

Corrosion Protection of Carbon Steel in Acidic Solution by Using Ylang-Ylang Oil as Green Inhibitor

H. Lgaz^{1,2}, M. Belkhaouda², M. Larouj¹, R. Salghi^{2,*}, S. Jodeh³, I. Warad³, H. Oudda¹, A. Chetouani⁴

¹ Laboratory separation processes, Faculty of Science, University Ibn Tofail PO Box 242, Kenitra, Morocco.

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

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

⁴ Laboratoire de Chimie Appliquée et environnement (LCAE-URAC18), Faculté des Sciences, 60000 Oujda, Morocco.

*Corresponding author. E-mail(R. Salghi) : salghi@uiz.ac.ma

Received 01 Nov 2015, Revised 08 Jan 2016, Accepted 09 Jan 2016

Abstract

The inhibition effect of ylang-ylang oil (**YYO**) and their adsorption on carbon steel surface in hydrochloric acid was realized at temperatures varying between 308 and 338 K by weight loss, EIS, and potentiodynamic polarization techniques. The tested compound showed inhibition efficiency that is superior 87 % for a concentration equal to 1.0 g/L. Polarization measurements indicate that the examined oil act as a mixed inhibitor with predominant anodic effectiveness and the protection efficiency increases with inhibitor concentration but this effect decreased with increasing of temperature. Data obtained from EIS studies were analyzed to model inhibition process through appropriate equivalent circuit models. The adsorption of **YYO** on carbon steel surface obeys Langmuir adsorption isotherm in acid medium and the activation were determined and discussed.

Keywords: Corrosion inhibition, ylang-ylang oil, electrochemical and gravimetric techniques,

1. Introduction

Alloys steel is the well-known materials used in various industrial applications and highly susceptible to dissolution problem in aqueous solutions and especially in acidic mediums [1-4]. To reduce this phenomenon, many organic and inorganic compounds are applied as corrosion inhibitors for metal and alloy in aggressive solution. Many researchers provide the inhibition of corrosion by adsorption of inhibitors molecules on the alloy surface [5-8]. Organic compounds containing nitrogen, sulfur or oxygen atoms are often used to protect alloys from dissolution by adsorption on the surface of electrode from the bulk of environment forming a protective film [8-10]. These compounds have been intensively investigated as effective corrosion inhibitors. Recently, research in corrosion is focused on green corrosion inhibitors

namely also ecofriendly inhibitor that shows good inhibition efficiency with low risk of environmental pollution and low cost [11-15]. The aim of this work is to study the effect of *ylang-ylang oil* on carbon steel corrosion in 1.0 M HCl using potentiodynamic polarization curves tests and electrochemical impedance spectroscopy (EIS) and gravimetric measurements.

2. Experiment

2.1. Electrodes and chemicals and test solution

Corrosion tests have been performed, using the gravimetric and electrochemical measurements, on electrodes cut from sheets of carbon steel with the 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 aggressive medium of molar hydrochloric acid used for all studies were prepared by dilution of analytical grade 37% HCl with double distilled water. The concentrations of **YYO** used in this investigates were varied from 0.01 to 1.00 g/L.

2.2. Gravimetric measurements

Gravimetric measurements were realized in a double walled glass cell equipped with a thermostat-cooling condenser. The carbon steel specimens used have a rectangular form with dimension of $2.5 \times 2.0 \times 0.2$ cm were abraded with a different grade of emery paper (320-800-1200) and then washed thoroughly with distilled water and acetone. After weighing accurately, the specimens were immersed in beakers which contained 100 ml acid solutions without and with various concentrations of **YYO** at temperature equal to 303 K remained by a water thermostat for 6h as immersion time. The gravimetric tests were performed by triplicate at same conditions.

The corrosion rates (C_R) and the inhibition efficiency (η_{wt} %) of carbon steel have been evaluated from mass loss measurement using the following equations:

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

$$\eta_{wt} \% = \frac{C_R^0 - C_R}{C_R^0} \times 100 \quad (2)$$

Where w is the average weight loss before and after exposure, respectively, S is the surface area of sample, t is the exposure time, C_R^0 and C_R is the corrosion rates of steel without and with the **YYO** inhibitor, respectively.

2.3. Electrochemical tests

The potentiodynamic polarization curves were conducted using an electrochemical measurement system PGZ 100 Potentiostat/Galvanostat controlled by a PC supported by the Voltmaster 4.0 Software. The electrochemical measurements were performed in a conventional three electrode glass cell with carbon steel as a working electrode, platinum as counter electrode (Pt) and a saturated calomel electrode used as a reference electrode. The working electrode surface was prepared as described above gravimetric section. Prior to each electrochemical test an immersion time of 30 min was given to allow the stabilization system at corrosion potential. The polarization curves were obtained by changing the electrode potential automatically

from -800 to -200 mV/SCE at a scan rate of 1 mV s⁻¹. The temperature is thermostatically controlled at desired temperature ± 1 K. The percentage protection efficiency (η_p %) is defined as:

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

Where, I_{corr}^0 are corrosion current in the absence of inhibitor, I_{corr} are corrosion current in the presence of inhibitor. Electrochemical impedance spectroscopy (EIS) measurements were carried out with same equipment used for potentiodynamic polarization study (Voltalab PGZ 100) at applied sinusoidal potential waves of 5mV amplitudes with frequencies ranging from 100 KHz to 10 mHz at corrosion potential. The impedance diagrams are given in the Nyquist representation. The charge transfer resistance (R_{ct}) was determined from Nyquist plots and double layer capacitance (C_{dl}) was calculated from CPE parameters of the equivalent circuit deduced using Zview software. In this case the percentage protection efficiency (η_z %) is can be calculated by the value of the charge transfer resistance (R_{ct})

$$\eta_z (\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (4)$$

Where R_{ct}^0 and R_{ct} were the polarization resistance of uninhibited and inhibited solutions, respectively.

3. Results and discussion

3.1. Polarization results

The anodic and cathodic polarization curves of carbon steel in 1.0 M HCl solution at 303 K in the absence and presence of various concentrations of **YYO** after 30 min of immersion time is exposed in Fig. 1. From this curves, corrosion current density (I_{corr}) were deduced graphically curve by extrapolating the cathodic and anodic Tafel slope to the corrosion potential (E_{corr}). The corrosion kinetic parameters and the percentage protection efficiency determined by the corrosion current density is listed in Table 1.

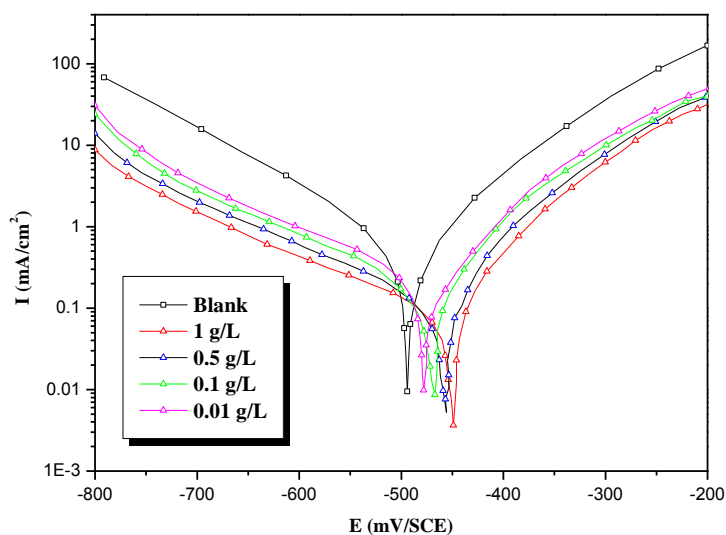


Figure 1. Polarisation curves of carbon steel in 1.0 M HCl for various concentrations of Ylang-ylang at 303K.

Comparing the curves for inhibited with that of uninhibited medium, it is observed that the E_{corr} values for carbon steel in 1 M HCl shift slightly toward more positive direction indicating that this compound can be classified as a mixed-style inhibitor with anodic predominance.

The cathodic diagrams (Fig. 1) offer to the parallel lines showing that the addition of **YYO** to the corrosive solution does not modify hydrogen reduction. The electrochemical data shows that, the addition of the **YYO** molecules to the corrosion solution reduces the aggressiveness of this medium per application on both anodic metal dissolution and cathodic hydrogen evolution reactions. This behavior can be explained by the adsorption of tested compound on electrode surface and which caused a barrier action for transfer of mass and charge for both reactions [16]. The increasing of the inhibition efficiency with the **YYO** concentration justifying that a higher surface coverage obtained in acidic solution with the optimum concentration of the inhibitor.

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

Inhibitor	Conc (g/L)	$-E_{\text{corr}}$ (mV/SCE)	$-\beta_c$ (mV dec ⁻¹)	I_{corr} ($\mu\text{A cm}^{-2}$)	η_p (%)	Θ
Blank	-	496.0	162	564.0	-	-
	1.00	449.8	166.37	72.5	87.14	0.871
Ylang-ylang oil	0.50	450.6	165.41	86.3	84.69	0.846
	0.10	451.2	176.53	131.9	76.61	0.766
	0.01	453.7	176.91	253.0	55.14	0.551

3.2. Electrochemical impedance spectroscopy measurements

The effect of addition of the **YYO** as inhibitor on the corrosion behavior of carbon steel in 1.0 M HCl solution was studied by electrochemical impedance spectroscopy measurements at 303 K after at 30 min immersion at open circuit potential (Fig. 2). The values of the electrochemical parameters that can be extracted from the Nyquist diagrams are collected in Table 2, Nyquist plots obtained for different concentrations of **YYO** are similar with the shape of blank solution; they exhibit single depressed semicircles across the frequency range studied, which denotes that the corrosion process was controlled by charge transfer resistance [17]. De size of semicircles increases with concentration of **YYO**. This depression can be attributed to the roughness of electrode surface and other inhomogeneity of the solid alloy caused by their dissolution during the attainment of corrosion potential [18]. An equivalent circuit model fitted from the Nyquist plots obtained by Zview software is arranged in such a way R_s in series with the parallel of CPE and R_{ct} (Fig. 3). To compensate for non-homogeneity in the system, the capacitances were ascribed as a constant phase element (CPE), defined by two values, Q and n . The impedance, Z , of CPE is presented by Eq.

$$Z_{CPE} = \frac{1}{Y_0(j2\pi f)^n} \quad (5)$$

Where Y_0 is a proportional factor, f is a frequency, $j^2 = -1$ and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [19]. The value of R_{ct} increases, while the double layer capacitance decreases with the change of inhibitor concentrations. The increase in R_{ct} values is attributed to the formation of an insulating protective film at the metal/solution interface. The decrease in CPE values can be attributed to a decrease in local dielectric constant and/or to an increase in the thickness

of the electrical double layer, suggesting that the inhibitor molecules are adsorbed at the metal/solution interface [20-21].

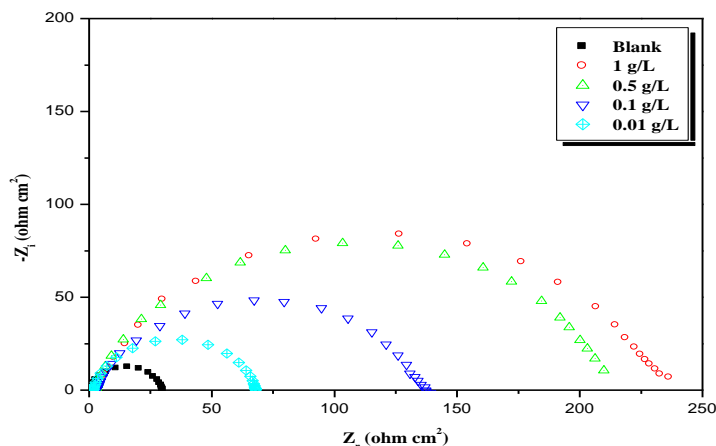


Figure 2. Nyquist diagrams for carbon steel in 1.0 M HCl containing different concentrations of Ylang-ylang oil at 303 K

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

Inhibitor	Conc (g/L)	R _{ct} (Ω cm ²)	n	Q×10 ⁻⁴ (s ⁿ Ω ⁻¹ cm ⁻²)	C _{dl} (μF cm ⁻²)	η _z (%)	Θ
Blank	-	29.35	0.91	1.7610	91.63	-	-
	1.00	230.0	0.93	0.2067	13.82	87.23	0.872
Ylang-ylang	0.50	210.3	0.92	0.4032	26.63	86.04	0.860
	0.10	132.5	0.92	0.6510	43.06	77.84	0.778
	0.01	66.44	0.89	0.8776	46.47	55.82	0.558

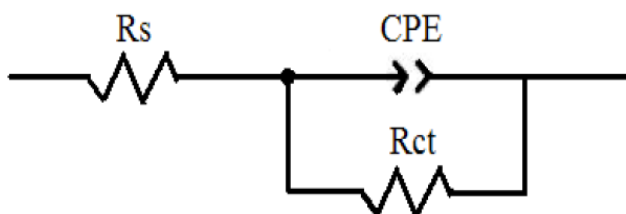


Figure 3. Equivalent electrical circuit corresponding to the corrosion process on the carbon steel in hydrochloric acid.

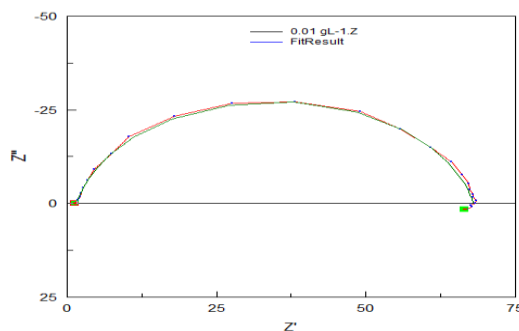


Figure 4. EIS Nyquist plots for carbon steel in 1.0 M HCl with 0.01 g/L Ylang-ylang oil interface: dotted lines experimental data; dashed line calculated.

3.3. Weight loss tests

Values of corrosion rate, inhibiting efficacies and cover surface obtained from weight loss method in different concentrations of ylang-ylang oil at 303 K are given in Table 3. It is clear from Table 3 and Fig. 5 that the addition of **YYO** in corrosive solution leads a decrease the corrosion rate of carbon steel, consequently, inhibition effect and coverage surface rise with concentration of tested compound. The explanation of this behavior can be justified by on the strong interaction of the inhibitor molecule onto the metal surface resulting in adsorption.

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

Inhibitor	Concentration (g/L)	C_R ($\text{mg cm}^{-2} \text{h}^{-1}$)	η_w (%)	Θ
Blank	-	1.135	-	-
Ylang-ylang oil	1.00	0.134	88.19	0.881
	0.50	0.162	85.73	0.857
	0.10	0.239	78.94	0.789
	0.01	0.469	58.68	0.586

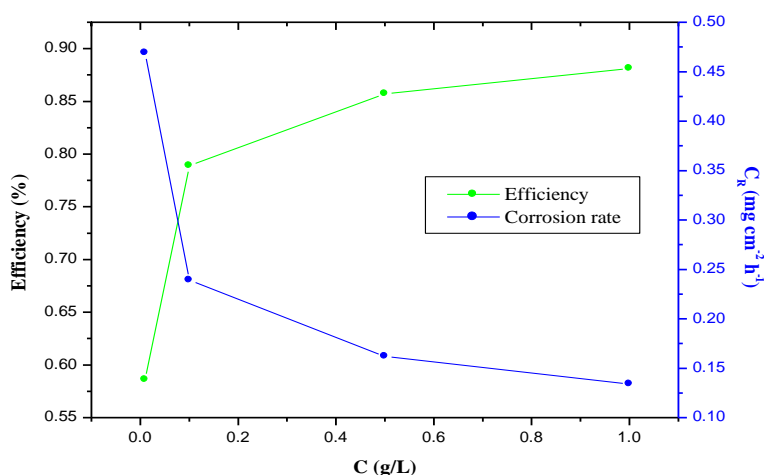


Figure 5. Relationship between the corrosion rate, the inhibition efficiency and Ylang-ylang concentrations for steel after 6 h immersion in 1.0 M HCl at 303 K.

3.4. Effect of temperature

The study of the temperature effect on the inhibition behavior is very important for understanding the adsorption of inhibitor molecules. Figs. 6 and 7 present the potentiodynamic polarization curves for carbon steel in the absence and presence of optimum concentration of the studied inhibitor in 1.0 M HCl at different temperatures. The electrochemical parameters deduced from this investigate are listed in Table 4.

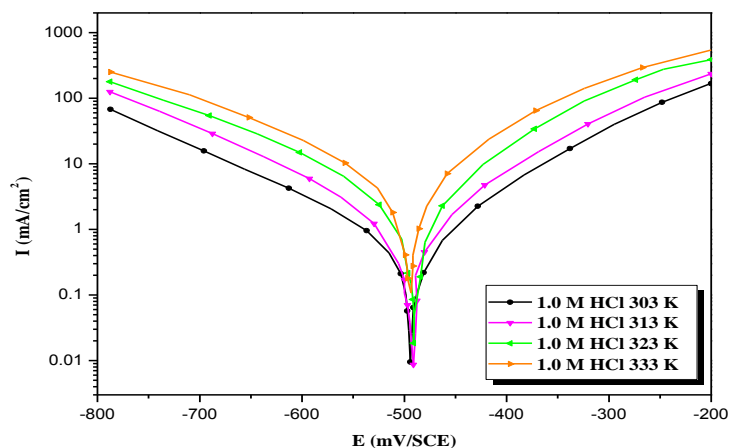


Figure 6. Potentiodynamic polarisation curves of carbon steel in 1.0 M HCl at different temperatures.

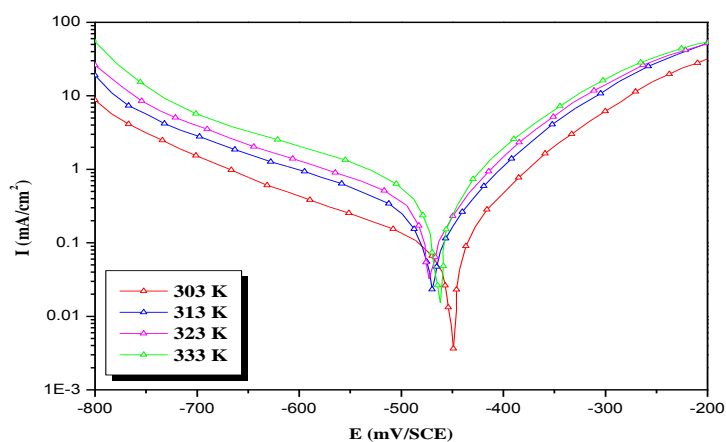


Figure 7. Potentiodynamic polarisation curves of carbon steel in 1.0 M HCl in the presence of 1 g/L Ylang-ylang oil at different temperatures.

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 + 1 g/L Ylang-ylang oil.

Inhibitor	Temperature (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	-
Ylang-ylang oil	303	449.8	166.37	72.5	87.14
	313	452.7	178.42	169.5	78.07
	323	455.2	187.08	418.7	66.34
	333	456.7	181.13	718.1	56.48

As may be note, the corrosion potential is affected slightly with increasing the medium temperature. On the other hand, the inhibition efficiency decreased with temperature. The increase in temperature accelerates of carbon steel dissolution reaction, justifying the rise of dissolution rate of metal. This result can be explained by decrease of adsorption of inhibitor molecules. Some researchers attributed this phenomenon to desorption of the inhibitor molecules from metal surface at higher temperatures. The effect of temperature on the corrosion current (I_{corr}) can be used for determines the activation parameters for dissolution process using the Arrhenius equation and transition state equation:

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

$$I_{\text{corr}} = \frac{RT}{Nh}.\exp\left(\frac{\Delta S^*}{R}\right).\exp\left(-\frac{\Delta H^*}{RT}\right) \quad (7)$$

Where E_a is the activation corrosion energy, ΔH^* is the enthalpy, ΔS^* is the entropy of activation, T is the absolute temperature in Kelvin, h is the Plank constant, N is the Avogadro number and R the molar gas constant. The linear regression between $\ln(I_{\text{corr}})$ and $1/T$ shown in Fig. 8 for uninhibited solution and inhibited by optimum concentration of **YYO**, we allowed to deduct the activation energy in the presence and absence of **YYO** inhibitor and the result is listed in Table 5. It is clearly from Table 5 that E_a value in the presence of the **YYO** inhibitor is higher compared to that in their absence, consequently leading to reduction in the metal dissolution. This result can be interpreted by formation of an adsorptive film of a physical electrostatic character. Some researches correlate this raising of E_a value with that the increased thickness of the double layer, which enhances the activation energy of the corrosion process [22]. The values of ΔH^* and ΔS^* evaluated from the slope ($\Delta H^*/R$) and the an intercept of $(\ln(R/Nh) + (\Delta S^*/R))$ of the plots of $\ln(I_{\text{corr}}/T)$ against $1/T$ are listed in Table 5. The positive signs of ΔH^* reflect the endothermic nature of dissolution process of the carbon steel suggesting that this dissolution is slowed. ΔS^* value is more positive in 1.0 M HCl solution containing **YYO** as an inhibitor than that make in the uninhibited solution. Some researches explained this behavior by replacement process of water molecules during adsorption of inhibitor molecules onto the electrode surface [23]. The thermodynamic reaction between the E_a and ΔH^* exposed in Table 5 is verified.

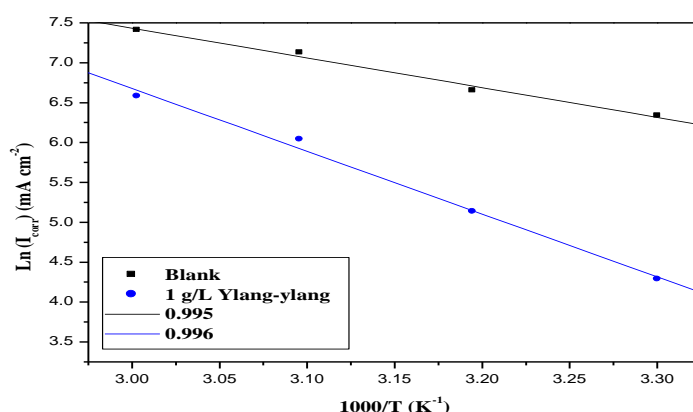


Figure 8. Arrhenius plots for carbon steel in 1.0 M HCl and 1.0 M HCl + 1 g/L Ylang-ylang.

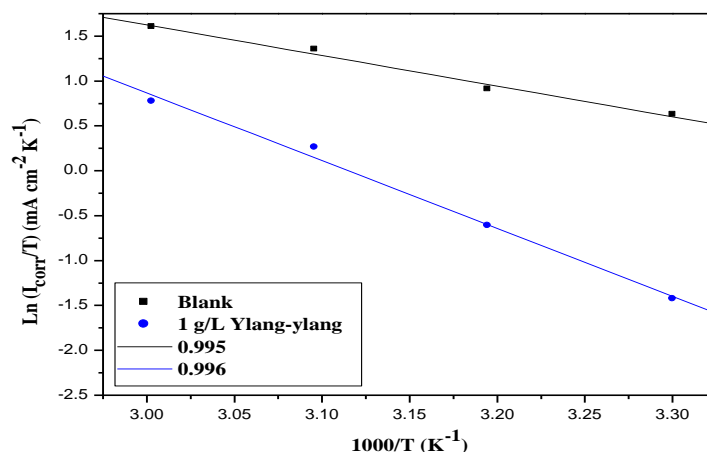


Figure 9. Transition state plots for carbon steel in 1.0 M HCl and 1.0 M HCl + 1 g/L Ylang-ylang.

Table 5. Corrosion kinetic parameters for carbon steel in 1.0 M HCl in the presence and absence of 1 g/L Ylang-ylang.

Inhibitor	E _a (kJ/mol)	ΔH* (kJ/mol)	ΔS* (J mol ⁻¹ K ⁻¹)	E _a - ΔH*
Blank	31.00	28.35	-98.8	2.65
1 g/L Ylang-ylang	65.38	62.74	-1.91	2.64

3.5. Adsorption considerations

The adsorption behavior of the inhibitor molecules on electrode surface can be used to elucidate the inhibition mechanism of inhibitors. The surface coverage values (θ) determined by polarization curves (Table 2) at different concentrations of **YYO** inhibitor in acidic solution were used to explain the excellent adsorption isotherm, consequently, establish the adsorption process from the experimental results obtained.

To investigate the inhibitor adsorption mechanism, several adsorption isotherms were fitted and the Langmuir adsorption isotherm gives the best description of the adsorption behavior of the inhibitor on carbon steel electrode according to Langmuir adsorption isotherm equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{inh} \quad (10)$$

where C_{inh} is the inhibitor concentration and k_{ads} is the adsorptive equilibrium constant.

The linear relationship of C_{inh}/θ versus C_{inh} in different concentrations of inhibitor presented in Fig. 10, possesses a slope near to unit with the correlation coefficient R^2 that is close to 1, thus, the adsorption of **YYO** on steel surface obeys the Langmuir adsorption isotherm.

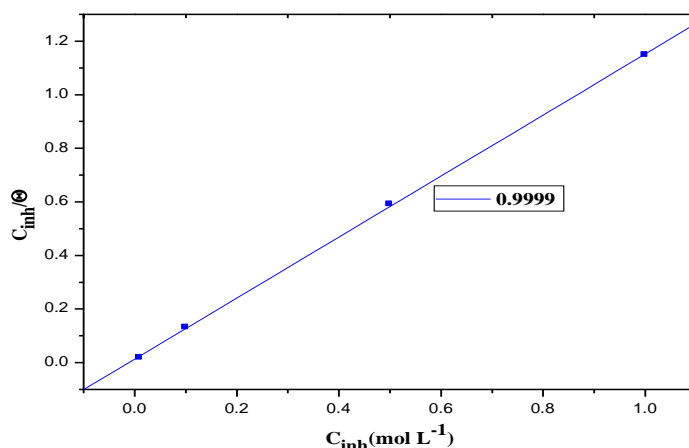


Figure 10. Langmuir adsorption of Ylang-ylang on the carbon steel surface in 1.0 M HCl solution at 303K.

4. Conclusion

This study demonstrates that *ylang-ylang oil* (YYO) is a good inhibitor of corrosion for carbon steel in corrosive environment. The polarization investigate showed YYO is a mixed-type inhibitor with anodic predominance inhibition. The adsorption of the tested inhibitor on interface between the carbon steel and molar hydrochloric acid obeys the Langmuir adsorption isotherm model. The inhibitory effect of YYO on the electrode surface increases with concentration of inhibitor and decrease with temperature. The inhibition efficiency evaluated from different measurements is in good agreement.

EIS measurement shows a single depressed semicircle observed from high to low frequencies region for uninhibited and inhibited solution illustrate that the corrosion process was controlled by charge transfer resistance. The increasing of charge transfer resistance (R_{ct}) and decreasing of double layer capacitance (C_{dl}) in the presence of inhibitor can be suggested by the adsorption the inhibitor molecules on the surface of carbon steel.

References

- [1] N.A. Negm, A.M. Al Sabagh, M.A. Migahed, H.M. Abdel Bary, H.M. El Din, Corros. Sci. 52 (2010) 2122– 2132.
- [2] Ashish Kumar Singh, M.A. Quraishi, Corros. Sci. 52 (2010) 152–160.
- [3] I. Ahamad, M.A. Quraishi, Corros. Sci. 51 (2009) 2006–2013.
- [4] L.F. Li, P. Caenen, J.P. Celis, Corros. Sci. 50 (2008) 804–810.
- [5] M. Lagrenee, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, Corros. Sci. 44 (2002) 573–588.
- [6] M.A. Quraishi, I. Ahamad, A.K. Singh, S.K. Shukla, B. Lal, V. Singh, Matar. Chem. Phys. 112 (2008) 1035–1039.
- [7] L. Li, Q. Qu, W. Bai, F. Yang, Y. Chen, S. Zhang, Z. Ding, Corros. Sci. 59 (2012) 249–257.
- [8] N. Soltani, M. Behpour, S.M. Ghoreishi, H. Naeimi, Corros. Sci. 52 (2010) 1351–1361.
- [9] S. K. Shukla, M. A. Quraishi, Corros. Sci. 52 (2010) 314–321
- [10] C. M. Goulart, A. Esteves-Souzaa, C. A. Martinez-Huitle, C. J. F. Rodrigues, M. A. M. Maciel, A. Echevarria, Corros. Sci. 67 (2013) 281–291
- [11] N. Soltani, N. Tavakkoli, M. Khayatkashani, M. R. Jalali, A. Mosavizade, Corros. Sci. 62 (2012) 122–135

- [12] X. Li, S. Deng, H. Fu, *Corrosion Science* 62 (2012) 163–175
- [13] A. Lecante, F. Robert, P.A. Blandinières, C. Roos, *Current Applied Physics* 11 (2011) 714-724
- [14] J. Huang, H. Cang, Q. Liu, J. Shao, *Int. J. Electrochem. Sci.*, 8 (2013) 8592 - 8602
- [15] M. Boudalia, A. Guenbour, A. Bellaouchou, A. Laqhaili, M. Mousaddak, A. Hakiki, B. Hammouti, E.E. Ebenso, *Int. J. Electrochem. Sci.*, 8 (2013) 7414 – 7424
- [16] A. M. Al-Sabagh, H. M. Abd-El-Bary, R. A. El-Ghazawy, M. R. Mishrif, B. M. Hussein, *Egypt. J. Petrol.* 20 (2011) 33–45.
- [17] M. Behpour, S.M. Ghoreishi, N. Mohammadi, N. Soltani, M. Salavati-Niasari, *Corros. Sci.* 52 (2010) 4046–4057.
- [18] F. Bentiss, M. Lebrini, M. Lagrenée, *Corros. Sci.* 47 (2005) 2915–2931.
- [19] A. Singh, I. Ahamad, V.K. Singh, M.A. Quraishi, *J. Solid State Electr.* 15 (2011)1087–1097.
- [20] P. Mourya, S. Banerjee, R.B. Rastogi, M.M. Singh, *Ind. Eng. Chem. Res.* 52 (2013) 12733-12747.
- [21] S.K. Singh, S.P. Tambe, G. Gunasekaran, V.S. Raja, D. Kumar, *Corros. Sci.* 51 (2009) 595-601.
- [22] R. Solmaz, G. Kardas, M. Çulha, B. Yazıcı, M. Erbil, *Electrochim. Acta* 53 (2008) 5941.
- [23] P. Li, J.Y. Lin, K.L. Tan, J.Y. Lee, *Electrochim. Acta.* 42 (1997) 605.