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Research paper

Lead corrosion inhibition by cedrus atlantica as a green inhibitor in 0.1M Na2CO3 solution

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Abstract

The inhibition of lead corrosion in 0.1 M Na_2CO_3 solution with the essential oil of Atlas cedar was studied by polarization and impedance. The studies of polarization showed that the essential oil of Cedrus atlantica acts as a cathodic inhibitor. The different thermodynamic and kinetic parameters were calculated to understand the energy changes associated during the inhibition process. The effectiveness increases with the concentration to reach 70% at concentration of 2000 ppm.

Keywords: *Basic Solutions; Cedrus Atlantica; Inhibition; Lead; Polarization.*

1. Introduction

In nature we can find an economic, ecological, renewable solution and easily realizable against corrosion metals, it is a green inhibitor. Several results were obtained by using these extracts from economic plants (Azzouyahar et al., 2013, 2014a, 2014b, Mounir et al. & Elmiziani et al. & Bensabah et al. 2014). The extracts obtained from the leaves, barks, seeds, fruits and roots of plants include an organic mixtures of contains Nitrogen, sulfur, oxygen and others (Chetouani et al. 2004, Etre et al. 2005, Bouyanzer et al. & Benbdellah et al. & Oguzie et al. 2006, Bouyanzer et al. 2007, Bothi et al. & Okafor et al. & Noor & Oguzie et al. 2008).
The effectiveness of corrosion inhibition of these extracts is generally allotted to the presence in their composition, complex organic species such as tannins, alkaloids, flavonoids, polyphenolic compounds, nitrogen bases, glycosides (Tavakoli et al. 2008).
In our laboratories, we found good effectiveness for a series of natural products: thyme (Houbairi et al. 2014a, 2014b), Ricinus (Houbairi et al. 2014c), green mint (Bensabah et al. 2013), cloves (Houbairi et al. 2014d), myrtle (Houbairi et al. 2015), eucalyptus (Elmiziani et al. 2014b) and Artemisia (Houbairi et al. 2014e).
The encouraging results obtained have prompted us to test new vegetable materials such as essential oil of Atlas cedar.
The aim of this work is to study the inhibition of lead corrosion in Na_2CO_3 .1M solution by natural essential oil of Atlas cedar by electrochemical measurements.

2. Material and methods

2.1. Extraction of essential oïl

The plant of Cedrus atlantica was collected in Sefrou region, in Morocco. The aerial parts of the plant were dried in laboratory at room temperature.
The essential oil was obtained by steam distillation using a Clevenger type during approximately 3h. The essential oil yield is 1.2 %. This average yield essential oil was calculated on the basis of the dry matter.
After extraction, part of oil was used for the analysis of the chemical composition by the technique of gas chromatography coupled with the mass spectrometry. The other part was used for testing the anti-corrosion activity. The oil obtained, after extraction, was recovered and preserved in an opaque bottle and stored at 4°Cbefore use.

2.2. Preparation of the solution

The solution of sodium bicarbonate Na_2CO_3 0.1 M was prepared with distilled water. Test solutions were freshly prepared before each experiment, by adding the oil directly to the corrosive solution. Experiments were conducted in three repetitions to allow determination of reproducibility.

2.3. Electrochemistry measurements

The electrochemical experiments were performed in a pyrex cell, equipped with a conventional three electrodes: lead as an electrode working disc cup-shaped with a geometric area of 1 cm^2, platinum as auxiliary electrode and a saturated calomel electrode SCE as reference electrode. The lead disk was abraded with sandpaper for different particle size up to 1200, degreased with acetone, rinsed with distilled water and dried before each test. The measurements are carried out with a mounting including a potentiostat-galvanostat PGZ100, type radiometer, associated with the "voltamaster4 "software.
The current-potential curves are obtained by potentiodynamic mode; the potential applied to the sample varies continuously with a scanning rate of 2 mV/sec, between -1000 and 1000 mV.
The electrochemical impedance spectroscopy measures (EIS) was carried out with similar previous electrochemical system. The

frequencies between 100 kHz and 10 Hz were superimposed on the corrosion potential. The impedance diagrams are given in the Nyquist representation.
The Chronoamperometric Curves were traced to a potential of 150 mV for 3600 seconds.

3. Results and discussion

3.1. Analyze of chemical composition of cedrus atlantica

The chemical composition of the essential oil shows that Cedrus atlantica is mainly composed by α-pinene (Fig. 1). The Table 1 summarizes the main constituents of the essential oil tested.

Table 1: Major Constituents of Cedrus Atlantica Essential Oil

Peak number	Retention time	Percentage (%)	Compound name
1	22.896	4.82	Decene
2	31.927	13.24	Menthyl acetate
3	35.620	15.56	1-tetradecene
4	36.540	10.69	caryophyllene
5	37.312	36.45	α-pinene

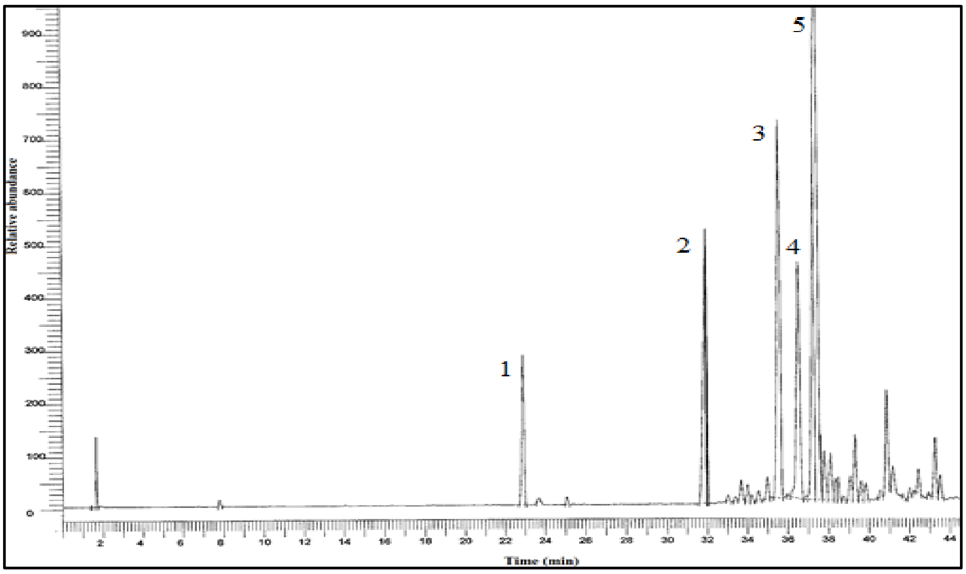

Fig. 1: Chromatogram of Cedrus Atlantica Essence.

3.2. Effect of concentration

3.2.1. The potentiodynamic polarization measurements

The cathodic and anodic polarization curves of lead, in 0.1M Na_2CO_3 solution with and without the essential oil of cedar tested at different concentrations are presented in Fig. 2. The electrochemical parameters derived from these curves are given in Table 1. The inhibitory efficacy of the compound is defined by the equation 1:

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

With I_{corr} and I'_{corr} are respectively the corrosion current densities determined by extrapolation of Tafel straights of the corrosion potential without and with addition of Cedrus atlantica.

The current densities of corrosion decrease with addition of green inhibitor CA. The maximum inhibitory action achieves 68% with 2000 ppm.
Fig.1 and table 2 show that Cedrus atlantica essential oil acted as a mixed type inhibitor for lead in Na_2CO_3 0.1M.
The addition of this inhibitor decreases also the passivation current density values from value of 136.4 at 61.05µA / Cm^2.

3.2.2. Chrono amperometry

The chrono amperometry curves obtained in alkaline solution at 150 mV as potential in absence and presence of inhibitor are presented in Fig. 3.

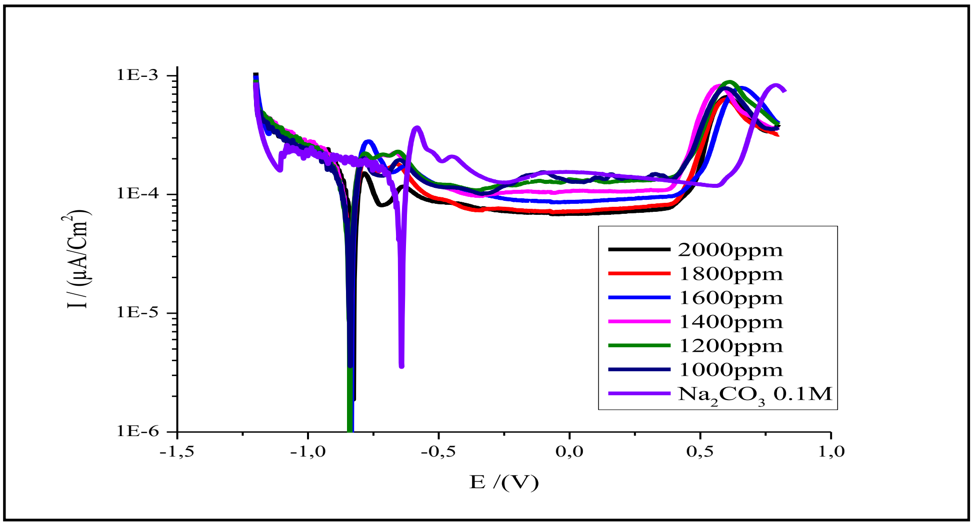

Fig. 2: Potentiodynamic Polarization Curves of Lead in Na_2CO_3 0.1 M in Absence and Presence of Cedrus Atlantica Essential Oil at Different Concentrations at 25°C.

Table 2: Electrochemical Parameters and Inhibitory Efficiency of Lead in Na_2CO_3 0.1 M Without and with Addition of the Essential Oil at Different Concentrations at 25°C

Inhibitor	C_{inh} / (ppm)	E_{corr} / (mV/ECS)	I_{corr} / (μA / Cm^2)	I_{pass} / (μA / Cm^2)	IE%
Blank	---	-644.5	28.4762	136.4	---
	1000	-733.9	11.664	124.9	59.04
	1200	-740.6	11.342	1226	60.17
	1400	-738.3	10.721	104.5	62.35
	1600	-733.9	10.171	86.62	64.28
Essential oil of CA	1800	-736.1	9.5338	70.21	66.52
	2000	-722.7	9.0383	62.63	68.26
	2200	-738.9	8.8447	61.05	68.94

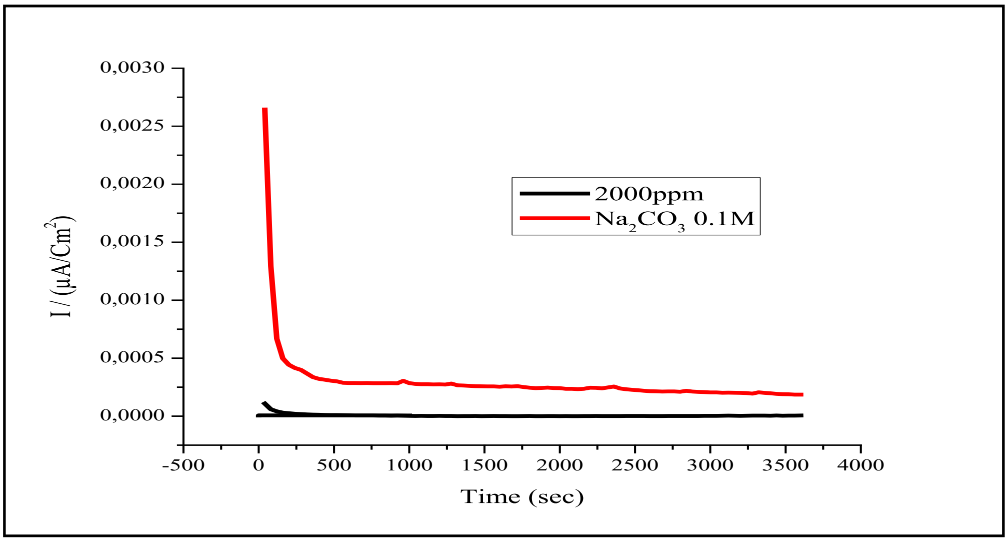

Fig. 3: Chronoamperometric Curves of Lead at 150 Mv in Na2co3 0.1m with and Without 2000 Ppm of Essential Oil at 25°C.

Fig. 3 reveals the existence of high values of current density in 0.1M Na_2CO_3 solution; this indicates the probability of formation of lead oxidation products (Mabille et al. 2003). Furthermore, the addition of 2000 ppm of cedar essential oil reduces greatly the current density values. Thus it could be an indication of the protective layer formed on the lead surface (Chikh et al. 2001, Ebntouhami et al. 2008).

3.2.3. The electrochemical impedance spectroscopy measurements (EIS)

The corrosion behavior of lead in Na_2CO_3 0.1M in presence and absence at different concentrations of cedar essential oil was also investigated by the electrochemical impedance spectroscopy (EIS) at 298K. Nyquist plots at various concentrations of this oil are presented in Fig. 4.

Table 3 gives values of charge transfer resistance, Rt double-layer capacitance, Cdl, and inhibition efficiency E (%).

The percent inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the equation 2:

$$E\ \% = \frac{R'_T - R_T}{R'_T} \times 100 \quad (2)$$

With Rt and Rt' are the charge transfer resistance values without and with the inhibitor, respectively.

From the impedance data (Table 3), it was clear that the values of charge transfer resistance (R_T) were increased in presence of the inhibitor and those of double layer capacitance, C_{dl}, are brought down with the increase of inhibitor concentration. These results confirm those of polarization measurements. This means that, this inhibitor was acting as adsorption inhibitor (Cheikh-Rouhou et al. 2008, Morikawa et al. 2013).

3.3. Effect of temperature

3.3.1. Polarization curves

Temperature can modify the interaction between the lead electrode and the alkaline medium in the absence and the presence of inhibitors. To assess the influence of temperature on corrosion and corrosion inhibition processes, polarization tests were carried out at various temperatures (298–328 K) in the absence and presence of 2000 ppm of Cedar essential oil, as shown in Fig. 5 and 6. Corresponding electrochemical data are given in Table 4.

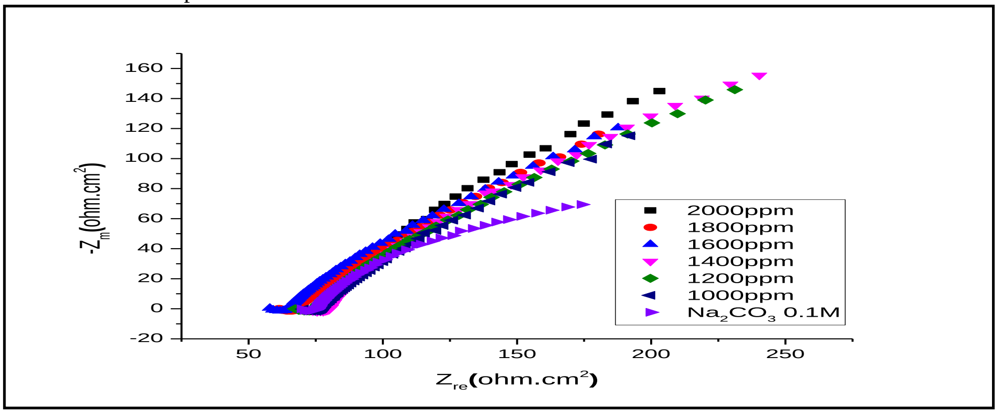

Fig. 4: Nyquist Representation of Lead in Na_2CO_3 0.1M at Different Concentrations of Cedar Essential Oil at 25°C.

Table 3: Electrochemical Parameters Characteristic of Lead Impedance Diagram at Various Concentrations of Inhibitor in Na_2CO_3 0.1M

inhibitor	Concentration in ppm	R_T / ohm.cm^2	C_{dl} / µF/cm^2	E%
Blank	0	236.9	67.16	-----
	1000	635.5	25.04	62.72
	1200	636.6	24.99	62.78
	1400	655.4	24.28	63.85
	1600	681.9	23.33	65.26
Essential oil of Cedrus atlantica	1800	745.0	21.36	68.20
	2000	788.2	20.19	69.94
	2200	790.9	19.86	70.05

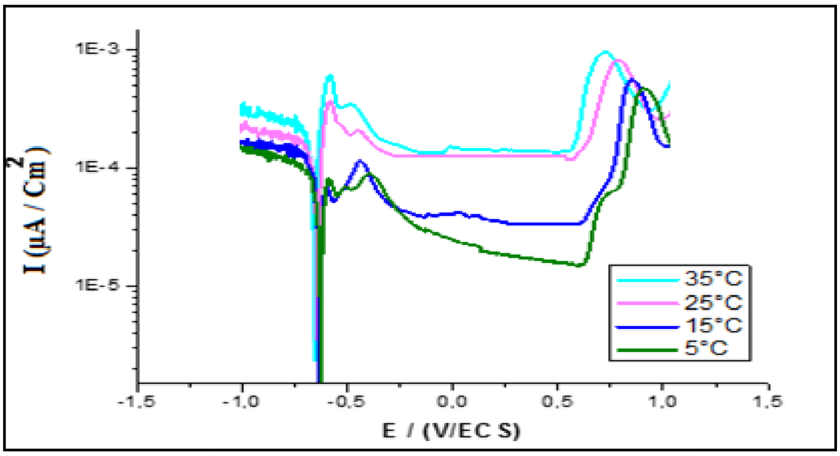

Fig. 5: Polarization Curves of Lead in $Na_2CO_3$0.1M Medium without Inhibitor at Different Concentrations.

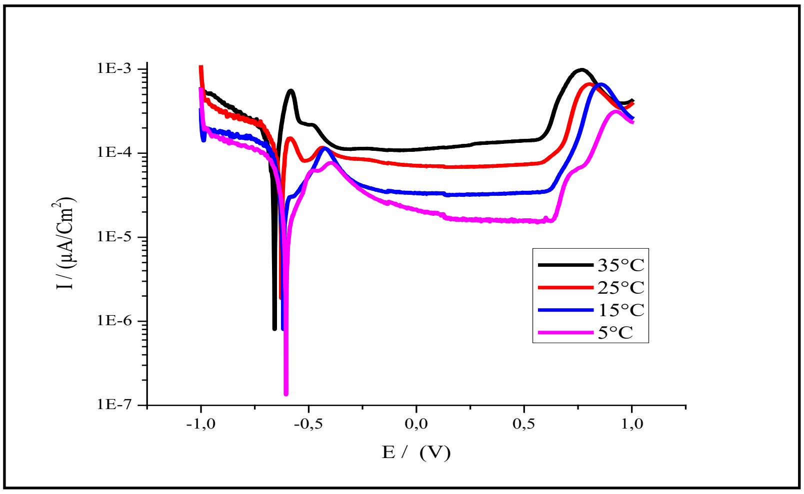

Fig. 6: Polarization Curves of Lead in $Na_2CO_3$0.1M Medium with 2000 Ppm of Inhibitor at Different Concentrations.

Table 4: Electrochemical Data of Lead in Na_2CO_3 0.1 M Medium Without and With 2000 Ppm of Cedar Essential Oil at Different Temperatures

Inhibitor	Temperature / (K)	E_{corr} / (mV/ECS)	I_{corr} / (μA / Cm^2)	I_{pass} / (μA / Cm^2)	IE%
Blank	278	-631.2	16.2547	19.22	---
	288	-633.4	20.426	36.64	---
	298	-644.5	28.476	136.4	---
	308	-658.5	35.322	147.2	---
2000 ppm of inhibitor	278	-707.5	3.5516	10.97	78.15
	288	-713.5	5.5619	32.49	72.77
	298	-722.7	9.0383	62.63	68.26
	308	-758.3	12.511	109.4	64.58

Inspection of Fig. 6 and table 4 shows that the corrosion rate increases both in the uninhibited and inhibited alkaline solution with the rise of temperature.

The presence of inhibitor leads to decrease of the corrosion rate. Also, we note that the efficiency (IE %) depends on the temperature and decreases with the rise of temperature from 278 to 308 K. 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 (Putilova et al. 1960). This is in accordance with the results reported by Ergun (Ebenso et al. 2008).

3.3.2. Electrochemical impedance spectroscopy (EIS)

The effect of temperature on lead corrosion behavior in Na_2CO_3 0.1M containing a concentration 2000 ppm of inhibitor was studied in a temperature range between 278 and 308 K using impedance diagrams (Fig. 7 and 8), the corresponding results are summarized in table 5.

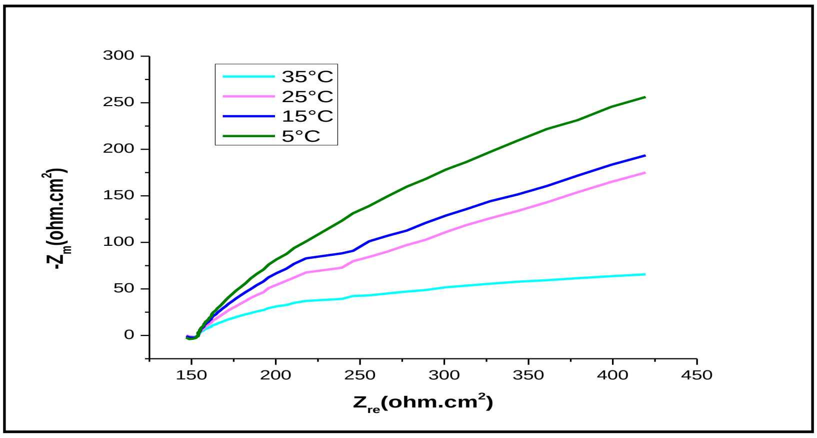

Fig. 7: Nyquist Curves of Lead in Na_2CO_3 0.1M at Different Temperatures.

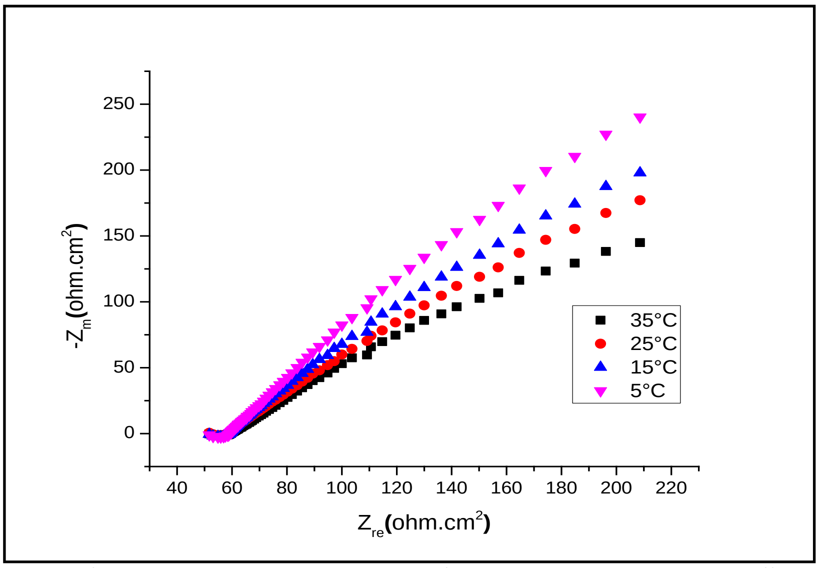

Fig. 8: Nyquist Curves of Lead in Na_2CO_3 0.1M with 2000 Ppm of Cedrus Atlantica Essential Oil at Different Temperatures.

Table 5: Temperature Effect on Lead Corrosion in Na_2CO_3 0.1M in Absence and Presence of 2000 Ppm of Essential Oil at Various Temperatures

Inhibitor	Temperature / (K)	R_T/ (Ω/ Cm^2)	C_{dl} / (μF / Cm^2)	IE%
Blank	278	1337	11.90	---
	288	874	18.20	---
	298	236	67.16	---
	303	153	70.36	---
2000 ppm of inhibitor	278	5606	32.33	76.15
	288	3271	29.76	73.28
	298	788	25.04	69.94
	303	442	12.34	65.41

In inhibited alkaline solution, R_T values are strongly increased. Furthermore, the inhibitor effectiveness is affected by temperature; this can be explained by the decrease in the force of adsorption at elevated temperature, there is a physisorption.

3.3.3. Determination of activation energy

The adsorption of organic compounds can be described by two main types of interactions: physical adsorption and chemisorption. They are influenced by the nature of metal charge, the chemical structure of the inhibitor, the pH, the type of electrolyte and temperature (Benabdellah et al. 2006).
Thus, in order to elucidate the inhibitory properties of Atlas cedar and the temperature dependence, the corrosion rate, the apparent activation energy (Ea) for the corrosion process in the absence and presence of the inhibitor was evaluated according to Equation 3 or 4:

$$I_{corr} = K \exp(-Ea/RT) \quad (3)$$

$$I'_{corr} = K' \exp(-E'a/RT) \quad (4)$$

Where k and k' are constants (pre-exponential parameter of Arrhenius),
E_a and E'_a are activation energy, in absence and presence of inhibitor respectively.
By drawing the graph Ln W = f (1000/T), Straight lines are obtained with a slope of (-Ea/R) for blank and (-E'a / R) for the essential oil Cedrus atlantica (Fig. 10), which allows us to calculate the activation energy in the presence of the inhibitors tested.
The estimated values of Ea of lead corrosion in absence and in presence of 2000 ppm of CA are listed in table 6.
Abiiola (Abiio et al. 2002), Ebenso (Ebenso et al. 2003) reported that the values of Ea>80 kcal/mol indicates chemical adsorption while Ea <80 kJ / mol reveals physical adsorption.
In this study, activation energy values support that the essential oil of Cedrus atlantica is physically adsorbed on lead surface.
According to table 6, the estimated Ea value in inhibited solution indicates that the interaction between metallic surface and the inhibitor is strong enough to reduce corrosion lead in alkaline solution.
The thermodynamic parameters such as enthalpy and entropy of corrosion process may be evaluated from 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 N is the Avogadro's number, h the Plank's constant, R is the perfect gas constant, ΔS* and ΔH* the entropy and enthalpy of activation, respectively.
Fig. 11 shows a plot of ln(Icorr/T) compared to 1/T. Straight lines are obtained with a slope of (-ΔH*/R) and an interception of (ln R/Nh + ΔS*/R) from which the values of ΔH* and ΔS* are calculated respectively and listed in Table 6.

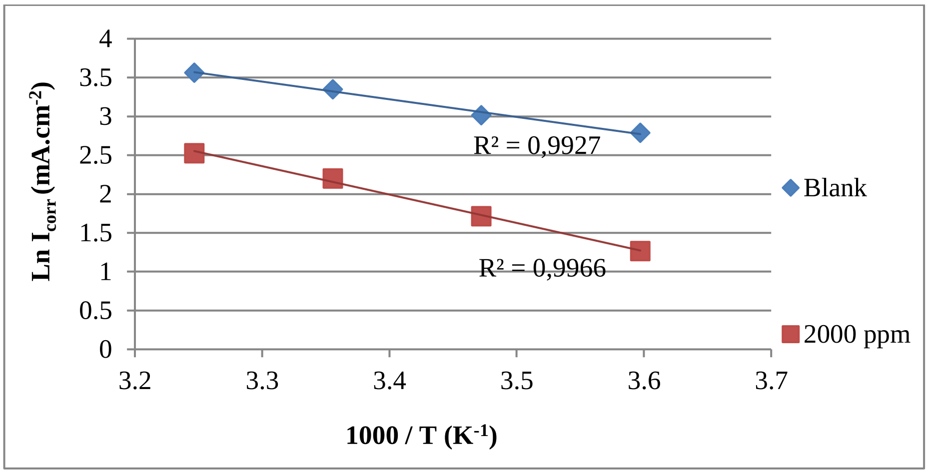

Fig. 10: Arrhenius Plots of Lead in 0.1 M Na_2CO_3 with and Without 2000 Ppm of CA.

Table 6: The Activation and Thermodynamic Parameters of Lead in Inhibited and Uninhibited Solution in 0.1M Na_2CO_3

Inhibitor	Ea KJ/mol	ΔH* (J/mol)	ΔS*(J/mol.K)
Blank	18.93	16.50	-161.92
2000 ppm	30.38	27.95	-133.18

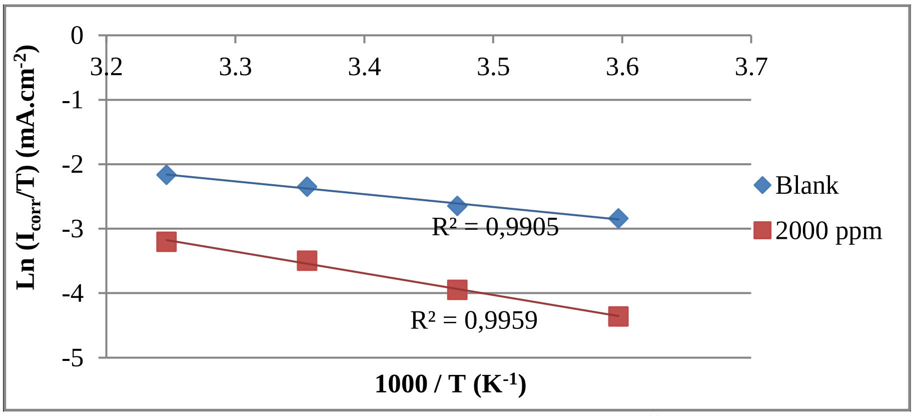

Fig. 11: Relation Between Ln (W_{corr}/T) And 1000/T in Acid at Different Temperatures.

The positive value of enthalpy (ΔH*) in the absence and presence of 2000 ppm of inhibitor reflects the endothermic nature of lead dissolution process (Quartarone et al. 1994). Furthermore, the negative values of entropy (ΔS*) 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 (Abdallah et al. 2006).

4. Conclusion

From this study, the following results might be extracted:

- The cedar essential oil is a good inhibitor against lead corrosion in 0.1 M Na_2CO_3 solution and the inhibition effectiveness increases with the oil concentration. At higher concentration of the inhibitor 2000 ppm, it achieves 70%.
- The Electrochemical impedance spectroscopy results indicate the increasing of the charge transfer resistance and the decreasing of the capacity of the double layer.
- The adsorption model obeys to physisorption.
- The obtained inhibition effectiveness results by electrochemical polarization and electrochemical impedance spectroscopy are in reasonable agreement.

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