"INHIBITION OF CORROSION OF TIN USING NATURAL LINSEED OIL IN Na_2CO_3 SOLUTION"

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Abstract

The inhibition effect of natural *linseed oil* on the corrosion of tin in 0.1M Na_2CO_3 solution was be studied using potentiodyanmic anodic polarization techniques. It was be found that the inhibition efficiency increased with an increase in the inhibitor concentration of this oil. The inhibitive action of *linseedoil* was be attributed to the adsorption on metal surface. The adsorption process follows the Langmuir adsorption isotherm. It was be found also that *linseed oil* provides good protection to tin against corrosion in bicarbonate sodium solutions.

Keywords: tin, Na2CO3,polarization techniques, linseed oil

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INTRODUCTION

The Mother Nature gave us an economic, eco-friendly, renewable and readily solution for corrosion of an almost metal, and the researchers who are interested explain that. We talk about 'green inhibitor'. Several surveys have been obtained using these extracts economic plants [1-6]. The extracts obtained from the leaves, peel, seeds, fruits and roots of plants include mixtures of organic compounds containing nitrogen, sulfur and oxygen and other [7-17]

The effectiveness of corrosion inhibition of these extracts is generally attributed to the presence in their composition, complex organic species such as tannins, alkaloids, flavonoids, polyphenolic compounds, nitrogen bases , glycosides and as well as their protein products of acid hydrolysis[18].
In our laboratories, we are reported a successful use of Eugenol [1] and Nigella sativa oil [2], and other extract as corrosion inhibitor for tin in Na_2CO_3. The encouraging results obtained by this research enthusiast us to test more plant materials extracts such us Linseed oil.
Linseed oil also known as flaxseed oil is made from the seeds of the flax plant. The oil contains substances, which promote good health because of their high levels of α-Linolenic acid [19-20].Linseed itself (ground or whole) also contains lignans, which may have antioxidant actions and may help protect against certain cancers, though not everyone agrees on this issue [21.22].

Linseed oil is a triglyceride, like other fats. Linseed oil is distinctive for its unusually large amount of αlinolenic acid, which has a distinctive reaction with oxygen in air.

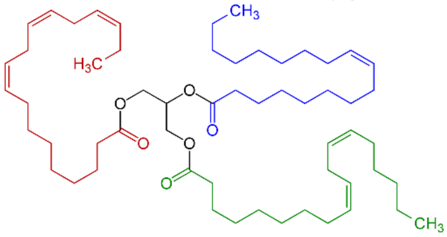

Figure 1: Representative triglyceride found in a linseed oil, a triester (triglyceride) derived of linoleic acid, alpha-linolenic acid, and oleic acid.

The present study seeks to investigate the potential of using Linseed oil as a cheap and environmentally safe corrosion control agent for tin inNa_2CO_3 solution. The assessment of the corrosion behavior was studied using weight loss, potentiodyanmic polarization measurement.

MATERIALS AND METHODS

Materiel

The working electrode was tin in a cylindrical shape with an exposed surface area of 1 cm^2. The samples was mechanically ground successively with emery paper grade 400, 800, and 1200, degreased in acetone and rinsed with distilled water before immersed in the test solution. The corrosive solutions were freshly prepared from analytical grade chemical reagents using distilled water.

Extraction of Linseed oil by Soxhlet technique

The linseeds were crushed and extracted with hexane for 3 h in a Soxhlet apparatus. The organic phase was then concentrated under vacuum and separated for 5 min in a rot vapor at 68.73C° (temperature of ebullition of solvent). Oil samples were stored and protected from sunlight prior analysis.The calculation for the yield of the Linseed oil is as follows[23]:

$$Yeild(\%) = \frac{\text{weight of linseed oil (g)} * 100}{\text{initial weight of sample(g)}} \quad (I)$$

Soxhlet extraction technique gave 39% of linseed oil.

Polarization measurements

Electrochemical polarization measurements were carried out in a conventional three-electrode cylindrical glass cell, platinum electrode was used as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The potentiodynamic polarization curves were recorded using Voltalab PGZ 301 piloted by ordinate associated to "Volta Master 4" software. The working electrode was initially kept at the free potential before recording the cathodic curves up to the -1200 mV vs. SCE at a scan rate of 1 mV/s.The inhibition efficiency E_p (%) was calculated using the following equation:

$$E_p(\%) = (1 - \frac{I_{cor}}{I°_{cor}}).100 \quad (II)$$

The surface coverage (θ) was calculated using the following equation:

$$\theta = \frac{I°cor - Icor}{I°cor} \quad (III)$$

Where I_{cor} and I_{cor} are the corrosion current densities of tin in the presence and absence of inhibitor, respectively.

Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy was carried out with a same equipment was used as for the potentiodynamic polarization measurements. The measuring ranged from 100 kHz down to 10 mHz with 10 mV peak to peak amplitude using sinusoidal potential perturbation at the open circuit potential. The impedance diagrams were plotted in the Nyquist representation. The inhibition efficiency E_{EIS} (%) was calculated using the following equation:

$$E_{EIS}(\%) = (1 - \frac{R_t}{R_t^0}).100 \qquad \text{(IV)}$$

Where Rtand R_t^0 are referred to as the charge transfer resistance of tin without and with the addition of the inhibitor, respectively.The values capacitance the double layer C_{dl}were obtained at maximum frequency (f_{max}), at which the imaginary component of the Nyquist plot is maximum, and calculated using the following equation:

$$C_{dl} = \frac{1}{2\pi . R_t . f_{max}} \qquad \text{(V)}$$

RESULTS AND DISCUSSION

Effect of linseed oil concentration

Potentiodyanmic polarization

Potentiodynamic anodic and cathodic polarization curves of tin specimens in 0,1 M Na_2CO_3solution in the absence and presence of different concentrations of linseed oil are shown in Fig. 2. The respective kinetic parameters including corrosion current density (I_{corr}), corrosion potential (E_{corr}), I_{pass} and inhibition efficiency E_p (%) are given in Table 1.

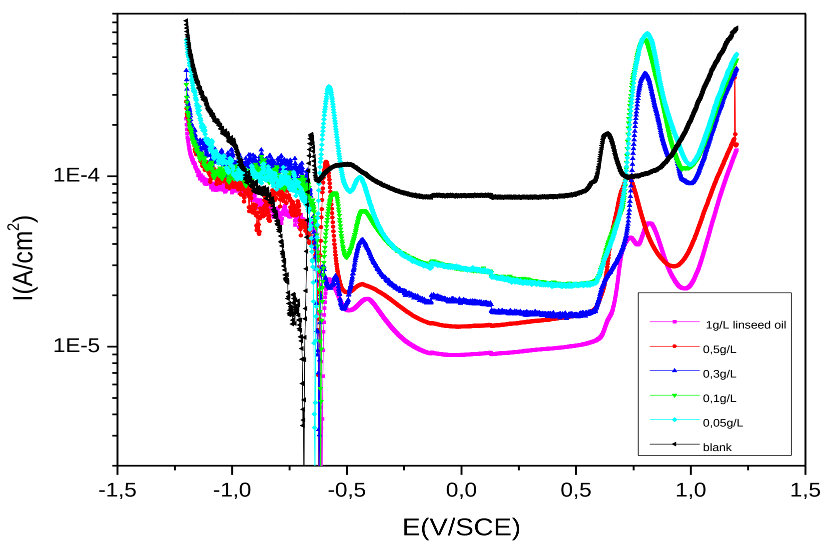

Figure2: Polarization curves for tin in 0.1 M Na_2CO_3 with and without linseed oil at 298 K.

Table 1:Electrochemical parameters derived from Tafel plots of tin in 0.1 M Na_2CO_3 with and without linseed oil at 298K.

C(g/L)	I_{corr} (µA/cm²)	E_{corr}(mv)	I_{pass}(µA/cm²)	E_p (%)	θ
bl	33	-687	80		
0,05	22	-633	31	33	0,33
0,1	15	-617	30	55	0,55
0,3	13	-625	19,4	61	0,61
0,5	8	-618	14,7	76	0,76
1	2	-608	9,45	92	0,92

As presented in Table 1, there is notable decrease in the value of corrosion rate with increasing oil concentration due to higher degree of surface coverage.

Electrochemical impedance spectroscopy measurements

The corrosion behavior of tin in 0.1 M Na_2CO_3 solution in the presence and absence differents concentrations of linseed oil is also investigated by the electrochemical impedance spectroscopy (EIS). The measures were performed at 298 K. Fig. 3 shows the corresponding Niquist diagram. The impedance parameters derived from these investigations are mentioned in Table 2.

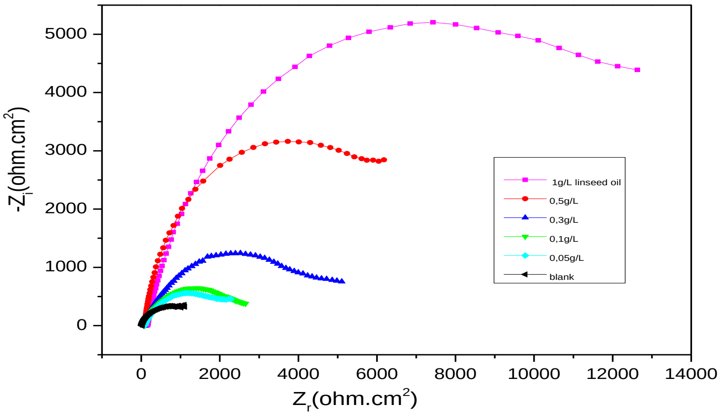

Figure 3.Nyquist plots for the corrosion of tin in 0.1 M Na_2CO_3 containing different concentrations of inhibitor at298K.

Table 2. Electrochemical impedance values of tin in 0.1 M Na_2CO_3containing different concentrations of inhibitor at 298K.

C (g/L)	R_s	R_t	f max	C_{dl} (µF/cm²)	E_{Rt}(%)
	(Ω.cm²)	(kΩ.cm²)	(Hz)		
blanc	11	1,2	2,84	46,69	--
0,05	75	2,21	2,88	25,00	46
0,1	66,4	2,6	2,85	21,47	54
0,3	60,74	4,64	2,83	12,13	74
0,5	90	7,43	2,86	7,5	84
1	150,4	13,86	2,74	4,2	91

From Table 2, it was clear that charge transfer resistance R_t values were increased and the capacitance values C_{dl}decreased with increasing inhibitors concentration. These results support those of polarization measurements that the inhibitor does not alter theelectrochemical reactions responsible for corrosion. It inhibits corrosion primarily through its adsorption on thetin surface[24-25].

Adsorption isotherm

Values of θ were be tested graphically for fit to different adsorption isotherms. As depicted in Fig. 1, a straight line is obtained when C/θ is plotted against C and the linear correlation coefficient of the fitted data is good (0,98). This confirms that the inhibition is due to the adsorption of the active organic compounds onto the metal surface and the adsorption obeys the Langmuir's adsorption isotherm [26] expressed as:

$$\frac{Cinh}{\theta} = nCinh + \frac{n}{Kads} \qquad (VI)$$

Free energy of adsorption was calculated using the relation:

$$Kads = \frac{1}{55,55} * \exp(-\frac{\Delta G0\ ads}{RT}) \quad \text{(VII)}$$

Where R is the universal gas constant and T is the absolute temperature. The value 55.55 in the above equation is the concentration of water in solution in mol L^{-1}. The negative value of ads ΔG^0_{ads}(-15kJ/mol^{-1}) means that the adsorption of LSO on tin surface is a spontaneous process[27]. Generally, the magnitude of ΔG^o_{ads} around −20 kJ.mol^{-1} or less negative indicates electrostatic interactions between inhibitor and the charged metal surface (i.e., physisorption)[28].

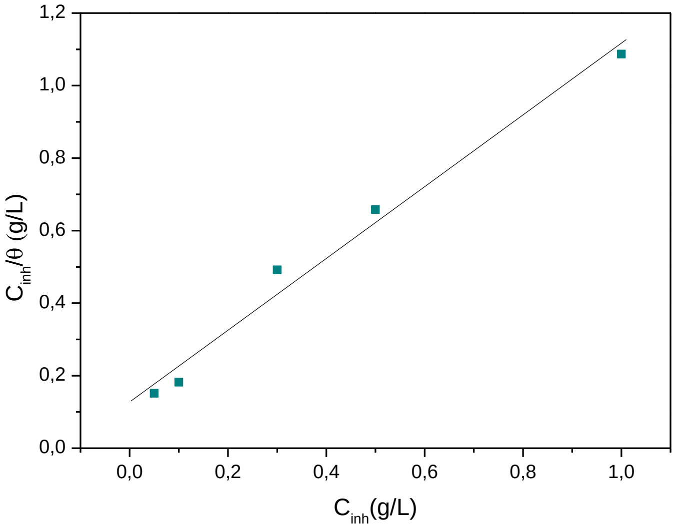

Figure 4.Langmuir isotherm plot for corrosion of tin in 0.1M Na_2CO_3containing different concentration of linseed Oil at 298K.

Effect of temperature

Temperature has a great effect on the corrosion phenomenon. Generally, the corrosion rate increases with the rise of the temperature. For this purpose, we made potentiodynamic polarization in the range of temperature 278 K to 308 K, in the absence and presence of *LSO* (1g/L). The corresponding data are shown in fig 5, 6 and Table 9.

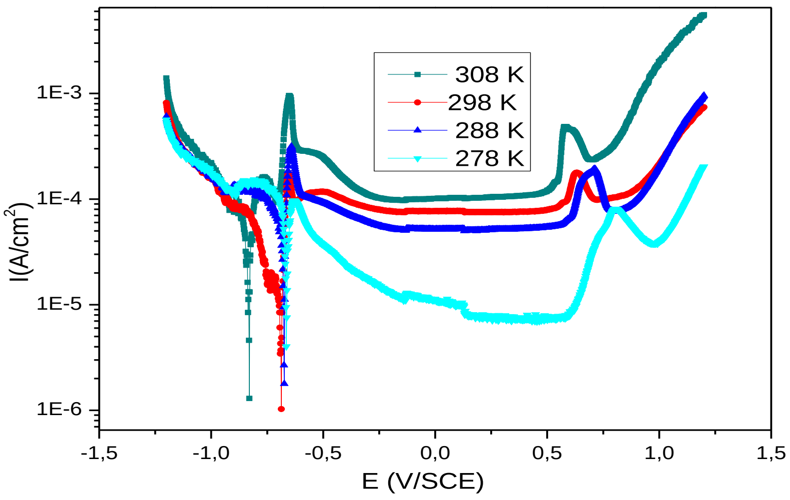

Figure 5.Tafel plots of tin in 0.1 M Na_2CO_3 at different temperatures.

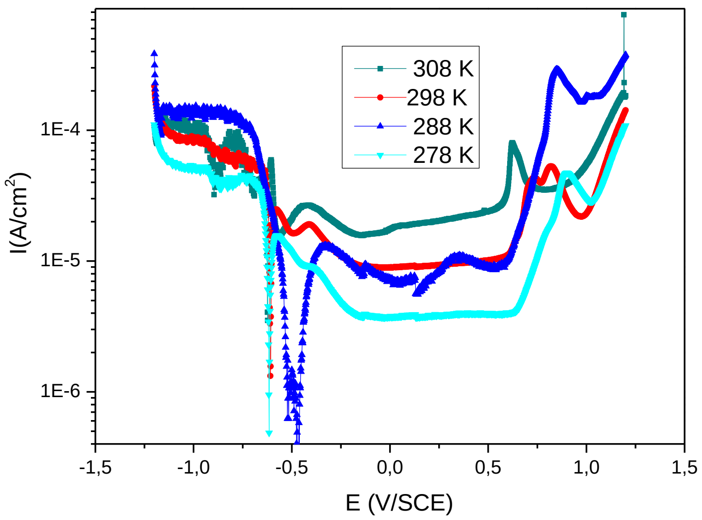

Figure 6. Tafel plots of tin in 0.1 M Na_2CO_3 with linseed oil (1g/L) at different temperatures.

Table 3 .Electrochemical parameters of tin in 0.1 M Na_2CO_3 with and without LSO (1g/L) at different temperatures

	T(K)	I_{corr}(μA/cm²)	E_{corr}(mv)	I_{pass}(μA/cm²)	%E
Blank	278	16,5	-596	12	
	288	28	-678	52	
	298	33	-687	75	
	308	51,32	-834	103	
1g/L	278	2,2	-596	22	87
	288	1	-464	8	96
	298	2,61	-608	9	92
	308	8,75	-761	19,4	83

Fig.6, Fig.5and table 3 indicate that there is a general increase in intensity of corrosion while the temperature increases. The solution become more corrosive with the rise of temperature, for that there was a marked decrease in the inhibition efficiencies. In addition, we can guess that linseed oil loss its character inhibitor with rise of high temperature.

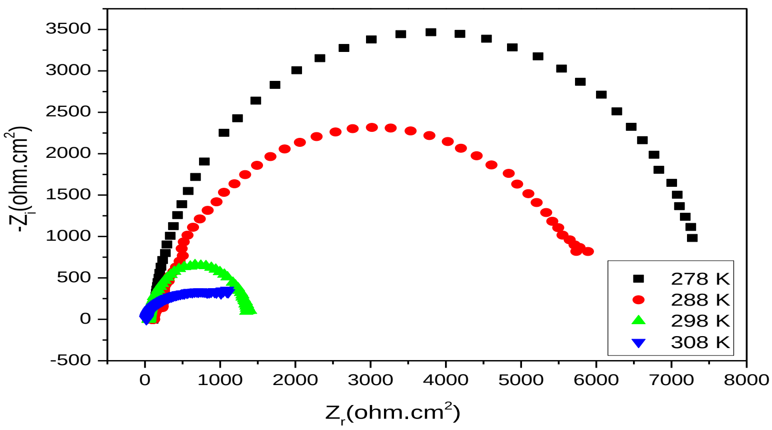

Figure 7 .Nyquist plots for tin in 0.1 M Na_2CO_3 at different temperatures

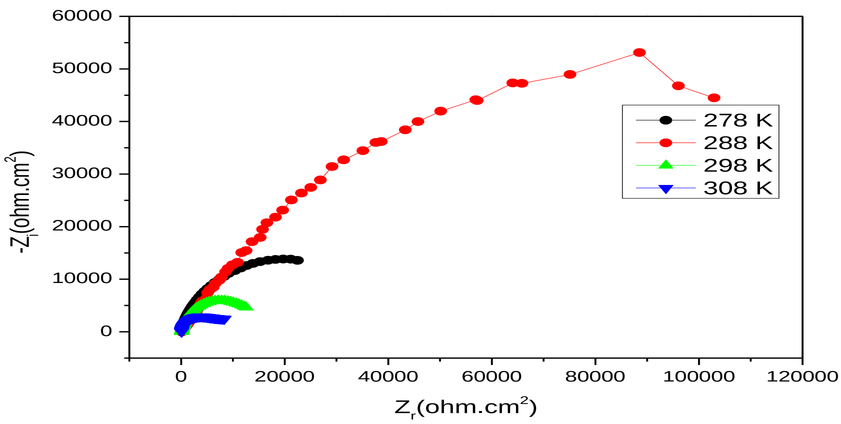

Figure8. Nyquist plots for tin in 0.1 M Na2CO3with LSO (1g/L) at different temperatures

Table 4. Impedance parameters of tin in 0.1 M $Na_2CO_3$with and without *LSO* (1g/L) at different temperatures

C(g/L)	T(K)	R_s(Ω.cm²)	R_t(kΩ.cm²)	C_{dl}(μF/cm²)	E_{Rt}(%)
	278	111	7,4	15.35	--
	288	119	5,9	21.34	--
blank	298	11	1,2	46.69	--
	308	56	1,4	16.5	
	278	108,8	37,47	3,07	80
	288	310,6	170	0,64	97
1	298	68,3	15,3	4,2	91
	308	73,32	6,94	2,8	83

It is clear that the increase of the corrosion rate is more pronounced with the rise of the temperature for blank solution. In the presence of the inhibitor, R_t is highly reduced. Also, the inhibition efficiency decreases slightly with increasing temperature. This can be explained by the decrease of the strength of the adsorption processes at elevated temperature and suggested a physical adsorption mode.

Kinetic parameters

The activation energies of corrosion process in free and inhibited acid were calculated using Arrhenius equation (VIII):

$$Icorr = A \exp\left(\frac{-Ea}{RT}\right) \quad \text{(VIII)}$$

Where A is Arrhenius factor, E_a is the apparent activation corrosion energy, R is the perfect gas constant and T the absolute temperature. Plotting (log I_{corr}) versus 1/T gives straight lines as revealed from Fig. 7.

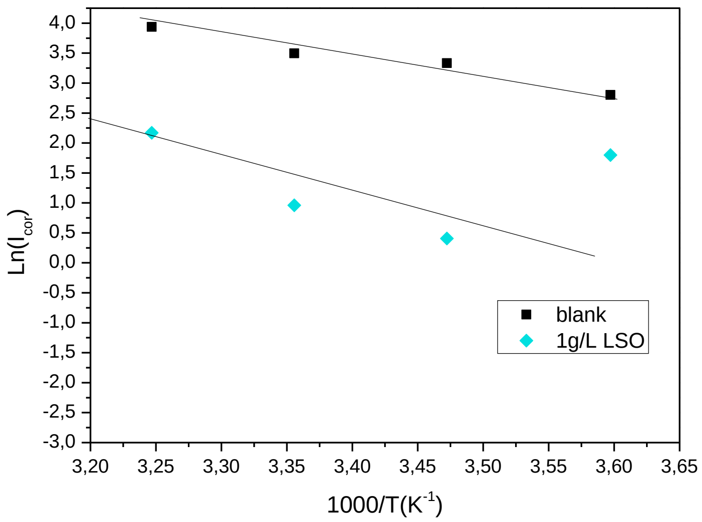

Figure 7. Arrhenius plots of tin in 0,1 M Na_2CO_3 with and without LSO (1 g/L).

The values of E_a found for LSO (50 Kj.mol^{-1}) is higher than that obtained for 0,1 M Na_2CO_3 solution(40 Kj.mol^{-1}) calculated by equation (8). The increase in the activation energy E_a with the additive inhibitor may be considered to be due to the physical adsorption of the inhibitor [29-30].
The activation parameters for the studied system (ΔH^* and ΔS^*) were estimated from the transition state equation [IX]:

$$Icorr = \frac{RT}{N_A h} . \exp\left(\frac{\Delta S^*}{R}\right) . \exp\left(-\frac{\Delta H^*}{RT}\right) \quad \text{(IX)}$$

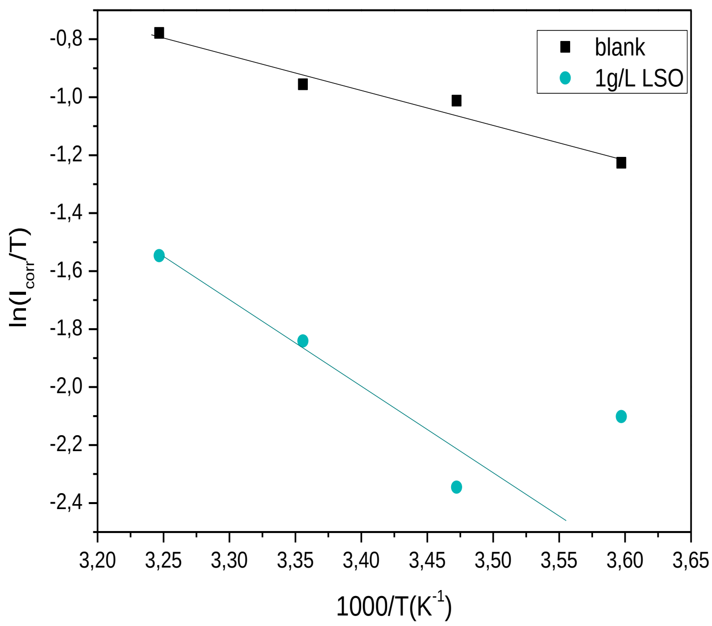

Figure 8. Arrhenius plots of log(I /T) for steel in 0,1 MNa_2C in the absence and the presence of LSO.

Where $\mathcal{N}_A$ 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.4 shows a plot of $\ln(I_{corr}/T)$ against 1/T for LSO. Straight lines are obtained with a slope of $(-\Delta H^*/R)$ and an intercept of $(\ln R/Nh + \Delta S^*/R)$ from which the values of $\Delta H^*$and ΔS^* are calculated respectively (Table 5).

Table 5. The values of activation parameters Ea , ΔH^* and ΔS^* for tin in 0.1 MNa_2CO_3 in the absence and the presence of 1 g /L of LSO.

Concentration of LSO (g/L)	ΔH ($kJ.mol^{-1}.k^{-1}$)	ΔS ($J.mol^{-1}.k^{-1}$)	E_a ($KJ.mol^{-1}$)
blank	10	-171,5	40
1	15,16	-192	50

Inspection of these data revealed that the thermodynamic parameters ($\Delta H^*$and ΔS^*) for dissolution reaction of tin steel in 0,1 M Na_2CO_3 in the presence of extract is higher (15 mol^{-1}) than that of in the absence of inhibitor (10 KJ mol^{-1}). The positive sign of reflect the endothermic nature of the tin dissolution process suggesting that the dissolution of tin is slow [31] in the presence of inhibitor.
it is clear that the entropy of activation decreases more negatively in the presence of LSO than in the absence of inhibitor, which reflects the formation of an ordered stable layer of the inhibitor on the steel surface [32].

CONCLUSION

From this study, the following results can be drawn:

-Linseed oil was found to inhibit the corrosion of tin in 0.1 M Na2CO3 solution and inhibition efficiency increases with increasing oil concentration. At the highest oil concentration of 1g/L, the inhibition efficiency is increased markedly and reached 97%.

-The electrochemical impedance spectroscopy results indicate an increase of the charge transfer resistance and a decrease of the reduced double layer capacitance values when the Linseed oil concentration increases.

-The adsorption model obeys the Langmuir adsorption isotherms model. Linseed oil inhibits the corrosion of tin in alkaline media by adsorption mechanism.

-Inhibitor efficiency values determined by electrochemical polarization and electrochemical impedance spectroscopy are in reasonable agreement.

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