

## Inhibition of Lead Corrosion in 0.1 M Na<sub>2</sub>CO<sub>3</sub> by *Artemisia* Oil

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### Abstract

The essential oil of *Artemisia herba alba* has been extracted and tested as an inhibitor of lead corrosion in 0.1 M Na<sub>2</sub>CO<sub>3</sub> medium, using stationary and transient electrochemical techniques. The results obtained show that the essential oil of *Artemisia* reduces the corrosion rate. The effectiveness of inhibition increases with the oil concentration to reach 77 % with 2000 ppm. The effect of temperature was also studied.

**Keywords:** corrosion, inhibition, lead, *Artemisia*, essential oil, adsorption.

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### Introduction

The growing need for corrosion inhibitors is becoming increasingly necessary to stop or delay the attack of a metal in an aggressive solution. The major application areas are: acid etching, cleaning with industrial acid, scaling and acidification.

Considerable efforts are made to find suitable compounds for use as corrosion inhibitors in various corrosive environments [1-8].

These organic compounds are either synthesized or extracted from spices and aromatic and/or medicinal plants. Naturally antioxidants, their use as corrosion inhibitors has been preferred, both for their economic value and for the environmental objectives. These benefits have encouraged us to pull a large part of our laboratory program to examine the inhibitory power of different extracts from natural substances. We found that thyme [9-10], castor [11], spearmint [12-13], verbena [14], cloves [15], myrtle [16], eucalyptus [17], etc., possess the power to be very effective corrosion inhibitors.

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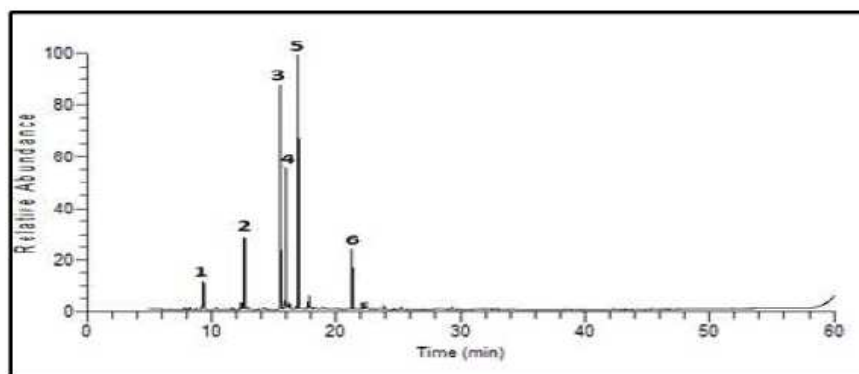
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The encouraging results achieved by the oil from *Artemisia herba alba* as steel corrosion inhibitor in HCl 1M solution [18], as well for copper in HNO<sub>3</sub> 2M [19], allowed us to expand its use in a basic solution. In fact, *Artemisia herba alba*, known in arabic such as Chih, is a spontaneous plant which abounds in desert of Middle East, Mediterranean Basin and sub-Saharan high plateau. *Artemisia herba alba* as aromatic plant is widely exploited for its essential oil. The latter is characterized by an extraordinary chemical polymorphism. The objective of this work is to study by polarization and electrochemical impedance methods, the effect of wormwood white oil on the lead corrosion in a solution of Na<sub>2</sub>CO<sub>3</sub> 0.1 M. The effect of temperature was also studied.

## Experimental

### *Extraction of artemisia herba alba essential oil*

*Artemisia herba alba* (Fig. 1) has been collected from the region of Agadir, Morocco. The aerial parts of the plant were air-dried in the laboratory at ambient temperature. The essential oil was obtained by steam distillation using a Clevenger type distiller for about 3 hours. The essential oil yield of *A. herba alba* is 1,1%. This essential oil yield has been calculated on the basis of the dry matter.



**Figure 1.** Chromatogram of *A. herba alba* essence.

After extraction, a part of the essential oil was analyzed for its chemical composition by gas chromatography coupled with mass spectrometry technique. The other part was tested for anticorrosive activity. The oil obtained after extraction, was recovered and stored in a dark bottle at 4 °C before use.

### *Preparation of the solution*

The solution of sodium bicarbonate (Sigma-Aldrich) Na<sub>2</sub>CO<sub>3</sub> 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.

### *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<sup>2</sup>, 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 "voltmaster4" 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.

## Results and discussion

### *Analysis of artemisia essential oil*

The analysis of the chemical composition *A. herba alba* essential oil shows the presence of chemotype to alpha thujone and camphor. Table 1 contains the main constituents of the essential oil.

**Table1.** Major constituents of the essential oil of *Artemisia herba alba*.

Name of the component	Peak number	Retention time	Percentage (%)
camphene	1	9.36	3.57
1.8-cineole	2	12.64	9.28
<b>alpha thujone</b>	<b>3</b>	<b>15.56</b>	<b>25.99</b>
beta thujone	4	15.98	16.01
<b>camphor</b>	<b>5</b>	<b>16.97</b>	<b>28.96</b>
myrtenal	6	21.31	6.44

### *Effect of concentration*

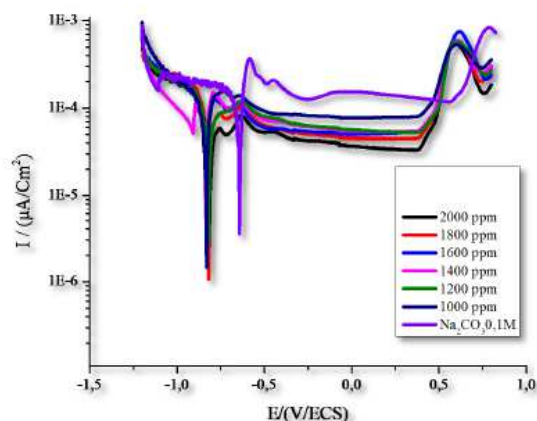
#### *The potentiodynamic polarization measurements*

Fig. 2 shows the plots of cathodic and anodic polarization of lead immersed in Na<sub>2</sub>CO<sub>3</sub> 0.1 M at 293 K in absence and presence of different concentrations of the inhibitor. The electrochemical data, corrosion potential (E<sub>corr</sub>), the corrosion current density (I<sub>corr</sub>), and passivation (I<sub>pass</sub>) are listed in the Table 2. The inhibition effectiveness (%) is calculated by equation 1:

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

where I<sub>corr</sub> and I'<sub>corr</sub> represent, respectively, the corrosion current density determined by extrapolation of Tafel straights of the corrosion potential without and with addition of the inhibitor.

The inspection of these results revealed that the corrosion density (I<sub>corr</sub>) decreased in the presence of the inhibitor. Indeed, with addition of 2000 ppm of the essential oil, the decrease of the corrosion intensity is noted by a factor of 4.3457; this behavior reflects its ability to inhibit the corrosion of lead in a solution of 0.1 M Na<sub>2</sub>CO<sub>3</sub>.



**Figure 2.** Potentiodynamic polarization curves of lead in  $\text{Na}_2\text{CO}_3$  0.1 M in absence and presence of *A. herba alba* essential oil at different concentrations at 25 °C.

**Table 2.** Electrochemical parameters and inhibitory efficiency of lead in  $\text{Na}_2\text{CO}_3$  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)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$I_{pass}$ ( $\mu\text{A}/\text{cm}^2$ )	IE%
Blank	---	-644.5	28.4762	136.4	---
The essential oil of <i>A.</i> <i>herba alba</i>	1000	-832.5	15.2029	77.32	46.61
	1200	-820.5	13.3056	55.79	53.27
	1400	-831.0	12.7067	54.37	55.37
	1600	-823.0	9.5282	49.67	66.54
	1800	-819.0	8.6226	40.57	69.72
	2000	-805.5	6.5526	38.51	76.98
	2200	-815.2	6.5003	38.02	77.17

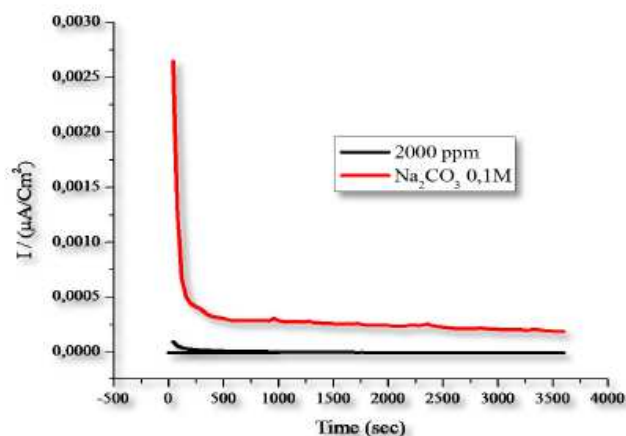
It is eventually clear from Fig. 2 and Table 2 that the adsorption of the inhibitor moves slightly the corrosion potential ( $E_{corr}$ ) in the most negative direction compared to blank, which means that the decrease in cathodic reaction is the main effect of this corrosion inhibitor[20]. Therefore, these results indicate that the essential oil of *A. herba alba* acts as an inhibitor of mixed type [21].

The increase of passivation current is also noted from a value of  $136\mu\text{A}/\text{cm}^2$  to a value of  $38\mu\text{A}/\text{cm}^2$ . Indeed, the addition of 2000 ppm decreases the passivation current  $I_{pass}$  by a factor of 3.5. This decrease is mainly due to the adsorption of oil on the metal surface.

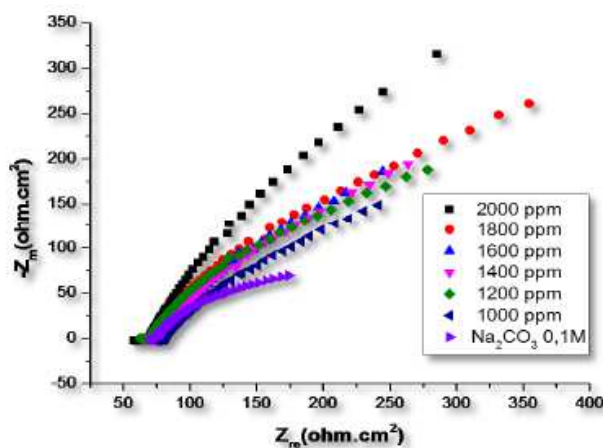
The inhibition efficiency increases with inhibitor concentration to reach 76% at 2000 ppm of *A. herba alba* essential oil by reducing the density current from a value of  $28.47\mu\text{A}/\text{cm}^2$  to a value of  $6.55\mu\text{A}/\text{cm}^2$ .

### Chronoamperometry

The chronoamperometric tests of the current as a function of time were performed to identify the type of lead corrosion in sodium bicarbonate solution in the absence and presence of the inhibitor. The chronoamperometric curves of lead measured at 150 mV in  $\text{Na}_2\text{CO}_3$  0.1 M without and with more than 2000 ppm of *Artemisia herba alba* essential oil are presented in Fig. 3.



**Figure 3.** Chronoamperometric curves of lead at 150 mV in  $\text{Na}_2\text{CO}_3$  0.1 M with and without 2000 ppm of essential oil at 25 °C.



**Figure 4.** Nyquist representation of lead in  $\text{Na}_2\text{CO}_3$  0.1 M at different concentrations of *Artemisia herba alba* essential oil at 25 °C.

It is clear that higher values of oxidation current of lead dissolution are recorded in  $\text{Na}_2\text{CO}_3$  solution without inhibitor; it is due to the corrosive attack of  $\text{OH}^-$  ions. The initial higher values of current occurs because lead dissolves in a first time to form  $\text{Pb}(\text{OH})_4$ , which is unstable thus is transformed to  $\text{PbO}_2$  when the current decreases with time due to the formation of an oxide layer ( $\text{PbO}_2$ ). The formation of such a layer provides a partial protection and doesn't allow current to rise [22]. Adding 2000 ppm of essential oil causes a sharp decrease in the current value, which is probably due to the adsorption of inhibitor on the surface of lead molecules, and the blocking of active sites, thus preventing its dissolution. These results are in good agreement with the polarization data, Fig. 2 and Table 2, and confirm the ability of *Artemisia herba alba* to inhibit lead corrosion.

#### *The electrochemical impedance spectroscopy measurements*

Nyquist performances for lead in  $\text{Na}_2\text{CO}_3$  0.1 M solution in absence and presence of different concentrations of *Artemisia herba alba* essential oil are given in Fig. 4.

The impedance spectra were simple semicircles, and their diameter increases with the increase of inhibitor concentration. The presence of a single semicircle indicates that the charge transfer occurs at the interface electrode / solution, and the transfer process reaction of lead corrosion in presence of the inhibitor doesn't change its dissolution mechanism [23].

The inhibitory effectiveness was determined by equation 2:

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

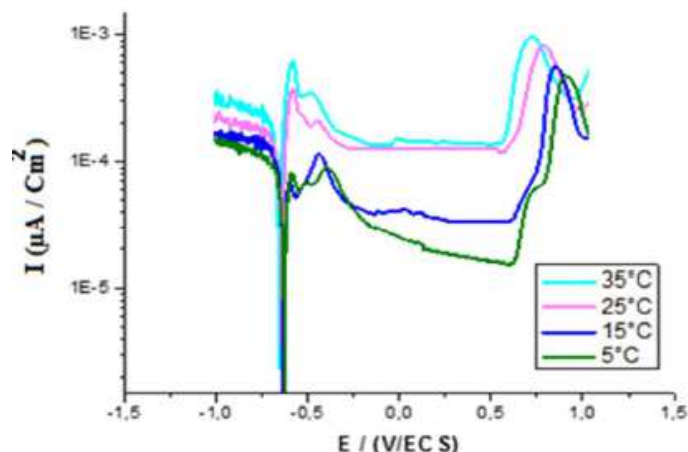
where  $R_T$  and  $R_T'$  are respectively the charge transfer resistance of lead in  $\text{Na}_2\text{CO}_3$  0.1 M medium in absence and presence of inhibitor.

The dielectric parameters are given in Table 3. The values of  $R_T'$  increase with the growth of inhibitor concentration while  $C_{dl}$  values are decrease. The increase of  $R_T'$  values may suggest the formation of a protective layer on the electrode surface [24].

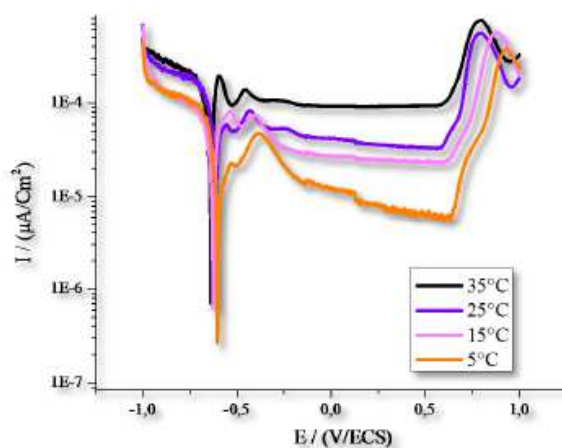
**Table 3.** Electrochemical parameters characteristic of lead impedance diagram with and without addition of inhibitor in  $\text{Na}_2\text{CO}_3$  0.1 M medium.

Inhibitor	Concentration in ppm	$R_T$ Ohm.cm <sup>2</sup>	$C_{dl}$ $\mu\text{F}/\text{cm}^2$	E%
Blank	0	236.9	67.16	-----
	1000	410.64	23.65	42.31
	1200	460.08	18.36	48.51
Essential Oil of <i>Artemisia herba alba</i>	1400	499.89	17.21	52.61
	1600	651.72	16.62	63.65
	1800	693.70	13.41	65.85
	2000	959.88	10.32	75.32
	2200	1029.10	9,414	76.98

The charge transfer resistance values ( $R_T$ ) were calculated according to the difference between impedance values at lower and higher frequencies. The  $C_{dl}$  values are considered inferior to those of blank value, which confirms that the adsorption of the inhibitor onto the metal surface forms a double electronic layer [25]. These results are in good agreement with those obtained by polarization where *Artemisia herba alba* essential oil is proved to be a good inhibitor for lead corrosion in basic medium  $\text{Na}_2\text{CO}_3$  0.1 M with an efficiency of 77 %.



**Figure 5.** Lead polarization curves in  $\text{Na}_2\text{CO}_3$  0.1 M medium without inhibitor at various concentrations.



**Figure 6.** Lead polarization curves in  $\text{Na}_2\text{CO}_3$  0.1 M medium with 2000 ppm of the inhibitor at different concentrations.

### *Effect of temperature*

Temperature is an important parameter that affects the corrosion phenomenon. The measurements are taken at different temperatures (278-308 K), in absence and presence of 2000 ppm of essential oil in 0.1 M  $\text{Na}_2\text{CO}_3$ .

### *Polarization measurement*

The effect of temperature without and with addition of *A. herba alba* essential oil, done by polarization measurements, is shown in Fig. 5 and 6, respectively,. The electrochemical parameters from these tests are given in Table 4.

The results in Fig. 5 and 6 and Table 4 indicate that there is a general increase in the intensity of the corrosion within the temperature of 278 to 308 K. The solution becomes more corrosive with rising temperature and the anticorrosive activity becomes less effective. This explains that *Artemisia herba alba* is adsorbed on the metal by electrostatic bonds (weak bonds). This type of links sensitive to temperature cannot fight effectively against corrosion when the temperature increases [26].

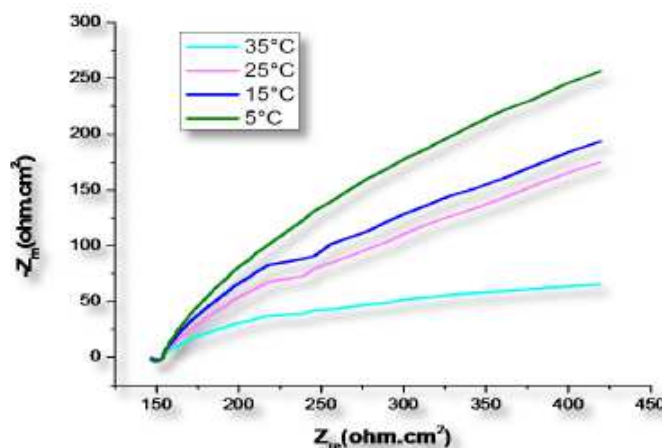


**Table 4.** Electrochemical parameters of lead in Na<sub>2</sub>CO<sub>3</sub> 0.1 M with and without 2000 ppm of *A. herba alba* essential oil at different temperatures.

Inhibitor	Temperature (K)	E <sub>corr</sub> (mV/ECS)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	I <sub>pass</sub> (μA/cm <sup>2</sup> )	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	-803.6	3.1631	6,786	80.54
	288	-809.7	4.2241	23.95	79.32
	298	-805.5	6.5526	38.51	76.98
	308	-816.6	10,769	91.35	69.51

### Electrochemical impedance spectroscopy (EIS)

The effect of temperature on lead corrosion behavior in Na<sub>2</sub>CO<sub>3</sub> 0.1 M containing a concentration of 2000 ppm of the 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.

**Figure 7.** Nyquist curves of lead in Na<sub>2</sub>CO<sub>3</sub> 0.1 M at different temperatures.

The increase of lead corrosion rate is more pronounced with higher temperature in Na<sub>2</sub>CO<sub>3</sub> 0.1 M. The inhibitor effectiveness is affected by temperature; the results show that *Artemisia herba alba* essential oil inhibitor effectiveness decreases when temperature increases.

### Determination of activation energy

To better explain the effect of temperature on the corrosion rate, it is useful to calculate the activation energy value by using the Arrhenius equation and therefore consider that the logarithm of the corrosion rate is a linear function of T<sup>-1</sup>.

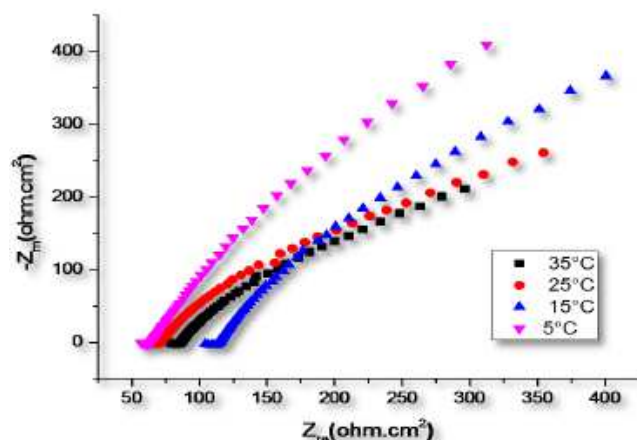
Thus, we can calculate the activation energies from the relations 3 and 4:

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

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



where  $K$  and  $K'$  are constants (pre-exponential parameter Arrhenius), and  $E_a$  and  $E'_a$  are the activation energies, respectively, in absence and presence of the inhibitor.

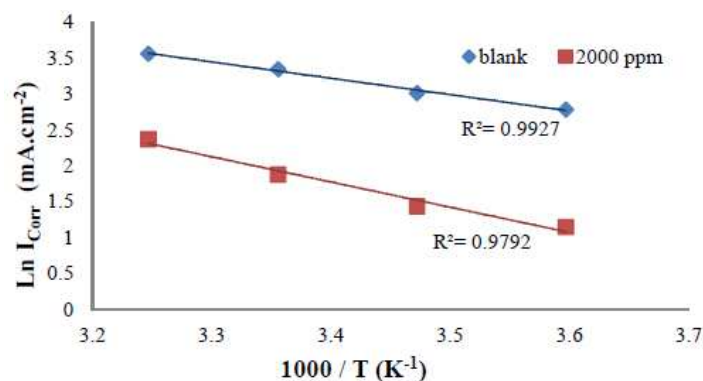


**Figure 8.** Nyquist curves of lead in  $\text{Na}_2\text{CO}_3$  0.1 M with 2000 ppm of *Artemisia herba alba* essential oil at different temperatures.

**Table 5.** Temperature effect on lead corrosion in  $\text{Na}_2\text{CO}_3$  0.1 M in absence and presence of 2000 ppm of essential oil at various temperatures.

Inhibitor	Temperature (K)	$R_T$ Ohm.cm <sup>2</sup>	$C_{dl}$ $\mu\text{F}/\text{cm}^2$	E%
Blank	278	1337	11.90	---
	288	874	18.20	---
	298	236	67.16	---
	303	153	70.36	---
2000 ppm of inhibitor	278	7282	7,358	81.64
	288	4072	9,640	78.54
	298	959	10.32	75.32
	303	515	19.21	70.32

Some conclusions on the mechanism of inhibitors action may be obtained by comparing  $E_a$  measured at a time in presence and absence of the corrosion inhibitor. Fig. 9 represents the Arrhenius plot coordinates of lead corrosion rate in  $\text{Na}_2\text{CO}_3$  0.1 M with and without essential oil of Artemisia to 2000 ppm.



**Figure 9.** Arrhenius plots of lead in  $\text{Na}_2\text{CO}_3$  0.1 M with and without inhibitor.

The variation of the logarithm of corrosion current as a function of  $T^{-1}$  gives lines indicating that the Arrhenius law is respected. The values of activation energies obtained from these lines are given in Table 6.

**Table 6.** Activation energy of lead corrosion in  $\text{Na}_2\text{CO}_3$  0.1 M without and with inhibitor.

Sample	Ea / (kJ / mol)
Blank	18.93
Essential Oil of <i>A. herba alba</i>	29.16

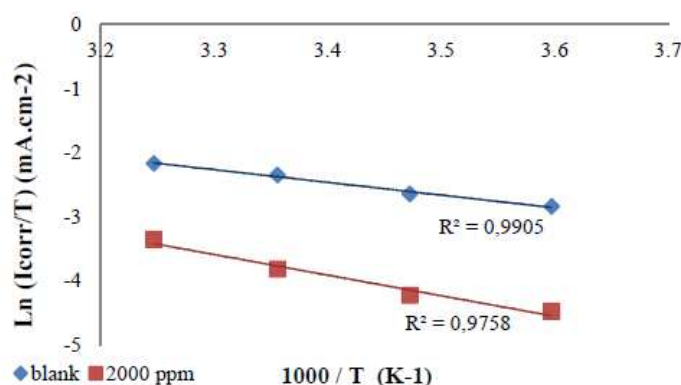
In view of the results of Table 6 it is clear that in presence of the inhibitor the activation energy increases, whereas IE% decreases when the temperature increases. This behavior demonstrates physisorption phenomenon of the inhibitor on metal surface. The recovery rate, low at higher temperatures, suggests that at these temperatures the destruction rate of the film physically adsorbed increases faster than its rate formation.

The values of activation energies obtained from Arrhenius lines are about  $18.93 \text{ KJ.mol}^{-1}$ , at a concentration 2000 ppm of inhibitor, which means that when the recovery rate is maximum, the value of activation energy in the presence of this oil is  $29.16 \text{ KJ.mol}^{-1}$ . This confirms the physical adsorption of *Artemisia herba alba* essential oil by formation of an effective superficial film.

The kinetic parameters, the enthalpy and entropy of the corrosion process are also evaluated from a study of the temperature effect. An alternative formulation of the Arrhenius equation (5) is [27]:

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

where  $h$  is the constant of Planck,  $N$  is the number of Avogadro,  $\Delta S^*$  is the entropy of activation and the  $\Delta H^*$  is the enthalpy of activation. Fig. 10 shows plots of  $\text{Ln}(I_{\text{corr}}/T)$  compared to  $1/T$ . The lines are obtained with a slope of  $-\Delta H^*/R$  and an interception of  $(\text{Ln}R/Nh + \Delta S^*/R)$ , from which the values of  $\Delta S^*$  and  $\Delta H^*$  can be calculated; these values are given in Table 7.



**Figure 10.** Relations between  $\text{Ln}(I_{\text{corr}}/T)$  and  $1000/T$  at different temperatures.

The inspection of these data revealed that the thermodynamic data ( $\Delta S^*$  and  $\Delta H^*$ ) for lead dissolution reaction in  $\text{Na}_2\text{CO}_3$  0.1 M in presence of the inhibitor is higher than that in its absence. The positive sign of  $\Delta H^*$  reflects the endothermic

nature of lead dissolution process, which suggests that lead dissolution is slow in presence of the inhibitor [28]. By comparing the values of activation entropy  $\Delta S^*$  given in the Table 7, it is clear that the activation entropy decreases negatively to a greater extent in presence of white wormwood essential oil, which reflects the formation of a stable layer controlled by the inhibitor on lead surface [28].

**Table 7.** Values of activation parameters  $\Delta H^*$  and  $\Delta S^*$  of lead in  $\text{Na}_2\text{CO}_3$  0.1 M in absence and presence of 2000 ppm of essential oil.

Inhibitor	$\Delta H^*$ (J/mole <sup>-1</sup> .K <sup>-1</sup> )	$\Delta S^*$ (kJ/mole)
Blank	16.5	-161.92
2000 ppm	26.73	-139.14

## Conclusions

The following conclusions can be drawn from this study:

- The *Artemisia herba alba* essential oil is an effective inhibitor of lead corrosion in a solution of  $\text{Na}_2\text{CO}_3$  0.1 M. The inhibition effectiveness increases with the concentration to achieve 77 % to 2000 ppm.
- The results of polarization studies suggest that this oil acts as mixed inhibitor.
- The positive value obtained from the activation energy reveals physisorption.
- The value of  $\Delta H$  shows that lead dissolution is endothermic.

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