Corrosion Inhibition of Aluminum in Hydrochloric Acid Solution Using Potassium Iodate Inhibitor

A.A. El Maghraby*

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

Abstract: The inhibition effect of potassium iodate on the corrosion of aluminum in 2M HCl has been studied by weight loss, polarization and electrochemical impedance spectroscopy (EIS) measurements. It has been found that KIO_3 acts as an excellent inhibitor. Inhibition efficiency with 100 ppm inhibitor was very high. Polarization curves reveal that the used inhibitor is a mixed type inhibitor. The surface adsorption of KIO_3 leads to a decrease of double layer capacitance as well as an increase of polarization resistance. The adsorption of the inhibitor on the aluminum surface is in agreement with Temkin adsorption isotherm.

Keywords: Aluminum, Corrosion inhibition, KIO_3, HCl.

1. INTRODUCTION

It has been reported that the cost due to corrosion in many countries is as high as 5% of the GNP [1]. This represents a huge amount of money which should have been channeled into the provision of basic social amenities in these countries. In practice corrosion can never be stopped but can be hindered to a reasonable level.

Corrosion of aluminum and its alloys has been a subject of numerous studies due to their high technological value and wide range of industrial applications especially in aerospace and house-hold industries. Aluminum and its alloys, however, are reactive materials and are prone to corrosion. Aluminum relies on the formation of a compact, strongly adherent and continuous passive oxide film is developed on aluminum upon exposure to the atmosphere or aqueous solutions. This is responsible for the corrosion resistance of aluminum in most environments. This surface film is amphoteric and dissolves substantially when the metal is exposed to high concentrations of acids or bases [2]. In addition, aluminum may be used in neutral solutions containing pitting agents such as chloride ions. These solutions cause pitting corrosion. Under these circumstances, corrosion inhibitors should be used because the solubility of the oxide film increases above and below pH4-9 range [3, 4] and aluminum exhibits uniform attack.

Aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their advantages. Hydrochloric acid (HCl) solutions are used for pickling, chemical and electrochemical etching of aluminum. It is very important to add corrosion inhibitors to prevent metal dissolution and minimize acid consumption [5]. Introduction of an oxidizing agent like KIO_3 into a corrosive acidic medium can lead to self-passivation of steel. Studies were also reported with IO_3^- as an effective inhibitor for corrosion of copper in acidic environments. IO_3^- behaves as an oxidizer at low concentrations and as a passivator at higher concentrations for copper dissolution, with strong adsorption of these ions on copper surface, forming Cu $(IO_3)_2$ [6]. It has also been found that the presence of IO_3^- in sulfuric and hydrochloric acids with a concentration higher than the critical one leads to the repair of the flawed regions of the naturally occurring oxide film and oxidation of the active sites on the corroding surfaces of Ti and Ti-6Al-4V alloy [7]. Based on their adsorption studies, Toraishi *et al*. observed that IO_3^- adsorption onto α-Fe_2O_3 occurred from pH 4 to10 [8]. KIO_3 possesses remarkable corrosion inhibition, anti-microbial and oxidizing properties. Recent studies project KI as an effective synergistic co- inhibitor for acidic environments [9-13]. Also iodide ions are the most absorbable of halide ions on steel. Until now, no research papers have been published on the use of KIO_3 as corrosion inhibitor for aluminum in acidic solutions.

The purpose of the present work is to study the inhibitive action of potassium iodate (KIO_3) on aluminum in 2M HCl using chemical (weight loss) and electrochemical methods including Tafel, linear polarization, open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) measurements. In addition, the adsorption isotherm of the inhibitor will be investigated.

MATERIALS AND METHODOLOGY

Aluminum sheets of the tube AA1060 and purity 98.8% were used in this study. Each sheet was 0.14 cm in thickness was mechanically press- cut into rectangular coupons of dimension 5 cm x 4 cm. The total surface area of the coupon used was 20 cm^2. These coupons were used as cut without further polishing. They were however degreased in absolute ethanol, dried in acetone, and stored in moisture- free desiccators prior to use [14]. All reagents used were BDH analytical grade. They were used as sourced without further purification. The used acid solutions were made from 37%HCl. Appropriate concentrations of acid were prepared by using double-distilled water. An aqueous solution of 2M HCl was used as a blank solution. Potassium iodate provided

*Address correspondence to this author at the Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt;
E-mail: maghraby04@yahoo.com

by merck, was used as inhibitor. The concentration range of employed inhibitor was 20- 200 ppm in 2M HCl. In each experiment, the cleaned aluminum coupon was weighed (m_1) and suspended with the aid of glass rod or hook in a beaker containing 100 ml 2M acid solution without and with different doses of KIO_3 concentrations ranged from 20- 200 ppm. The coupon was then taken out of the test solution after 60 mins, washed in 70% nitric acid for 2 min to remove the corrosion products using bristle brush, rinsed with distilled water, dried and re- weighed (m_2). The weight loss was taken as the difference between the weight at a given time and the initial weight of the test coupon. The average weight loss for two determinations is reported in this study. The temperature was adjusted to 30 $\pm$ 0.1°C using MEMERT thermostat.

Corrosion rate and inhibition efficiencies were calculated from the following equations [15, 16]:

$$C.\ R. = \frac{m_1 - m_2}{A\ T} \quad (1)$$

$$IE_w\ \% = \frac{(C.\ R.)_o - (C.\ R.)}{(C.\ R.)_o} \times 100 \ldots\ldots\ldots\ldots \quad (2)$$

where m is the weight loss in milligram, A is the total surface area in cm^2, T is the time of exposure in minutes, $(C.\ R)_o$ and (C. R.) are the corrosion rates in ($mg\ cm^{-2}\ min^{-1}$) without and with different concentrations of KIO_3 additives, respectively.

The inhibition efficiency depends on the degree of coverage of the aluminum surface by molecules of the inhibitor and can be expressed as in the following equation [16].

$$\theta = \frac{(C.\ R.)_o - (C.\ R.)}{(C.\ R.)_o} \quad (3)$$

Electrochemical experiments were carried out using potentiostat model 273 / 81 under stirring conditions. In case of Tafel polarization method, scan rate of potential was 5 mV/s and potential was scanned in the range of -1150 to - 550mV. Three compartment with a saturated calomel reference electrode (SCE) and a platinum auxiliary electrode was used. A sheet cut of 98.8 % pure aluminum of exposed area of 2 cm^2 was used for both Tafel and linear polarization studies. The electrode was polished using different grades of emery papers and degreased. For linear polarization studies, the scan rate was 1.66 x 10^{-4} mV/s and the polarization resistance (R_p) values were measured in the absence and presence of 100 ppm KIO_3 concentration as an optimum dose. Open circuit potential studies were carried out to explore the direction of potential shifting in the presence and absence of inhibitor.

The inhibitor efficiency was evaluated from Tafel polarization curves using the following equation [17].

$$IE_p\ \% = \left(1 - \frac{i_{corr}}{i_{0\ corr}}\right) \times 100 \quad (4)$$

where $i_{0\ corr}$ and i_{corr} correspond to uninhibited and inhibited corrosion current densities, respectively.

Electrochemical impedance measurements were carried out in the frequency range of 10 KHZ-0.1HZ by applying 5mV sine wave ac signal. Double layer capacitance (C_{dl}) and charge transfer resistance (R_t) values were calculated from Nyguist plots as described elsewhere [18].

3. RESULTS AND DISCUSSION

3.1. Gravimetric Measurement

The corrosion rate of aluminum in the absence and presence of potassium iodate at room temperature $\simeq$ 30°C was studied using weight loss technique. The results in Fig. (**1**) show that KIO_3 actually inhibited the corrosion of aluminum in 2 M HCl solutions. The corrosion rate was found to depend on the concentration of the inhibitor. Increasing the concentration of potassium iodate increases the inhibition efficiency IE% up to a maximum value of 90% at nearly 100 ppm inhibitor. No appreciable increase in IE% was noticed above this concentration. This indicates that the protective effect of KIO_3 is not solely due to their reactivity with HCl. The inhibitory action of KIO_3 against Al corrosion can be attributed to the adsorption of its molecules on the Al surface, which limits the dissolution of the latter by blocking its corrosion sites and hence decreasing the weight loss, with increasing efficiency as the concentration increases.

The percentage inhibition efficiency IE % and the degree of surface coverage (θ) were calculated using the following equations:

$$IE\ \% = \frac{W_o - W}{W_o} \times 100 \quad (5)$$

$$\theta = \frac{W_o - W}{W_o} \quad (6)$$

where W_0 and W are the weight loss of the Al coupon in 2M HCl in the absence and presence of KIO_3. Fig. (**2**) shows the effect of immersion time on the performance of inhibitor at its optimum dose (100 ppm). The inhibitor shows good performance up to 1 hour with 87% inhibition efficiency.

3.2. Adsorption Considerations

It is generally assumed that the adsorption of the inhibitor at the metal / solution interface is the first step in the mechanism of inhibition aggressive media. It is also widely acknowledged that adsorption isotherms provide useful insights into the mechanism of corrosion inhibition. The surface coverage, θ, was calculated according to equation (6). Surface coverage values (θ) for the inhibitor were obtained from the weight loss measurement for various concentrations at $\simeq$ 30ºC. The best – fitted straight line is obtained for the plot of surface coverage (θ) versus logarithmic of inhibitor concentration (Log C) (Fig. **3**).

3.3. Open Circuit Potential Measurement

Fig. (**4**) shows the OCP variation when Al electrode was exposed to aggressive 2M HCl environment (curve A). When this experiment was carried out with 100ppm KIO_3 as an optimum dose, it was observed that the OCP remained almost unchanged (curve B). This observation is attributed to the presence of IO_3^- ions in 2M HCl solution which inhibit the corrosion of the aluminum surface and enhance the growth of the pre- immersion oxide film on aluminum.

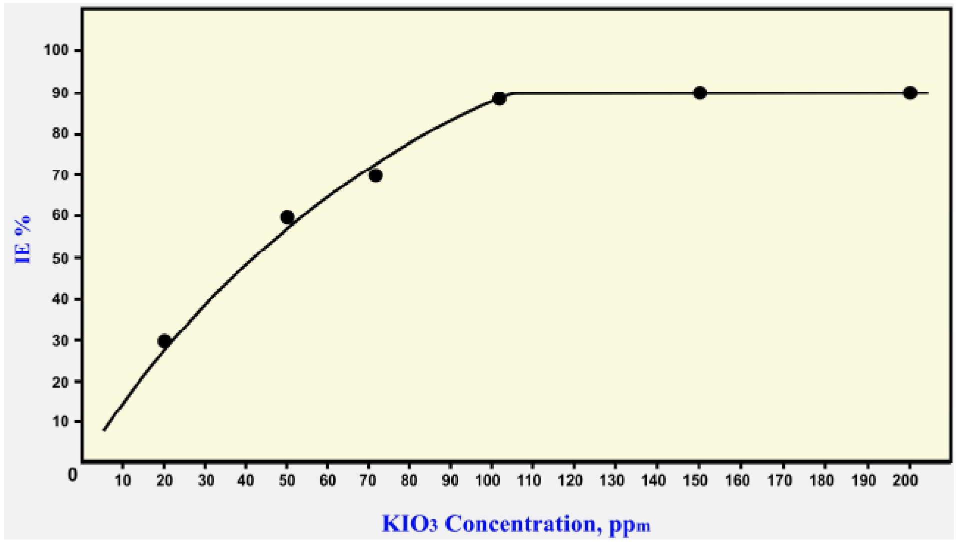

Fig. (1). Variations of the inhibition efficiency calculated from weight loss measurements at different concentrations of KIO_3 in 2M HCl at 30°C.

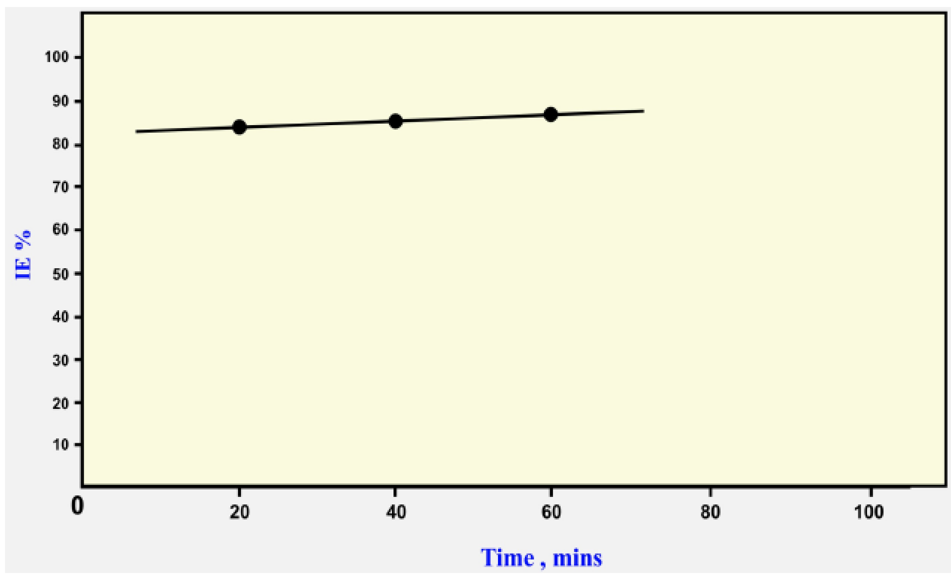

Fig. (2). Effect of immersion time on the I E% of KIO_3 inhibitor for Al coupons in 2M HCl at 30°C.

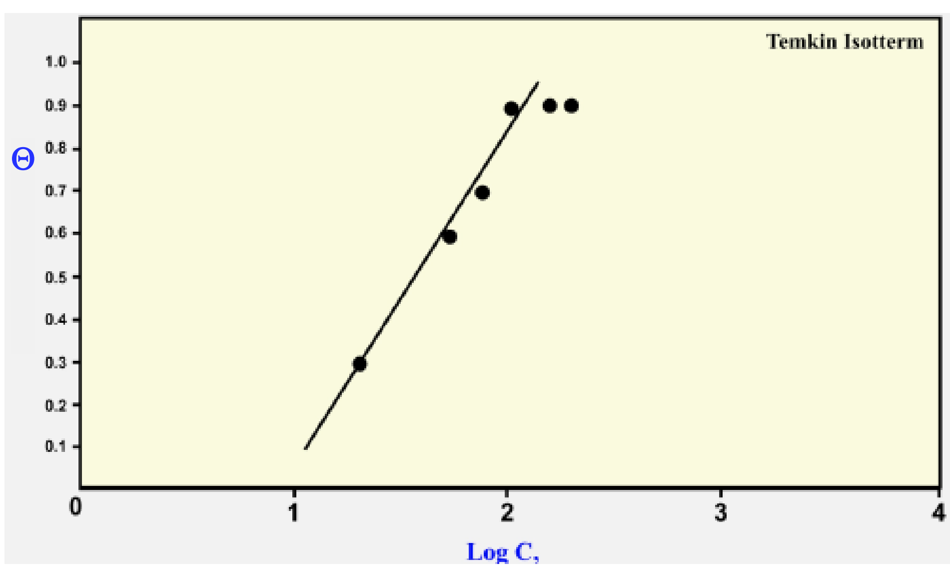

Fig. (3). Temkin adsorption plot as θ against Log C for KIO_3 at 30°C.

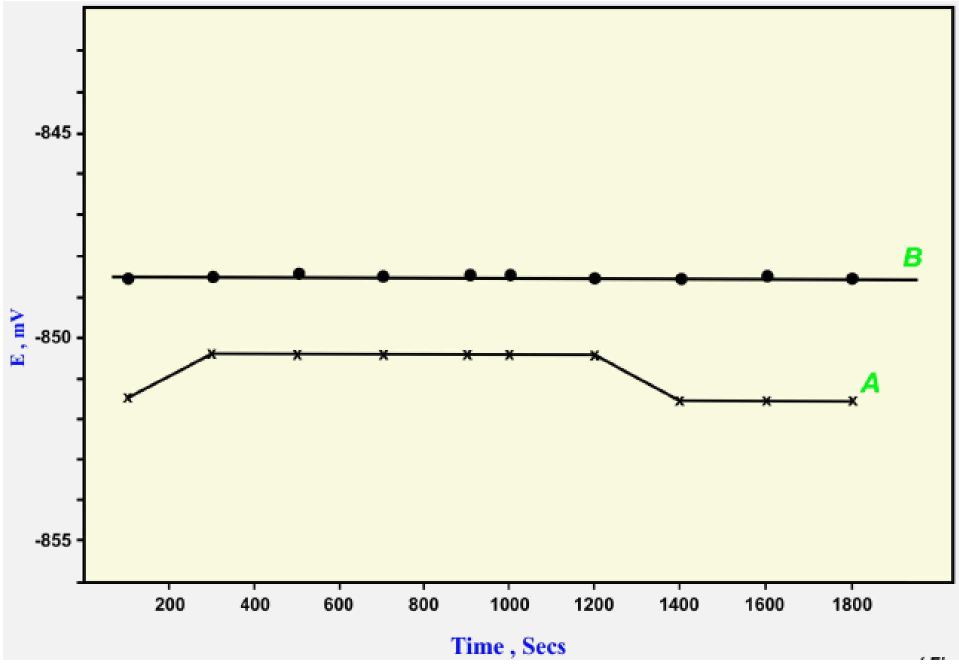

Fig. (4). Potential Vs. time plots for Al in 2M HCL at 30°C: (**A**) Blank. (**B**) 100 ppm KIO_3.

3.4. Polarization

Figs. (**5**, **6**) represent Tafel polarization curves of aluminum in 2M HCl in the presence of 100 ppm KIO_3 and absence of inhibitor (blank solution). It is observed that, both of the cathodic and anodic curves show lower current density in the presence of KIO_3 than recorded for the blank solution. This behavior indicated that KIO_3 effects on both cathodic and anodic reactions of corrosion process. Therefore potassium iodate could be classified as mixed type (anodic/cathodic) inhibitor. The electrochemical parameters (i_{corr}, E_{corr}, β_a and β_c) associated with polarization measurements and the inhibitor efficiency IE% at 100 ppm inhibitor concentration at 30°C, are listed in Table **1**, where i_{corr}, $E_{corr,}$ β_a and β_c are the corrosion current density, the corrosion potentials and anodic and cathodic Tafel slopes, respectively. Since the corrosion rate is directly related to the corrosion current density (i_{corr}), the inhibition efficiency IE% at 100 ppm inhibitor concentration was calculated from the equation:

$$IE\% = 100 \text{ x} \left(1 - \frac{i_{corr}}{i_{0\ corr}} \right) \quad (7)$$

where $i_{o\ corr}$ and i_{corr} are the corrosion current densities in the absence and presence of inhibitor. According to data

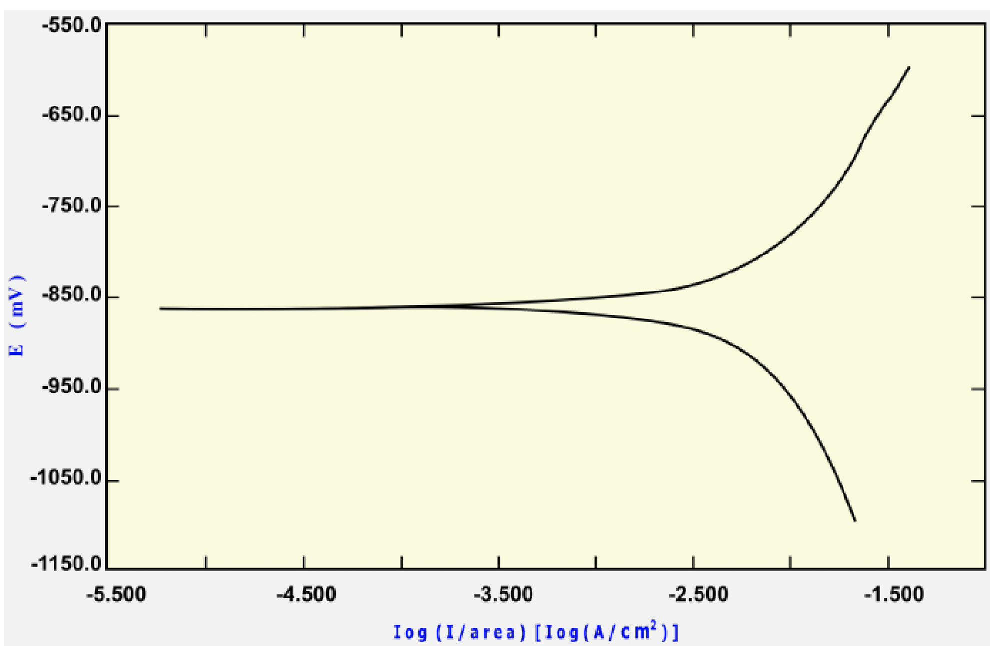

Fig. (5). Tafel polarization curve obtained for aluminum at 30°C in 2M HCl.

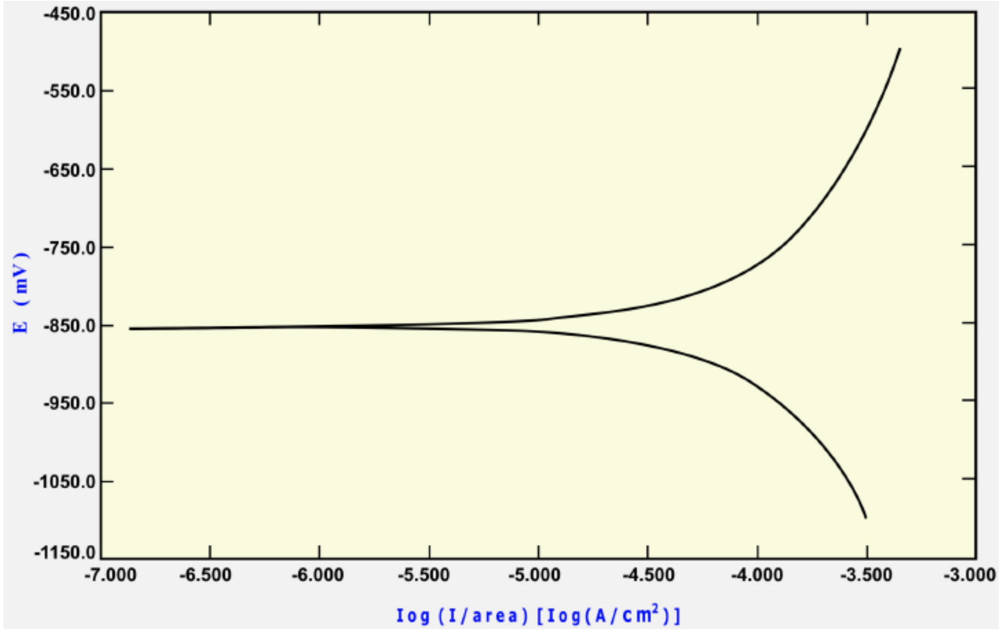

Fig. (6). Tafel polarization curve obtained for aluminum at 30°C in 2M HCl containing 100 ppm inhibitor.

obtained in Table **1**, inhibition efficiency with the inhibitor was 98.63%, which indicates that KIO_3 compound acts as adsorption inhibitor. This idea has been examined in section 3.2; by plotting the suitable adsorption isotherm. Linear polarization measurements were conducted over the potential region, E_{corr} $\pm$20mV at a sweep rate of 1.66 x 10^{-4} mVs^{-1}. Typical linear- polarization curves at room temperature 30°C are shown in Figs. (**7**, **8**). Polarization resistance (R_p) was obtained from the slopes of such polarization curves. These data showed that as was expected, R_p value was 1.072 KΩ for 100 ppm KIO_3 inhibitor. In addition, the percentage corrosion inhibition efficiency with the inhibitor was in agreement to that obtained from Tafel-line method, Table **1**. These measurements confirmed that KIO_3 is an excellent inhibitor for Al- corrosion in 2M HCl at room temperature.

3.5. Electrochemical Impedance Spectroscopy (EIS)

Impedance measurements provide information about both the resistive and capacitive behavior of the interface and makes possible to evaluate the performance of KIO_3 as possible inhibitor against aluminum corrosion. The methods for analysis of the experimental data, developed recently, enable the identification of the choice of adequate structural modes of the interface [19, 20]. This method is widely used for investigation of the corrosion inhibition processes [21].

The effect of 100 ppm KIO_3 concentration on the impedance behavior of Al in 2M HCL solution has been studied (Fig. **9**). Inspection of the data reveals that, the impedance spectra consist of a large capacitive loop at high frequencies (HFS) followed by a small inductive one at low frequency (LF) rang. The HFS capacitive loop is usually related to the charge transfer of the corrosion process and the inductive loop may be attributed to the relaxation processes in the oxide film covering electrode surface [22]. The equivalent circuit model used to fit the experimental results is given in Fig. (**10**) as described elsewhere [23, 24]. The frequency response analyzer is used for impedance data analysis and the fit parameters are listed in Table **2** where R_t, C_{dl} and R_s are the charge transfer resistance, double layer capacitance and solution resistance, respectively. The inhibition efficiency of 100 ppm KIO_3 concentration was calculated from the following equation:

$$IE\% = \left(1 - \frac{C_{dl}}{C^{\circ}_{dl}}\right) \quad (8)$$

where C°_{dl} and C_{dl} are the double layer capacitance of the electrode without and with the inhibitor, respectively. Inspection of Table **2** reveals that R_t value will be higher in presence of 100 ppm KIO_3, and lower with respect to C_{dl}. This is due to surface coverage by the inhibitor, which leads to higher IE%. The electrochemical theory shows that C_{dl} is proportional to the corrosion rate [24]. From the resistance R_t that represnts the corrosion process, the surface coverage may be calculated as follows,

$$\frac{R_t\,(0)}{R_t\,(100)} = \frac{162.3}{1310} = \frac{1/S(0)}{1/S(100)}$$

where S is the area of surface on which no inhibitor adsorbs.

$$\frac{S(100)}{S(0)} = \frac{162.3}{1310}$$

$$\Theta = \frac{S(0) - S(100)}{S(0)} = \frac{1310 - 162.3}{1310} = 0.876$$

The polarization resistance calculated from polarization Table **1** and impedance technique Table **2**, was found to increase in presence of iodate ion. This means that EIS measurements are in good agreement with polarization measurements.

Table 1. Electrochemical Parameters of Corrosion of Al in 2M HCL at 30°C without and with 100ppm KIO_3 and Corresponding Inhibition Efficiencies Obtained from Polarization Method

	E_{corr}(mV)	βa(V/dec)	β_c(V/dec)	R_p(Ωcm^{-2})	i_{corr}	C. R.	IE%
Blank	-862.5	333.5×10^{-3}	372.6×10^{-3}	4.7	5.547mA/cm^2	7.138×10^3mpy	---
100ppm KIO_3	-853.7	386×10^{-3}	381×10^{-3}	1072	75.68μA/cm^2	97.38mpy	98.63%

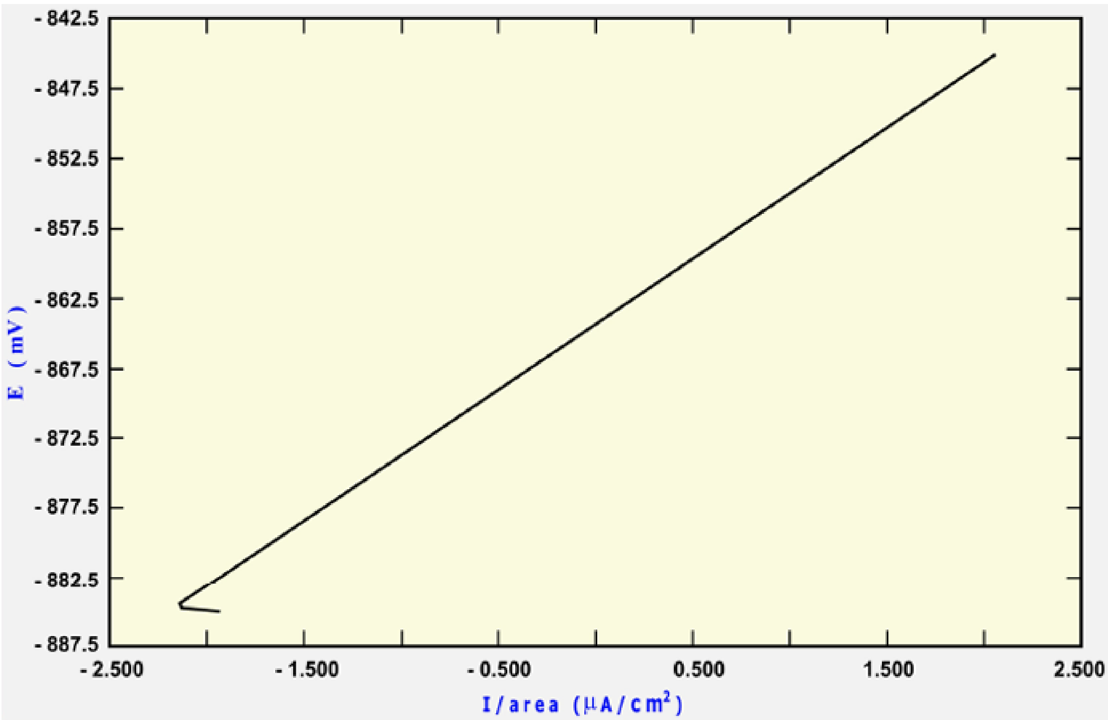

Fig. (7). Polarization resistance measurement for Al in 2M HCl at 30°C.

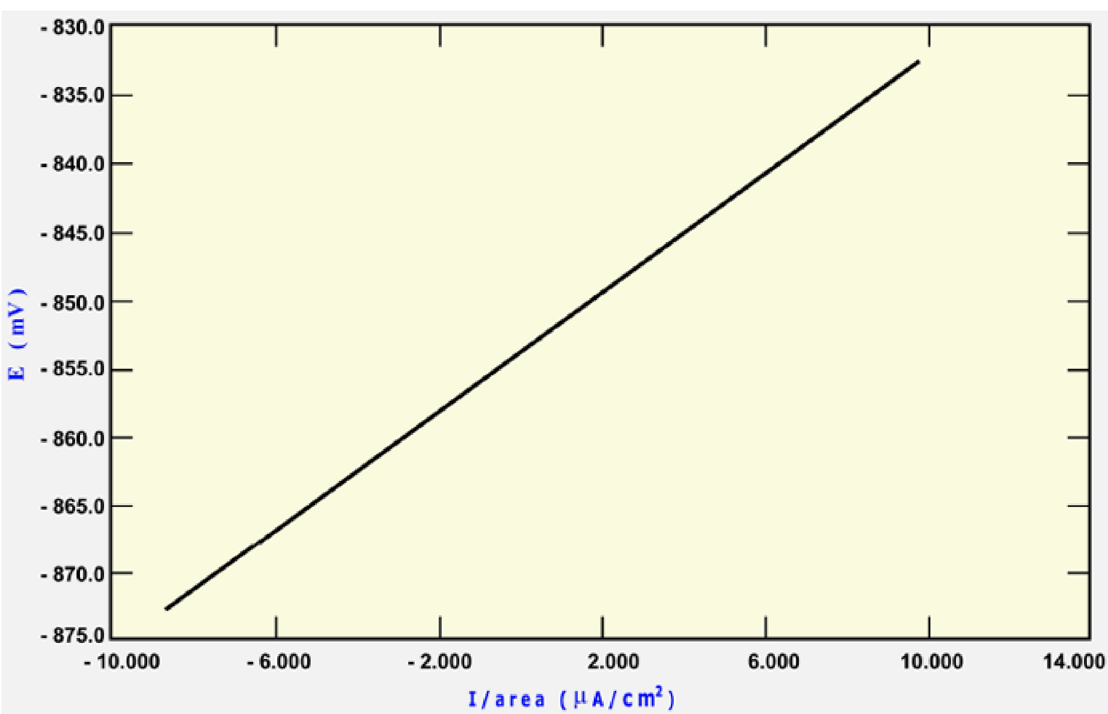

Fig. (8). Polarization resistance measurement for Al in 2M HCl at 30°C containing 100 ppm KIO_3.

Table 2. Impedance Parameters and Corresponding Inhibition Efficiency for the Corrosion of Aluminum in 2M HCl

	$C_{inh.}$	$R_s(\Omega cm^{-2})$	$R_t(\Omega cm^{-2})$	$C_{dl}(\mu F)$	IE%
Blank	----	1.6	162.3	25.83	---
KIO_3	100ppm	3.21	1310	1.04	96.34

4. CONCLUSION

Chemical and electrochemical measurements were used to study the corrosion inhibition of Al in 2M HCl solution at the corrosion potential using potassium iodate as corrosion inhibitor. The principle conclusions are:

1) KIO_3 was found to be effective inhibitor for aluminum in 2M HCl solution.

2) The corrosion process is inhibited by the adsorption of its molecules on aluminum surface.

3) Double layer capacitance decreases with respect to the blank solution when the inhibitor is added; this fact may be explained on the basis of adsorption of KIO_3 on the aluminum surface.

4) In determining the corrosion rates, electrochemical studies and weight loss measurements are coincide.

5) The data obtained from weight loss technique fit well the Temkin adsorption isotherm.

6) The corrosion inhibition efficiency of iodate anion was found to be 90% by weight loss, 98% by Tafel polarization and 96% by EIS measurements.

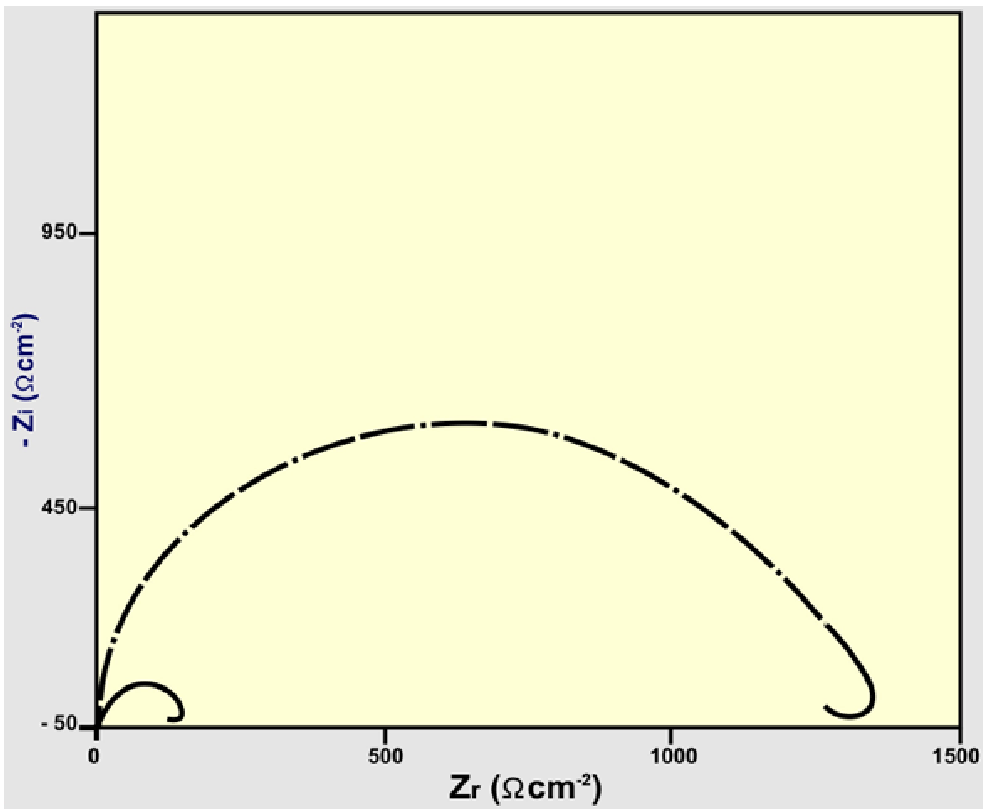

Fig. (9). Impedance plot obtained at 30°C for Al in 2M HCl containing 100 ppm KIO_3 inhibitor.

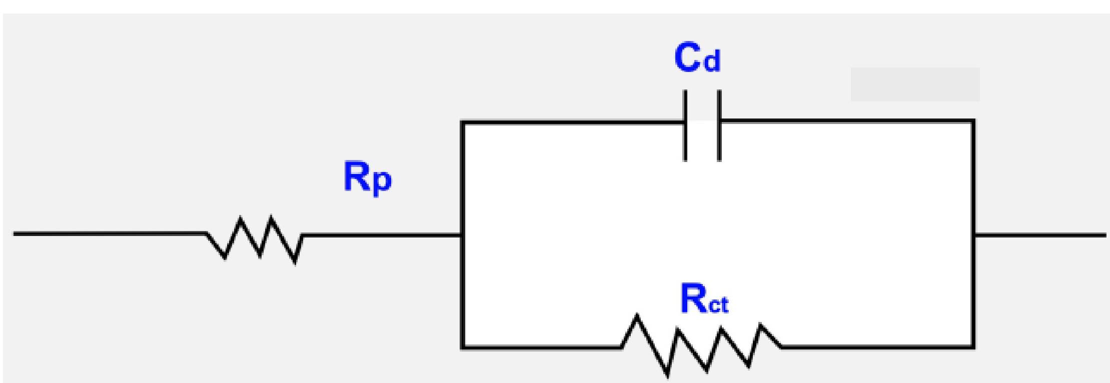

Fig. (10). The equivalent circuit model used to fit the experimental results.

REFERENCES

[1] Ergun U, Yuzer D, Emregul KC. The inhibitory effect of bis-2, 6-(3, 5-dimethylpyrazolyl) pyridine on the corrosion behaviour of mild steel in HClsolution. Mater Chem Phys 2008; 109: 492-9.

[2] Hurlen T, Lian HH, Odegard OS, Valand TV. Corrosion and passive behaviour of aluminium in weakly acid solution. Electrochim Acta 1984; 29: 579-85.

[3] El-Etre AY. Inhibition of aluminum corrosion using opuntia extract. Corrosion Sci 2003; 45: 2485-95.

[4] Pourbaix M. Atlas of electrochemical equilibriua in aqueous solutions. New York: Pergamon Press 1966.

[5] Abdullah M. Antibacterial drugs as corrosion inhibition for corrosion of aluminum in hydrochloric acid solution. Corrosion Sci 2004; 46: 1981-96.

[6] Luo Q. Copper dissolution behavior in acidic iodate solutions. Langmuir 2000; 16: 5154-8.

[7] Mogoda A, Ahmead Y, Badawy W. Corrosion inhibition of Ti-6Al-4V alloy in sulfuric and hydrochloric acid solutions using inorganic passivators. Mater Corrosion 2004; 55: 449-56.

[8] Toraishi T, Nagaski S, Tanaka S. In: Tokyo Daigaku Genshiryoku Kenkyo Sogo Senta Shin Ponjumu, 1999, 8th, 1999; p. 152.

[9] Azim SS, Muralidharan S, Iyer SV, Muralidharan B, Vasudhevan T. Synergistic influence of iodide ions in inhibition of corrosion of mild steel in H_2SO_4 by N-Phynylthiourea. Br Corrosion J 1998; 33: 297-301.

[10] Feng Y, Siow KS, Teo WK, Hsieh AK. The synergistic effects of propargyl alchol and potassium iodide on the inhibition of mild steel in 0.5M sulfuric acid solution. Corrosion Sci 1999; 41: 829-52.

[11] Quraishi MA, Rawat I, Ajmal M. Synergistic effect of iodide ions on inhibitive performance of substituted dithiobiurets during corrosion of mild steel in hot hydrochloric acid. Corrosion (Houston) 1999; 55: 919-23.

[12] Oguzie EE, Unaegbu C, Okolue CN, Onuchukwu AI. Inhibition of mild steel corrosion in sulfuric acid using indigo dye and synergistic halide additives. Mater Chem Phys 2004; 84: 363-8.

[13] Oguzie EE. Influence of halide ions on the inhibitive effect of congo red dye on the corrosion of mild steel in sulfuric acid solution. Mater Chem Phys 2004; 87: 212-7.

[14] Umoren SA, Obot IB, Akpabia LE, Etuk SE. Adsorption and corrosive inhibitive properties of viga unguiculate in alkaline and acidic media. Pigment Resin Technol 2008; 37: 98-106.

[15] Khaled KF. New synthesized guanidine derivative as a green corrosion for mild steel in acidic solutions. Int J Electrochem Sci 2008; 3: 462-75.

[16] Khaled KF. Molecular simulation, quantum chemical calculations and electrochemical studies for inhibition of mild steel by triazoles. Electrochim Acta 2008; 53: 3484-92.

[17] Kendig M, Jeanjaquet S. Cr (VI) and CE (III) inhibition of oxygen reduction on copper. J Electrochem Soc 2002; 149: B47-B51.

[18] Hosseini MG, Mertens SFL, Gorbani M, Arshadi MR. Assymmetrical Schiff bases as inhibitiors of mild steel corrosion in sulphoric acid media. Mater Chem Phys 2003; 78: 800-8.

[19] Stoynov ZB, Grafov BM, Savova-Stoynova B, Elkin VV. Electrochemical impedance. Moscow: Nauka 1991.

[20] Gabrielli G. Identification of electrochemical processes by frequency response analysis. Technical Report 004/83, 1984; 120.

[21] Lopez DA, Simison SN, de Sanchez SR. The influence of steel microstructure on corrosion. EIS Studies on the inhibition efficiency of benzimidazole. Electrochim Acta 2003; 48: 845-54.

[22] Abd El-Rehim SS, Hassan HH, Amin MA. Corrosion inhibition of aluminum by 1,1 (Lauryl amido) propyl ammonium chloride in HCl solution. Mater Chem Phys 2001; 70: 64-72.

[23] Sekine I, Satongi M, Hagiuda H, *et al.* Corrosion inhibition of steel by cationic and anionic polymers in cooling water system. J Electrochem Soc 1992; 139: 3167-73.

[24] Lorenz WJ, Masfeld F. Determination of corrosion rates by electrochemical DC and AC methods. Corrosion Sci 1981; 21: 647-72.

Received: March 23, 2009 Revised: May 8, 2009 Accepted: May 17, 2009