



Investigation of the Effect of Natural Extract on Corrosion Behavior of Tin in Na₂CO₃ Solution

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ABSTRACT

The inhibition effect of eugenol oil (EO) on the corrosion of tin in 0.1 M Na₂CO₃ has been studied by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization technics. The effect of temperature on the corrosion behavior of tin in 0.1 M Na₂CO₃ with and without addition of eugenol oil was studied in the temperature range 278-308 K. This compound inhibits the corrosion of tin at low concentration. At 4g/L eugenol oil the inhibition efficiency calculated by potentiodynamic polarization and EIS techniques is 70% and 82%, respectively. The inhibition efficiency increased with increase of the inhibitor concentration and decreased with increase of medium temperature. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition. Polarization curves reveal that EO acts as a mixed-type inhibitor in corrosive solution. The results obtained from the different corrosion evaluation techniques are in good agreement.

Indexing terms/Keywords

Electrochemical Impedance Spectroscopy; Potentiodynamic Polarization; corrosion inhibition; tin; Eugenol Oil; 0.1 M Na₂CO₃.



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INTRODUCTION

The interest on the corrosion and inhibition behaviour of tin is due to its important technological application. The corrosion behavior of this metal in aqueous medium has been the subject of several investigators [1-5]. The use of pure tin is greatly restricted by its high fusibility, high price, low hardness, corrosion resistance, wettability and ease of forming alloys[6]. As a result, tin's functionality is typically found in the form of a thin coating or as an alloy with other metal[7]. Because of its utility, the reserch of tin corrosion and its inhibition has become verry impotant.

Recently the research has been focused on the use of the natural products of plant origin contain different organic compounds, and most are known to have inhibitive action [8-14]. Other authors have also shown that the inhibitive effect of some plants solution extract is due to the adsorption of molecules of phytochemicals present in the plant on the surface of the metal, which blocks the metal surface and thus doesn't permit the corrosion process to take place. The encouraging results obtained by this research permit us to test more plant materials extacts.

The electrochemical studies of tin are closely related to its wide applications in industry. Very little work has been carried out in carbonate solutions [15-18], it's reported that'is in bicarbonnate media, potentiodynamic polarization is characterized by formation a layer of passivation without a break down of passivity and the appearance of two anodic peaks assigned to the formation of Sn(II) an d Sn(IV) species[17,19-20].

The present work was devoted to study the corrosion inhibition of tin in bicarbonnate sodium solution using a series of green inhibitors by electrochemical impedance spectroscopy and potentiodynamic techniques. The influence of the concentration and temperature was also investigated.

2. EXPERIMENTAL PART

2-1 Materiel

The working electrode was pure tin in a cylindrical shape with an exposed surface area of 0.5cm². The samples was mechanically ground successively with 300, 800, and 1200 grit emery paper, degreased in acetone and rinsed with bidistilled water before immersed in the test solution. The corrosive solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water.

We investigated the efficiency of eugenol, thymol and the carvacrol oil as corrosion inhibitors in 0.1 M Na₂CO₃ media. These oils are supplied by company called Fluka.

2-3 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 polarisation curves were recorded using a potentiostat PGZ 301. The working electrode was initially kept at the free potential for 30 min 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:

$$E_p(\%) = \left(1 - \frac{I_{cor}}{I_{cor}^0}\right) \cdot 100 \quad (1)$$

where I_{cor} and I_{cor}^0 are the corrosion current densities of tin in the presence and absence of inhibitor, respectively.

2-4 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:

$$E_{EIS}(\%) = \left(1 - \frac{R_t}{R_t^0}\right) \cdot 100 \quad (2)$$

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

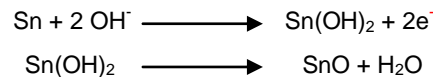
$$C_{dl} = \frac{1}{2 \pi \cdot R_t \cdot f_{max}} \quad (3)$$

3. RESULTS AND DISCUSSION

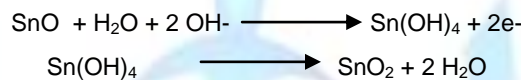
3-1 Electrochemical study of tin in 0,1M Na₂CO₃ solution

Potentiodynamic polarization plots for tin specimen in 0.1 M Na₂CO₃ solution at 298 K is shown in Fig. 1. The curves were swept between -1200 and 1200 mV/SCE at scan rate of 1 mV.s⁻¹. The active dissolution region involves two anodic peaks (I and II) prior to permanent passive region. These results are similar to those reported by Refaey for tin electrode in carbonate solutions [10, 20] and for tinplate by our laboratory [21].

The first anodic peak located at about -0.65 V/SCE is due to the formation of Sn(OH)₂ or SnO according to the following reaction:



The second anodic peak located about -0.55 V/SCE corresponds to the formation of Sn(OH)₄ or SnO₂ according to the following reaction:



The same explanation is introduced by several authors [2,21-23]. Dehydration of the thermodynamically unstable Sn(OH)₄ leads to the stable SnO₂[24]. When the surface is covered with passive film, the anodic current density falls to the lowest value *I*_{pass} indicating a permanent passivation.

The third peak (III) observed about 0.64 V/SCE beyond the passivity plateau, it cannot be assigned to any particular anodic oxidation reaction [5]. Several authors attributed the observation of the transpassive region in alkaline media to a solid phase transformation[5,10-12]. It is generally believed that oxygen evolution occurs most probably on a film of metastannic acid (H₂SnO₃)[12].

For more raised anodic potentials, the field of transpassivity is reached due to the oxidation of solvent according to the reaction:



The effect of the addition of eugenol, thymol and carnabol oil at 2g/L on potentiodynamic polarization curves for tin in 0.1 M Na₂CO₃, pH = 10.9 is shown in Fig. 2.

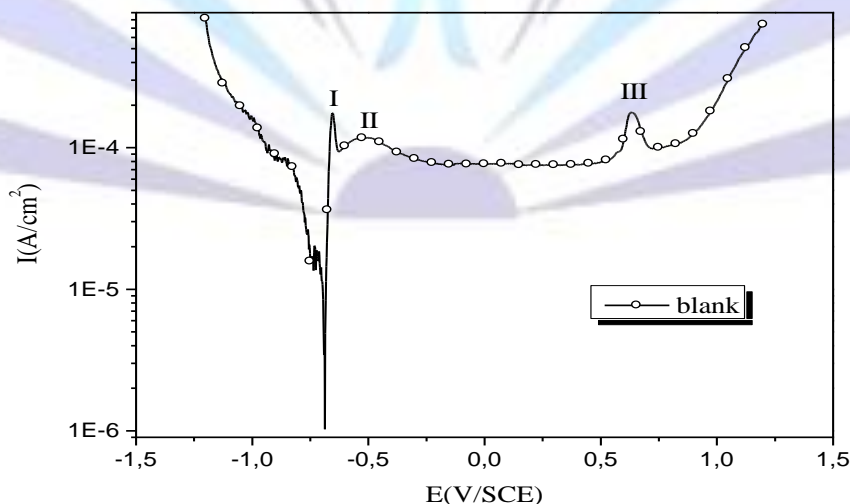


Fig. 1. Potentiodynamic polarisation curves for tin electrode in 0.1 M Na₂CO₃ at 298 K

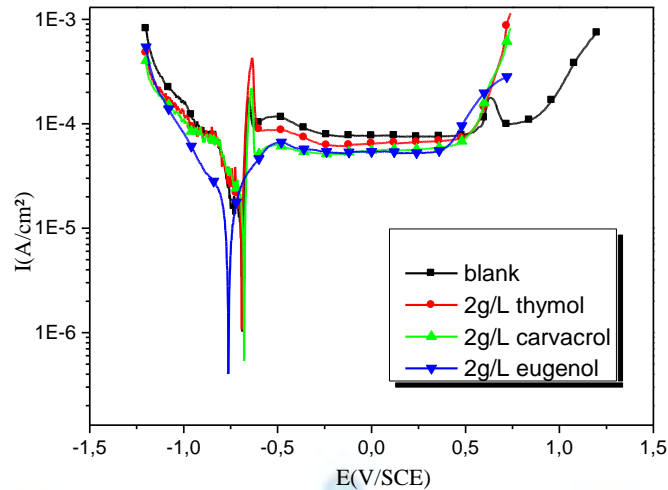


Fig. 2. Polarization curves for tin in 0.1 M Na_2CO_3 without and with different inhibitors at 298 K.

the curves of thymol oil and carvacrol oil are almost more confused with that of the free acid solution (blank) reflects the non-functionality of these oils as corrosion inhibitors in these conditions, Except that eugenol oil. The results encourage us to follow the study with this inhibitor.

Eugenol, extract the essential oil of cloves, also known as 4-allyl-2-methoxyphenol (Fig. 3) is an aromatic compound of the family phenylpropenes, a subclass of phenylpropanoid, the empirical formula $\text{C}_{10}\text{H}_{12}\text{O}_2$ is used in some products for medical and dental fields because of its analgesic and antiseptic properties [14,25-28].

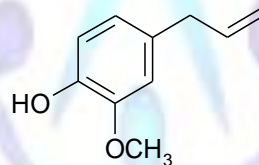


Fig. 3. Chemical structure of Eugenol

3-2. Effet of eugenol concentration

3-2-1. Potentiodynamic polarization

The effect of eugenol oil concentration on the anodic and cathodic polarization behavior of tin in 0.1 M Na_2CO_3 solution has been studied by polarization measurements and the recorded Tafel plots are shown in Fig.4.

Table 1 shows the electrochemical parameters of tin determined from polarization measurements such as; corrosion potential (E_{cor}), corrosion current density (I_{cor}), passivation current density (I_{pass}) and inhibition efficiency $E_p(\%)$ calculated from I_{cor} values using equation (1). It is clear from Fig. 4 that anodic metal dissolution of tin were inhibited after the addition of eugenol oil in corrosive solution.

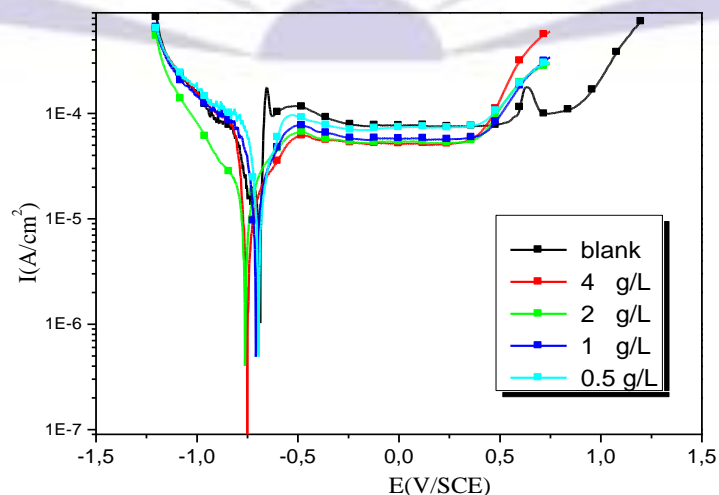


Fig. 4. Polarization curves for tin in 0.1 M Na_2CO_3 with and without eugenol oil at 298 K.

Table 1 : Electrochemical parameters derived from Tafel plots of tin in 0.1 M Na₂CO₃ with and without eugenol oil at 298K.

Concentration (g/L)	I_{cor} ($\mu A/cm^2$)	E_{cor} (mV/CSE)	I_{pass} ($\mu A/cm^2$)	E_p (%)
blank	30	-688	75	--
0.5	21	-693	69	32
1.0	19	-703	56	38
2.0	15	-757	52	50
4.0	10	-754	50	70

From the figure 4 and table 1, it is clear that the inhibition efficiency ($E_p\%$) increases with the increase of eugenol oil concentration reaching a maximum value at a higher concentration (4g/L). This suggests that increase in the inhibitor concentration increases the number of molecules adsorbed over the tin surface, blocking the active sites of solution attack and thereby protecting the metal from corrosion. We note the small variation of I_{pass} values. The values of corrosion potential nearly remain constant with the addition of eugenol oil. These results indicate that EO acts as a mixed-type inhibitor [29-30].

3-2-2 Electrochemical impedance spectroscopy

The Nyquist impedance plots for tin in 0.1 M Na₂CO₃ in the absence and presence of different concentrations of eugenol oil are shown in Fig. 5. From this Figure, the obtained impedance diagrams almost a semi-circular appearance, indicates that a charge transfer process mainly controls the corrosion of tin, whose size increases with increasing eugenol oil concentration.

The impedance parameters derived from these investigations are listed in Table 2. The values of charge transfer resistance (R_t) increased with the increase of the concentration of Eugenol oil. The decrease in C_{dl} means that the adsorption of this oil takes place on the metal surface[31]. It shows that eugenol is an effective inhibitor for the tin in 0.1 M Na₂CO₃ solutions.

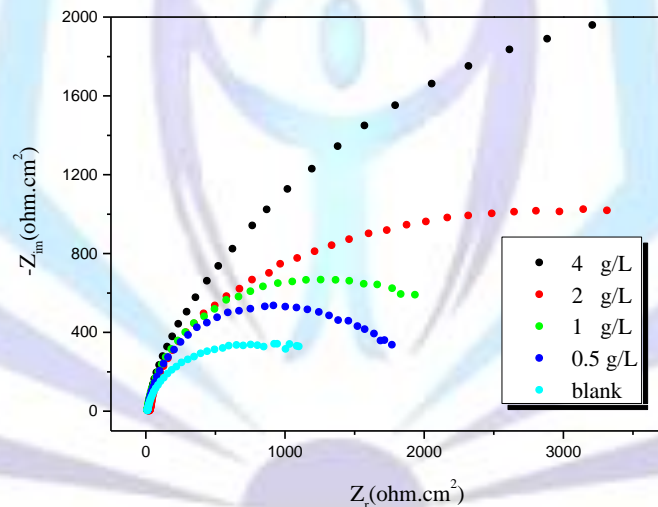


Fig. 5. Nyquist plots for tin in 0.1 M Na₂CO₃ at various concentrations of eugenol oil at 298 K.

Table 2. Impedance parameters derived from EIS plots of tin in 0.1 M Na₂CO₃ at various concentrations of eugenol oil at 298 K.

C (g/L)	R_s ($\Omega .cm^2$)	R_t ($k\Omega .cm^2$)	C_{dl} ($\mu F/cm^2$)	E_{EIS} (%)
Blank	12	1.195	53	--
0.5	13	1.697	44	30
1.0	10	1.955	40	39
2.0	3	2.770	33	57
4.0	5	6.600	24	82

the inhibition efficiency values obtained from impedance and polarization measurements are in good agreement, confirming that the inhibition action of eugenol for tin corrosion 0.1 M Na_2CO_3 .

3-3.Effet of temperature

The temperature is an essential parameter affecting the phenomenon of corrosion. Electrochemical steady state measurements are taken at various temperatures (278-308 K) in the absence and presence of Eugenol oil 2 g/L in 0.1 M Na_2CO_3 .

3-3-1 polarisation curves

The effect of temperature on the inhibition efficiency of eugenol oil on the potentiodynamic polarisation curves are shown in Fig. 6 and Fig.7. The respective electrochemical parameters derived from the above plots are given in Table 3.

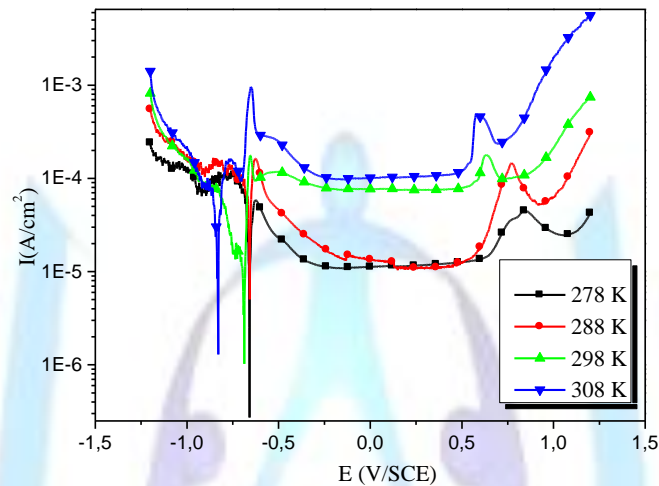


Fig. 6. Tafel plots of tin in 0.1 M Na_2CO_3 at different temperatures .

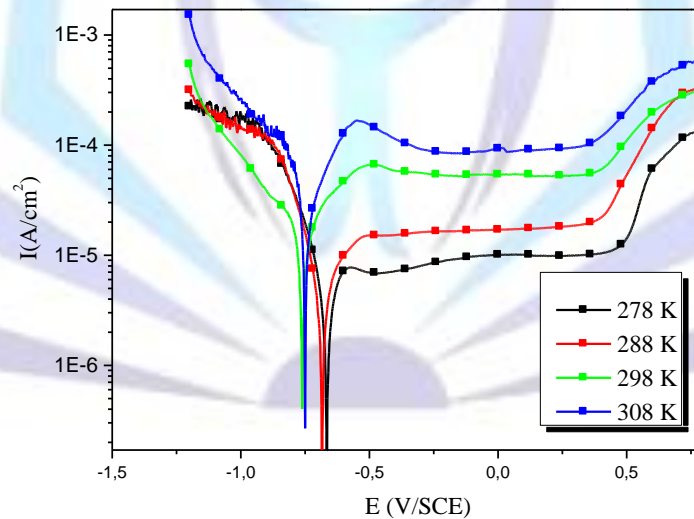


Fig. 7. Tafel plots of tin in 0.1 M Na_2CO_3 with eugenol oil (2g/L) at different temperatures.

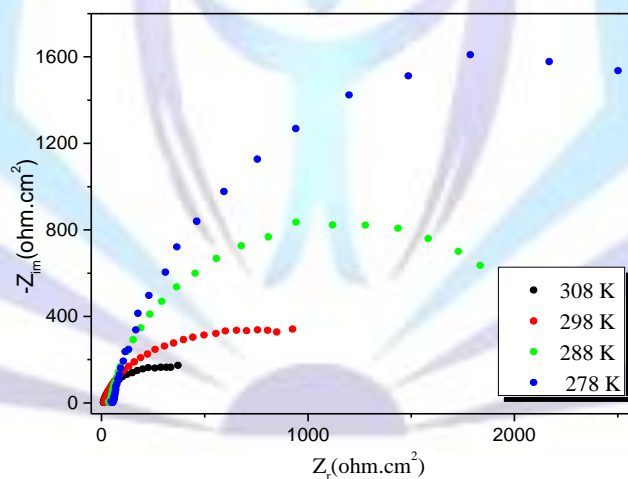
**Table3 : Electrochemical parameters of tin in 0.1 M Na₂CO₃ with or without eugenol oil (2g/L) at different temperatures.**

C (g/L)	Temperature (K)	I _{cor} (μA/cm ²)	E _{cor} (mV/SCE)	I _{pass} (μA/cm ²)	E _p (%)
Blank	278	18	-658	11	--
	288	30	-656	51	--
	298	33	-688	75	--
	308	48	-831	97	--
2	278	2	-662	10	89
	288	12	-681	42	60
	298	15	-757	52	55
	308	32	-744	84	33

Fig 6 ,fig 7 and table3 indicates that there is a general increase in intensity of corrosion while the temperature increase from 278 to 308 K. The solution become more corrosive with the rise of temperature, for that there was a marked decrease in the inhibition efficiencies. Also we can guess that the molecule of eugenol oil loss its character inhibitor with rise of temperature.

3-3-2 Electrochemical impedance spectroscopy (EIS).

The effect of temperature on the corrosion behaviour of tin in 0.1 M Na₂CO₃ containing inhibitor concentration (2g/L) is studied in the temperature range 278-308 K using impedance diagrams measurements (Fig. 8 and Fig. 9), the corresponding results are summarised in Table 4.

**Fig.8. Nyquist plots for tin in 0.1 M Na₂CO₃ at different temperatures.**

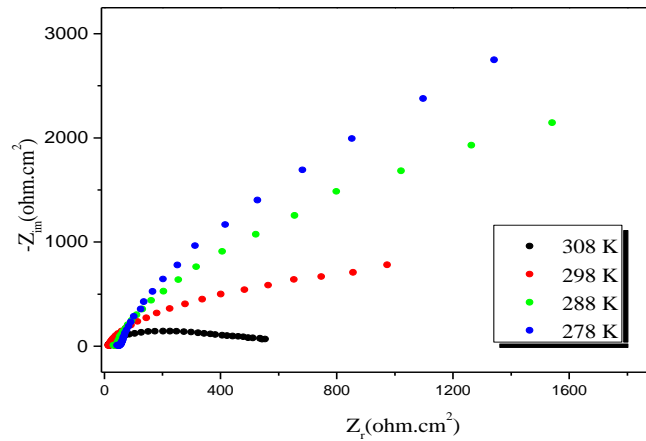


Fig.9. Nyquist plots for tin in 0.1 M Na₂CO₃ with eugenol (2g/L) at different temperatures.

Table 4: Impedance parameters of tin in 0.1 M Na₂CO₃ with and without eugenol (2g/L) at different temperatures.

C (g/L)	Temperature (K)	R _s (Ω.cm ²)	R _t (kΩ.cm ²)	C _{dl} (μF/cm ²)	E _{EIS} (%)
blank	278	55	3.55	20	--
	288	20	1.60	29	--
	298	12	1.20	42	--
	308	12	0.42	24	--
2	278	39	10.47	12	66
	288	3	3.96	36	60
	298	4	2.77	32	57
	308	8	0.55	18	24

The increase in corrosion rate is more pronounced with the rise of temperature for the uninhibited 0.1 M Na₂CO₃ solution. The presence of inhibitor leads to decrease of the resistance of transfer. E_{EIS} (%) depends upon the temperature and decreases with temperature.

3-4. Determination of the activation parameters

It has been pointed out by number of authors [32-33] that the logarithm of the corrosion rate (k) is a linear function with the reciprocal of the absolute temperature 1/T (Arrhenius equation):

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

where E_a is the apparent effective activation energy, T the absolute temperature, R the universal gas constant, and A is Arrhenius pre-exponential factor. The average activations energy for the dissolution of tin in 0.1 M Na₂CO₃ solution between 278 and 308 K were illustrated on Figs.10 and 11.

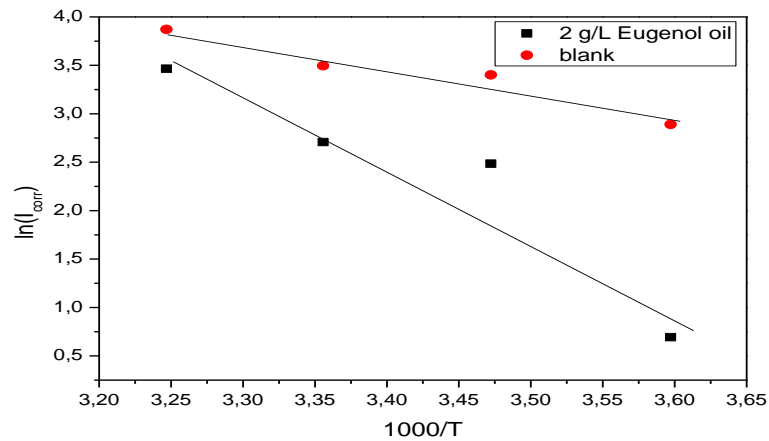


Fig 10. Arrhenius plots of tin in carbonate medium in the absence and presence of EO (Polarisation curves)

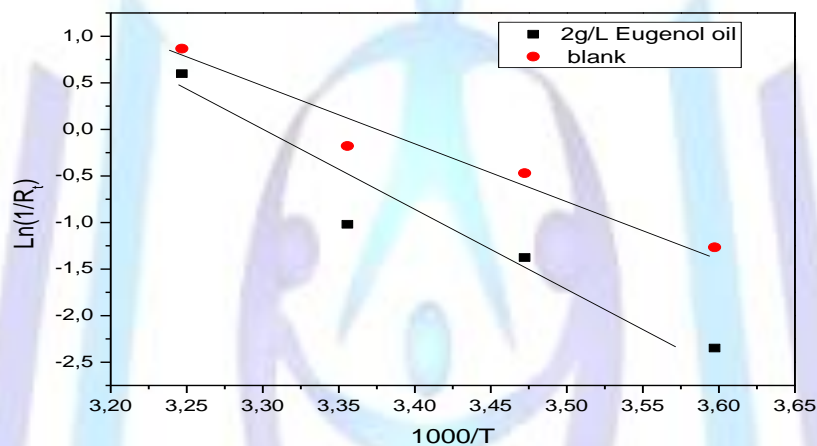


Fig 11. Arrhenius plots of tin in carbonate medium in the absence and presence of EO (EIS)

Table 5 : Activation Energy E_a for tin corrosion in the absence and presence of EO.

C(g/L)	Polarization curves	EIS
	E_a (kJ.mol ⁻¹)	E_a (kJ.mol ⁻¹)
blank	40	47
2	61	65

The values of E_a for the corrosion reaction in absence and presence of eugenol oil (Table 5) are calculated by equation (4). 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[34-35].

4- CONCLUSION

From the overall experimental results the following conclusions can be deduced:

1. Eugenol oil acts as an mixed-type inhibitor for corrosion of tin in 0.1 M Na₂CO₃ solution.
2. The inhibition efficiency increases with increase in the concentration of eugenol oil but decreases with increase in temperature.
3. The inhibition is due to the presence of some the constituents in the eugenol oil which is adsorbed on the surface of the tin metal.
4. The values of E_a suggest that the inhibitors were strongly adsorbed on the tin metal surface.

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