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Inhibitive Action of *Anethum graveolens* L. oil on Aluminium Corrosion in Acidic Media

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The inhibition effect of *Anethum graveolens* L. essential oil on the corrosion of aluminium in 1 M hydrochloric acid solution was investigated by weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods. Inhibition efficiency increased with increasing oil concentration, but decreased with temperature. The adsorption of *Anethum graveolens* L. essential oil obeys Langmuir adsorption isotherm. Polarization curves show that *Anethum graveolens* L. essential oil in acidic medium behaves as cathodic inhibitor. The Nyquist plots showed that on increasing the inhibitor concentration, the charge transfer resistance increased, confirming the adsorption process mechanism. Values of inhibition efficiency obtained from weight loss and electrochemical measurements are in good agreement.

Keywords: *Anethum graveolens* L., corrosion inhibition, aluminium, acidic media.

1. INTRODUCTION

It is well known that a compact, strongly adherent and continuous film is developed on aluminium upon exposure to the atmosphere or aqueous solutions. This film is responsible for the corrosion resistance of aluminum in most environments [1,2].

Nevertheless, aluminum may be exposed to high concentrations of acids, especially hydrochloric acid which are used for pickling, chemical and electrochemical etching of aluminium. These solutions dissolve the passive film and under these circumstances, corrosion inhibitors should be used. Corrosion inhibitors are chemical compounds usually used in small concentrations which are added to aggressive medium to reduce corrosion. Corrosion inhibition occurs *via* adsorption of their molecules on the corroding metal surface and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular conditions [3].

The protection of aluminium and its oxide film against the corrosive action of acids has been extensively investigated and a great number of inhibitors have been studied [4-8].

In the recent years, there is an increasing awareness of environment and development of a new branch of chemistry so called green chemistry. Therefore, many studies were conducted to use as corrosion inhibitors the environmental friendly substances, instead of harmful synthetic chemicals.

In the 21st century, the research in the field of green or eco-friendly corrosion inhibitors has been addressed to plant extracts [9-12]. The inhibition performance of plant extracts is ascribed to the presence of complex organic species in their composition including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products. These organic compounds usually contain polar functions with nitrogen, sulphur or oxygen atoms as well as triple or conjugated double bonds or aromatic rings, which act as the major adsorption centres. Recently, we have reported the corrosion inhibition ability of *Lavandula angustifolia* L. for Al-3Mg corrosion in neutral medium [13]. This study is a continuation of the research of inhibiting effects of aromatic plants of Mediterranean origin.

Dill (*Anethum graveolens* L.) is a green leafy medicinal and aromatic plant belonging to *Apiaceae* (*Umbelliferae*) family widely used as spice and medicine. It has been reported that it is a possible source of antioxidant compounds and also has anti-microbial properties [14].

The goal of this research was to investigate the effects of *Anethum graveolens* L. essential oil as complex system on corrosion of aluminium in 1 M HCl solution. The investigation of corrosion parameters was performed by weight loss and electrochemical measurements (potentiodynamic polarization and electrochemical impedance spectroscopy).

2. EXPERIMENTAL METHODS

2.1. Materials

Corrosion tests were performed using coupons prepared from 99.85% pure aluminium. The other components (wt %) were: Fe 0.08, Si 0.06 and Cu 0.001. Aluminium was mechanically press-cut into coupons of dimension 2 cm × 2 cm × 0,5 cm. The sample surface was abraded with emery paper to an 800 metallographic finish, rinsed with distilled water and dried in acetone.

The aggressive acid solutions were made from analytical grade hydrochloric acid (HCl). Appropriate concentration of acid (1 M) was prepared by using deionised water and used in absence and presence of inhibitor concentration. Pure 100% *Anethum graveolens* L. essential oil was provided by “Aromara, Zagreb”. The stock solution of oil was prepared by dissolving it in ethanol as 30% (v/v) solution which was used as inhibitor. A specific volume was taken from the stock solution and added directly to 1 M HCl solution to prepare the desired concentrations in range from 20 ppm to 300 ppm (v/v). The density of oil is 0.892 g cm^{-3}.

2.2. Weight loss measurements

In each experiment, the cleaned aluminium coupon was weighed and suspended in a beaker containing 100 mL test solution with the aid of glass rod and hook. The temperature was controlled using a thermostat. All the aggressive acid solutions were open to air. The immersion time for the weight loss test was 3 h at 25 °C, 40 °C, 60 °C and 75 °C in non-de-aerated test solutions. The coupon was then taken out from the test solution, washed with distilled water, dried and re-weighed.

The corrosion rate (W) and the inhibition efficiency η_w (%) were calculated from equations (1) and (2):

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

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

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.

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

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

where θ is the surface coverage.

2.3. Potentiodynamic polarization and EIS measurements

Potentiodynamic polarization measurements and electrochemical impedance spectroscopy studies (EIS) were carried out in a conventional three electrode cylindrical glass cell containing 500 mL of electrolyte at 298 K under atmospheric conditions. All measurements were performed using a potentiostat type VersaSTAT 3 (Princeton Applied Research), controlled by a personal computer.

A saturated calomel electrode (SCE) and graphite electrode were used as reference and auxiliary electrodes, respectively. The working electrode (WE) cut from aluminium was mounted in Teflon holder so that exactly 1 cm^2 area was exposed to corrosive solution. In order to minimize ohmic contribution, the Luggin capillary was placed close to the working electrode.

Before measurements the working electrode was abraded successively on test face with emery paper to an 800 metallographic finish, and then the metal surface was rinsed with distilled water, dried in acetone and finally dipped into the electrolytic cell. Each experiment was repeated at least three times to check the reproducibility. The electrochemical measurements were performed in the test solution after reaching the open-circuit potential (E_{ocp}). Potentiodynamic polarization studies were performed at scan rate of 0.4 mV s^{-1} in the potential range from ±150 mV with respect to the E_{ocp}. All reported potentials refer to SCE.

In the case of electrochemical measurements, equation (4) was used to determine the inhibition efficiency:

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

where I_{corr} and I'_{corr} are the corrosion current densities in the absence and presence of inhibitor to be determined by the intersection of the extrapolated cathodic Tafel lines at the experimentally measured open-circuit potential, and corrosion potential (E_{corr}), respectively.

Electrochemical impedance spectroscopy (EIS) measurements were carried out at the open circuit potential 30 minute after the electrode had been immersed in the test solution. EIS were performed in the frequency range from 100 kHz to 30 mHz with an a.c. voltage amplitude perturbation of 10 mV with five data points per decade.

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

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

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

3. RESULTS AND DISCUSION

3.1. Weight loss measurements, adsorption isotherm and effect of temperature

The values of inhibition efficiency η_w%, corrosion rate and surface coverage obtained from weight loss measurements with the addition of different concentrations of *Anethum graveolens* L. essential oil after 3 h immersion in 1 M HCl solutions at 298 K are summarized in Table 1. It can be seen from Table 1 that the used dill oil inhibit the corrosion rate of aluminium in 1 M HCl solution at all concentrations investigated. The corrosion rate values (mg cm^{-2} h^{-1}) decrease as *Anethum graveolens* L. oil concentration increases, i.e., corrosion inhibition efficiency enhances with the increase of inhibitor concentration. The maximum η_w% is reached with addition of 300 ppm dill oil (96.9 %), although the addition of only 20 ppm causes significant inhibition efficiency (78.5 %), which indicates that *Anethum graveolens* L. essential oil acts as a very good inhibitor for aluminium in 1 M HCl solution.

Table 1. Corrosion rate and inhibition efficiency data obtained from weight loss measurements for aluminium in 1 M HCl solution in the absence and presence of different concentrations of *Anethum graveolens* L. oil at 298 K, after 3 h immersion time.

c (ppm)	W (mg cm^{-2} h^{-1})	θ	η_W (%)
0	0.466	-	-
20	0.1002	0.785	78.5
50	0.0806	0.827	82.7
100	0.0601	0.871	87.1
150	0.0438	0.906	90.6
200	0.0288	0.938	93.8
250	0.0223	0.952	95.2
300	0.0144	0.969	96.9

Anethum graveolens L. essential oil contains mainly carvone (76 %) and limonene (18 %) and their molecular structures are given in Fig.1. From the inspection of carvone molecule, we assume that these molecules can be adsorbed on the metal surface *via* the lone pairs of electrons of an oxygen atom, while limonene molecules can be adsorbed on the basis of interactions between π-electrons of double bonds in aromatic ring and vacant p-orbitals of Al [3,7]. The adsorption of these compounds on aluminium surface reduces the surface area that is available for the attack of the aggressive chloride ions, (Cl^-) from the aggressive solution.

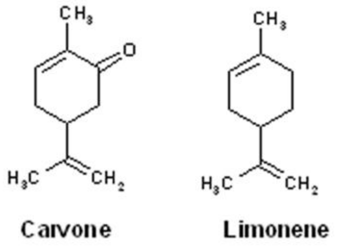

Figure 1. Molecular structures of the main components of *Anethum graveolens* L. essential oil.

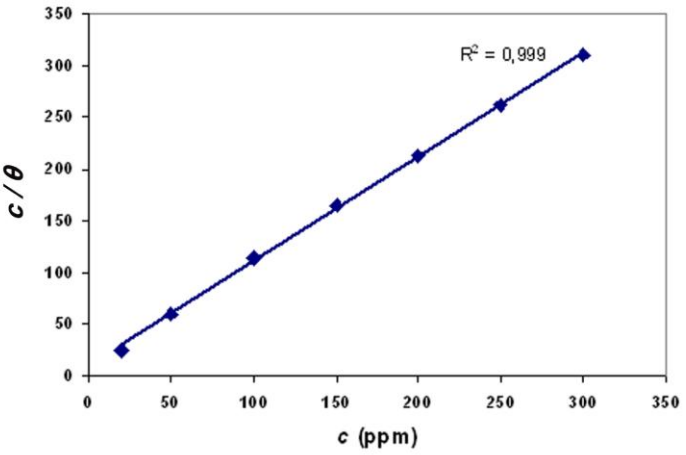

Figure 2. Langmuir adsorption isotherm for *Anethum graveolens* L. essential oil on aluminium in 1 M HCl solution at 25°C.

Basic information on the interaction between the inhibitor molecules and metal surface could be provided from the adsorption isotherms, i.e. the relationship between surface coverage θ and the bulk concentration of the inhibitor at constant temperature [15]. Attempts were made to fit θ values to various isotherms including Frumkin, Temkin, Langmuir and Freundlich isotherm. When surface coverage is plotted against dill oil concentration (c / θ), a straight line with almost unit slope is obtained (R^2=0.999), as shown in Fig. 2.

This behaviour suggests that the dill oil compounds adsorbed onto the aluminium surface follow the Langmuir adsorption isotherm expressed as (6):

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

where K represents the equilibrium constant for the adsorption/desorption process of the inhibitor molecules on the metal surface [15,16]. A Langmuir isotherm assumes that the solid surface contains a fixed number of adsorption sites and each hold one adsorbed species but there is no interaction between the adsorbed molecules [5].

For better understanding adsorption process of active molecules from dill oil on aluminium surface in acidic media, weight loss measurements were done in the temperature range of 298–348 K. Two concentrations of dill oil were investigated, namely 100 ppm and 300 ppm during 3 h immersion time. The variation of inhibition efficiency with temperature is given in Fig. 3.

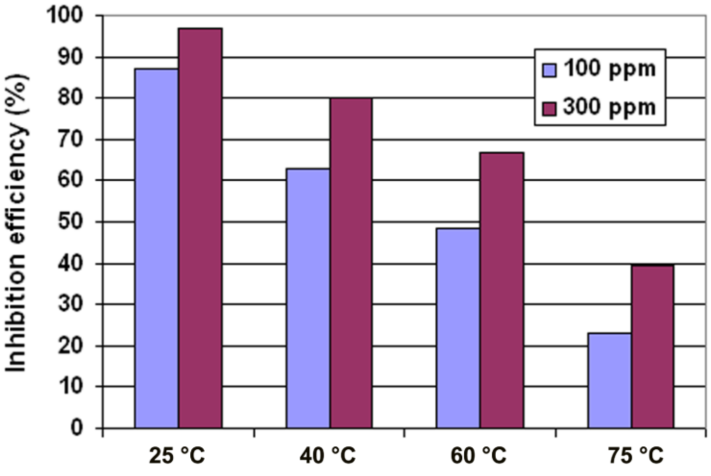

Figure 3. Inhibition efficiency (%) of *Anethum graveolens* L. essential oil on aluminium corrosion in 1 M HCl solution at different temperature obtained by weight loss method.

The results revealed that, on increasing temperature, there is a decrease in inhibition efficiency. The effect of temperature on the inhibited acid-metal reaction is very complex. Many changes such as rapid etching desorption of inhibitor, as well as inhibitor decomposition occur on the metal surface. Generally, the metallic corrosion in acidic media is accompanied by the evolution of hydrogen gas, and rise in the temperature usually accelerates the corrosion reactions resulting in higher dissolution rate of the metal. A decrease in inhibitor efficiency with temperature can be attributed to the increased desorption of inhibitor molecules from the aluminium surface at elevated temperature suggesting a physical adsorption mode [17].

The reduction of corrosion inhibition efficiencies by increasing the temperature may be due to thermal degradation of its organic content. Although inhibition efficiency decreases with temperature, the values of η_w% at 75°C are quite high, 23 % and 40 %, for 100 ppm and 300 ppm, respectively. These results confirm that *Anethum graveolens* L. oil components act as efficient inhibitors in the range temperature studied.

3.2. Potentiodynamic polarization

Potentiodynamic polarization curves for aluminium in 1 M HCl solution with various concentrations of *Anethum graveolens* L. oil at 298 K are shown in Fig. 4. The presence of inhibitor causes a remarkable decrease in current density values. In acidic solutions, concentration of H^+ ions is sufficiently high and oxygen is eliminated from the solution, therefore the main anodic reaction is the dissolution of aluminium in the form of Al^{3+} aqueous complexes and their passage from the metal surface into the solution. Meanwhile the main cathodic reaction is a reduction of hydrogen ions and evolution of hydrogen gas [18]. The inhibitor may affect either the anodic or the cathodic reaction, or both.

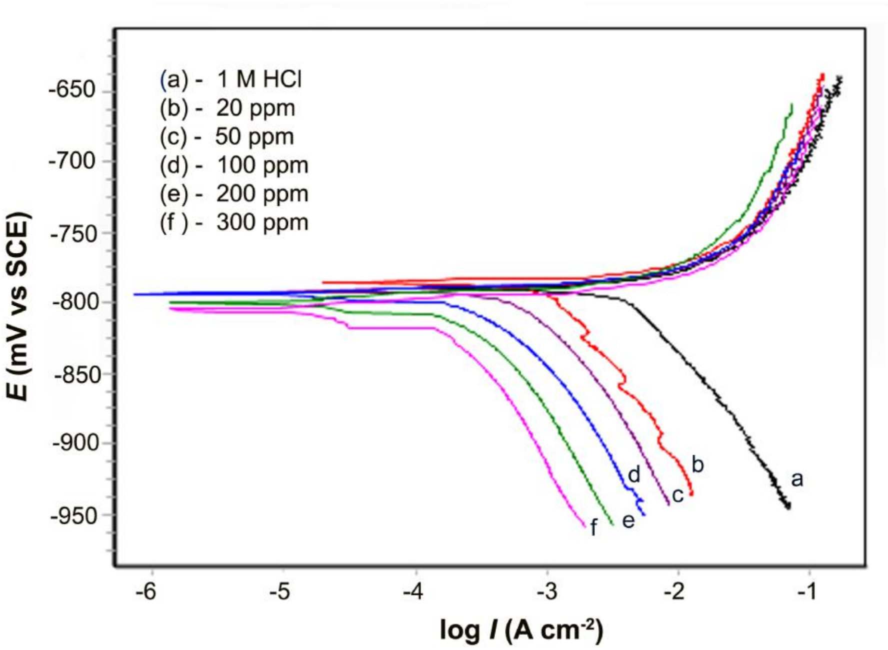

Figure 4. Potentiodynamic polarization curves for aluminium in 1 M HCL solution in the absence and presence of various concentrations of *Anethum graveolens* L. oil at 298 K.

Inspection of Fig. 4 indicates that the addition of the dill oil reduces only the cathodic current density. The suppression of cathodic process can be due to the surface covered with monolayer of the dill oil molecules investigated i.e. due to the adsorbed inhibitor molecules [3]. The form of anodic polarization curves for aluminium in the presence of the inhibitor resembles the curve obtained in a pure 1 M HCl solution. This means that active molecules from dill oil do not affect anodic metal dissolution.

Parameters including corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c), surface coverage (θ) and the inhibition efficiency (η_p) are listed in Table 2.

Since the plateau of anodic currents were invisible, the corrosion current density values in the presence and the absence of inhibitor in HCl solutions were determined by the extrapolation of cathodic Tafel slopes to the respective corrosion potentials. It is clearly seen that the corrosion current density values decrease considerably with increasing oil concentrations (8.47 mA cm^{-2} for uninhibited solution and 0.168 mA cm^{-2} with addition of 300 ppm dill oil), probably because of the formation of a barrier film on aluminium surface, while inhibition efficiency values increase with oil concentration and the maximum is up to 98% for addition of 300 ppm *Anethum graveolens* L. oil.

Compared to the uninhibited solution in the presence of *Anethum graveolens* L. oil, the E_{corr} values shifted towards more negative direction, and these results suggest that the hydrogen evolution reaction is retarded. Therefore, this oil could be classified as cathodic inhibitor [19].

Table 2. Potentiodynamic polarization parameters obtained for aluminium in 1 M HCl solution in absence and presence of different concentration of *Anethum graveolens* L. oil at 25 °C.

c (ppm)	E_{corr} (mV_{SCE})	I_{corr} (mA cm^{-2})	$-b_c$ (mV dec^{-1})	θ	η_p (%)
0	-790	8.475	130	-	-
20	-785	1.477	123	0.826	82.6
50	-792	0.973	121	0.885	88.5
100	-793	0.539	128	0.936	93.6
150	-797	0.472	127	0.944	94.4
200	-800	0.343	125	0.959	95.9
250	-801	0.295	132	0.965	96.5
300	-804	0.168	136	0.980	98.0

Table 2. shows that the cathodic Tafel slopes (b_c) are almost unchanged upon addition of the inhibitor and are slightly greater (around -130 mV dec^{-1}) than that expected for H_2 evolution according to the Volmer-Tafel mechanism (-118 mV dec^{-1}) [20]. This suggests that aluminium electrode is covered with Al oxide and presence of the oxide film can markedly influence the surface reduction process, by imposing a barrier to charge transfer through the oxide film. The fact that b_c values are almost equal in unhibited and inhibited solutions suggests that the inhibitor simply blocks the electrode surface without changing the mechanism of aluminium corrosion [21].

3.3. Electrochemical impedance spectroscopy (EIS)

The effects of different concentrations of *Anethum graveolens* L. oil on the impedance behaviour of aluminium in 1 M HCl solution at 298 K have been studied and corresponding Nyquist plots are given in Figure 5. As can be seen from Fig. 5, the impedance spectra consist of a large capacitive loop at high frequencies followed by a large inductive loop at low frequencies, but only for inhibitor concentration in the range from 20 ppm to 100 ppm. Furthermore, at concentrations higher than 100 ppm of *Anethum graveolens* L. oil inductive loop in the Nyquist plots completely disappears, which indicates prevention of local corrosion [22]. From this observation conclusion can be made that if the dill oil concentration is > 100 ppm, a compact and coherent layer is formed on aluminium surface, acting as a physical barrier to prevent the localized corrosion attack of the hydrochloric acid solution.

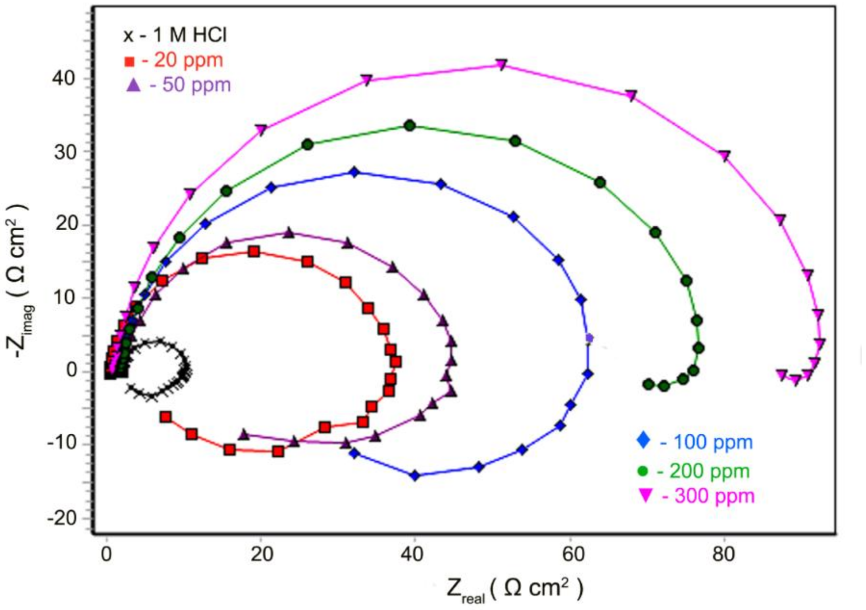

Figure 5. Nyquist plots for aluminium in 1 M HCl solution without and with presence of different concentrations *Anethum graveolens* L. oil at 298 K.

The capacitive loop at high frequencies is usually related to the charge transfer of the corrosion process and double layer behaviour, and according to some authors [23,24] the high frequency capacitive loop could be also attributed to the oxide layer on aluminium surface. So, this loop can be correlated with dielectric properties of formed [metal-oxide-hydroxide-inhibitor]$_{ads}$ complex. The low frequency inductive loop is quite common for aluminium in hydrochloric acid solutions [3,6,25]. Thus the inductive loop may be determined by the relaxation process of hydrogen and Cl$^-$ adsorption, and Al dissolution.

Some authors [26,27] confirmed that the inductive loop is closely related to the existence of a passive film on aluminium, while the other [28] suggest that inductive behaviour is characteristic of the pitted active state and is attributed to the surface area modulation.

The spectra show that the impedance changes rapidly with the change in inhibitor concentrations, e.g. the recorded impedance values increase with increasing the inhibitor concentration indicating that the metal surface is more protected [29].

According to an ac circuit theory, an impedance plot obtained for an electrochemical system can be correlated to one or more equivalent circuits. The EIS data were analyzed by fitting to the equivalent circuit model shown in Fig. 6a (blank solution and solution with inhibitor concentrations in range from 20 ppm – 100 ppm) and 6b (solution with inhibitor concentrations in range from 150 ppm – 300 ppm).

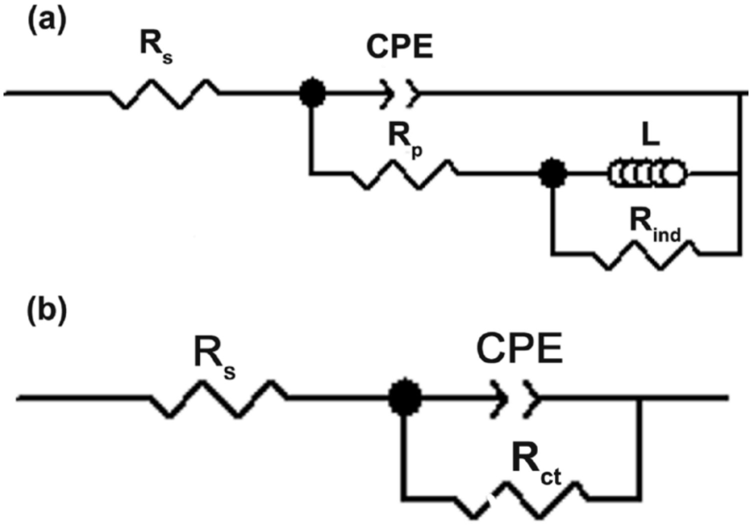

Figure 6. The equivalent circuit used to simulate the impedance data.

The circuit from Fig. 6a is previously reported [6,8,22] for aluminium and in this equivalent circuit, R_s is the solution resistance, *CPE* is a constant phase element and R_p is the polarization resistance. R_{ind} and L represent the inductive element. The charge transfer resistance R_{ct} correspond to the sum of R_p and R_{ct}. Noticeably, capacitive loops are not perfect semicircles which can be attributed to the frequency dispersion as result of the roughness and inhomogenity of electrode surface, so *CPE* was used instead of an ideal capacitor [30]. The impedance, $Z_{CPE,}$ of *CPE* is described by the expression (7):

$$Z_{CPE} = A^{-1}(i\omega)^{-n} \qquad (7)$$

where the coefficient A is a combination of properties related to the both the surface and electroactive species. When the values of n is close to 1, the CPE behaves like an ideal capacitor [28,31].

The calculated equivalent circuit parameters for aluminium in 1 M HCl solution containing different concentrations of dill oil are presented in Table 3.

Table 3. Electrochemical impedance parameters and the corresponding inhibition efficiencies for aluminium in 1 M HCl solution in the absence and in presence of different concentrations of *Anethum graveolens* L. oil at 298 K.

c (ppm)	R_s (Ω cm^2)	R_p (Ω cm^2)	CPE (μF cm^{-2})	n	R_{ind} (Ω cm^2)	L (H cm^2)	R_{ct} (Ω cm^2)	η_{eis} (%)
0	1.73	0.75	495.6	0.989	7.32	9.93	8.07	-
20	0.38	4.31	115.8	0.953	30.38	19.3	34.69	76.7
50	1.78	10.21	96.4	0.907	31.29	35.9	41.50	80.6
100	1.33	15.69	67.2	0.910	43.78	42.4	59.47	86.4
150	0.37	-	61.3	0.922	-	-	65.24	87.6
200	1.59	-	53.5	0.935	-	-	74.70	89.2
250	1.12	-	51.2	0.948	-	-	78.12	89.7
300	0.90	-	43.6	0.917	-	-	91.76	91.2

Inspection of Table 3. reveals that R_{ct} values increase prominently with increasing dill concentrations, while *CPE* values decrease. The highest inhibitor efficiency which was calculated from the equation (6) was observed in the presence of 300 ppm of dill oil (91 %). A comparison of the inhibiting efficiencies obtained from weight loss method and using a.c. and d.c. methods shows that acceptable agreement is achieved.

It must be noted that all the studied systems give n values close to 1, indicating the predominance of capacitive behaviour. The increase of charge transfer resistance R_{ct} values and decrease of *CPE* values with increasing inhibitor concentrations suggests the formation of a protective layer on electrode surface. This layer acts as a barrier for mass and charge transfer [32].

3.4. Mechanism of corrosion inhibition

In the present study, from the previously reported results and from the molecular structures of main constituents of *Anethum graveolens* L. essential oil (carvone and limonene), two modes of adsorption process could be suggested to explain the inhibitory action of *Anethum graveolens* L. essential oil on aluminium corrosion in 1 M HCl solution. Thus, in aqueous acidic solutions, carvone molecules exist either as neutral molecules or in the form of protonated species (cations), while limonene molecules exist as neutral species.

In one mode, the neutral molecules may be adsorbed on the metal surface through the chemisorption, involving the displacement of water molecules from the metal surface and the sharing electrons between the oxygen atoms and aluminium. These molecules can also be adsorbed on the metal surface on the basis of donor–acceptor interactions between π-electrons of double bonds in aromatic ring and vacant p-orbitals of Al [33].

Physical adsorption depends on the electric charge of the metal surface and the type of charged species in the solution. According to the literature data [34] it is evident that aluminium surface is positively charged at pH 1, which is the pH value of HCl solution that was used in this investigation. In acidic media active molecules from *Anethum graveolens* L. oil exist in the form of protonated species and also as neutral molecules, therefore it is difficult for the protonated compounds to approach the positively charged aluminium surface due to the electrostatic repulsions. Since chloride ions have a smaller degree of hydration and being specifically adsorbed [35], the anodic dissolution of Al in hydrochloric acid follows the steps (8) and (9):

$$Al+Cl^{-} \leftrightarrow AlCl^{-}_{ads} \tag{8}$$

$$AlCl^{-}_{ads}+Cl^{-} \leftrightarrow AlCl^{+}_{2}+3e^{-} \tag{9}$$

Chloride ions present in the test solutions facilitate adsorption of protonated inhibitor species by forming intermediate bridges between the metal surface and the inhibitor, thus the reaction shown by step (9) can be prevented. It is noteworthy that such protonated species are often adsorbed on the metal surface at the cathodic sites and hence retard the hydrogen evolution reaction [36,37], which is probably responsible for the pronounced cathodic inhibiting effect of *Anethum graveolens* L. essential oil at 25 °C.

If we assume that the adsorption phenomenon is only made by carvone and limonene as the principal constituents of the *Anethum graveolens* L. oil, then it is clear that initial step of inhibition of aluminium acidic corrosion by this oil is due to adsorption of these molecules on metal surface, especially at higher inhibitor concentration (>100 ppm).

However, *Anethum graveolens* L. oil must be considered as a mixture of inhibitors in which its constituents may act synergistically to retard aluminium corrosion in hydrochloric acid solution.

4. CONCLUSIONS

Anethum graveolens L. oil acts as good inhibitor for aluminium corrosion in 1 M HCl solution. The inhibition action of this essential oil can be attributed to the adsorption of organic compounds present, mainly carvone and limonene. The adsorption behaviour can be described by the Langmuir adsorption isotherm. The results of potentiodynamic measurements revealed clearly that *Anethum graveolens* L. oil is a good cathodic inhibitor for aluminium corrosion in acidic solutions. The inhibition efficiency increases with increased oil concentration and decreases with increased temperature. From the EIS measurements is evident that the increase of *Anethum graveolens* L. oil concentration increases the charge transfer resistance, while at concentrations higher than 100 ppm of *Anethum graveolens* L. oil inductive loop in the Nyquist plots completely disappears, which indicates prevention of local corrosion. From these observations it can be concluded that if the dill oil concentration is > 100 ppm, a compact and coherent layer is formed on aluminium surface, acting as a physical barrier to prevent the localized corrosion attack of the hydrochloric acid solution.

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References

1. L. Young, Anodic Oxide Films, Academic Press, New York, 1961, pp. 4–9.
2. M. Pourbaix, in 'Atlas of Electrochemical Equilibria in Aqueous Solutions', Pergamon Press, New York, (1966).
3. K. F. Khaled, M.M. Al-Qahtani, *Mater. Chem. Phys.*, 113 (2009) 150.
4. S.A. Umoren, Y. Li, F.H. Wang, *J. Solid. State. Electrochem.*,14 (2010) 2293.
5. *I.B. Obot,, N.O. Obi-Egbedi, S.A. Umoren, Int. J. Electrochem. Sci.,* 4 (2009) 863.
6. A. Yurt, S. Ulutas, H. Dal, *Appl. Surf. Sci.*, 253 (2006) 919.
7. J. Halambek, M. Jukić, K Berković, J. Vorkapić-Furač, *Int. J. Electrochem. Sci.*, 7 (2012) 1580.
8. M. Metikoš-Huković, R Babić, Z Grubač, *J. Appl. Electrochem.*, 32 (2002) 35.
9. I. Radojčić, K. Berković, S. Kovač, J. Vorkapić-Furač, *Corros. Sci.* 50 (2008) 1498.
10. I.B. Obot, N.O. Obi-Egbedi, *Int. J. Electrochem. Sci.*, 4 (2009) 1277.
11. X-H. Li, S-D. Deng, H. Fu, *J. Appl. Electrochem.*, 40 (2010) 1641.
12. T. H. Ibrahim, M. A. Zour, *Int. J. Electrochem. Sci.*, 6 (2011) 6442.
13. J. Halambek, K. Berković, J. Vorkapić-Furač, *Corros. Sci.*, 52 (2010) 3978.
14. M. Solouki1, S. B. Hoseini1, B. A. Siahsar, A. Tavassoli, *Afr. J. Biotech.*, 11 (2012) 3649.
15. Z. Tao, S. Zhang, W. Li, B. Hou, *Corros. Sci.*, 51 (2009) 2588.
16. O. K. Abiola, J.O.E. Otaigbe, *Corros. Sci.*, 51 (2009) 2790.
17. F. Bentiss, M. Lebrini, M. Lagrenee, *Corros. Sci.*, 47 (2005) 2915.
18. M. Šeruga, D. Hasenay, *J. Appl. Electrochem.*, 31 (2001) 961.
19. A. Yurt, Ozlem Aykın, *Corros. Sci.*, 53 (2011) 3725.
20. J. M. Bockris, A.K.N. Reddy, Modern Electrochemistry, Vol. 2 , Plenum Press, New York, (1974).
21. S.S. Abd El Rehim, H.H. Hasan, M.A. Amin, *Mater. Chem. Phys.*, 78 (2002) 337.
22. M. Kliškić, J. Radošević, S. Gudić, V. Katalinić, *J. Appl. Electrochem.*, 30 (2000) 823.
23. J. Bessone, C. Mayer, K. Jutter, W. Lorenz, *Electrochim. Acta*, 28 (1983) 171.
24. C. M.A. Brett, *Corros. Sci.*, 33 (1992) 203.
25. Q. Zhang, Y. Hua, *Mater. Chem. Phys.*, 119 (2010) 57.
26. G.T. Burstein, R.J. Cinderey, *Corros. Sci.*, 32 (1991) 1195.
27. R.J. Cinderey, G.T. Burstein, *Corros. Sci.*, 33 (1992) 475.
28. J.B. Bessone, D.R. Salinas, C. Mayer, M. Ebert, W.J. Lorenz, *Electrochim. Acta*, 37 (1992) 2283.
29. E.A. Noor, *Mater. Chem. Phys.*, 114 (2009) 533.
30. M. Lebrini, M. Langreneé, H. Vezin, M. Traisnel, F. Bentis, *Corros. Sci.* 49 (2007) 2254.
31. Z. Stoynov, *Electrochim. Acta*, 35 (1990) 1493.
32. S. Şafak, B. Duran, A. Yurt, G. Tűrkoğlu, *Corros. Sci.* 54 (2012) 251.
33. E. I. Atinga, S. A. Umoren, I. I. Udousoro, E. E. Ebenso, A. P. Udoh, *Green Chem. Lett. Rev.*, 3 (2010) 61.
34. E.A. Noor, *J. Appl. Electrochem.*, 39 (2009) 1465.
35. X. Li, S. Deng, H. Fu, *Corros. Sci.*, 53 (2011) 1529.
36. H. Ashassi-Sorkhabi, D. Seifzadeh, M.G. Hosseini, *Corros. Sci.*, 50 (2008) 3363.
37. El-Sayed, M. Sherif, *Int. J. Electrochem. Sci.*, 6 (2011) 1479.