

Natural corrosion inhibitor for lead in 0.1 M Na₂CO₃ solution

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Abstract— *The primary objective of this work is the study of the behavior of lead corrosion in a 0.1M Na₂CO₃ medium, and the inhibitory effect of the extract of Eucalyptus camaldulensis. To do this, we used the polarization techniques, chrono-amperometry and impedance spectroscopy. The effect of temperature on the lead with and without inhibitor in 0.1M Na₂CO₃ medium was studied in the range of 5 to 35°C. The results show that the corrosion rate in the presence of lead decreases the essential oil tested, where the effectiveness of inhibition increases with the concentration of the inhibitor to reach 75.81% at 1800ppm. The adsorption isotherm and the activation energy were determined.*

Index Terms—Lead; corrosion; inhibition; essential oil; Eucalyptus camaldulensis; adsorption.

I. INTRODUCTION

Lead is a heavy metal that is naturally extracted from copper ore. Since ancient times, lead has been very popular because of its malleability and ductility. It was heavily used not only in the manufacture of pipes for potable water, dishwashers, gutters, roofing plates but also for creating railings. Until now, the lead has been used to contain liquid sulfuric acid, which resists producing a protective layer of insoluble lead sulfate. Indeed, it is remarkable in electric accumulators or batteries [1]. The corrosive environment degrades and the material and battery performances are affected [2]. Corrosion problems in industries and the manufacture of batteries in general have been resolved through the selection of appropriate materials and/or by changing the environment to make it less aggressive [3]. The solutions (acid or base) are widely used in industry. Important areas where these solutions are the most applied are, pickling, and industrial cleaning scaling. Corrosion inhibitors are needed to reduce the rate of corrosion of metallic materials in aggressive environments [5-10]. An inhibitor is usually added in small quantities in order to slow the rate of corrosion by the mechanism of adsorption [11, 12]. Over the years, many inhibitors have been synthesized and it was found that the best inhibitors consist of one or more functional groups (-nh), hydroxide (-oh), mercapto (-sh), phosphonate (-po3h), sulfonate (-so3h), carboxyl (-cooh), and their derivatives. However, these products are generally obtained by chemical synthesis and therefore have a negative impact on the

environment. This has led many researchers around the world to use new non-polluting natural molecules to the environment. Spearmint [13], lippia spicata [14] thymus saturoides [15,16], jojoba oil [17], rosemary oil [18], eugenol [19] bgugaine [20] wormwood. [21] The encouraging results obtained by natural compounds as corrosion inhibitor of different metals prompted us to examine other natural substances against corrosion of lead. The aim of this work is to study the inhibitory activity of the essential oil of eucalyptus camaldulensis against corrosion of lead in 0.1 m na2co3 medium by the methods of electrochemical polarization, chrono-amperometry and spectroscopy electrochemical impedance methods. The effect of temperature was also studied.

II. EXPERIMENTAL PART

A. Extraction of essential oil of Eucalyptus camaldulensis

Leaves of Eucalyptus were collected in January 2014, in the region of Khouribga, Morocco. They were cut into small pieces and dried in the laboratory in the shade at room temperature for three days, to reduce its moisture content. The oil was obtained by the steam distillation method using the Clevenger apparatus. The extraction time is about 3 hours in average. The essential oil was recovered in a dark bottle and stored at 4 °C. A portion of the oil was used for the analysis of the chemical composition by gas chromatography, and the other part was used for the tests of the anti-corrosion activity.

B. Preparation of the solution

The solution of 0.1 M sodium bicarbonate (Sigma-Aldrich) was prepared with distilled water. Test solutions were freshly prepared before each experiment by adding the oil directly to the etching solution. Experiments were repeated three times to verify reproducibility.

C. Electrochemical measurements

The electrochemical experiments were performed in a pyrex cell, equipped with a conventional three-electrode assembly: working electrode lead as cup-shaped disc with a geometric area of 1 cm², platinum as a counter electrode and the electrode SCE as saturated calomel reference electrode. The lead disc was abraded with sandpaper to increasing particle size up to 1200, degreased with acetone, rinsed with distilled water and dried before each test. The measurements are performed with

an assembly comprising a potentiostat-galvanostat PGZ100, radiometer type coupled with "voltmaster4" software. The current-potential curves are obtained by potentiodynamic method; the potential applied to the sample varies continuously with a scanning rate of 2 mV/s between 1000 and -1000mV. Chrono- amperometric curves were plotted at a potential of 150 mV for 3600 seconds. The measures of electrochemical impedance spectroscopy (EIS) were performed with the same electrochemical system. The frequencies between 100 Hz and 10 kHz were superposed on the corrosion potential. The diagrams given in the impedances are Nyquist representation.

III. RESULTS AND DISCUSSION

A. Analysis of the chemical composition of the oil

The average yield of the essential oil extracted from the plant of *Eucalyptus camaldulensis* is studied in the range of 1.2%.

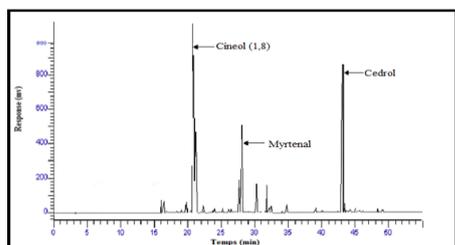


Fig 1. Chromatogram Essential oil of *eucalyptus camaldulensis*

Table 1. Chemical components of the essential oil of *Eucalyptus camaldulensis*

Peak	Time (min)	Area %	Compose
1	15.793	1.31	Anisole
2	16.189	1.14	Tricyclene
3	19.501	1.01	carene(2)
4	20.508	34.22	cineol (1,8)
5	20.807	10.56	cymen (para)
6	20.874	4.51	limonene
7	21.949	0.58	ocimene (trans)
8	23.640	0.37	camphenone (6)
9	24.828	0.31	campholenal (alpha)
10	26.006	0.17	camphene hydrate
11	27.300	3.84	terpineol 4

12	27.797	11.34	myrtenal
13	29.828	2.81	carvone
14	31.302	2.66	Nopol
15	31.671	0.40	Thymol
16	31.939	0.52	Menthyl acetate
17	34.171	0.61	Citronellyl acetate
18	38.388	0.26	Gurjunese «gamma-»
19	42.525	16.13	Cedrol
20	42.542	6.28	Guafol
21	42.671	0.71	Eudesmol «beta-»
22	44.195	0.22	Isoelemicin«trans-»

B. Electrochemical study of lead in a Na_2CO_3 solution 0.1 M

Figure 2 shows polarization curves in a lead 0.1 M sodium bicarbonate solution at 25 °C.

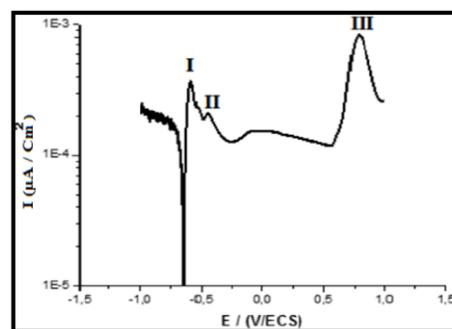
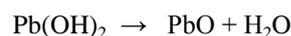
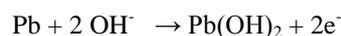


Fig 2. Lead polarization curves in 0.1 M Na_2CO_3 at 25°C.

The anodic portion of the curve contains three peaks (I, II, and III), the first peak is located at -0582 I V / SCE, which is due to the formation of $\text{Pb}(\text{OH})_2$ or PbO by the following reactions [22]:



The second anodic peak is located at -0.45 V/SCE corresponding to the training $\text{Pb}(\text{OH})_4$ or PbO_2 by the following reactions [22]:





The thermodynamically unstable dehydration of Pb(OH)_4 results in the formation of PbO_2 responsible for the formation of a passive film, making the coated surface, and the anode current density falls to a lower value (I_{pass}) indicating passivation [23]. The third peak (III) is observed at about 0.789 V/ECS beyond the plateau of passivity, it cannot be particularly assigned to any anodic oxidation reaction, several authors attributed this observation to the region of transpassivity, which is generally due to release of oxygen which occurs most likely on acid film H_2PbO_3 [24]. For higher anodic potentials, the field of transpassivity is achieved due to the oxidation of the solvent according to the following reaction:



C. Effect of concentration

1. Measurement of polarization:

Figure 3 shows the effect of the concentration of eucalyptus oil on the cathodic and anodic behavior of lead in a solution of 0.1 M Na_2CO_3 , which was studied by measurements of polarization. Table 2 shows the parameters of electrochemical lead, determined from measurements of polarization, such as; corrosion potential (E_{corr}), corrosion current density (I_{corr}), passivation current density (I_{pass}) and efficacy of inhibition E (%) calculated by Equation 1:

$$E \% = \frac{I_{\text{corr}} - I'_{\text{corr}}}{I_{\text{corr}}} \times 100 \quad (1)$$

Where I'_{corr} and I_{corr} respectively the current density with and without addition of inhibitor.

It is clear from Figure 3 that the anodic dissolution of the metal was inhibited with the addition of eucalyptus oil in the corrosive solution.

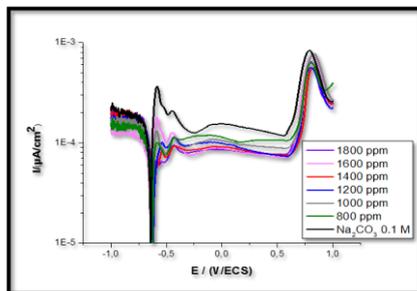


Fig 3. Lead polarization curves in a 0.1 M Na_2CO_3 solution with and without inhibitor at 25°C.

From figure 3 and table 2 it is clear that the effectiveness of inhibition (E_p %) increases with increasing concentration of eucalyptus oil to reach a maximum value of 75% at a concentration 1800 ppm. This suggests that increasing the concentration of inhibitor increases the number of lead molecules adsorbed on the surface, blocking the active sites and protect the metal. From Table 1 we see that the passivation current increase from $1.5366 \cdot 10^{-4} \mu\text{A}/\text{cm}^2$ to

$8.5026 \cdot 10^{-5} \mu\text{A}/\text{cm}^2$. Indeed the addition of 2000 ppm I_{pass} decreases by a factor of 1.8. This decrease is mainly due to the adsorption of oil on the surface of the metal. There was a wide variation in I_{pass} values. The corrosion potential values remain constant with the addition of eucalyptus oil. These results indicate that the inhibitor acts as an inhibitor of the mixed type [25-26].

2. Chrono-amperometry:

Experiences of time - current chrono- amperometric were conducted to identify the type of lead corrosion in a solution of sodium bicarbonate in the absence and presence of inhibitor. The chrono- amperometric curves measured at 150 mV of lead 0.1M Na_2CO_3 medium without and with addition of 1800 ppm of eucalyptus essential oil are shown in Figure 4.

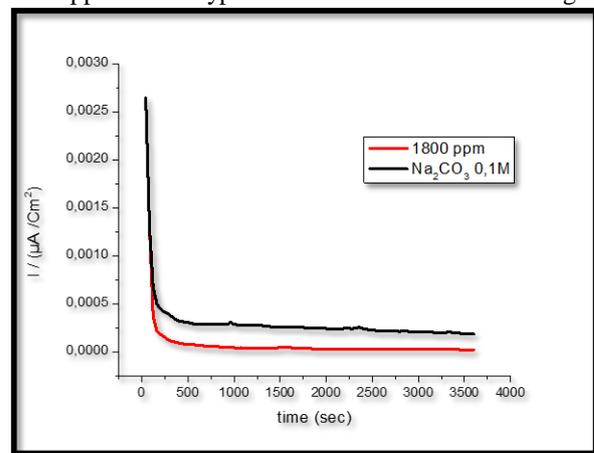


Fig 4. Chrono-amperometric curves at 150 mV for lead in 0.1 M Na_2CO_3 solution with and without 1800 ppm Eucalyptus oil at 25°C.

Table 2: Parameters derived electrochemical Tafel free lead in 0.1 M Na_2CO_3 with and without inhibitor at 25°C

Concentration en ppm	I_{corr} ($\mu\text{A}/\text{Cm}^2$)	E_{corr} (mV/ECS)	I_{pass} ($\mu\text{A} / \text{Cm}^2$)	E_p %
0	28.4762	-644.5	$1.5366 \cdot 10^{-4}$	-----
800	19.8735	-630.2	$1.1023 \cdot 10^{-4}$	30.21
1000	17.5336	-635.5	$1.0946 \cdot 10^{-4}$	38.47
1200	15.1041	-634.1	$1.0209 \cdot 10^{-4}$	46.95
1400	11.4832	-631.0	$8.9955 \cdot 10^{-4}$	59.67
1600	9.8508	-623.9	$8.6741 \cdot 10^{-5}$	65.40
1800	6.9424	-641.2	$8.6428 \cdot 10^{-5}$	75.62
2000	6.8883	-640.3	$8.5026 \cdot 10^{-5}$	75.81

It is clear that the lead in solution Na_2CO_3 alone recorded higher values of oxidation current of the lead dissolution by corrosive attack of OH^- ions. The initial increase in current occurs because the lead dissolves in a first time to form the $\text{Pb}(\text{OH})_4$ which is unstable and is transformed into PbO_2 where the current decreases with time due to the formation of an oxide layer (PbO_2). The formation of such a layer provides partial protection and does not allow the current to rise [27]. Adding 1800 ppm of eucalyptus essential oil causes a great decrease in current values, which is probably due to adsorption of the inhibitor on the surface of lead molecules, blocking the active sites and thereby preventing its dissolution. These results are in good agreement with the polarization data, where Figure 3 and Table 2, both confirm that the inhibitor has the ability to inhibit the corrosion of lead.

3. Electrochemical impedance spectroscopy:

Nyquist Impedance curves of lead in 0.1 M Na_2CO_3 in the absence and presence of different concentrations of eucalyptus oil are shown in Figure 5. The effectiveness EEIS inhibition (%) was calculated using Equation 2:

$$E_{\text{EIS}} \% = \frac{R_T - R_T'}{R_T} \times 100 \quad (2)$$

Where R_T and R_T' are the charge transfer resistances with and without inhibitor respectively. Double layer capacity C_{dl} values were obtained at the maximum frequency (f_{max}), where the imaginary part of the Nyquist curve is maximum, and calculated using the equation 3:

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

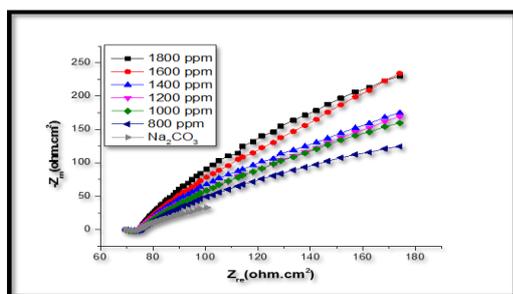


Fig 5. Lead Nyquist curves in 0.1 M Na_2CO_3 at various concentrations of eucalyptus oil to 25 °C.

From Figure 5, the impedance diagrams obtained are almost semi-circular appearance, indicating the corrosion of lead is mainly controlled by a charge transfer, the size increases with the concentration of the oil eucalyptus. Parameters derived from these studies are presented in Table 3. It was found that the charge transfer resistance R_t increases, it increases from 236.9 $\Omega \cdot \text{cm}^2$ to 926.7 $\Omega \cdot \text{cm}^2$ by adding 1800 ppm of essential oil. Indeed, the film formed has low conductivity. Similarly, there was a remarkable decrease in the value of the capacitance of the double layer which passes from 67.16 $\mu\text{F}/\text{cm}^2$ to 17.17 $\mu\text{F}/\text{cm}^2$ for the same addition.

Table 3. Impedance parameters of lead in 0.1 M Na_2CO_3 at different concentrations of eucalyptus oil at 25 °C.

Concentration in ppm	R_s ($\Omega \cdot \text{cm}^2$)	R_t ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	EEIS (%)
0	74.47	236.9	67.16	-----
800	76.03	357.2	52.94	33.68
1000	77.52	374.5	48.65	36.74
1200	80.68	425.6	37.38	44.34
1400	93.50	607.9	29.05	61.03
1600	120.09	736.5	21.60	67.83
1800	151.90	926.7	17.17	74.43
2000	155.22	932.3	16.12	74.59

D. Effect of temperature

Temperature is an important parameter that affects the corrosion phenomenon. Measurements are taken at different temperatures (278-308 K) in the absence and presence of 1800 ppm of eucalyptus oil in 0.1 M Na_2CO_3 .

a. Measurement of polarization:

The effect of temperature on the lead without and with addition of eucalyptus oil, carried by the polarization measurements is respectively given in Figure 6 and 7. The electrochemical parameters derived from these figures are given in Table 4.

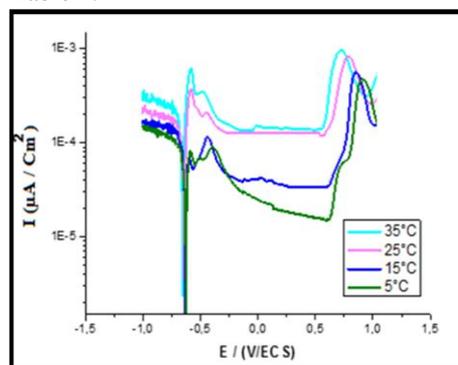


Fig 6. Lead polarization curves in a 0.1 M Na_2CO_3 solution without inhibitor at different temperatures.

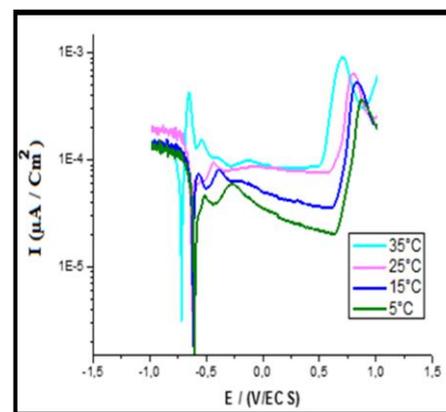


Fig 7. Polarization curves lead in a 0.1 M Na_2CO_3 solution with 1800 ppm inhibitor at different temperatures.

Table 4. Electrochemical parameters lead in a 0.1 M Na₂CO₃ solution with and without 1800 ppm eucalyptus oil at different temperatures.

Concentration in ppm	Temperature (K)	I _{corr} (μA/cm ²)	E _{corr} (mV/SCE)	I _{pass} (μA/cm ²)	Ep (%)
Blank	278	16.2547	-631.2	1.88839.10 ⁻⁵	---
	288	20.4262	-633.4	3.59821.10 ⁻⁵	---
	298	28.4762	-644.5	1.5366.10 ⁻⁴	---
	308	35.3222	-658.5	1.41384.10 ⁻⁴	---
1800 ppm	278	2.5649	-605.1	3.13393.10 ⁻⁵	84.22
	288	4.2159	-619.3	4.17857.10 ⁻⁵	79.36
	298	6.9424	-641.2	8.6428.10 ⁻⁵	75.62
	308	8.3561	-655.7	9.65625.10 ⁻⁵	67.85

Figure 6 and 7 and Table 4 indicate that there is a general increase in the intensity of corrosion with increasing temperature of 278-308 K. The solution becomes more corrosive with the temperature rise and the corrosive power becomes less effective. This implies that this inhibitor is adsorbed on the metal by electrostatic bonds (weak bonds). This type of temperature-sensitive links cannot fight effectively against corrosion with increasing temperature [28].

b. Electrochemical impedance spectroscopy (EIS).

The effect of temperature on the behavior of the lead corrosion in 0.1M Na₂CO₃ containing an inhibitor concentration of 1800 ppm is considered in the temperature range of 278-308 K using of diagrams impedance (Fig. 8 and Fig. 9), the corresponding results are summarized in Table 5.

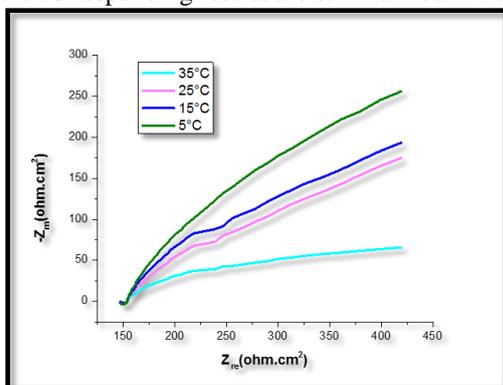


Fig 8. Lead Nyquist curves in 0.1 M Na₂CO₃ at different temperatures.

Concentration in ppm	Temperature (K)	Rs (Ω. Cm ²)	Rt (KΩ. Cm ²)	C _{dl} (μF/cm ²)	E _{EIS} (%)
Blank	278	107.1	1.337	11.90	---
	288	81.56	0.874	18.20	---
	298	74.47	0.236	67.16	---
	308	65.22	0.153	70.36	---
1800 ppm	278	293.11	7.494	11.36	82.16
	288	180.60	3.848	14.96	77.29
	298	151.90	0.926	17.17	74.43
	308	122.98	0.463	19.32	66.96

Table 5. Electrochemical parameters of lead Na₂CO₃ 0.1 M with and without 1800 eucalyptus oil at different temperatures ppm.

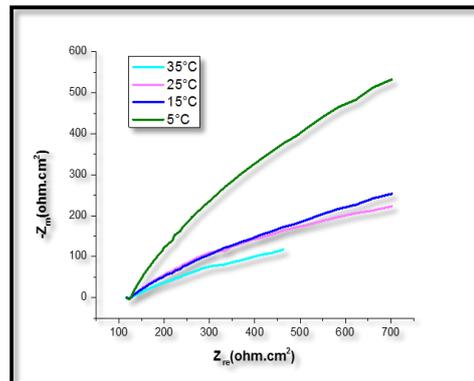


Fig 9. Nyquist curves of lead in 0.1M Na₂CO₃ with 1800 ppm of eucalyptus oil at different temperatures.

The increased rate of corrosion of lead is more pronounced with increasing temperature in 0.1M Na₂CO₃ solution. The effectiveness of the inhibitor is affected by the temperature hereby decreasing as the temperature increases.

c. Determination of the activation energy:

It was noted by some authors [29-30] that the logarithm of the corrosion rate (k) is a linear function with the inverse of the absolute temperature 1 / T (Arrhenius equation 4):

$$\ln k = -\frac{E_a}{R.T} + A \quad (4)$$

Where E_a is the activation energy, T the absolute temperature, R is the gas constant, and A is the Arrhenius pre-exponential factor.

The average activation energy for the dissolution of lead in a solution of 0.1 M Na₂CO₃ between 278 and 308 K are shown in Figure 10.

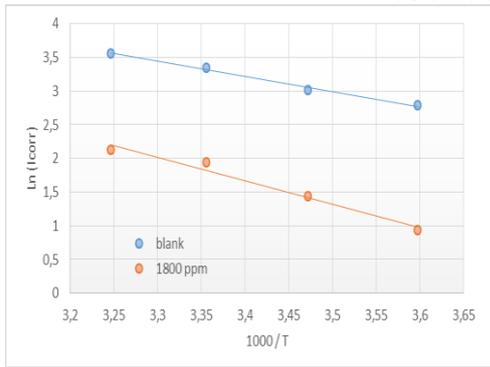


Fig 10. Curves Arrhenius plots of lead in Na₂CO₃ 0.1 M in the absence and presence of inhibitor.

Table 6. The activation energy of the lead with and without inhibitor.

	Blank	1800 ppm eucalyptus oil
E _a (J / mol)	18.93	28.90

The activation for the reaction in the absence of corrosion and eucalyptus oil (Table 6) the presence of energy values are computed by equation (4). The increase of the activation energy of the inhibitor can be considered due to the physical adsorption of the inhibitor. [31-32] The kinetic parameters, the enthalpy and entropy of the corrosion process are also estimated from the study of the effect of temperature. An alternative formulation of Arrhenius equation 5 is:

$$I_{corr} = \frac{RT}{Nh} \times \exp\left(\frac{\Delta S^*}{R}\right) \times \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (5)$$

Where h is Planck's constant, N is the Avogadro number, ΔS* is the entropy of activation, ΔH* is the activation enthalpy. Figure 11 shows plots of Ln(I_{corr}/T) compared to 1/T. straight lines are obtained with a spawning -ΔH*/R is an intercept (LnR/Nh+ΔS*/R), from which the values ΔS* and ΔH* can be calculated, these values are given in Table 7:

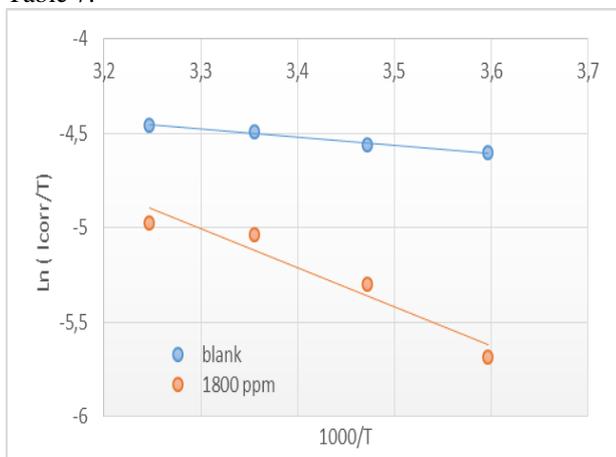


Fig 11. Relationship between Ln (I_{corr}/T) and 1000/T at different temperatures.

Table 7: The values of the activation parameters of lead in Na₂CO₃ in the absence and presence of 1600 ppm of the essential oil of eucalyptus.

Inhibitor	ΔH* (KJ/mol)	ΔS*(J/mol.K)
Blank	35.63	-222.99
1600 ppm	171.28	-182.63

Inspection of these data revealed that the thermodynamic data (ΔS* and ΔH*) for the reaction of dissolution of lead in Na₂CO₃ 0.1 M in the presence of the inhibitor is higher than in the absence of inhibitor. The positive sign of ΔH* reflects the endothermic nature of the process of dissolution of lead, which suggests that the slow dissolution of the lead is in the presence of inhibitor [33]. By comparing the values of the activation data ΔS* entropy in Table 7, it is clear that the activation entropy decreases more negatively to a great extent in the presence of inhibitor than in its absence, which reflects the formation of a stable layer controlled the inhibitor on the surface of the lead [34].

The value of the enthalpy of the free energy ΔG* is derived by the equation 6:

$$\Delta G^* = -RT \times \ln(55.5 \times K) \quad (6)$$

Where K is the adsorption equilibrium constant, and 55.5 is the water concentration in mol/l. ΔG* = -22.57 kJ/mol at 25°C this indicates the physisorption of the inhibitor on the surface of the metal and the negative sign indicates the spontaneity of the adsorption process.

d. Adsorption isotherm:

The adsorption behavior provides information on the interaction between the adsorbed molecules and their interactions with the surface of the electrode [35]. It has been reported that the adsorption of the adsorbate depends on adsorbent interactions / and in particular the nature of the adsorbed species and the nature of the solid surface [36]. The adsorption Temkin, Frumkin, and Langmuir isotherms were used to represent the eucalyptus oil adsorption on the surface of the lead. The correlation coefficient, R², was used to choose the isotherm that best matches the experimental data. The recovery rate (θ) at different concentrations for the inhibitor tested in 0.1M Na₂CO₃ was assessed from measurements of polarization.

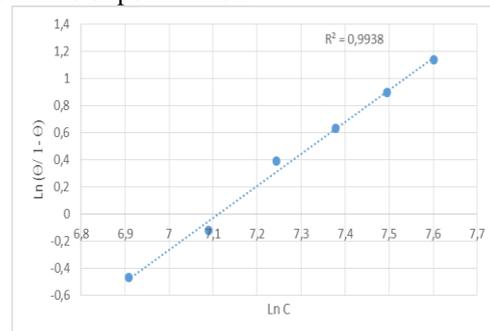


Fig 12. Model Langmuir isotherm for adsorption of eucalyptus oil on the surface of the lead in 0.1 M Na₂CO₃ at 25 °C.

The curve representing $\ln(\theta / (\theta - 1))$ as a function of $\ln [C]$, where C is the concentration of inhibitor, is a straight line (Figure 12) indicating that the adsorption of the inhibitor on the surface of the plate Lead is according to the Langmuir model (Equation 7)

$$\ln(\theta / (1 - \theta)) = K \ln [C] \quad (7)$$

The strong correlation ($R^2 = 0.9938$) for the plot of the isotherm of adsorption according to Langmuir confirms the validity of this approach.

IV. CONCLUSION

From the results, the following conclusions can be deduced:

1. Eucalyptus oil acts as a mixed type inhibitor for the corrosion of lead in a Na_2CO_3 solution 0.1M
2. Inhibition efficiency increased to 75.81% with the increase in concentration of eucalyptus oil.
3. The negative value of the enthalpy of the free energy results in spontaneous adsorption. ΔG is around -22 KJ / mol; this has shown that a physisorption has occurred.
4. Adsorption is modeled on Langmuir.

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