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Plants extract as green corrosion inhibitors: The case of eugenol from *Clove*

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ABSTRACT

Corrosion inhibition of aluminium in carbonate sodium solution was investigated by weight loss and electrochemical techniques using eugenol oil as inhibitor. The inhibition efficiency increase when the eugenol concentration enhance. The obtained data revel that the tested oil acts as an excellent inhibitor for the corrosion of aluminium in Na_2CO_3 solution. The value of some thermodynamic, kinetic parameters was calculated from the experimental data. The adsorption of eugenol on the metal surface followed the Langmuir adsorption isotherm.

Keyword: Corrosion, Inhibition, Aluminium, Eugenol, Activation parameters.

INTRODUCTION

Aluminium and its alloys are widely used in automobile and aerospace industries, these applications are linked to many prominent electrical properties. In aggressive medium these materials are affected by the corrosion phenomenon many techniques are used for protected their structure respecting the environment. Among these methods many research in corrosion field are oriented to the development of green corrosion inhibitor. Plant extracts are an extremely wealthy source of natural organic compounds that can be extracted with low cost and environment friendly. These factors have encouraging many researchers to use natural compounds as inhibitors for corrosion of metal and alloy [1-4]. Many natural compounds plant (seeds, fruits, leaves, and flowers) have been employed as efficient corrosion inhibitors of different metals and/ or alloy in corrosive solution, oil form [5-7] and extracts [8-10].

Eugenol is a member of the allyl benzene class of chemical compounds. it is usually soluble in organic solvents. Clove-like is used in cuisine as a spice, in perfumeries as a aroma and essential oil of eugenol in medicine as a local antiseptic and anaesthetic [11-15]. Eugenol iol acts as a good inhibitor of corrosion for tin in bicarbonate solution [16]. Eugenol molecule containing functional groups with oxygen and doubles bonding responsible to their adsorption on aluminium surface

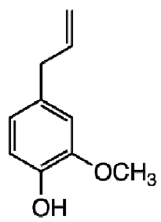


Figure 1: the structure of Eugenol

The present study report on the corrosion inhibition and adsorption behaviour of the eugenol on aluminum in 0.1M Na_2CO_3 solution at the temperature range of 278 to 308K by gravimetric measurement, electrochemical impedance spectroscopy methods and completed by SEM (Scanning electron microscopy).

MATERIALS AND METHODS

Aluminum specimens with electrode area of 1.0 cm^2 were used for weight loss and potentiostatic polarization measurements. The electrodes was polished successively with emery papers of different grades, degreased with acetone and rinsed by distilled water.

2.1. Gravimetric measurements

Weight loss measurements expressed in $mg/h/cm^2$ of the electrode area for aluminum was estimated without and with tested compounds with various concentrations. Experiments conditions of weight loss are described previously [17]. The inhibition efficiency E_w(%) from the corrosion rate of aluminum in the absence and in the presence inhibitor was calculated according to equation:

$$E_w\% = (1 - \frac{w}{w_0}).100 \qquad \text{Eq (1)}$$

2.2. Electrochemical tests

2.2.1. Polarization curves

The potentiodynamic polarization curves were recorded using Voltalab PGZ 301 and a three electrode cell system. Before each recording the curves the working electrode was initially kept at the free potential during 30 mn at a scan rate of 1 mV/s. The inhibition efficiency Ep (%) was evaluated using the following equation:

$$E_p(\%) = (1 - \frac{I_{cor}}{I^\circ_{cor}}).100 \qquad \text{Eq (2)}$$

Where $I_{cor}^0$and I_{cor} are the corrosion current density values without and with inhibitor, respectively. The value of corrosion current density is estimed by extrapolation of cathodic Tafel lines to the corrosion potential. The value of surface coverage (θ) was calculated according to equation:

$$\theta = \frac{I^\circ_{cor} - I_{cor}}{I^\circ_{cor}} \qquad \text{Eq (3)}$$

2.2.2. Electrochemical impedance spectroscopy tests

The experiments related to electrochemical impedance spectroscopy were carried out with a same equipment was used as for the potentiodynamic polarization measurements. The EIS measurement was carried out in the 100 kHz - 10 mHz frequency range at corrosion potential. The impedance diagrams were given in the Nyquist plan. The inhibition efficiency in this case was determined using the following equation:

$$E_{Rt}(\%) = (1 - \frac{R_t}{R_t'}).100 \qquad \text{Eq (4)}$$

Where $R_{t'}$ and R_t are the charge transfer resistance values in the presence and absence of inhibitor, respectively. The values of double layer capacitance Cdl were obtained at frequency (fmax) which corresponding to the maximum value of imaginary component on the Nyquist plot and can be calculated by:

$$C_{dl} = \frac{1}{2\pi . R_t . f_{max}} \qquad \text{Eq (5)}$$

2.3. Characterization of surface morphology

The surface morphology of the aluminum specimen after immersion in 0,1 M Na_2CO_3 solution containing of eugenol inhibitor at 4g/L was compared by recording the scanning electron microscopy images of the samples in the absence of inhibitor. The immersion times of the electrode for the SEM analysis were 20 days.

RESULTS AND DISCUSSION

3.1. Gravimetric measurements

Table 1 represents the corrosion rate of aluminum alloy in carbonate medium and the inhibition efficiency percentages of eugenol at different concentrations.

Table 1. The corrosion rate (w) and of aluminum alloy and inhibition efficiency of eugenol

C (g/L)	w ($mg.cm^{-2}.h^{-1}$)	E_w(%)
blank	4.73 $x10^{-4}$	--
0.5	3.64 $x10^{-4}$	30
1.0	2.41$x10^{-4}$	49
2.0	2.08 $x10^{-4}$	52
3.0	1.60 $x10^{-4}$	66
4.0	1.32 $x10^{-4}$	72

It is clear that the weight loss diminish with increasing of inhibitor concentration. The value of inhibition efficiency rises when the concentration of eugenol increases.

3.2. Polarisation curves

The anodic and cathodic polarisation curves for aluminum in corrosive medium with and without eugenol oil were showed in Fig. 2. The corresponding electrochemical parameters are down in Table 2. Inspection this result, it's clear that the dissolution rate decreases with increasing of eugenol concentration.

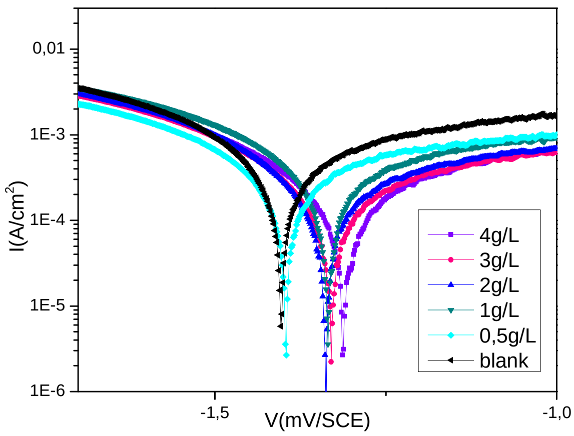


Figure 2: Polarization curves for aluminum in 0.1M Na_2CO_3 solution in the presence and absence of eugenol oil at 298K

Table 2. Corrosion parameters for aluminum in 0.1M Na_2CO_3 solution in the presence and absence of eugenol at 298K

C (g/L)	I_{cor} (µA/cm²)	E_{cor} (mV/SCE)	ba (mV/dec)	bc (mV/dec)	E_p (%)
blank	108	-1405	94	-79	--
0,5	72	-1424	76	-56	33
1.0	47	-1357	100	-83	56
2.0	35	-1368	71	-61	67
3.0	26	-1378	47	-40	75
4.0	20	-1364	27	-47	81

From the Fig. 2 and Table 2, it is clear that the inhibition efficiency Ep(%) increases with increasing of eugenol oil concentration and reaches a maximum value at concentration equal to 4g/L. This proposed considers that increase in the inhibitor concentration leads to increases the number of molecules adsorbed over the aluminum surface, this adsorption blocking the active sites of solution and consequently protection of alloy surface from corrosion.

3.3 – EIS measurements

The Nyquist diagram of aluminum in carbonate medium in the absence and presence for different concentrations of eugenol are exposed in Fig. 3. The impedance parameters obtained from this investigation are presented in Table 3.

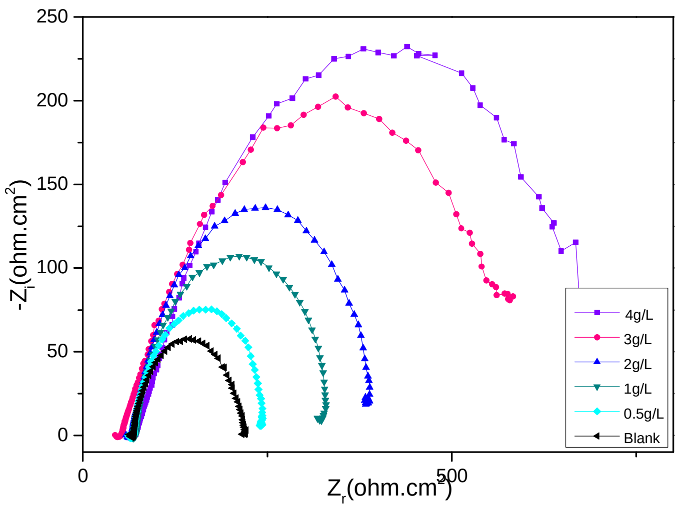


Figure 3. Nyquist plots of aluminum in 0.1 M Na_2CO_3 of eugenol at different concentrations

Table 3: Tafel polarization parameters for aluminum in 0.1 M Na_2CO_3 of eugenol at different concentrations

C (g/L)	R_s (ohm.cm²)	R_t (kohm.cm²)	F_{max} (Hz)	C_{dl} (µF/cm²)	E_{Rt} (%)
blank	69	147	79	14	--
0.5	69	179	28	11	18
1.0	71	269	25	7,5	45
2.0	67	337	31	6	56
3.0	57	554	20	4	73
4.0	74	775	12,5	2	81

As can seen that the value of charge transfer resistance R_t increases with increasing of eugenol concentration, but the values of C_{dl} decreases. These variations can be explained by adsorption of inhibition, at the metal/solution interface testifying the formation of protective layer on aluminum surface.

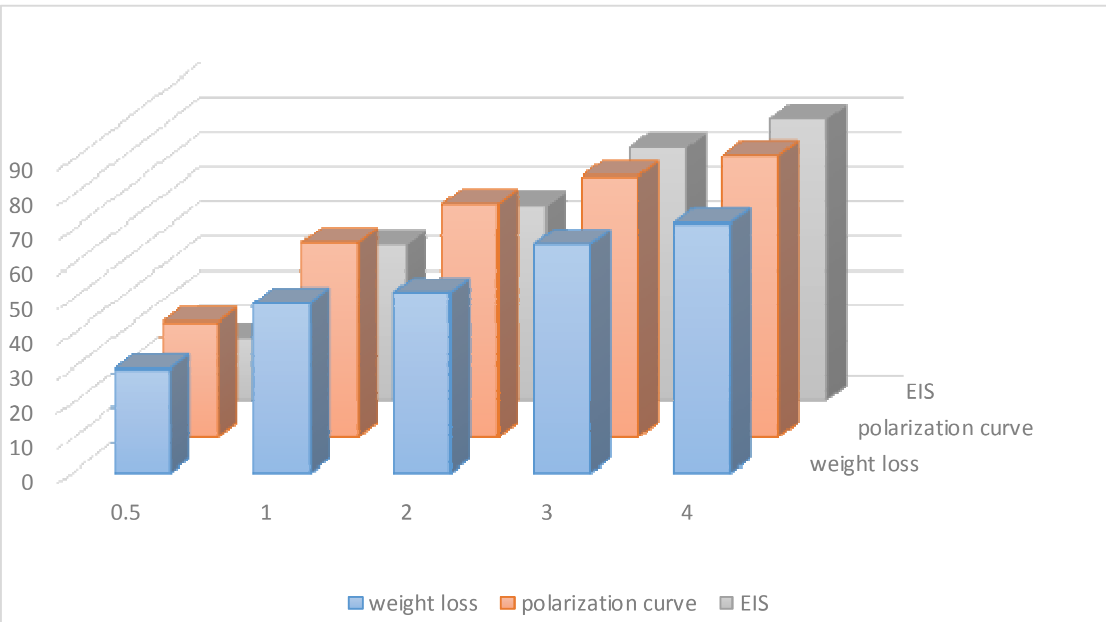


Figure 4: Inhibition efficiency E (%) values obtained by different methods

The comparative study of inhibitory efficiencies obtained by different techniques is represented in Fig.4. It's clear that the obtained results are in good agreement.

We can be concluded that the oil eugenol is a good inhibitor for corrosion of aluminum in the carbonate medium.

3.4-Adsorption Isotherms

The surface coverage values for the eugenol at different concentrations (Table 2), from potentiodynamic polarization curve, were fitted into Langmuir adsorption isotherm model according to the following equation [18]:

$$\frac{C_{\mathrm{inh}}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \qquad \text{Eq (6)}$$

Where C_{inh} is the concentration of eugenol and k_{ads} is the adsorption equilibrium constant of the adsorption process.

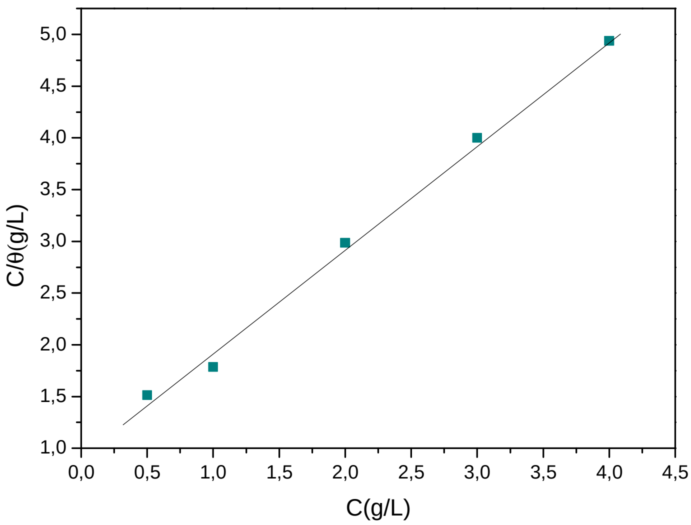


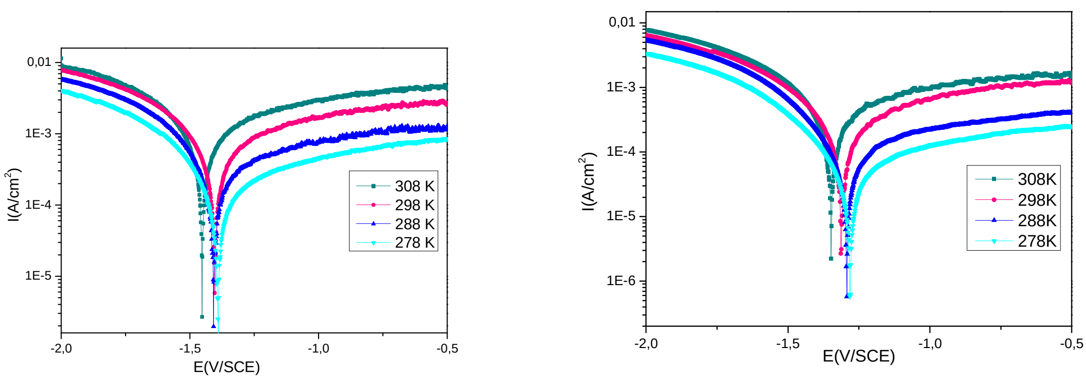
Figure 5: Langmuir isotherm of eugenol on aluminum in 0.1M Na_2CO_3 at 298K

The linear relationship between C_{inh}/ θ vs. C_{inh} so obtained confirmed the suggesting the adsorption of inhibitor molecules follow the Langmuir adsorption model onto the aluminum surface (Fig. 5).

3.5- Temperature effect on the aluminum corrosion

Weight loss tests

The influence of temperature on the behavior of aluminum corrosion is given in Table 4. The results revealed that the increasing temperature leads to the increase for inhibition efficiency of corrosion until 298K, after this temperature a slow shift in inhibition efficiency is marked.



(a) ***(b)***

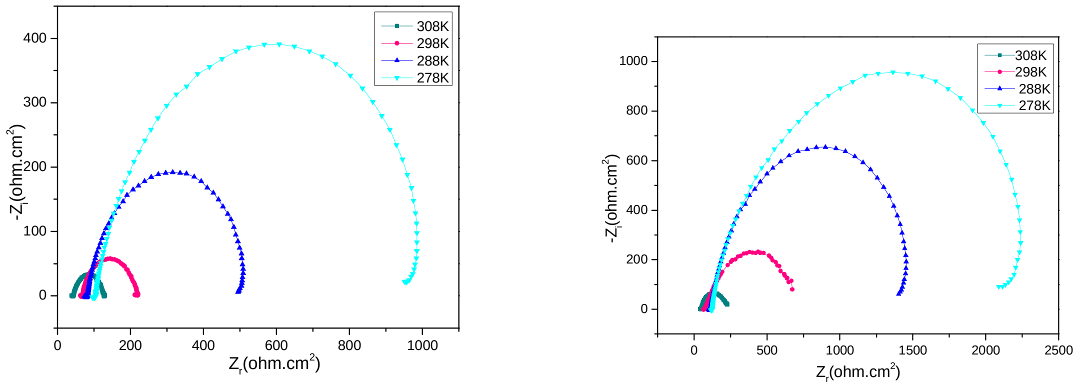
Figure 6: Effect of temperature on polarization curve of aluminum in 0.1 M Na_2CO_3 without (a) and with eugenol (b) at (4g/L)

Polarization curves

The effect of temperature on corrosion behaviour was also studied by potentiodyanmic polarization curves in corrosive medium with and without of inhibitor at concentration equal to 4 g L^{-1} in the temperature range 278-308K (Fig. 6 (a) and (b)). Polarization parameters and the corresponding inhibition efficiency are summarized in Table 4.

Electrochemical impedance spectroscopy (EIS)

Fig. 7 shows EIS measurements obtained for uninhibited and for inhibited solution by eugenol molecule at 4g. L^{-1} in the temperature range 278-308 K.



(a) (b)

Figure 7. Effect of temperature on Nyquist plots for aluminium in 0.1 M Na_2CO_3 (a) and 0.1 M Na_2CO_3 + 4g/L of eugenol (b)

Table 4. The effect of temperature on electrochemical parameters for aluminium in 0,1 M Na_2CO_3 in absence and presence of inhibitor at 4g/L by different methods

		Polarization curves			EIS				Weight loss
T (K)	C (g/L)	I_{cor} (µA/cm²)	E_{cor} (mV/SCE)	Ep (%)	R_s (Ω.cm²)	R_t (kΩ.cm²)	C_{dl} (µF/cm²)	E_{Rt} (%)	E_w (%)
308	0	161	-1454	--	43,78	0,83	12	--	--
	4	74	-1349	54	46	1,90	5	56	60
298	0	108	-1405	--	69,3	0,147	14	--	--
	4	20	-1364	80	74	0,775	2	81	82
288	0	60	-1408	--	83,56	0,438	14,5	--	--
	4	14	-1308	77	100	1,7	5	74	79
278	0	26	-1392	--	106	0,94	27	--	--
	4	10	-1283	62	135	2,5	11	62	66

From Figs. 6 and 7 and Table 4, the dissolution rate is more increased with the rise of temperature in the case of uninhibited medium. The adding of inhibitor in corrosive solution leads to a decrease in the dissolution of aluminum. For the temperature less than 298 K, we note the increase in inhibition efficiencies. However, for temperature more than 298 K, we can guess that eugenol lose its inhibitor character with rise of temperature. For that, the inhibition efficiency is reduced when the temperature increases.

The calculate of activation energy, Ea, of the corrosion process can be treated using Arrhenius plot (Fig. 8) and by the following Arrhenius equation type [19-20]:

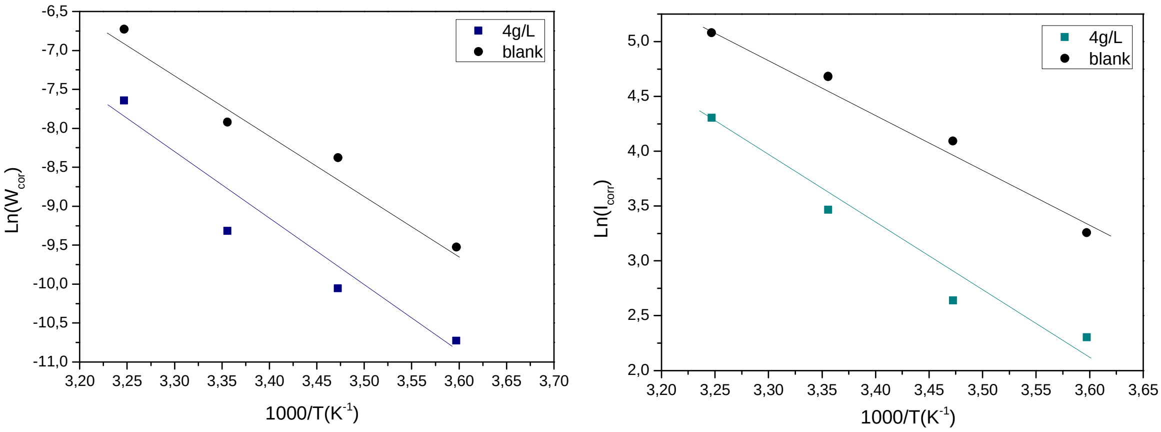
$$I_{cor} = \text{A} \exp\left(-\frac{E_a}{\text{RT}}\right) \qquad \text{Eq (8)}$$

Where A is the Arrhenius pre-exponential factor, R is the universal gas constant, and T is the absolute temperature.

The values of Ea determined in medium containing eugenol (48,3 $kJ.mol^{-1}$) is higher than that obtained for uninhibited solution (38,3 $kJ.mol^{-1}$). The increase in the activation energy Ea with the additive inhibitor may be considered to be due to the physical adsorption of the inhibitor molecules on aluminum surface [21], other researchers have attributed this receding due to decreased in the adsorption of eugenol molecules on metal surface with increase in temperature [22-23].

The entropy (ΔS*) and enthalpy of activation (ΔH*) for the investigated system were evaluated from the transition state equation:

$$I_{cor} = \frac{RT}{hN_A}.\exp\left(\frac{\Delta S^*}{R}\right).\exp\left(-\frac{\Delta H^*}{RT}\right) \qquad \text{Eq (9)}$$



(a) (b)

Figure 8. Arrhenius plots of aluminum in 0,1M Na_2CO_3 (a) and in 0,1 M Na_2CO_3 +4 g/L of eugenol(b)

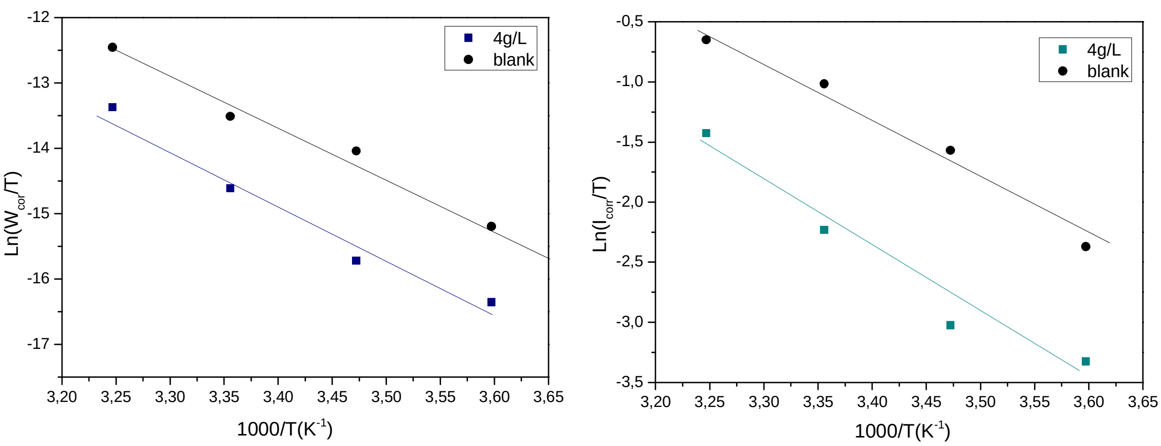


Figure 9. Arrhenius plots of log (I /T) for aluminum in 0, 1 MNa_2CO_3 in the absence and the presence of eugenol

Where N_A is the Avogadro's number, h the Plank's constant, A plot of ln (I_{cor}/T) against 1/T shown in Fig.9 offer straight line. The slope is (-ΔH*/R) and the intercept is (ln R/N_Ah + ΔS*/R) from which the values of ΔH*and ΔS* are evaluated (Table 5).

Table 5. The values of activation parameters for aluminum in 0,1 MNa_2CO_3 in the absence and the presence of eugenol

C(g/L)	Polarisation curve			Weight loss		
	E_a (kJ/mol/K)	ΔH^* (kJ/mol/K)	ΔS^* (J/mol/K)	Ea (kJ/mol/K)	ΔH* (kJ/mol/K)	ΔS* (J/mol/K)
0	38	41	-69	43	45	-72
4	48	46	-61	51	49	-69

Examination of these data showed that the value of activation parameters for corrosion reaction of aluminum in inhibited solution by eugenol is higher than that in absence of inhibitor. The activation entropy decreases more negatively in inhibited medium than in the uninbited solution, which reflects the formation of an ordered stable layer of the inhibitor on the aluminum surface. The activation parameters estimated by the different techniques are in good agreement.

3.6- Surface analysis by SEM

The SEM images of corroded surface of aluminum after 20 days of immersion are given in Fig. 11, which shows degradation of aluminum, with uniform attack in carbonate sodium solution.

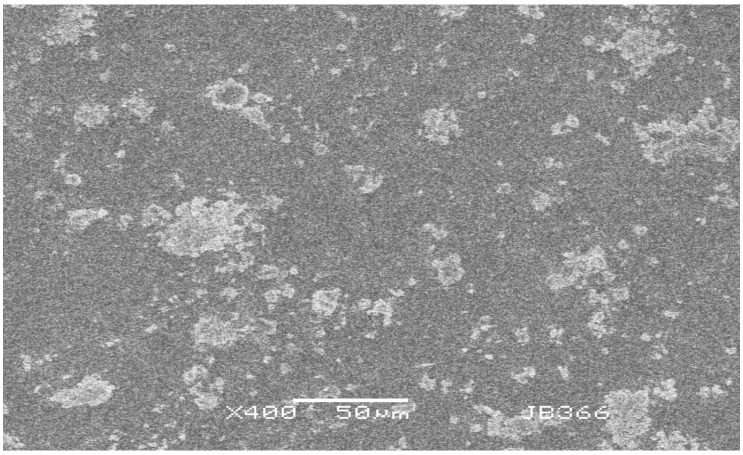


Figure 11. MEB images of the surface of aluminum 3003 after immersion 20 days in 0,1 M Na_2CO_3 in the absence of eugenol

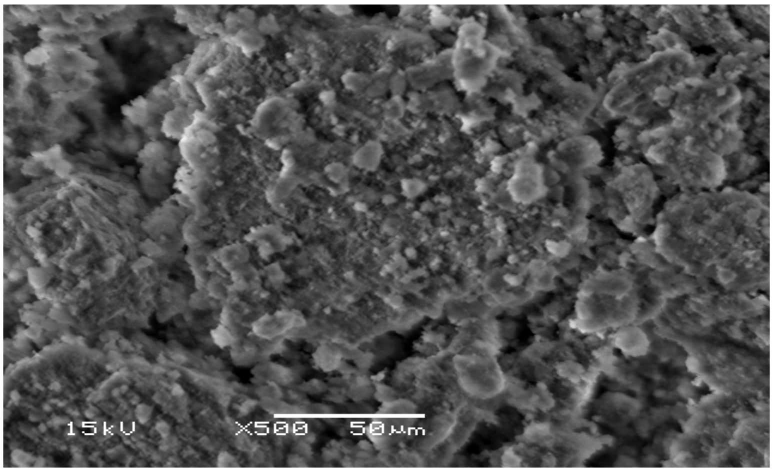


Figure 12. MEB images of the surface of aluminum 3003 after immersion 20 days in 0,1 M Na_2CO_3 in the presence of eugenol

Fig. 12 represents the aluminum surface after treating with eugenol concentration 4g/L. It indicates the reduction in the corrosion by eugenol due to an adsorption film formed on aluminum surface forming a protective inhibitor layer on the electrode surface. This result justifies the observed high inhibition efficiency of the inhibitor at this concentration.

CONCLUSION

From the experimental results of study the effect of eugenol oil on the aluminum corrosion in carbonate medium the conclusions can be deducted:

- Eugenol is a good inhibitor for aluminum corrosion in 0.1 M Na_2CO_3 media.
- E% increased with rise in the concentration of eugenol and with increase in temperature up to 298K.
- The values of Ea propose that the inhibitor molecules were effectively adsorbed on the aluminum metal surface.
- The adsorption model obeys the Langmuir adsorption isotherms model. Eugenol inhibits the corrosion of aluminum in carbonate media.
- Inhibitor efficiency values determined by weight loss, electrochemical polarization and electrochemical impedance spectroscopy are in reasonable agreement.

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