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Nigella Sativa Oil as Green Corrosion Inhibitor for Aluminum in Na_2CO_3 Solution

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ABSTRACT

Nigella Sativa Oil was investigated as the corrosion inhibitor of aluminum in Na_2CO_3 solution using weight loss measurements, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods. The results revealed that Nigella sativa oil was a good inhibitor, the corrosion inhibition efficiency increases on increasing plant oils concentration. The inhibition efficiencies obtained from different methods were in good agreement. The effect of temperature on the corrosion behavior of aluminum in Na_2CO_3 with and without addition of nigella sativa oil was studied in the temperature range 278–318 K. The adsorption of this oil on the aluminum surface obeys the Langmuir adsorption isotherm.

Keywords: EIS, Polarization Curves, weight loss, corrosion inhibition, aluminum, Nigella Sativa Oil, 0.1 M Na_2CO_3.

INTRODUCTION

Aluminum is a lightweight metal having good electrical and thermal conductivity, recycling and can be combined with good atmospheric corrosion resistance as well as corrosion resistance to many aqueous media [1]. The importance of aluminum alloys, especially in the automotive and aviation industries, has been growing in recent years. The need for aluminum and its alloys products continues to grow year after year and much attention has been paid to the use of aluminum in acid [2-15], alkaline [16-20] and non-aqueous systems [21-24]. It is well known that a compact, strongly adherent and continuous oxide film is developed on aluminum upon exposure to the atmosphere or aqueous solutions. This film is responsible for the corrosion resistance of aluminum in most environments [1,22]. In these solutions, the passive film may be dissolved.

Recently, many works shows that adding the green inhibitor is the most practice and economic solution via adsorption of their molecules on the metal surface forming a protective barrier. Our previous work [14] reported a successful use of Artemisia as corrosion inhibitor for aluminum in high acidic solution. The seeds of Nigella sativa (family: Ranunculaceae), commonly known as Black Seed, Black Cumin, have long been used as a spice, food preservative and in folk medicine in the Arabian region, East Asia, and Europe[25-27],many articles had described the healing powers of the Black Seeds against a variety of diseases [28-36]. Over 150 studies have been conducted over the last five decades to investigate chemical and pharmacological properties of Black Seeds. Phytochemical studies of Black Seed showed the presence of >100 constituents [37].

The essential oil of black cumin seeds, Nigella sativa L., was tested for a possible antioxidant activity. A rapid evaluation for antioxidants, showed that thymoquinone and the components carvacrol, t-anethole and 4-terpineol demonstrated respectable radical scavenging property [38]. For that we propose in present paper to study the effect of its exact oil on both the corrosion and kinetics of corrosion process of aluminum in 0,1 M carbonate sodium solution, it have been investigated using weight loss, potentiostatic polarization measurements and electrochemical impedance spectroscopy. The effect of temperature was also studied.

MATERIALS AND METHODS

Materials: Coupons with surface area of 1.0 cm^2 were used for weight loss and potentiostatic polarization measurements. The electrodes were polished with different grades of emery papers, degreased with acetone and rinsed by distilled water.

Extraction of Nigella sativa exact oil by Soxhelt technique: 150 g seeds were crushed and extracted with hexane for 3 h in a Soxhelt 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 exact oil is as follows [39]:

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

The Soxhelt technique gave 43% of nigella sativa oil.

Weight loss measurements: In the weight loss experiments, 3 aluminum coupons was immersed completely in a 250 ml beaker containing the corroding and inhibitors with the aid of glass rod and hooks. The beakers were placed in a constant thermo stated bath maintained at 278-318 K. The coupons were retrieved for 1 h, then for 2 min to remove the corrosion product, finally, the coupons were washed with distilled water, dried and weighed again in order to obtain the final weight (w_i). The inhibition efficiency of nigella sativa oil acting as inhibitor in 0.1 M Na_2CO_3 was calculated using the following expression [40-42]:

$$\text{Ew }(\%) = \left(1 - \frac{wi}{w0}\right) \times 100 \quad (2)$$

Where W_0 and W_i are the weight loss of the aluminum coupons in the absence and presence of inhibitor respectively in 0.1 M Na_2CO_3 at the same temperature. The inhibition efficiency depends on the degree of coverage of the aluminum alloy surface by molecules of the inhibitor, and can be expressed as in the following equation:

$$\theta = \left(1 - \frac{wi}{w0}\right) \quad (3)$$

Polarization measurements: Electrochemical measurements were carried out in a conventional three electrodes cylindrical glass cell. The working electrode (WE) cut from aluminum alloy had a geometric area of 1 cm^2. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The inhibition efficiency Ep (%) was calculated using the following equation:

$$E_p(\%) = (1 - \frac{I_{cor}}{I°_{cor}}).100 \quad (4)$$

Where I_{cor} and I°_{cor} are the corrosion current densities of aluminum in the presence and absence of inhibitor, respectively.

Electrochemical impedance spectroscopy measurements: Impedance measurements were carried out at the open circuit potential in the frequency range of 100 kHz to 10 mHz peak to peak amplitude using sinusoidal potential perturbation at the open circuit potential. The impedance diagrams were plotted in the Nyquist representation. The charge transfer resistance (R_t) and double layer capacitance values were evaluated. The inhibitor efficiency was calculated using the formula [23]:

$$E_{EIS}(\%) = (1 - \frac{R_t}{R_t^0}).100 \qquad (5)$$

Where R_t and R_t^0 are referred to as the charge transfer resistance of aluminum 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.

$$C_{dl} = \frac{1}{2\,\pi.R_t.f_{max}} \qquad (6)$$

RESULTS AND DISCUSSION

Weight loss measurements and adsorption isotherm : The weight loss results obtained for the corrosion of aluminum specimens for different concentrations of nigella sativa oil in 0.1M Na_2CO_3 solution at 298K are given in table 1. It was observed from the table1 that increase in inhibitor concentration decreased the Weight loss and therefore the corrosion inhibition strengthened. The increase in inhibitor efficiency may result from the fact that adsorption and surface coverage increases with the increase in concentration. As concentration increases more inhibitor molecules are adsorbed on the metal surface, thus resulting larger surface coverage.

Table1. Corrosion parameters for aluminum in 0.1M Na_2CO_3 solution in the presence and absence of nigella sativa oil at 298K for 1 h.

C (g/L)	Weight loss (mg/h)	E_w (%)	Surface coverage (Ɵ)
blank	10.8	--	--
1	4.9	55	0.55
2	2.2	80	0.80
3	1.5	86	0.86
4	1	91	0.91
6	0.5	95	0.95

Several adsorption isotherms were assessed to fit h values, but the best fit was found to obey Langmuir adsorption isotherm, which may be expressed by:

$$\frac{Cinh}{\theta} = nCinh + \frac{n}{Kads} \qquad (7)$$

Where C_{inh} is inhibitor concentration and n is equilibrium constant of adsorption. Fig. 1 represents the plot of (C_{inh}/θ) against Cinh for investigated Nigella sativa oil.

Potentiodynamic polarization studies: The anodic and cathodic polarization curves for the corrosion of aluminum in the absence and presence of different concentrations of nigella sativa oil are shown in figure 2. Electrochemical parameters such as E_{cor}, I_{cor}, anodic and cathodic Tafel slopes (ba, and bc) are given in table 2.

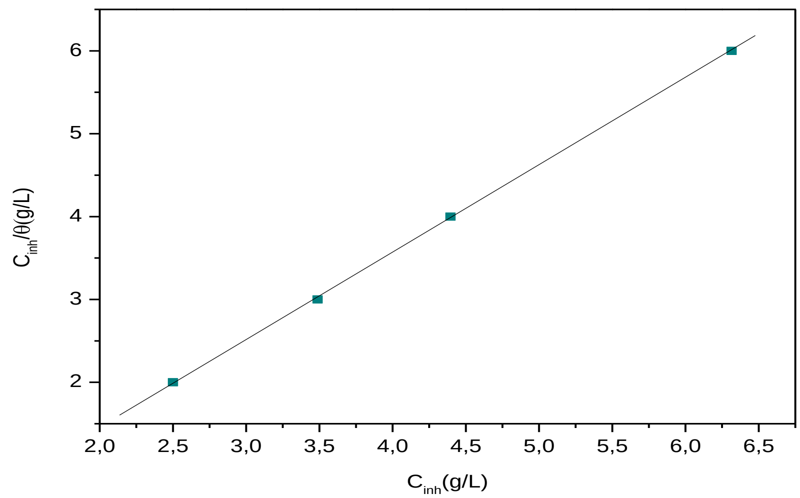

Figure 1. Langmuir adsorption isotherm plot for corrosion of aluminum in 0.1M Na_2CO_3 containing different oncentration of nigella sativa oil at 298K.

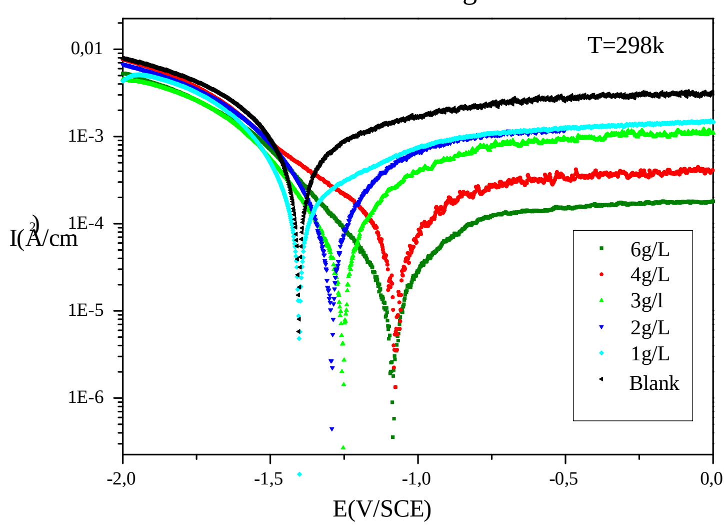

Figure 2: Polarization curves for aluminum in 0.1M Na_2CO_3 solution in the presence and absence of nigella sativa oil at 298K.

Table 2: Tafel polarization parameters for the corrosion of aluminum in 0.1M Na_2CO_3 solution in the presence and absence of nigella sativa oil at 298K.

C(g/L)	I_{cor}(µA/cm²)	E_{cor} (mV/SCE)	b_a (mV/dec)	b_c (mV/dec)	R_p (Ω.cm^2)	E_p (%)
0	92	-1405	81	-68	128.53	--
1	54	-1404	95	-83	281	41
2	20	-1240	70,5	-74,6	615	78
3	10	-1256	60	-56	900	89
4	8,3	-1081	68	-46	1860	91
6	3,3	-1081	60	-54	2940	96

In the presence of different concentrations of inhibitor the corrosion current density was lowered and E_{cor} values were shifted to more positive side in the presence of inhibitor solutions confirming the inhibitive nature of nigella sativa oil.

Electrochemical impedance spectroscopy (EIS) measurements: Nyquist plots of aluminum in 0.1M Na_2CO_3 solution in the absence and presence of different concentrations of NSO are given in Fig. 3. Where it can be concluded that the Nyquist diagrams is recorded at the corrosion potential and represents a slight semicircle at high frequencies followed at the lower frequencies, by a straight line superimposed at 45° to both axes, which is corresponding to diffusion process (Warburg diffusion) [43,44].

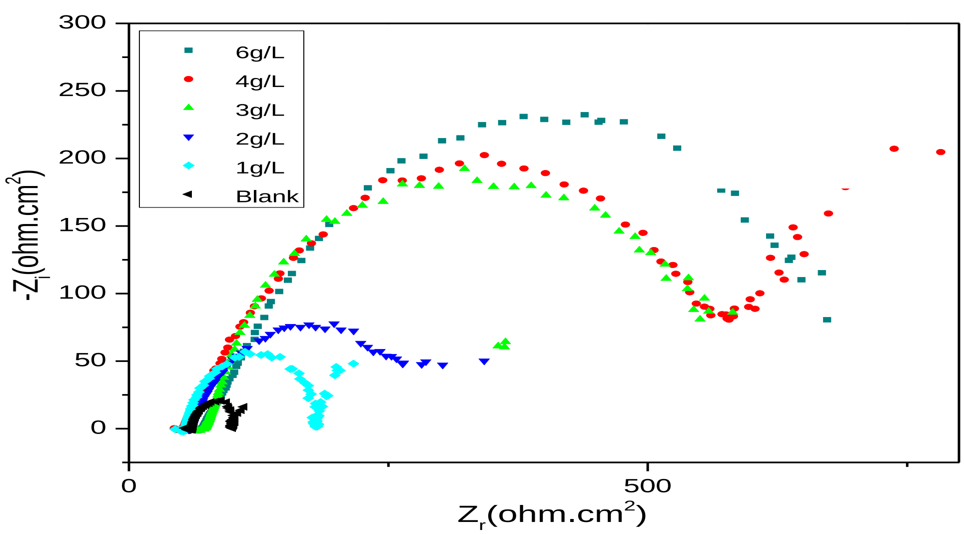

Figure 3. Nyquist plots for the corrosion of aluminum in 0.1 M Na_2CO_3 containing different concentrations of inhibitor 298K.

Table 3: Electrochemical impedance values of aluminum in 0.1 M Na_2CO_3 containing different concentrations of inhibitor 298K.

C (g/L)	R_s (Ω.cm²)	R_t (Ω.cm²)	f_{max} (Hz)	C_{dl} (µF/cm²)	E_{Rt} (%)
Blank	62	50	223	14.30	--
1	55	133	178	6.73	55
2	60	212	223	3.37	76
3	75	475	125	2.68	89
4	52	554	158	1.82	91
6	74	775	178	1.15	94

Table 3 shows the EIS data where the C_{dl} values decrease and the R_t values increase with the increase of the NSO concentrations. This increase is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the electrode surface, and decreasing the extent of dissolution reaction. The decrease in the C_{dl} can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [45] suggested that the inhibitor molecules function by adsorption at the electrode/solution interface.

Effect of temperature: The corrosion rate of aluminum with temperature was studied in 0.1 M Na_2CO_3 in the absence and presence of inhibitor at concentration (4 g L^{-1}) in the temperature range 318–278K using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy method.

Weight loss measurements: The effect of increasing temperature on the corrosion rate values is given in Table 4. The results revealed that on increasing temperature there is an increase for inhibition efficiency of corrosion until 298K, after that a slow shift in inhibition efficiency is marked.

Table 4. Inhibition efficiency for aluminum in 0.1M Na_2CO_3 solution at different temperatures.

C	E_w (%)				
(g/L)	278K	288K	298K	308K	318K
4	70	77	95	74	68

Polarization curves: The effect of temperature on polarization curves of aluminum in 0.1 Na_2CO_3 in the absence and presence of inhibitor at concentration (4 g L^{-1}) in the temperature range 318–278K are shown in Fig. 4 and Fig. 5 and summarized in table 5.

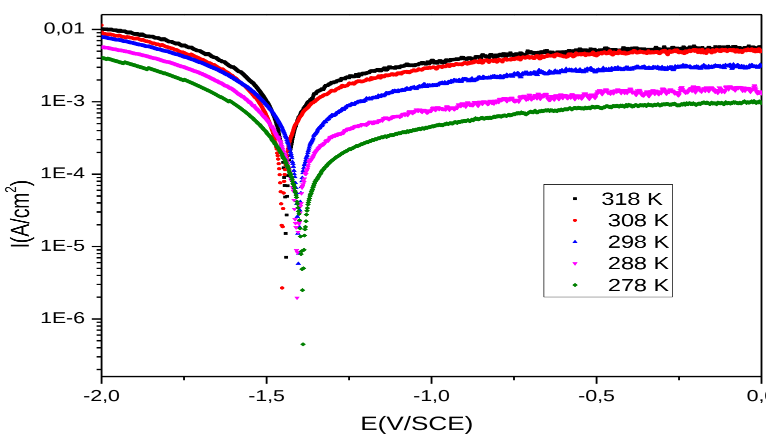

Figure 4. Tafel plots of aluminum in 0.1 M Na_2CO_3 at different temperatures.

From fig 4, fig 5 and table 5, generally the corrosion rate is more increased with the rise of temperature for uninhibited carbonate medium. The presence of inhibitor leads to a decrease in the corrosion rate. For the temperature less than 298 K, we note increase in inhibition efficiencies. However, for temperature more than 298K, we can guess that NSO loss its character inhibitor with rise of temperature. For that, the inhibition efficiency decreases while the temperature increase.

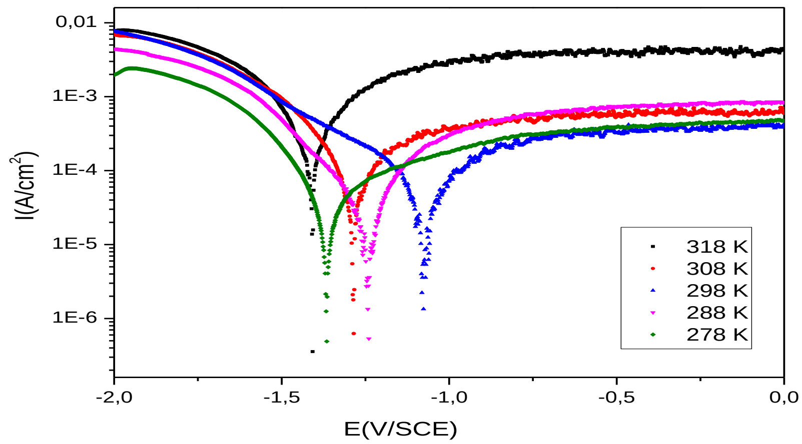

Figure 5. Tafel plots of aluminum in 0.1 M Na_2CO_3 with nigella sativa oil (4g/L) at different temperatures.

Table 5 : Electrochemical parameters of aluminum in 0.1 M Na_2CO_3 with and without nigella sativa oil (4g/L) at different temperatures.

T (K)	C (g/L)	Ic_{orr} (µA/cm²)	E_{corr} (mV/SCE)	b_a (mV/dec)	b_c (mV/dec)	R_p ($\Omega.cm^2$)	E_p (%)
278	blank	24	-1392	75.7	-57	441	--
288		66	-1410	110	-83	231	--
298		92	-1405	81	-68	128.53	--
308		148	-1456	77	-69	128.53	--
318		261	-1444	106	-95	61	--
278	4	9	-1370	79	-58	1100	63
288		7	-1244	65	-72	1410	89
298		8	-1081	54.7	-46	1860	91
308		32	-1290	126.7	-97	458	78
318		103	-1412	83.8	-104	124.6	61

Electrochemical impedance spectroscopy (EIS): Fig. 6 and fig. 7 shows EIS measurements obtained in 0.1 M Na_2CO_3 in the absence and presence of (4g L^{-1}) of NSO in the temperature range 278-318 K.

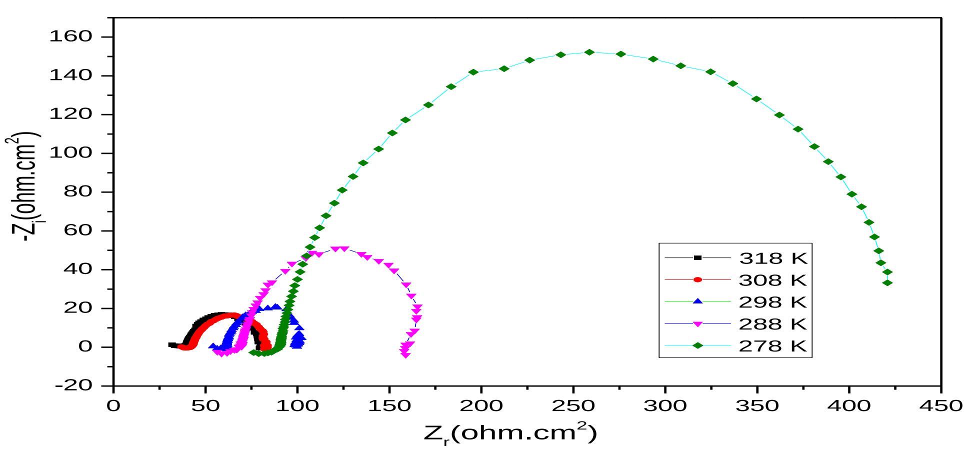

Figure 6. Nyquist plots for aluminum in 0.1 M Na_2CO_3 at different temperatures.

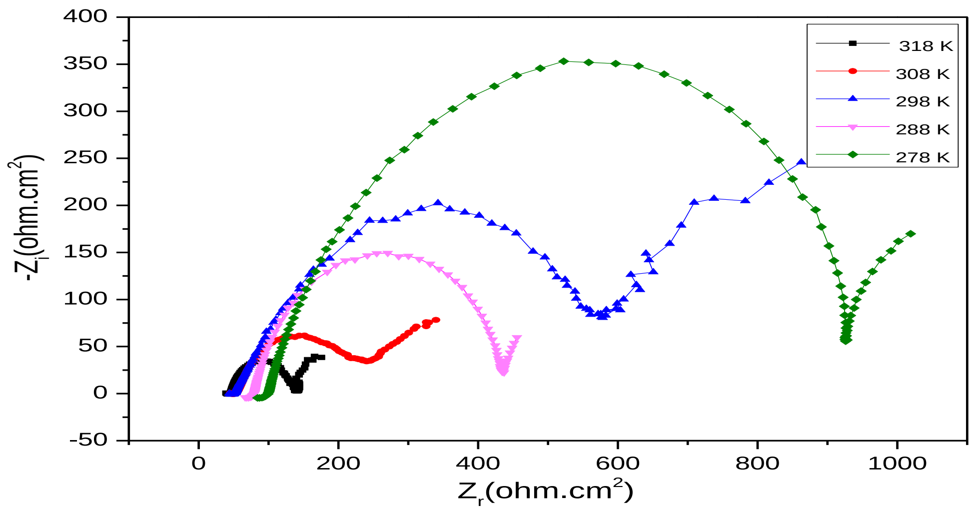

Figure 7. Nyquist plots for aluminum in 0.1 M Na_2CO_3 with nigella sativa oil (4g L^{-1}) at different temperatures.

Table 6: Impedance parameters of aluminum in 0.1 M Na_2CO_3 with and without nigella sativa oil (4g L^{-1}) at different temperatures

T (K)	C (g/L)	Rs (Ω.cm²)	R_t (Ω.cm²)	f_{max} (Hz)	C_{dl} (μF/cm²)	E_{Rt} (%)
278	blank	91.39	338	31.64	14.9	--
288		70.36	103	12.4	125	--
298		61.66	50	223.21	14.3	--
308		42.92	42	8.51	445	--
318		36.66	40	9.9	400	--
278	4	101	943	28	6.03	64
288		80.67	400	158	2.52	74
298		52	554	158	1.82	91
308		55.25	180	8.92	99	77
318		45.61	102	10	156	61

Generally, the Nyquist plots of aluminum in 0.1M Na_2CO_3 solution at 4g/L of NSO for various temperature have the same shape, a slight semicircle at high frequencies followed at the lower frequencies, by a straight line superimposed at 45° to both axes, which is corresponding to diffusion process [46, 47]. It is clear from fig. 6, fig.7 and table 6, that R_s has high values at less temperature. Its value decreases with the rise of temperature as a result of increasing the solution conductivity [48]. The value of charge transfer resistance R_t attaint au maximum at 298 K. After this temperature, the R_t decrease with increase of temperature . There is a good agreement between results of weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy method.

Determination of the activation parameters: The logarithm of the corrosion rate (in mg cm^{-2} min^{-1}) is a linear function with 1/T following Arrhenius equation type [49, 50] :

$$\ln(CR) = -\frac{Ea}{RT} + A \quad (9)$$

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).

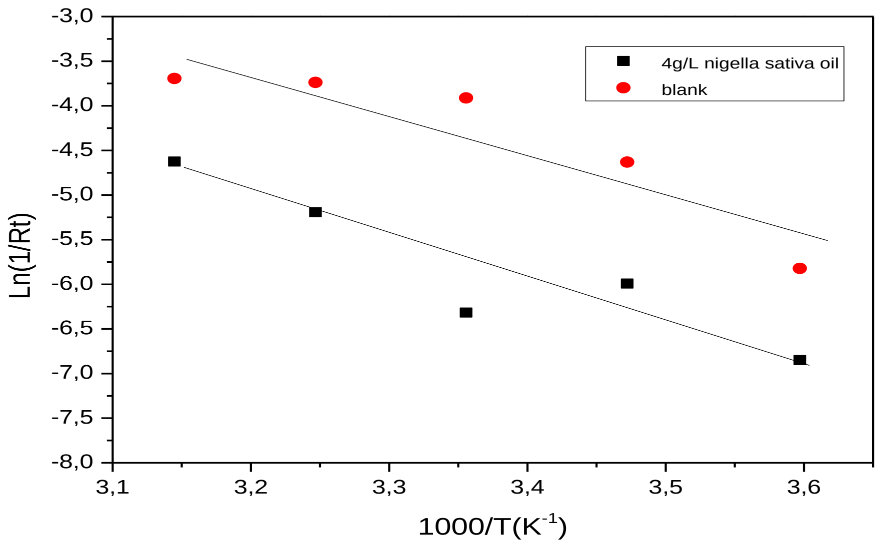

Figure 8. Arrhenius plots of aluminum in carbonate medium in the absence and presence of nigella sativa oil (4g L^{-1}).

Inspection of the slope of the straight line shows that the presence of the NSO increases the value of activation energy for aluminum compared to the blank (0.1M Na_2CO_3) from 38 to 41kJ mol^{-1} indicating the adsorption of NSO on the surface of the metal.

APPLICATIONS

These results revealed that Nigella sativa oil is useful as a good inhibitor, the corrosion inhibition efficiency increases on increasing plant oils concentration.

CONCLUSIONS

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

- Nigella Sativa Oil acts as a good inhibitor for corrosion of aluminum in 0.1 M Na_2CO_3 solution.
- The inhibition efficiency increases with increase in the concentration of nigella sativa oil and with increase in temperature up to 298K (91% for 4g L^{-1} at 298K).
- The inhibition is due to the presence of some the constituents in nigella sativa oil, which is adsorbed on the surface metal.
- The values of E_a suggest that the inhibitors were strongly adsorbed on the aluminum metal surface.
- The adsorption behavior of the Nigella Sativa oil is consistent with Langmuir adsorption model.

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