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Study of Corrosion Inhibition for Mild Steel in Hydrochloric Acid Solution by *Limbarda crithmoides* (L.) Essential Oil of Corsica

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Abstract

The inhibitive effect of *Limbarda crithmoides* (L.) essential oil on the corrosion of mild steel in 1M HCl solution has been investigated by weight loss measurement. The results obtained showed that inhibition efficiency increases with inhibitor concentration to attain 77.85% at 2 g/L of essential oil. The temperature effect on the corrosion behavior of steel in 1M HCl without and with the inhibitor at 2 g/L was studied in the temperature range from 303 and 343 K. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. The adsorption of the essential oil components on the mild steel surface obeyed the Langmuir adsorption isotherm. Gibbs free energy of adsorption indicated that the adsorption process is spontaneous and the molecules adsorbed on the metal surface by the process of physical adsorption.

Keywords : Adsorption, Corrosion Inhibition, Essential oil, Mild steel, *Limbarda crithmoides* (L.).

1. Introduction

Corrosion is gradual destruction of a material because of its reaction with environment. It is a major industrial problem that has attracted a lot of investigators in recent years [1,2]. Indeed, corrosion control is an essential issue from application point of view and it has been reported that inhibitors are needed to be used which act as a barrier to reduce the aggressiveness of the environments against the corrosion attack [3,4]. An attempt to find corrosion inhibitors that are environmentally safe and readily available has been a growing trend in the use of natural products such as essential oils as corrosion inhibitors for metals in acid cleaning processes. The effectiveness of inhibiting corrosion by an essential oil is closely related for its phytochemical constituents, which includes a non-polar, hydrophobic, consisting of hydrocarbon molecules and a polar, hydrophilic, which presents one or more functional groups [5]. These organic compounds can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate. However, synergistic (and antagonistic) effects are often expected with these mixtures of compounds that may affect their inhibition efficiency. We have previously reported that the essential oils of many plants are excellent inhibitors for corrosion of steel in acidic solutions [6-9].

In the present work, we have been investigated the corrosion inhibition capacity of *Limbarda crithmoides* (L.) essential oil from Corsica. *Limbarda crithmoides* (L.) was a common *Asteraceae* widespread on wetlands of Corsica and Mediterranean Sea, French Atlantic coasts, Great Britain channel and West European seaboards [10]. The chemical composition of *L. crithmoides* essential oil from Corsica was recently reported by S.

Andreani *et al* (2013) [11]. *Para*-cymene, thymol methyl ether and two *p*-cymenene derivatives 3-methoxy-*p*-cymenene and 2,5 dimethoxy *p*-cymenene, were identified as main constituents.

2. Materials and methods

2.1. Preparation of inhibitor

Essential oil of *Limbarda crithmoides* was obtained by hydrodistillation using a *Clevenger*-type apparatus according to the method recommended in the European pharmacopoeia [12] as described by S. Andreani *et al.* (2013) [11].

2.2. Preparation of materials

The aggressive solutions of 1 M HCl was prepared by dilution of AR grade 37% HCl with distilled water. The material used in this study was mild steel (2 cm x 2 cm x 0.05 cm) with a chemical composition (in wt. %) of 0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron (Fe). For all the experiments, the mild steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (grades 400, 600 and 1200), then washed thoroughly with double-distilled water, degreased with AR grade ethanol, and finally dried at room temperature before use.

2.3. Weight loss measurements

2.3.1. Effect of concentration of L. crithmoides essential oil

Weight loss tests were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. Tests were performed on a total volume of 100 mL with and without *L. crithmoides* essential oil, added to the system in different concentrations in a range from 0.25 to 2g/L. The immersion time for the weight loss was 6 h at 298 K. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Triplicate experiments were performed in each case and the mean value of the weight loss is reported using an analytical balance (precision ± 0.1 mg). Weight loss allowed us to calculate the mean corrosion rate as expressed in $mg.cm^{-2}\ h^{-1}$.

The corrosion rate (W) and inhibition efficiency E_w (%) were calculated according to the Eqs. (1) and (2) respectively:

$$W = \frac{\Delta m}{St} \qquad (1)$$

$$E_W\ \% = \frac{W_{corr} - W_{corr(inh)}}{W_{corr}} \times 100 \qquad (2)$$

where Δm (mg) is the specimen weight before and after immersion in the tested solution, W_{corr} and $W_{corr(inh)}$ are the values of corrosion weight losses ($mg/cm^2.h$) of mild steel in uninhibited and inhibited solutions, respectively, S is the area of the mild steel specimen (cm^2) and t is the exposure time (h).

2.3.2. Effect of temperature

The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition. The change of the corrosion rate with the temperature was studied in 1 M HCl during 1 h of immersion, both in the absence and presence of inhibitor at a concentration corresponding to the maximum inhibition efficiency. For this purpose, gravimetric experiments were performed at different temperatures (303–343 K).

To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. (3) and transition state Eq. (4) were used [13]:

$$W = A\exp\left(-\frac{E_a^{\circ}}{RT}\right) \qquad (3)$$

$$W = \frac{RT}{Nh}\exp\left(\frac{\Delta S^{\circ}_{a}}{R}\right)\exp\left(-\frac{\Delta H^{\circ}_{a}}{RT}\right) \quad (4)$$

where E°a is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius pre-exponential factor, h is the Plank's constant, N is the Avogrado's number, ΔS°_{a} is the entropy of activation and ΔH°_{a} is the enthalpy of activation.

2.4. Adsorption isotherm

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitors must be calculated with several adsorption isotherms, including Langmuir, Frumkin, and Temkin. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitor in acidic media have been evaluated from the Weight loss measurements.

3. Results and discussion

3.1. Corrosion tests

3.1.1. Effect of Inhibitor Concentration

The values of percentage inhibition efficiency Ew (%) and corrosion rate (W) obtained from weight loss method at different concentrations of *L. crithmoides* essential oil at 298 K are summarized in Table 1 and Figure 1.

Table 1 : Weight loss results of mild steel in 1 M HCl without and with different concentrations of *L. crithmoides* essential oil (*t*= 6h, *T*= 298 K).

Inhibitor	C (g/L)	W (mg/h.cm^2)	E_w (%)
L. crithmoides essential oil	0	0.381	--
	0.25	0.381	43.39
	0.5	0.216	57.14
	1	0.163	66.50
	1.5	0.128	73.11
	2	0.102	77.85

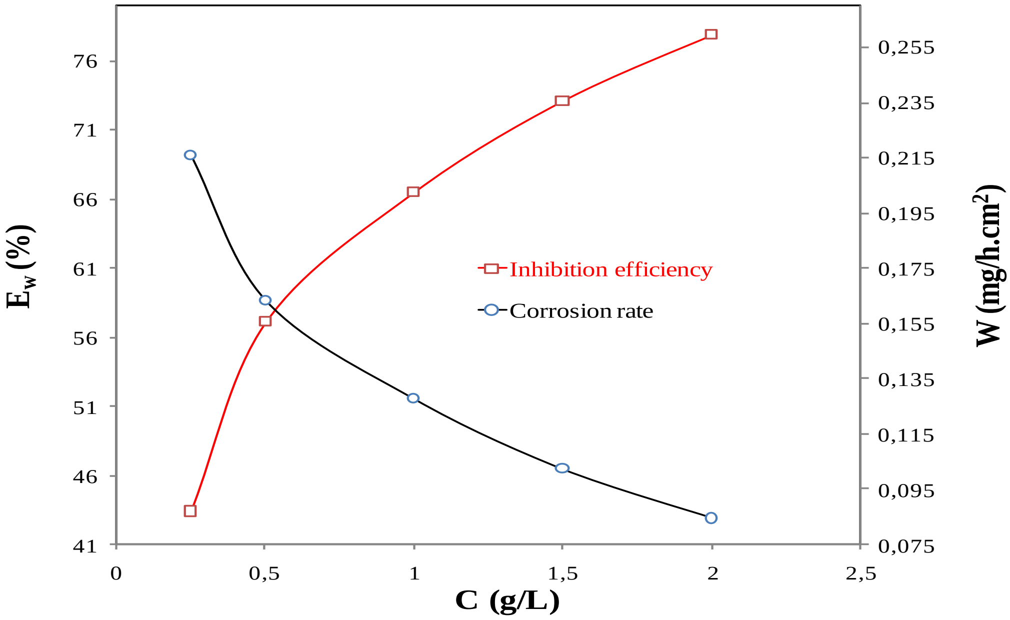


Figure 1: Variation of corrosion rate (W) and inhibition efficiency (E_w) of corrosion of mild steel in 1 M HCl with different concentration of *L. crithmoides* essential oil.

The results obtained in Table 2 and Figure 1 indicated that the corrosion rate (W) of mild steel decreased continuously with increasing the inhibitor concentration, ie, the corrosion of steel is retarded by *L. crithmoides* essential oil. However, the inhibition efficiency E_w increases sharply with increase in concentration of inhibitor reaching a maximum value of 77.85% at 2 g/L. This behavior could be explained by the adsorption of phytochemical components of the essential oil onto the mild steel surface resulting in the blocking of the reaction sites, and protection of the mild steel surface from the attack of the corrosion active ions in the acid medium [9]. Consequently, we can conclude that the *L. crithmoides* essential oil is a good corrosion inhibitor for mild steel in 1 M HCl solution.

3.1.2. Effect of temperature.

The effect of temperature on the corrosion behaviour of steel in 1 M HCl containing *L. crithmoides* essential oil at 2 g/L is studied in the temperature range 303-343 K using weight loss measurements at 1 h. The data of corrosion rates (W) and corresponding efficiency (E_w) collected were presented in Table 2 and Figure 2.

Table 2 : Corrosion parameters obtained from weight loss for mild steel in 1 M HCl containing 2 g/L of *L. crithmoides* essential oil at different temperatures.

T (K)	W_{inh} mg/cm^2.h	W_0 mg/cm^2.h	E_w %
303	1.114	4.178	73.33
313	2.535	7.419	65.83
323	4.826	11.178	56.82
333	9.843	17.369	43.33
343	12.855	19.369	33.63

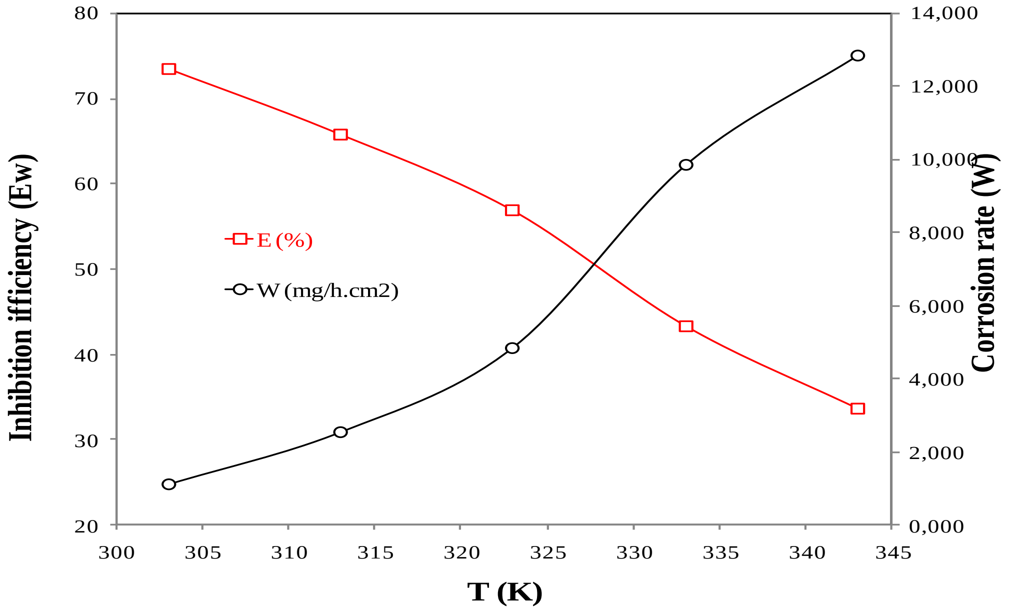


Figure 2 : Influence of temperature on corrosion rate (W) and inhibition efficiency (E_w) of mild steel 1 M HCl in the presence of 2g/L of *L. crithmoides* essential oil.

Inspection of these results reveals that the corrosion rate (W) increases with temperature both in uninhibited and inhibited solutions especially goes up more rapidly in the absence of inhibitor. This result indicates that the presence of inhibitor leads to decrease of the corrosion rate. Also, we note that the efficiency (E_w) depends on the temperature and decreases with the rise of temperature from 303 to 343 K. the efficiency (E_w) reached a high values of 73.33 % in 1 M HCl solution at 303 K, which represents excellent inhibitive ability of *L. crithmoides* essential oil. The decrease in inhibition efficiency with increase in temperature may be attributed to the increased desorption of inhibitor molecules from metal surface and the increase in the solubility of the protective film or the reaction products precipitated on the surface of the metal that might otherwise inhibit the reaction [14].

3.2. Activation parameters $E°_a$, $\Delta S°_a$, $\Delta H°_a$

In order to calculate activation parameters of the corrosion reaction such as activation energy $E°_a$, activated entropy $\Delta S°_a$ and enthalpy $\Delta H°_a$, the Arrhenius equation (Eq. (3)) and its alternative formulation called transition state equation (Eq. (4)) were employed [13]. Plotting the logarithm of the corrosion rate (W) versus reciprocal of absolute temperature (1/T), the activation energy can be calculated from the slope (-E°a/R). Figure 3 shows the variations of Ln W with the presence and absence of inhibitor with the (10^3/T).

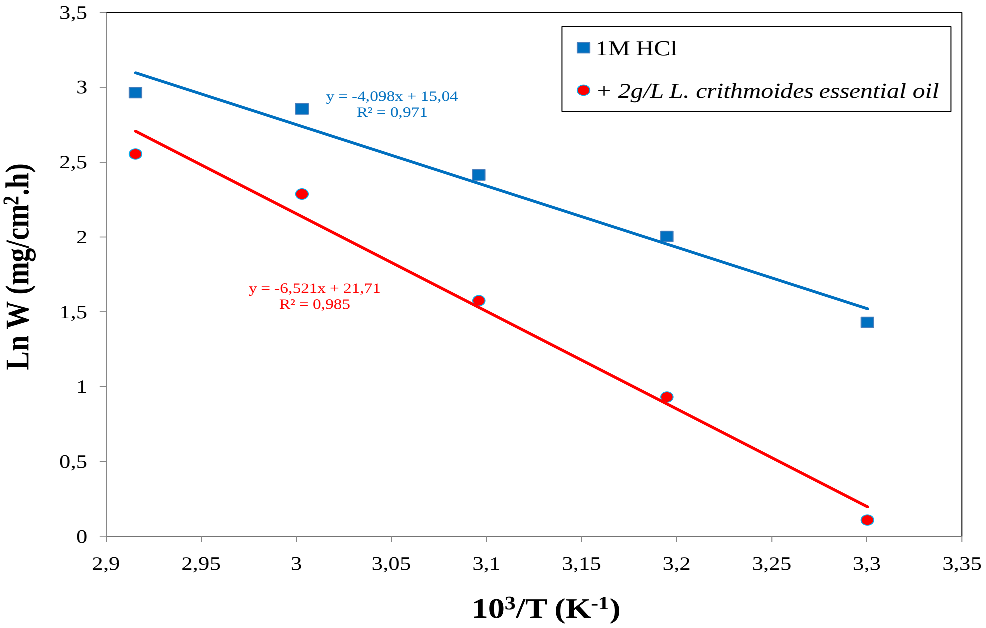


Figure 3 : Arrhenius plots for mild steel corrosion rates (W) in 1 M HCl in absence and in presence of 2 g/L of *L. crithmoides* essential oil.

The logarithm of the corrosion rate of steel (Ln W) can be represented as straight-lines function of (10^3/T) with the linear regression coefficient (R^2) was close to 1, indicating that the corrosion of steel in hydrochloric acid without and with inhibitor follows the Arrhenius equation. The activation energy ($E°_a$) values were calculated from the Arrhenius plots (Figure 3) and the results are shown in Table 3.

Table 3 : Activation parameters $E°_a$, $\Delta S_a°$, $\Delta H°_a$ of the dissolution of mild steel in 1 M HCl in the absence and presence of 2 g/L of *L. crithmoides* essential oil.

Inhibitor	$E°_a$ (KJ. mol^{-1})	$\Delta H°_a$ (KJ.mol^{-1})	$E–\Delta H°_a$ (KJ. mol^{-1})	$\Delta S°a$ (J. $mol^{-1}.K^{-1}$)
1M HCl	34.10	31.41	2.69	-128.86
+2 g/L *L. crithmoides* essential oil	54.26	51.57	2.69	-73.38

Further, using Eq. (4), plots of Ln (W/T) versus 10^3/T gave straight lines (Figure 4) with a slope of (-ΔH°a/R) and an intercept of (Ln(R/Nh) + (ΔS°a/R)) from which the values of ΔH°a and ΔS°a were calculated and are listed in Table 4. The calculated values of activation energies from the slopes are 34.10 and 71.98 KJ.mol^{-1} for free acid and with the addition of 2 g/L of *L. crithmoides* essential oil, respectively. We remark that the activation energy increases in the presence of inhibitor. Generally, the higher $E°_a$ value leads to the lower corrosion rate and indicate that a strong inhibitive action of the additives by increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the mild steel surface [15]. In addition, the value of $E°_a$ that is around 40–80 KJ.mol^{-1} can be suggested to obey the physical adsorption (physiosorption) mechanism [16].

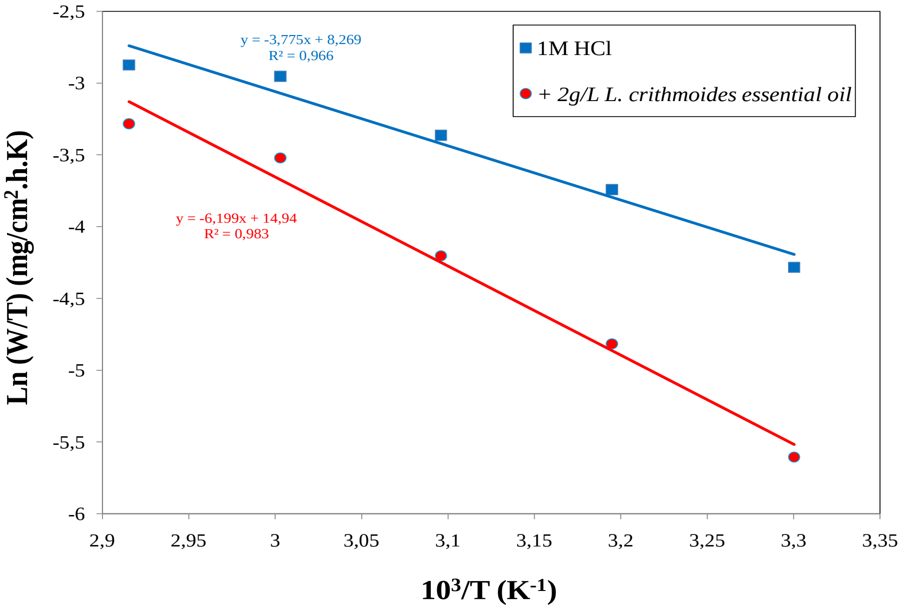


Figure 4 : Transition-state plots for mild steel corrosion rates (W) in 1 M HCl in absence and in presence of 2 g/L of *L. crithmoides* essential oil.

Moreover, inspection of the data of Table 4 reveals that the positive signs of $\Delta H°_a$ both in the absence and presence of 2 g/L of *L. crithmoides* essential oil reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow [17]. Typically, enthalpy of physical adsorption process is lower than 80 KJ.mol^{-1} while the enthalpy of chemisorption process approaches 100 KJ.mol^{-1} [18]. The value of the obtained enthalpy, therefore, suggests physical adsorption of the components of the *L. crithmoides* essential oil on the surface of the metal. Contrariwise, the negative values of entropies of activation ($\Delta S°a$) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [19].

On the other hand, the average difference value of the $E°a–\Delta H°a$ is 2.69 kJ.mol^{-1}, which is approximately equal to the average value of RT (2.69 kJ.mol^{-1}) at the average temperature (323 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known Eq. (5) of perfect gas:

$$E°a - \Delta H°a = RT \qquad (5)$$

3.3 Adsorption isotherm considerations

It is know that the adsorption process of inhibitor depends on its electronic characteristics, the nature of metal surface, temperature, steric effects and the varying degrees of surface-site activity. In fact, the solvent H_2O molecules could also be adsorbed at the metal/solution interface. In the aqueous solution, the adsorption of inhibitor molecules can be considered as a quasi-substitution process between the inhibitor in the aqueous phase $Inh_{(sol)}$ and water molecules at the electrode surface $H_2O_{(ads)}$ [20] :

$$Org_{(sol)} + xH_2O_{(ads)} \leftrightarrow xH_2O_{(sol)} + Org_{(ads)} \qquad (6)$$

where x is the size ratio, that is, the number of water molecules re-placed by one organic inhibitor.

This equation showed that the interaction force between metal and inhibitor must be greater than the interaction force of metal and water molecule. The corrosion adsorption processes can be understood using adsorption isotherm. Langmuir adsorption isotherm is attributing to physisorption or chemisorption phenomenon while Temkin adsorption isotherm gives an explanation about the heterogeneity formed on the metal surface.

Chemisorption is attributed to Temkin isotherm [21]. Here, Langmuir, Frumkin and Temkin adsorption isotherms were applied in order to explain the adsorption process of *L. crithmoides* essential oil on the mild steel surface :

$$\text{Lamgmuir}:\frac{C_{inh}}{\theta}=\frac{1}{K}+C_{inh} \qquad (7)$$

$$\text{Temkin}:\text{Ln}\left(\frac{C_{inh}}{\theta}\right)=\text{LnK}-g\theta \qquad (8)$$

$$\text{Frumkin}:\text{Ln}\left(C_{inh}*\left(\frac{\theta}{1-\theta}\right)\right)=\text{LnK}+g\theta \qquad (9)$$

where θ is the surface coverage, K is the adsorption–desorption equilibrium constant, C_{inh} is the concentration of inhibitor and g is the adsorbate parameter.

Again, the weight loss measurements were employed in this experiment with the concentration range 0.25 to 2 g/L at 298 K. The corresponding plots are shown in Fig. 5, where the R^2 value for Langmuir isotherm (Figure 5a) was 0.998, Temkin isotherm (Figure 5b) was 0.985 and Frumkin isotherm (Figure 5c) was 0.997. Consequently, Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the *L. crithmoides* essential oil on the mild steel surface. This result indicated that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species [22].

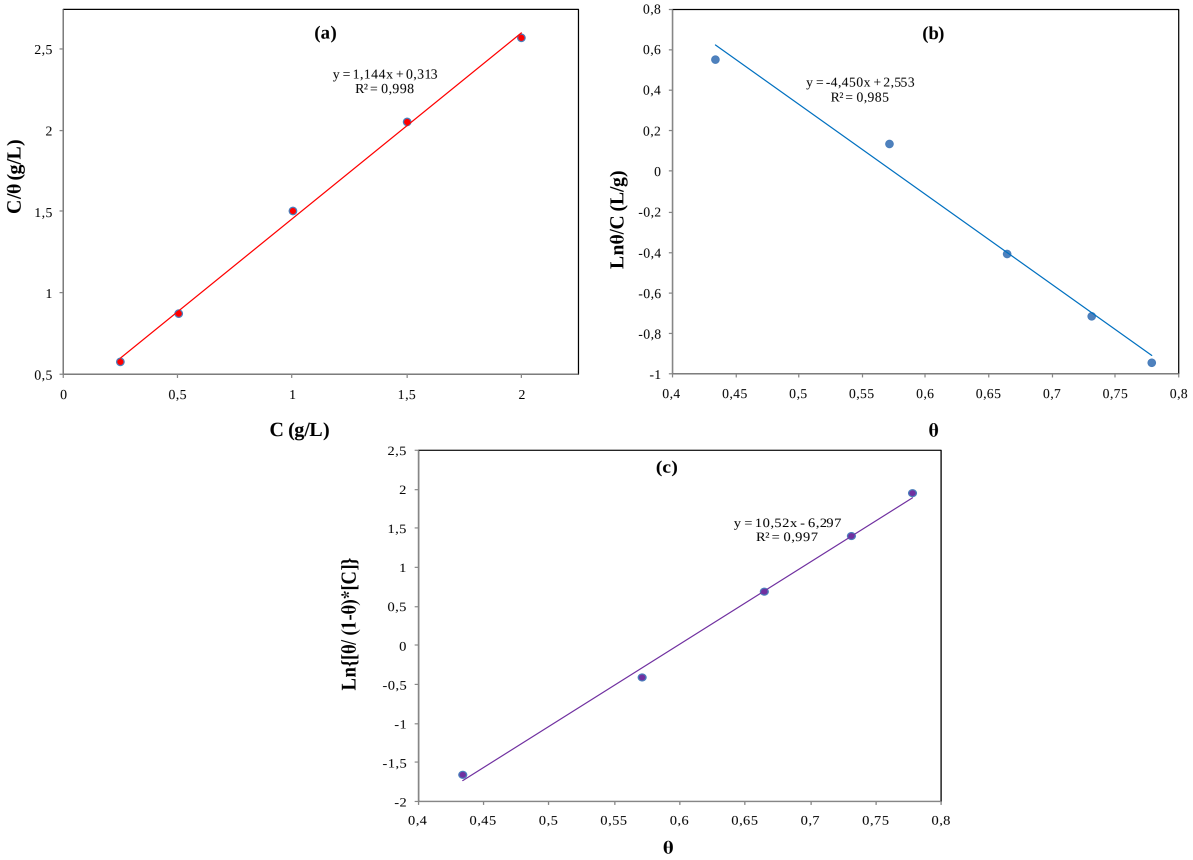


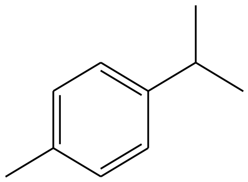
Figure 5 : (a) Langmuir, (b) Temkin and Frumkin (c) isotherm for the adsorption of *L. crithmoides* essential oil on the surface of mild steel in 1 M HCl.

Thermodynamic parameters are important to further understand the adsorption process of inhibitor on steel/solution interface. The equilibrium adsorption constant, K is related to the standard Gibb's free energy of adsorption ($\Delta G°_{ads}$) with the following equation :

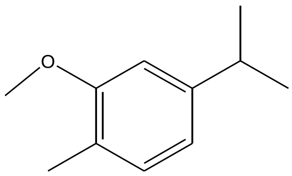
$$K=\frac{1}{55.5}.\exp\left(-\frac{\Delta G°_{ads}}{RT}\right) \qquad (10)$$

where R is the universal gas constant, T is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution in mol/L (10^3 g/L).

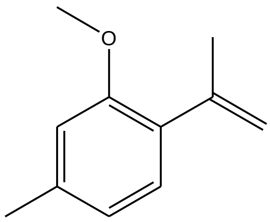
Since the natural oil contains infinite compounds at various contents, we assume that the inhibition process is essentially due to the synergistic intermolecular phenomenon between molecules of natural product at major levels [23-27]; we cite that para-cymene, thymol methyl ether and two p-cymenene derivatives 3-methoxy-p-cymenene and 2,5 dimethoxy p-cymenene, were identified as main constituents [11].



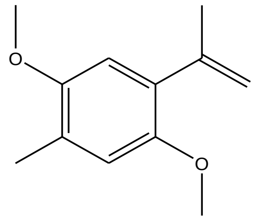
p-cymene



Methyl thymol ether



3-methoxy-p-cymenene



2,5 dimethoxy p-cymenene

3.4. Mechanism of inhibition

Accordingly, the effectiveness of inhibiting corrosion by an essential oil could be attributed to the adsorption of its phytochemical components on the mild steel surface. Owing to the complex chemical composition of the *L. crithmoides* essential oil, it is quite difficult to assign the inhibitive effect to a particular constituent. This makes it difficult to assign the inhibitive effect to adsorption of any particular constituent since some of these constituents including aromatic, oxides, esters and alcohols compounds. These compounds contain the hetero-atom oxygen in functional groups (C=O, C–O, O–H) and π-electrons of the aromatic ring and the double bonds (C=C) in their structure, which meets the general characteristics of typical corrosion inhibitors. Also, these organic molecules of *L. crithmoides* essential oil exist either as neutral molecules or in the form of protonated organic molecules (cation) in aqueous acidic solution. Therefore, the effectiveness of a corrosion inhibitor can be related to its molecular electronic structure.

Generally, two modes of adsorption are considered on the metal surface in acid media. In first mode, the neutral molecules may be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the oxygen atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor–acceptor interactions between their π-electrons and vacant d-orbitals of surface iron. In second mode, since it is well known that it is difficult for the protonated molecules to approach the positively charged mild steel surface (H_3O^+/metal interface) due to the electrostatic repulsion. Since Cl^- have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favour more adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed Cl^- ions and protonated inhibitors [28, 29].

Conclusion

The inhibition action of this essential oil can be attributed to the adsorption of its phytochemical compounds especially their oxygenated terpenes. The inhibition efficiency values increased with increase in inhibitor concentration but decreased with increase in temperature. The value of apparent activation energy increased with the increase in the inhibitor concentration. Enthalpy of activation reflects the endothermic nature of the mild steel dissolution process. Entropy of activation increased with increasing inhibitor concentration; hence increase in the disorderliness of the system. The adsorption behavior can be described by the Langmuir adsorption isotherm. Gibbs free energy of adsorption indicated that the adsorption process is spontaneous and the molecules adsorbed on the metal surface by the process of physical adsorption.

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