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Eco-friendly Inhibition Corrosion of Carbon Steel in Acidic Solution using the Oil of Citrus Leaves

L. Adardour¹, M. Larouj¹, H. Lgaz^{1,2}, M. Belkhaouda², R. Salghi^{2*}, S. Jodeh^{3*},
A. Salman^{4*}, H. Oudda¹ and M. Taleb⁵

¹Laboratory Separation Processes, Faculty of Science, University Ibn Tofail PO Box 242, Kenitra, Morocco

²Laboratory of Applied Chemistry and Environment, ENSA, Université Ibn Zohr, PO Box 1136, 80000 Agadir, Morocco

³Department of Chemistry, An-Najah National University, P. O. Box 7, Nablus, Palestine

⁴Department of Computer and Information Technology, An-Najah National University, P. O. Box 7, Nablus, Palestine

⁵Département de Chimie, Faculté des Sciences Dhar El Mehraz FES B.P. 1796 Atlas Fès Morocco

ABSTRACT

The influence of oil of citrus leaves (**OCL**) concentration and the effect of medium temperature on the carbon steel corrosion in aqueous 1.0 M hydrochloric acid was realized experimentally using electrochemical impedance spectroscopy, potentiodynamic polarization curves and gravimetric technique. Results showed that the **OCL** is the excellent inhibitor for steel corrosion and the polarization curves data revealed that the tested compound acts as a mixed type inhibitor with predominant anodic. The study of temperature effect was investigated and leads to the determination of thermodynamic activation parameters. Electrochemical impedance spectroscopy result exhibit one capacitive loop indicating that, the corrosion reaction is controlled by charge transfer process and the presence of this compound decreases the double layer capacitance and increases the charge transfer resistance. The oil of citrus leaves act by adsorption on the carbon steel surface according to a Langmuir isotherm adsorption model.

Keywords: Corrosion, inhibition, Carbon steel, Oil of Citrus Leaves, electrochemical and gravimetric methods

INTRODUCTION

Iron and its alloys, especially, steel is the most important engineering material particularly in automobile industries [1-3]. In many industries applications the use of acidic solutions leads to destruction of structure of these alloys [4-5]. The employ of different organics inhibitors can be classed as an excellent technique to minimize the dangers that may be caused by dissolution phenomenon [6-7]. These inhibitors act usually by adsorption on the metal surface by the formation of the bonds between the reactive centers of organic inhibitor and steel [8-9]. For economic and environmental reason, the researchers seek the other alternative using extracts and oils of natural substances [10-11]. Many natural compounds such as plant extracts and oils were used as effective corrosion inhibitors of iron alloys in aggressive solution [12-13].

The objectives realized in present work (a) to investigate the effect of temperature and concentration of **OCL** (oil of citrus leaves) on the corrosion inhibition of carbon steel in acidic medium, (b) to deduct the activation thermodynamic parameters and (c) determine of model adsorption type. Potentiodynamic polarization curves, EIS and gravimetric methods have been used to evaluate corrosion rate of carbon steel and its inhibition by citrus oil leaves of inhibitor in molar hydrochloric acid solution.

MATERIALS AND METHODS

1.1. Preparation of working electrode and test solutions

The alloy employed in this investigation has been carbon steel with a chemical composition: 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. The working electrode was prepared prior each test; mechanically abraded by different grades of emery papers (600, 800 and 1200), washed with double distilled water, degrease with acetone, dried with soft paper and introduce into the glass cell containing test solution. The aggressive medium used, molar hydrochloric acid, was freshly prepared by dilution of an analytical reagent grade 37% HCl with bidistilled water. The experimental tests were executed in 1.0 M HCl solution in the absence and presence of different concentrations of oil of citrus leaves (OCL).

1.2. Weight loss experiment

The gravimetric tests were performed on the carbon steel samples with size (length = 2.5 cm, width = 1.2 cm, thickness = 0.2 cm). After and before 6h immersion of electrode specimens in 1.0 M HCl medium with and without various concentrations of citrus oil leaves (1to 6 g/L) , the sample weighed accurately by a digital balance with high sensitivity. The corrosion rate value (C_R) of carbon steel was evaluated by the following relation:

$$C_R = \frac{w}{St} \quad (1)$$

Where w are the difference mass loss before and after immersion, S are the surface of specimen and t are the immersion time.

The inhibition efficiency (η_{wt} %) of carbon steel have been determined from this method using the following equations:

$$\eta_{wt} \% = \left(1 - \frac{C_R}{C_R^0}\right) \cdot 100 \quad (2)$$

Where C_R^0 and C_R is the corrosion rates of carbon steel without and with the citrus oil leaves, respectively.

1.3. Electrochemical measurements

The potentiodynamic polarization curves and EIS measurements were performed with a potentiostat/galvanostat PGZ 100 piloted with VoltaMaster4 software. Electrochemical tests were realized in a conventional three electrode electrochemical cell with the carbon steel as a working electrode, a platinum counter electrode and saturated electrode as reference electrode. Before each electrochemical measurements, the working electrode were immersed in the test solution during 30 min for establish the stabilization potential. The polarization curves were plotted in the range of -800 to -200 mV/SCE atscan rate of 1 mVs⁻¹.

The inhibition efficiency (η_p (%)) can be evaluated from this technique using the following equation:

$$\eta_p (\%) = \left(1 - \frac{I_{corr}}{I_{corr}^0}\right) \times 100 \quad (3)$$

Where I_{corr} and I_{corr}^0 represent corrosion current density values with and without oil of citrus leaves, respectively.

Electrochemical impedance spectroscopy experiment were realized at corrosion potential upon a frequency range of 10 mHz–100 kHz and the sinusoidal potential perturbation was 5 mV in amplitude. The impedance data were fitted to most appropriate equivalent circuit by using Zview2 software. The value double layer capacitance (C_{dl}) is evaluated from CPE (Q) and a resistor (Rct), using the following relation[14-15]:

$$C_{dl} = (Q \cdot R_{ct}^{1-n})^{1/n} \quad (4)$$

Where Q is the constant phase element (CPE) and n is a coefficient can be used as a measure of surface inhomogeneity. For n = 0, CPE represents a resistance, for the ideal electrodes, the CPE are an ideal capacitance when n = 1 and for n = 0.5 a Warburg element.

The inhibition efficiency η_z (%) is determined from the value of the charge transfer resistance for uninhibited (R_{ct}^0) and inhibited solution (R_{ct}), using the following equation:

$$\eta_z (\%) = \left(1 - \frac{R_{ct}^0}{R_{ct}}\right) \times 100 \quad (5)$$

RESULTS AND DISCUSSION

1.4. Polarization results

The potentiodynamic polarization curves, given in Fig. 1, presents the corrosion behavior of carbon steel in 1.0 M HCl without and with addition of different concentrations of oil of citrus leaves (OCL) at 303K. We can see from I-E curves that the anodic and cathodic current densities decrease with rise of concentration of OCL. The intersection of lines of anodic and cathodic Tafel obtained by their extrapolation up to intersection at a point where corrosion current density (I_{corr}) and corrosion potential (E_{corr}) are obtained. The corresponding electrochemical parameters to fig. 1 and η_p (%) calculated by equation (3) are listed in Table 1.

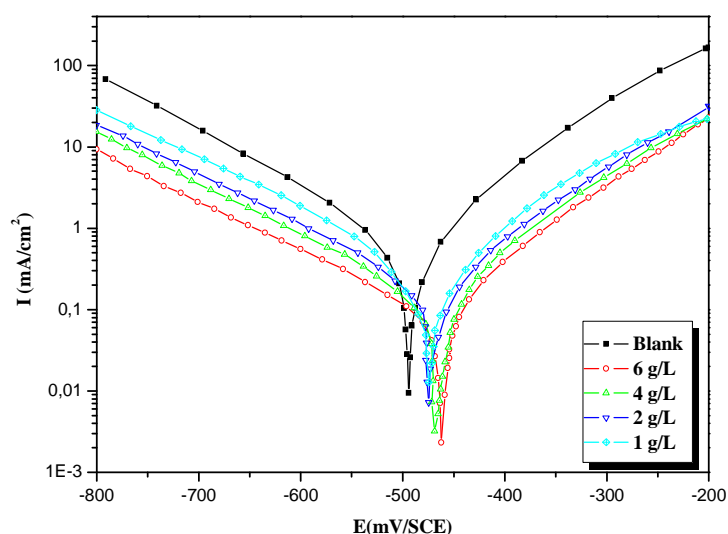


Figure 1. Polarization curves of carbon steel in 1.0 M HCl for various concentrations of OCL at 303K

Table 1. Polarization data of carbon steel in 1.0 M HCl without and with various concentrations of OCL at 303 K

Inhibitor	Conc (g/L)	$-E_{corr}$ (mV/SCE)	$-\beta_c$ (mV dec ⁻¹)	I_{corr} ($\mu\text{A cm}^{-2}$)	η_{Tafel} (%)	Θ
Blank	-	496.0	162.00	564.0	-	-
Citrus oil	6	452.1	175.41	63.3	88.95	0.889
	4	454.8	164.87	99.7	82.32	0.823
	2	457.3	156.21	156.7	72.21	0.722
	1	456.9	147.77	180.5	67.99	0.679

It's clear that the tested compound can be classified as mixed inhibitor with anodic predominant because we see the small displacement of corrosion potential with respect to corrosion potential of the blank test toward positive value and not exceed 85 mV [16].

The result in Table 2 and Fig.2 shows that when the concentration of oil of citrus leaves increased in acidic medium, the inhibition efficiency increases and the corrosion current density decreased considerably. These changes can be due to the adsorption layer of the inhibitor molecules on the steel surface.

1.5. Electrochemical impedance spectroscopy measurements

Fig.3 presents the Nyquist diagrams of carbon steel in corrosive medium without and with OCL inhibitor at various concentrations. The general shape of all Nyquist plots corresponds to a single depressed semi-circle indicating that the corrosion process is related to charge transfer to interface steel/solution. This behavior may be clarified with the help of a simple equivalent circuit, used to model the iron/acid interface (Fig. 3), and composed of double layer capacitance (C_{dl}) that is in parallel with the impedance due to the charge transfer reaction (R_{ct}) and solution resistance (R_s) [17]. The equivalent circuits parameters using Z view 2 software and the example of fitted curve are submit in Table 2 and Fig. 4, respectively.

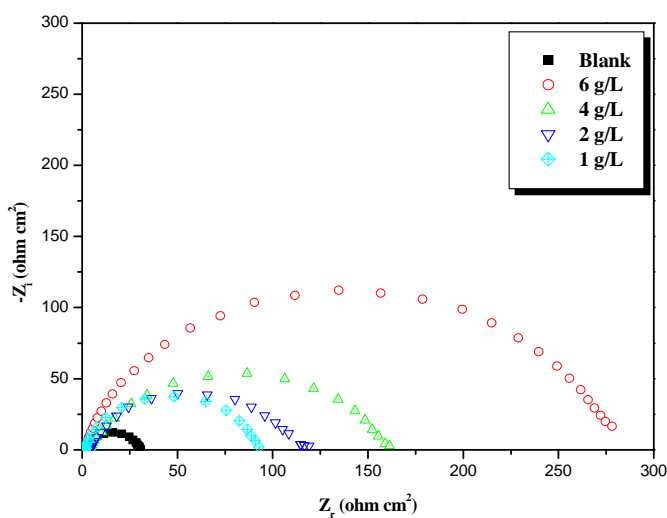


Figure 2. Nyquist diagrams for carbon steel in 1.0 M HCl containing different concentrations of OCL at 303 K

Table 2. Impedance parameters for corrosion of carbon steel in 1.0 M HCl in the absence and presence of different concentrations of OCL at 303 K

Inhibitor	Conc (g/L)	R_{ct} ($\Omega \text{ cm}^2$)	n	$Q \times 10^{-4}$ ($\text{s}^2 \Omega^{-1} \text{ cm}^{-2}$)	C_{dl} ($\mu\text{F cm}^{-2}$)	η_z (%)	Θ
Blank	-	29.35	0.91	1.7610	91.63	-	-
Oil of citrus leaves	6	274.9	0.90	0.3444	20.52	89.32	0.893
	4	157.6	0.89	0.4873	26.69	81.38	0.813
	2	109.3	0.92	0.6966	45.58	73.15	0.731
	1	88.48	0.88	1.0485	55.38	66.83	0.668

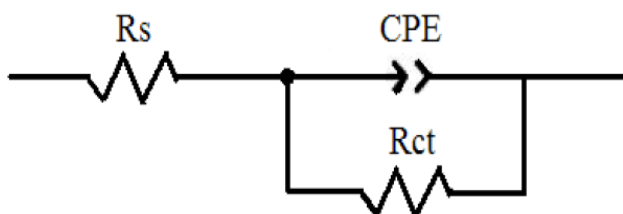


Figure 3. Equivalent electrical circuit corresponding to the corrosion process on the carbon steel in hydrochloric acid

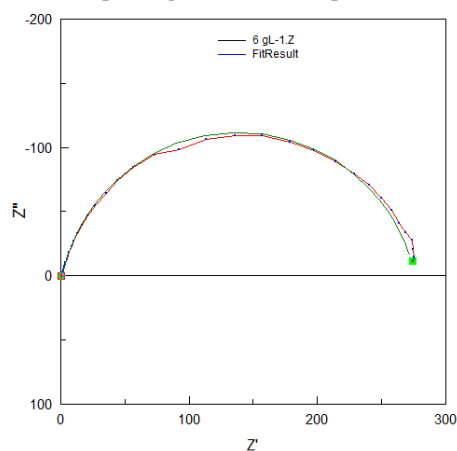


Figure 4. EIS Nyquist plots for carbon steel in 1.0 M HCl with 6 g/L OCL: dotted lines experimental data; dashed line calculated

Charge transfer resistance presented by diameter of Nyquist plots increases on increasing the OCL concentration. This suggested that the formed inhibitive layer was strengthened by addition of citrus oil compounds.

The C_{dl} values decreased and resistance of charge transfer increased with the addition of the OCL and this variation is more pronounced with increasing concentration of tested inhibitor. The decrease in the double layer capacitance caused by a decrease in local dielectric constant and/or an increase in the thickness of double layer that can be attributed to the gradual replacement of adsorbed molecules on the surface generally water molecules by adsorption of citrus oil molecules on the metal surface [18-19].

1.6. Weight loss tests

Table 3 show the variation of corrosion rate, inhibition efficiency and surface coverage for carbon steel in acidic solution containing different concentrations of studied oil of citrus leaves. These results prove that the addition of OCL in aggressive medium decreases the corrosion rate of carbon steel, whereas inhibition efficiency (η_w) and surface coverage (θ) increase with increasing inhibitor concentration (Fig. 5). The gravimetric results confirm those obtained by potentiodynamic polarization methods and electrochemical impedance spectroscopy.

Table 3. Corrosion parameters obtained from weight loss measurements for carbon steel in 1.0 M HCl containing various concentration of OCL at 303 K

Inhibitor	Concentration (g/L)	C_R ($\text{mg cm}^{-2} \text{h}^{-1}$)	η_w (%)	θ
Blank	-	1.135	-	-
Oil of citrus leaves	6	0.101	91.10	0.911
	4	0.143	87.40	0.874
	2	0.244	78.50	0.785
	1	0.339	70.13	0.701

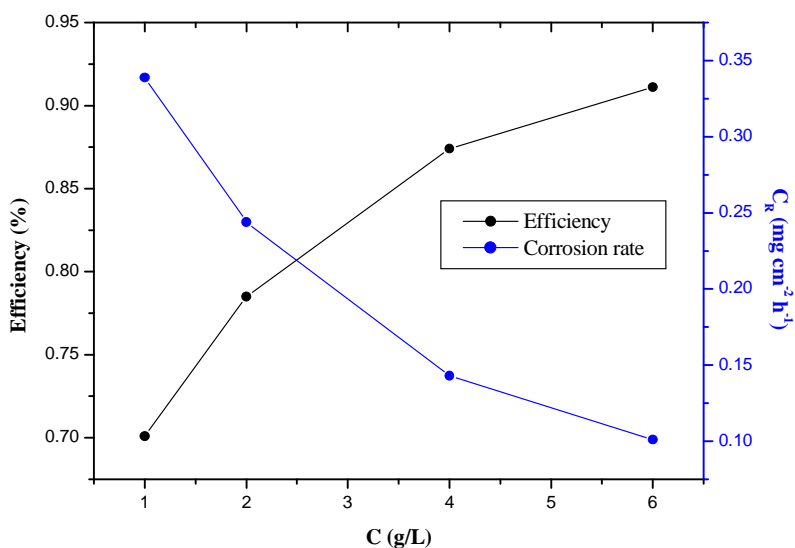


Figure 5. Relationship between the corrosion rate, the inhibition efficiency and OCL concentrations for carbon steel after 6 h immersion in 1.0 M HCl at 303 K

1.7. Effect of temperature

To estimate the activation energies of the dissolution process of carbon steel and to study the mechanism of corrosion and its inhibition, polarization measurements were conducted at different temperatures in the absence and presence of oil of citrus leaves at 6g/L (Figs.6. and 7.). The effect of temperature in the range 298–328 K on the electrochemical parameters of carbon steel are, with and without of OCL at 6g/L, listed in Table 4. It is clear from Table 3 that the increase of corrosion rate is more pronounced with the rise of temperature for uninhibited solution. The presence of the OCL leads to a decrease in the corrosion rate. The inhibitory action of inhibitor is slightly increased at elevated temperature from 298 to 328 K leading to the increase of inhibition efficiency. This decrease can be due to the desorption phenomena of some molecules from the carbon steel surface by increasing the temperature.

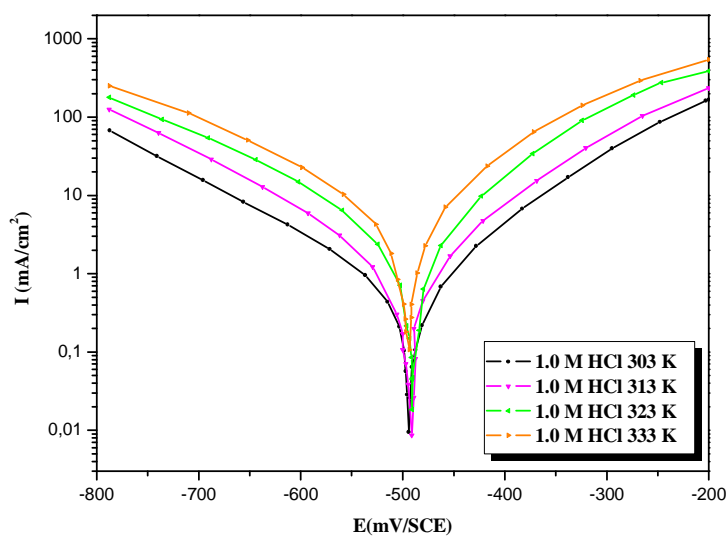


Figure 6. Potentiodynamic polarization curves of carbon steel in 1.0 M HCl at different temperatures

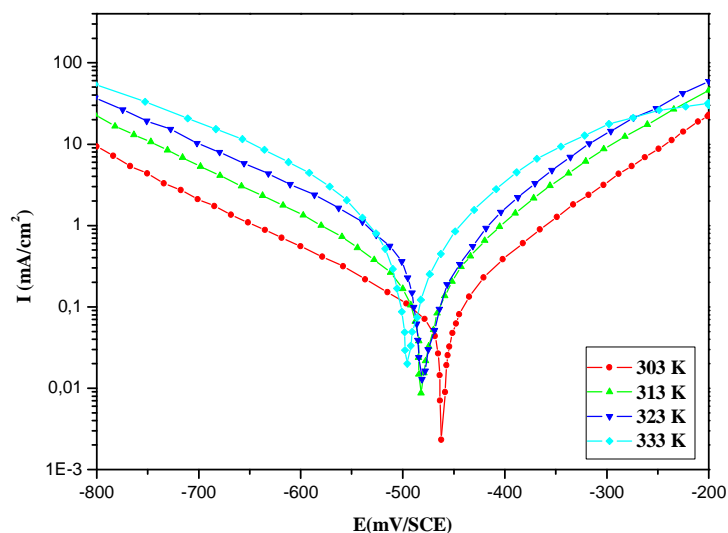


Figure 7. Potentiodynamic polarization curves of carbon steel in 1.0 M HCl in the presence of 6 g/L OCL at different temperatures

Table 4. The influence of temperature on the electrochemical parameters for carbon steel electrode immersed in 1.0 M HCl and 1.0 M HCl + 6 g/L OCL

Inhibitor	Temp (K)	$-E_{\text{corr}}$ (mV/SCE)	$-\beta_c$ (mV dec ⁻¹)	I_{corr} ($\mu\text{A cm}^{-2}$)	η_{Tafel} (%)
Blank	303	496	162.5	564	-
	313	498	154.5	773	-
	323	492	176.0	1244	-
	333	497	192.0	1650	-
Oil of citrus leaves	303	452.1	175.41	63.3	88.95
	313	483.7	152.07	161.7	79.08
	323	484.8	163.36	367.8	70.43
	333	495.2	170.52	632.5	61.67

The activation parameters such as apparent activation energy (E_a), the change of activation enthalpy (ΔH_a^*) and the change of activation entropy (ΔS_a^*) for the corrosion process were calculated from Arrhenius type plot (Eq. (6)) and transition-state (Eq. (7)) [20], respectively:

$$I_{\text{corr}} = A \cdot \exp\left(-\frac{E}{R \cdot T}\right) \quad (6)$$

$$I_{\text{corr}} = \frac{RT}{Nh} \cdot \exp\left(\frac{\Delta S_a^*}{R}\right) \cdot \exp\left(-\frac{\Delta H_a^*}{RT}\right) \quad (7)$$

Where I_{cor} is the corrosion current density, A is the Arrhenius constant, and R is the universal gas constant, N is Avogadro's constant, h is Planck's constant.

Figs. 8 and 9 represent the data plots of $\ln(I_{\text{corr}})$ versus $10^3/T$ and $\ln(I_{\text{corr}}/T)$ versus $10^3/T$, respectively, without and with optimum concentration of citrus oil. The calculated values of activation parameters are given in Table 5.

From this table, the obtained values of ΔH_a^* and E_a for inhibited solutions are higher than that obtained for uninhibited solutions, showing that the energy barrier of the corrosion reaction increased in the presence of the tested inhibitor without changing the mechanism of dissolution [21]. The positive sign of ΔH_a^* reflects the endothermic nature of the carbon steel corrosion process indicating that the dissolution of steel is slowed by addition of the tested compound [22].

The entropy of activation (ΔS_a^*) increases more positively with the inhibited solution than the uninhibited solution suggesting the formation of an ordered stable film of the tested compound on the electrode surface [23]. In the presence of inhibitor, one can notice the E_a and ΔH_a^* values vary in the same way (Table 5). These results permit to verify the known thermodynamic relation between the E_a and ΔH_a^* [24-25]:

$$\Delta H_a^* = E_a - RT \quad (8)$$

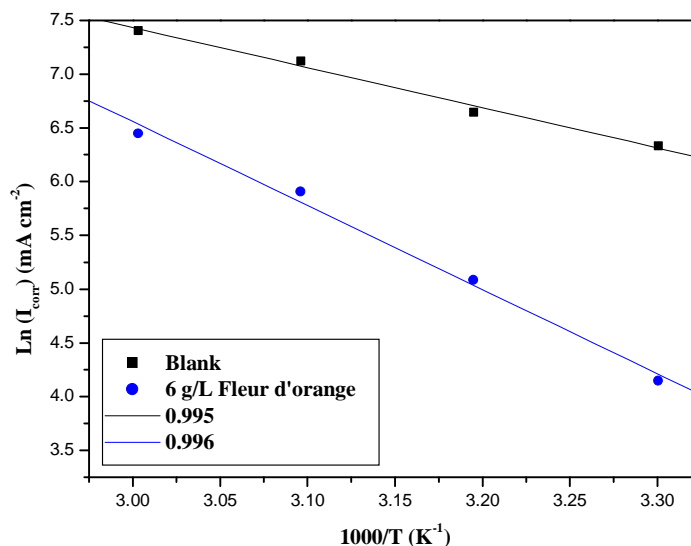


Figure 8. Arrhenius plots for carbon steel in 1.0 M HCl and 1.0 M HCl + 6 g/L OCL

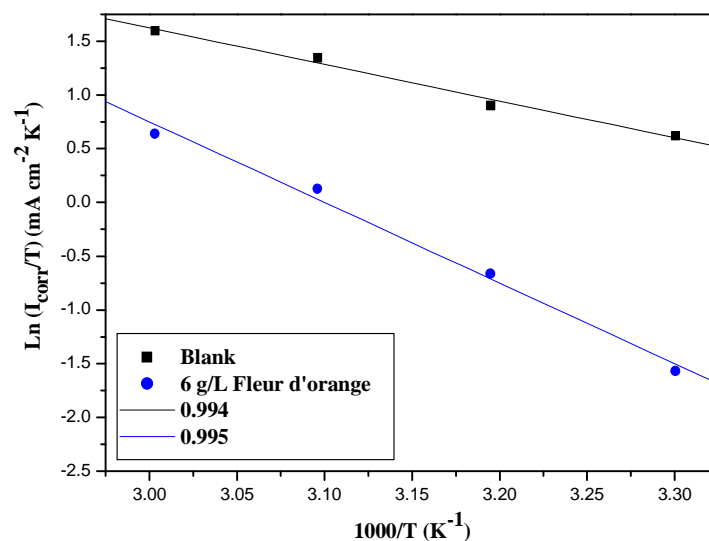


Figure 9. Transition state plots for carbon steel in 1.0 M HCl and 1.0 M HCl + 6 g/L OCL

Table 5. Corrosion kinetic parameters for carbon steel in 1.0 M HCl in the presence and absence of 6 g/L OCL

Inhibitor	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J mol ⁻¹ K ⁻¹)	$E_a - \Delta H_a$
Blank	31.00	28.35	-98.8	2.65
6 g/L oil citrus	64.96	62.32	-4.16	2.64

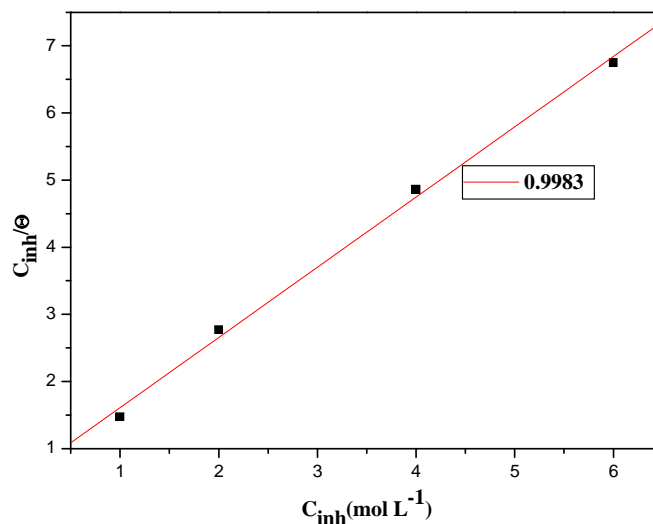


Figure 10. Langmuir adsorption of OCL on the carbon steel surface in 1.0 M HCl solution at 303K

1.8. Adsorption considerations

The mechanism of corrosion inhibition for carbon steel can be introduced on the basis of adsorption behavior of the oil citrus inhibitor on the electrode surface. The degree of surface coverage (θ) estimated for different concentrations of the study inhibitor in 1M HCl has been evaluated using electrochemical measurements, where θ is the ratio $\eta_{Tafel}(\%)/100$. The tests were made to fit the θ values to the adsorption isotherms frequently used that are Langmuir adsorption isotherms, Temkin, Frumkin and Flory-Huggins. Many adsorption isotherms were plotted. The best description of the adsorption behavior of the studied inhibitor can be accorded to Langmuir isotherm where the

regression coefficient related to (C_{inh}/θ) versus C_{inh} plot is almost equal to 1 (Fig. 10). And which may be represented by the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{inh} \quad (9)$$

Where C_{inh} is the concentration of OCL and k_{ads} is the adsorption equilibrium constant of the adsorption process.

CONCLUSION

The oil of citrus leaves may act as an eco-friendly corrosion inhibitor for carbon steel in molar hydrochloric solution. The potentiostatic polarization data indicate that oil of citrus leaves acted as a mixed type inhibitor with predominant anodic effectiveness.

The inhibition efficiencies of tested oil obtained by EIS, by polarization and by gravimetric methods were in good reasonably agreement. He increases with the inhibitor concentration, and decreases with temperature of medium. The adsorption of citrus oil on the steel surface obeys to the Langmuir isotherm model.

From result of EIS, values of the obtained double layer capacitance (C_{dl}) have shown a tendency to decrease, which can result from a decrease in local dielectric constant and/or an increase in thickness of the electrical double layer. Consequently, the inhibition function of the tested compound is through adsorption at the steel/solution interface.

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REFERENCES

- [1] G. Trabaneli, *Corrosion*, **1991**, 47, 410–419.
- [2] H Wang, H Fan, J Zheng, *Mater. Chem. Phys.* **2003**, 77, 655-661.
- [3] I Ahamad, R Prasad, MA Quraishi, *Corros. Sci.* **2010**, 52, 3033–3041.
- [4] M Lagrenée, B Mernari, M Bouanis, M Traisnel, FBentiss, *Corros. Sci.* **2002**, 44, 573-581.
- [5] M Abdallah, *Corros. Sci.* **2003**, 45, 2705-2713.
- [6] M Outirite, MLagrenée, M Lebrini, M Traisnel, C Jama, H Vezin, F Bentiss, *Electrochim.Acta*, **2010**, 55, 1670–1681
- [7] E A Noor, A H Al-Moubaraki, *Mater. Chem. Phys.* **2008**, 110, 145–154.
- [8] G Quartarone, L Ronchin, AVavasori, C Tortato, L Bonaldo, *Corrosi. Sci.*, **2012**, 64, 82–89
- [9] M AHegazy, *Corrosi. Sci.*, **2009**, 51, 2610–2618.
- [10] M Znini, L Majidi, ABouyanzer, J Paolini, JM Desjobert, J Costa, B Hammouti. *Arabian J. of Chem.* **2012**, 5, 467–474
- [11] A Lecante, F Robert, PA Blandinières, C Roos, *Current Appl. Phys.* **2011**, 11, 714-724
- [12] N I Kairi, JKassim, *Int. J. Electrochem. Sci.*, **2013**, 8, 7138 – 7155.
- [13] M Belkhaouda, L Bammou, R Salghi, O Benali, AZarrouk, E Ebenso, B Hammouti, *J. Mater. Environ. Sci.* **2013**, 5 (6), 1042-1051.
- [14] S Martinez, M Metikos-Hukovic, *J. Appl. Electrochem.* **2003**, 33, 1137.
- [15] H Ma, X Cheng, G Li, S Chen, Z Quan, S Zhao, LNiu, *Corros. Sci.* **2000**, 42, 1669
- [16] ES Ferreira, C Giancomelli, FC Giacomelli, A Spinelli, *Mater. Chem. Phys.* **2004**, 83, 129-134.
- [17] H B Ouici, M Belkhoua, O Benali, R Salghi, L Bammou, A Zarrouk, B Hammouti, *Res Chem Intermed.* **2015**, 41, 4617-4634
- [18] JAljourani et al., *Corros. Sci.* **2009**, 51, 1836–1843.
- [19] AK Singh, MA Quraishi, *Corros. Sci.* **2009**, 51, 2752–2760.
- [20] JOM. Bockris, AKN Reddy, *Modern Electrochemistry*, vol. 2, Plenum Press, New York, **1977**. p. 1267.
- [21] ST Arab, K Memran, *Inter. J. App. Chem.* **2007**, 3, 69–84.
- [22] N.M. Guan, L. Xueming, L. Fei, *Mater. Chem. Phys.* **2004**, 86, 59–68.
- [23] A Yurt, ABalaban, SU Kandemir, G Bereket, BERk, *Mater. Chem. Phys.* **2004**, 85, 420.
- [24] K JLaidler, *Reaction kinetics* vol. 1, first ed., Pergamon Press, New York, **1963**. p. 1.
- [25] F Bentiss, M Bouanis, B Mernari, M Traisnel, H Vezin, MLagrenée, *Appl. Surf.Sci.* **2007**, 253, 3696.