Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(2):704-712

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

New possibility of mild steel corrosion inhibition by organic heterocyclic compound

A. Ghazoui[1], A. Zarrouk[1], N. Bencaht[1], R. Salghi[2], M. Assouag[3], M. El Hezzat[4],
A. Guenbour[5] and B. Hammouti1[1]

[1]*LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, Oujda, Morocco*
[2]*Laboratory of Environmental Engineering and Biotechnology, ENSA, University Ibn Zohr, Agadir, Morocco*
[3]*Laboratory Separation Processes, Faculty of Science, University Ibn Tofail, Kenitra, Morocco*
[4]*Laboratoire de Physico-Chimie du Solide (LPCS), Faculté des Sciences, Université Ibn Tofail, Kenitra, Morocco*
[5]*Laboratoire d'Electrochimie et de Corrosion, Faculté des Sciences, Rabat, Morocco*

ABSTRACT

The corrosion inhibition properties of 2-(3-methyl-6-oxopyridazin-1(6H)-yl)accetohydrazide (GK1) for mild steel corrosion in HCl solution were analysed by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and gravimetric methods. The results of these techniques indicated that the inhibition efficiency increased with the concentration of inhibitor. Potentiodynamic polarization study clearly revealed that pyridazine derivative acted as mixed type inhibitor. EIS plots indicated that the addition of GK1 increases the charge-transfer resistance (R_{ct}), decreases the double-layer capacitance (C_{dl}) of the corrosion process. Adsorption of inhibitor obeyed Langmuir adsorption isotherm model.

Keywords: Mild Steel, HCl, Pyridazine derivative, Potentiodynamic polarization, EIS

INTRODUCTION

Acid solutions, especially hydrochloric and sulfuric acids, are widely used in various industrial processes, such as pickling of iron, chemical cleaning, descaling of boilers, and oil well acidification in petroleum exploration. The use of inhibitors is one of the most practical methods for corrosion protection of metallic objects in acidic media, as well as for reduction of acid consumption occurring during the course of corrosion. The corrosion for metals and alloys is a problem of serious concern which considerably affects both economy and safety. Steel is widely used in industries and machinery and many other fields [1]. The efficiency of an organic compound as an inhibitor depends on its ability to get adsorbed on the metal surface by replacing water molecule from metal surface [2]. Generally the compounds containing hetero atoms like O, N, S, and P are found to work as very effective corrosion inhibitors. The efficiency of these compounds depends upon electron density present around the hetero atoms, the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption, and formation of metallic complexes [3-29].

This article reported our attempt to use electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss method to investigate the nature of adsorption of 2-(3-methyl-6-oxopyridazin-1(6H)-yl)accetohydrazide (GK1) on the mild steel surface. The structure of this compound is shown in Figure 1.

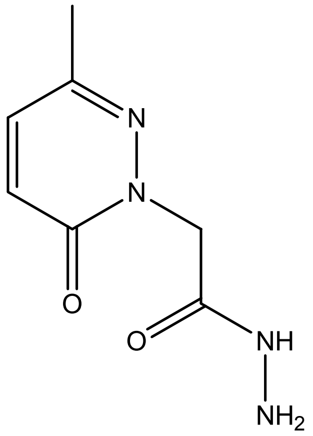

Figure 1. Structure of pyridazine derivative molecule

EXPERIMENTAL SECTION

Materials

The steel used in this study is a mild steel (MS) with a chemical composition (in wt%) of 0.21 % C, 0.38 % Si, 0.05 % Mn, 0.05 % S, 0.09 % P, 0.01 % Al and the remainder iron (Fe).

Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. The organic compound tested is 2-(3-methyl-6-oxopyridazin-1(6H)-yl)accetohydrazide (GK1). The concentration range of this compound was 10^{-3} to 10^{-6} M.

Weight loss measurements

The mild steel (MS) sheets of 1 × 1 × 0.05 cm were abraded with a series of emery papers SiC (120, 600 and 1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in an 80 mL beaker containing 50 mL

1.0 M HCl solution with and without addition of different concentrations of GP0. All the aggressive acid solutions were open to air. After 6 h the specimens were taken out, washed, dried, and weighed accurately. In order to get good reproducibility experiments were carried out in triplicate. The average weight loss of three parallel MS sheets was obtained. The tests were repeated at 308 K. The corrosion rate (ν) and the inhibition efficiency (η_{WL}) were calculated by the following equations [30]:

$$\nu = \frac{W}{St} \times 100 \tag{1}$$

$$\eta_{WL}(\%) = \frac{\nu_0 - \nu}{\nu_0} \times 100 \tag{2}$$

where W is the three-experiment average weight loss of the mild steel, S is the total surface area of the specimen, t is the immersion time and ν_0 and ν are values of the corrosion rate without and with addition of the inhibitor, respectively.

Polarization measurements

Electrochemical impedance spectroscopy

The electrochemical measurements were carried out using Volta lab (Tacussel- Radiometer PGZ 100) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode of surface area of 1 cm^2. The working electrode was mild steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to a establish steady state open circuit potential (*E*ocp). After measuring the *E*ocp, the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 308 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit

0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the *x*-axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation [31]:

$$\eta_z\% = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \qquad (3)$$

where R_{ct} and $R_{\mathrm{ct\ (inh)}}$ were the values of polarization resistance in the absence and presence of inhibitor, respectively.

Potentiodynamic polarization

The electrochemical behaviour of mild steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1.0 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -800 to 200 mV versus corrosion potential at a scan rate of 1 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). From the polarization curves obtained, the corrosion current (I_{corr}) was calculated by curve fitting using the equation:

$$I = I_{corr}\left[exp\left(\frac{2.3\Delta E}{\beta_a}\right) - exp\left(\frac{2.3\Delta E}{\beta_c}\right)\right] \qquad (4)$$

The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$\eta_{Tafel}\% = \frac{I^{\circ}_{corr} - I^{i}_{corr}}{I^{\circ}_{corr}} \times 100 \qquad (5)$$

where, I°_{corr} and I^{i}_{corr} are the corrosion current density in absence and presence of inhibitor, respectively.

RESULTS AND DISCUSSION

Potentiodynamic polarization measurements

Potentiodynamic polarization curves of mild steel in 1.0 M HCl in the absence and presence of 10^{-6} to 10^{-3} M concentrations of GK1 is given in Figure 2. The potentiodynamic polarization parameters i.e. Corrosion potential (E_{corr}), cathodic Tafel slopes (β_c), corrosion current density (I_{corr}) and percentage inhibition efficiency (η_{Tafel} %) were also calculated and given in Table 1. It can be seen from table that I_{corr} value decreases from 605.3 $\mu A\ cm^{-2}$ to 217.3 $\mu A\ cm^{-2}$ on increasing concentration from 10^{-6} to 10^{-3} M this depicted that the rate of electrochemical reaction was reduced due to the formation of a barrier layer over the mild steel surface by the pyridazine derivative molecule.

From Table 1, it is also clear that the values of cathodic Tafel slope constant are slightly changed in the presence of GK1. This suggest that GK1 was first adsorbed onto the mild steel surface and impeded by merely blocking the reaction sites of the metal surface without affecting the cathodic reaction [32]. Maximum reduction of I_{corr} for each inhibitor is obtained at 10^{-3} M. From table, it is also observed that E_{corr} values did not change significantly in presence of GK1 suggesting that it is a mixed type inhibitor [33].

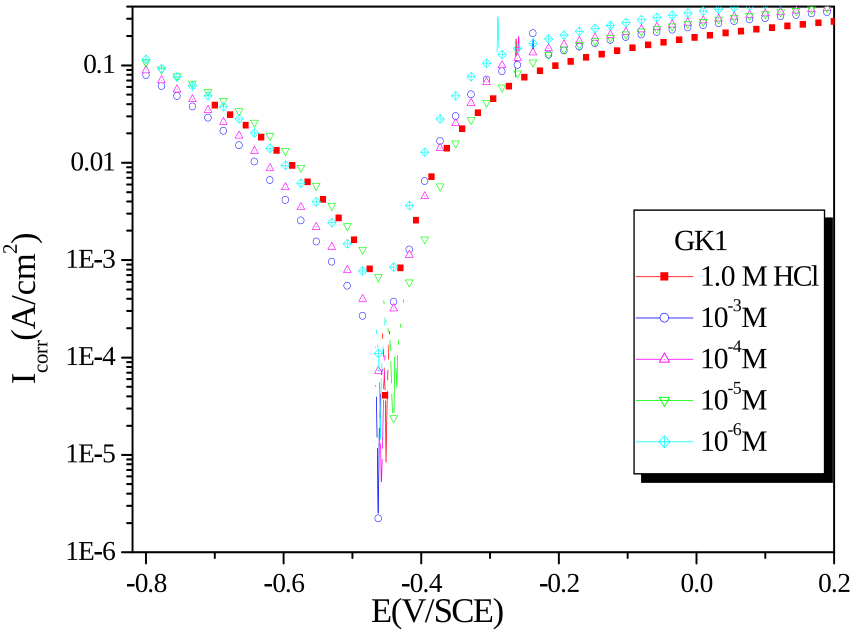

Figure 2. Potentiodynamic polarization curves for the corrosion of mild steel in 1.0 M HCl solution without and with various concentrations of GK1 at 308 K

Table 1. Effect of concentration of GK1 on the electrochemical parameters calculated using potentiodynamic polarization technique for the corrosion of mild steel in 1.0 M HCl at 308 K

Inhibitor	Conc (M)	$-E_{corr}$ (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} ($\mu A/cm^2$)	η_{Tafel} (%)
Blank	1.0	455.2	127.3	815.7	------
GK1	10^{-3}	467.4	114.4	217.3	73.4
	10^{-4}	462.8	112.2	324.8	60.2
	10^{-5}	444.7	117.1	523.6	35.8
	10^{-6}	463.7	113.5	605.3	25.8

Electrochemical Impedance Spectroscopy

The corrosion behaviour of mild steel in 1.0 M HCl in absence and presence of different concentrations of GK1 were investigated by EIS after immersion for 30 min at 308 ± 1 *K*. Nyquist plot of mild steel in uninhibited and inhibited acid solutions containing various concentrations of GK1 is presented in Figure. 3. From figure it is clear that diameter Nyquist plot increases with concentration. The increasing diameter of Nyquist plot in 1.0 M HCl in presence of GK1 indicated the corrosion inhibition of mild steel. For corrosion reactions which are strictly charge transfer controlled, impedance behavior can be explained with the help of a simple and commonly used equivalent circuit [Figure 4] composed of a double layer capacitance, charge transfer resistance (R_{ct}) and solution resistance (R_s). The resistor *Rs* is in series to the double layer capacitance and R_{ct}, while double layer capacitance is parallel to R_{ct}. The double layer capacitance is in parallel with the impedance due to the charge transfer reaction. This type of circuit is used to model the iron/acid interface [34]. The *EIS* parameters for GK1 such as R_s, R_{ct} and C_{dl} were derived from the Nyquist plot are given in Table 2. It is depicted from Table 2, that the impedance of the inhibited system amplified with increase and the C_{dl} values decreased with increase in GK1 concentration.

The double layer capacitance (C_{dl}) was calculated by using following equation [35]:

$$C_{dl} = Y_0 \left(\omega_{\max}\right)^{n-1} \tag{6}$$

where, Y_0 is *CPE* coefficient, *n* is *CPE* exponent (phase shift), ω is the angular frequency. The $\omega_{\max}$ represents the frequency at which the imaginary component reaches the maximum. This decrease in C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that pyridazine derivative molecules inhibit the mild steel corrosion by adsorption at the metal/acid interface [36]. As stated earlier the diameter of Nyquist plot increases with increasing concentration of GK1. The decrease of diameter in Nyquist plot is a feature for solid electrodes and often referred to as frequency dispersion and attributed to the roughness and other in homogeneities of the solid electrode [37].

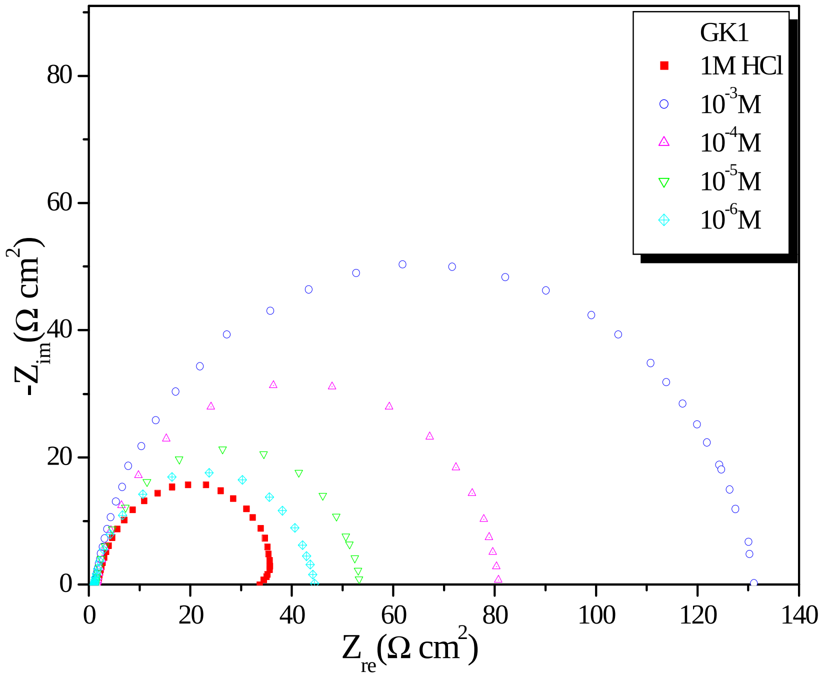

Figure 3. Nyquist diagrams for mild steel in 1.0 M HCl containing different concentrations of GK1 at 308K

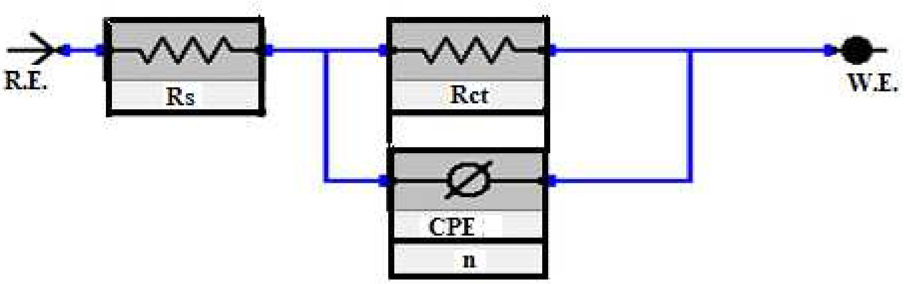

Figure 4. The electrochemical equivalent circuit used to fit the impedance measurements

Table 2. Corrosion parameters obtained by impedance measurements for mild steel in 1.0 M HCl at various concentrations of GK1

Inhibitor	Conc (M)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	η_z (%)
Blank	1.0	1.68	33.23	50.00	95.8	-----
GK1	10^{-3}	1.15	130.19	20.00	61.2	74.5
	10^{-4}	1.24	79.71	31.65	63.1	58.3
	10^{-5}	1.31	52.63	31.65	95.6	36.9
	10^{-6}	1.45	44.22	31.65	113.8	24.8

Weight loss measurements

Weight loss measurements were carried out using different concentrations of inhibitor. The weight loss, inhibition efficiency and corrosion rate are reported in the Table3. It is observed that the inhibition efficiency increases with increase in concentration of inhibitor up to 10^{-3} M and further increase in concentration does not show any appreciable rise in inhibition efficiency. The inhibitor showed a maximum efficiency of 74.2% in HCl at an optimum concentration of 10^{-3} M.

Table 3. Corrosion parameters for mild steel in aqueous solution of 1.0 M HCl in the absence and presence of different concentrations of GK1 from weight loss measurements at 308K

Inhibitor	Conc (M)	ν (mg/cm^2 h)	η_{WL} (%)	θ
Blank	1.0	1.142	----	----
GK1	1×10^{-3}	0.294	74.2	0.742
	5×10^{-4}	0.300	73.7	0.737
	1×10^{-4}	0.449	60.6	0.606
	5×10^{-5}	0.531	53.4	0.534
	1×10^{-5}	0.740	35.1	0.351
	1×10^{-6}	0.840	26.3	0.263

The evolution of both the corrosion rates and the inhibition efficiencies evaluated from weight loss measurements for different GK1 concentrations in 1.0 M HCl is illustrated in Fig 5. The addition of GK1 diminished the corrosion rate and hence inhibited mild steel corrosion in acid solution. The decrease in CR with increasing inhibitor concentration suggests that the inhibiting action was concentration dependent. The inhibition efficiency (η_{WL}(%)) attained its maximum (74.2%) at 10^{-3}M.

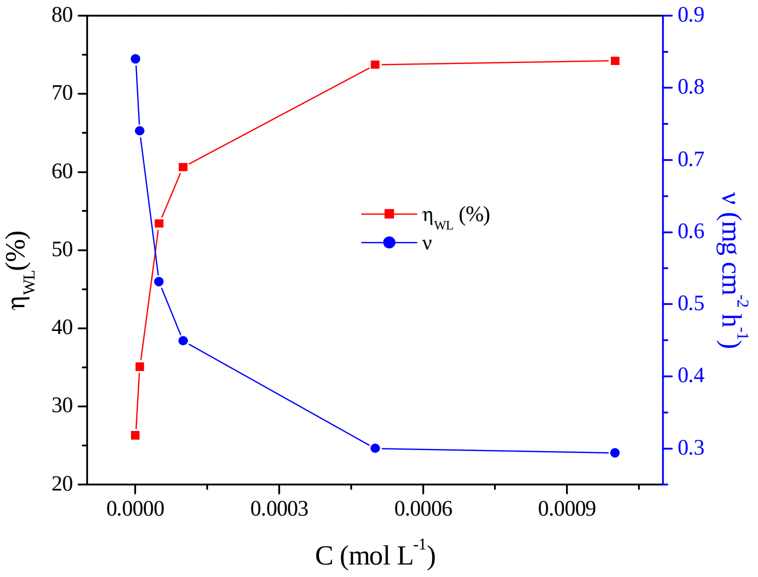

Figure 5. Variation of the corrosion rate and inhibitive efficiency against the GK1concentrations

Adsorption considerations

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds, and the adsorption depends on the compounds' chemical composition, the temperature and the electrochemical potential at the metal/solution interface. In fact, the water molecules could also adsorb on metal/solution interface. Thus, the so-called adsorption can be regarded as a quasi-substitution process between the pyridazine derivative in the aqueous phase [$GK1_{(sol)}$] and water molecules at the electrode surface [$H_2O_{(ads)}$]:

$$Gk1_{(sol)} + nH_2O_{(ads)} \rightleftharpoons GK1_{(ads)} + nH_2O_{(sol)}$$

Where GK1(sol) and GK1(ads) are the pyridazine derivative dissolved in the aqueous solution and adsorbed onto the metallic surface, respectively.

According to Langmuir adsorption isotherm, θ is related to equilibrium adsorption constant (K_{ads}) and C by the equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (7)$$

Fig. 6 shows the straight lines of C/θ vs. C at 308 K. The parameters obtained from C/θ vs. C plots were listed in Table 4. These results show that the linear correlation coefficients (R^2) is almost equal to 1 and the slope is close to 1, which confirmed that the adsorption of the pyridazine derivative on mild steel surface good obeyed Langmuir adsorption isotherm.

The free energy of inhibitor adsorption ΔG°_{ads} on mild steel surface can be evaluated using the following equation:

$$K_{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \tag{8}$$

where the value 55.5 is the concentration of water in solution in M, R is the universal gas constant and T is absolute temperature.

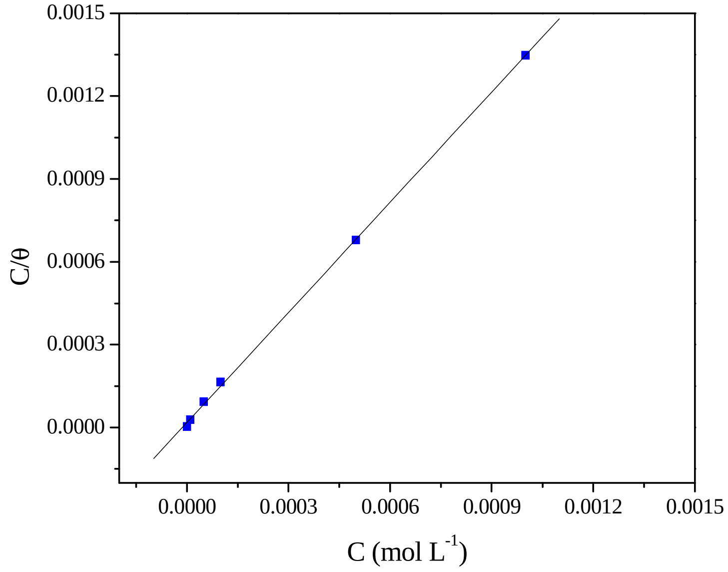

Figure 6. Langmuir adsorption isotherm for mild steel in 1.0 M HCl containing different concentrations of GK1 at 308 K

The negative value of ΔG°_{ads} and the higher value of K_{ads} reveal the spontaneity of adsorption process and they are characteristic of strong interaction and stability of the adsorbed layer with the mild steel surface. In general, the standard free energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, resulting in physisorption and those of -40 kJ mol^{-1} or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, resulting in chemisorption [38]. The value of ΔG°_{ads} *in* case of GK1 is found to be around -38 kJ mol^{-1}, showing that GK1 is adsorbed by mixed mode of adsorption which involes both physical and chemical adsorption [39].

Table 4. Some parameters from Langmuir model for mild steel in 1.0 M HCl at 308K

Inhibitor	Slope	K_{ads} (M^{-1})	r	ΔG°_{ads} (kJ/mol)
GK1	1.22	54796.62	0.99981	-38.22

CONCLUSION

The inhibition effect of the pyridazine compound on mild steel in hydrochloric acid was examined by weight loss methods, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results of inhibition efficiency determined by so-called measurements are in good agreement. GK1 acts as a good corrosion inhibitor in 1.0 M HCl solutions. Inhibition efficiency value increases with the increasing of the inhibitor concentration. Polarization curves indicated that the extract acts as mixed type inhibitor in 1.0 M HCl solutions. EIS measurement results indicated that the resistance of the mild steel electrode increased greatly and its capacitance decreases by increasing the inhibitor concentration. The inhibition is accomplished by adsorption of the GK1 on the mild steel surface, and the adsorption is spontaneous and obeys the Langmuir isotherm.

REFERENCES

[1] Q. B. Zhang, Y.X. Hua, *Electrochim. Acta.* **2009**, 54, 1887.
[2] A.S. Fouda, A.S. Ellithy, *Corros. Sci.,* **2009**, 51, 875.
[3] M. Yadav, S. Kumar, U. Sharma, P.N. Yadav, *J. Mater. Environ*. Sci., *2013*, 4 (5), 691.
[4] A. K. Singh, M. A. Quraishi, *J. Mater. Environ. Sci.,* **2010**, 1, 101.
[5] M. Prajila, J. Sam, J. Bincy, J. Abraham, *J. Mater. Environ. Sci.,* **2012**, 3, 1045.
[6] U.J. Naik, V.A. Panchal, A.S. Patel, N.K. Shah, *J. Mater. Environ. Sci.,* **2012**, 3, 935.
[7] A. Zarrouk, H. Zarrok, R. Salghi, B. Hammouti, F. Bentiss, R. Touir, M. Bouachrine, *J. Mater. Environ. Sci.,* **2013**, 4, 177.
[8] D. Ben Hmamou, R. Salghi, A. Zarrouk, H. Zarrok, S.S. Al-Deyab, O. Benali, B. Hammouti, *Int. J. Electrochem. Sci*., **2012**, 7, 8988.
[9] B. Hammouti, A. Zarrouk, S.S. Al-Deyab and I. Warad, Orient. J. Chem., 27 **(2011)** 23.
[10] A. Zarrouk, M. Messali, H. Zarrok, R. Salghi, A.A. Ali, B. Hammouti, S.S. Al-Deyab, F. Bentiss, *Int. J. Electrochem. Sci*., **2012**, 7, 6998.
[11] H. Zarrok, A. Zarrouk, R. Salghi, Y. Ramli, B. Hammouti, S. S. Al-Deyab, E. M. Essassi, H. Oudda, *Int. J. Electrochem. Sci*., **2012**, 7, 8958.
[12] A. Zarrouk, B. Hammouti, S.S. Al-Deyab, R. Salghi, H. Zarrok, C. Jama, F. Bentiss, *Int. J. Electrochem. Sci*., **2012,** 7, 5997.
[13] D. Ben Hmamou, M. R. Aouad, R. Salghi, A. Zarrouk, M. Assouag, O. Benali, M. Messali, H. Zarrok, B. Hammouti, *J. Chem. Pharm. Res*., **2012,** 4, 3489.
[14] A. Zarrouk, H. Zarrok, R. Salghi, B. Hammouti, S.S. Al-Deyab, R. Touzani, M. Bouachrine, I. Warad, T. B. Hadda, *Int. J. Electrochem. Sci*., **2012**, 7, 6353.
[15] H. Zarrok, R. Saddik, H. Oudda, B. Hammouti, A. El Midaoui, A. Zarrouk, N. Benchat, M. Ebn Touhami, *Der Pharm. Chem*., **2011**, 3, 272.
[16] A. Zarrouk, B. Hammouti, A. Dafali, H. Zarrok, *Der Pharm. Chem*., **2011**, 3, 266.
[17] A. Ghazoui, R. Saddik, N. Benchat, B. Hammouti, M. Guenbour, A. Zarrouk, M. Ramdani, *Der Pharm. Chem*., **2012**, 4, 352.
[18] D. Ben Hmamou, R. Salghi, A. Zarrouk, B. Hammouti, S.S. Al-Deyab, Lh. Bazzi, H. Zarrok, A. Chakir, L. Bammou, *Int. J. Electrochem. Sci*., **2012**, 7, 2361.
[19] A. Zarrouk, B. Hammouti, H. Zarrok, M. Bouachrine, K.F. Khaled, S.S. Al-Deyab, *Int. J. Electrochem. Sci*., **2012**, 6, 89.
[20] A. Zarrouk**,** B. Hammouti, H. Zarrok, I. Warad, M. Bouachrine, *Der Pharm. Chem*., **2011**, 3, 263.
[21] A. H. Al Hamzi, H. Zarrok, A. Zarrouk, R. Salghi, B. Hammouti, S. S. Al-Deyab, M. Bouachrine, A. Amine, F. Guenoun, *Int. J. Electrochem. Sci*., **2013**, 8, 2586.
[22] A. Ghazoui, N. Bencaht, S. S. Al-Deyab, A. Zarrouk, B. Hammouti, M. Ramdani, M. Guenbour, *Int. J. Electrochem. Sci*., **2013** 8, 2272.
[23] D. Ben Hmamou, R. Salghi, A. Zarrouk, M. Messali, H. Zarrok, M. Errami, B. Hammouti, Lh. Bazzi , A. Chakir, *Der Pharm. Chem*., **2012**, 4, 1496.
[24] A. Zarrouk, H. Zarrok, R. Salghi, N. Bouroumane, B. Hammouti, S. S. Al-Deyab, R. Touzani, *Int. J. Electrochem. Sci*., **2012**, 7, 10215.
[25] H. Bendaha, A. Zarrouk, A. Aouniti, B. Hammouti, S. El Kadiri, R. Salghi, R. Touzani, *Phys. Chem. News*, **2012**, 64, 95.
[26] J. Hmimou, A. Rochdi, R.Touir, M. Ebn Touhami, E.H. Rifi, A. El Hallaoui, A. Anouar, , D. Chebab, *J. Mater. Environ. Sci.,* **2012**, 3, 543.
[27] Y. Aouine, M. Sfaira, M. Ebn Touhami, A. Alami, , B. Hammouti, M. Elbakri, A. El Hallaoui, R. Touir, *Int. J. Electrochem. Sci*., **2012**, 7, 5400.
[28] M. Cenoui, N. Dkhireche, O. Kassou, M. Ebn Touhami, R. Touir, A. Dermaj, N. Hajjaji, *J. Mater. Environ. Sci.,* **2010**, 1, 84.
[29] M. ELbakri, R. Touir, M. Ebn Touhami, A. Srhiri, , M. Benmessaoud, *Corros. Sci.,* **2008**, 50, 1538.
[30] X.H. Li, S.D. Deng, H. Fu, G.N. Mu, N. Zhao, *Appl. Surf. Sci*., **2008**, 254, 5574.
[31] H. Zarrok, , A. Zarrouk, , B. Hammouti, , R. Salghi, , C. Jama, , F. Bentiss, *Corros. Sci*., **2012**, 64, 243.
[32] F. Xu, J. Wang, Y. Tian, *Synth. Commun*., **2008**, 38, 1299.
[33] G. Moretti, G. Quartarone, A. Tassan, A. Zingoles, *Electrochem. Acta*, **1996**, 41, 1971.
[34] W.H. Li, Q. He, C.L. Pei, B.R. Hou, *Electrochim. Acta*, **2007**, 52, 6386.
[35] C. S. Hsu and F. Mansfeld, *Corrosion,* **2001**, 57, 747.

---

[36] Ashassi-Sorkhabi, D. Seifzadeh, M.G. Hosseini, *Corros. Sci*., **2008**, 50, 3363.
[37] A. Popova, M. Christov, *Corros. Sci.*, **2006**, 48, 3208.
[38] M. Ehteshamzadeh, T. Shahrabi, M. Hosseini, *Anti. Corros. Methods Mater*. **2006**, 53, 296.
[39] K.F. Khaled, *Electrochim. Acta*, **2008**, 53, 3492.