Inhibiting effects 4,5-Diphenyl-1H-Imidazole-2-Thiol for C38 steel in 1 M HCl : Electrochemical study

D. Ben Hmamou[1], M. R. Aouad[2], R. Salghi [1*], A. Zarrouk [3], M. Assouag [4], O. Benali [5], M. Messali [2], H. Zarrok [4], B. Hammouti [3]

[1] Equipe de Génie de l'Environnement et Biotechnologie, ENSA, Université Ibn Zohr, BP1136 Agadir, Morocco.
[2] Chemistry department, Faculty of Science, Taibah University, 30002, Al-Madinah AlMounawara, Saudi Arabia
[3]LCAE-URAC18, Faculté des Sciences, Université Mohammed 1er, Oujda, Morocco.
[4]Laboratory of the Separation Processes, University Ibn Tofail, Faculty of the Sciences, P.O. Box 1246 Kénitra Morocco.
[5]Départment de Biologie, Faculté des sciences et de la technologie, Université Dr. Tahar Moulay - Saïda

ABSTRACT

4,5-Diphenyl-1H-Imidazole-2-Thiol (DIT) as C38 steel corrosion inhibitor in 1 M HCl solution was studied by using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Polarization curves indicate that inhibition efficiencies of DIT increase with increasing inhibitors concentration. Inhibition efficiency of DIT reached 92.74% at 10^{-2} M. The adsorption of DIT on C38 steel surface obeys the Langmuir isotherm. The negative values of $\Delta G°_{ads}$ indicate the spontaneous adsorption of the inhibitor on steel surface.

Keywords: Corrosion inhibition; Adsorption; C38 Steel; Electrochemical measurements.

INTRODUCTION

Acidic solutions are used in many industrial areas. The most important applications are acid pickling, industrial acid cleaning, acid descaling, and oil well acidizing [1-2]. Steel has found wide applications in a broad spectrum of industries and machinery; despite its tendency to corrosion [3–4]. The use of inhibitor is one of the most practical methods to protect metals from corrosion, especially in aggressive media [5-8]. The higher inhibition efficiency (E%) is essentially due to the presence of heteroatoms and the presence of triple bonds or aromatic rings in their structures increase the adsorption process and should follow the sequence O < N < S < P [9–25].

In this work, a 4,5-Diphenyl-1H-Imidazole-2-Thiol (DIT) had been studied on the corrosion inhibition of C38 steel in 1M HCl solutions by weight loss and electrochemical methods studies. The chemical structure of the studied compound was given in Fig. 1.

_____
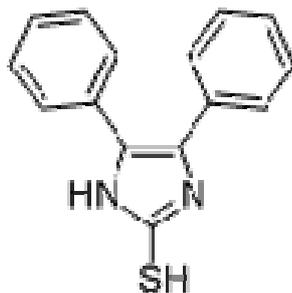
Figure 1. The chemical structure of the 4,5-Diphenyl-1H-Imidazole-2-Thiol

EXPERIMENTAL SECTION

Electrochemical tests
The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster software. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was the same used for gravimetric measurements. The surface area exposed to the electrolyte is 0.094 cm^2.

Potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5 mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from –800 mV to –400 mV at 298 K. The solution test is there after de-aerated by bubbling nitrogen. Gas bubbling is maintained prior and through the experiments. The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} 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.

Solutions preparation
The aggressive solution (1M HCl) was prepared by dilution of Analytical Grade 37 % HCl with double-distilled water. The organic compound tested was 4,5-Diphenyl-1H-Imidazole-2-Thiol **(DIT)**. The concentration range of this compound was 10^{-2} to 10^{-6} M. The studied organic compound was synthesized as described elsewhere [26-27].

RESULTS AND DISCUSSION

Polarization curves
The current–potential relationships (cathodic and anodic) for C38 steel in 1 M HCl in the presence of the different concentrations of **(DIT)** at 298 K are shown in Fig. 2. Values of associated electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (b_c), and the calculated P(%) are presented in Table 1. In this case, the inhibition efficiency is defined as follows[28-30]:

$$P\% = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100 \tag{1}$$

where I_{corr}^0 is the corrosion current density in uninhibited acid and I_{corr} is the corrosion current density in inhibited acid.

As can been seen from Figure 2, both anodic and cathodic reactions of corrosion process were significantly inhibited while the imidazole derivative is added to the acid solution. The addition of the studied compound decreased the current densities in a large domain anodic and cathodic of potential. In literature, it has been reported that [31-32] if the displacement in E_{corr} 1) is >85 mV with respect to E_{corr}, the inhibitor can be seen as a cathodic or anodic type and 2) if the displacement in E_{corr} is <85 mV, the inhibitor can be seen as mixed type. In our study, the maximum displacement in E_{corr} value is 25 mV towards cathodic region, which indicates that **DIT** studied is mixed-type inhibitors [33]. The increase in inhibition efficiency with increasing inhibitor concentration may be attributed to the formation of a barrier film, which prevents the attack of acid on the metal surface [34-35]. Moreover, these

_____

inhibitors cause no change in the anodic and cathodic Tafel slopes, indicating that the inhibitors are first adsorbed onto steel surface and therefore impedes by merely blocking the reaction sites of iron surface without affecting the anodic and cathodic reaction mechanism [36]. The best inhibition efficiency was about 92.74% at concentration 10^{-2} M.
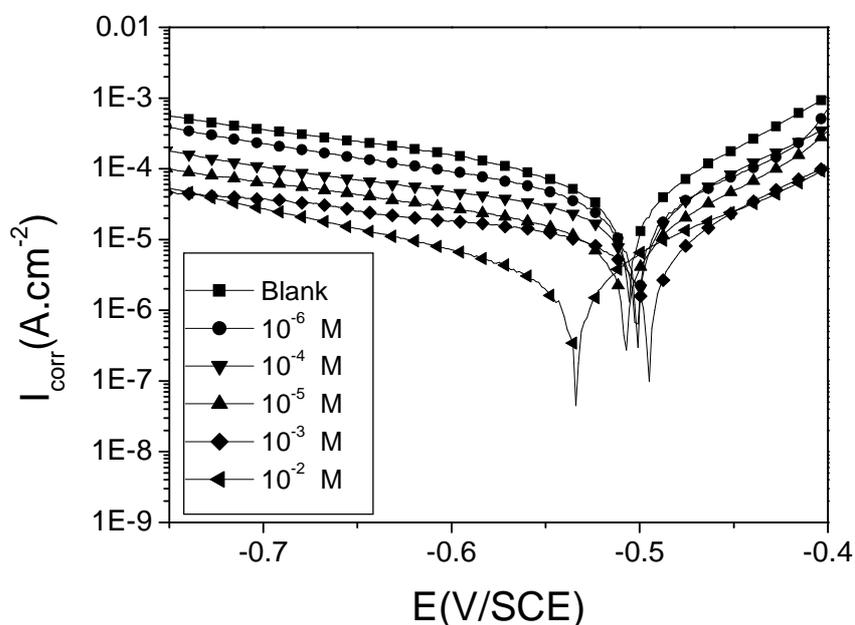
Figure 2. Potentiodynamic polarisation curves of C38 steel in 1M HCl in the presence of different concentrations of DIT

Table 1. Electrochemical parameters of C38 steel at various concentrations of *DIT* in 1M HCl and corresponding inhibition efficiency.

Conc. (Mol /L)	E_{corr} (mV/SCE)	I_{corr} ($\mu A/cm^2$)	$-b_c$ (mV/dec)	E_I (%)
Blank	-507	124	225	---
10^{-6}	-501	65	217	**47.58**
10^{-5}	-502	57	196	**54.03**
10^{-4}	-508	39	155	**68.54**
10^{-3}	-495	31	360	**75.00**
10^{-2}	-532	9	221	**92.74**

Electrochemical impedance spectroscopy measurements:
Nyquist plots in 1 M HCl solutions of **DIT** in the absence and presence of various concentrations are given in Fig. 3. The impedance spectra show that a single semicircle and the diameter of semicircle increases with increasing inhibitor concentration. These diagrams exhibit that the impedance spectra consist of one capacitive loop at high frequency, the high frequency capacitive loop was attributed to charge transfer of the corrosion process [28].

Impedance parameters derived from the Nyquist plots, percent inhibition efficiencies, P (%) and the equivalent circuit diagram are given in table 2 and figure 4, respectively.

_____
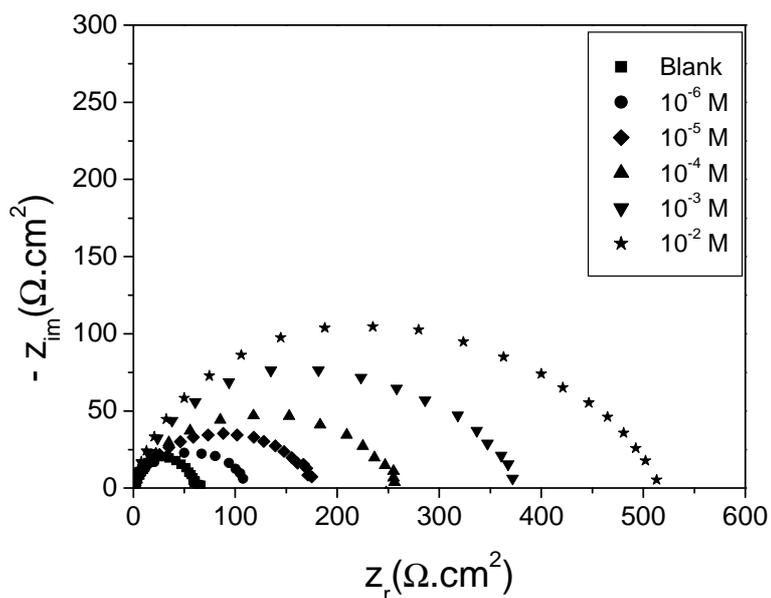
Figure 3. Nyquist diagrams for C38 steel electrode with and without DIT at E$_{corr}$ after 30 min of immersion.

Figure 4. The equivalent circuit of the impedance spectra obtained for DIT

Figure 5 gives an example of fitting curve, where we see clearly that the fitted data match the experimental.
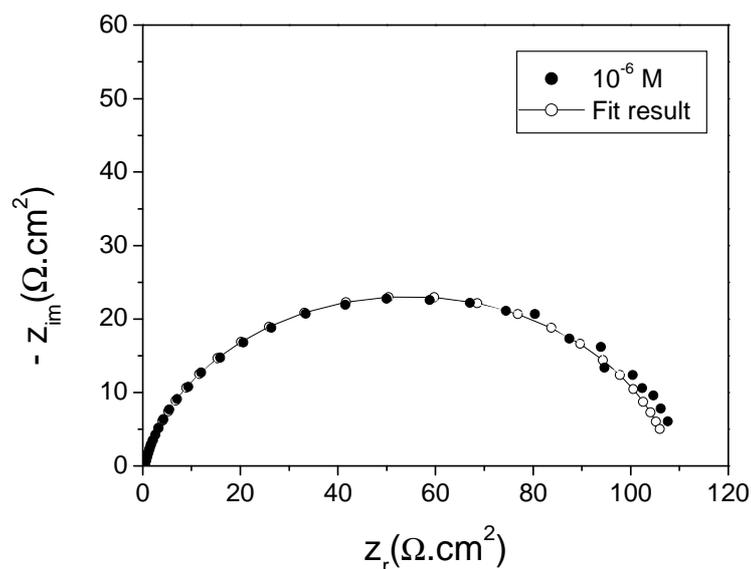
Figure 5. Curves fitting of EIS data of C38 steel in 1 M HCl with 10^{-6} M of DIT to Nyquist plots at Ecorr

To describe the observed depression of the capacitive semicircle it is necessary to replace the capacitor by some element, which has frequency dispersion like the constant phase element (CPE). This element is a generalised tool,

_____

which can reflect exponential distribution of the parameters of the electrochemical reaction related to energetic barrier at charge and mass transfer, as well as impedance behaviour caused by fractal surface structure [37].

The dispersion of the capacitive semicircle is explained also by surface heterogeneity due to surface roughness, impurities or dislocations [38-39], distribution of activity centres, inhibitors adsorption and formation of porous layers [28-30, 40]. The impedance of the CPE is [41-42] :

$$Z_{CPE} = Q^{-1} (j\omega)^{-n} \qquad (2)$$

where Q is a proportionality coefficient and n an exponent related to the phase shift. For whole numbers of n = 1, 0, -1, CPE is reduced to the classical lumped elements capacitor (C), resistance (R) and inductance (L), respectively. The value of n = 0.5 corresponds to Warburg impedance (W). Values of n can serve as a measure of the surface heterogeneity [38-39, 43].

The percent inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the equation:

$$P\% = \frac{R'_t - R_t}{R'_t} \times 100 \qquad (3)$$

where R_t and R'_t are the charge transfer resistance values without and with inhibitor, respectively.

Table 2. Electrochemical Impedance parameters for corrosion of C38 steel in acid medium at various contents of DIT

Conc (M)	R_t ($\Omega.cm^2$)	n	$Q(s^n/\Omega.cm^2)$	C_{dl} ($\mu F/cm^2$)	E_{Rt} (%)
Blank	51.42	0.89	1.91×10^{-4}	107.88	----
10^{-2}	501.9	0.88	6.79×10^{-5}	42.88	**89.75**
10^{-3}	203.7	0.86	8.76×10^{-5}	45.46	**74.75**
10^{-4}	178.3	0.84	1.46×10^{-4}	72.83	**71.16**
10^{-5}	142.8	0.85	1.61×10^{-4}	82.65	**63.99**
10^{-6}	87.11	0.86	1.92×10^{-4}	98.67	**40.97**

From this table we can see that, the R_t values of investigated product increase with increasing inhibitor concentration. The greatest effect was observed at a concentration of 10^{-2} M, which produced R_t value of 501.9 $\Omega.cm^2$. At the same time the C_{dl} has opposite trend at the whole concentration range. These observations clearly bring out the fact that the corrosion of C38 steel in 1 M HCl is controlled by a charge transfer process. The decrease in C_{dl} is due to the gradual replacement of water molecules by the adsorption of the organic molecules at metal/solution interface, leading to a protective film on the C38 steel surface, and then decreasing the extent of dissolution reaction [44]. The decrease of the values of n when compared with 1 M HCl and with concentration can be explained by some increase of surface heterogeneity, due to the adsorption of the inhibitor on the most active desorption sites [39].

Note that the capacitances were calculated from Q and R_t using the equation [45-46] :

$$Q = \frac{(C R_t)^n}{R_t} \qquad (4)$$

These results are in reasonably good agreement with the values of inhibitor efficiency obtained from polarization technique.

Adsorption consideration

Assuming the corrosion inhibition was caused by the adsorption of **DIT** on the C38 steel in HCl 1 M, the degree of surface coverage, θ, of the metal surface was calculated from potentiodynamic polarisation and EIS measurements using the following relations [47]:

$$\theta = \frac{I_{corr} - I'_{corr}}{I_{corr}} \qquad (5)$$

where I_{corr} and I'_{corr} are the current densities for the blank and the inhibited solutions, respectively.

And[48],

_____

$$\theta = \frac{R'_t - R_t}{R'_t} \times 100 \qquad\qquad (6)$$

where R'_t and R_t are the charge transfer resistance values without and with inhibitor, respectively.

The adsorption of an organic adsorbate at a metal solution interface can be represented as a substitutional adsorption process between the organic molecules in the aqueous solution Org $_{(sol)}$ and the water molecules on the metallic surface $H_2O_{(ads)}$ [49].

$$Org_{(sol)} + x\,H_2O_{(ads)} \quad \rightleftharpoons \quad Org_{(ads)} + x\,H_2O_{(sol)} \qquad (7)$$

where $Org_{(sol)}$ and $Org_{(ads)}$ are the organic molecules in the aqueous solution and adsorbed on the metallic surface, respectively, $H_2O_{(ads)}$ is the water molecules on the metallic surface, x is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate.

According to Bockris and Drazic [50], the inhibition mechanism could be explained by the Fe-(inh)$_{ads}$ reaction intermediates :

$$Fe + Inh \quad \rightleftharpoons \quad Fe(Inh)_{ads} \quad \rightleftharpoons \quad Fe^{n+} + n\,e + Inh \qquad (8)$$

At first, where there is not enough Fe(Inh)$_{ads}$ to cover the metal surface, because the inhibitor concentration is low or because the adsorption rate is slow, metal dissolution takes place on sites of the C38 steel surface free of Fe(Inh)$_{ads}$. With high inhibitor concentration, a compact and coherent inhibitor overlayer forms on the C38 steel surface, reducing chemical attack of the metal [51].

When the equilibrium of the process described in Eq. (8) is reached, it is possible to obtain different expressions of the adsorption isotherm plots.

Of the known adsorption isotherm's, the data of θ values were found to fit well with Langmuir isotherm. The isotherm is given by :

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad\qquad (9)$$

with

$$K = \frac{1}{55,5} \exp\left(-\frac{\Delta G^0{}_{ads}}{RT}\right) \qquad\qquad (10)$$

where C is the concentration of the inhibitor in the bulk of the solution, K the adsorptive equilibrium constant and $\Delta G^\circ{}_{ads}$ the free energy of adsorption.

According to this isotherm a plot of $\dfrac{C}{\theta}$ against C should give a straight live with a slope of unity. Fig. 12 shows such these plots. For all the plots, straight lines were obtained with slopes very close to 1, which indicates that the adsorption of inhibitor onto C38 steel surface accords with the Langmuir adsorption isotherm. The result means that there were no interactions among the adsorbed species [52]. The linear regression between $\dfrac{C}{\theta}$ and C were calculated by the computer, and parameters are listed in Table 5. It can be seen from this table that the adsorption equilibrium constant (K) values increased with increasing temperature, which indicated that **DIT** was easily adsorbed strongly onto the C38 steel surface at higher temperatures.

Table 3. Some parameters of the linear regression between C/θ and C

	Slope	K	-ΔG$_{ads}$ (kJ/mol)
From Eq. 5	1.06	1.35×10^4	**33.51**
From Eq. 6	1.07	1.56×10^4	**33.87**

_____
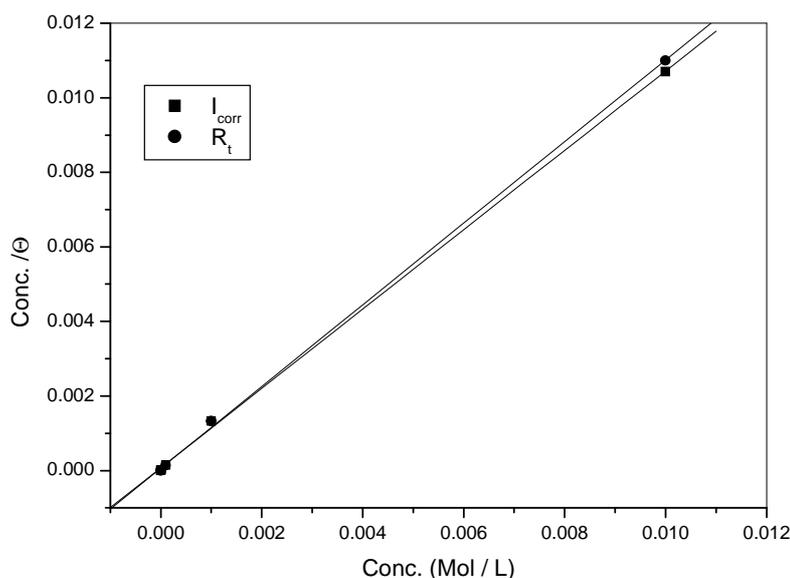
Figure 6. Curves fitting of the corrosion data of C38 steel in the presence of DIT to Langmuir isotherm at 298K

The value of ΔG_{ads} from the Langmuir adsorption isotherm in 1.0 M HCl is calculated to be -34 kJ / mol. The large negative value of ΔG_{ads} reveals that the adsorption of **DIT** molecules on the C38 steel surface is spontaneous and the adsorptive layer is highly stable [53-55]. Generally, the magnitudes of ΔG_{ads} around -20 kJ / mol or less negative are assumed for electrostatic interactions between inhibitor and the charged metal surface (physisorption), and those around -40 kJ / mol or more negative are indicative of charge sharing or transferring from organic species to the metal surface to form a coordinate type of metal bond (chemisorption) [53]. Accordingly, the value of ΔG_{ads}, -34 kJ / mol suggests that the physisorption of **DIT** molecules occurs together with the chemisorption on the C38 steel surface. In fact, due to the strong adsorption of water molecules on the surface of steel, it may be assumed that adsorption occurs first due to the physical forces, and then the removal of water molecules from the surface is accompanied by chemical interaction between the metal surface and the adsorbate [56-57].

CONCLUSION

It can be concluded that:
• **DIT** is a good inhibitor for C38 steel corrosion in 1 M HCl, and inhibition efficiency increases with the increase in the concentration of **DIT**.
• As a mixed-type inhibitor **DIT** inhibits the reduction of H^+ ions by merely blocking the reaction sites of C38 steel surface.
• A good agreement is obtained between the polarization data and electrochemical impedance spectroscopy measurements.
• **DIT** prevents C38 steel from corrosion through the spontaneous adsorption on steel surface, and the process accords with Langmuir isotherm.

REFERENCES

[1] D.Chebabe ; Z. Ait Chikh ; N. Hajjaji ; *Corros. Sci.*, **2003**, 45, 309-320.
[2] K. F Khaled.; N Hackerman;. *Mater. Chem. Phys.*, **2003**, 82, 949-960.
[3] Z. Wahbi ; A. Guenbour ; H. Abou El Makarim ; A. Ben Bachir ; S. El Hajjaji ; *Porg. Org. Coat.*, **2007**, 60, 224.
[4] K.F. Khaled, *Electrochim. Acta*, **2008**, 53, 3484.
[5] D. Ben Hmamou ; R. Salghi ; A. Zarrouk ; H. Zarrok ; B. Hammouti ; S. S. Al-Deyab ; M. Bouachrine ; A.Chakir ; M. Zougagh, *Int. J. Electrochem. Sci.* , **2012**, 7, 5716.
[6] B. Hammouti ; R. Salghi ; S. Kertit, *J. Electrochem Soc. India.*, **1998**, 47, 31.
[7] H. Zarrok ; H. Oudda ; A. Zarrouk ; R. Salghi ; B. Hammouti ; M. Bouachrine ; *Der Pharma Chemica*, **2011**, 3 (6), 576.
[8] M. Mihit ; S. El Issami ; M. Bouklah ; L. Bazzi ; B. Hammouti ; E. Ait Addi ; R. Salghi ; S. Kertit, *Applied Suf Sci.*, **2006**, 252 (6), 2389.

_____

[9] K. Barouni ; L. Bazzi ; R. Salghi ; M. Mihit ; B. Hammouti ; A. Albourine ; S. El Issami, *Mater. Lett.*, **2008**, 62, 3325.

[10] S. El Issami ; L. BAZZI ; M. Mihit ; M. Hilali ; R. Salghi ; El. Ait Addi, *J. Phys. IV*, **2005**, 123, 307.

[11] S. El Issami ; L. Bazzi ; M. Hilali ; R. Salghi ; S. Kertit, *Ann. Chim. Sci. Mat*, **2002**, 27, 63.

[12] S. El Issami ; L. Bazzi ; M. Mihit ; B. Hammouti ; S. Kertit ; E. Ait Addi ; R. Salghi, *Pig. Res.. Tech.*, **2007**, 36(3), 161.

[13] R. Salghi ; L. Bazzi ; B. Hammouti ; S. Kertit, *Bull. of. Electrochem.*, **2000**, 16 (6), 272.

[14] M. Mihit ; K. Laarej ; H. Abou El Makarim ; L. Bazzi ; R. Salghi ; B. Hammouti, *Arab J. Chem.*, **2010**,3, 55.

[15] A. Zarrouk ; A. Dafali ; B. Hammouti ; H. Zarrok ; S. Boukhris ; M. Zertoubi ; *Int. J. Electrochem. Sci.*, **2010**, 5, 46.

[16] A. Zarrouk ; T. Chelfi ; A. Dafali ; B. Hammouti ; S.S. Al-Deyab ; I. Warad ; N. Benchat ; M. Zertoubi ; *Int. J. Electrochem. Sci.*, **2010**, 5, 696.

[17] A. Zarrouk ; B. Hammouti ; A. Dafali ; H. Zarrok, *Der Pharma Chemica.*, **2011**, 3, 266.

[18] A. Zarrouk ; B. Hammouti ; R. Touzani ; S. S. Al-Deyab ; M. Zertoubi ; A. Dafali ; S. Elkadiri, *Int. J. Electrochem. Sci.*, **2011**, 6, 4939.

[19] A. Zarrouk ; B. Hammouti ; H. Zarrok, *Der Pharma Chemica*, 2011, 3 (5), 263.

[20] H. Zarrok ; R. Saddik ; H. Oudda ; B. Hammouti ; A. El Midaoui ; A. Zarrouk ; N. Benchat ; M. Ebn Touhami, *Der Pharma Chemica*, **2011**, 3 (5), 272.

[21] A. Zarrouk ; B. Hammouti ; A. Dafali ; H. Zarrok ; R. Touzani ; M. Bouachrine ; M. Zertoubi, *Res. Chem. Intermed.,* **2011,** DOI 10.1007/s11164-011-0444-2.

[22]. A. Zarrouk ; B. Hammouti ; H. Zarrok ; M. Bouachrine ; K.F. Khaled ; S.S. Al-Deyab ; *Int. J. Electrochem. Sci*., **2012**, 6, 89.

[23] A. Zarrouk ; B. Hammouti ; H. Zarrok ; R. Salghi ; A. Dafali ; L. Bazzi ; L. Bammou ; S. Al-Deyab, *Der Pharma Chemica.*, **2012**, 4 (1), 337.

[24] H. Zarrok ; R. Salghi ; A. Zarrouk ; B. Hammouti ; H. Oudda ; L. Bazzi ; L. Bammou ; S. Al-Deyab, *Der Pharma Chemica.*, **2012**, 4 (1), 407.

[25] H. Zarrok ; H. Oudda ; A. El Midaoui ; A. Zarrouk ; B. Hammouti ; M. Ebn Touhami ; A. Attayibat ; S. Radi ; R. Touzani, *Res. Chem. Intermed.*, **2012,** DOI: 10.1007/s11164-012-0525-x).

[26] M. Messali ; S. A. Ahmed, *Green Sust. Chem.*, **2011**, 1, 70-75.

[27] M. Messali, *Arab. J. Chem.*, **2011**, doi:10.1016/j.arabjc.2011.06.030.

[28] O. Benali ; L. Larabi ; S. M. Mekelleche ; Y. Harek, *J. Mater. Sci.,* **2006**, 41, 7064.

[29] S. Merah ; L. Larabi ; O. Benali ; Y. Harek ; *Pig. Res. Tech.,* **2008**, 37(5), 291.

[30] O. Benali ; L. Larabi ; Y. Harek*, J. App. Electrochem.,* **2009**, 39, 769.

[31] O. L. Riggs Jr., "Corrosion Inhibitors (2nd Edition)," C. C. Nathan, Houston, **1973**.

[32] E. S. Ferreira ; C. Giancomelli ; F. C. Giacomelli ; A. Spinelli, *Mater. Chem.Phys*, **2004**, 83, 129.

[33] G. Lyberatos ; L. Kobotiatis, *Corrosion*, **1991**, 47 (11), 820.

[34] O. Benali ; M. Ouazene, *Arab. J. Chem.*, **2011**, 4, 443.

[35] O. Benali ; L. Larabi ; Y. Harek, *J. Saudi Chem. Soc.*, **2010**, *14(2), 231.*

[36] S.S. Abdel-Rehim ; A.M. Magdy ; K.F. Khaled, *Mater. Chem. Phys.*, **2001**, 70, 268.

[37] A. Popova ; M. Christov, *Corros. Sci.,* **2006***,* 48, 3208.

[38] Z. B. Stoynov ; B. M. Grafov ; B. Savova-Stoynova ; V. V. Elkin, *Electrochemical Impedance*, Nauka, Moscow, **1991**.

[39] F. B. Growcock ; R. J. Jasinski, *J. Electrochem. Soc.,***1989***,* 136, 2310.

[40] U. Rammelt ; G. Reinhard, *Corros. Sci.* , **1987**, 27, 373.

[41] Z. Stoynov, *Electrochim. Acta* , **1990**, 35, 1493.

[42] J. R. Macdonald, *J. Electroanal. Chem.,* **1987***,* 223, 233.

[43] D. A. Lopez ; S. N. Simison ; S. R. De Sanchez ; *Electrochim. Acta*, **2003**, 48, 845.

[44] C. Selles ; O. Benali ; B. Tabti ; L. Larabi ; Y. Harek, *J. Mater. Environ. Sci.,* **2012***,* 3 (1) 206.

[45] X. Wu ; H. Ma ; S. Chen ; Z. Xu ; A. Sui, *J. Electrochem. Soc.*, **1999**, 146, 1847.

[46] H. Ma ; S. Chen ; B. Yin ; S. Zhao ; X. Liu, *Corros. Sci.,* **2003**, 45, 867.

[47] L. Larabi ; Y. Harek ; O. Benali ; S. Ghalem, Prog. Org. Coat., **2005**, 54, 256.

[48] L. Larabi ; O. Benali ; Y. Harek, *Mater. Lett.*, **2007**, 61, 3287.

[49] J. O'M Bockris ; D. A. J. Swinkels, *J . Electrochem. Soc.*, **1964**, 111, 736.

[50] J. O'M Bockris ; D. Drazic, *Electrochim. Acta*, **1962**, 7, 293.

[51] V. Branzoi ; F. Branzoi ; M. Baibarac, *Mater. Chem. Phys.,* **2000**, 65, 288.

[52] A. Y. El- Etre, *Corros. Sci.*, **2001**, 43, 1031.

[53] J. Aljourani ; K. Raeissi ; M.A. Golozar, *Corros. Sci.*, **2009**, 51, 1836.

[54] H. Amar ; A. Tounsi ; A. Makayssi ; A. Derja ; J. Benzakour ; A. Outzourhit ; *Corros. Sci.,* **2007**, 49, 2936.

[55] G. Avci, *Colloids Surf., A*, **2008**, 317, 730.

[56] L. M. Vracar ; D.M. Drazic, *Corros. Sci.*, **2002**, 44, 1669.

_____

[57] F. Zhang ; Y. Tang ; Z. Cao ; W. Jing ; Z. Wu, Y. Chen, *Corros. Sci.,* **2012**, 61, 1.