J. Mater. Environ. Sci. 7 (5) (2016) 1751-1758
ISSN : 2028-2508
CODEN: JMESC

Study of corrosion inhibition by Electrochemical Impedance Spectroscopy method of 5083 aluminum alloy in 1M HCl solution containing propolis extract

H. Hachelef [1], A. Benmoussat[1], A. Khelifa[2], D. Athmani[3], D. Bouchareb[2]

1Materials and Corrosion Equip of LAEPO Research Laboratory - Tlemcen University –Algeria

2 Research laboratory of processes Genius, Department of Industrial Chemistry, Faculty of Technology, Saâd Dahlab University of Blida ,BP 270, 09000, Blida, Algeria

3 Research center of technology Bab Ahcen Algeria

Received 08 Dec 2015, Revised 22 Feb 2016, Accepted 05 Mar 2016
**Corresponding author. E-mail: hachelefhakima@yahoo.fr (H. Hachelef)*

Abstract

The effect of propolis extract on the corrosion inhibition of Al in acid medium was studied. The inhibition studies were carried out on Al in 1 M HCl with the propolis extract using Electrochemical Impedance Spectroscopy (EIS) . Parameters, such as concentration of the inhibitor, temperature were varied and optimized. The results revealed that the increase of the temperature and concentration of acid can decrease the performance of the inhibitor. Thermodynamic parameters demonstrate that the physisorption of the inhibitor molecules on Al surface obeys Langmuir isotherm.

Keywords: Alloy of aluminium; propolis; acid corrosion; inhibition; electrochemical impedance Spectroscopy (EIS)

1-Introduction:

The corrosion inhibition process helps in reducing the safety and economic input of corrosion damage. Each metal is subjected to its own unique corrosion process [1]. Aluminum (Al) is the most reactive metal compared to copper and steel. The significant property of Al is its tendency to form strongly bonded passivating oxide film on its surface. The thickness of the oxide film varies according to temperature..., environment and alloy elements. If the oxide film is damaged by scratch, new oxide film will immediately form on the bare metal. For this reason, it offers excellent resistance to corrosion and provides years of maintenance free service in natural atmosphere. As a result, Al and its alloys are used extensively both in industrial and domestic applications [2]. The corrosion of metals in acid solutions can be inhibited by a wide range of substances, which may be synthetic or natural inhibitors, such as the biomaterials. Synthetic compounds containing multiple bonds and hetero atoms are effective inhibitors, but at the same time the processing time, cost and their toxic nature have compelled the researchers to look for eco-friendly, nontoxic and low cost inhibitors for the corrosion protection of metals. Many corrosion prevention works have been carried out using extracts of various plants as corrosion inhibitors [3-14]. The use of plants' extracts has been found to be viable alternative. The bioactive compounds in the plant extract are as effective as synthetic inhibitors. These bioactive compounds act as inhibitors in acid solution which interact with metals and affect the corrosion reaction in a number of ways, some of which may occur simultaneously. Propolis is a resinous substance prepared by honeybees from buds, leaves and exudates of trees and plants mixed with pollen, wax and enzymes secreted from the bees [2,3]. Some important characteristics have been reported concerning this substance, such as antimicrobial and antioxidant effects, anesthetic properties and others, it found that the propolis extracts represent an important functional product, rich in flavonoids and polyphenols [4.5]. The used raw propolis have been obtained in harvest month of April from the region of Bordj El – Menaiel in septembre 2014 Al alloy behaviour in a hydrochloric acid solution 1 M with and without propolis extract as corrosion inhibitors motivate our research. The objective is to bring a better comprehension of corrosion damage mechanisms and corrosion inhibition using biomaterials for environment in order to reduce pollution. Appropriate models for corrosion parameters, such as corrosion, current density (Icorr), corrosion potential (Ecorr), polarization resistance (Rp), are used to fit the experimental data and extract the parameters which characterize the corrosion process. Electrochemical impedance spectroscopy (EIS) was carried out. We present experimental data obtained by electrochemical measurements by taking cutting Al alloy 5083.

2. Materials and methods

2.1 Materials:

An aluminum alloy (5083) of dimension Rectangular 1cm ^{2} is used as a sample. The chemical compositions of the alloy used are shown below in Table1 determined by spectrometry kind "SPECTROLAB".

Table 1: Chemical composition of the tested aluminum alloy 5083:

	Al	**Mn**	**Si**	**Mg**	**Fe**	**Cu**
%	93.6	0.60	0.139	5.13	0.224	0.142

The cutting process was chosen as it does not alter the microstructure and corrosion test at the coupon surface, due to its low heat input and the absence of mechanical damage by avoiding the zones affected thermically. Pre-treatment of Al samples surfaces was carried out by grinding with emery paper of 600- 1200 grit, rinsing with bidistilled water, and ultrasonic degreasing in acetone and dried at room temperature before us. . All tests have been performed at 30± 1°C.

2.2 Solution preparation

Sample of *propolis* extract shave been obtained in harvest month of April-from the region of Bordj El – Menaiel in Algeria. The extract was prepared by dissolving 20g of propolis in 100 ml of ethanol at 70%. The solution 1M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water. This extract was used to study the corrosion inhibition properties and to prepare the required concentrations. The solution tests are freshly prepared before each experiment. Experiments were carried out in triplicate to ensure the reproducibility

2.2 Electrochemical tests

The electrochemical study was carried out using a potentiostat Autolab brand piloted by Nova 1.7 software~~.~~ connected to a cell with three electrode thermostats and~~-~~double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode have been used as reference and auxiliary electrodes, respectively. The surface area exposed to the electrolyte is 1cm^2.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Autolab 1.7 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

3. Results and discussion:

3.1 Effect of inhibitor concentration:

The impedance spectra for Al 5083 in acidic solution at 298 K with different concentrations of propolis are presented as Nyquist and Bode plots in Fig. 1. The electrochemical impedance parameters derived from these investigations are mentioned in Table 2. The inhibition efficiency got from the charge transfer resistance is calculated by:

$$E_{RT}\% = 100*(R_t\text{-}R_{t0})\ Rt \qquad (1)$$

Were Rt and Rt_0 are the charge transfer resistances in inhibited and uninhibited solutions respectively. The charge transfer resistance (Rt) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [6]. The Nyquist plots of figure 1 show two parts: the capacitive loop in the high-frequency region, the inductive loop in the low-frequency region. The high-frequency capacitive loop can be attributed to the charge transfer resistance (Rt). The inductive loop might have been caused by the adsorbed intermediate complex. Adsorption or desorption equilibrium of surface-active species, or corrosion inhibitors, on a metal surface has also been reported as a possible source of induction in EIS spectra [7]. However, in literatures the inductive loop of aluminum has also been attributed to some other phenomena [8]. For example, it has been referred to surface or bulk relaxation of species in the oxide layer [9]. Cinderey and Burstein's measurements [10–11- 12] confirmed that the inductive loop was closely related to the existence of a passive film on aluminum. The double layer capacitance (C_{dl}) values were obtained at maximum frequency (fmax), at which the imaginary component of the Nyquist plot is maximum and calculated using the following equation:

$$C_{dl}=1/\ 2\ \pi\ f_{max}\ Rt \qquad (2)$$

with C_{dl}: double layer capacitance ($\mu F.cm^{-2}$); f_{max}: maximum frequency (Hz) and R_t: Charge transfer resistance ($\Omega.Cm^2$).

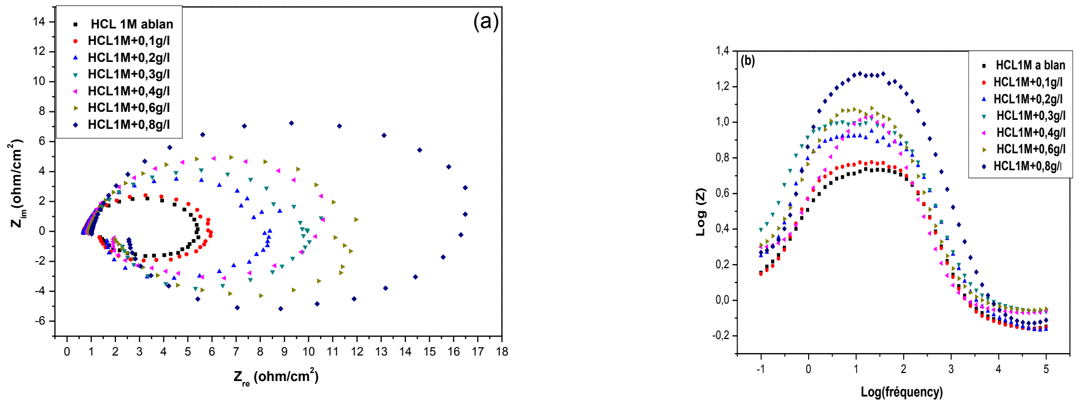

Figure 1: Nyquist (a) and Bod (b) of modul plots of Al in 1 M HCl with and without different concentrations of *propolis* extract at 298 K

Table 2. Impedance parameters for corrosion of aluminum in 1 M HCl in the absence and presence of different concentrations of *propolis extract* at 298 K.

Inhibitor	C(g/l)	Rt ($\Omega.cm^2$)	f_{max}(Hz)	C_{dl} ($\mu F/cm^2$)	E_{Rt} (%)
Blank	0	5.413	202.358	145.37	_
Propolis extract	0.2	8.396	202.368	93.72	35.52
	0.4	10.616	354.64	42.26	49.01
	0.6	11.956	355.65	37.44	54.72
	0.8	16.487	415.14	23.26	67.17

as we perceive in figure 1, impedance diagrams show a semi-circular appearance, indicating a charge transfer process mainly controls the corrosion of aluminium. From the impedance data, we notice an increase in the charge transfer resistance and decrease of the double layer capacitance with increasing inhibitor concentration indicates that the *propolis extract* inhibits the corrosion rate of aluminum by an adsorption mechanism [6].

Therefore, the decrease in the C_{dl} value can be attributed to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules function by adsorption at the metal/solution interface as a consequence of the replacement of water molecules by the inhibitor molecules [13].

3.1.1Mechanism of adsorption:

The adsorption behavior of inhibitor molecule on metal surface can be assessed by several adsorption isotherms, among which the most commonly used ones include Temkin isotherm, Langmuir isotherm, Frumkin isotherm. In order to obtain the isotherm, surface coverage degree (θ), as a function of inhibitor concentration, was calculated by charge transfer resistance values using the following equation [14, 15] :

$$\theta = 1 - R_{t0} / Rt \qquad (3)$$

R_t: charge transfer resistance with inhibitor ($\Omega.Cm^2$), R_{t0} charge transfer resistance without inhibitor ($\Omega.Cm^2$). Attempts were made to fit the values of θ to various isotherms mentioned above and the best fit was obtained using the Langmuir adsorption isotherm, which can be described by the following equation [16–17]:

$$C / \theta = 1/K_{ads} + C_{inh} \qquad (4)$$

where C_{inh} is the concentration of inhibitor in mg L^{-1}, K_{ads} is the adsorptive equilibrium constant in $mg.L^{-1}$, which can be obtained from the intercept of the straight line on the C / θ versus C plot and the related standard free energy of adsorption (ΔG_{ads}) can be estimated
by the following equation [18 ,19 ,20,21, 22]:

$$\Delta G^0{}_{ads} = -RT \ln(55,5K_{ads}) \qquad (5)$$

Figure 2 shows the Langmuir propolis extract adsorption plot on the Al 5083 surface. The plot of
C/θ versus C yielded a straight line with a slope close to 1 and a correlation coefficient of 0.9987, which confirms that the propolis extract adsorption on the Al 5083 surface in HCl solution obeys the Langmuir adsorption isotherm.

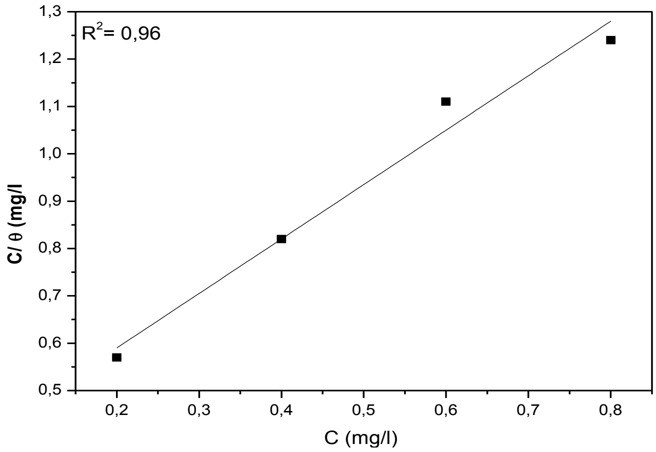

Figure 2: Langmuir adsorption plot for Al 5083 HCL1M containing different concentrations propolis extract from Charge transfer resistance at 298 k.

3.2. Effect of temperature:

In order to study the effect of temperature on the inhibition efficiency of propolis , Charge transfer resistance was carried out in the temperature range 298–333 K, in the presence of propolis at 0.8 g/l . Resulting Charge transfer resistance data are given in table 3. Results presented in table3 showed decreases of values with increasing temperature.

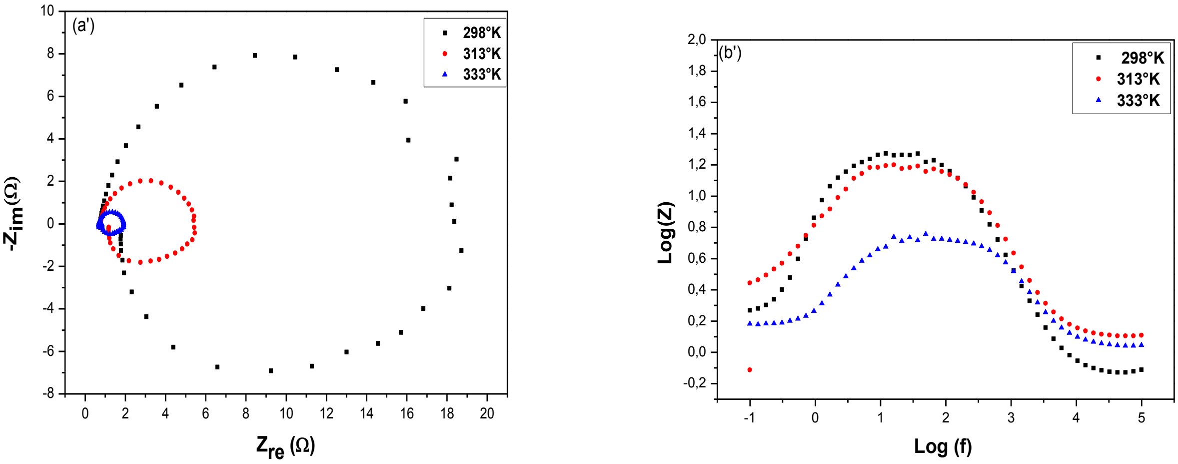

Figure 3: Nyquist and Bod respectively (a) and (b) of modul plots of Al in 1 M HCl with 0.8g/l of inhibitor at different temperatures

Table (3): Impedance parameters for corrosion of aluminum in 1 M HCl in the presence of 0.8 g/l of *propolis extract* at different temperatures.

Temperatures K	**Rt ($\Omega.cm^2$)**	**f_{max}(Hz)**	**C_{dl} ($\mu F/cm^2$)**
298	16.487	415.14	23.26
313	12.189	355.65	36.73
333	5.3040	109.67	273.74

3.2.1. Mechanism of adsorption:

Fig. 4 shows the Langmuir adsorption plot of propolis on the aluminium surface. The plot of C / θ versus C yielded a straight line, which confirms that the adsorption of propolis on the aluminium surface in HCl solution obeys the Langmuir adsorption isotherm. The value of K_{ads} ΔG , ΔH, ΔS were calculated .

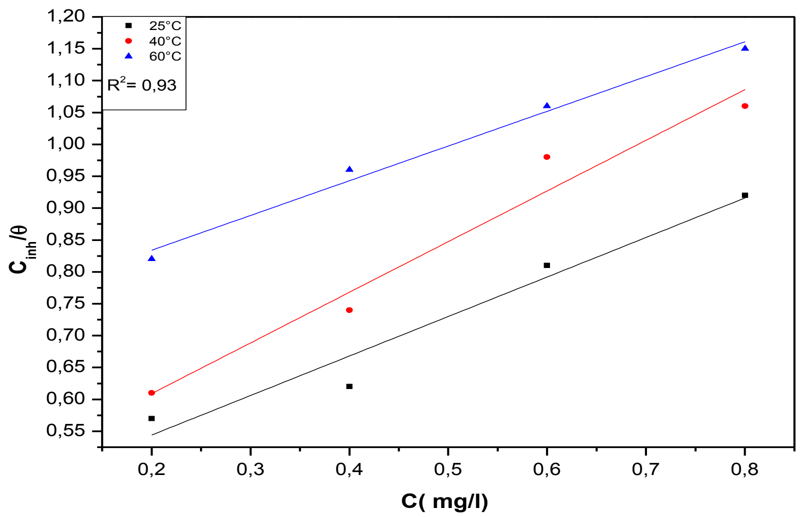

Figure 4: Langmuir adsorption plot for Al 5083 in HCL 1M at different concentrations of *propolis extract* at different temperatures

The negative values of ΔG_{ads} (Table 4) clearly indicated the spontaneous adsorption of propolis extract on Aluminium surface and strong interactions between inhibitor molecules and the metal surface [20, 21]. Generally, the values of ΔG_{ads} up to -20 KJ/mol signify physisorption, which is consistent with electrostatic interaction between charged molecules and a charged metal. The values around - 40 KJ/mol or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [22, 23].

Table 4. Thermodynamics parameters for corrosion of aluminium in 1 M HCl at different temperatures.

Temperatures K	K_{ad}	Δ G (kJ/mol)	ΔH(kJ/mol)	ΔS (kJ/mol)
298	2.595	-12.314	32.945	-0.149
313	2.222	-12.529		
333	9.523	-17.359		

3.3. Scanning Electron Microscopy (SEM) studies

Corrosion inhibition shown in SEM microscopy (figure 5) indicated that Al alloy shows that the inhibiting effectiveness of the propolis extract varies according to the concentration of the inhibitor; and the immersion time indicates that *propolis extract* inhibits the corrosion rate of aluminum by an adsorption mechanism of the extract on metal surface. These studies supplement the results of EIS measurement.

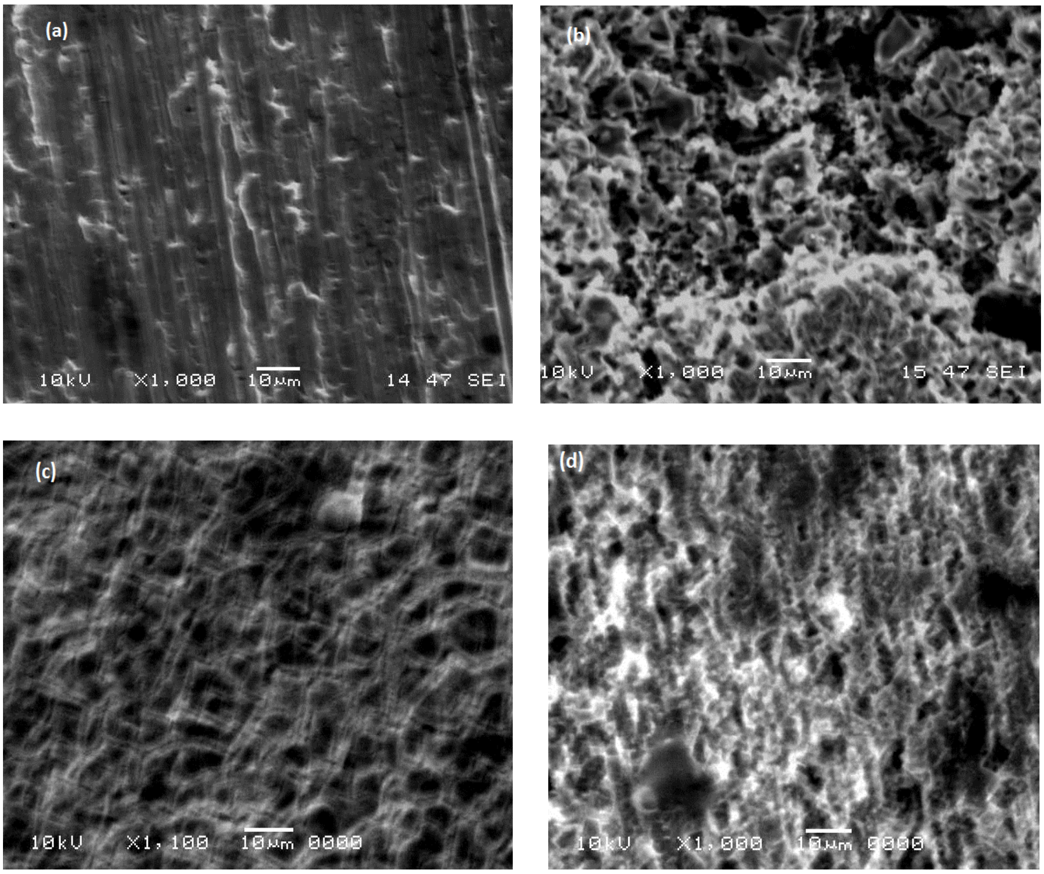

Figure 5 : SEM figures of Al 5083 at different concentration of propolis extract and immersion time, (a) Al 5083 without immersion (b) after 4h immersion in HCL 1M , (c) after 4h immersion in HCL 1M +0.4g/l (d) after 4h immersion in HCL 1M+0.8g/l

Figure (6) below shows the FTIR spectrum of the propolis extract the spectrum shows the existence of a band corresponds to the C_6H_5OH in 3476.2 Cm^{-1} and a band in 2933 Cm^{-1}corresponds to the CH stretching vibration of the methyl group , a band between 1676 Cm^{-1} - 1634 Cm^{-1} corresponds to the CO stretching vibration of aromatic group.

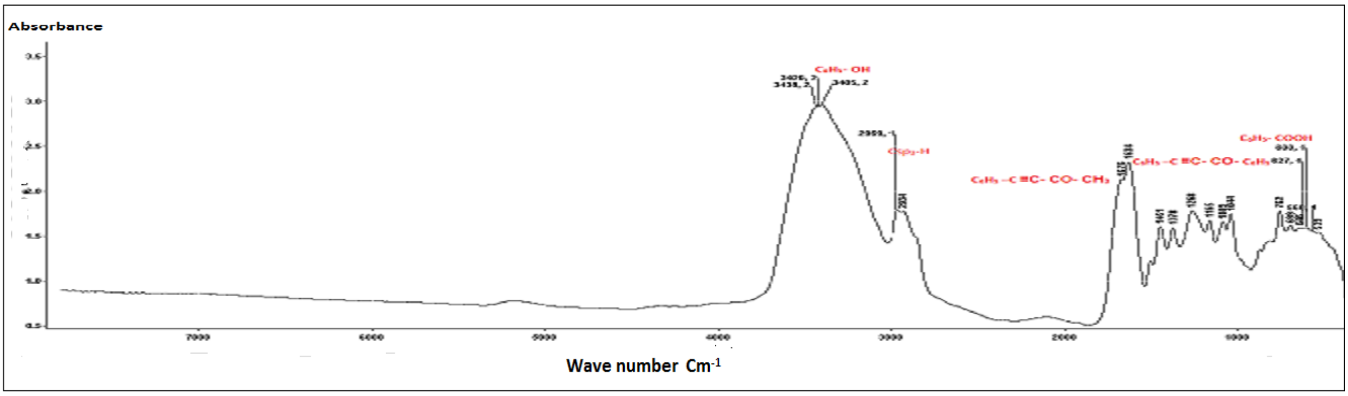

Figure 6: FTIR spectra of propolis extract

Conclusion

- Aluminum alloy behavior in a hydrochloric acid solution 1 M with and without propolis extract as corrosion inhibitors have been carried out using EIS method.
- Results of EIS measurement reveals that charge transfer resistance increases with increase in concentration of propolis extract, indicating that the inhibition increases with increase in concentration.
- Charge transfer resistance from EIS measurement decreases with increase of the temperature, which confirms that the adsorption of propolis on the aluminum surface in HCl solution obeys the Langmuir adsorption isotherm.
- SEM study confirm that the inhibition of corrosion Al 5083 is through adsorption of the extract on surface of metal and these studies also supplement the results of EIS measurement.

Acknowledgements: We would like to express our gratitude to Prof. A. Khelifa, from the Research laboratory of processes Genius, Department of Industrial Chemistry, Faculty of Technology Saâd Dahlab University of Blida for his kind permission to work in his laboratory. We are also profoundly thankful to the members of the Research center of technology Bab Ahcen Algeria for their hospitality and help.

Reference

1. Zenati A., Benmoussat A., *J. Mater. Environ.Sci*. 6 (7) (2015) 1896-1901
2. Krishnaveni K., Ravichandran J., *Nonferrous Met. Soc. China* 24 (2014) 2704−2712
3. Noore A., *Journal of Appl Electrochem*. 39 (2009) 1465−1475.
4. Beatriz C, Mello S , Miriam B. Hubinger D., *Inter. J. Food Sci and Techn*. 47 (2012) 2510–2518.
5. Coral O. et al., *J. Cancer Sci. Ther*. 5 (10) (2013) 1948-5956.
6. Tsuru T., Haruyama S., GijutsuB., *J. Jpn. Soc. Corros. Eng*. 27 (1978) 573
7. Ashassi-Sorkhabi H., Asghari E., *J. Appl. Electrochem*. 40 (2010) 631
8. MetikosHukovic M., Baic R., Grubac Z., *J. Appl. Electrochem*. 32 (2002) 35
9. Freres SE, Stefenel MM, Mayer C., Chierchie T., *J. Appl. Electrochem*. 20 (1990) 996
10. Brustein GT, Cinderey R., *J. Corros. Sci*. 32 (1991) 1195
11. Cinderey RJ, Brustein G.T, *Corros. Sci*. 33 (1992) 499
12. Ladha D.G., Wadhwani P.M., Kumar S., Shah N.K., *J. Mater. Environ. Sci*. 6 (5) (2015) 1200-1209
13. Ogundele G.I., White W.E., *Corros. Sci*. 42 (1986) 71

14. Dan Wang, Bin Xiang, Yuanpeng Liang, Shan Song, Chao Liu, *Corros. Sci*. 85 (2014) 77-86
15. Khadraoui A., Khelifa A., Touafri L., Hamitouche H., Mehdaoui R., *J. Mater. Environ. Sci.* 4(5) (2013) 663-670
16. Mobin M., Mosarrat Parveen,. Rafiquee M.Z.A , *Arabi. J. Chem*., 10 (2013) 1878-5352
17. OngunYuce A., Kardas G., *Corros. Sci.* (58) (2012) 86–94.
18. Pournazari S., Moayed M.H., Rahimizadeh M., *Corros. Sci.* 71 (2013) 20–31
19. Doner A., Sahin E.A, Kardas G, Serindag O., *Corros. Sci*. 66 (2013) 278–284
20. Hegazy M.A , Badawi A.M, Abd El Rehim S.S, Kamel W.M., *Corros. Sci*. (69) (2012) 110–122
21. Bouanane Z., Bounekhel M., Ellkoli1 M., Takfaoui A., Abrigach F., Boyaala R., Touzani R., *J. Pure & Appl. Sci. 1* (2) (2015) 62- 73
22. Lotfi N., Lgaz H., Belkhaouda M., Larouj M., Salghi R., Jodeh S., Oudda H.,. Hammouti B., *Arab J. Chem. and Environ. Resear.* 1 (1) (2014) 13–23
23. Behpour M., Ghoreishi S.M., Khayatkashani M., Soltani N., *Corros. Sci.* 53 (2011) 2489–2501
24. Bouklah M., Hammouti B., Lagrenee M., Bentiss F.; *Corros. Sci*. 48 (2006)2831–2837
25. Avci Gulsen, *Colloids Surf.* (317) (2008) .730–736

(2016) ; http://www.jmaterenvironsci.com/