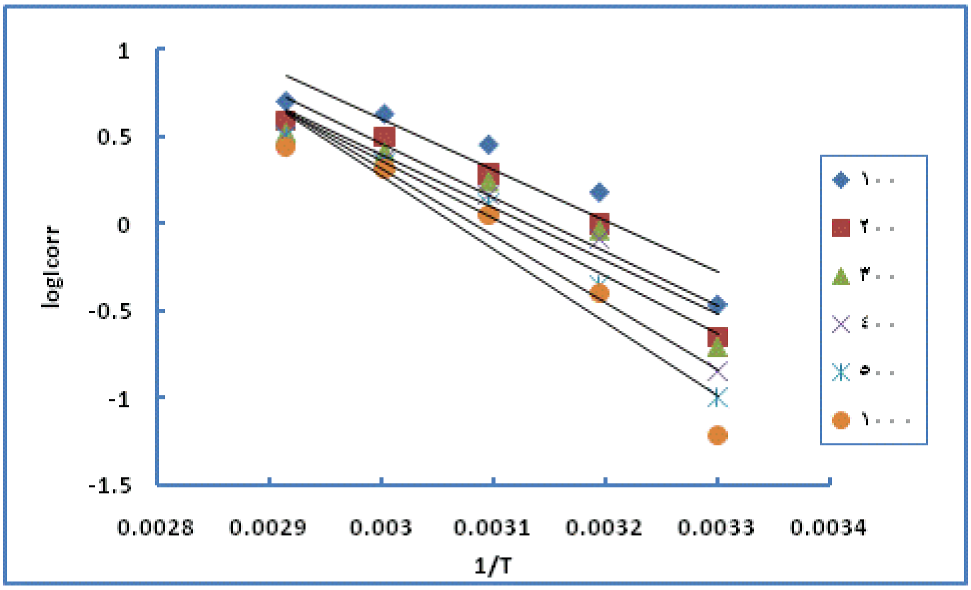

Fig 8: Arrhenius plot for corrosion of carbon steel in inhibited 2M HCl solutions at different concentrations.

Table 5: Activation parameters of carbon steel corrosion in free and inhibited 2M HCl solutions at different concentrations of *Melissa officinalis* extract.

C, ppm	***Ea kJ/mol***	***ΔH* kJ/mol***	***ΔS* kJ/mol K***
100	**56.12**	**53.44**	**-0.074**
200	**58.61**	**55.93**	**-0.070**
300	**59.43**	**56.77**	**-0.067**
400	**63.55**	**60.87**	**-0.056**
500	**74.06**	**71.40**	**-0.026**
1000	**80.59**	**77.91**	**-0.007**

Other activation parameters were calculated using the transition state equation:

$$\log\frac{I_{corr}}{T} = \left[\log\left(\frac{R}{hN}\right)\right] + \left[\frac{\Delta S^*}{2.303\ R}\right] - \frac{\Delta H^*}{2.303\ RT} \qquad (7)$$

where, R is the universal gas constant (8.314 J/mol.K), *N* is the Avogadro's number (6.02 x 10^{23}), *h* is the Plank's constant (6.62 × 10^{-34} m^2 kg /s) where Δ*S** and Δ*H** are the entropy and the enthalpy changes of activation corrosion energies for the transition state complex, respectively. Plotting log (I_{corr}/T) versus 1/T gives straight lines Fig 9 from which the activation parameters are determined and represented in Table 5.

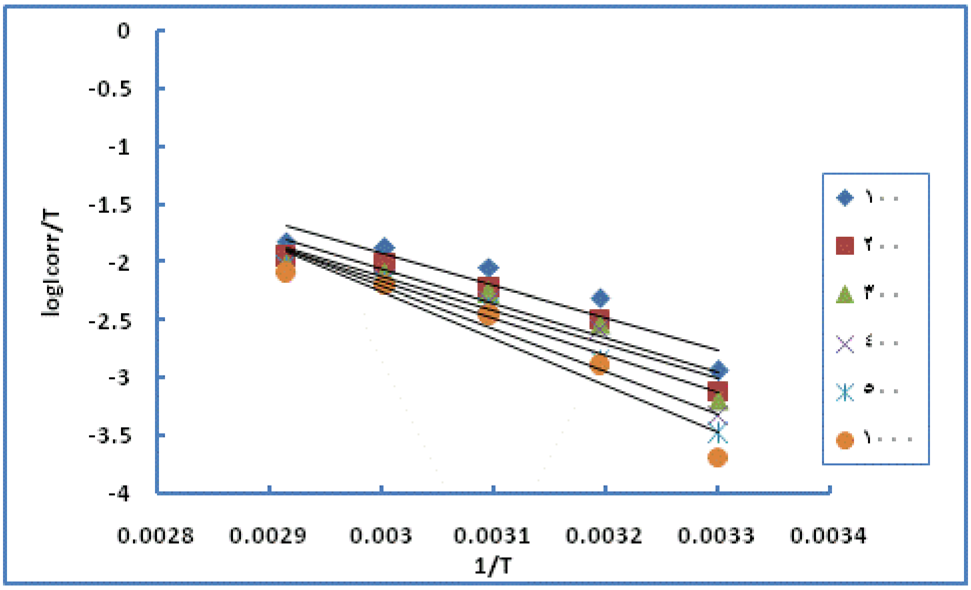

Fig 9: Transition state plot for corrosion of carbon steel in inhibited 2 M HCl solutions at different concentrations.

According to the data recorded in Table 5 the following discussion can be written:

i. The results show positive sign of Δ*H**, reflecting the endothermic nature of the corrosion process.

ii. It is obviously seen that the apparent activation energy strongly increases in the presence of inhibitor. Some authors [41-43] attributed this result to that the inhibitor species are physically adsorbed on the metal surface.

As observed, the trend of (*E*a) for the studied inhibitors is not the same with that obtained from inhibition efficiency. The lower activation energy for *Valerian officinals* extract as compared to that of *Hierochuntica Anastatica*or *Melissa officinalis* may be explained according to Riggs and Hurd [44], as they stated that at higher level of surface coverage the corrosion process may proceed on the adsorbed layer of inhibitor and not on the metal surface leading to a decrease in the apparent activation energy and in some cases becomes less than that obtained in the absence of inhibitor.

4. Conclusions

- The ***Melissa officinali*** Extract act as good inhibitors for acid corrosion of C-steel.
- The inhibition efficiency increases with increased concentration
- The inhibition efficiency decreases as the temperature was increased.
- The adsorption of extract on steel surface is a spontaneous process and follows Langmuir adsorption isotherm.

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