*Full Length Research Paper*

# Eco-friendly chalcones derivatives as corrosion inhibitors for carbon steel in hydrochloric acid solution

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The inhibiting effect of some chalcones derivatives on the corrosion of carbon steel in 1 M HCl was studied by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. The results showed that the inhibition efficiency increases with increasing the inhibitor concentration, while it decreases with increasing the temperature. The adsorption of chalcones derivatives on the carbon steel surface obeys Langmuir adsorption isotherm. Some thermodynamic parameters were calculated and discussed. The values of free energy of adsorption for investigated inhibitors were calculated. Polarization curves showed that chalcones derivatives are mixed-type inhibitors but the cathode is more polarized than the anode. The variation in inhibition efficiency depends on the type of the substituent groups in the benzene ring. It was found that the presence of donating group (such as $OCH_3$) better facilitates the adsorption of molecules on the surface than in the case with withdrawing groups (such as – Cl and $NO_2$). The data obtained from the four different methods were in good agreement.

**Key words:** Carbon steel, HCl, corrosion inhibition, electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM), chalcones derivatives.

## INTRODUCTION

Hydrochloric acid is often used as a pickling acid for iron and its alloys. Also, the corrosion inhibition of carbon steel becomes of such interest to do because of its widely used as a constructional material in many industries and this is due to its excellent mechanical properties and low cost. To make secure from attack of acid, inhibitors are frequently used (Trabanelli, 1991; Abd El Rehim et al., 2001). Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms. Among them, organic inhibitors have many advantages such as high inhibition efficiency, low price, low toxicity and easy production (Dey et al., 1993; Malhotra et al., 1992; Noor et al., 1993; Raspini, 1993;

Abd El Rehim et al., 2003; Aljourani et al., 2009; Amar et al., 2007; Arab and Noor, 1993). Organic heterocyclic compounds have been used for the corrosion inhibition of iron (Arawaki et al., 1987; Ashassi-Sorkhabi and Ghalebsaz-Jeddi, 2005; Banerjee and Malhotra, 1992; Bayol et al., 2007; Benabdellah et al., 2007; Benalli et al., 2007), copper (Bessone et al., 1983), aluminum Bosch et al., 2001; Branzoi et al., 2002; Da Costa and Agostinho, 1989), and other metals (Damaskin et al., 1971; Elachouri et al., 1995) in different corroding media.

It has been observed that the adsorption of corrosion inhibitors depends mainly on certain physico-chemical properties of the molecule such as functional groups,

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**Table 1.** The molecular structures, names, molecular weights and molecular formulas of investigated inhibitors.

| Inhibitor | Structure | IUPAC name | Molecular weight | Chemical formula |
|---|---|---|---|---|
| (1) | H₃C–N(CH₃)–C₆H₄–CH=CH–C(O)–C₆H₄–OH | 3-(4-(dimethylamino)phenyl) -1-(4-hydroxyphenyl) prop-2-en-1-one | 267. 32 | $C_{17}H_{17}NO_2$ |
| (2) | HO–C₆H₄–CH=CH–C(O)–C₆H₄–OH | 3-(3-hydroxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one | 240. 25 | $C_{15}H_{12}O_3$ |
| (3) | C₆H₅–CH=CH–C(O)–C₆H₄–OH | 1-(4-hydroxyphenyl)-3-phenylprop-2-en-1-one | 224.25 | $C_{15}H_{12}O_2$ |
| (4) | O₂N–C₆H₄–CH=CH–C(O)–C₆H₄–OH | 1-(4-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en- 1-one | 269. 25 | $C_{15}H_{12}O_2$ |

steric factors, aromaticity, electron density at the donor atoms and π orbital character of donating electrons (El-Sherbiny, 1999; Epelboin et al., 1972; Fouda et al., 2006; Fouda and Elattar, 2012; Granese et al., 1992; Granese, 1988), and also on the electronic structure of the molecules (Guo et al., 2002; Hajjaji et al., 1993; Khaled and Hackerman, 2003).

The objective of the present work is to investigate the inhibiting action of the eco-friendly chalcones derivatives in 1 M HCl at 25 to 55°C using chemical and electrochemical techniques.

**MATERIALS AND METHODS**

Tests were performed on carbon steel specimens of the following composition (weight %): 0.200% C, 0.350% Mn, 0.024% P, 0.003% S, and the remainder Fe.

**Inhibitors**

Chalcones are important intermediates for the synthesis of many flavones and chromones molecules. A fast and very rapid procedure is reported for the synthesis of chalcones from the ketones and aldehydes under the microwave (MW) irradiation. Most of the chalcones were found to have very promising antibacterial and antifungal activities. This motivated us to prepare these chalcones derivatives in order to use them as save corrosion inhibitors for carbon steel in HCl solutions. These chalcones derivatives were prepared as reported earlier (Khamis 1990) and are listed in Table 1.

**Solutions**

The aggressive solutions, 1 M HCl were prepared by dilution of analytical grade (37%) HCl with bi-distilled water. The concentration

range of the inhibitors used was $1 \times 10^{-6} – 21 \times 10^{-6}$ M.

**Chemical technique (weight loss method)**

Seven parallel carbon steel sheets of 2.5 × 2.0 × 0.06 cm were abraded with emery papers (grade 320–500–800) and then washed with bi-distilled water and acetone. After accurate weighing, the specimens were immersed in a 250 ml beaker, which contained 100 ml of HCl with and without addition of different concentrations of investigated inhibitors. All the aggressive acid solutions were open to air. After 2 h, the specimens were taken out, washed, dried and weighed accurately. The average weight loss of seven parallel carbon steel sheets could be obtained. The inhibition efficiency (% IE) and the degree of surface coverage, θ, of chalcones derivatives for the corrosion of carbon steel were calculated from Equation 1:

$$\% \text{ IE} = \theta \times 100 = [(W_o – W)/ W_o] \times 100 \qquad (1)$$

Where $W_o$ and W are the values of the average weight losses without and with addition of the inhibitor, respectively.

**Electrochemical technique**

All electrochemical measurements were carried out in a conventional three-electrode cell with a platinum counter electrode (1 cm²) and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode. The working electrode was in the form of a square cut from carbon steel embedded in epoxy resin of polytetrafluoroethylene (PTFE) so that the flat surface was the only surface of the electrode. The working surface area was 1.0 × 1.0 cm. Tafel polarization curves were obtained by changing the electrode potential automatically from -500 to +500 mV at open circuit potential with a scan rate of 1 mVs⁻¹. All experiments were carried out in freshly prepared solution at constant temperature (25 ± 1°C) using a thermostat.

Stern-Geary method (Lipkowski and Ross, 1992) used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines to a point  which gives log $i_{corr}$ and
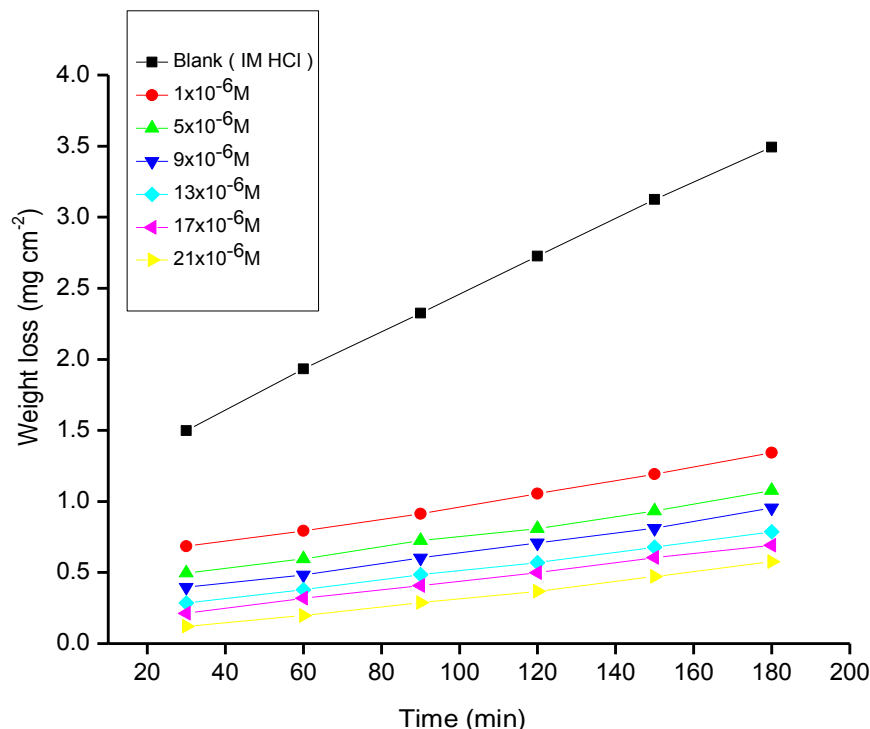
**Figure 1.** Weight loss- time curves for carbon steel in 1 M HCl in the absence and presence of different concentrations of inhibitor (1) at 25°C.

the corresponding corrosion potential ($E_{corr}$) for inhibitor free acid and for each concentration of inhibitor. Then, $i_{corr}$ was used for calculation of inhibition efficiency and surface coverage ($\theta$) as in Equation 2:

$$\% \text{ IE} = \theta \times 100 = [(i_{corr} - i_{corr (inh)}) / i_{corr}] \times 100 \qquad (2)$$

Where $i_{corr}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively.

Impedance measurements were carried out in frequency range from 100 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using ac signals at open circuit potential. The experimental impedance were analyzed and interpreted on the basis of the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer $R_{ct}$ (diameter of high frequency loop) and the capacity of double layer $C_{dl}$ which is defined in Equation 3:

$$C_{dl} = 1/ (2 \pi f_{max} R_{ct})$$
$$\qquad (3)$$

Where $f_{max}$ is the maximum frequency.

The inhibition efficiencies and the surface coverage ($\theta$) obtained from the impedance measurements were defined by Equation 4:

$$\% \text{ IE} = \theta \times 100 = [1 - (R^{\circ}_{ct} / R_{ct})] \times 100 \qquad (4)$$

Where $R^{\circ}_{ct}$ and $R_{ct}$ are the charge transfer resistance in the absence and presence of inhibitor, respectively.

The electrochemical frequency modulation technique (EFM) provides a new tool for electrochemical corrosion monitoring. With the electrochemical modulation technique (EFM), a potential perturbation by two sine waves of different frequencies is applied to the system. As a corrosion process is nonlinear in nature, responses are generated at more frequencies than the frequencies of the applied signal. The current responses can be measured at zero, harmonic and intermodulation frequencies. Analysis of these current responses can result in the corrosion current density and Tafel parameters. Electrochemical frequency modulation (EFM) is a nondestructive technique as electrochemical impedance spectroscopy (EIS) that can directly and rapidly give values of the corrosion current without a prior knowledge of Tafel constants. The great strength of the EFM is the causality factor, which serves as an internal check on the validity of the EFM measurement. With the causality factors, the experimental EFM can be verified (Luo et al., 1998; Maayta and Al-Rawashdeh, 2004). The electrode potential was allowed to stabilize 30 min before starting the measurements. All the experiments were conducted at 25 ± 1°C. Measurements were performed using Gamry (PCI 300/4) Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry framework system based on the ESA 400.

Gamry applications include DC105 for corrosion measurements, EIS300 for electrochemical impedance spectroscopy and EFM140 software for electrochemical frequency modulation along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.

## RESULTS AND DISCUSSION

### Weight loss measurements

The weight loss-time curves of carbon steel with the addition of inhibitor (1) in 1 M HCl at various concentrations is shown in Figure 1 (similar curves were

**Table 2.** Variation of inhibition efficiency (% IE) of different compounds with their molar concentrations at 25°C from weight loss measurements at 2 h immersion in 1 M HCl.

| Compound | Concentration (M) | CR (mg cm$^{-2}$ min$^{-1}$) | % IE |
|---|---|---|---|
| Blank | - | 0.028 | - |
| 1 | $1 \times 10^{-6}$ | 0.012 | 57.1 |
|  | $5 \times 10^{-6}$ | 0.009 | 67.9 |
|  | $9 \times 10^{-6}$ | 0.007 | 75.0 |
|  | $1.3 \times 10^{-5}$ | 0.006 | 78.6 |
|  | $1.7 \times 10^{-5}$ | 0.005 | 82.1 |
|  | $2.1 \times 10^{-5}$ | 0.003 | 89.3 |
| 2 | $1 \times 10^{-6}$ | 0.015 | 46.4 |
|  | $5 \times 10^{-6}$ | 0.012 | 57.1 |
|  | $9 \times 10^{-6}$ | 0.010 | 64.3 |
|  | $1.3 \times 10^{-5}$ | 0.008 | 71.4 |
|  | $1.7 \times 10^{-5}$ | 0.007 | 75.0 |
|  | $2.1 \times 10^{-5}$ | 0 .006 | 78.6 |
| 3 | $1 \times 10^{-6}$ | 0.018 | 35.7 |
|  | $5 \times 10^{-6}$ | 0.015 | 46.4 |
|  | $9 \times 10^{-6}$ | 0.012 | 57.1 |
|  | $1.3 \times 10^{-5}$ | 0.011 | 60.7 |
|  | $1.7 \times 10^{-5}$ | 0.009 | 67.9 |
|  | $2.1 \times 10^{-5}$ | 0.007 | 75.0 |
| 4 | $1 \times 10^{-6}$ | 0.022 | 21.4 |
|  | $5 \times 10^{-6}$ | 0.017 | 39.3 |
|  | $9 \times 10^{-6}$ | 0.015 | 46.4 |
|  | $1.3 \times 10^{-5}$ | 0.013 | 53.6 |
|  | $1.7 \times 10^{-5}$ | 0.011 | 60.7 |
|  | $2.1 \times 10^{-5}$ | 0.009 | 67.9 |

obtained in presence of the other inhibitors, but not shown). The curves of Figure 1 show that the weight loss values of carbon steel in 1 M HCl solution containing investigated inhibitor decrease as the concentration of the inhibitor increases; that is, the corrosion inhibition strengthens with the inhibitor concentration, this appear in Table 1. This trend may result from the fact that the adsorption of inhibitor on the carbon steel increases with the inhibitor concentration thus the carbon steel surface is efficiently separated from the medium by the formation of a film on its surface (Table 2) (Mazzone et al., 1983; Mernari et al., 2001).

**Potentiodynamic polarization technique**

Figure 2 shows the anodic and cathodic Tafel polarization curves for carbon steel in 1 M HCl in the absence and presence of varying concentrations of inhibitor 1 at 25°C.

Similar curves were obtained in presence of the other inhibitors (not shown). From Figure 2, it is clear that both anodic metal dissolution and cathodic $H_2$ reduction reactions were inhibited when investigated inhibitors were added to 1 M HCl and this inhibition was more pronounced with increasing inhibitor concentration. Tafel lines are shifted to more negative and more positive potentials with respect to the blank curve by increasing the concentration of the investigated inhibitors. This behavior indicates that the undertaken inhibitors act as mixed-type inhibitors (Migahed et al., 2009, 2004). Table 3 shows that $i_{corr}$ decreases by adding the additives and by increasing their concentrations. In addition, $E_{corr}$ does not change obviously, but the Tafel slopes ($\beta_a$, $\beta_c$) are approximately constant indicating that the retardation of the two reactions (cathodic hydrogen reduction and anodic metal dissolution) were affected without changing the dissolution mechanism (Moretti et al., 1994; Moussa et al., 2007; Mu et al., 1996).

**Table 3.** Corrosion parameters of carbon steel electrode in 1 M HCl solution containing different concentrations of inhibitors at 25°C from potentiodynamic technique.

| Compound | Concentration (M) | $-E_{corr}$ (mV versus SCE) | $i_{corr}$ (mA cm$^{-2}$) | $\beta_c$ (mV dec$^{-1}$) | $\beta_a$ (mV dec$^{-1}$) | $\Theta$ | % IE | CR (mmy$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 M HCl | 00 | 521 | 483 | 42 | 22 | - | - | 220.6 |
| | $1 \times 10^{-6}$ | 520 | 261 | 26 | 13 | 0.459 | 45.9 | 119.5 |
| | $5 \times 10^{-6}$ | 496 | 177 | 48 | 20 | 0.634 | 63.4 | 80.9 |
| Inhibitor 1 | $9 \times 10^{-6}$ | 506 | 101 | 47 | 39 | 0.791 | 79.1 | 45.9 |
| | $1.3 \times 10^{-5}$ | 499 | 90 | 82 | 50 | 0.814 | 81.4 | 41.2 |
| | $1.7 \times 10^{-5}$ | 498 | 80 | 74 | 47 | 0.834 | 83.4 | 36.6 |
| | $2.1 \times 10^{-5}$ | 473 | 45 | 127 | 85 | 0.906 | 90.6 | 20.9 |
| | $1 \times 10^{-6}$ | 519 | 284 | 32 | 41 | 0.412 | 41.2 | 130 |
| | $5 \times 10^{-6}$ | 510 | 211 | 46 | 33 | 0.563 | 56.3 | 96.2 |
| Inhibitor 2 | $9 \times 10^{-6}$ | 501 | 165 | 85 | 54 | 0.658 | 65.8 | 75.4 |
| | $1.3 \times 10^{-5}$ | 490 | 137 | 116 | 70 | 0.716 | 71.6 | 62.4 |
| | $1.7 \times 10^{-5}$ | 494 | 98 | 106 | 76 | 0.797 | 79.7 | 45.1 |
| | $2.1 \times 10^{-5}$ | 494 | 63 | 83 | 57 | 0.869 | 86.9 | 29.2 |
| | $1 \times 10^{-6}$ | 518 | 300 | 32 | 27 | 0.378 | 37.8 | 137.2 |
| | $5 \times 10^{-6}$ | 517 | 253 | 29 | 24 | 0.476 | 47.6 | 115.8 |
| Inhibitor 3 | $9 \times 10^{-6}$ | 506 | 203 | 48 | 67 | 0.579 | 57.9 | 92.9 |
| | $1.3 \times 10^{-5}$ | 523 | 152 | 22 | 20 | 0.685 | 68.5 | 69.3 |
| | $1.7 \times 10^{-5}$ | 518 | 117 | 23 | 23 | 0.757 | 75.7 | 53.5 |
| | $2.1 \times 10^{-5}$ | 507 | 84 | 28 | 17 | 0.825 | 82.5 | 38.7 |
| | $1 \times 10^{-6}$ | 532 | 369 | 37 | 36 | .0.236 | 23.6 | 186.5 |
| | $5 \times 10^{-6}$ | 513 | 263 | 61 | 42 | 0.455 | 45.5 | 120.1 |
| Inhibitor 4 | $9 \times 10^{-6}$ | 507 | 206 | 71 | 51 | 0.573 | 57.3 | 94.3 |
| | $1.3 \times 10^{-5}$ | 499 | 160 | 80 | 58 | 0.668 | 66.8 | 73.3 |
| | $1.7 \times 10^{-5}$ | 506 | 123 | 64 | 46 | 0.745 | 74.5 | 56.2 |
| | $2.1 \times 10^{-5}$ | 486 | 96.8 | 122 | 82 | 0.800 | 80.0 | 44.2 |

**Electrochemical impedance spectroscopy (EIS)**

The effect of inhibitor concentration on the impedance behavior of carbon steel in 1 M HCl solution at 25°C is presented in Figure 3. The curves show a similar type of Nyquist plots for carbon steel in the presence of various concentrations of inhibitor (1). Similar curves were obtained for other inhibitors but not shown. The existence of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. Deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, and formation of porous layers and in homogenates of the electrode surface (Osman et al., 1997; Parr et al., 1978). Inspections of the data reveal that each impedance diagram consists of a large capacitive loop with one capacitive time constant in the Bode–phase plots (Figure 4). The electrical equivalent circuit model is shown in Figure 5. It used to analyze the obtained impedance data. The model consists of the solution resistance ($R_s$), the charge-transfer resistance of the interfacial corrosion reaction ($R_{ct}$) and the double layer capacitance ($C_{dl}$). Excellent fit with this model was obtained with our experimental data.

EIS data in Table 3 show that the $R_{ct}$ values increase and the $C_{dl}$ values decrease with increasing the inhibitor concentrations. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, decreasing the extent of dissolution reaction. The higher ($R_{ct}$) values are generally associated with slower corroding system (Raspini, 1993; Rosenfeld, 1981). The decrease in the $C_{dl}$ can result from the decrease of the local dielectric constant and/or from
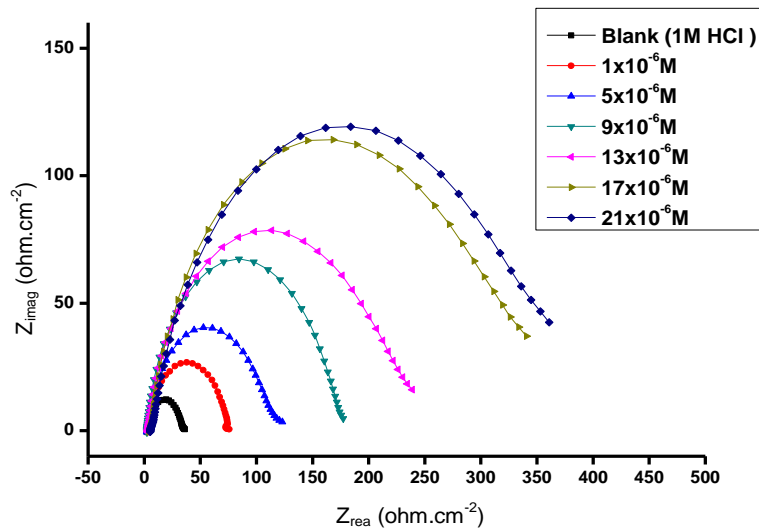
**Figure 3.** Nyquist plots for carbon steel in 1 M HCl at different concentrations of inhibitor (1) at 25°C.
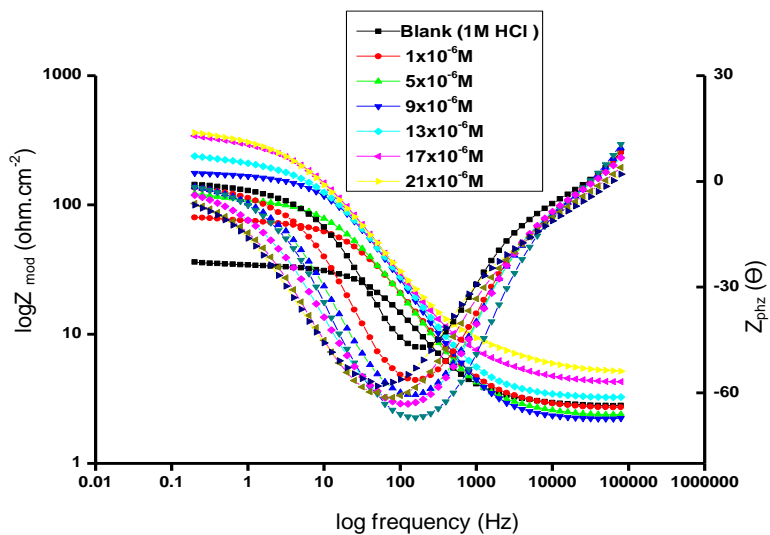


**Figure 4.** The Bode plots for C-steel in 1 M HCl at different concentrations of inhibitor (1) at 25°C.
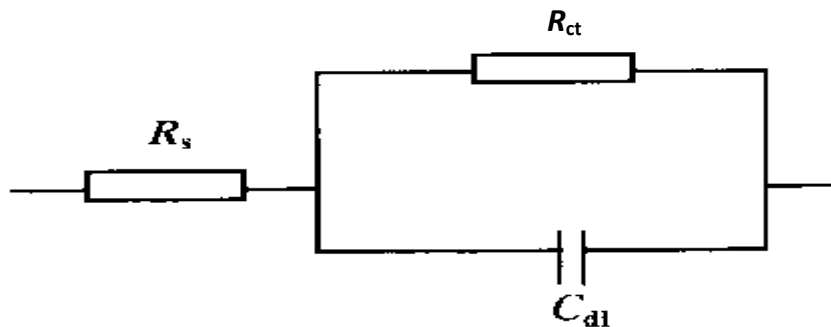


**Figure 5.** Electrical equivalent circuit model used to fit the results of impedance.

**Table 4.** EIS data of carbon steel in 1 M HCl and in the absence and presence of different concentrations of investigated inhibitors at 25°C.

| Compound | Concentration (M) | $C_{dl} \times 10^{-3}$ ($\mu F cm^{-2}$) | $R_{CT}$ ($\Omega$ cm$^2$) | $\theta$ | %IE |
|---|---|---|---|---|---|
| 1 M HCl | 00 | 117.9 | 31.8 | - | - |
| | $1 \times 10^{-6}$ | 91.4 | 74.3 | 0.572 | 57.2 |
| | $5 \times 10^{-5}$ | 86.3 | 110.9 | 0.715 | 71.5 |
| Inhibitor 1 | $9 \times 10^{-5}$ | 79.6 | 168.4 | 0.812 | 81.2 |
| | $13 \times 10^{-5}$ | 73.1 | 219.6 | 0.856 | 85.6 |
| | $17 \times 10^{-5}$ | 64.9 | 330.4 | 0.904 | 90.4 |
| | $21 \times 10^{-5}$ | 57.6 | 364.3 | 0.913 | 91.3 |
| | $1 \times 10^{-6}$ | 93.7 | 51.6 | 0.386 | 38.6 |
| | $5 \times 10^{-5}$ | 88.9 | 81.68 | 0.613 | 61.3 |
| Inhibitor 2 | $9 \times 10^{-5}$ | 81.2 | 134 | 0.764 | 76.4 |
| | $13 \times 10^{-5}$ | 78.9 | 178.3 | 0.822 | 82.2 |
| | $17 \times 10^{-5}$ | 63.6 | 197.3 | 0.839 | 83.9 |
| | $21 \times 10^{-5}$ | 61.7 | 244 | 0.870 | 87.0 |
| | $1 \times 10^{-6}$ | 97.2 | 42.6 | 0.256 | 25.6 |
| | $5 \times 10^{-5}$ | 90.4 | 65.96 | 0.528 | 51.8 |
| Inhibitor 3 | $9 \times 10^{-5}$ | 84.9 | 101.4 | 0.688 | 68.8 |
| | $13 \times 10^{-5}$ | 79.4 | 168.4 | 0.811 | 81.1 |
| | $17 \times 10^{-5}$ | 69.3 | 176 | 0.821 | 82.1 |
| | $21 \times 10^{-5}$ | 66.2 | 224 | 0.859 | 85.9 |
| | $1 \times 10^{-6}$ | 102.5 | 37.5 | 0.147 | 14.7 |
| | $5 \times 10^{-5}$ | 92.3 | 47.8 | 0.339 | 33.9 |
| Inhibitor 4 | $9 \times 10^{-5}$ | 86.1 | 66.1 | 0.521 | 52.1 |
| | $13 \times 10^{-5}$ | 79.1 | 72.5 | 0.563 | 56.3 |
| | $17 \times 10^{-5}$ | 77.4 | 97.71 | 0.676 | 67.6 |
| | $21 \times 10^{-5}$ | 69.8 | 139.7 | 0.773 | 77.3 |

the increase of thickness of the electrical double layer suggested that the inhibitor molecules function by adsorption at the metal/solution interface (Schmitt and Bedbur, 1985). The % IE obtained from EIS measurements are close to those deduced from polarization measurements. The order of inhibition efficiency obtained from EIS measurements is as follows (Table 4): 1 > 2 > 3 > 4.

**Electrochemical frequency modulation technique (EFM)**

The results of EFM experiments are a spectrum of current response as a function of frequency. The spectrum is called the intermodulation spectrum. Figure 6 shows the intermodulation spectrum of $1 \times 10^{-6}$ M of compound (1) for example. Similar intermodulation spectrum for the effect of addition of various concentrations of inhibitors to 1 M HCl acid solution for

carbon steel were obtained, but not shown. The larger peaks were used to calculate the corrosion current density ($i_{corr}$), the Tafel slopes ($\beta_c$ and $\beta_a$) and the causality factors (CF-2 and CF-3). These electrochemical parameters were simultaneously determined and are listed in Table 5. As can be seen from this table, the corrosion current densities decrease in the presence of different concentrations of chalcones derivatives than in the presence of 1 M HCl solution alone in case of carbon steel. The causality factors also indicate that the measured data are of good quality. The inhibition sufficiency obtained from this method is in the order: 1 > 2 > 3 > 4.

**Adsorption isotherm**

Organic molecules inhibit the corrosion process by the adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitutional
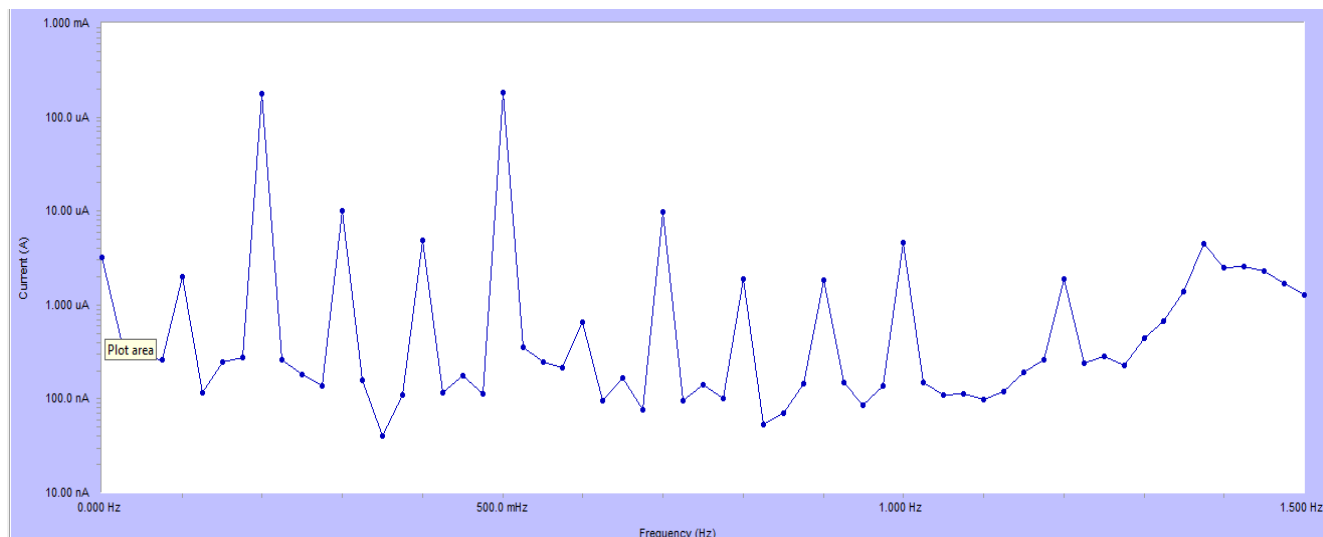
**Figure 6.** EFM spectra for carbon steel in the presence of 1 M HCl in presence of $1 \times 10^{-6}$ M of inhibitor (1) at 25°C.

**Table 5.** Electrochemical kinetic parameters obtained by EFM for carbon steel in 1 M HCl solution, in the absence and presence of different concentration of inhibitors at 25°C.

| Component | Concentration (M) | $i_{corr}$ ($\mu$ A cm$^{-2}$) | $\beta_1$ (mVdec$^{-1}$) | $\beta_2$ (mVdec$^{-1}$) | Causality factor (2) | Causality factor (3) | CR (mmy$^{-1}$) | %IE |
|---|---|---|---|---|---|---|---|---|
| 1 M HCl | 00 | 808.5 | 112.9 | 163.7 | 2.09 | 1.75 | 370.2 | - |
| | $1 \times 10^{-6}$ | 327.6 | 147.7 | 149.7 | 2.18 | 1.98 | 149.7 | 59.5 |
| | $5 \times 10^{-6}$ | 168 | 94.8 | 97.11 | 1.70 | 2.87 | 77.1 | 79. 2 |
| Inhibitor 1 | $9 \times 10^{-6}$ | 140 | 87.9 | 149.5 | 1.93 | 3.32 | 64.1 | 82.7 |
| | $13 \times 10^{-6}$ | 94.9 | 87.6 | 125.1 | 2.08 | 3.82 | 43.4 | 88.3 |
| | $17 \times 10^{-6}$ | 85.9 | 129.4 | 152.1 | 1.78 | 1.27 | 34.6 | 89.4 |
| | $21 \times 10^{-6}$ | 75.7 | 113.7 | 119.4 | 1.35 | 3.01 | 39.3 | 90.6 |
| | $1 \times 10^{-6}$ | 434.9 | 95.9 | 137 | 2.03 | 3.3 | 198.7 | 46.2 |
| | $5 \times 10^{-6}$ | 313 | 101.9 | 144 | 2.02 | 2.36 | 143.1 | 61.3 |
| Inhibitor 2 | $9 \times 10^{-6}$ | 197.5 | 114.4 | 120 | 2.1 | 3.15 | 90.2 | 75.6 |
| | $13 \times 10^{-6}$ | 141.3 | 110.9 | 115.7 | 1.37 | 2.18 | 64.6 | 82.5 |
| | $17 \times 10^{-6}$ | 120.7 | 106.3 | 109.1 | 1.44 | 3.77 | 55.2 | 85.1 |
| | $21 \times 10^{-6}$ | 99.8 | 104.4 | 116.1 | 1.54 | 1.37 | 45.6 | 87.7 |
| | $1 \times 10^{-6}$ | 505.1 | 97.9 | 133.8 | 2.03 | 2.96 | 231.8 | 37.5 |
| | $5 \times 10^{-6}$ | 375.4 | 111.5 | 118.7 | 2.01 | 3.1 | 171.5 | 53.6 |
| Inhibitor 3 | $9 \times 10^{-6}$ | 219.1 | 94.9 | 108.2 | 2.01 | 2.83 | 100.2 | 72.9 |
| | $13 \times 10^{-6}$ | 140.2 | 87.9 | 149.5 | 1.93 | 3.32 | 64.1 | 82.7 |
| | $17 \times 10^{-6}$ | 132.6 | 100.6 | 103.5 | 1.37 | 2.22 | 56.5 | 83.6 |
| | $21 \times 10^{-6}$ | 129.1 | 125.4 | 157.6 | 1.99 | 2.62 | 58.9 | 84.1 |
| | $1 \times 10^{-6}$ | 599.9 | 98.9 | 136.6 | 2.04 | 3.23 | 274.1 | 25.8 |
| | $5 \times 10^{-6}$ | 453.9 | 101.4 | 125.6 | 1.95 | 3.09 | 207.4 | 43.9 |
| Inhibitor 4 | $9 \times 10^{-6}$ | 374.5 | 112 | 117.8 | 2.05 | 3.08 | 172 | 53.7 |
| | $13 \times 10^{-6}$ | 272.7 | 96.6 | 100.7 | 1.73 | 2.61 | 124.6 | 66.3 |
| | $17 \times 10^{-6}$ | 233.1 | 91.9 | 118.1 | 1.97 | 2.57 | 106.5 | 71.2 |
| | $21 \times 10^{-6}$ | 152.6 | 104.7 | 110.7 | 1.49 | 1.83 | 69.7 | 81.1 |
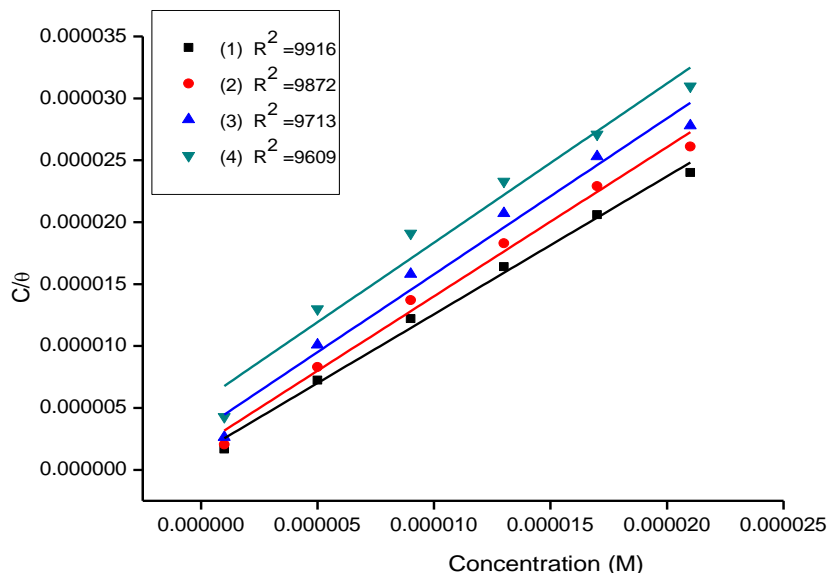
**Figure 7.** Langmuir adsorption isotherm plots for C-steel in 1 M HCl containing various concentrations of investigated inhibitors at 25°C.

**Table 6.** Equilibrium constant and adsorption free energy of the investigated inhibitors adsorbed on carbon steel surface at 25°C.

| Inhibitor | Kinetic model | | | Langmuir isotherm | | | |
| | $1/y$ | $K \times 10^{-5}$ $(M^{-1})$ | $-\Delta G°_{ads.}(kJmol^{-1})$ | $K \times 10^{-5}$ $(M^{-1})$ | $-\Delta G°_{ads.}$ $(kJmol^{-1})$ | Slope | $R^2$ |
|---|---|---|---|---|---|---|---|
| (1) | 2.2 | 16.35 | 45.4 | 6.97 | 43.3 | 1.113 | 0.991 |
| (2) | 2.3 | 6.83 | 43.3 | 5.07 | 42.5 | 1.206 | 0.972 |
| (3) | 2.08 | 2.62 | 40.9 | 3.12 | 41.3 | 1.259 | 0.956 |
| (4) | 1.69 | 1.25 | 39.1 | 1.82 | 40.0 | 1.285 | 0.976 |

process in which an inhibitor molecule, I, in the aqueous phase substitutes an "x" adsorbed on the metal surface (Stupnisek-Lisac et al., 1992; Tan et al 2011) namely:

$$I_{(aq)} + xH_2O_{(sur)} \rightarrow I_{(sur)} + xH_2O_{(aq)} \qquad (8)$$
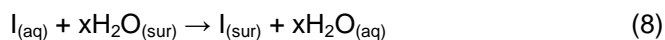
Where x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule.

The adsorption depends on the structure of the inhibitor, the type of the metal and the nature of its surface, the nature of the corrosion medium and its pH value, the temperature and the electrochemical potential of the metal-solution interface. Also, the adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the metal surface. The values of surface coverage, θ, for different concentration of the studied compound at different temperatures have been used to explain the best isotherm to determine the adsorption process. By far, the results of investigated inhibitors were best fitted by Langmuir adsorption isotherm. Figure 7

show the plotting of C/θ against C at 25°C for investigated inhibitors, respectively. These plots gave straight lines with unit slope indicating that the adsorption of investigated compounds on carbon steel surface follows Langmuir adsorption isotherm (Tan et al 2011).

$$C/\theta = 1/K + C \qquad (9)$$

Where C is the concentration of inhibitor, θ the fractional surface coverage and $K_{ads}$ is the adsorption equilibrium constant related to the free energy of adsorption (Singh and Dey, 1993):

$\Delta G°_{ads}$ as:

$$K_{ads} = 1/55.5 \exp(-\Delta G°_{ads}/RT) \qquad (10)$$

Where R is the universal gas constant, T is the absolute temperature. The value 55.5 is the concentration of water on the metal surface in mol/ l.

Value of $K_{ads}$ and $\Delta G°_{ads}$ for chalcones derivatives were calculated and are recorded in Table 6. In all cases, the
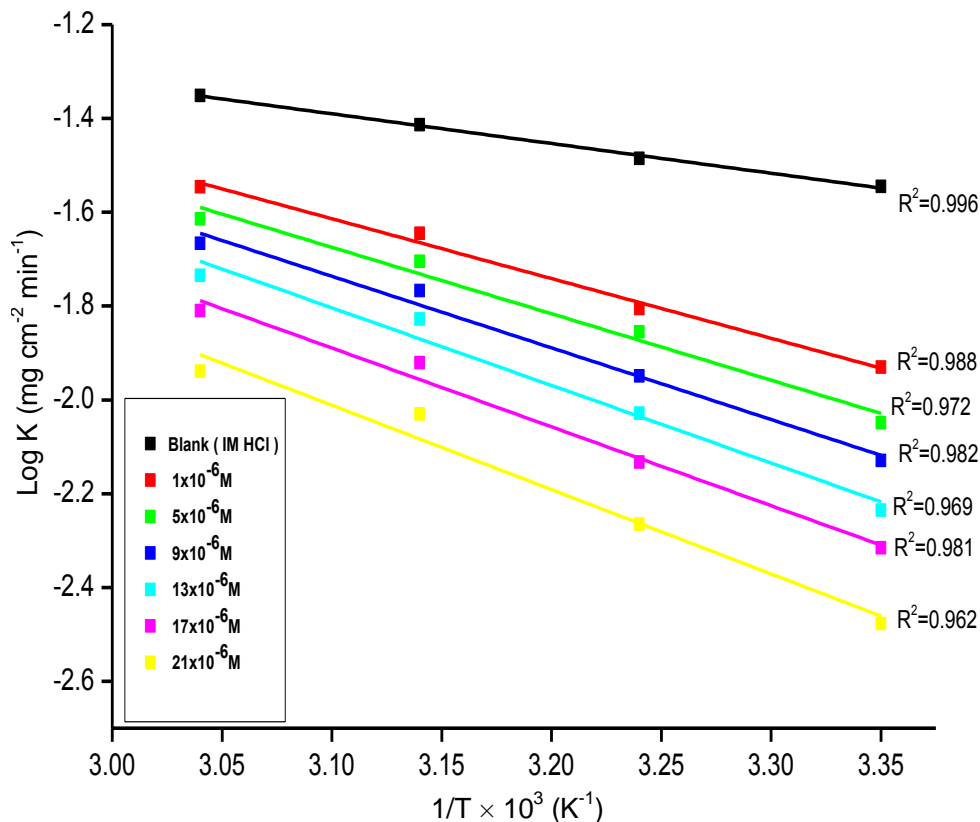
**Figure 8.** Log k – 1/T curves for carbon steel dissolution in 1 M HCl in the absence and presence of compound (1).

values were greater than zero indicating a Langmuir adsorption isotherm. High negative values of $\Delta G°_{ads}$ indicate that these derivatives are strongly adsorbed on carbon steel surface. The negative value ensures spontaneity of the adsorption process and the stability of adsorbed layer on the carbon steel surface. The values of $K_{ads}$ were found to run parallel to the % IE ($K_1 > K_2 > K_3 > K_4$). This result reflects the increasing capability due to structural formation on the metal surface (Trabanelli and Corrosion, 1991).

**Effect of temperature**

The effect of temperature on the rate of corrosion of carbon steel in 1 M HCl containing different concentration from investigated inhibitors was tested by weight loss measurements over a temperature range from 25 to 55°C. The effect of increasing temperature on the corrosion rate and IE obtained from weight loss measurements. The results revealed that, the rate of corrosion increases as the temperature increases and decreases as the concentration of these compounds increases for all compound used. The activation energy ($E_a^*$) of the corrosion process was calculated using

Arrhenius equation:

$$k = A \exp (-E_a^* / RT) \tag{11}$$

Where k is the rate of corrosion, A is the Arrhenius constant, R is the gas constant and T is the absolute temperature.

Figure 8 presents the Arrhenius plots in the presence and absence of compound (1). Similar curves were obtained in the presence of other inhibitors, but not shown. $E_a^*$ values determined from the slopes of these linear plots are shown in Table 7. The linear regression ($R^2$) is close to 1 which indicates that the corrosion of carbon steel in 1 M HCl solution can be elucidated using the kinetic model. Table 7 showed that the value of $E_a^*$ for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of carbon steel is slow in the presence of inhibitor and can be interpreted as due to physical adsorption (Villamil et al., 1999). It is known from Equation 11 that the higher $E_a^*$ values lead to the lower corrosion rate. This is due to the formation of a film on the carbon steel surface serving as an energy barrier for the carbon steel corrosion (Zhao and Mu, 1999). Enthalpy and entropy of activation ($\Delta H^*$, $\Delta S^*$) of the corrosion process were calculated from the transition

**Table 7.** Activation parameters for dissolution of carbon steel in the absence and presence of different concentration of inhibitors in 1 M HCl.

| Inhibitors | Concentration (M) | $E_a^*$ (kJ mol$^{-1}$) | $\Delta H^*$ (kJ mol$^{-1}$) | $-\Delta S^*$ (J mol$^{-1}$K$^{-1}$) | Regression coefficient ($R^2$) |
|---|---|---|---|---|---|
| | Blank (1 M HCl) | 12.2 | 9.6 | 108.6 | 0.9941 |
| 1 | $1 \times 10^{-6}$ | 24.4 | 21.8 | 74.8 | 0.9859 |
| | $5 \times 10^{-6}$ | 27.1 | 24.5 | 67.5 | 0.9658 |
| | $9 \times 10^{-6}$ | 29.2 | 26.7 | 64.9 | 0.9785 |
| | $1.3 \times 10^{-5}$ | 31.7 | 29.1 | 62.1 | 0.9636 |
| | $1.7 \times 10^{-5}$ | 32.2 | 29.6 | 55.9 | 0.9787 |
| | $2.1 \times 10^{-5}$ | 34.4 | 31.9 | 51.3 | 0.9562 |
| 2 | $1 \times 10^{-6}$ | 21.1 | 18.6 | 83.5 | 0.9844 |
| | $5 \times 10^{-6}$ | 22.7 | 20.2 | 80.1 | 0.9381 |
| | $9 \times 10^{-6}$ | 23.7 | 21.2 | 78.2 | 0.9834 |
| | $1.3 \times 10^{-5}$ | 24.8 | 21.9 | 77.6 | 0.9969 |
| | $1.7 \times 10^{-5}$ | 24.8 | 22.3 | 77.1 | 0.9849 |
| | $2.1 \times 10^{-5}$ | 25.64 | 23.1 | 67.9 | 0.9563 |
| 3 | $1 \times 10^{-6}$ | 18.7 | 16.1 | 90.3 | 0.9875 |
| | $5 \times 10^{-6}$ | 20.1 | 17.5 | 87.3 | 0.9867 |
| | $9 \times 10^{-6}$ | 20.9 | 18.3 | 86.1 | 0.9915 |
| | $1.3 \times 10^{-5}$ | 20.9 | 18.4 | 86.9 | 0.9849 |
| | $1.7 \times 10^{-5}$ | 22.4 | 19.8 | 83.4 | 0.9743 |
| | $2.1 \times 10^{-5}$ | 25.8 | 23.3 | 74.3 | 0.9655 |
| 4 | $1 \times 10^{-6}$ | 15.4 | 12.8 | 99.8 | 0.9921 |
| | $5 \times 10^{-6}$ | 17.6 | 15.1 | 94.1 | 0.9917 |
| | $9 \times 10^{-6}$ | 19.3 | 16.8 | 89.7 | 0.9868 |
| | $1.3 \times 10^{-5}$ | 19.9 | 16.9 | 90.3 | 0.9907 |
| | $1.7 \times 10^{-5}$ | 21.3 | 18.8 | 85.7 | 0.9845 |
| | $2.1 \times 10^{-5}$ | 21.7 | 19.6 | 84.2 | 0.9718 |

state theory (Table 7) (Bayol et al., 2007):

$$\text{Rate} = (RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (12)$$

Where h is Planck's constant and N is Avogadro's number.

A plot of log (Rate/ T) versus 1/ T for carbon steel in 1 M HCl at different concentrations from investigated compounds gives straight lines as shown in Figure 9 for compound (1). Similar curves were obtained in presence of the other inhibitors, but not shown. The positive signs of $\Delta H^*$ reflect the endothermic nature of the steel dissolution process. Large and negative values of $\Delta S^*$ imply that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex (Zucchi et al., 1992). The order of the inhibition efficiencies of chalcones derivatives as gathered from the increase in $E_a^*$ and $\Delta H^*$ values and decrease in $\Delta S^*$ values are as follows: (1) > (2) > (3) > (4).

**Conclusions**

1) The tested chalcones derivatives establish a very good inhibition for carbon steel corrosion in HCl solution.
2) Chalcones derivatives inhibit carbon steel corrosion by adsorption on its surface and act better than the passive oxide film.
3) The inhibition efficiency is in accordance to the order: 1 > 2 > 3> 4.
4) The inhibition efficiencies of the tested compounds increase with increasing of their concentrations.
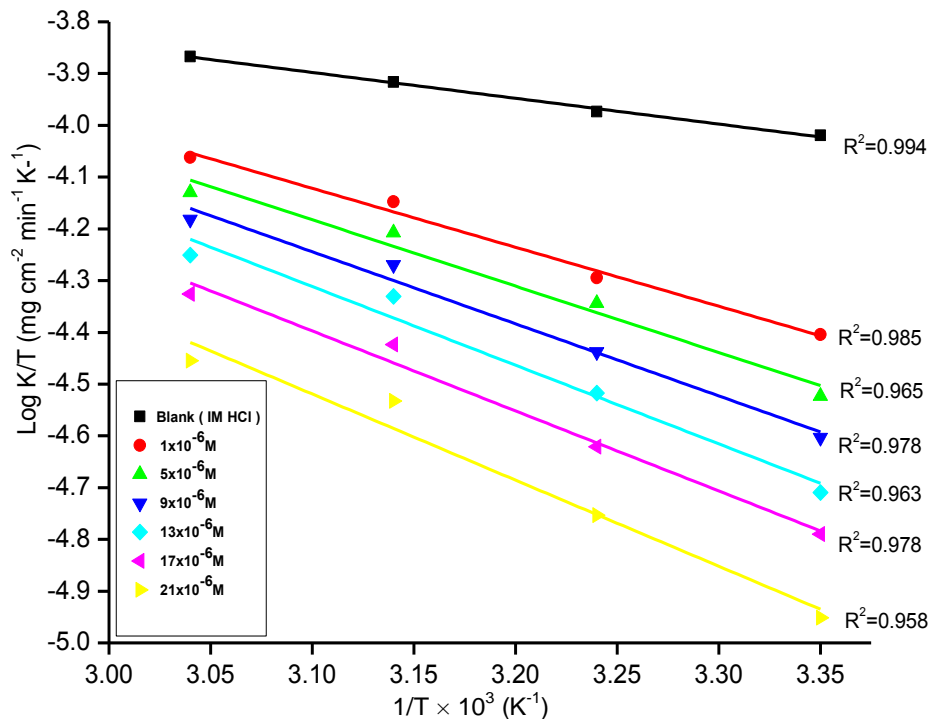5) Double layer capacitances decrease with respect to blank solution when the inhibitor added. This fact may be

**Figure 9.** Log k/T – 1/T curves for carbon steel dissolution in 1 M HCl in the absence and presence of different concentrations in the investigated compound (1).

explained by adsorption of the inhibitor molecule on the carbon steel surface.

6) The adsorption of these compounds on carbon steel surface in HCl solution follows Langmuir adsorption isotherm.

7) The values of inhibition efficiencies obtained from the different independent techniques used showed the validity of the obtained results.

## REFERENCES

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

Abd El-Rehim SS, Hassan H, Amin MA (2003). The corrosion inhibition study of sodium dodecyl benzene sulphonate to aluminum and its alloys in 1 M HCl solution. Mater. Chem. Phys. 78:337-348.

Aljourani J, Raeissi K, Golozar MA (2009). Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution. Corros. Sci. 51:1836-1843.

Amar H, Tounsi A, Makayssi A, Derja A, Benzakour J, Outzourhit A (2007). Corrosion inhibition of Armco iron by 2-mercaptobenzimidazole in sodium chloride 3% media. Corros. Sci. 49:2936-2945.

Arab ST, Noor EA (1993). Inhibition of acid corrosion of steel by some S Alkylisothiouronium iodides. Corrosion 49:122-129.

Arawaki K, Hagiwara N, Nishihara H (1987). The synergistic effect of anions and the ammonium cation on the inhibition of iron corrosion in acid solution. Corros. Sci. 27:487-497.

Ashassi-Sorkhabi H, Ghalebsaz-Jeddi N (2005). Inhibition effect of polyethylene glycol on the corrosion of carbon steel in sulphuric acid. Mater. Chem. Phys. 92:480-486.

Banerjee G, Malhotra SN (1992). Contribution to the adsorption of

aromatic amines on mild steel surfaces from HCl solutions by impedance, UV and Raman spectroscopy. Corrosion 48:10-15.

Bayol E, Kayakirilmaz K, Erbil M (2007). The inhibitive effect of hexamethylene tetramine on the acid corrosion of steel. Mater. Chem. Phys. 104:74-82.

Benabdellah M, Touzan R, Aouniti A, Dafali AS, El-Kadiri S, Hommouti B, Benkaddour M (2007). Inhibitive action of some bipyrazolic compounds on the corrosion of steel in 1 M HCl: Part I: Electrochemical study. Mater. Chem. Phys. 105:373-379.

Benalli O, Larabi L, Traisnel M, Gengembra L, Harek Y (2007). Electrochemical, theoretical and XPS studies of 2-mercapto-1 methylimidazole adsorption on mild steel in 1 M HClO$_4$. Appl. Surf. Sci. 253: 6130-6139.

Bessone MJC, Tuttner K, lorenz WJ (1983). AC-impedance measurements on aluminum barrier type oxide films. Electrochim. Acta 28:171-180.

Bosch HRWJ, Bogaerts WF, Syrett BC (2001). Electrochemical frequency modulation: A new electrochemical technique for online corrosion monitoring. Corrosion 57:60-70.

Branzoi V, Golgovici F, Branzoi F (2002). Aluminum corrosion in hydrochloric acid solutions and the effect of some organic inhibitors. Mater. Chem. Phys. 78:122-131.

Da Costa SLFA, Agostinho SML (1989). Electrochemical studies of Cu-Al alloys in sulphate. Corrosion 45:472-477.

Damaskin BB, Petrii OA, Batrakov VV (1971). Adsorption of Organic compounds on Electrodes, Plenum Press, New York.

Elachouri M, Hajji MS, Salem M, Kertit S, Coudert R, Essassi EM (1995). Some surfactants in the series of 2-(alkyldimethylammonio) alkanol bromides as inhibitors of the corrosion of iron in acid chloride solution. Corros. Sci. 37:381-389.

El-Sherbiny EF (1999). Effect of some ethoxylated fatty acids on the corrosion behavior of mild steel in sulphuric acid solution. Mater. Chem. Phys. 60:286-290.

Epelboin I, Keddam M, Takenouti H (1972). Use of impedance measurements for the determination of the instant rate of metal corrosion. J. Appl. Electrochem. 2:71-79.

Fouda AS, Al-Sarawy AA, El-Katori EE (2006). Pyrazolone derivatives as corrosion inhibitors for Mild steel HCl solution. Desalination 201:1-13.

Fouda AS, Elattar KM (2012). Corrosion inhibition of carbon steel by new enaminonitrile derivatives in HCl solutions. J. Sci. Ind. Res. 48(4):477.

Granese SL, Rosales BM, Oviedo C, Zerbino JO (1992). The inhibition action of heterocyclic nitrogen organic compounds on Fe and steel in HCl media. Corros. Sci. 33:1439-1453.

Granese SL (1988). Study of the inhibitory action of nitrogen- containing compounds, Corrosion 44:322-327.

Guo R, Liu T, Wei X (2002). Effects of SDS and some alcohols on the inhibition efficiency of corrosion for nickel. Colloids. Surf. A. 209:37-45.

Hajjaji N, Ricco I, Srhiri A, Lattes A, Soufiaoui M, Benbachir A (1993). Effect of N-Alkylbetaines on the Corrosion of Iron in 1 M HCl Solution. Corrosion. 49:326-334.

Khaled KF, Hackerman N (2003). Investigation of the inhibitive effect of *ortho* substituted anilines on corrosion of iron in 1 M HCl solutions. Electrochim. Acta. 48:2715-2723.

Khamis E (1990). Effect of temperature on the acidic dissolution of steel in the presence of inhibitors. Corrosion. 46:476-482.

Lipkowski J, Ross PN (1992). Adsorption of Molecules at Metal Electrodes, VCH, New York.

Luo H, Guan YC, Han KN (1998). Inhibition of mild steel corrosion by sodium dodecyl benzene sulfonate and Sodium Oleate in Acidic Solutions. Corrosion. 54:619-627.

Maayta AK, Al-Rawashdeh NAF (2004). Inhibition of acidic corrosion of pure aluminum by some organic compounds. Corros. Sci. 46:1129-1140.

Mazzone G, Puglisi G, Bonina F, Corsaro A (1983). A new synthesis of symmetrical 2,5-diaryl-1,3,4-thiadiazoles, J. Heterocyclic. Chem. 20:1399-1401.

Mernari B, Elkadi L, Kertit S (2001). 2,5 Bis (2-Thienyl)-1,3,4-oxadiazole as corrosion inhibitor of mild steel in acidic media. Bull. Electrochem. 17:115-120.

Migahed MA, Azzam EMS, Morsy SMI (2009). Electrochemical behavior of carbon steel in acid chloride solution in the presence of dodecylcysteine hydrochloride self-assembled on gold nanoparticles. Corros. Sci. 51:1636-1644.

Migahed MA, Azzam EMS, Al-Sabagh AM (2004). Corrosion inhibition of mild steel in 1 M sulfuric acid solution using anionic surfactant. Mater. Chem. Phys. 85:273.

Moretti G, Quartanone G, Tassan A, Zingales A (1994). an investigation of some Schiff bases as corrosion inhibitors foraustenitic chromium–nickel steel in $H_2SO_4$. Wekst. Korros. 45:641-247.

Moussa MNH, El-Far AA, El-Shafei AA (2007). The use of water-soluble hydrazones as inhibitors for the corrosion of C-steel in acidic medium. Mater. Chem. Phys. 105:105-113.

Mu GN, Zhao TP, Liu M, Gu T (1996). Effect of metallic cations on corrosion inhibition of an anionic surfactant for mild steel. Corrosion. 52:853-856.

Osman MM, Omar AM, Al-Sabagh AM (1997). Corrosion inhibition of benzyl triethanol ammonium chloride and its ethoxylate on steel in sulphuric acid solution. Mater. Chem. Phys. 50:271-274.

Parr RG, Donnelly DA, Levy M, Palke M (1978). Electronegativity: The density functional viewpoint. J. Chem. Phys. 68:3801-3807.

Raspini IA (1993). Influence of Sodium Salts of Organic Acids as Additives on Localized Corrosion of Aluminum and Its Alloys. Corrosion 49:821-828.

Rosenfeld IL (1981). Corrosion Inhibitors, McGraw-Hill, New York.

Schmitt G, Bedbur K (1985). Investigations on structural and electronic effects in acid inhibitors by AC impedance. Werkst. Korros. 36:273-280.

Singh DN, Dey AK (1993). Synergistic Effects of inorganic and organic cations on inhibitive performance of propargyl alcohol on steel dissolution in boiling hydrochloric acid solution. Corrosion 49:594-600.

Stupnisek-Lisac E, Meticos-Hukovic M, Lencic D, Vorkapic-Furac J, Berkovic K (1992), Structural investigation of N-arylpyrroles as iron corrosion inhibitors in hydrochloric acid. Corrosion 48:924-930.

Tan Nhut Doan, Dao Thanh Tran (2011). Eco- friendly synthesis and antimicrobial activity of chalcones. Pharmacol. Pharm. 2:282-297.

Trabanelli G (1991). Whitney award lecture: Inhibitors — An old remedy for a new challenge 47(6):410-419.

Villamil RFV, Corio P, Rubim JC, Siliva Agostinho ML (1999). Effect of sodium dodecylsulfate on copper corrosion in sulfuric acid media in the absence and presence of benzotriazole. J. Electroanal. Chem. 472:112-119.

Zhao TP, Mu GN (1999). The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid, Corros.Sci. 41:1937-1944.

Zucchi F, Trabanelli G, Brunoro G (1992). The influence of the chromium content on the inhibitive efficiency of some organic compounds. Corros. Sci. 33:1135-1139.