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Research Article

Inhibition of Tin Corrosion in Na_2CO_3 Medium by Oil of Nigella Sativa

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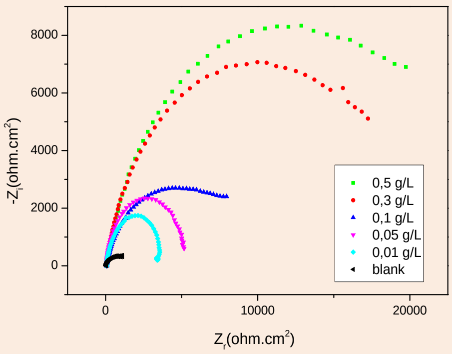
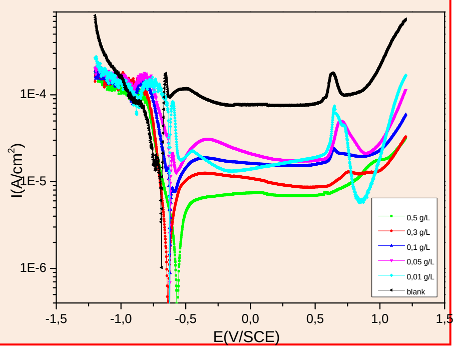
Abstract

The character inhibitive of Nigella Sativa Oil (NSO) on the corrosion of tin in Na_2CO_3 was studied using potentiodynamic polarization curve and electrochemical impedance spectroscopy (EIS) measurements. The results indicate that the oils functioned as a good inhibitor in carbonate medium environments and inhibition efficiency increases with oil concentration to attain 95% at 0.5 g/L at 298 K. E(%) values obtained from various methods used are reasonably good agreement. The effect of temperature on the corrosion behavior of tin in Na_2CO_3 without and with addition of 0.5 $g.L^{-1}$ of NSO was studied in the temperature range from 278 to 308 K. The adsorption of Nigella Sativa Oil on the surface of the tin follows the Langmuir adsorption isotherm.





Keywords: Corrosion Inhibition, Tin, Nigella Sativa Oil, 0.1 M Na_2CO_3, EIS, Potentiodynamic Polarization.

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Introduction

The Tin has been in use since ancient times and it has played an important role in the humankind history. It was used in other implements as complement because it provides an important hardening effect [1]. The importance of tin grew rapidly when the ancients understood its potential for making everything from tools, to weapons, and even coating, food-packaging materials [2].

Tin has been used safely for many years, but responding to the increasing consumer interest in understanding the exact science of the metals behavior in the environment and the human body. The laboratory and industry has come together to carry out new research [3-7], but the corrosion is the biggest difficulty who restrict the use of tin.

The addition of inhibitor in solution is the most practice method, 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 [8–20].

In our latest work [21], we are reported a successful use of Eugenol as corrosion inhibitor for tin in Na_2CO_3. The encouraging results obtained by this research enthusiast us to test more plant materials extracts.Nigella Sativa namely called black cumin is a medicinal plant with rich historical and religious background. It grows in the Mediterranean region and western Asian countries. From far days, it has been employed as a spice, food preservative and traditional remediation [22-24], pharmaceutical and cosmetic industries and become a subject of many works [25-27], for that we can suggest that a nigella sativa seed is one of the most miracles spices in the world.

The aim of this paper is to evaluate the effect of the addition of nigella sativa oil on the corrosion of tin in Na_2CO_3 solution taking account the variation of both medium temperature and inhibitor concentration.

Experimental Part
Materiel

The working electrode was pure 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 Nigella sativa exact oil by Soxhlet technique

150 g seeds 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 Nigella Sativa Oil is as follows [28]:

$$\text{Yield}(\%) = \frac{\text{weight of nigella sativa oil collected(g)} * 100}{\text{initial weight of sample(g)}} \quad (1)$$

The Soxhlet technique gave **40%** of nigella sativa 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:

$$E_p(\%) = (1 - \frac{I_{cor}}{I^{\circ}_{cor}}).100 \quad (2)$$

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

$$\theta = \frac{I^{\circ}cor - Icor}{I^{\circ}cor} \quad (3)$$

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:

$$E_{EIS}(\%) = (1 - \frac{R_t}{R_t^0}).100 \quad (4)$$

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:

$$C_{dl} = \frac{1}{2\,\pi.R_t.f_{max}} \quad (5)$$

Results and Discussion

Effect of nigella sativa oil concentration

Potentiodynamic polarization

The effect of NSO 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.1. 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).

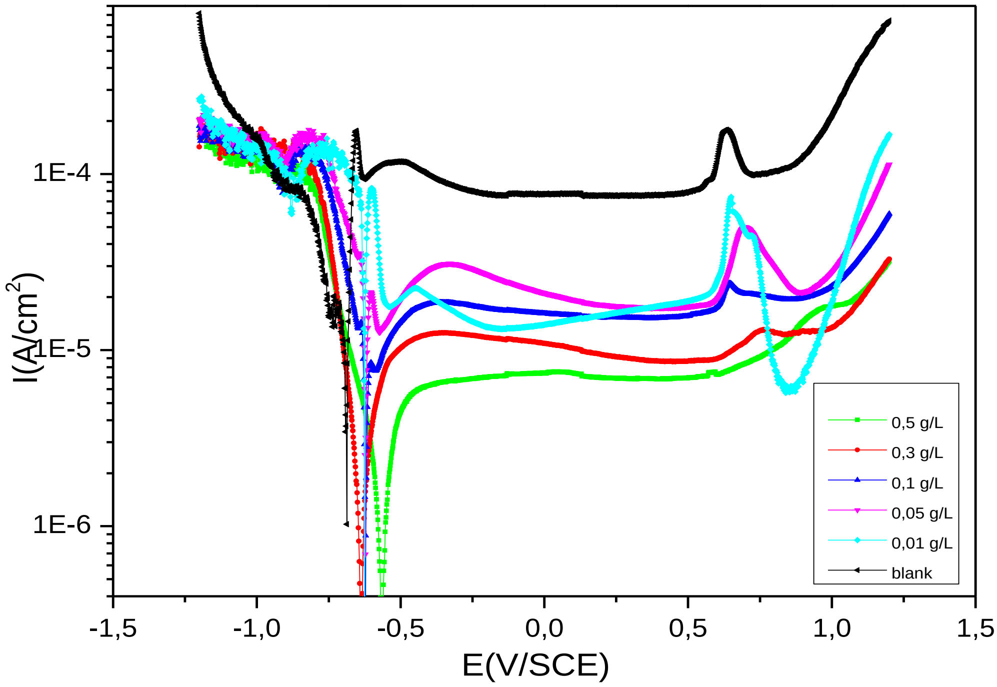

Figure 1 Polarization curves for tin in 0.1 M Na_2CO_3 with and without nigella sativa oil at 298 K.

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

C(g/L)	I_{cor} (µA/cm²)	E_{cor} (mV/SCE)	I_{pass} (µA/cm²)	E_p (%)
Blank	35	-687	80.40	--
0.01	14.80	-625	18.27	58
0.05	8.13	-622	17.00	77
0.10	5.20	-622	15.57	85
0.30	2.46	-636	8.80	93
0.50	1.31	-565	6.84	96

It is clear from Fig. 1 that anodic metal dissolution of tin were inhibited after the addition of nigella sativa oil in corrosive solution.

Electrochemical impedance spectroscopy measurements

Nyquist plots of tin in 0.1M Na_2CO_3 solution in the presence of nigella sativa oil at different concentrations are given in Fig. 2, where it can be concluded that the curves approximated by a single capacitive semicircles, showing that the corrosion process was mainly charge-transfer controlled [29]. The increase in capacitive loop suggests that the inhibition action of these inhibitors is due to their adsorption on the metal surface [30].

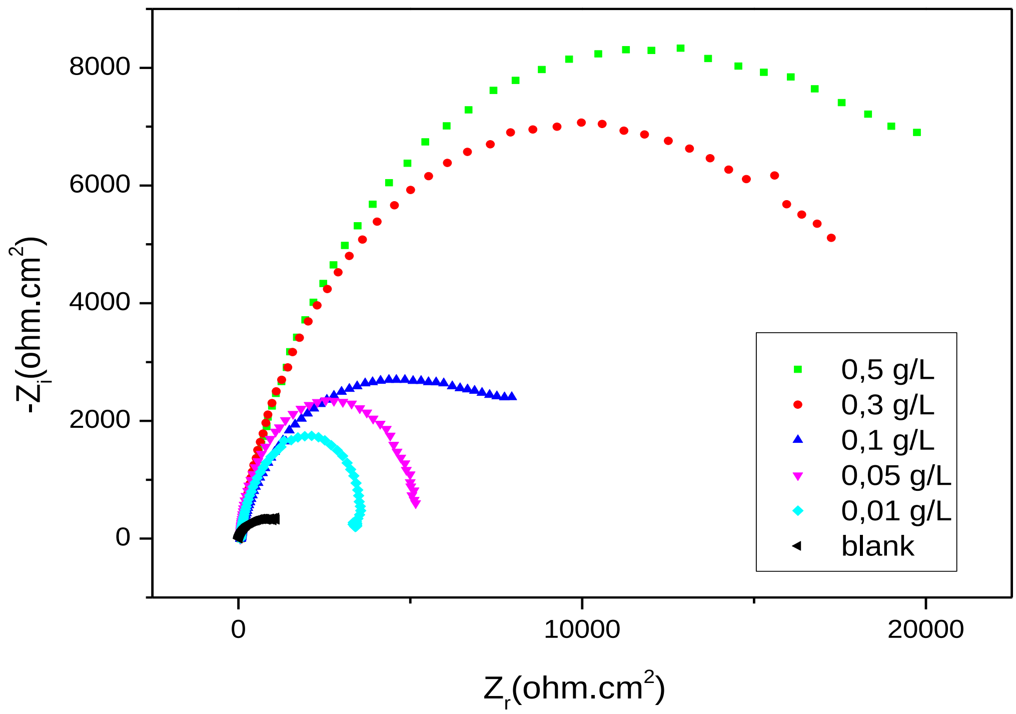

Figure 2 Nyquist plots for the corrosion of tin in 0.1 M Na_2CO_3 containing different concentrations of inhibitor at 298K.

Table 2 Electrochemical impedance values of tin in 0.1 M Na_2CO_3 containing different concentrations of inhibitor at 298K.

C (g/L)	R_s (Ω.cm²)	R_t (kΩ.cm²)	f_{max} (Hz)	C_{dl} (µF/cm²)	E_{Rt}(%)
blank	11	1.20	2.840	46.69	--
0.01	70	3.69	2.800	15.41	67
0.03	58	5.24	2.829	10.74	77
0.10	55	8.25	2.753	7.01	85
0.30	53	15.05	2.837	3.73	92
0.50	56	20.57	2.765	2.80	94

We also note the increase of the value of R_t with the inhibitor concentration leading to an increase in the corrosion inhibition efficiency. A good agreement is observed between potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) results.

Adsorption isotherm

Adsorption isotherms are very important to understand the mechanism of inhibition corrosion reactions. The curve obtained clearly shows that the data fit well with Langmuir adsorption isotherm (Fig.3) was found to be the best description of the adsorption behavior of the studied inhibitor, which obeys

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{inh} \qquad (6)$$

Where C_{inh} is the concentration of nigella sativa oil and k_{ads} is the adsorption equilibrium constant of the adsorption process [31].

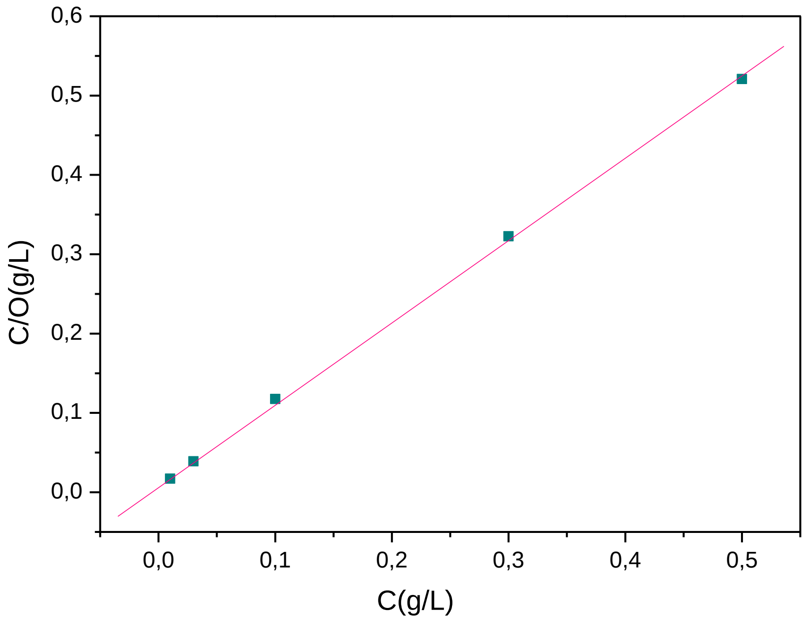

Figure 3 Langmuir adsorption isotherm plot for corrosion of tin in 0.1M Na_2CO_3 containing different concentration of Nigella Sativa Oil at 298K.

Effect of temperature

The corrosion rate of tin with temperature was studied in 0.1M Na_2CO_3 both in the absence and presence of inhibitor at optimum concentration (0.5 g/L) in the temperature range 278– 308 K using potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) measurements.

Polarization curves

The effect of temperature on the inhibition efficiency of nigella sativa oil on the potentiodynamic polarization curves are shown in Fig. 4 and Fig.5. The respective electrochemical parameters derived from the above plots are given in Table 3.

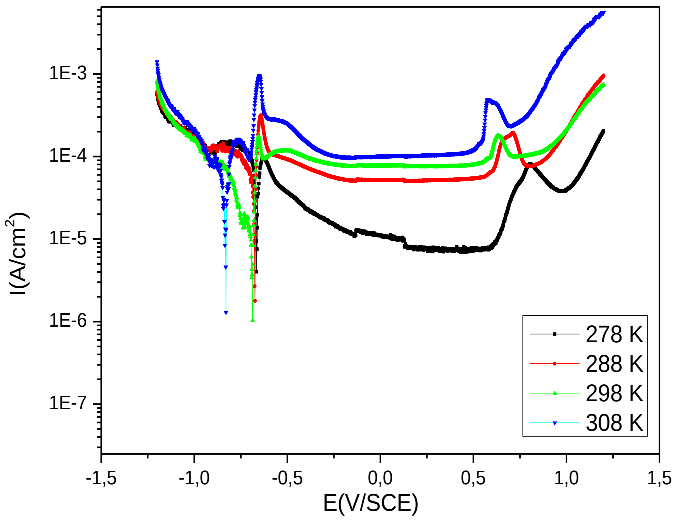

Figure 4 Tafel plots of tin in 0.1 M Na_2CO_3 at different temperatures.

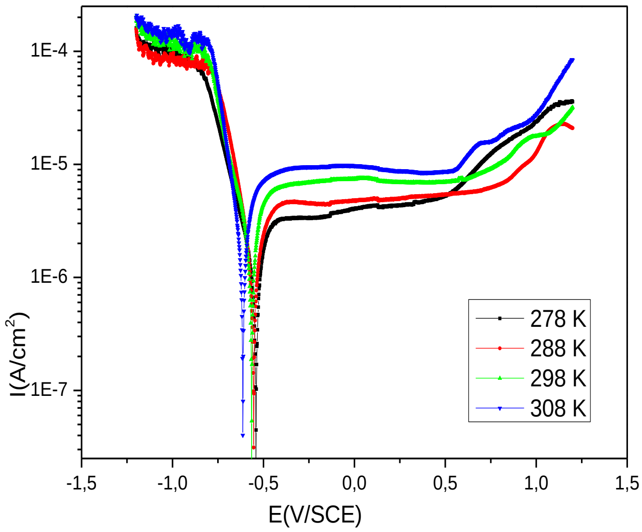

Figure 5 Tafel plots of tin in 0.1 M Na_2CO_3 with NSO (0.5g/L) at different temperatures.

Table 3 Electrochemical parameters of tin in 0.1 M Na_2CO_3 with and without NSO (0.5g/L) at different temperatures.

C(g/L)	T(K)	I_{cor}(µA/cm²)	E_{cor}(mV/SCE)	I_{pass}(µA/cm²)	E_p(%)
blank	278	18	-668	12	--
	288	30	-676	52	--
	298	35	-687	75	--
	308	48	-629	103	--
0.5	278	1.96	-556	51	89
	288	2.56	-543	41	91
	298	1.31	-565	6.84	96
	308	1.61	-610	9.3	97

Fig.4, Fig.5 and 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 nigella sativa oil loss its character inhibitor with rise of high temperature.

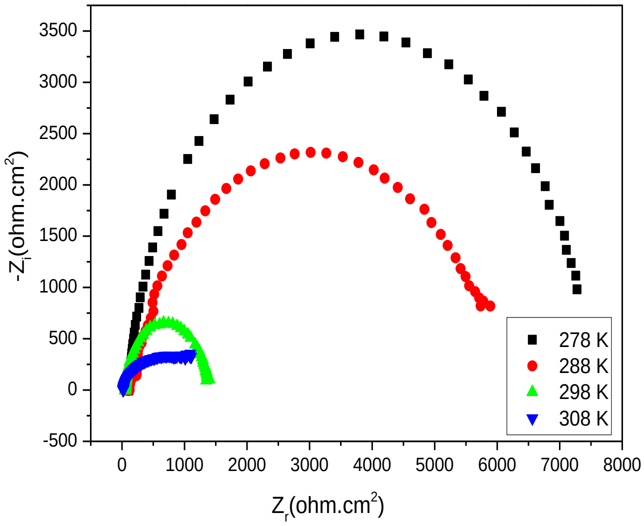

Figure 6 Nyquist plots for tin in 0.1 M Na_2CO_3 at different temperatures

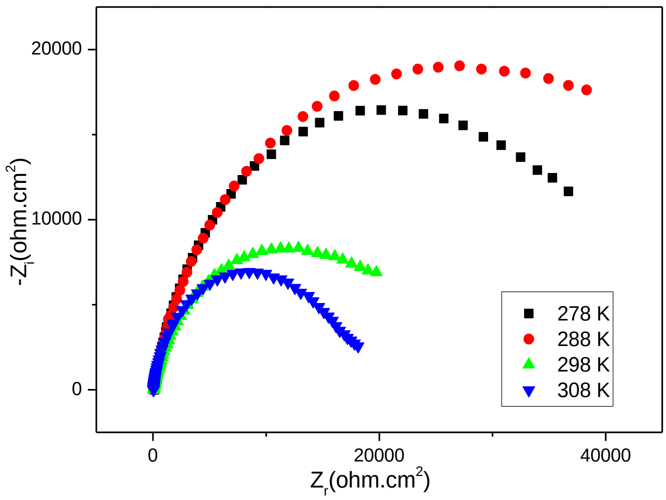

Figure 7 Nyquist plots for tin in 0.1 M $Na_2CO_3$with NSO (0.5g/L) at different temperatures

Table 4 Impedance parameters of tin in 0.1 M Na_2CO_3 with and without nigella sativa oil (0.5g/L) at different temperatures

C(g/L)	T(K)	R_s(Ω.cm²)	R_t(kΩ.cm²)	C_{dl}(µF/cm²)	E_{Rt}(%)
blank	278	111	7.4	15.35	--
	288	119	5.9	21.34	--
	298	56	1.4	16.5	--
	308	11	1.2	46.69	--
0,5	278	114	43	2.6	83
	288	83	46.01	2.77	87
	298	43	16.77	1.32	92
	308	56	20.57	0.17	94

From this result, it can be concluded that the value of corrosion current density increases in both case, in the absence and presence of inhibitor, and the value of inhibition efficiency increases with the increase in the temperature. In the absence of NSO inhibitor, the elevation of corrosion rate when the electrolyte temperatures increase. After addition of the tested inhibitor in corrosive medium, the dissolution of tin is extensively retarded.

Determination of the activation parameters

The activation energy of the corrosion process was calculated using the Arrhenius equation [32-33]:

$$\ln(CR) = -\frac{Ea}{RT} + A \qquad (7)$$

Where C_R is the corrosion rate, A is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. The apparent activation energy was calculated by linear regression between ln (C_R) and 1/T (Fig. 8).

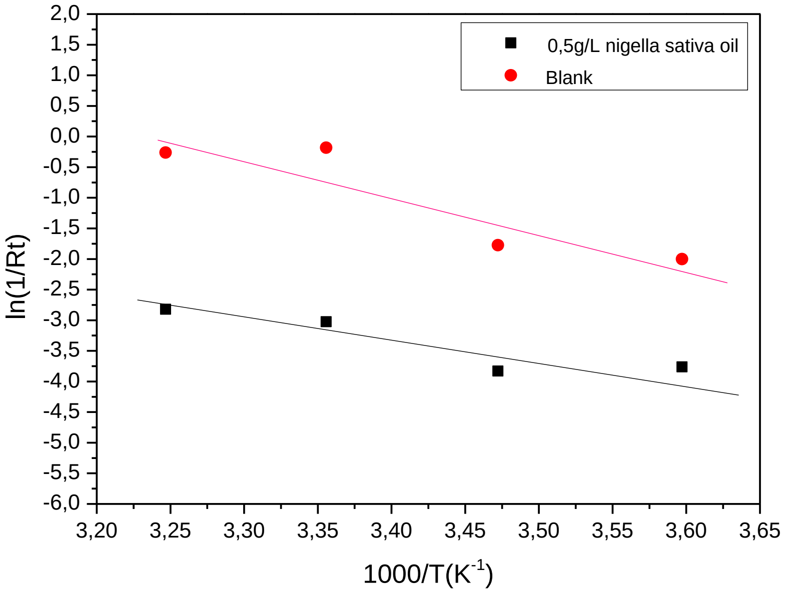

Figure 8 Arrhenius plots of tin in carbonate medium in the absence and presence of nigella sativa oil (0,5g/L).

The value of E_a can be obtained from the slope of the straight line which was found to be 54 kJ $.mol^{-1}$ and 84,43 kJ mol^{-1} in the absence and presence of 0.5g/L nigella sativa oil, respectively. The higher value of E_a in the presence of extract than its absence indicates a strong inhibitive action of the extract by increasing the energy barrier for the corrosion process.

Conclusion

From this study, the following results can be drawn:

Nigella sativa oil was found to inhibit the corrosion of tin in 0.1 M Na_2CO_3 solution and inhibition efficiency increases with increasing oil concentration. At the highest oil concentration of 0.5g/L, the inhibition efficiency is increased markedly and reached 96%.

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 Nigella sativa oil concentration increases.

The adsorption model obeys the Langmuir adsorption isotherms model. Nigella sativa 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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