

***Ocimum basilicum* L. Oil as Corrosion Inhibitor for Aluminium in Hydrochloric Acid Solution**

Jasna Halambek*, Anja Žutinić, Katarina Berković

Faculty of Food Technology and Biotechnology, Department for Chemistry and Biochemistry, Laboratory for Physical Chemistry and Corrosion, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia

*E-mail: jhalambe@pbf.hr

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Ethanol solution of *Ocimum basilicum* L. oil was studied as corrosion inhibitor for aluminium in 0.5 M HCl. Its inhibition effect was performed using weight loss measurements, potentiodynamic polarization and EIS methods. Potentiodynamic polarization measurements show that presence of basil oil in HCl solution influence on current densities decreasing. EIS results confirmed that investigated compound formed protective layer on aluminium surface. Thermodynamic adsorption parameters show that compounds present in basil oil are adsorbed on aluminium surface by an exothermic process, indicating that the adsorption mechanism is physisorption, with the adsorptive layer having an electrostatic character.

Keywords: Aluminium, corrosion inhibition, EIS, *Ocimum basilicum* L., polarization.

1. INTRODUCTION

Aluminium show excellent corrosion resistance due to the formation of a thin and protective, naturally formed oxide film on its surface [1]. Unfortunately, when aluminium is exposed to aggressive environments such as acid pickling solutions, chemical etching, industrial cleaning or scale dissolving, these processes lead to significant mass loss of aluminium [2]. In order to prevent and minimize aluminium dissolution, different corrosion inhibitors are used, especially organic compounds, which in their structure contain atoms of nitrogen, sulphur, oxygen, phosphor etc. [3-5]. Despite the large number of suitable inhibitors to prevent corrosion of metal, the discovery and development of novel corrosion inhibitors is required, because a lot of known and used inhibitors are dangerous to the environment and human health [6]. The plant extracts as cheap and "eco-friendly"

corrosion inhibitors are widely used, due to increasing environmental awareness and vigilance of the importance of protecting and preserving the nature [7,8]. Recently, some studies have confirmed the efficiency of plant materials as corrosion inhibitors for aluminium in various media [9-12]. The inhibition efficiency of plant materials is ascribed to the presence of complex organic compounds with variety of different adsorption centers (heteroatoms, double bonds, aromatic rings etc.).

Ocimum basilicum L. (Lamiaceae), known as basil, is an aromatic herb and traditionally extensively utilized as a flavoring agent in food industry, as well as in perfumery and medical industry. Numerous laboratory studies have shown various effects of *Ocimum* sp., including bactericidal, antioxidative, chemopreventive, blood-sugar lowering etc. [13,14]. On the basis on main component, essential oils isolated from *O. basilicum* L., can be classified in four major basil essential oil chemotypes: (1) methyl chavicol-rich, (2) linalool-rich, (3) methyleugenol-rich, (4) methyl cinnamate-rich, and numerous subtypes [15].

Presently, to the best of our knowledge, there is no reported work on inhibitive effects of *Ocimum basilicum* L. ct linalool essential oil on acidic corrosion of aluminium. Therefore, the aim of this work is to investigate the essential oil of basil (*Ocimum basilicum* L., chemotype linalool) as potential inhibitor of the aluminium corrosion in 0.5 M HCl. The study was done by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The effect of temperature was also studied, and some thermodynamic and kinetic parameters were calculated, too.

2. EXPERIMENTAL METHODS

2.1. Materials

Gravimetric and electrochemical tests were performed on 99.85% pure aluminium and the other components (wt%) were: Fe 0.08, Si 0.06 and Cu 0.001. The aggressive solution (0.5 M HCl) was made from analytical grade hydrochloric acid (37%) and deionised water. Pure 100% *Ocimum basilicum* L., ct. linalool, essential oil was provided by "Oshadhi". The density of basil oil is 0.956 g cm^{-3} . Chemical composition of oil was obtained from the supplier and is: linalool (65%), eugenol (4.5%), 1,8-cineole (4.4 %), geraniol (3.5%), camphor (0.25%), monoterpenes (4.5%), sesquiterpenes (7.8%), bornyl acetate (1.5%) etc. The essential oil was dissolving in 96% ethanol and 30% (v/v) solution was used as inhibitor (stock solution). A specific volume was taken from the stock solution and added directly to 0.5 M HCl solution to prepare the desired concentrations in range from 0.2 to 5.7 g L^{-1} .

2.2. Weight loss measurements

Weight loss measurements were performed on aluminium coupons dimension $2.0 \text{ cm} \times 2.0 \text{ cm} \times 0.5 \text{ cm}$. Before measurements coupons were abraded with emery paper up to 1200 grade, rinsed with distilled water, degreased with acetone and dried between filter paper prior to use. Prepared aluminium coupons were weighed and suspended in a beaker containing 150 mL test solution (without

and with inhibitor, respectively) with the aid of glass rod and hook. The immersion period for the weight loss test was 24 h at 30 °C and 2 h at 45 °C, 65 °C and 85 °C (in thermostat) in non-deaerated test solutions. After immersion time the coupons were then taken out from the test solution, washed with distilled water, dried with hot air stream and re-weighed. The corrosion rate (W), surface coverage (θ) and the inhibition efficiency η_w (%) were calculated from equations (1), (2) and (3):

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

$$\theta = \frac{W_{corr} - W'_{corr}}{W_{corr}} \quad (2)$$

$$\eta_w = \theta \times 100 \quad (3)$$

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

2.3. Potentiodynamic polarization and EIS measurements

Potentiodynamic polarization and electrochemical impedance spectroscopy studies (EIS) were carried out in a conventional three electrode glass cell. The saturated calomel electrode (SCE) was used as reference, while two graphite electrodes were auxiliary electrodes. The working electrode (aluminium) was mounted in Teflon holder (1 cm^2 area was exposed to corrosive solution) and the Luggin capillary was used in order to minimize ohmic contribution. Before measurements the aluminium electrode was prepared on the same way as is described in section 2.2. Each experiment was repeated at least three times to check the reproducibility. All polarization measurements were performed in the test solution (500 mL) after reaching the open-circuit potential (E_{ocp}) with scan rate of 0.5 mV s^{-1} in the potential range from $\pm 150 \text{ mV}$ with respect to the E_{ocp} .

All electrochemical measurements were carried out using Potentiostat type VersaSTAT 3 (Princeton Applied Research), controlled by a personal computer. In the case of polarization measurements, equation (4) was used to determine the inhibition efficiency:

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

where I_{corr} and I'_{corr} are the corrosion current densities in the absence and presence of inhibitor.

Electrochemical impedance spectroscopy (EIS) measurements were conducted at the open circuit potential after the electrode had been immersed in the test solution for 30 min. EIS measurements were performed in the frequency range of 100 kHz - 30 mHz with an AC voltage amplitude perturbation of 10 mV with five data points per decade.

Inhibition efficiency (η_{eis} %) is calculated using the equation (5):

$$\eta_{eis}(\%) = \left(\frac{R_{ct}' - R_{ct}}{R_{ct}'} \right) \times 100 \quad (5)$$

where R_{ct}' and R_{ct} are charge transfer resistance with and without inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements, adsorption isotherm, thermodynamic and kinetic parameters

Weight loss measurements at 303 K after 24 h of immersion period was used to study the potentially inhibitory action of *Ocimum basilicum* L. oil on the corrosion of aluminium in 0.5 M HCl solution. The obtained values of corrosion rate, surface coverage and inhibition efficiency in the absence and presence of various concentrations of basil oil are listed in Table 1.

Table 1. Corrosion rate, surface coverage and inhibition efficiency data obtained from weight loss measurements for aluminium in 0.5 M HCl solution in the absence and presence of various concentrations of *Ocimum basilicum* L. oil at 303 K, after 24 h immersion time.

| c (g L ⁻¹) | W (mg cm ⁻² h ⁻¹) | θ | η_w (%) |
|-----------------------------|---|----------|-----------------|
| - | 1.027 | - | - |
| 0.2 | 0.340 | 0.668 | 66.8 |
| 0.6 | 0.332 | 0.677 | 67.7 |
| 1.0 | 0.315 | 0.693 | 69.3 |
| 1.9 | 0.302 | 0.705 | 70.5 |
| 3.8 | 0.265 | 0.742 | 74.2 |
| 5.7 | 0.222 | 0.784 | 78.4 |

The results show that the basil oil influenced on reducing the dissolution of aluminium in 0.5 M HCl solution at all concentrations used. The inhibition efficiency of *Ocimum basilicum* L. oil increased with increasing concentrations and reached the maximum value of 78.4 % in the presence of 5.7 g L⁻¹, while at the same time the corrosion rates significantly decreased.

These results also confirm that *Ocimum basilicum* L. oil can acts as effective inhibitor for aluminium corrosion in acid solution in the concentrations range studied. The primary step in the action of organic inhibitors in acid solutions is generally agreed to be adsorption on the metal surface [16,17]. The adsorption of organic molecules provides information about the interaction between the adsorbed molecules themselves as well as their interaction with the metal surface. When the fraction of the surface covered is determined as a function of the concentration at a constant temperature, adsorption isotherm could be evaluated at equilibrium conditions. The degree of surface coverage (θ) for different concentrations of inhibitor in 0.5 M HCl was calculated from weight loss measurements (Table 1) and was tested graphically for fitting a suitable adsorption isotherm as indicated in Fig. 1.

Fig. 1 shows the straight lines of c/θ vs. c (g L^{-1}) obtained for basil oil, where the obtained linear correlation coefficient are close to 1 (0.9987), confirming that the adsorption of active molecules on the aluminium surface obeys Langmuir adsorption isotherm. The Langmuir model is given by the following equation (6):

$$\frac{c}{\theta} = c + \frac{1}{K} \quad (6)$$

where K is the adsorptive equilibrium constant, c the inhibitor concentration, and θ is surface coverage [11,17].

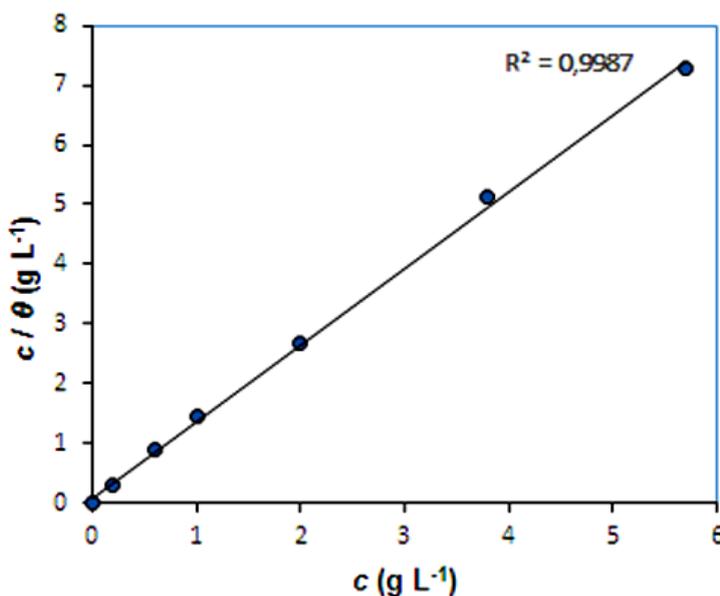


Figure 1. Langmuir adsorption isotherm for *Ocimum basilicum* L. oil on aluminium in 0.5 M HCl solution at 303 K obtained from weight loss measurements.

The adsorptive equilibrium constant obtained for basil oil at different temperatures are listed in Table 2. K_{ads} value can be related to the standard free energy of adsorption (ΔG_{ads}^0) by the following

equation (7):

$$K = \frac{1}{c_{H_2O}} \exp\left(\frac{-\Delta G_{ads}^0}{RT}\right) \quad (7)$$

where c_{H_2O} is the concentration of water in solution expressed in g L^{-1} , R ($\text{kJ mol}^{-1} \text{K}^{-1}$) is the universal gas constant and T (K) is temperature. It must be noted that the concentration unit of water molecules has to be similar to that of the inhibitor (the unit of c_{H_2O} is g L^{-1} with the value of approximate 1×10^3), and the calculated ΔG_{ads}^0 values (at different temperatures) are listed in Table 2.

In this work, the calculated ΔG_{ads}^0 values are ranging between $-13.2 \text{ kJ mol}^{-1}$ and $-17.1 \text{ kJ mol}^{-1}$, indicating that the adsorption mechanism of basil essential oil on aluminium in 0.5 M HCl solution at the studied temperatures is physisorption with adsorptive layer having electrostatic character [2,19]. This is concluded on the fact that values of ΔG_{ads}^0 up to -20 kJ mol^{-1} are consistent with physisorption, while those around -40 kJ mol^{-1} or higher are associated with chemisorption [18].

Table 2. Thermodynamic parameters for the adsorption of *Ocimum basilicum* L. oil and linalool molecules on the aluminium surface in 0.5 M HCl solution at different temperatures.

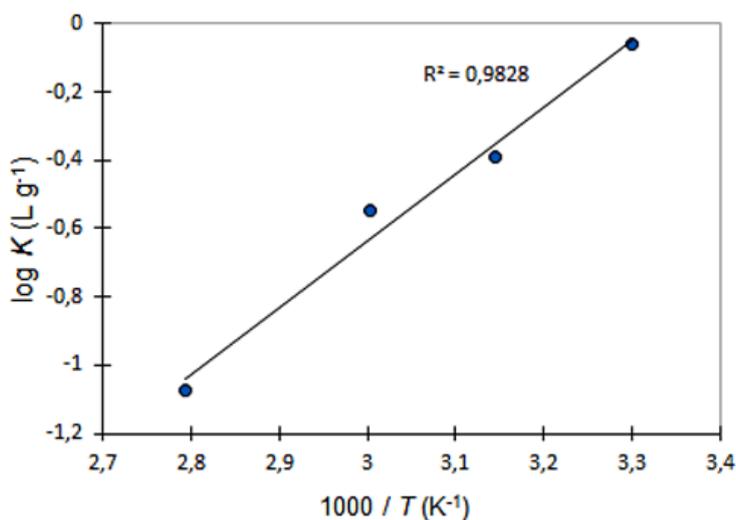
| Inhibitor | Temperature (K) | K_{ads} (L g ⁻¹) | ΔG_{ads}^0 (kJ mol ⁻¹) | ΔH_{ads}^0 (kJ mol ⁻¹) |
|----------------------------|-----------------|--------------------------------|--|--|
| <i>Ocimum basilicum</i> L. | 303 | 0.875 | -17.1 | -38.4 |
| | 318 | 0.408 | -15.9 | |
| | 333 | 0.283 | -15.6 | |
| | 358 | 0.084 | -13.2 | |

Different thermodynamic parameters can be important for prediction the adsorption of inhibitor on aluminium/solution interface. The standard adsorption enthalpy (ΔH_{ads}^0) can be calculated on the

basis of Van't Hoff equation (8):

$$\frac{d \ln K}{dT} = \frac{\Delta H_{ads}^0}{RT^2} \quad (8)$$

where R is the gas constant, T the absolute temperature (K), and K is adsorptive equilibrium constant (L g⁻¹) [20]. To obtain the adsorption enthalpy, the linear regression between $\log K$ and $1/T$ was figured and shown in Fig. 2.

**Figure 2.** Van't Hoff plot obtained for aluminium in 0.5 M HCl solution in the presence of 1.9 g L⁻¹ of *Ocimum basilicum* L. oil.

ΔH_{ads}^0 is calculated from the slope ($-\Delta H_{ads}^0/R$) and listed in Table 2. The negative sign of ΔH_{ads}^0 suggests that the inhibitor molecules adsorption is an exothermic process, which means that inhibition efficiency decreases with rise in the temperature. This behavior is correlated to the fact that increasing temperature stimulate desorption of some adsorbed inhibitor molecule from the aluminium surface. Moreover, in an exothermic process, chemisorption is distinguished from physisorption by considering the absolute value of ΔH_{ads}^0 . For exothermic process is also known, that the heat of adsorption is low

and therefore this type of adsorption is stable only at relatively low temperatures. Moreover, on the basis of literature [21] for the chemisorption process, ΔH_{ads}^0 approaches 100 kJ mol^{-1} , while for the physisorption process, it is less than 40 kJ mol^{-1} . In the present study, the ΔH_{ads}^0 value is smaller than the common physical adsorption enthalpy ($-38.4 \text{ kJ mol}^{-1}$), once again confirming that physical adsorption takes place. The same results were obtained by other authors [22].

To evaluate the stability of adsorbed layer of inhibitor on aluminium surface as well as activation parameters of the corrosion process of aluminium in acidic medium, weight loss measurements were carried out in the range of temperature 303-358 K in the absence and presence of 1.9 g L^{-1} basil oil during 2 h immersion time. Arrhenius suggested the equation which evaluates the temperature dependence of the corrosion rate (10):

$$\log \frac{W_2}{W_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (10)$$

where E_a represent the apparent activation energy, R is gas constant, while W_1 and W_2 are corrosion rates at temperatures T_1 and T_2 , respectively [23]. Plotting $\log W$ (corrosion rate in $\text{mg cm}^{-2} \text{ h}^{-1}$) versus $1000/T$ gives a straight line, as revealed by Fig. 3.

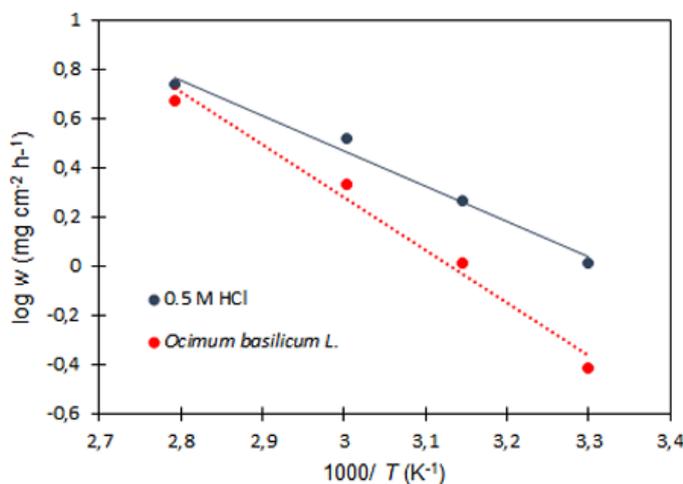


Figure 3. Activation energy determination for aluminium in 0.5 M HCl solution without and in the presence of *Ocimum basilicum L.* oil.

Calculated E_a value for the inhibited solution with basil oil is 38.9 kJ mol^{-1} and are higher than that for the uninhibited one (26.3 kJ mol^{-1}). The higher values of E_a suggest that dissolution of aluminium in the presence of inhibitors is slow, indicating a strong inhibitive action of the investigated compounds, which leads to increasing the energy barrier for the corrosion process [17]. Indeed, linalool molecules (the main component of basil oil) are easily protonated and exist in acidic medium in cationic form. Therefore, it is logical to assume that in this case the electrostatic cation adsorption is responsible for the good protective properties of this compound.

3.3. Polarization measurements

Potentiodynamic polarization curves for aluminium in 0.5 M HCl solution in the absence and presence of different concentrations of *O. basilicum* L. oil at 303 K are shown in Fig. 3.

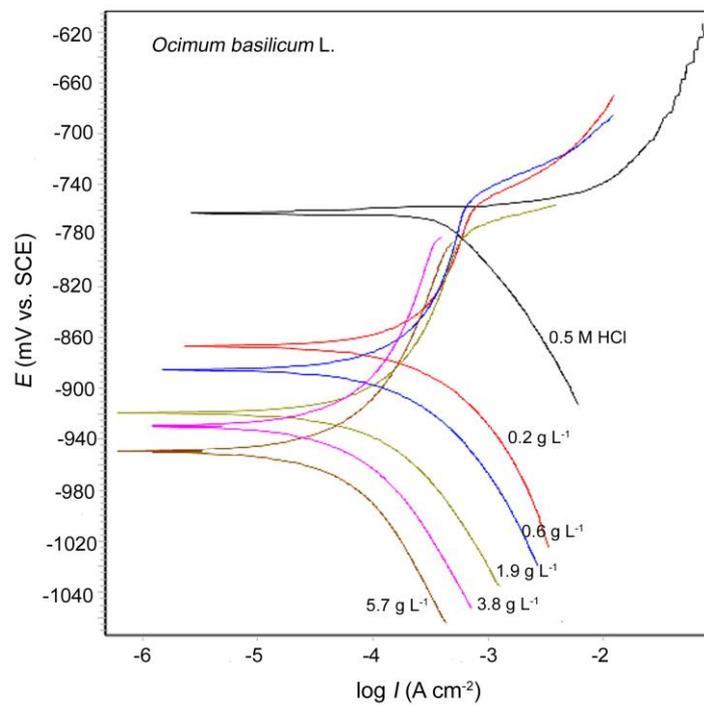


Figure 4. Potentiodynamic polarization curves for aluminium in 0.5 M HCl solution in the absence and presence of different concentrations of *Ocimum basilicum* L. oil at 303 K.

It is evident that presence of basil oil causes a prominent decrease in current densities, i.e. shifts the cathodic curves to lower values of current densities. It is known that corrosion behaviour (resistance) of aluminium is determined essentially by the behaviour of its oxide layer, in which the surface state plays a significant role and the oxide film on aluminium is in fact impossible to reduce electrochemically in aqueous solution [24]. As long as acid media are able to dissolve the oxide film spontaneously formed on aluminium surface during or before transferring electrode to the electrolytic cell with medium, it is expected that the combined action of acid and chloride leads to conditions similar to that of pitting [1,25]. Chlorides may substitute oxygen atoms in the oxide network, and this leads to a decrease in the oxide film resistance, which facilitates the release of aluminium atoms that diffuse into the hydrochloric acid solution.

From Fig. 4. is quite clear that in 0.5 M HCl solution without inhibitor there was no passive film formation during the anodic polarization, since the existence of potential plateaus on anodic curves is not observed. Strong dissolution of the preimmersion oxide air formed film occurs, probably due to the high concentration of H^+ ions (pH 0.5 M HCl is around 1), in other words, the dissolution rate of the film is greater than its rate of formation and a strongly local metal dissolution occur [26].

The shape of anodic curves observed in the HCl solution in presence of *O. basilicum* L. oil is quite different from those recorded in the solution without inhibitor. When inhibitor are added to the hydrochloric acid solution the existence of potential plateaus is observed. The shape of the curves confirms that basil oil affects the cathodic hydrogen evolution, and blocked anodic electron transfer reaction, indicating the passive behaviour of the aluminium surface due to the formation of a thin barrier passive film. It is quite obvious that the anodic process on Al in presence of basil oil is not only the simple dissolution of bare aluminium and that other processes are also involved such as adsorption of inhibitor molecules on electrode surface.

When the potential of approximately -750 mV vs. SCE was reached, the form of anodic polarization curves in the presence of basil oil resemble the curve obtained in a pure hydrochloric acid solution. After this potential (-750 mV vs. SCE), simultaneous destruction of the formed film on aluminium surface and the continuous dissolution of the bare metal were achieved. Since no linear Tafel regions were observed in anodic parts of polarisation curves, cathodic Tafel lines were extrapolated to the corrosion potential in order to determine polarisation parameters obtained for aluminium corrosion in 0.5 M HCl solution in absence and presence of various concentrations of *O. basilicum* L. oil at 303 K. Similar fitting method had been used for aluminium in HCl solution previously [2,3]. Corrosion potentials (E_{corr}), corrosion current densities (I_{corr}), cathodic Tafel slope values (b_c) deduced from the polarisation curves, corresponding inhibition efficiencies ($\eta_p(\%)$) and surface coverage degrees (θ) are listed in Table 3.

Table 3. Potentiodynamic polarization parameters obtained for aluminium in 0.5 M HCl solution in the absence and presence of various concentrations of *Ocimum basilicum* L. oil at 303 K.

| | c_{inh} (ppm) | E_{corr} (mV) | I_{corr} (mA cm ⁻²) | $-b_c$ (mV dec ⁻¹) | θ | η_p (%) |
|----------------------------|---------------------------|---------------------------|---|-----------------------------------|----------|-----------------|
| 0.5 M HCl | 0 | -762 | 0.786 | 104 | - | - |
| <i>Ocimum basilicum</i> L. | 0.2 | -866 | 0.456 | 63 | 0.419 | 41.9 |
| | 0.6 | -885 | 0.288 | 74 | 0.633 | 63.3 |
| | 1.0 | -896 | 0.233 | 110 | 0.704 | 70.4 |
| | 1.9 | -919 | 0.218 | 112 | 0.722 | 72.2 |
| | 3.8 | -930 | 0.148 | 116 | 0.811 | 81.1 |
| | 5.7 | -949 | 0.078 | 121 | 0.901 | 90.1 |

The shift of corrosion potentials in the cathodic direction and decrease of corrosion currents with the increase of inhibitor concentration indicate the adsorption of these molecules at the cathodic site of the aluminium surface [27]. By addition of basil oil to the HCl solution, the change in the mechanism of corrosion process and an improvement in corrosion behaviour are obvious. This could be mainly attributed to the physical adsorption process of active molecules, which additionally form protective layer on aluminium surface.

3.4. Electrochemical impedance spectroscopy (EIS)

The obtained Nyquist diagrams for aluminium in 0.5 M HCl solution at 303 K without and in the presence of various concentrations of *Ocimum basilicum* L. oil is given in Fig. 5.

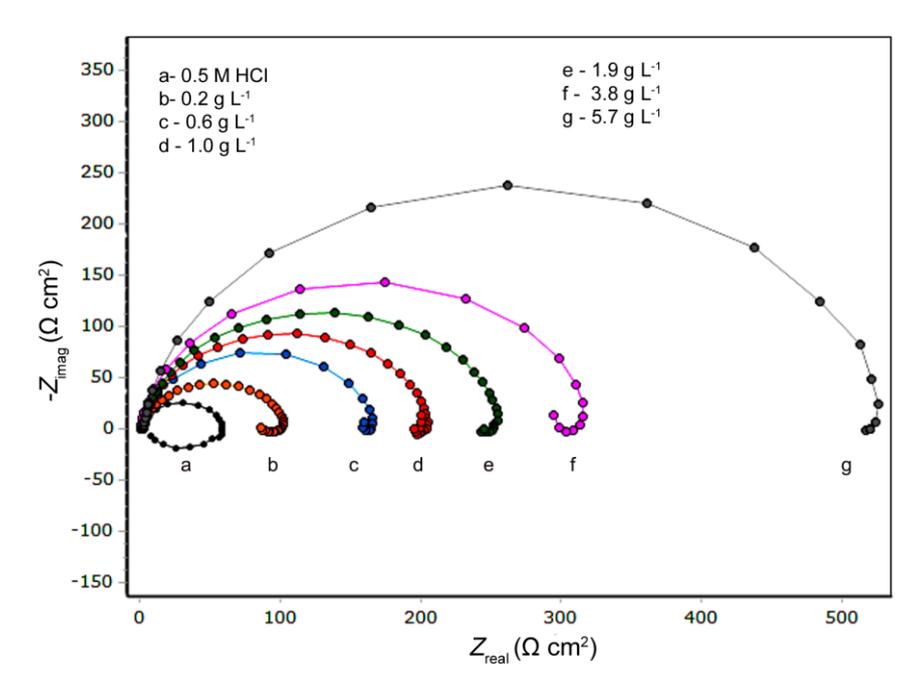


Figure 5. Nyquist plots for aluminium in 0.5 M HCl solution without and in the presence of *Ocimum basilicum* L. oil at 303 K.

As can be seen from Fig. 5, the impedance spectra recorded for aluminium in HCl solution consist from capacitive loop and inductive loop.

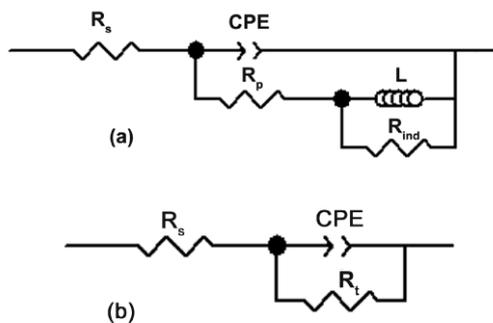


Figure 6. The equivalent circuit used to simulate the impedance data.

It must be noted that the low frequency inductive loop is quite common for aluminium in hydrochloric acid solutions [2,28]. The observed inductive loop on aluminium in HCl solution can be

caused by Cl^- adsorption, and Al dissolution. Furthermore, with addition of basil oil in acid solution the inductive loop in the Nyquist plots completely disappear. This changes in impedance behaviour of aluminium can indicate on prevention of local corrosion, actually pitting corrosion [29]. Obtained results also confirmed that compact and coherent protective film of inhibitors molecule is formed on aluminium surface, acting as a physical barrier to prevent the corrosion attack of the hydrochloric acid solution. Furthermore, the diameter of the capacitive loop in the presence of inhibitors is larger than that in blank solution, and enlarges with the increased inhibitor concentration.

The EIS results can be explained by equivalent circuit models shown in Fig. 6a (blank solution) and 6b (solution with inhibitor), where R_s represents the solution resistance, CPE is a constant phase element and R_p is the polarization resistance. Inductive elements (R_{ind} and L) are quite common for aluminium impedance behaviour in acid solution [2,30]. Meanwhile, the charge transfer resistance R_{ct} correspond to the sum of R_p and R_{ind} . CPE was used instead of an ideal capacitor, since capacitive loops are not perfect semicircles, and this can be correlated to the frequency dispersion as result of the inhomogeneity and roughness of electrode surface [31].

The impedance parameters derived from Nyquist plots obtained for aluminium in 0.5 M HCl solution are given in Table 4.

Table 4. Impedance parameters for aluminium in 0.5 M HCl solution at 303 K.

| R_s ($\Omega \text{ cm}^2$) | R_p ($\Omega \text{ cm}^2$) | CPE ($\mu\text{F cm}^{-2}$) | n | R_{ind} ($\Omega \text{ cm}^2$) | L (H cm^2) | R_{ct} ($\Omega \text{ cm}^2$) | η_{eis} (%) |
|------------------------------------|------------------------------------|------------------------------------|--------|--|---------------------------|---------------------------------------|---------------------|
| 1.725 | 7.389 | 45.46 | 0.9323 | 48.25 | 32.07 | 55.6 | - |

The impedance parameters and inhibition efficiencies η_{eis} (%) for addition of basil oil in HCl solution were obtained from equivalent circuit given in Figure 6b, and these parameters are shown in Table 5.

Table 5. Electrochemical impedance parameters and the corresponding inhibition efficiencies for aluminium in 0.5 M HCl solution in presence of various concentrations of *Ocimum basilicum* L. oil at 303 K.

| Inhibitor | c_{inh} (ppm) | R_s ($\Omega \text{ cm}^2$) | CPE ($\mu\text{F cm}^{-2}$) | n | R_{ct} ($\Omega \text{ cm}^2$) | η_{eis} (%) |
|----------------------------|--------------------|------------------------------------|------------------------------------|-------|---------------------------------------|---------------------|
| <i>Ocimum basilicum</i> L. | 0.2 | 2.457 | 24.61 | 0.914 | 102.7 | 45.9 |
| | 0.6 | 1.539 | 17.01 | 0.925 | 163.5 | 65.9 |
| | 1.0 | 2.364 | 12.00 | 0.927 | 208.2 | 73.3 |
| | 1.9 | 1.910 | 10.51 | 0.908 | 264.4 | 78.9 |
| | 3.8 | 1.184 | 8.97 | 0.942 | 309.8 | 82.0 |
| | 5.7 | 2.374 | 4.82 | 0.922 | 523.4 | 89.4 |

Inspection of Table 5 reveal that R_{ct} values increases prominently, while CPE decreases with the increasing concentration of basil oil. This decrease of CPE values in comparison with that in HCl solution without basil oil can result from an increase in the thickness of the electrical double layer and suggests that molecules present in basil oil blocking the metal surface by their adsorption at the metal/solution interface [32]. The highest inhibitor efficiency of 89.4% which was calculated from the equation (6) was observed in the presence of 5.7 g L^{-1} of basil oil and these results are in good agreement with those obtained from potentiodynamic polarization method.

3.5. Explanation for inhibition

The inhibitory action of *Ocimum basilicum* L. oil is due to the presence of linalool (chemical composition of oil is given in section 2.1.), which is the major component of this oil (65%). Linalool (2,6-dimethyl-2,7-octadien-6-ol) is a naturally occurring terpene alcohol found in many flowers and spice plants with many commercial applications [33]. As we previously obtained and reported [34,35] that plants whit linalool in their composition (*Lavandula angustifolia* L. and *Laurus nobilis* L. essential oils) showed excellent inhibition properties for pitting corrosion of aluminium alloy, we assume that *Ocimum basilicum* L. oil could be a good inhibitor especially in acidic solution. As discussed above the thermodynamic and kinetic parameters, the adsorption is mainly electrostatic. The adsorption based on pure electrostatic interaction is fast and reversible because of the low activation energy. Besides the fact that linalool molecules could be protonated in the acid solution, they also contain oxygen atom in O–H functional group and double bonds in their structure which are the major characteristic for typical corrosion inhibitors [36].

As it is known, physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution. The chloride ions can be specifically adsorbed on the metal surface [37], so this ions can improve adsorption of the organic cations in solution by forming intermediate bridges between the metal surface and the protonated inhibitor molecule. Corrosion inhibition synergism thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions. In view of the above the adsorption mechanism may occur as follows: firstly, the acid anions (Cl^-) adsorb electrostatically on the positively charged oxide-metal surface, giving rise for a net negative charge on the metal surface; secondly, the organic cations are physically attracted to the anions layer which is formed on the metal surface (cathodic area), forming electrostatic protective layer on aluminium.

4. CONCLUSIONS

Ocimum basilicum L. oil acts as good inhibitor for aluminium corrosion in 0.5 M HCl solution. Inhibition efficiency increases with the inhibitor concentration, but decreases with increasing temperature. Thermodynamic adsorption parameters show that the inhibitor under investigation is adsorbed on aluminium surface by an exothermic process, indicating that the adsorption mechanism of

compounds present in basil oil on aluminium in 0.5 M HCl solution at the temperatures studied is physisorption. Potentiodynamic polarization curves for aluminium in 0.5 M HCl solution show that presence of basil oil cause a prominent decrease in current densities, and shift the E_{corr} values to more cathodic direction. This behavior of the inhibitor can be explained on the basis of the fact that in acidic solution, basil oil components largely exist in the protonated form (especially linalool) and these protonated species are adsorbed on the cathodic site of the aluminium and thereby decrease the hydrogen evolution reaction. R_{ct} values increase prominently, while CPE decrease with the increasing concentrations of basil oil. This confirmed that compact and coherent layer is formed on aluminium surface, acting as a physical barrier thus preventing the localized corrosion attack.

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