

New (Z)-N'-(1-phenylethylidene) benzohydrazide as Corrosion Inhibitors for Carbon Steel in 1 M HCl Solutions

A.S. Fouda¹, K. Shalabi¹, A.E.El-Shennawi², R.M. Abo Shohba², A.A.El-Naggar²

Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt¹

Department of Chemistry, Faculty of Science (girls), El-Azhar University, Egypt²

Abstract: The corrosion inhibition of carbon-steel in 1 M HCl by some (Z)-N'-(1-phenylethylidene) benzohydrazide derivatives (PEBH) has been investigated using weight loss method, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Results obtained showed that these investigated compounds are good inhibitors and their inhibition efficiencies increase with increasing inhibitor concentration and decrease with increase in temperature. Moreover, polarization studies clearly revealed that the presence of inhibitors changes the mechanism of hydrogen evolution and the metal dissolution i.e. they act as mixed type inhibitors. EIS study showed that charge transfer resistance increases with the increase of inhibitor concentration but the capacitance of double layer decreases. The adsorption of investigated compounds obeys Langmuir's adsorption isotherm. The activation parameters were determined and discussed. The mechanism of adsorption had been explained on the basis of chemical structure of the investigated inhibitors. It was found that there is a good agreement between the different tested techniques.

Keywords: Carbon steel, HCl, potentiodynamic polarization, EIS, EFM.

I. INTRODUCTION

Carbon steel is an alloy of iron it is widely used in petrochemical, chemical and metallurgical industries. It is also used as a construction material owing to its excellent mechanical properties and cost effectiveness. However, it is easily undergoes corrosion in various environmental conditions. Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidising, because of the general aggressiveness of acid solutions, the practice of inhibition is commonly used to reduce the corrosive attack on metallic materials. Inhibitors are generally used for this purpose to control the metal dissolution. Most of the well-known inhibitors are organic compounds containing nitrogen, sulphur and /or oxygen atoms. It has been observed that the most of the organic inhibitors act by adsorption on the metal surfaces [1]. The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecules such as functional group, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density at the donor atoms and π -orbital character of donating electrons [2-6], and also, on the electronic structure of molecules [7-10]

The aim of the present work is to study the inhibitive action of some new (Z)-N'-(1-phenylethylidene) benzohydrazide derivatives (PEBH) towards the corrosion of C-steel in 1 M hydrochloric acid solution using chemical and electrochemical techniques. Moreover, the effect of temperature on the dissolution of carbon steel, as well as, on the inhibition efficiency of the studied compounds was also investigated and discussed.

II. EXPERIMENTAL

2.1. Materials and reagents

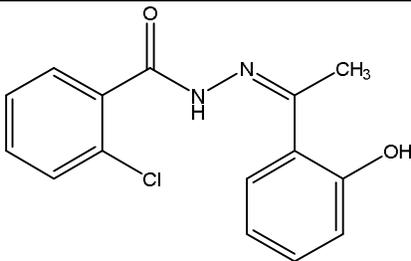
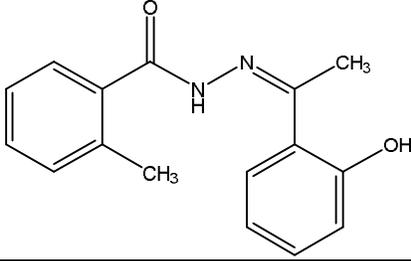
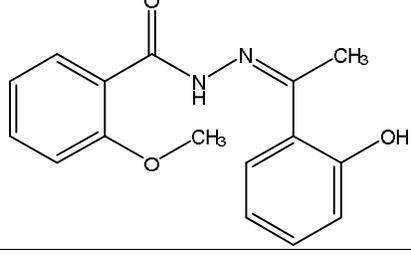
Carbon steel strips (BDH grade) containing (weight %): 0.2 C, 0.024 P, 0.003 Si, 0.35 Mn, and rest Fe were used in this investigation. All chemicals used were of AR grade. Specimens of C-steel strips were abraded successively by emery papers of different grades, i.e. 320, 400, 600, 800 and 1000 finally polished with a 4/0 emery paper to obtain mirror like finish, then degreased ultrasonically with ethyl alcohol and rinsed with bidistilled water several times and dried between two filter papers. AR grade hydrochloric acid (37 %) was used for preparing the corrosive solutions.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

Appropriate concentration of aggressive solutions used (1 M HCl) was prepared using bidistilled water. The structures of the investigated compounds are shown below [11]:

Compounds	Structures	Names	Chemical formulas and molecular weights
1		(Z)-2-chloro-N'-(1-(2-hydroxyphenyl) ethylidene) benzohydrazide	$C_{15}H_{13}ClN_2O_2$ 288.73
2		(Z)-N'-(1-(2-hydroxyphenyl) ethylidene)-2-methylbenzohydrazide	$C_{16}H_{16}N_2O_2$ 268.31
3		(Z)-N'-(1-(2-hydroxyphenyl) ethylidene)-2-methoxybenzohydrazide	$C_{16}H_{16}N_2O_3$ 284.31

2.2. Weight loss measurements

For weight loss measurements, rectangular C-steel specimens of size 20 x 20 x 2 mm were immersed in 100 ml inhibited and uninhibited solutions and allow to stand for several intervals at 25°C in water thermostat. Therefore, the weight losses given by:

$$\Delta m = (m_1 - m_2) \quad (1)$$

where m_1 and m_2 are the weights of metal before and after exposure to the corrosive solution, respectively. The percentage inhibition efficiency (% IE) and the degree of surface coverage (θ) of the investigated compounds were calculated using equation (2):

$$\% \text{ IE} = \theta \times 100 = [1 - (\Delta m_{\text{inh}} / \Delta m_{\text{free}})] \times 100 \quad (2)$$

where Δm_{free} and Δm_{inh} are the weight losses per unit area in the absence and presence of additives, respectively.

2.3 Electrochemical measurements

A three electrode electrochemical cell was used. The working electrode was C-steel of surface area of 1 cm². Before each experiment, the electrode was abraded using emery papers as before. After this, the electrode was cleaned ultrasonically with ethyl alcohol and washed by bidistilled water. All potentials were given with reference to the saturated calomel electrode (SCE). The counter electrode was a platinum plate of surface area of 1 cm². The working

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

electrode was immersed in the test solution during 30 min until a steady state open circuit potential (E_{ocp}) was obtained. The polarization curves were recorded by polarization from -0.6 V to 0.2 V under potentiodynamic conditions corresponding to 1 mV/s (sweep rate) and under air atmosphere. All measurements were carried out with C-steel electrode in 1 M HCl in the absence and presence of different concentrations (15×10^{-6} – 27×10^{-6} M) of the investigated inhibitors at 25 °C. All experiments were carried out at 25 ± 1 °C. The inhibition efficiency and surface coverage (θ) were calculated from equation (3):

$$\% IE = \theta \times 100 = [1 - (i_{corr(inh.)} / i_{corr(free)})] \times 100 \quad (3)$$

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

Electrochemical impedance spectroscopy measurements were performed using the same cell that used in polarization experiments. The EIS carried out over a frequency range of 1 Hz to 100 kHz, with a signal amplitude perturbation of 10 mV.

The inhibition efficiency (% IE) and surface coverage (θ) of the investigated compounds obtained was calculated from equation (4):

$$\% IE = \theta \times 100 = [(R_{ct} - R_{ct}^{\circ}) / R_{ct}] \times 100 \quad (4)$$

where R_{ct}° and R_{ct} are the charge transfer resistance values in the absence and presence of the inhibitors, respectively.

Electrochemical frequency modulation is a non-destructive technique as electrochemical impedance spectroscopy that can directly and rapidly give values of the corrosion current without a prior knowledge of Tafel constants. The great of the EFM is the causality factors, which serves as an internal check on the validity of the EFM measurement. With the causality factors the experimental EFM data can be verified [12-13]. Identical cell assembly was used as in impedance studies. All electrochemical measurements were carried out using Potentiostat /Galvanostat / Zra analyzer (Gamry PCI300/4). A personal computer with DC105 software for potentiodynamic, EIS300 software for EIS and EFM140 software for EMF and Echem Analyst 5.21 was used for data fitting.

3. RESULTS AND DISCUSSION

3.1 Weight – loss measurements

Figure 1 shows the effect of concentration of compound (3) on the weight loss vs. time of C-steel at 25°C. Similar curves were obtained for the other two compounds not shown. It is obvious that the weight loss of C-steel in presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface and, therefore, impede the corrosion process [14].

The calculated values of the percentage inhibition efficiency (% IE) at different concentrations of investigated compounds in 1 M HCl at different temperatures (25- 40°C) are given in Tables 1 and 2. From these Tables, the inhibition efficiencies increase by increasing inhibitors concentrations and decreases by increasing in temperature. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface. At one and the same inhibitor concentration % IE increases in the following order: (1) < (2) < (3).

3.2 Adsorption isotherm

Basic information on the interaction between the inhibitors and the C-steel can be provided by the adsorption isotherm. Two main types of interaction can describe the adsorption of the organic compound: physical adsorption and chemical adsorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and nature of the metal. The surface coverage, θ , of the metal surface by the adsorbed inhibitor was evaluated from weight loss measurements using equation (2). The θ values of different inhibitor concentrations at 25 °C were tested by fitting to various isotherms including, Frumkin, Langmuir, Temkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm is given as [15]:

$$\theta / 1-\theta = K_{ads} C \quad (5)$$

where C is the inhibitor concentration and K_{ads} is the equilibrium constant of adsorption process and is related to the standard free energy of adsorption ΔG_{ads}° by Eq. (6) :

$$K_{ads} = 1/55.5 \exp (-\Delta G_{ads}^{\circ}/RT) \quad (6)$$

The value of 55.5 is the concentration of water in solution expressed in mole per liter, R is the universal gas constant and T is the absolute temperature .

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

A plot of $(\theta/1-\theta)$ against C , for all concentrations of inhibitors (Figure 2) a straight line relationship was obtained in all cases with correlation coefficients (R^2) in more than 0.994.

The deviation of the slope from unity as observed from this study could be interpreted that there are interactions between adsorbed species on the metal surface as well as changes in adsorption heat with increasing surface coverage [16, 17], factors that were ignored in the derivation of Langmuir isotherm. The negative $\Delta G_{\text{ads}}^{\circ}$ values (Table 3) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the C-steel surface [18].

It is generally accepted that the values of $\Delta G_{\text{ads}}^{\circ}$ up to -20 kJ mol^{-1} the types of adsorption were regarded as physisorption, the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1} or smaller, were seen as chemisorptions, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form covalent bond [19-20]. The $\Delta G_{\text{ads}}^{\circ}$ values obtained in this study range from -36.2 to $-36.7 \text{ kJ mol}^{-1}$. It suggested that the adsorption mechanism of investigated inhibitors on C-steel in 1 M HCl solution was typical of physisorption.

3.3 Kinetic-thermodynamic corrosion parameters

As noticed previously, the adsorption process was well elucidating by using a thermodynamic model, in addition a kinetic-thermodynamic model was another tool to explain the mechanism of corrosion inhibition for an inhibitor. The apparent effective activation energies (E_a^*) for the corrosion reaction of C-steel in HCl in the absence and presence of different concentrations of investigated compounds were calculated from Arrhenius-type equation [21]:

$$k = A \exp(-E_a^* / RT) \quad (7)$$

where A is the Arrhenius pre-exponential factor. A plot of $\log k$ (corrosion rate) vs. $1/T$ gave straight lines as shown in (Figure 3). The entropy of activation (ΔS^*) and the enthalpy of activation (ΔH^*) for the intermediate complex in the transition state for the corrosion of C-steel in HCl in the absence and presence of different concentrations of investigated compounds were obtained by applying the transition-state equation [22-24]

$$k = RT / Nh \exp(\Delta S^*/R) \exp(-\Delta H^* / RT) \quad (8)$$

where h is the Planck's constant and N is the Avogadro's number

A plot of $\log k$ (corrosion rate) / T vs. $1/T$ should give a straight lines (Figure 4), with a slope of $(-\Delta H^* / 2.303R)$, and an intercept of $[(\log(RT / Nh)) + (\Delta S^*/2.303R)]$ [25-26], from which the values of ΔH^* and ΔS^* were calculated, respectively. (Table 4) exhibited values of apparent activation energy, apparent enthalpies ΔH^* and entropies ΔS^* for C-steel dissolution in 1 M HCl solution in the absence and presence of different investigated compounds. The presence of inhibitors decreased the activation energies of C-steel indicating strong adsorption of the inhibitor molecules on the metal surface and the presence of these additives induces the adsorption of these additives on the surface of C-steel. Values of the entropy of activation ΔS^* in the absence and in presence of the studied compounds are negative. This implies that the activated complex in the rate determining step represents an association rather than a dissociation step [27]. This means that the activated molecules were in higher order state than that at the initial stage [28-29].

3.4 Polarization curves

Figure.5 illustrates the polarization curves of carbon steel in 1 M HCl solution without and with various concentrations of compound (3) at 25°C . The presence of investigated compounds shift both anodic and cathodic branches to the lower values of corrosion current densities and thus causes a remarkable decrease in the corrosion rate. The parameters derived from the polarization curves in (Figure 5) are given in Table 5. In 1 M HCl solution, the presence of the investigated compounds cause a remarkable decrease in the corrosion rate i.e., shifts both anodic and cathodic curves to lower current densities. In other words, both cathodic and anodic reactions of carbon steel electrode are retarded by the investigated compounds in hydrochloric acid solution. The Tafel slopes of β_a and β_c at 25°C do not change remarkably upon addition of the investigated compounds, which indicates that the presence of investigated compounds does not change the mechanism of hydrogen evolution and the metal dissolution process. Generally, an inhibitor can be classified as cathodic or anodic type if the shift of corrosion potential in the presence of the inhibitor is more than 85 mV with respect to that in the absence of the inhibitor [30, 31]. In the presence of investigated compounds, E_{corr} shifts to less negative but this shift is very small (about 20-30 mV), which indicates that investigated compounds can be arranged as a mixed-type inhibitor, with predominant anodic effectiveness. The % inhibition increased with increasing the concentration of the compounds, the inhibition efficiency of the three tested compounds measured by polarization

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

method increased in the following order: (1) < (2) < (3). This sequence is in accordance with that obtained from weight-loss measurements.

3.5 Electrochemical impedance spectroscopy

Figures 6 and 7 show the Nyquist and Bode diagrams of carbon steel in 1 M HCl solutions containing different concentrations of compound (3) at 25°C. All the impedance spectra exhibit one single depressed semicircle. The diameter of semicircle increases with the increase of the investigated compounds concentration. The impedance spectra exhibit one single capacitive loop, which indicates that the corrosion of steel is mainly controlled by a charge transfer process [32] and the presence of the investigated compounds does not change the mechanism of carbon steel dissolution [33]. In addition, these Nyquist diagrams are not perfect semicircles in 1 M HCl that can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface [34]. Furthermore, the diameter of the capacitive loop in the presence of inhibitor is larger than that in the absence of inhibitor (blank solution), and increased with the inhibitor concentration. This indicates that the impedance of inhibited substrate increased with the inhibitor concentration. [33,34]. This behavior is usually attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena [35], which is typical for solid metal electrodes [36]. Generally, when a non-ideal frequency response is presented, it is commonly accepted to employ the distributed circuit elements in the equivalent circuits. What is most widely used is the constant phase element (CPE), which has a non-integer power dependence on the frequency [37]. Thus, the equivalent circuit depicted in Figure 8 is employed to analyze the impedance spectra, where R_s represents the solution resistance, R_{ct} denotes the charge-transfer resistance, and a CPE instead of a pure capacitor represents the interfacial capacitance. The impedance of a CPE is described by the equation 9:

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \quad (9)$$

where Y_0 is the magnitude of the CPE, j is an imaginary number, ω is the angular frequency at which the imaginary component of the impedance reaches its maximum values, and n is the deviation parameter of the CPE: $-1 \leq n \leq 1$. The values of the interfacial capacitance C_{dl} can be calculated from CPE parameter values Y_0 and n using equation 10 [38]:

$$C_{dl} = Y_0 (\omega_{max})^{n-1} \quad (10)$$

The values of the parameters such as R_s , R_{ct} , through EIS fitting as well as the derived parameters C_{dl} and η % are listed in Table 6. The order of inhibition efficiency obtained from EIS measurements is as follows: (1) < (2) < (3). This sequence is in accordance with that obtained from weight-loss and polarization measurements.

3.6 Electrochemical Frequency Modulation Technique (EFM)

The EFM is a nondestructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Like EIS, it is a small AC signal. Intermodulation spectra obtained from EFM measurements of carbon steel in 1 M HCl solution, in the absence and presence of different concentrations of compound (3) at 25°C are presented in Figure 9. Each spectrum is a current response as a function of frequency. The calculated corrosion kinetic parameters at different concentrations of the investigated compounds in 1 M HCl at 25°C (i_{corr} , β_a , β_c , CF-2, CF-3 and η %) are given in Table 7. From this Table, the corrosion current densities decreased by increasing the concentration of investigated compounds, the inhibition efficiencies increase by increasing investigated compounds concentrations. The causality factors CF-2 and CF-3 in Table 7 are very close to theoretical values that according to EFM theory [39] should guarantee the validity of Tafel slopes and corrosion current densities. Values of causality factors (Table 7) indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2 and 3, respectively. The causality factor is calculated from the frequency spectrum of the current response. If the causality factors are approximately equal to the predicted values of 2 and 3, there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable [12]. When CF-2 and CF-3 are in the range 0-2 and 0-3, respectively, then the EFM data is valid. The deviation of causality factors from their ideal values might due to that the perturbation amplitude was too small or that the resolution of the frequency spectrum is not high enough also another possible explanation that the inhibitor is not performing very well [13].

3.7 Mechanism of Corrosion inhibition

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

From the observations drawn from the different methods, corrosion inhibition of C-steel in acid chloride solution by the investigated inhibitors as indicated from weight loss, potentiodynamic polarization, EIS and EFM techniques was found to depend on the concentration and the nature of the inhibitor.

The adsorption of organic molecules on the solid surfaces cannot be considered only as purely physical or as purely chemical adsorption phenomenon. In addition to the chemical adsorption, inhibitor molecules can also be adsorbed on the steel surface via electrostatic interaction between the charged metal surface and charged inhibitor molecule if it is possible. The free energy of adsorption value is not very greater than -40 kJ mol^{-1} should indicate contribution of physical adsorption. If the contribution of electrostatic interactions takes place, the following adsorption process can additionally be discussed. The investigated compounds have basic character and expected to be protonated in equilibrium with the corresponding neutral form in strong acid solutions. Because Csteel surface carried positive charge, Cl^- ions should be first adsorbed onto the positively charged metal surface. Then the inhibitor molecules adsorb through electrostatic interactions between the negatively charged metal surface and positively charged inhibitor molecule and form a protective layer. In this way, the oxidation reaction of Fe can be prevented [40]. The protonated inhibitors molecules are also adsorbed at cathodic sites of metal in competition with hydrogen ions. The adsorption of protonated inhibitors molecules reduces the rate of hydrogen evolution reaction [41].

The order of increased inhibition efficiency for investigated derivatives is: $3 > 2 > 1$ as indicated from the different methods. Compound (3) is the most efficient inhibitor. Exhibit excellent inhibition power due to: (i) The presence of two N and three O atoms which are electron denoting atoms which increase the electron charge density on the molecule and (ii) these atoms may add an additional active centers. Compound (2) comes after compound (3) in inhibition efficiency due to the presence of two N and two O atoms with less one O atom than in compound (3). This will decrease the charge density on the molecules and hence, the inhibition efficiency decreased. Compound (1) is the least efficient inhibitor, in spite of the presence of two N and two O atoms. This is due to the presence of Cl atom which is very withdrawing group.

CONCLUSIONS

From the overall experimental results the following conclusions can be deduced:

1. (Z)-N'-(1-phenylethylidene)benzohydrazide derivatives are good inhibitors and act as mixed type but mainly act as anodic inhibitors for carbon steel corrosion in 1 M HCl solution.
2. The results obtained from all electrochemical measurements showed that the inhibiting action increases with the inhibitors concentration and decreases with the increasing in temperature.
3. Double layer capacitances decrease with respect to blank solution when PEBH is added. This fact confirms the adsorption of the investigated compounds molecules on the carbon steel surface.
4. The adsorption of PEBH on the carbon steel surface at different temperature was found to obey the Langmuir adsorption isotherm and this adsorption is physisorption
5. The values of inhibition efficiencies obtained from the different independent quantitative techniques used show the validity of the results.

REFERENCES

- [1] S.S. Abd El-Rehim, M.A.M. Ibrahim and K.F. Khaled, "4 Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution," *J. Appl. Electrochem.*, vol. 29, pp. 593-599, 1999.
- [2] I. Dehri and M. Ozcan, "The effect of temperature on the corrosion of mild steel in acidic media in the presence of some sulphur containing organic compounds," *Mater. Chem and Phys.*, vol. 98, pp. 316-323, 2006.
- [3] M.G. Hosseini, M. Ehteshamzadeh and T. Shahrabi, "Protection of mild steel corrosion with Schiff bases in 0.5 M H₂SO₄ solution" *Electrochim. Acta*, vol. 52, pp. 3680- 3685, 2007.
- [4] M.M. El-Naggar, "Corrosion inhibition of mild steel in acidic medium by some sulfa drugs compounds," *Corros.Sci.*, vol. 49, pp. 2226-2236, 2007.
- [5] I.L. Rosenfeld, *Corrosion Inhibitors*, New York: McGraw- Hill, 1981.
- [6] S.T. Selvi, V. Raman and N. Rajendran, "Corrosion inhibition of mild steel by benzotriazole derivatives in acidic medium," *J. Appl. Electrochem.*, vol. 33, pp. 1175-1184, 2003.
- [7] M. Özcan, I. Dehri and M. Erbil, "Organic sulphur containing compounds as corrosion inhibitors for mild steel: Correlation between inhibition efficiency and chemical structure," *App. Surf. Sci.*, vol. 236, pp. 155-164, 2004.
- [8] S.L. Granese, B.M. Rosales, G. Oviedo and J.O. Zerbino, "The inhibition action of heterocyclic nitrogen organic compounds on Fe and steel in HCl media," *Corros. Sci.*, vol. 33, pp.1439-1453, 1992.
- [9] A.S. Fouda, H.A. Mostafa, F. El-Taib and G.Y. Elewady, "Synergistic influence of iodide ions on the inhibition of corrosion of carbon steel in sulphuric acid by some aliphatic amines," *Corros. Sci.*, vol. 47, pp.1988-1996, 2004.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

- [10] M. Abdallah, "Corrosion behavior of 304 stainless steel in sulphuric acid solutions and its inhibition by some substituted pyrazolones," *Mater. Chem. Phys.*, vol. 82, pp.786 -792, 2003.
- [11] N. M. Hosny, "Synthesis and Characterization of Transition Metal Complexes Derived from (E)-N-(1-(Pyridine-2-yl)ethylidene)benzohydrazide (PEBH)," *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 41:736-742, 2011.
- [12] R. W. Bosch, J. Hubrecht, W. F. Bogaerts and B. C. Syrett, "Electrochemical Frequency Modulation: A New Electrochemical Technique for Online Corrosion Monitoring," *Corrosion*, vol. 57, pp. 60-70, 2001.
- [13] S.S. Abdel-Rehim, K.F. Khaled and N.S. Abd-Elshafi "Electrochemical frequency modulation as a new technique for monitoring corrosion inhibition of iron in acid media by new thiourea derivative," *Electrochim. Acta*, vol. 51, pp. 3269-3277, 2006.
- [14] M. Abdallah, "Antibacterial drugs as corrosion inhibitors for corrosion of aluminium in hydrochloric solution," *Corros. Sci.* vol. 46, pp. 1981-1996, 2004.
- [15] I. Langmuir, "The Constitution and Fundamental Properties of Solids and Liquids," *J. Am. Chem. Soc.*, vol. 39, pp.1848-1906, 1917.
- [16] J. I. Bhat, V. D. P. Alva, "Inhibition Effect of Nevirapine an Antiretroviral on the Corrosion of Mild Steel Under Acidic Condition," *J. Korean. Chem. Soc.*, vol. 55, pp. 835-841, 2011.
- [17] E. E. Oguzie, B. N. Okolue, E. E. Ebenso, G. M. Onuoha and A. I. Onuchukwu, "Evaluation of the inhibitory effect of methylene blue dye on the corrosion of aluminium in hydrochloric acid" *Mater. Chem. Phys.*, vol. 87, 394-401, 2004.
- [18] A. Popova, E. Sokolova, S. Raicheva, and M. Chritov, "AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives," *Corros. Sci.*, vol. 45, pp. 33-58, 2003.
- [19] Z. Szlarska-Smialowska and J. Mankowski, "Crevice corrosion of stainless steels in sodium chloride solution" *Corros. Sci.*, vol. 18, pp. 953-960, 1978.
- [20] A. Yurt, S. Ulutas, and H. Dal, "Electrochemical and theoretical investigation on the corrosion of aluminum in acidic solution containing some Schiff bases," *Appl. Surf. Sci.*, vol. 253, pp. 919-925, 2006.
- [21] J.O.M. Bochrus and A.K. N. Reddy, *Modern Electrochemistry*, New York: Plenum Press, 1970.
- [22] S. Martinez and I. Stern, "Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in the low carbon steel/mimoso tannin/sulfuric acid system," *Appl. Surf. Sci.* vol. 199, pp. 83-89, 2002.
- [23] K. Tebbji, I. Bouabdellah, A. Aouniti, B. Hammouti, H. Oudda, M. Benkaddour and A. Ramdani, "N-benzyl-N,N-bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]amine as corrosion inhibitor of steel in 1 M HCl," *Mater. Lett.* vol. 61, pp.799-804, 2007.
- [24] M. Mihit, S. El-Issami, M. Bouklah, L. Bazzi, B. Hammouti, E.A. Addi, R. Salghi and S. Kertit, "The inhibited effect of some tetrazolic compounds towards the corrosion of brass in nitric acid solution," *Appl. Surf. Sci.*, vol. 252, pp. 2389-2395, 2006.
- [25] M. Bouklah, B. Hammouti, M. Lagrenee and F. Bentiss, "Thermodynamic properties of 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole as a corrosion inhibitor for mild steel in normal sulfuric acid medium" *Corros. Sci.*, vol. 48, pp. 2831-2842, 2006.
- [26] M. Bouklah, N. Benchat, B. Hammouti, A. Aouniti and S. Kertit, "Thermodynamic characterisation of steel corrosion and inhibitor adsorption of pyridazine compounds in 0.5 M H₂SO₄," *Mater. Lett.*, vol. 60, pp. 1901-1904, 2006.
- [27] S.S. Abd El-Rehim, M.A.M Ibrahim and K.F. Khaled, "4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution," *J. Appl. Electrochem.*, vol. 29, pp. 593-599, 1999.
- [28] M. Abdallah, "Ethoxylated fatty alcohols as corrosion inhibitors for dissolution of zinc in hydrochloric acid," *Corros. Sci.*, vol. 45 pp. 2705-2716, 2003.
- [29] A.S. Fouda, A.A. Al-Sarawy and E.E. El-Katori, "Pyrazolone derivatives as corrosion inhibitors for C-steel in hydrochloric acid solution," (2006). *Desalination*, vol. 201, pp.1-13, 2006.
- [30] Z.H. Tao, S.T. Zhang, W.H. Li and B.R. Hou, "Corrosion inhibition of mild steel in acidic solution by some oxo-triazole derivatives," *Corros. Sci.*, vol. 51, pp. 2588-2595, 2009.
- [31] E.S. Ferreira, C. Giacomelli, F.C. Giacomelli and A. Spinelli, "Evaluation of the inhibitor effect of L-ascorbic acid on the corrosion of mild steel," *Mater. Chem. Phys.*, vol. 83, pp.129-134, 2004.
- [32] M. Behpour, S.M. Ghoreishi, N. Mohammadi, N. Soltani and M. Salavati-Niasari, "Investigation of some Schiff base compounds containing disulfide bond as HCl corrosion inhibitors for mild steel" *Corros. Sci.*, vol. 52, pp.4046-4057, 2010.
- [33] L. Larabi, Y. Harek, M. Traianel and A. Mansri, "Synergistic Influence of Poly(4-Vinylpyridine) and Potassium Iodide on Inhibition of Corrosion of Mild Steel in 1M HCl," *J. Appl. Electrochem.*, vol.34, pp.833-839, 2004.
- [34] M. Lebrini, M. Lagrenee, H. Vezin, M. Traisnel, F. Bentiss, "Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds", *Corros. Sci.*, vol. 49, pp.2254-2269, 2007.
- [35] S. Martinez and M. Metikoš-Hukovic, "S. Martinez and M. Metikoš-Hukovic," *J. Appl. Electrochem.*, vol. 33, pp. 1137-1143, 2003," *J. Appl. Electrochem.*, vol. 33, pp. 1137-1143, 2003.
- [36] M.N. El-Haddad and A.S. Fouda, "Corrosion Inhibition and Adsorption Behavior of Some Azo Dye Derivatives on Carbon Steel in Acidic Medium: Synergistic Effect of Halide Ions," *Chem. Eng. Comm.*, vol. 200, pp. 1366-1374, 2013.
- [37] J.L. Trinstancho-Reyes, M. Sanchez-Carrillo, R. Sandoval-Jabalera, V.M. Orozco-Carmona, F. Almeraya-Calderon, J.G. Chacon-Nava, J.G. Gonzalez-Rodriguez and A. Martínez-Villafane, "Electrochemical Impedance Spectroscopy Investigation of Alloy Inconel 718 in Molten Salts at High Temperature" *Int. J. Electrochem. Sci.*, vol. 6, pp. 419-431, 2011.
- [38] C.S. Hsu and F. Mansfeld, "Concerning the Conversion of the Constant Phase Element Parameter Y₀ into a Capacitance," *Corrosion*, vol. 57, pp.747-748, 2001.
- [39] F. Bentiss, M. Bouanis, B. Mernari, M. Traisnel, H. Vezin and M. Lagrenee, "Understanding the adsorption of 4H-1,2,4-triazole derivatives on mild steel surface in molar hydrochloric acid," *Appl. Surf. Sci.*, vol. 253, pp.3696-3704, 2007.
- [40] H. Keles, M. Keles, I. Dehri and O. Serindag, "The inhibitive effect of 6-amino-*m*-cresol and its Schiff base on the corrosion of mild steel in 0.5 M HCl medium," *Mater. Chem. Phys.*, vol. 112, pp. 173-179, 2008.
- [41] A. Yurt, A. Balaban, S. Ustün Kandemir, G. Bereket, B. Erk, "Investigation on some Schiff bases as HCl corrosion inhibitors for carbon steel", *Mater. Chem. Phys.*, vol.85, pp. 420-426, 2004.

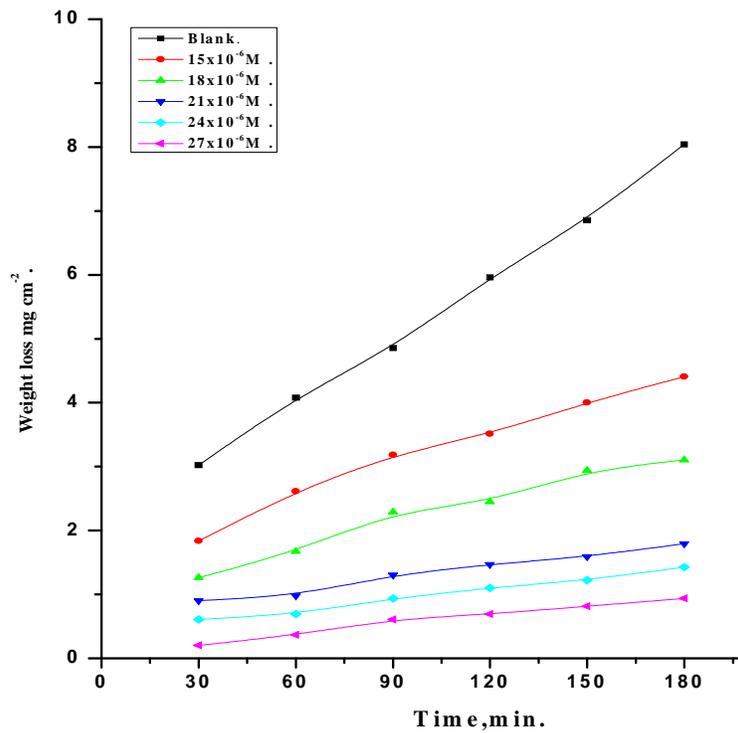


Fig. 1: Weight loss-time curves for the dissolution of C-steel in 1 M HCl in the absence and presence of different concentrations of compound (3) at 25°C

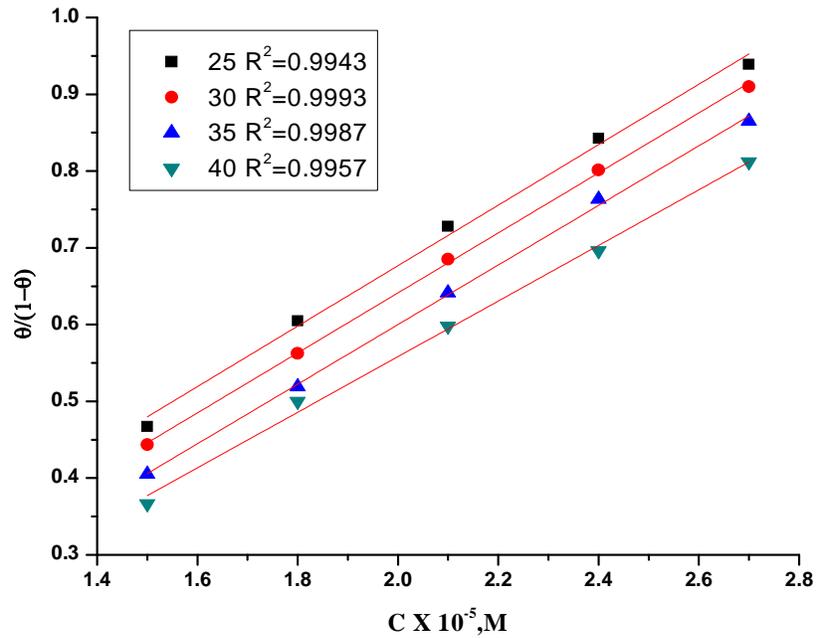


Fig. 2: Langmuir adsorption isotherm of compound (3) on C-steel surface in 1 M HCl at different temperatures

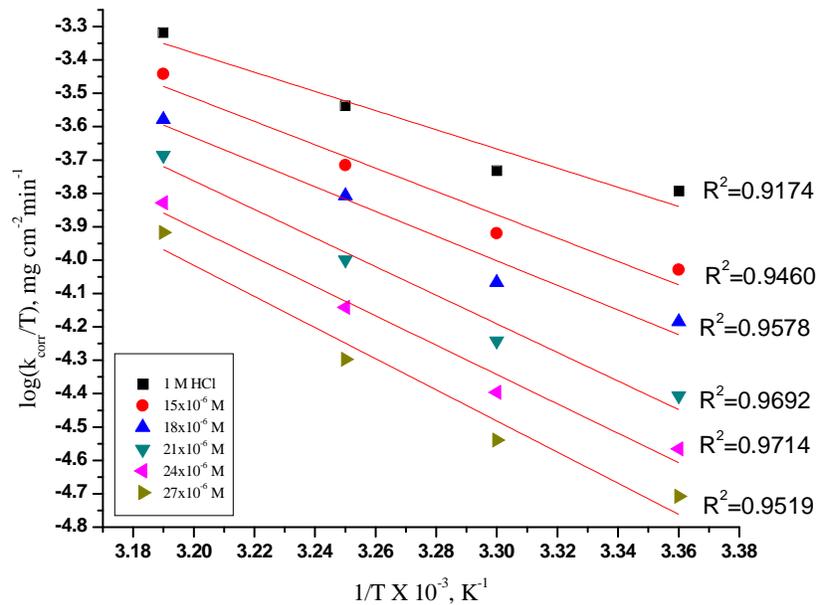


Fig. 3: Arrhenius plots for C-steel corrosion rates (k_{corr}) after 120 minutes of immersion in 1 M HCl in the absence and presence of different concentrations of compound (3)

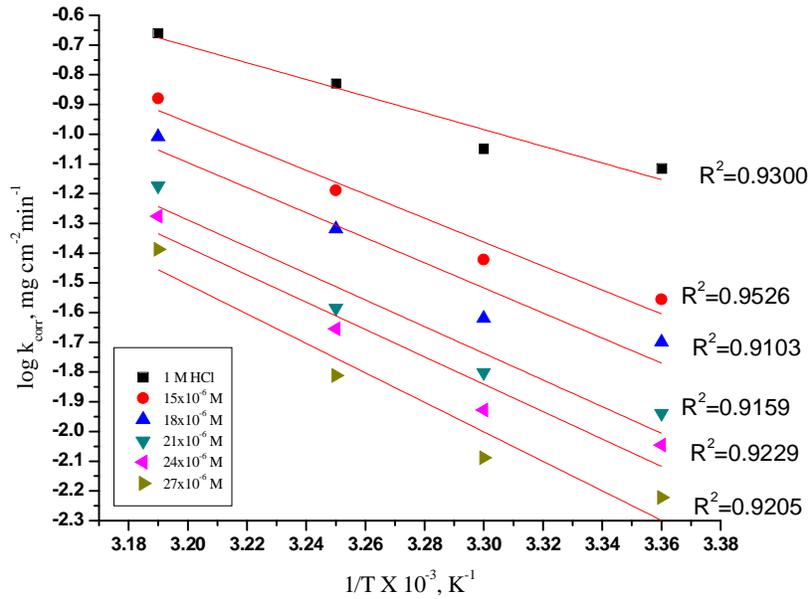


Fig. 4: Plots of $(\log k_{\text{corr}}/T)$ vs. $1/T$ for corrosion of C-steel in 1M HCl in the absence and presence of different concentrations of compound (3)

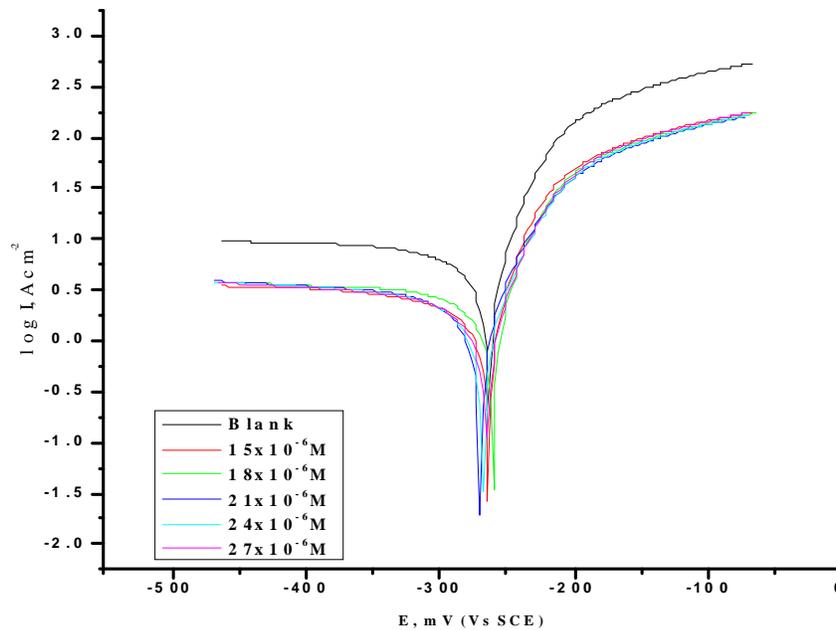


Fig. 5: Potentiodynamic polarization curves for the corrosion of C-steel in 1M HCl in the absence and presence of different concentrations of compound (3) at 25°C

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

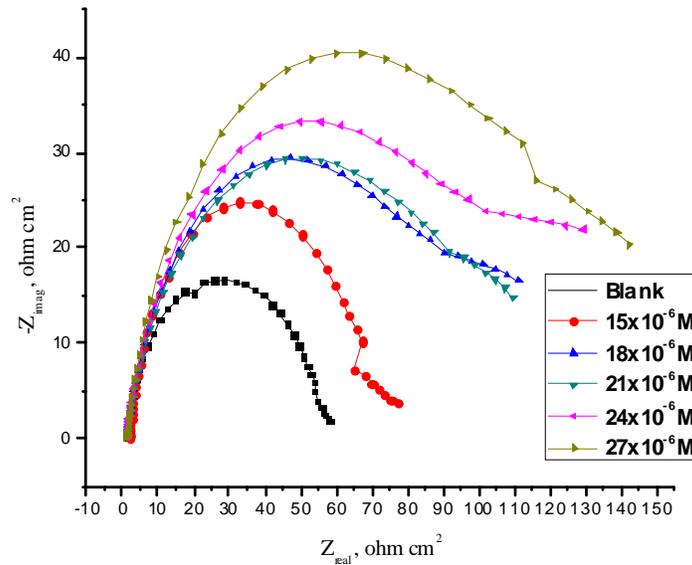


Fig. 6: The Nyquist plots for corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of compound (3) at 25°C

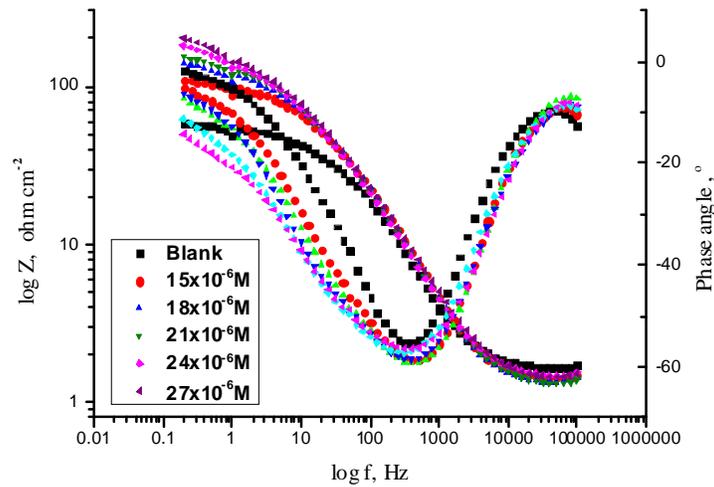


Fig. 7: The Bode plots for corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of compound (3) at 25°C

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

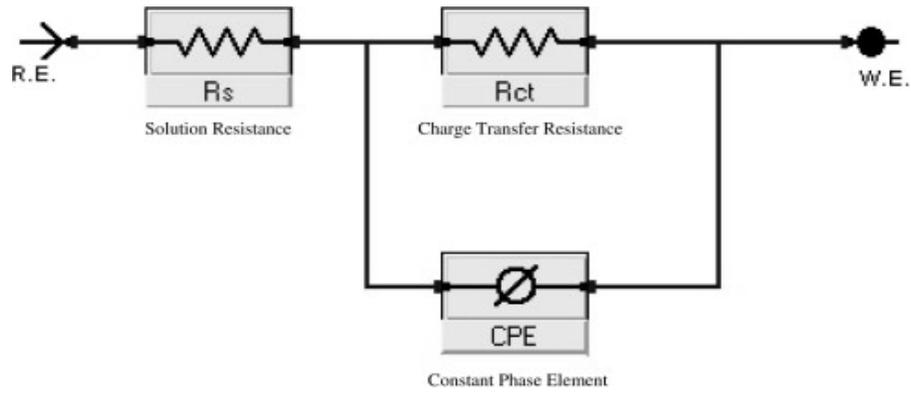


Fig.8: Equivalent circuit model used to fit experimental EIS

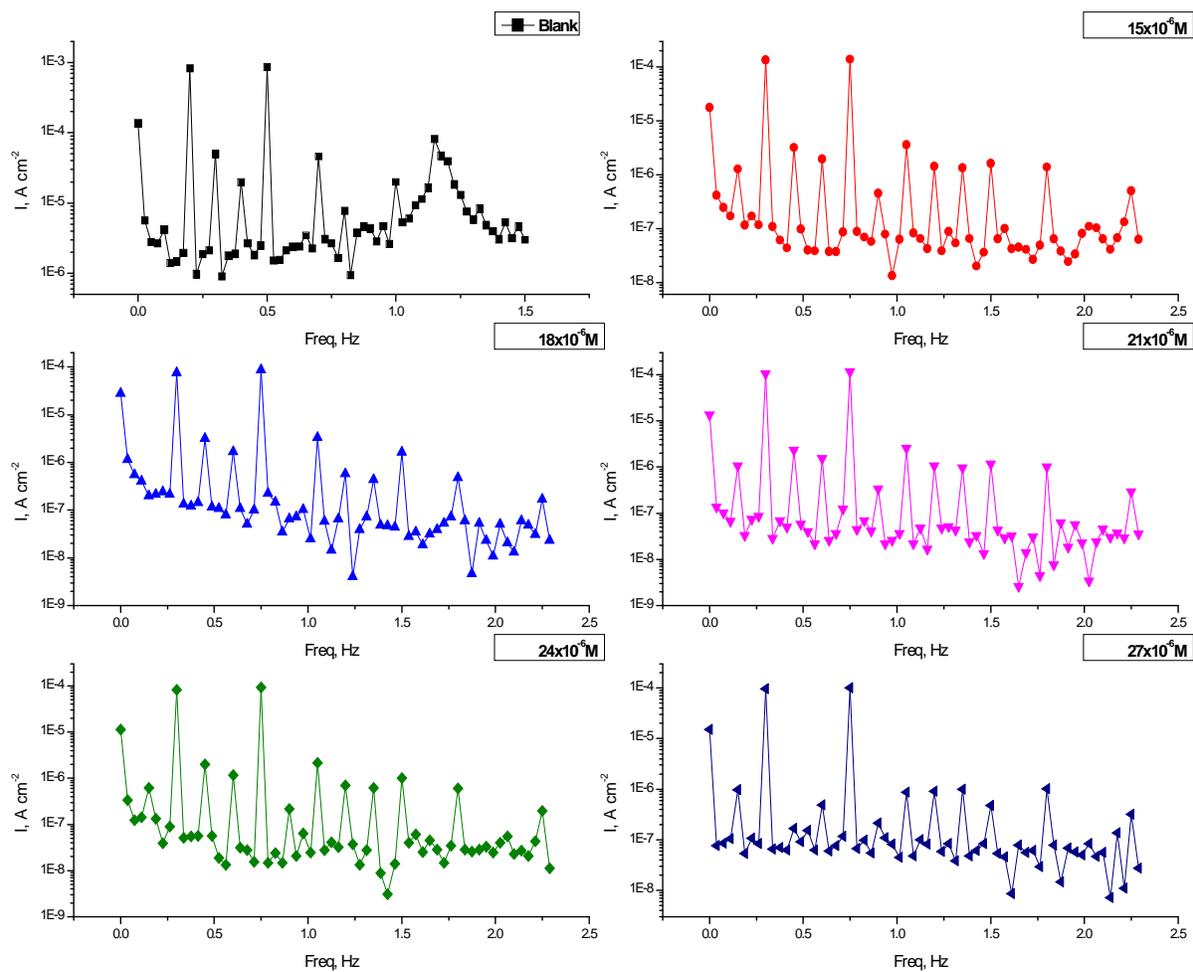


Fig. 9: EFM spectra for C-steel in 1 M HCl in the presence of different concentrations of compound (3) at 25° C

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

Table 1: Data of weight loss measurements for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of investigated inhibitors at 25°C

Compound	Conc., x 10 ⁶ M	Corrosion Rate (CR), mg cm ⁻² min ⁻¹	θ	% IE
Blank		0.050	----	----
1	15	0.029	0.411	41.1
	18	0.020	0.589	58.9
	21	0.012	0.754	75.4
	24	0.009	0.815	81.5
	27	0.006	0.884	88.4
2	15	0.034	0.314	31.4
	18	0.025	0.493	49.3
	21	0.016	0.685	68.5
	24	0.012	0.760	76.0
	27	0.007	0.864	86.4
3	15	0.040	0.205	20.5
	18	0.028	0.431	43.1
	21	0.017	0.658	65.8
	24	0.014	0.722	72.2
	27	0.009	0.826	82.6

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

Table 2: Data of weight loss measurements for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of investigated inhibitors at different temperature

Compound	Conc., x 10 ⁶ M	30C		35C		40C	
		θ	% IE	θ	% IE	θ	% IE
Blank		----	-----	----	----	----	----
1	15	0.390	39.0	0.344	34.4	0.332	33.2
	18	0.545	54.5	0.445	44.5	0.423	42.3
	21	0.746	74.6	0.699	69.9	0.602	60.2
	24	0.804	80.4	0.777	77.7	0.688	68.8
	27	0.861	86.1	0.836	83.6	0.759	75.9
2	15	0.270	27.0	0.173	17.3	0.143	14.3
	18	0.459	45.9	0.323	32.3	0.290	29.0
	21	0.646	64.6	0.583	58.3	0.558	55.8
	24	0.745	74.5	0.717	71.7	0.692	69.2
	27	0.833	83.3	0.800	80.0	0.759	75.9
3	15	0.199	19.9	0.141	14.1	0.123	12.3
	18	0.357	35.7	0.257	25.7	0.223	22.3
	21	0.629	62.9	0.587	58.7	0.465	46.5
	24	0.692	69.2	0.672	67.2	0.558	55.8
	27	0.740	74.0	0.725	72.5	0.659	65.9

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

Table 3: Thermodynamic parameters for the adsorption of three compounds on carbon steel surface in 1M HCl at different temperatures

Compounds	Temp., K	$K_{ads} \times 10^{-8}, M^{-1}$	$-\Delta G_{ads}^{\circ}, kJ mol^{-1}$	$-\Delta H_{ads}^{\circ}, kJ mol^{-1}$	$-\Delta S_{ads}^{\circ}, J mol^{-1}K^{-1}$
1	298	4.92	36.2	5.5	103
	303	1.49	36.8		
	308	1.46	37.4		
	313	1.45	37.8		
2	298	3.39	36.7	1.8	116
	303	1.43	37.3		
	308	1.42	37.8		
	313	1.41	38.4		
3	298	3.23	36.7	3.1	112
	303	1.42	37.3		
	308	1.41	37.9		
	313	1.40	38.4		

Table 4: Activation parameters for the dissolution of carbon steel in the presence and absence of different concentrations of inhibitors in 1 M HCl

Inhibitor	Conc., $\times 10^{-6}$ M	Activation parameters		
		$E_a^{\circ}, kJ mol^{-1}$	$\Delta H^{\circ}, kJ mol^{-1}$	$-\Delta S^{\circ}, J mol^{-1}K^{-1}$
Blank		56.4	24.9	78.1
1	15	80.5	30.4	40.9
	18	84.4	32.1	29.9
	21	89.4	37.2	4.7
	24	91.9	38.2	9.3
	27	98.9	40.4	23.7
2	15	77.6	29.8	44.6
	18	82.4	31.3	34.6
	21	84.9	32.9	25.9
	24	86.7	34.2	18.9
	27	95.6	36.1	7.5
3	15	68.2	26.9	65.2
	18	72.8	28.5	55.2
	21	81.3	30.9	39.7
	24	85.6	33.6	22.1
	27	93.6	35.1	13.6

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

Table 5: The effect of concentration of the investigated compounds on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), degree of surface coverage θ , and inhibition efficiency (% IE) for the corrosion of carbon steel 1 M HCl at 25 °C

Comp.	Conc., x 10 ⁻⁶ M	-E _{corr} , mV(vs SCE)	i _{corr} , μA cm ⁻²	β _a , mV dec ⁻¹	-β _c , mV dec ⁻¹	θ	% IE
1	Blank	262	5.0446	39	334	----	-----
	15	263	1.8291	37	403	0.637	63.7
	18	259	1.6217	36	207	0.679	67.9
	21	268	1.4479	43	180	0.713	71.3
	24	268	1.3014	40	158	0.742	74.2
	27	265	.9966	33	103	0.802	80.2
2	15	260	2.4958	34.9	96.5	0.505	50.5
	18	336	2.1467	74.0	274.5	0.574	57.4
	21	275	1.9183	59	339	0.620	62.0
	24	263	1.5231	43	225	0.968	96.8
	27	266	1.1880	38	152	0.765	76.5
3	15	267	4.2720	48	261	0.153	15.3
	18	268	3.6600	43	199	0.2744	27.44
	21	270	2.7496	39	128	0.455	45.5
	24	266	2.0807	35	97	0.588	58.8
	27	264	1.9197	31	84	0.619	61.9

Table 6: Electrochemical kinetic parameters obtained by EIS technique for in 1 M HCl without and with various concentrations of investigated compounds at 25 °C

Comp.	Conc., x 10 ⁻⁶ M	R _s , Ωcm ²	Y ₀ , x 10 ⁻³ μΩ ⁻¹ s ⁿ	n	R _{ct} , Ω cm ²	C _{dl} , μFcm ⁻²	θ	%IE
1	Blank	1.54	344.8	773.8	53.1		----	-----
	15	1.26	345.2	753.8	101.4	1.89	0.476	47.6
	18	1.18	373.3	745.6	124.6	1.86	0.574	57.4
	21	1.15	422.2	731.8	140.6	1.49	0.662	62.2
	24	1.28	508.2	712.6	164.3	1.31	0.677	67.7
	27	1.20	526.2	695.3	184.6	1.15	0.712	71.2
2	15	1.48	316.6	773.7	80.0	1.20	0.336	33.6
	18	1.55	353.0	740.7	100.8	1.09	0.473	47.3
	21	1.37	290.9	777.5	106.4	1.07	0.501	50.1
	24	1.20	341.2	756.0	115.2	1.02	0.539	53.9
	27	1.44	228.5	804.9	133.1	0.97	0.601	60.1
3	15	1.72	369.7	830.1	68.1	1.74	0.220	22.0
	18	1.35	394.1	762.4	95.9	1.47	0.447	44.7
	21	1.17	433.2	745.9	97.9	1.42	0.458	45.8
	24	1.14	373.3	765.1	109.4	1.40	0.515	51.5
	27	1.20	341.3	779.3	126.8	1.39	0.581	58.1

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 3, March 2014

Table 7: Electrochemical kinetic parameters obtained by EFM technique for carbon steel in the absence and presence of various concentrations of inhibitors in 1 HCl at 25°C

Comp.	Conc., x 10 ⁻⁶ M	i _{corr.} , μAcm ⁻²	β _c mVdec ⁻¹	β _a mVdec ⁻¹	CF-2	CF-3	CR mpy	θ	%IE
	Blank	1231	80.6	112.0	2.4	5.1	562.0	-	-
1	15	248.0	129	108	1.889	2.856	113.7	0.799	79.9
	18	211.0	214	140	1.932	3.635	96.55	0.829	82.9
	21	203.5	131	111	1.830	3.264	93.00	0.835	83.5
	24	185.3	153	125	1.90	3.057	84.65	0.849	84.9
	27	174.3	118	114	1.083	3.663	97.73	0.858	85.8
2	15	289.1	122	101	1.930	3.320	132.1	0.765	76.5
	18	232.6	121	103	1.846	3.080	106.3	0.811	81.1
	21	224.4	126	106	1.945	2.982	102.5	0.818	81.8
	24	208.1	118	110	1.583	2.836	95.09	0.831	83.1
	27	204.7	127	121	1.494	3.61	67.93	0.834	83.4
3	15	375.1	91.7	105.7	1.8	2.8	124.5	0.695	69.5
	18	304.9	148	141	1.292	3.366	101.2	0.752	75.2
	21	295.4	150	134	1.779	3.187	98.05	0.760	76.0
	24	283.7	102	96	1.497	2.923	94.15	0.770	77.0
	27	250.4	147	131	1.867	2.990	83.09	0.797	79.7