Int. J. Electrochem. Sci., 8 **(2013)** 1409 - 1421

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Chemical and Electrochemical Investigations of L- Arginine as Corrosion Inhibitor for Steel in Hydrochloric Acid Solutions

K.F.Khaled[1,2] and N. S. Abdel-Shafi[1,3]*

[1]Electrochemistry Research Laboratory, Ain Shams University, Faculty of Education, Chemistry Department, Roxy, Cairo, Egypt
[2]Materials and Corrosion Laboratory, Taif University, Faculty of Science, Chemistry
[3]Department, Taif, Hawiya 888, Kingdom of Saudi Arabia
Chemistry Department, Hail University, Faculty of Science, Chemistry Department
[*]E-mail: khaledrice2003@yahoo.com

Received: 13 November 2012 / *Accepted:* 4 December 2012 / *Published:* 1 January 2013

The corrosion inhibition effect of L-arginine has been used as possible corrosion inhibitor for steel in 1.0 M HCl. Several chemical (weight loss) and electrochemical (potentiodynamic polarization, electrochemical impedance spectroscopy, EIS and electrochemical frequency modulation, EFM) measurements have been used. Data obtained from chemical and electrochemical measurements were in good agreement with the results obtained from EFM.Tafel polarization studies have shown that L-arginine affects both the cathodic and anodic corrosion processes and thus it acts as mixed-type inhibitor. The results of EIS indicate that the value of constant phase elements, CPEs tends to decrease and both charge transfer resistance and inhibition efficiency tend to increase by increasing the inhibitor concentration. This result can be attributed to increase of the thickness of the electrical double layer. A comparative study between EFM and other conventional corrosion monitoring techniques has been performed. EFM was used as an effective method for corrosion rate determination in corrosion inhibition studies. By using EFM measurements, corrosion current density was determined without prior knowledge of Tafel slopes. Data obtained using EFM, were compared to that obtained from other chemical and electrochemical techniques and found to be comprable. The measurements demonstrated that under the chosen experimental conditions L-arginine offers sufficient protection against steel corrosion in 1.0 M HCl solutions.

Keywords: Corrosion inhibition; L-arginine; EFM; EIS ; Potantiodynamic Polarization

1. INTRODUCTION

Carbon steel is widely applied as the constructional material in many industries due to its excellent mechanical properties and low cost. As some of the important fields of application are acid pickling, industrial cleaning, acid descaling, oil-well acidizing and petrochemical processes, the main problem of applying steel is its dissolution in acidic solutions. Several methods are present for corrosion prevention. One of such methods is the use of the organic inhibitors [1-9]

Corrosion inhibitors are needed to reduce the corrosion rates of metallic materials in these media. Most of the efficient inhibitors used in industry are organic compounds, which mainly contain oxygen, sulphur, nitrogen atoms, and multiple bonds in the molecule through which they are adsorbed on metal surface [10-20]

Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to corrodent attack. The adsorption bond strength is dependent on the composition of the metal and corrodent, inhibitor structure and concentration as well as temperature. Despite the broad spectrum of organic compounds, the final choice of the appropriate inhibitor for a particular application is restricted by several factors. As the environmental awareness increased , the need to promote environmentally friendly (green) corrosion inhibitors is raised [21].

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by Khaled et al.[22, 23], Eddy et al. [24-26] and Kamal et al.,[27-29].

This study aims to gain some insight into the corrosion of steel in HCl in the presence of L-arginine as possible corrosion inhibitor. The inhibitor effect of this compound on the corrosion of steel in 1.0 M HCl was investigated by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, EIS and electrochemical frequency modulation, EFM.

2. EXPERIMENTAL

The materials used in this study include steel specimens with composition (C = 0.12 wt %, S = 0.04 wt %, Si = 0.015 wt %, Mn = 0.8 wt %, and Fe = balance). The steel coupons of 3.0 cm x 1.0 cm x 0.20 cm with an exposed total area of 7.6 cm^2 were used for weight loss measurement studies. A steel rod of the same composition was mounted in Teflon with an exposed area of 0.28 cm^2 used for potentiodynamic polarization, electrochemical impedance spectroscopy EIS, and electrochemical frequency modulation, EFM measurements. The coupons were polished, dried and weighted and then suspended in a 100-cm^3 aerated solution of 1.0 M HCl with and without the different concentrations of L-arginine for exposure period (6 h).

Inhibitor compound was obtained from Aldrich chemical co. It was added to the corrosive medium (1.0 M HCl) (Fisher Scientific) at concentrations of 100, 300, 700, 900 mg/l.

After the designated exposure to the test solution, the specimens were rinsed with distilled water, washed with acetone to remove a film possibly formed due to the inhibitor, dried between two tissue papers, and weighted again. Weight-loss measurements were made in triplicate and the loss of weight was calculated by taking an average of these values. Prior to all measurements, the steel samples are abraded with a series of emery paper up to 4/0 grit size. The specimens are washed thoroughly by bidistilled water degreased and dried with acetone.

Electrochemical experiments were carried out using a conventional electrolytic cell with three-electrode arrangement: saturated calomel reference electrode (SCE), platinum mesh as a counter electrode, and the working electrode (WE) had the form of a rod. The counter electrode was separated from the working electrode compartment by fritted glass. The reference electrode was connected to a Luggin capillary to minimize IR drop. Solutions were prepared from bidistilled water of the resistivity 13MΩcm, Prior to each experiment, the specimen was polished with a series of emery papers of different grit sizes up to 0000 grit size, polished with Al_2O_3 (0.5 mm particle size), washed several times with bidistilled water then with acetone and dried using a stream of air. The electrode potential was allowed to stabilize 60 minutes before starting the measurements. All experiments were conducted at 25 ± 1 °C.

Potentiodynamic polarization curves were obtained by changing the electrode potential automatically from (-700 to -250 mV *vs* SCE) at open circuit potential with scan rate of 0.1 mV s^{-1}.

EIS measurements were carried out in a frequency range of 100 kHz to 40 mHz with amplitude of 5 mV peak-to-peak using ac signals at open circuit potential.

Electrochemical frequency modulation, EFM, was carried out using two frequencies 2 Hz and 5 Hz. The base frequency was 1 Hz, so the waveform repeats after 1 second. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit.

Measurements were performed with a Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry Framework system based on the Reference 3000^{TM} Potentiostat/Galvanostat/ZRA, Gamry applications that include DC105 for dc corrosion measurements, EIS300 for electrochemical impedance spectroscopy measurements to calculate the corrosion current and the Tafel constants along with a computer for collecting the data. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

Corrosion rates of steel in the absence and presence of the L-arginine amino acid at various concentrations (100–900 mg/l) in 1.0 M HCl were determined. The obtained data showed that the corrosion rate decreased from 5.2 mg cm^{-2} h^{-1} in blank to 2.0 mg cm^{-2} h^{-1} in presence of 900 mg/l. The inhibition efficiency at different concentrations on steel corrosion were calculated from equation 1, is shown in Table 1 .

$$E_w\% = \frac{(\mathrm{CR})_o - (\mathrm{CR})}{(\mathrm{CR})_o} \times 100 \qquad (1)$$

where $(CR)_0$ and (CR) are the corrosion rates in (mg cm^{-2} h^{-1}) without and with L-arginine, respectively.

Table 1. Corrosion rate of steel in 1.0 M HCl in absence and presence of L-arginine calculated by weight loss method at 25 ± 1 °C

Conc. mg/l	Corrosion Rate mg cm^{-2} h^{-1}	E_w%
0.00	5.2	-----
100	4.1	21.5
300	3.6	29.3
700	3.1	40.8
900	2.0	61.2

The corrosion parameters such as inhibition efficiency (E_w%) and corrosion rate CR at different concentration of L-arginine in 1.0 M HCl at 25 ± 1 °C are presented in Table 1. As can be seen from Table 1, L-arginine inhibits the corrosion of steel at all concentrations. Data in Table 1 reveals that the inhibition efficiency increases with increasing concentration of L-arginine. Table 1 shows that the inhibition efficiency increases from 20% to 60% with increasing L-arginine concentration from 100 to 900 mg/l

3.2 Electrochemical studies

Electrochemical methods used here were potentiodynamic polarization, electrochemical polarization measurements and electrochemical frequency modulation.

3.2.1 Potentiodynamic polarization study

Corrosion phenomena can be explained in terms of electrochemical reactions. Therefore, the electrochemical techniques can be used to study these phenomena. A complete current-potential plot of a specimen can be measured in a few hours, or in some cases in a few minutes [30-33].

When a steel electrode is dipped in a 1.0 M HCl, both hydrogen reduction and iron oxidation processes occur on its surface. Typically the steel corrodes and the acid is reduced. The steel electrode can function as both anode and cathode, and both anodic and cathodic currents occur on the steel surface. Any corrosion processes that occur are usually a result of anodic currents. When a steel electrode is in contact with 1.0 M HCl and the steel is not connected to the potentiostate, the steel assume a potential (relative to a SCE electrode) termed the corrosion potential, E_{corr}. A steel electrode at E_{corr} has both anodic and cathodic currents present on its surface. However, these currents are exactly equal in magnitude so there is no net current to be measured. The steel electrode is at equilibrium with the acid solution (even though it may be visibly corroding). E_{corr} can be defined as the potential at which the rate of oxidation is exactly equal to the rate of reduction. Experimentally one measures polarization characteristics by plotting the external current response as a function of the applied potential. Since the measured current can vary over several orders of magnitude, usually the log current function is plotted vs. potential on a semi-log chart. This plot is termed as a potentiodynamic polarization plot. The corrosion current density, i_{corr}, is obtained from Tafel plot by extrapolating the linear portion of the curve to E_{corr}, as shown in Figure 1.

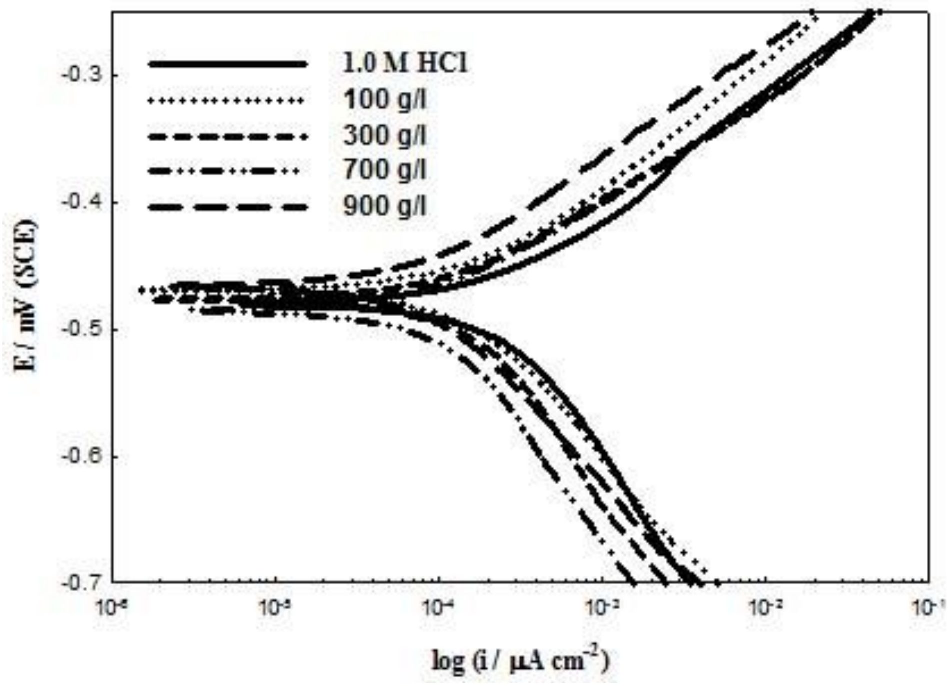

Figure 1. Anodic and cathodic Tafel polarization curves for mild steel in the absence and presence of various concentrations of L-arginine in 1.0 M HCl at 25 ± 1 °C.

The corrosion rate can be calculated from corrosion current by using equation 2 [34].

$$\text{Corrosion rate (mpy)} = \frac{0.13\, i_{\text{corr}}\ (E.W.)}{\text{d}} \qquad (2)$$

Where i_{corr} is corrosion current density, µA/cm^2, E.W. = equivalent weight of the corroding species, g, d = density of the corroding species, g/cm^3

Potentiodynamic polarization plots can provide a direct measure of the corrosion current, which can be related to corrosion rate. Tafel plots for the steel specimen immersed in 1.0 M HCl in the absence and in the presence of different concentrations of L-arginine is presented in Fig. 1.

Table 2. Electrochemical parameters calculated from polarization measurements on the steel electrode in 1.0 M HCl solutions without and with various concentrations of L-arginine at 25 ± 1 °C.

Conc. mg/l	I_{corr} $\mu A.cm^{-2}$	$-E_{corr}$ mV	b_a $mV.dec^{-1}$	$-b_c$ $mV.dec^{-1}$	C.R mpy	$E_T\%$
0.00	258	480	103.7	195	117.9	-----
100	174	470	170	104	79.36	32.55
300	144	477	181	88.6	65.78	44.18
700	110	485	180.9	88.1	50.22	57.36
900	89.5	466	148	93.3	40.88	65.31

Figure 1 shows that the addition of L-arginine to the acid solution shifts the anodic polarization to more positive and the cathodic polarization to more negative values. The effect of L-arginine is more pronounced on anodic polarization than on cathodic polarization. Values of the electrochemical parameters and the percentage inhibition efficiency $E_T\%$ are given in Table 2. The inhibition efficiency $E_T\%$ is given from the equation 3 [30, 35]:

$$E_T\%=(1-\frac{i_{corr}}{i^{o}_{corr}})\times 100 \qquad \textbf{(3)}$$

Where i^{o}_{corr} and i_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of Tafel lines. The values of i_{corr} decrease with increasing concentration, the decrease in i_{corr} is associated with no definite trend for E_{corr}. These results suggest that L-arginine behaves as mixed-type inhibitor. The slopes b_a and b_c change both electrode reaction, and their shift depends on inhibitor concentration.

The electrochemical polarization data of the steel in presence of the tested inhibitor is listed in Table 2.

It is seen from Table 2 that addition of L-arginine is decreasing the values of i_{corr} with increasing concentration. This indicates that L-arginine inhibits the corrosion of steel in HCl. Inspection of Table 2 shows that maximum inhibition (lowest corrosion current density) achieved at highest concentration (65%). It can also be seen that increasing concentrations of L-arginine shifts the corrosion potential E_{corr} with no definit direction, thereby showing that L-arginine is adsorbed on the metal surface and this kind of inhibitor behaves as mixed-type inhibitors. The anodic and cathodic Tafel constants (b_a and b_c) do not change significantly with increasing concentration of the inhibitor, i.e. L-arginine affects both the anodic and cathodic overpotentials and shifts Tafel lines in both directions. This suggests that the inhibiting action of L-arginine occurs by simple site blocking of the electrode, thus decreasing the surface area available for corrosion reactions [36]. The values of Tafel slops (b_a and b_c) are in good agreement with the values reported previously for steel in 1.0 M HCl [37].

3.2.2 Electrochemical impedance study, EIS

For Nyquist plot AC signals of 5 mV amplitude and a frequency spectrum from 100 kHz to 40 mHz was impressed. The impedance data was analyzed using the equivalent circuit described in Fig. 2.

Nyquist plots of steel in uninhibited and inhibited solutions containing various concentrations of L-arginine is shown in Fig. 3.

Figure 3 shows that EIS spectra obtained consists of one depressed capacitive loop (one time-constant in Bode-phase representation). The diameter of the capacitive loop obtained in 1.0 M HCl solution increases in the presence of L-arginine indicating inhibition of the corrosion process as shown in Fig. 3. Parameters derived from EIS measurements (equivalent circuit described in Fig. 3) and inhibition efficiency is given in Table 3.

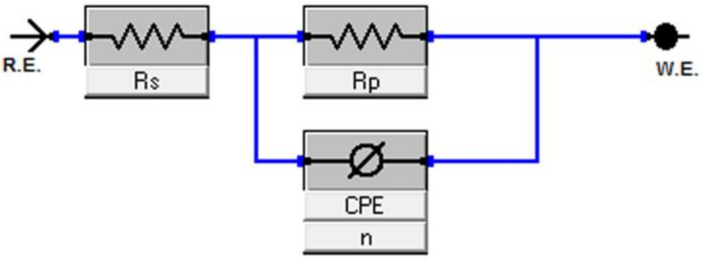

Figure 2. Equivalent circuit model for steel /HCl interface.

Table 3. Electrochemical parameters calculated from EIS measurements on steel electrode in 1.0 M HCl solutions without and with various concentrations of L-arginine at 25 ± 1 °C.

Conc. mg/l	R_s Ω^{-1} cm^2	R_p $\Omega^{-1}.cm^2$	*CPE* $\mu\Omega^{-1}cm^{-2}S^n$	n	E_{IMP}%
	1.2	189.5	30	0.81	-----
100	0.9	290	20	0.75	34.86
300	1.5	363	18	0.79	47.91
700	1.2	483	15	0.65	60.92
900	1.2	640.2	13	0.85	70.53

From Table 3, the inhibition efficiency, E_{IMP}% of L-arginine for the steel electrode can be calculated from the polarization resistance as follows [37]:

$$E_{IMP}\% = (1 - \frac{R_p^o}{R_p}) \times 100 \qquad (4)$$

where R_p^o and R_p are the polarization resistances for uninhibited and inhibited solutions, respectively.

When the complex plane impedance plots contains a “depressed” semicircle with the center below the real axis, this behavior is characteristic for solid electrodes (as steel electrode) and often referred to as frequency dispersion, which have been attributed to roughness and inhomogeneities of the surface [38]. The parallel network polarization resistance-double layer capacity (Rp-C_{dl}) is usually a poor approximation.

Two ways are used in the literature to describe the EIS spectra for the inhomogeneous films on the metal surface or rough and porous electrodes. One is the finite transmission line model [39]. and the other is the filmed equivalent circuit model, which is usually proposed to study the degradation of coated metals [40, 41]. It has been suggested that the EIS spectra for the metal covered by inhibitor films are very similar to the failed coating metals [42].

Therefore, in this work the filmed equivalent circuit model is used to describe the inhibitors-covered metal/solution interface. The circuit model used for failed coating metal/solution interface is shown in Fig. 2.

When there is a non-ideal frequency response, it is common practice to employ distributed circuit elements in an equivalent circuit [43]. The most widely used is the constant phase element (CPE), which has a non-integer power dependence on the frequency. Its impedance is described by equation 5:

$$Z_{CPE} = Y^{-1}(i\omega)^{-n} \qquad (5)$$

where Y is a proportional factor, i is $\sqrt{-1}$, ω is $2\pi f$ and n is a phase shift [44].

Often a CPE is used in a model in place of a capacitor to compensate for non-homogeneity in the system. For example, a rough or porous surface can cause a double-layer capacitance to appear as a CPE with an n value between 0.65 and 0.85 43..

For n=0, Z_{CPE} represents a resistance with $R=Y^{-1}$, for n=1 a capacitance with $C=Y$, for n=0.5 a Warburg element and for n=-1 an inductance with $L=Y^{-1}$.

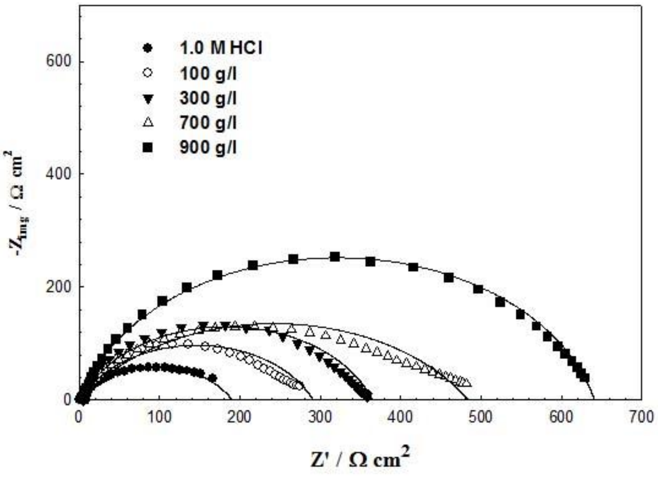

Figure 3. Measured (symbols) and simulated (solid lines) complex plane impedance plots of steel corrosion in 1.0 M HCl solutions at E_{corr} in the absence and presence of L-arginine at 25±1 °C.

Figure 2 shows the electrical equivalent circuits employed to analyze the impedance plots. R_s is the electrolyte resistance (Ω cm^2), R_{ct} is the charge transfer resistance (Ω cm^2). Y ($\Omega^{-1}cm^{-2}S^n$) and n are parameters used in equation 5. Excellent fit with this model was obtained with our experimental data (see solid lines in Fig. 3). It is observed that the fitted data matches the experimental, with an average error of about 3.1 % all through.

3.2.3 Electrochemical frequency modulation, EFM

The electrochemical frequency modulation (EFM) technique is a recent tool for monitoring the corrosion electrochemically. The theory of EFM technique is described in our previous work [45-49]. Electrochemical frequency modulation technique has many features, non-destructive technique, rapid test, gives directly values of the corrosion current without a prior knowledge of Tafel constants and has a great strength due to the causality factors, which serve as an internal check on the validity of the EFM measurements [50-55].

Table 4 shows the electrochemical corrosion kinetic parameters such as inhibition efficiency ($E_{EFM}\,\%$), corrosion current density (μA/cm^2), Tafel constants (b_a , b_c) and causality factors (CF-2, CF-3) at different concentration of L-arginine in 1.0 M HCl at 25 ± 1 °C.

Table 4. Electrochemical kinetic parameters, inhibition efficiency recorded for steel in 1.0 M HCl solutions without and with various concentrations of L-arginine at 25 ± 1 °C calculated by EFM method

Conc. mg/l	I_{corr} μA.cm^{-2}	b_a mV.dec^{-1}	$-b_c$ mV.dec^{-1}	C.R mpy	E_{EFM}%	C.F-2	C.F-3
0.00	198.8	90.78	148.1	324.4	-----	1.88	2.01
100	149.1	101.2	139.6	243.3	25.00	1.99	2.98
300	125.24	98.6	143.1	204.36	37.00	1.89	2.76
700	107.35	90.8	139.6	175.17	46.00	2.0	2.90
900	75.54	87.8	142.4	123.26	62.00	1.88	3.01

Figure 4 representing the EFM intermodulation spectra of steel in 1.0 M HCl in absence and presence of various concentrations of L-arginine at 25°C±1.The inhibition efficiency, $E_{EFM}\,\%$, of L-arginine was calculated at different concentration using equation presented below [47]:

$$E_{EFM}\,\% = (1 - \frac{i_{corr}}{i^{o}_{corr}})\ \times 100 \qquad (6)$$

where i^{o}_{corr} and i_{corr} are corrosion current density in the absence and presence of L-arginine compound, respectively.

The calculated electrochemical parameters (i_{corr}, b_c, b_a, CF-2, CF-3 and $E_{EFM}\,\%$) are given in Table 4. As can be seen from Table 4, the corrosion current densities decrease with increase in L-arginine concentrations. The causality factors in Table 4 indicate that the measured data is of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The causality factor is calculated from the frequency spectrum of the current response. If the causality factors differ significantly from the theoretical values of 2.0 and 3.0, then it can be deduced that the measurements are influenced by noise. If the causality factors are approximately equal to the predicted values of 2.0 and 3.0, there is a causal relationship between the perturbation signal and the response signal. Then the data is assumed to be reliable [56]. When CF-2 and CF-3 are in the range 0–2 and 0–3, respectively, then the EFM data is valid.

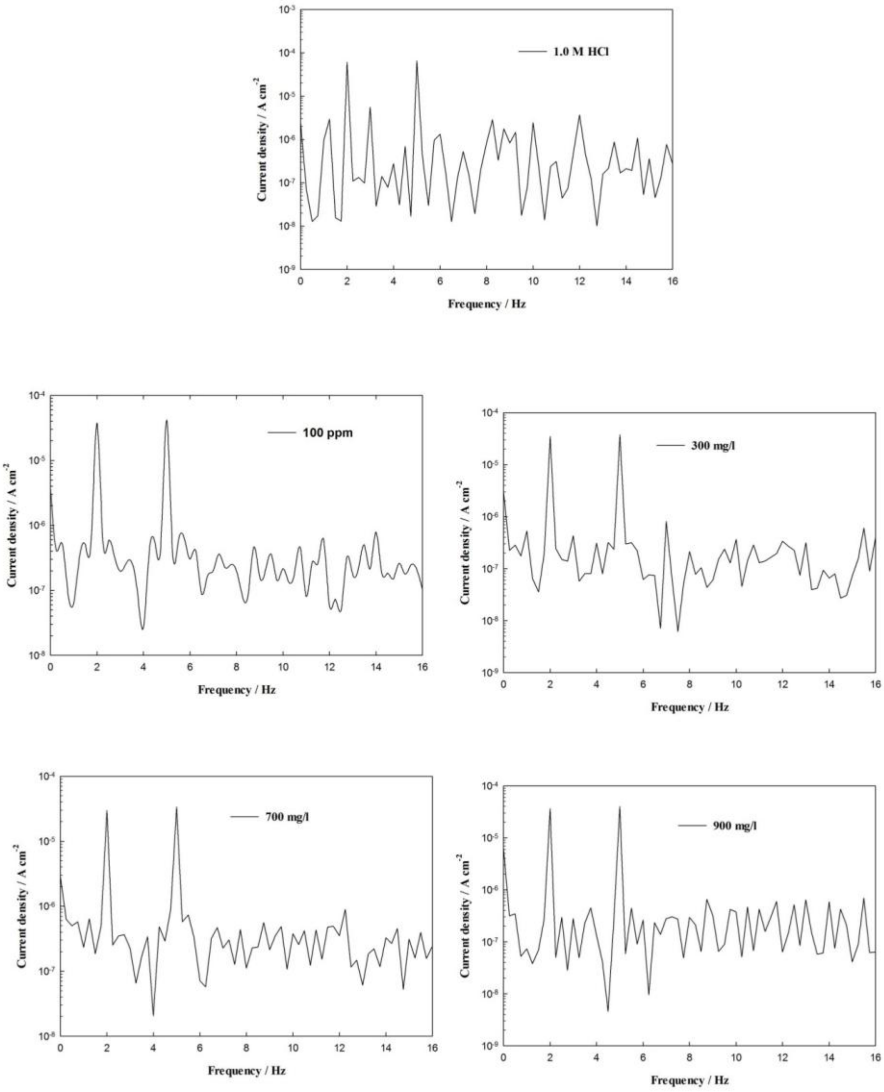

Figure 4. Intermodulation spectra for steel in 1.0 M HCl in the absence and presence of various concentrations of L- arginine in 1.0 M Hcl at 25 ±1 °C.

In Table 4, Addition of increasing concentration of L-arginine to 1.0 M HCl solutions decreases the corrosion current density (i_{corr}), indicating that L-arginine inhibits the corrosion of steel through adsorption. The calculated inhibition efficiency $E_{EFM}\%$ enhances with L-arginine concentration.

3.3. Inhibition mechanism

The adsorption of an L-arginine on the steel surface can be described by two major types of interactions: physisorption and chemisorption. Physisorption occurs due to the presence of electrical charges on both steel surface and L-arginine in 1.0 M HCl solutions. The surface charge of the steel is due to the electric field existing at the steel/1.0 M HCl interface. Chemisorption process involves charge sharing or charge transfer from the L-arginine molecules to the vacant d-orbital in the steel surface to form a coordinate type of a bond. Generally, the two types of mechanisms of inhibition were proposed

4. CONCLUSION

Both chemical and electrochemical measurements demonstrated that L-arginine offers sufficient protection against steel corrosion in 1.0 M HCl solutions. Electrochemical frequency modulation, EFM can be used as a rapid and non destructive technique for corrosion rate measurements without prior knowledge of Tafel constants which give this technique an advantage over the conventional dc and ac techniques. The results of EIS indicate that the value of CPEs tends to decrease and both charge transfer resistance and inhibition efficiency tend to increase by increasing the inhibitor concentration. This result can be attributed to increase of the thickness of the electrical double laye. Tafel polarization studies have shown that the L-arginine amino acid affects both the cathodic and anodic processes and thus it acts as mixed-type inhibitor. Data obtained from chemical and electrochemical measurements were in good agreement with the results obtained from EFM.

ACKNOWLEDGMENTS
Authors would like to thank King Abdul Aziz City for Science and Technology, KACST for the financial support of this work provided through project # AT-30-66 titled" Development of a new corrosion protection strategy for water-ammonia refrigerating systems ".

References

1. Sudheer, M.A. Quraishi, E.E. Ebenso, M. Natesan, *Int. J. Electrochem. Sci*, 7 (2012) 7463-7475.
2. A. Chetouani, K. Medjahed, S.S. Al-Deyab, B. Hammouti, I. Warad, A. Mansri, A. Aouniti, *Int. J. Electrochem. Sci,* 7 (2012) 6025-6043.
3. J.-M. Zhao, J. Li, *Acta Physico-Chimica Sinica*, 28 (2012) 623-629.
4. M. Behpour, S.M. Ghoreishi, M. Khayatkashani, N. Soltani, *Mater. Chem. Phys*., 131 (2012) 621-633.
5. N.A. Negm, N.G. Kandile, E.A. Badr, M.A. Mohammed, *Corros. Sci.*, 65 (2012) 94-103.
6. A.Y. Musa, R.T.T. Jalgham, A.B. Mohamad, *Corros. Sci.,* 56 (2012) 176-183.

7. D. Kesavan, M.M. Tamizh, M. Gopiraman, N. Sulochana, R. Karvembu, *Journal of Surfactants and Detergents*, 15 (2012) 567-576.
8. P. Mohan, R. Usha, G.P. Kalaignan, V.S. Muralidharan, *Journal of Chemistry*, (2013).
9. A.Y. Musa, A.B. Mohamad, A.A.H. Kadhum, M.S. Takriff, *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*, 43A (2012) 3379-3386.
10. M.A. Quraishi, D. Jamal, *Mater. Chem. Phys*., 71 (2001) 202-205.
11. M.A. Quraishi, D. Jamal, *Mater. Chem. Phys*., 68 (2001) 283-287.
12. K. Khaled, N. Al-Mobarak, *Int. J. Electrochem. Sci*, 7 (2012) 1045-1059.
13. K. Khaled, N. Abdel-Shafi, N. Al-Mobarak, *Int. J. Electrochem. Sci*, 7 (2012) 1027-1044.
14. K.F. Khaled, S.S. Abdel-Rehim, G.B. Sakr, *Arabian Journal of Chemistry*, 5 (2012) 213-218.
15. Zarrouk, B. Hammouti, H. Zarrok, M. Bouachrine, K.F. Khaled, S.S. Al-Deyab, *Int. J. Electrochem. Sci*, 7 (2012) 89-105.
16. K. Khaled, Corros. Sci., (2011).
17. K. Khaled, N. Abdel-Shafi, *Int. J. Electrochem. Sci*, 6 (2011) 4077-4094.
18. K. Khaled, *J. Appl. Electrochem*., 41 (2011) 277-287.
19. K.F. Khaled, *Electrochim. Acta*, 56 (2011) 10292-10292.
20. K.F. Khaled, *Mater. Chem. Phys.*, 130 (2011) 1396-1396.
21. E.E. Oguzie, *Corros. Sci*., 50 (2008) 2993-2998.
22. K. Khaled, *J. Solid State Electrochem*., 13 (2009) 1743-1756.
23. K. Khaled, *Int. J. Electrochem. Sci*, 3 (2008) 462-475.
24. N.O. Eddy, *Pigment & Resin Technology*, 39 (2010) 348-354.
25. N.O. Eddy, *Portugaliae Electrochimica Acta*, 27 (2009) 579-589.
26. N.O. Eddy, F.E. Awe, A.A. Siaka, L. Magaji, E.E. Ebenso, *Int. J. Electrochem. Sci*, 6 (2011) 4316-4328.
27. A. Kalendová, D. Veselý, *Anti-Corros Method* M., 55 (2008) 175-190.
28. C. Kamal, M.G. Sethuraman, *Ind. Eng. Chem. Res*., 51 (2012) 10399-10407.
29. C. Kamal, M.G. Sethuraman, *Arabian Journal of Chemistry*, 5 (2012) 155-161.
30. A.E.R.S.S. K.F. Khaled, N. Hackerman, 2003.
31. K. Khaled, N. Hackerman, *Electrochim. Acta*, 48 (2003) 2715-2723.
32. K. Khaled, N. Hackerman, *Mater. Chem. Phys*., 82 (2003) 949-960.
33. A.E.R. K.F. Khaled, S. S., N. Hackerman, 2003.
34. S.S.A. El-Rehim, M.A.M. Ibrahim, K. Khaled, *J. Appl. Electrochem.*, 29 (1999) 593-599.
35. K.F. Khaled, *Electrochim. Acta*, 48 (2003) 2493-2503.
36. S.S. Abd El-Rehim, M.A.M. Ibrahim, K.F. Khaled, *J. Appl. Electrochem*., 29 (1999) 593-599.
37. K.F. Khaled, S.S. Abdel-Rehim, G.B. Sakr, *Arabian Journal of Chemistry*, 5 (2012) 213-218.
38. K.F. Khaled, *Appl. Surf. Sci*., 230 (2004) 307-318.
39. J.R. Park, D.D. Macdonald, *Corros. Sci.*, 23 (1983) 295-315.
40. G.W. Walter, *Corros. Sci*., 32 (1991) 1331-1352.
41. G.W. Walter, *Corros. Sci*., 32 (1991) 1353-1359.
42. F. Mansfeld, *Electrochim. Acta*, 35 (1990) 1533-1544.
43. Z.f. Windows, Electrochemical Impedance Software Operatin Manual, in, Scibner Associates Inc., Southern Pines, NC,, 1998.
44. S. Lenhart, M. Urquidi-Macdonald, D.D. Macdonald, *Electrochim. Acta*, 32 (1987) 1739-1741.
45. S.S. Abdel-Rehim, K.F. Khaled, N.S. Abd-Elshafi, *Electrochim. Acta*, 51 (2006) 3269-3277.
46. N.A. Al-Mobarak, K.F. Khaled, M.N.H. Hamed, K.M. Abdel-Azim, *Arabian Journal of Chemistry*, 4 (2011) 185-193.
47. K.F. Khaled, *J. Appl. Electrochem*., 39 (2009) 429-438.
48. K.F. Khaled, *Mater. Chem. Phys*., 112 (2008) 290-300.
49. K.F. Khaled, *Mater. Chem. Phys*., 112 (2008) 104-111.
50. N.A. Al-Mobarak, K.F. Khaled, O.A. Elhabibc, K.M. Abdel-Azim.

51. S. Abdel-Rehim, K. Khaled, N. Abd-Elshafi, *Electrochim. Acta*, 51 (2006) 3269-3277.
52. K. Khaled, *Mater. Chem. Phys.*, 112 (2008) 290-300.
53. K.F. Khaled, *Appl. Surf. Sci.*, 255 (2008) 1811-1818.
54. K. Khaled, *J. Appl. Electrochem.*, 39 (2009) 429-438.
55. K. Khaled, *J. Electrochem. Soc.*, 157 (2010) C116.
56. R.W. Bosch, F. Moons, J.H. Zheng, W.F. Bogaerts, *Corrosion*, 57 (2001) 532-539.