

Inhibition Performance of Eugenol and Linalool on Aluminium Corrosion: A Comparative Study

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Received: 25 September 2019 / Accepted: 7 November 2019 / Published: 30 November 2019

It is well known that corrosion inhibition performance of organic compounds in acidic media depend on their concentration and molecular structures. Therefore, the comparative study of inhibition efficiency of eugenol as aromatic and linalool as linear molecules on aluminium corrosion in 0.5 M HCl solution was performed. The study was done by weight loss, potentiodynamic polarization and EIS methods, while surface morphology of aluminium was examined by SEM method. All used methods confirmed inhibition efficiency of both investigated compounds on aluminium corrosion in acidic medium. From the obtained potentiodynamic polarization curves is evident that presence of eugenol and linalool in acid media cause a prominent decrease in current densities, and shift of the E_{corr} values to more cathodic direction in comparison with 0.5 M HCl without inhibitors. EIS method confirmed that the maximum inhibition was achieved with addition of 0.012 mol L⁻¹ eugenol (92.4%) and 0.035 mol L⁻¹ linalool (85.1%) in HCl solution. Thus, these concentrations can be assumed as optimum for corrosion inhibition of aluminium. SEM results are in accordance with the results obtained by weight loss and electrochemical measurements, confirming the existence of protective inhibitor film on the Al surface.

Keywords: aluminium, corrosion, eugenol, inhibition, linalool.

1. INTRODUCTION

The use of corrosion inhibitors in the industry has a long tradition, because it provides good protection of metals and thus minimize economic loses. In the 21st century there is still an increasing awareness on environment and human health protection, therefore the studies must be conducted to use as corrosion inhibitors the environmental friendly, biodegradable and non-toxic compounds, instead of harmful synthetic ones [1]. Corrosion of aluminium, especially in high acidic media such as hydrochloric acid is pronounced when processes such as acid pickling, descaling and corrosion product removing

were obtained. Detection of corrosion inhibitor with high inhibition efficiency is particularly based on their molecular structure, mainly on the availability of electron-rich atoms (N, S, O, P) in the inhibitor molecule, and equally the presence of multiple bonds or aromatic rings [2]. The majority of organic compounds used as corrosion inhibitors, act by adsorption on the metal surface, creating a protective layer. Adsorption process mainly depends not only on charge of metal in corrosive medium, but also on the molecular structure of the inhibitor, where electron-rich atoms can serve in adsorption process as adsorption centers. Many studies confirmed that inhibitors which in their structure possesses multiple bonds and heteroatoms, such as aromatic rings [3-6] show better inhibition performance than molecules with linear structure [7,8]. Regarding to replacement of toxic corrosion inhibitors with environmentally friendly types such as natural products of plant origin, and compounds used in food industry for flavouring or thickening [9-13], in this work, eugenol and linalool were examined as potential corrosion inhibitors for aluminium in high acidic medium. Eugenol (2-Methoxy-4-(prop-2-en-1-yl) phenol) and linalool (3,7-dimethyl-1,6-octadien-3-ol), which are the principal components of many essential oils, possess some typical adsorption centres attributable to good corrosion inhibitors. These naturally occurring antioxidants are used, not only for food products stabilization, but also in pharmaceuticals and cosmetics [14, 15]. Comparative study of inhibition efficiency of eugenol as aromatic and linalool as linear molecules on aluminium corrosion in 0.5 M HCl solution was performed. Their inhibition efficiency was examined by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. In addition, the scanning electron microscopy (SEM) analysis was used to confirm eugenol and linalool inhibition performance on aluminium surfaces.

2. EXPERIMENTAL

2.1. Materials, Reagents and Solutions.

Eugenol and linalool were provided by Sigma-Aldrich. The stock solution of eugenol ($C_{10}H_{12}O_2$, $\rho = 1.067 \text{ g mL}^{-1}$) and linalool ($C_{10}H_{18}O$, $\rho = 0.87 \text{ g mL}^{-1}$) were prepared by dissolving it in ethanol as 30% (v/v) solution. A specific volume of the stock solution with corrosion inhibitors was taken and added directly to 0.5 M HCl solution (prepared from analytical grade hydrochloric acid and deionised water) to prepare the desired concentration (c_{inh}) in the range of 0.001 - 0.035 mol L⁻¹. Aluminium coupons prepared from 99.85% pure aluminium were used for weight loss and electrochemical investigations.

2.2. Weight Loss measurements.

For weight loss measurements cleaned aluminium coupons dimension of $2 \times 2 \text{ cm}$ were used in each experiment, weighed and suspended in a 100 mL beaker containing 0.5 M HCl as the test solution, with or without inhibitors. After 2 h of immersion at 30 °C in non-de-aerated test solutions the coupon was taken out, dried and re-weighed. The corrosion rate (W_{corr}) and the inhibition efficiency (η_w) were calculated from equations (1) and (2):

$$W_{corr} = \frac{\Delta m}{S \cdot t} \quad (1)$$

$$\eta_w(\%) = \left(\frac{W'_{\text{corr}} - W_{\text{corr}}}{W'_{\text{corr}}} \right) \times 100 \quad (2)$$

where Δm is average weight loss of three parallel aluminium coupons (mg), S is the area of the Al coupons (cm^2), t is immersion time (h), W_{corr} and W'_{corr} are the corrosion rates of Al coupons, with and without inhibitor, respectively.

The inhibition efficiency depends on the degree of aluminium surface coverage (θ) by molecules of the inhibitor and can be expressed by the equation (3):

$$\theta = \frac{W'_{\text{corr}} - W_{\text{corr}}}{W'_{\text{corr}}} \quad (3)$$

2.3. Electrochemical and SEM methods.

All electrochemical measurements were conducted in the cylindrical glass cell containing 600 mL of electrolyte, where saturated calomel electrode (SCE) and graphite electrode were used as reference and auxiliary electrodes, respectively. The working electrode (WE) cut from Al with surface area of 1 cm^2 was exposed to test solution and each experiment was repeated at least three times to check the reproducibility. Electrochemical measurements were recorded with a potentiostat type VersaSTAT 3, Princeton Applied Research, controlled by a personal computer. Potentiodynamic polarization measurements were performed at scan rate of 0.5 mV s^{-1} after open circuit potential was reached. The inhibition efficiency (η_p) was calculated according to equation (4):

$$\eta_p(\%) = \left(\frac{I'_{\text{corr}} - I_{\text{corr}}}{I'_{\text{corr}}} \right) \times 100 \quad (4)$$

where I'_{corr} and I_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively. Corrosion current densities values were determined by the intersection of the extrapolated cathodic Tafel lines at the corrosion potential (E_{corr}).

EIS measurements were performed in the frequency range from 10 kHz to 30 mHz with an AC voltage amplitude perturbation of 10 mV and obtained data was analysed using ZSimpWin 3.00 software (EG&G, USA). The inhibition efficiency (η_e) of eugenol and linalool was calculated using the following equation (5):

$$\eta_e(\%) = \frac{R'_{\text{ct}} - R_{\text{ct}}}{R'_{\text{ct}}} \times 100 \quad (5)$$

where R'_{ct} and R_{ct} are charge transfer resistance in the presence and absence of the inhibitor, respectively. The SEM micrographs of the samples were made by JEOL JSM 6460 LV scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements.

Weight loss measurement of aluminium coupons was performed at 30°C in the absence and presence of different concentrations of eugenol and linalool after 2 h immersion in 0.5 M HCl. The

obtained corrosion rates W_{corr} ($\text{mg cm}^{-2} \text{ h}^{-1}$), surface coverage (θ) and inhibition efficiency values ($\eta_w\%$) were shown in Table 1. It can be seen that both used inhibitors decreased the corrosion rate of aluminium in 0.5 M hydrochloric acid solution at all studied concentrations. Increasing the concentration of the used inhibitors results in a significant decrease in the corrosion rate, which in turn leads to an increase in the surface coverage and inhibition efficiency values.

Table 1. Corrosion rate and surface coverage values of eugenol and linalool on aluminium in 0.5 M HCl solution obtained after 2 h immersion time, at 30°C by weight loss method.

Inhibitor	c (mol L^{-1})	W_{corr} ($\text{mg cm}^{-2} \text{ h}^{-1}$)	θ	$\eta_w\%$
Blank	0	1.0272	-	-
Eugenol	0.001	0.4237	0.5875	55.75
	0.003	0.3196	0.6888	68.88
	0.006	0.2104	0.7951	79.51
	0.012	0.1817	0.8230	82.30
	0.024	0.2013	0.8041	80.41
	0.035	0.1929	0.8122	81.22
Linalool	0.001	0.5725	0.4426	44.26
	0.003	0.8304	0.5033	50.33
	0.006	0.4330	0.5785	57.85
	0.012	0.3459	0.6632	66.32
	0.024	0.2897	0.7179	71.79
	0.035	0.2289	0.7716	77.16

From this results are evident that maximum surface coverage of aluminium was achieved for addition of 0.012 mol L^{-1} eugenol (0.8230), while for linalool the maximum surface protection was obtained after addition 0.035 mol L^{-1} (0.7716). It must be noted that further increases of eugenol concentration ($> 0.012 \text{ mol L}^{-1}$) did not cause any significant change of surface coverage and the inhibition efficiency values. This could be occurred due to desorption process of inhibitor molecules, when its concentration is beyond the optimum [16]. Also, these results confirmed that both molecules act as good corrosion inhibitors for aluminium in high acidic media and these molecules are probably adsorbed on aluminium surface via adsorption centres presents in their structure [17,18].

On the basis of weight loss measurements, it can be drawn that eugenol and linalool acted as good corrosion inhibitors for aluminium in high acidic media and they are probably adsorbed on aluminium surface via adsorption centres presented in their structure (Figure 1).

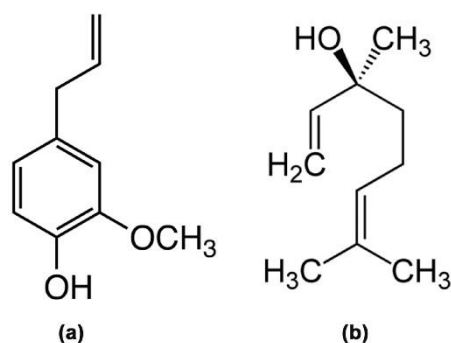


Figure 1. Molecular structures of eugenol (a) and linalool (b).

The primary step in the action of organic inhibitors in acid solutions is generally agreed on their adsorption on the metal surface [19]. In this content, the adsorption behavior of molecules used in this work was investigated in terms of Langmuir adsorption isotherm (Figure 2.), in order to check which, type of interaction is occurred, i.e. adsorption of inhibitors on aluminium surface or interaction between adsorbed molecules. From Figure 2. is evident that the linear correlation between c/θ vs c was obtained for eugenol and linalool molecules, confirming that their adsorption on the aluminium surface obeys Langmuir adsorption isotherm. The gained isotherm postulate that there is no interaction between the adsorbed molecules, and on the metal surface is a fixed number of adsorption sites, while each can hold one adsorbed species [5].

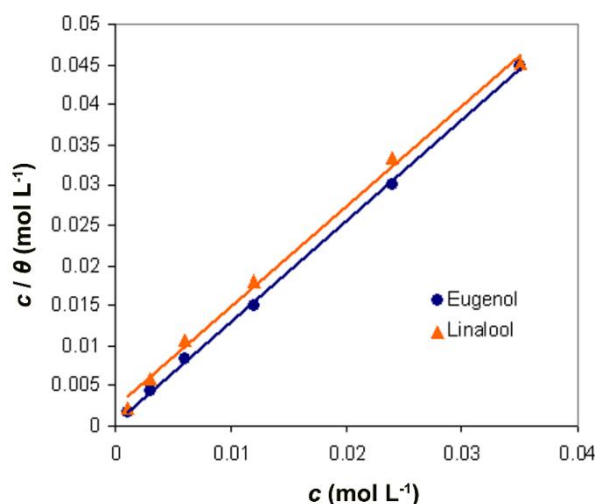


Figure 2. Langmuir adsorption isotherms of eugenol and linalool on aluminium in 0.5 M HCl solution obtained after 2 h of immersion, at 30°C by weight loss method.

Since it is found that the experimental data obtained from weight loss measurements fitted Langmuir's adsorption isotherm, some thermodynamic parameters such as the adsorption constant, K_{ads} and the Gibbs energy of adsorption, ΔG_{ads}^0 can be calculated. From the expression for Langmuir's adsorption isotherm (6):

$$\frac{\theta}{1-\theta} = K_{ads}c \quad (6)$$

where c is the inhibitor concentration in mol dm^{-3} , θ the surface coverage, K_{ads} was calculated, while the Gibbs energy of adsorption (ΔG_{ads}^0) was given from the following equation (7):

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5 K_{\text{ads}}) \quad (7)$$

where 55.5 mol dm^{-3} is the molar concentration of water in the solution, R is the gas constant ($8,314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the temperature (K) [19].

Thermodynamic parameters obtained from Langmuir's adsorption isotherms for eugenol and linalool are given in Table 2. According to the obtained values for ΔG_{ads}^0 which are between $-28.41 \text{ kJ mol}^{-1}$ and $-21.63 \text{ kJ mol}^{-1}$ some conclusions can be made. Firstly, negative value for ΔG_{ads}^0 indicates that adsorption process of eugenol and linalool molecules on aluminium surface is spontaneous, and secondly, the calculated values of Gibbs energy are typical for electrostatic interaction, i.e., physisorption [20,21]. So, it can be observed that the adsorption process of eugenol and linalool molecules on the aluminium surface in the present study is mainly physisorption.

Table 2. Adsorption constant (K_{ads}) and free energy of adsorption (ΔG_{ads}^0) obtained from Langmuir adsorption isotherms for eugenol and linalool, at 30°C

Inhibitor	$c \text{ (mol L}^{-1}\text{)}$	K_{ads} (L mol^{-1})	$-\Delta G_{\text{ads}}^0$ (kJ mol^{-1})
Eugenol	0.001	1424.2	28.41
	0.003	737.8	26.75
	0.006	646.7	26.42
	0.012	387.5	25.13
	0.024	170.7	23.06
	0.035	123.6	22.25
Linalool	0.001	749.0	26.79
	0.003	337.8	24.78
	0.006	229.6	23.81
	0.012	164.2	22.96
	0.024	106.0	21.86
	0.035	96.6	21.63

3.2. Electrochemical Measurements

3.2.1. Potentiodynamic Polarization.

The cathodic and anodic polarization curves of aluminium in 0.5 M hydrochloric acid solution in the absence and presence of different concentrations of eugenol and linalool are shown in Figures 3a and 3b, respectively. Potentiodynamic polarization parameters were calculated from Tafel plots and are given in Table 3.

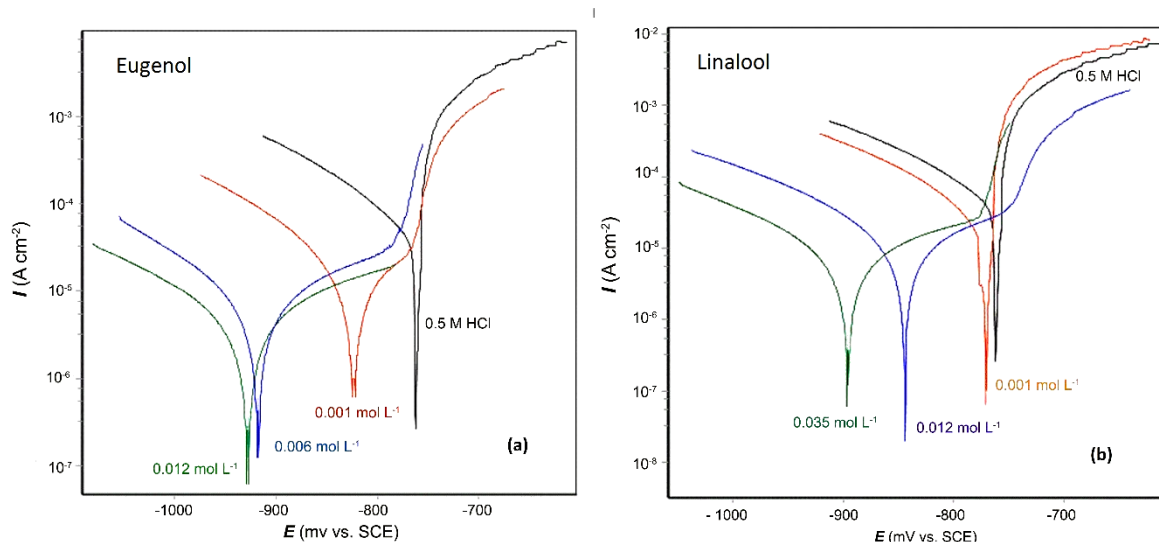


Figure 3. Potentiodynamic polarization curves for aluminium in 0.5 M HCl solution in the absence and presence of different concentrations of eugenol (a) and linalool (b) at 30°C.

The corrosion current density values in the presence and absence of inhibitor in hydrochloric acid were determined by the extrapolation of cathodic Tafel slopes to the respective corrosion potentials. It is apparent that I_{corr} decreases considerably in the presence of used inhibitor, and decreases with rises of their concentration. Maximum decrease of I_{corr} values (0.042 mA cm^{-2}) and maximum inhibition efficiency (94.7 %) was obtained with addition of 0.012 mol L^{-1} eugenol in 0.5 M HCl solution. This trend is also observed for weight loss measurements which points out that both applied methods are in good correlation. Since the higher concentration ($> 0.012 \text{ mol L}^{-1}$) of eugenol did not cause further increase in current densities value, these polarisation curves are not presented. From Table 3, it can be seen that addition of eugenol even at quite low concentration (0.001 mol L^{-1}) cause prominent decrease of corrosion current density values (0.148 mA cm^{-2}) with a quite high (81.2 %) inhibition efficiency. For comparison, at the same concentration of linalool the inhibition efficiency is only 31.4 %.

Table 3. Potentiodynamic polarization parameters obtained for aluminium in 0.5 M HCl solution in the absence and presence of various concentrations of eugenol and linalool at 30°C.

Inhibitor	C_{inh} (mol L^{-1})	E_{corr} (mV)	I_{corr} (mA cm^{-2})	$-b_c$ (mV dec^{-1})	θ	η_p (%)
Blank	0	-762	0.786	104	-	-
Eugenol	0.001	-825	0.148	91	0.812	81.2
	0.003	-884	0.093	115	0.882	88.2
	0.006	-918	0.063	110	0.919	91.9
	0.012	-928	0.042	112	0.947	94.7
Linalool	0.001	-771	0.539	136	0.314	31.4
	0.003	-825	0.282	93	0.641	64.1
	0.006	-832	0.265	133	0.663	66.3
	0.012	-844	0.203	139	0.741	74.1
	0.024	-870	0.178	124	0.773	77.3
	0.035	-896	0.108	128	0.862	86.2

Since the eugenol is aromatic molecule which can be adsorbed on aluminium surface with planar orientation, and the linalool is linear molecule which can be adsorbed via vertical one, we assumed that their structural differences (Figure 1) are influenced on the level of aluminium protection. In this content, at the same used concentration, eugenol can cover larger aluminium surface than linalool, holding a nearly flat orientation with respect to the aluminium. This planar adsorption configuration increases the contact area and prevents the water molecule to pass from aggressive solution into the aluminium surface. The similar observations were previously studied for some aromatic molecules [23-26].

From Figures 3a and 3b is evident that the corrosion potential shifts in the negative direction with increases of concentrations of investigated inhibitors. It is obvious that eugenol prevents localized attack on the aluminium electrode surface, causing E_{corr} shift with appearing of passive region for all used concentration. This passive region means that the shape of anodic curves observed in the HCl solution in the presence of eugenol as well as in the presence of higher concentration of linalool ($>0.006 \text{ mol L}^{-1}$) is quite different from those recorded in the solution without inhibitor. The shape of the polarization curves confirms that both inhibitors mainly retard the cathodic evolution of hydrogen, and blocked reaction of electron transfer on anodic site, indicating on the passive behavior of the aluminium surface, probably due to the formation of a protective layer. Similar behavior of aluminium was observed previously [27,28].

Shape of polarization curves also indicates that after the potential of approximately -760 mV vs. SCE was reached, a significant destruction of the resulting film on the aluminum surface and aluminium dissolution were achieved. Furthermore, in the presence of either compound, the slight change of b_c indicates that the corrosion mechanism of aluminium does not change significantly, confirming that utilized inhibitors acted by simple blocking of the available surface area via adsorption process [28].

Furthermore, from the potentiodynamic polarization curves for aluminium in 0.5 M HCl solution can be seen that presence of eugenol and linalool cause a significant decrease in current densities, and at the same time, shift the E_{corr} values to more cathodic direction. This behaviour can be explained on the basis of the fact that in acidic solution these molecules existed in the protonated form (especially linalool), and as such can be easily adsorbed on the cathodic site of the aluminium, decreasing the hydrogen evolution reaction. Linalool molecules could be easily protonated in the high acid solution such as 0.5 M HCl , moreover, this molecule also contained oxygen atom in O-H functional group and double bonds, typical for corrosion inhibition activity via adsorption. Similarly, the eugenol molecule (Figure 1) contained functional groups with oxygen and doubles bond also responsible for adsorption and protection of aluminium surface.

3.2.2. Electrochemical Impedance Spectroscopy.

The effect of eugenol and linalool on the impedance behaviour of aluminium in 0.5 M hydrochloric acid solution has been studied and the results are given in Figure 4. as Nyquist plots. Results obtained from the inspections of the impedance spectra for pure 0.5 M hydrochloric acid solution and the equivalent circuit model used to fit the experimental results was given previously [27].

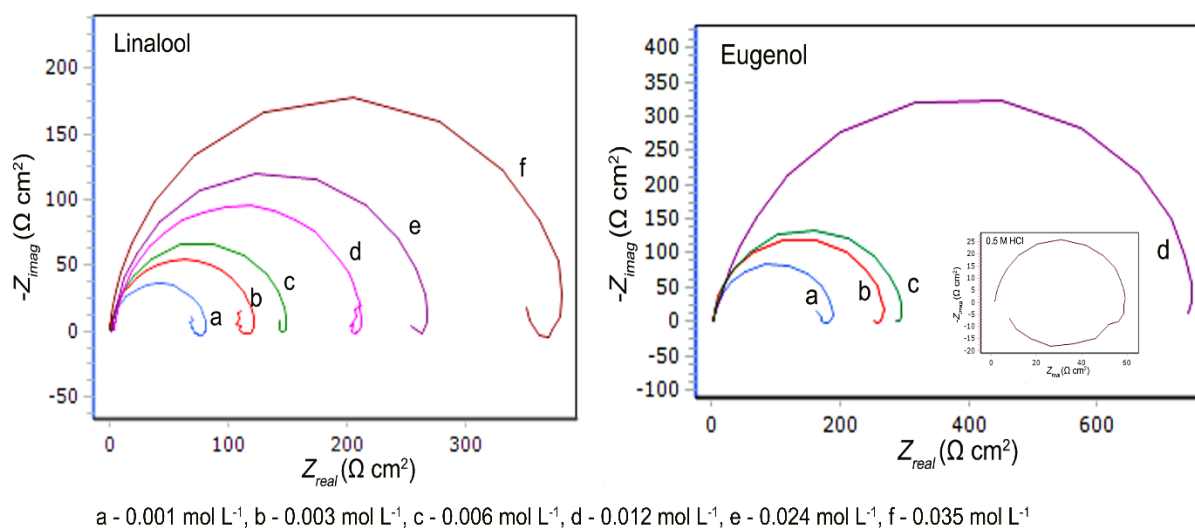


Figure 4. Nyquist plots obtained for aluminium in 0.5 M HCl solution in the absence and presence of different concentrations of linalool (a) and eugenol (b) at 30°C.

Table 4. Electrochemical impedance parameters obtained for aluminium in 0.5 M HCl solution in absence and presence of different concentrations of eugenol and linalool at 30°C.

Inhibitor	C_{inh} (mol L ⁻¹)	R_s (Ω cm ²)	CPE (μ F cm ⁻²)	R_{ct} (Ω cm ²)	η_{eis} (%)
Blank	0	1.725	45.46	55.6	-
Eugenol	0.001	1.629	13.97	181.1	69.3
	0.003	1.740	9.69	260.9	78.7
	0.006	1.678	6.87	305.7	81.8
	0.012	1.859	3.43	737.5	92.4
Linalool	0.001	1.196	31.68	79.84	30.3
	0.003	0.953	20.75	121.9	54.3
	0.006	1.784	17.04	146.7	62.2
	0.012	2.068	12.01	210.7	73.6
	0.024	2.204	9.50	266.3	79.1
	0.035	0.996	6.77	373.6	85.1

EIS data summarised in Table 4 show that the R_{ct} values increase and the constant phase element (CPE) values decreases with increasing eugenol and linalool concentrations. The increase of the charge transfer resistance (R_{ct}) values with increases of inhibitor concentration suggests the formation of a protective layer on the electrode surface, which acts as a barrier for mass and charge transfer. Furthermore, the decrease in CPE can result from the increase of thickness of the electrical double layer, once again confirming inhibitor molecules adsorption at the metal/solution interface. The inhibition efficiencies (η_e) calculated from R_{ct} values indicate that both investigated inhibitors acted as good corrosion inhibitors of aluminium in hydrochloric acid solution. Due to the fact that the maximum inhibition efficiency was achieved with addition of 0.012 mol L⁻¹ eugenol (92.4%) and 0.035 mol L⁻¹ linalool (85.1%) in HCl solution, this concentration can be assumed as optimum concentration for

aluminium protection. Furthermore, the results obtained from the EIS measurements are in very good agreement with those obtained from weight loss and polarization measurements, suggesting that linalool must be added in higher concentration than eugenol for achieving similar inhibition efficiency.

3.3. Scanning Electron Microscopy (SEM).

The SEM images of aluminium surface after 2 h of immersion in 0.5 M HCl solution in absence and presence of optimum concentration of eugenol and linalool are given in Figure 5.

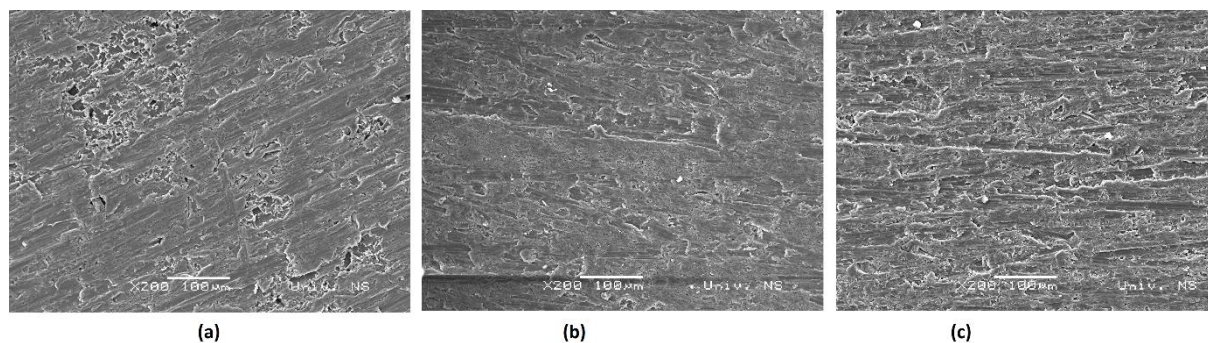


Figure 5. SEM images of aluminium surface after 2 h of immersion in 0.5 M HCl solution in absence (a) and presence of optimum concentration of eugenol (b) and linalool (c).

Figure 5a shows uniform attack of the aggressive HCl solution on aluminium surface and appearance of some shallow pits. On the other hand, SEM images of aluminium samples immersed in HCl solution in presence of 0.012 mol L^{-1} eugenol and 0.035 mol L^{-1} linalool are presented in Figure 5b and 5c, indicating on significant improvements in surface morphology as compared to that in the aggressive medium without inhibitors. It is obvious that on aluminium surface is present the layer of adsorbed inhibitor, which provided efficient corrosion inhibition of aluminium. Thus, these results are in accordance with those obtained by weight loss and electrochemical measurements, especially when is evident that surface morphology of aluminium samples shows better improvement with addition of eugenol than linalool in HCl solution.

4. CONCLUSIONS

Eugenol and linalool act as effective corrosion inhibitors for aluminium in 0.5 M HCl solution. Potentiodynamic polarization curves indicated that presence of eugenol and linalool in HCl cause the shift of corrosion potentials in the cathodic direction and decrease of corrosion currents with the increase of inhibitor concentration. The results obtained from the EIS measurements are in very good agreement with those obtained from weight loss and polarization measurements, suggesting that linalool must be added in higher concentration than eugenol for achieving similar inhibition efficiency. Thus, to attain the maximum inhibition efficiency, the optimum concentrations of eugenol and linalool are 0.012 mol L^{-1} and 0.035 mol L^{-1} , respectively. The surface morphology of aluminium samples shows better

improvement with addition of eugenol than linalool in HCl solution. This could be due to the differences between chemical structures of eugenol and linalool, where is well known that molecules with aromatic ring possessed better adsorption and inhibition behavior on metal surface in comparison with linear ones.

ACKNOWLEDGEMENTS

This paper was produced as part of the “Atrium of Knowledge” project co-financed by the European Union from the European Regional Development Fund and the Operational Programme Competitiveness and Cohesion 2014-2020.)

References

1. K. Xhanari, M. Fingšar, M. Knez-Hrnčić, U. Maver, Ž. Knez, B. Seiti, *RSC Adv.*, 7 (2017) 27299.
2. K. F. Khaled, M.M. Al-Qahtani, *Mater. Chem. Phys.*, 113 (2009) 150.
3. F. Bentiss, M. Traisnel, H. Vezin, M. Lagrenée, *Corros. Sci.*, 45 (2003) 371.
4. M. Finšgar, I. Milošev, *Corros. Sci.*, 52 (2010) 2737.
5. I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, *Corros. Sci.*, 51 (2009) 1868.
6. E. Chaieb, A. Bouyanzer, B. Hammouti, M. Benkaddour, *Appl. Surf. Science* 246 (2005) 199.
7. G.Y. Elewady, I.A.El-Said and A.S.Fouda, *Int. J. Electrochem. Sci.*, 3 (2008) 644.
8. O. K. Abiola, N.C. Oforka, S.S. Angaye, *Mater. Lett.*, 58 (2004) 3461.
9. L. Divya, S. Nisha, T. Suresh, L. Mohsin, J. Prakash, *Pigm. Resin Technol.*, 45 (2016) 106.
10. T.Y. Soror, *Europ. Chem. Bull.*, 2 (2013) 191.
11. S.A. Umoren, E.E. Ebenso, *Pigm. Resin Technol.*, 37 (2008) 173.
12. A.Ninčević Grassino, J. Halambek, S. Djaković, S. Rimac Brnčić, M. Dent, Z. Grabarić, *Food Hydrocoll.*, 52 (2016) 265.
13. L. Divya, S. Nisha, T. Suresh, L. Mohsin, J. Prakash, *Pigm. & Resin Technol.*, 45 (2016) 106.
14. P. Hernández Sánchez, S. López Miranda, C. Lucas Abellán, E. Núñez Delicado, *Food Nutr. Sci.*, 3 (2012) 716.
15. J. Prakash, S.K. Gupta, *J. Ethnopharmacol.*, 72 (2000) 29.
16. M.H. Hussin, M.J. Kassim, *Mater. Chem. Phys.*, 125 (2011) 461.
17. P.M. Ejikeme, S.G. Umana, O.D. Onukwuli, *Portugalie Electrochim. Acta*, 30 (2012) 317.
18. P.B. Raja, M.G. Sethuraman, *Mater. Letter.*, 62 (2008) 113.
19. S. Ghareba, S. Omanovic, *Electrochim. Acta*, 56 (2011) 3890.
20. J. Aljourani, K. Raeissi, M.A. Golozar, *Corros. Sci.*, 51 (2009) 1836.
21. M.A. Amin, S.S. Abd El Rehim, H.T.M. Abdel-Fatah, *Corros. Sci.*, 51 (2009) 882.
22. S. Deng, X. Li, *Corros. Sci.*, 64 (2012) 253–262.
23. J.J. Fu, S.N. Li, L.H. Cao, Y. Wang, L.H. Yan, L.D. Lu, *J. Mater. Sci.*, 45 (2010) 979.
24. A.S. Patel, V.A. Panchal, N.K. Shah, *Bull. Mater. Sci.*, 35 (2012) 283.
25. M.Abdallahab, E.A.M.Gad, M.Sobhiad, J. H. Al-Fahemia, M.M. Alfakeer, *Egyptian J. Petrol.*, 28 (2019) 173.
26. M. Metikoš-Huković, R. Babić, Z. Grubač, *J. Appl. Electrochem.*, 32 (2002) 35.
27. J. Halambek, A. Žutinić, K. Berković, *Int. J. Electrochem. Sci.*, 8 (2013) 11201.
28. S. Ghareba, S. Omanovic, *Corros. Sci.*, 52 (2010) 2104.