Experimental and Theoretical Studies on Corrosion Inhibition Performance of Phenanthroline for Cast Iron in Acid Solution

B. Idir^{1,2*} and F. Kellou-Kerkouche¹

¹USTHB, Laboratoire d'Electrochimie-Corrosion, Métallurgie et Chimie Minérale Faculté de Chimie BP32 El-Alia Bab-Ezzouar Alger-Algérie

²Research center in industrial technologies (CRTI), P.O. Box 64, Cheraga 16014 Algiers, Algeria

ABSTRACT

The corrosion inhibition of cast iron in 1 M HCl by Phenanthroline (Phen) was investigated using potentiodynamic polarization (PDP) curves, electrochemical impedance spectroscopy (EIS), surface analysis and theoretical calculations. It is found that Phen exhibits high inhibition activity towards the corrosive action of HCl and its adsorption obeys the Langmuir adsorption isotherm model. The results showed that inhibition efficiency increases with Phen concentration up to a maximum value of 96% at 1.4 mM, and decreases slightly with the increase in temperature. The free adsorption energy value indicates that Phen adsorbs on cast iron surface in 1 M HCl via a simultaneous physisorption and chemisorption mechanism. Scanning electron microscopy (SEM) micrographs, atomic force microscopy (AFM) and FTIR analysis confirmed the formation of a protective film on cast iron surface, resulting in the improvement of its corrosion resistance in the studied aggressive solution. Quantum chemical calculations at the DFT level were achieved to correlate electronic structure parameters of Phen molecules with their adsorption mode.

Keywords : Cast iron, Corrosion inhibition, Phenanthroline, Acid solution, DFT

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1. Introduction

Ductile cast iron is specifically useful in pipelines, agriculture, some vehicle components and wind turbine parts [1-3]. It has been recognized as the most appropriate material for a wide variety of industrial applications due to its good machinability, high castability, and other various advantages [4-6]. With its unique microstructure, this material provides manufacturers an exceptional combination of toughness and reliability at a considerably lower cost [7].

Acidic solutions are widely employed in the industry for acid pickling and acid cleaning; they are also added to oil and gas production. It should be emphasized that hydrochloric acid (HCl) is the most used for this purpose [8,9]. Unfortunately, because of the

presence of Cl^- ions this acid is highly corrosive. The use of organic inhibitors is the most practical and effective method for the protection of ferrous materials [10-17]. Generally, molecules containing nitrogen, sulfur, oxygen and aromatic rings are preferred [18-20]. The efficiency of these molecules depends mainly on their ability to adhere to the metal surface [21].

Phenanthroline is a classic chelating bidentate ligand for transition metal ions, which has played an important role in the development of coordination chemistry; the presence of nitrogen and multiple bonds with high electron density in its flat molecular structure facilitates its ability to inhibit corrosion of most metals. Banerjee [22] reported the corrosion inhibition of Phenanthroline on mild steel in aerated 0.5 M H_2SO_4 , whereas its adsorption on the aluminum surface was investigated by Xianghong Li in 1 M HCl solution [23]. Obi-egbedi et al have tested a

*E-mail address: idirbrahim2016@gmail.com

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synthesized Phenanthroline derivative as a corrosion inhibitor for mild steel in 0.5 M H₂SO₄ solution [24]. Furthermore, Xia Liu et al. [25] have studied the effect of Phenanthroline and its cobalt complex on the corrosion of mild steel in 0.1 M H₂SO₄ solution. However, an overview of the literature revealed that few studies were devoted to the corrosion inhibition of various categories of cast iron in acidic medium. One can cite the influence of sodium dodecyl benzene sulfonate on the corrosion behavior of an elaborated cast iron alloy in sulfuric acid [26]. Recently, many studies [27-30] have reported that some expired drugs, carbohydrates, Schiff base derivatives and some plant extracts are effective corrosion inhibitors of cast iron corrosion in various environments.

In this context, the current work describes the inhibitive performance of Phenanthroline on cast iron corrosion in aerated hydrochloric acid, using electrochemical measurements. The inhibited metallic surface was examined by scanning electron microscopy, atomic force microscopy, and FTIR spectroscopy. The donor-acceptor relationship between inhibitor molecules and cast iron surface was achieved by the calculated theoretical parameters of the neutral Phen molecule and its protonated specie, in aqueous phase, using quantum chemical calculations.

2. Experimental

2.1 Material

The chemical composition (in wt.%) of the commercial studied cast iron is: 3.70% C, 1.98% Si, 0.25% Mn, 0.019% P, 0.017% S, 0.093% Cr, 0.01% Al, 0.021% Ni, 0.007% Cu, 0.059% Mg, 0.01% Ti and balance Fe. A round rod with an exposed area of 1.76 cm² was assembled as the working electrode. Before introducing it in the electrochemical cell, the exposed face of the electrode was ground mechanically with silicon carbide papers of graded grit ranging from 600 to 1200 grit, then rinsed with bi-distilled water and degreased with acetone.

2.2 Corrosive and inhibitive solutions

The corrosive 1 M HCl solution was prepared using analytical reagent HCl in double distilled water. Phenanthroline (Fig. 1) was added to the acid solution at different concentrations. Phenanthroline and its derivatives have been employed as a ligand in coordination chemistry; forming stable complexes

Fig. 1. Chemical molecular structure of Phenanthroline.

with most metal ions [31].

2.3 Electrochemical methods

Electrochemical experiments were performed in a conventional three-electrode cell. The cast iron sample was used as the working electrode (WE); a saturated Ag/AgCl electrode and a platinum foil (surface area of 1.0 cm²) were used as reference and counter electrode, respectively. Electrochemical impedance spectroscopy measurements were achieved at the open circuit potential for the frequency range of 100 KHz to 10 mHz, using a peak-to-peak voltage excitation of 10 mV. Potentiodynamic polarization curves were plotted from -300 to +300 mV versus open circuit potential (E_{cor}) at the scan rate of 1 mV/s.

All electrochemical measurements were carried out using a Potentiostat-Galvanostat (Princeton Applied Research Versastat 3). Corr-View and Z-view software's were used for Tafel extrapolations and the fit of EIS diagrams, respectively. Before performing EIS diagrams and potentiodynamic polarization curves, the sample has been immersed in 1 M HCl solution with and without addition of inhibitor for 30 minutes until a steady state open circuit potential (E_{cor}) is reached.

2.4 Quantum chemical calculations

Theoretical calculations were performed using density functional theory (DFT) in Spartan 08 program package, at B3LYP/6-31 G (d, p) level of theory. Optimization of the molecules structure was accomplished in a water phase [32]. It is believed that this level optimizes accurately and provides right electronic properties for a wide range of organic molecules. Some parameters such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}) and dipole moments (μ) were obtained. Absolute electronegativity (χ), hardness (η), global

electrophilicity (ω) and global nucleophilicity (ε) were calculated from the following equations:

$$\chi = \frac{I + A}{2} \quad (1)$$

$$\eta = \frac{I - A}{2} \quad (2)$$

Where ionization potential $I = -E_{\text{HOMO}}$ and electron affinity $A = -E_{\text{LUMO}}$.

Global electrophilicity index (ω) is as follow [33]:

$$\omega = \frac{\chi^2}{2\eta} \quad (3)$$

Nucleophilicity (ε) is the inverse of electrophilicity ($1/\omega$).

To get more insight about ability of inhibitor molecules to interact with iron atoms, and to predict the most favorable adsorbed inhibitor, Pearson [34] has shown that the fraction of electrons transferred (ΔN) between the inhibitor molecules and the iron atom could be calculated by the following equation:

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})} \quad (4)$$

Where χ_{Fe} , χ_{inh} , η_{Fe} , η_{inh} are electronegativities and hardness values of iron and inhibitor molecule, respectively. Recently, Kokalj [35] has shown that the use of work function (Φ) of the iron surface instead of χ_{Fe} is a more appropriate value of iron electronegativity. In this study, we have considered Fe(110) because it is the most stable plane and it presents a dense surface package, hence derived theoretical values of iron (110) have been considered: $\Phi_{\text{Fe}(110)} = 4.82 \text{ eV}$ and $\eta_{\text{Fe}} = 0 \text{ eV}$ [35].

The Fukui indices are calculated by taking the finite difference approximations from Mulliken population's analysis (MPA) of atoms for Phen and Phen- H^+ as follows:

$$f_k^+ = q_k(N+1) - q_k(N) \quad (5)$$

$$f_k^- = q_k(N) - q_k(N-1) \quad (6)$$

Where $q_k(N)$, $q_k(N+1)$ and $q_k(N-1)$ are the atomic charges of the systems with N , $N+1$, and $N-1$ electrons, respectively.

2.5 Surface characterization

The cast iron specimens were in first polished with

a series of emery paper to obtain a surface mirror, rinsed with double distilled water and thereafter degreased with acetone. The cleaned specimens were immersed in 1 M HCl solution with and without the optimum concentration of Phen (1.4 mM). After 04 hours of exposure to the tested solutions, the cast iron specimens were taken out, cleaned with double distilled water and finally dried with a cold air blower. Surface characterization was carried out using a ZEISS EVO MA 25 scanning electron microscope at an accelerating voltage of 20 kV.

The topology measurements (on the samples immersed for 03 hours in the above testing solutions) were performed using a Bruker Dimension Icon AFM atomic force microscope. Before starting the tests, the samples were cleaned and dried thoroughly with a cold air blower to eliminate all corrosion products.

Infrared spectra of the pure Phen and the scraped layer collected from specimen immersed during 6 hours in HCl solution containing 1.4 mM of inhibitor (Phen) were recorded via FTIR spectrometer (Agilent Cary 630) measured in the range of 4000-600 cm^{-1} .

3. Results and Discussion

3.1 Electrochemical measurements

3.1.1 Polarization studies at 25°C

The inhibitive properties of Phenanthroline were

Fig. 2. Potentiodynamic polarization curves of cast iron in 1 M HCl containing Phen at different concentrations: 0.36, 0.76, 1 and 1.40 mM at 25°C with a scan rate of 1 mV/s.

analyzed by potentiodynamic polarization curves and electrochemical impedance spectroscopy diagrams. The polarization curves of cast iron in 1 M HCl solution in the absence and presence of various concentrations of Phen are illustrated in Fig. 2. Different

electrochemical kinetic parameters were determined by extrapolating the linear Tafel regions to the corrosion potential (Table 1): the corrosion current density (i_{cor}), the corrosion potential (E_{cor}), cathodic Tafel slope (b_c), anodic Tafel slope (b_a), as well as the inhibition efficiency ($IE\%$) which is defined as follows:

$$IE(\%) = \frac{i_{\text{cor}} - i_{\text{cor(inh)}}}{i_{\text{cor}}} \times 100 \quad (7)$$

Where: i_{cor} and $i_{\text{cor(inh)}}$ are the uninhibited and inhibited corrosion current densities, respectively.

As can be seen in Fig. 2, anodic and cathodic current densities decrease with increasing inhibitor concentration. This is an indication that the organic compound under study reduces the hydrogen evolution reaction as well as the anodic cast iron dissolution. The parallel Tafel lines obtained from cathodic branches indicate that hydrogen evolution reaction is activation controlled and the addition of Phen does not modify the mechanism of this process, however, the proton discharge process is delayed. The anodic curves of cast iron in 1 M HCl in the presence of organic compound show that the tested molecule has markedly hindered the anodic reaction in the potential range from E_{cor} to -200 mV, however, at the highest anodic potentials the curves ideally overlapped; this phenomenon can be attributed to the desorption of the inhibitive molecules from iron surface [36].

The data in Table 1 showed that corrosion current densities (i_{cor}) are significantly decreased with increasing Phen concentration, which means that the iron sample has become more resistant to corrosion. The values of the anodic and cathodic Tafel slopes, b_a and b_c , respectively, have nearly the same order of magnitude in the free and inhibitive solutions, which indicates that the corrosion mechanism of the cast

Fig. 2. a) Nyquist plots and b) Bode plots of cast iron corrosion in 1 M HCl without and with different concentrations of Phen: 0.36, 0.76, 1 and 1.40 mM at 25°C.

Table 1. Tafel and EIS parameters of cast iron in 1 M HCl solution with and without Phen at 25°C

Tafel						EIS						
C/ 10 ⁻⁴ (M)	E_{cor} / mV vs Ag/ AgCl	i_{cor} / mA cm ⁻²	b_a / mV/dec	$-b_c$ / mV/dec	IE%	R_s / Ωcm ²	R_{ct} / Ωcm ²	Y_0 / μΩ ⁻¹ S ⁿ cm ⁻²	n	C_{dl} / (μF cm ⁻²)	IE%	χ^2
0	-397	3.25	134	147	/	1.71	4.16	617.8	0.85	260.1	/	0.0007
3.6	-408	0.58	123	116	82	1.69	28.5	281.9	0.85	132.1	85.4	0.0011
7.6	-417	0.42	198	114	87	1.85	69.6	198.7	0.84	88.5	94.0	0.0041
10	-415	0.34	171	111	89	1.52	98.1	120.6	0.84	56.1	95.7	0.0045
14	-407	0.19	104	121	94	1.58	127.1	92.5	0.83	41.1	96.7	0.0053

iron is unaffected by the addition of Phen. On the other hand, the corrosion potential (E_{cor}) has not undergone any significant variation, meaning that the organic inhibitor is adsorbed on the anodic and cathodic sites of the metal surface. So, it can be recognized that Phen acts as a mixed-type inhibitor [37]. The value of inhibition efficiency ($IE\%$) increases up to 94% with increasing the concentration of Phen at the optimum value of 1.4 mM.

3.1.2 EIS studies at 25°C

The impedance diagrams (Fig. 3a) represented in a complex plane, describe the behavior of cast iron in a solution of HCl without and with inhibitor at different concentrations. It can be seen that all EIS diagrams display a single depressed capacitive semicircle. These imperfect semicircles may be attributed to the surface roughness, the frequency dispersion, as well as the heterogeneity of the cast iron surface [38]. Nyquist plots of the blank and inhibited solutions show similar behavior, indicating that the cast iron corrosion reaction is mainly controlled by charge transfer, and the addition of the inhibitor does not modify the mechanism of the process [39]. The semicircles diameters in the presence of Phen are larger than that observed in its absence; this phenomenon could be attributed to the adsorption of the investigated inhibitor on the cast iron surface by blocking its active sites, leading to the improvement of cast iron protection against corrosion [40].

The impedance plots are fitted accurately with a good chi-squared coefficient (χ^2) using the Randles equivalent circuit (R_s (R_{ct}/CPE)) having a single time constant, as shown in the insert of Fig. 3a. In this circuit, R_s is the solution resistance, R_{ct} is the charge transfer resistance related to the OCP corrosion reaction, while the CPE represents a constant phase element related to the non-ideal capacity (C_{dl}). A similar circuit was proposed in several works [41-44]. The constant phase element (CPE) is introduced to simulate the non-ideal capacitive behavior of cast iron/HCl interface, and its impedance is defined as follows [43]:

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^n} \quad (8)$$

Where Y_0 is a CPE constant, j is the imaginary number, ω is the angular frequency ($\omega = 2\pi f$, f represents the AC frequency in Hz), n is a phase shift,

Fig. 3. Adsorption isotherms of inhibitor on cast iron surface in 1 M HCl.

which is related to the system homogeneity, when the CPE display a pure capacitance, $n = 1$. The electrical double layer capacitance (C_{dl}) was determined by the following equation [45]:

$$C_{\text{dl}} = Y_0(\omega_{\text{max}})^{n-1} \quad (9)$$

The EIS parameters of the cast iron immersed in uninhibited and inhibited solutions are summarized in Table 1. The results obtained are consistent with those deduced from the Tafel method. Indeed, the charge transfer resistance increases with the increase in Phen concentration, while the capacitance decreases, indicating that this inhibitor has reduced the aggressiveness of the acid solution.

The inhibition efficiency ($IE\%$) was calculated, using the charge transfer resistance values (R_{ct}), by the following equation:

$$IE\% = \left(\frac{R_{\text{ct}}(\text{inh}) - R_{\text{ct}}}{R_{\text{ct}}(\text{inh})} \right) \times 100 \quad (10)$$

Where $R_{\text{ct}}(\text{inh})$ and R_{ct} represent the charge transfer resistance derived from the inhibited and uninhibited solutions, respectively.

The highest value of R_{ct} bound to lowest C_{dl} value corresponds to the highest inhibition efficiency recorded at the optimum concentration of Phen (1.4 mM); which means the effective adsorption of Phen which causes the slowing of the cast iron corrosion process.

According to the Helmholtz model, the decrease of the C_{dl} value (Eq.11) indicates an increase in the double layer thickness (d), which can be attributed to the

development of a compact protective film on the metal surface by the inhibitor adsorption [46].

$$C_{dl} = \frac{\varepsilon^0 \times \varepsilon S}{d} \quad (11)$$

Where d is the thickness of the film, ε^0 is the permittivity of the air, ε is the medium dielectric constant, and S represents the surface area of the working electrode.

Bode and phase angle plots are given in Fig. 3b, they can provide complementary information on the complicated corrosion process. The impedance modulus, at low frequencies, increases with the increase of the inhibitor concentration, indicating that the adsorption of the inhibitive molecules improves the corrosion resistance of the studied cast iron in the corrosive HCl solution [47]. It is also evident, that the mid-frequency phase angle values have evolved in the negative direction with increasing inhibitor concentration, indicating the improvement of Phen adsorption on the metal surface. In addition, there is only one peak in the phase angle plots that confirms the existence of a single time constant at the metal/solution interface.

The results obtained from the electrochemical measurements are in reasonable agreement and confirm once more that Phenanthroline shows good inhibition performance (above 95%) for cast iron in hydrochloric acid solution. A comparison of corrosion inhibition efficiency of phenanthroline with various phenanthroline derivatives reported as corrosion inhibitors is presented in Table 2 [22-25, 48-52].

3.2 Adsorption isotherm

The electrochemical measurements evidenced the Phen adsorption on the cast iron surface and therefore the inhibition of general corrosion of the metal surface, by forming a barrier for the hydrated corrosive ions. Consequently, it would be very useful to describe the adsorption process by an appropriate adsorption isotherm. The relative coverage area (θ) is proportional to the inhibition efficiency ($IE\%$), which is determined directly as follow [47]:

$$\theta = \frac{IE\%}{100} \quad (12)$$

Adsorption isotherms are usually used to describe the adsorption process of inhibitors. Their determina-

Table 2. Comparison of corrosion inhibition efficiency of phenanthroline with other phenanthroline derivatives reported as corrosion inhibitors in the literature.

Inhibitor	Corrosive medium	material	Inhibition efficiency (%)			Reference
			Weight loss	Tafel	EIS	
Phenanthroline	H ₂ SO ₄ (0.5 M)	Mild steel	92	54	/	[22]
Phenanthroline	H ₂ SO ₄ (0.5 M)	Steel	67	82	/	[48]
Phenanthroline+ NaCl	H ₂ SO ₄ (0.5 M)		96	99	/	
Phenanthroline	HCl (1 M)	Aluminum	95	98	96	[23]
phenanthroline	H ₃ PO ₄ (1 M)	Steel	58	/	/	[49]
Phenanthroline +NaCl	H ₃ PO ₄ (1 M)		96	85	/	
2-(6-methylpyridin-2-yl)-1H-imidazo[4,5-f] [1,10] phenanthroline	H ₂ SO ₄ (0.5 M)	Mild steel	72	/	/	[24]
2-Mesityl-1H-imidazo[4,5-f] [1,10]phenanthroline	H ₂ SO ₄ (0.5 M)	Mild steel	87	/	/	[51]
2-(6-methylpyridin-2-yl) oxazolo [5,4 f][1,10] phenanthroline	H ₂ SO ₄ (0.5 M)	Mild steel	90	/	/	[50]
1H-benzimidazole phenanthroline	HCl (1 M)	Mild steel	92	84	84	[52]
Phenanthroline	H ₂ SO ₄ (0.1 M)	Carbon steel	/	69	80	[25]
Cobalt phenanthroline complex			/	95	92	
Phenanthroline	HCl (1 M)	Cast iron	/	94	96	This work

Fig. 4. Nyquist plots of cast iron in 1 M HCl (a) in absence and (b) in presence of 1.4 Mm of Phen at various temperatures (between 25 and 55°C).

tion can provide important clues about the nature of metal-inhibitor interactions [53]. The surface coverage (θ) values obtained from the Tafel and EIS methods, corresponding to different Phen concentrations at 25°C, were used to deduce the best isotherm. Several attempts have been made to identify among all the adsorption isotherms; the best fit was obtained with the Langmuir adsorption isotherm modeled by the following equation [54]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (13)$$

The plot of C_{inh}/θ vs C_{inh} is characterized by a straight line (Fig. 4).

The slope of the plot was close to 1, indicating that

Phen molecules interact significantly with cast iron surface to form an inhibiting film that corresponds to a single layer [55]. The hypothesis of this isotherm implies that all the adsorption sites are equivalent and that the adsorption capacity of the molecules on a given site is independent for the occupation of neighboring sites [56].

In addition, with using this model (Langmuir isotherm), the Gibbs free energy (ΔG_{ads}^o), which can be used to describe the stability of the adsorption bond between the compound and the metal, was determined using K_{ads} in the following equation:

$$\Delta G_{ads}^o = -RT \ln 55.5 K_{ads} \quad (14)$$

It is generally accepted that the values of ΔG_{ads}^o revolving around -20 kJ mol^{-1} , indicate that the adsorption is considered as a physisorption, the inhibition occurs via electrostatic interactions between the charged molecules and the charged metal [57], while the values around -40 kJ mol^{-1} or smaller (more negative) are seen as chemisorption, which is due to the charge sharing or electrons transfer from the inhibitor molecules to the metal surface [58]. The values of ΔG_{ads}^o deduced from the potentiodynamic polarization curves and the EIS measurement are $-35.53 \text{ kJ mol}^{-1}$ and $-36.38 \text{ kJ mol}^{-1}$, respectively. A large negative value of ΔG_{ads}^o indicates the greater adsorption capacity of Phen molecules on cast iron surface. In addition, calculated ΔG_{ads}^o values exceed electrostatic interactions range and are close to the chemical interactions region. This confirms the mixed mode of adsorption where physisorption and chemisorption contribute to the whole adsorption process [59].

3.3 Temperature effect and thermodynamic parameters

Temperature has a great influence on the corrosion process and generally, it increases the corrosion rate [60]. For this purpose, EIS measurements were performed in the temperature range of 25-55°C for the cast iron sample immersed in 1 M HCl solution, without and with the optimal Phen concentration (Fig. 5a-b).

Examination of Nyquist plots in Fig. 5a-b reveals that the rising in temperature does not change the profile of diagrams, which means that the corrosion process is charge transfer controlled [61]. The non-

ideal circular shape of these diagrams could be attributed to the frequency dispersion and heterogeneity of the cast iron surface resulting from the interfacial phenomena [61-63]. The size of these

Fig. 5. a) Arrhenius plots and b) transition state plots for cast iron in 1 M HCl (blank) and in the solution containing 1.4 mM of Phen.

imperfect semi-circles decreases with increasing temperature; this is probably attributed to the decrease of cast iron corrosion resistance resulting from the partial desorption of the inhibitive molecules [63]. The equivalent electrical circuit used to fit the EIS data is shown in the inset of Fig. 5a-b. The deduced results are summarized in Table 3.

It can be seen from table 3 that the temperature increase reduced the value of the charge transfer resistance R_{ct} in the presence or absence of inhibitor and simultaneously the double layer capacitance value increased. However, it should be noted that the inhibition efficiency remains almost constant, which provides evidence for the existence of chemisorption because this adsorption type has a great adsorption heat and it is usually irreversible [64]. It follows from the above that Phen is an effective corrosion inhibitor for cast iron immersed in the acidic solution since even at 55°C its inhibition efficiency is about 95%.

It would be interesting to investigate the corrosion kinetics of cast iron in HCl solution in the presence and absence of inhibitor, using the Arrhenius equations as follows:

$$i_{cor} = A \exp\left(\frac{-E_a}{RT}\right) \quad (15)$$

$$i_{cor} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^*}{R}\right) \exp\left(\frac{-\Delta H_a^*}{RT}\right) \quad (16)$$

Where A ($A \text{ cm}^{-2}$) represents a pre-exponential factor, E_a (J mol^{-1}) is the apparent activation energy, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant and T (K) is the absolute temperature, N is the Avogadro's number, h is the plank's constant, ΔH_a^* and ΔS_a^* are the

Table 3. Temperature effect on the EIS parameters for the cast iron immersed in 1 M HCl with and without the optimal concentration of Phen

T/ °C	C / (10^{-3} M)	R_s / ($\Omega \text{ cm}^2$)	R_{ct} / ($\Omega \text{ cm}^2$)	Y_0 / $\mu\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	n	C_{dl} / ($\mu\text{F cm}^{-2}$)	IE%	χ^2
25	/	1.81	4.16	617.8	0.85	260.1	/	0.0007
	1.4	1.58	127.1	92.5	0.83	41.1	96.7	0.0053
35	/	1.92	3.18	645.8	0.86	287.9	/	0.0009
	1.4	1.37	94.6	118.2	0.83	50.1	96.6	0.0041
45	/	1.96	2.29	692.9	0.87	338.8	/	0.0010
	1.4	1.98	64.2	139.9	0.83	54.9	96.4	0.0045
55	/	1.91	1.47	705.5	0.87	364.6	/	0.0007
	1.4	1.36	29.5	146.1	0.84	60.6	95.1	0.0022

Fig. 6. The optimized chemical structure, topology of HOMO and LUMO orbitals and Molecular Electrostatic Potential (MEP) for neutral and protonated Phen.

enthalpy and entropy of activation, and i_{cor} ($A\ cm^{-2}$) represents the corrosion current densities computed from the charge transfer resistance R_{ct} at various temperatures in the presence and absence of Phen using the following equation:

$$i_{cor} = \frac{RT}{zFR_{ct}} \quad (17)$$

Herein; R_{ct} represents the charge transfer resistance, z is the valence of iron ($z=2$), F is the Faraday constant ($F = 96485\ C$), R and T retain the earlier meaning in the previous equation.

The plots $\ln(i_{cor})$ versus $\frac{1}{T}$ (Fig. 6a) corresponding to the blank and inhibitive solutions are linear throughout the temperature range, which indicates that the corrosion and corrosion inhibition processes follow the kinetics Arrhenius. The apparent activation energy values deduced from the slopes of the two straight lines are: $30.50\ kJ\ mol^{-1}$ and $40.78\ kJ\ mol^{-1}$ in the blank and inhibitive solution respectively. It has been reported [65-67] that inhibitors whose inhibition efficiency decreases with increasing

Table 4. Activation parameters for the corrosion of cast iron in 1 M HCl in the presence and absence of Phen

Solutions	$E_a/$ $kJ\ mol^{-1}$	$\Delta H^*/$ $kJ\ mol^{-1}$	$\Delta S^*/$ $J\ mol^{-1}$
Blank	30.50	27.69	-200.81
Phen	40.78	38.02	-195.27

temperature have a higher apparent activation energy value than that of the blank solution, due to physical adsorption of inhibitors on the metal surface. In the present study, the increase of the activation energy value in the presence of Phen indicates that the adsorption of Phen molecules occurs primarily through physical interactions.

The representative plots of $\ln(\frac{i_{cor}}{T})$ versus $\frac{1}{T}$ corresponding to the acidic and inhibitive solutions are linear (Fig. 6b), with a great coefficient of correlation. The slope $-\frac{\Delta H_a^*}{R}$ gives ΔH_a^* and the intercept $\ln$

$(\frac{R}{Nh}) + \frac{\Delta S_a^*}{R}$ gives ΔS_a^* . The calculated values are gathered in Table 4.

The positive values of ΔH_a^* reflected the endothermic nature of the cast iron dissolution process. The value of ΔS_a^* for the uninhibited solution is lower than that for the inhibited solution. This phenomenon means a decrease in randomness has occurred going from reactants to the activated complex. This could be the result of the adsorption of the organic inhibitor on the electrode surface. The great negative value of entropy in the inhibited solution means that the disorder on cast iron surface decreased in the presence of Phen.

3.4 Theoretical study

3.4.1 Molecular orbital theory and quantum molecular descriptors

Theoretical calculations can provide detailed information for understanding the reactive behavior of corrosion inhibiting molecules. Density Functional Theory (DFT) has become a very useful tool for analyzing experimental data to elucidate the corrosion inhibition mechanism [68]. The optimized molecular structure and the frontier orbitals density distributions (HOMO and LUMO) of neutral Phen and Phen-H⁺ molecules in aqueous phase are shown in Fig. 7. It

Fig. 7. SEM micrographs of cast iron samples a) As polished, b) immersed in 1 M HCl during four hours without inhibitor, b') Magnified image of cast iron sample immersed in the uninhibited solution and c) in the presence of 1.4 mM of Phen.

can be seen that the two chemical structures are planar which favors their efficient adsorption leading to high coverage of cast iron surface. The highest occupied molecular orbital (HOMO) is related to the ability of a molecule to donate electrons to empty metal orbitals, while the lowest unoccupied molecular orbital (LUMO) represents the capacity of the molecule to

accept electrons from full metal orbitals (Fig. 7). It can be seen that the electron densities HOMO and LUMO of Phen and Phen- H^+ are distributed in the whole area of the molecules, thus, the most likely adsorption mode is in parallel on cast iron surface [69].

Inspection of determined quantum parameters, listed in Table 5, reveals that after Phen protonation,

Table 5. Quantum chemical parameters of Phen and Phen-H⁺

	$E_{\text{HOMO}}/\text{eV}$	$E_{\text{LUMO}}/\text{eV}$	$\Delta E/\text{eV}$	μ/Debye	χ	η	ω	ε	ΔN
Phen	-6.30	-1.43	4.87	4.65	3.86	2.44	3.05	0.33	0.197
Phen-H ⁺	-6.76	-2.38	4.38	5.33	4.57	2.20	4.74	0.21	0.057

E_{HOMO} becomes more negative, suggesting that protonation reduces the ability to donate electrons to unoccupied metal orbitals [70]. It is well known that the higher the HOMO energy of the inhibitor, the higher its ability to donate electrons and the higher its corrosion inhibition efficiency. In addition, the E_{LUMO} value of Phen-H⁺ shifts to the negative value compared to the E_{LUMO} value of Phen neutral, suggesting that the protonated molecule has more ability to accept electrons from iron [71]. On the other hand, the energy gap (ΔE) of the protonated molecule is slightly lower than that of the neutral molecule; this suggests that it has more ability to react than the neutral molecule. Recently several authors introduced the electrophilicity index (ω), which describes the electrophilic capacity of a molecule [33]. In the current study, Phen-H⁺ has the highest value of ω which implies the protonated form's greater ability to accept electrons from the iron atoms. According to the literature [71,72], a molecule with a low electrophilicity index is a good corrosion inhibitor, for this reason, it can be stated that the neutral inhibitor is more effective against the corrosion of iron in acid solution.

The organic inhibitor adsorption is usually considered as a substitution process between the organic molecules in the aqueous solution $\text{Org}_{(\text{sol})}$ and the water molecules $\text{H}_2\text{O}_{(\text{ads})}$ adsorbed on the electrode surface [73]:

Where: $\text{Org}_{(\text{sol})}$ and $\text{Org}_{(\text{ads})}$ are the organic molecules in the solution and adsorbed on the metal surface, respectively. $\text{H}_2\text{O}_{(\text{ads})}$ is the water molecules adsorbed on the metal surface, and x is the size ratio representing the number of water molecules replaced by an adsorbed organic molecule.

The dipole moment (μ) values of Phen and Phen-H⁺ shown in Table 4 are higher than that of water ($\mu_{\text{H}_2\text{O}} = 1.84$ Debye), which implies that the displacement of the water molecules from the metal surface is favorable [74].

According to Lukovits et al. [75], the ΔN value indicates the donating ability of electrons from molecule to metal if $\Delta N > 0$ and vice versa if $\Delta N < 0$. They also suggest that if $\Delta N < 3.6$, the inhibition efficiency increases with increasing electron donating ability. In the present study, the results in Table 5 show that Phen and its protonated form are electrons donors, which means the strong and stable adsorption of these species on the cast iron surface in hydrochloric solution. Therefore, all of these factors indicate that the inhibitive molecules could involve both electrostatic interaction and chemical bond, resulting in higher inhibition efficiency.

3.4.2 Local reactivity properties

Molecular electrostatic potential (MEP) illustrated in Fig.7 is a visual method that allows us to distinguish the location of the electron density. In these maps, different colors are observed, where the red represents the zone with the negative potential of MEP, associated with reactive electrophilic sites, the blue color is adapted to the zone with the positive potential and represents the suitable center of the nucleophilic attacks [76]. The red colored region in the neutral molecule is concentrated mainly on the hetero-atoms, while the blue region is located around the phenanthrene. However, in the case of Phen-H⁺, the positive charge is obviously concentrated on the protonated nitrogen and concerning the negative charge, it is localized on the non-protonated nitrogen atom and also on the adjacent carbon atoms. This presentation separates electron density and electrostatic potential surfaces with clarity and compactness. The main disadvantage is that it provides information only on the contact surface and does not reveal how far electron-rich and electron-poor areas extend beyond the surface.

In addition to the MEP surfaces, the Fukui indices are more accurate indicators of the molecule parts disposed to electrophilic or nucleophilic attacks, they describe changes in atomic electron density as a result of adding or removing a charge.

The Fukui indices f_k^+ and f_k^- shown in Table 6,

were calculated to predict the most likely atomic sites for nucleophilic and electrophilic attacks respec-

Fig. 8. 3D AFM micrographs of cast iron samples a) as polished, b) immersed in 1 M HCl during three hours in the absence of inhibitor and c) in the presence of 1.4 mM of Phen.

tively. They can also explain the charge transfer as they indicate the reactive sites in the molecule. Atoms that have a high absolute f_k^+ are more susceptible to nucleophilic attacks, while higher absolute f_k^- are more prone to attack by species that have electrons deficiencies.

For nucleophilic attack, the most reactive sites are N10 and N14 for the neutral Phenanthroline and C11 and C13 for the protonated Phenanthroline, which can accept electrons from cast iron surface to form back donating bond. On the other hand, the highest f_k^- coincide on C5 and C6 for both the neutral and protonated Phen, which may denote electrons transfer to the metal to form a coordinate bond. According to these findings, it can be suspected a likely donor-acceptor interaction engaged by inhibitor molecules and iron surface. Overall, the chemical reactivity of Phen and Phen- H^+ can be regarded as π -excessive, thus the adsorption could be achieved simply by the geometric blocking effect. The theoretical study demonstrates the ability of Phen molecules to offer electrons to unoccupied d -orbital of iron, and also to accept electrons from the iron surface, which is consistent with the obtained adsorption isotherm.

3.5 Surface analysis

Scanning electron microscope (SEM) was used in

Table 6. The values of Fukui indices for Phen and Phen- H^+ considering Mulliken population analysis (MPA)

Atom	Mulliken charge		f_k^+		f_k^-	
	Phen	Phen- H^+	Phen	Phen- H^+	Phen	Phen- H^+
C1	0.1193	0.1714	0.0408	0.0623	0.0368	0.0391
C2	0.1145	0.2342	0.0433	0.0371	0.0095	0.0179
C3	0.1145	0.3666	0.0433	0.0608	0.0095	0.0304
C4	0.1193	0.1296	0.0408	0.0025	0.0368	0.0116
C5	-0.1159	-0.1209	0.0007	0.0367	0.1074	0.1321
C6	-0.1159	-0.1195	0.0007	0.0025	0.1074	0.1263
C7	-0.0422	-0.0916	0.0603	0.0109	0.0601	0.0609
C8	-0.1087	-0.0998	0.0568	0.0304	0.0091	0.0015
C9	0.0852	0.1213	0.0333	0.0316	0.0758	0.0743
N10	-0.5432	-0.5685	0.0904	0.0425	0.0634	0.0823
C11	-0.0422	-0.0214	0.0603	0.1465	0.0601	0.0562
C12	-0.1087	-0.1035	0.0568	0.0223	0.0091	0.0014
C13	0.0852	0.2173	0.0333	0.1144	0.0758	0.0534
N14	-0.5432	-0.5968	0.0904	0.0569	0.0634	0.0829

order to demonstrate that the corrosion inhibition is mainly due to the formation of an adsorptive layer on the metal surface. Fig. 8a shows the surface of the freshly polished cast iron alloy, which consists of iron matrix embedded graphite nodules; this surface is very smooth, except some defects which had arisen during polishing.

After immersion in the uninhibited solution (Fig. 8b), the cast iron surface is strongly damaged due to the uniform dissolution of the matrix. In addition, graphite nodules peeled off from the surface caused by galvanic corrosion leading to wide and deep holes, as shown in the magnified image (Fig. 8b'). However, in the presence of Phen at its optimal concentration (Fig. 8c) the cast iron surface is smooth, intact and well improved. These observations confirm that Phenanthroline forms a protective layer by adsorption, which blocks the matrix dissolution, leading to the lowering of cast iron corrosion rate.

The 3D AFM image of the freshly polished sample (Fig. 9a) shows a regular and smooth surface, his average roughness (R_a) is 17 nm. After immersing the sample in the blank solution (Fig. 9b), the average roughness increases to 275 nm, as a result of severe damage of the surface. However, in the presence of Phen (Fig. 9c) the average roughness decreases to 97 nm, due to the formation of a protective film by adsorption of Phen molecules on the metal surface.

The FTIR spectra for pure Phen and scrapped adsorbed layer on the cast iron (Fig. 9) have been recorded to determine if Phen effectively adsorbs on the metal surface. The FTIR spectrum of pure phen shows a broad water band at 3365 cm^{-1} attributed to O-H stretching. The absorption band at 3050 cm^{-1} is related to the aromatic C-H stretching mode, and the strong absorption bands around 1585 cm^{-1} , 1558 cm^{-1} are assigned to C=N stretching vibrations. The peaks at 1502 and 1418 cm^{-1} are associated with the carbocyclic ring vibrations (C=C), the presence of band at 1134 cm^{-1} corresponds probably to the in-plane hydrogen deformation modes or ring vibrations, and other peaks at 850 and 736 cm^{-1} correspond to the hydrogen (C-H) out of plane bending on the benzene and the heterocyclic rings. A full vibrational assignment of phenanthroline molecule has been previously published [77]. The most bands observed in the FTIR spectra of the adsorbed layer on cast iron surface closely resemble those appearing in the pure Phen

Fig. 9. (a, a') FTIR spectra of pure Phen and adsorbed layer formed on cast iron surface after 6 hours' immersion in 1 M HCl solution with 1.4 mM of Phen.

spectra. A broad band around 3300 cm^{-1} attributed to O-H stretching, which further indicates the formation of FeOOH on the adsorbed layer. the aromatic C-H stretching band has vanished from 3050 to 3029 cm^{-1} . The shifted to higher wavenumbers of the C=N and C=C bands confirm the involvements of these centers in the adsorption. in addition, the absorption bands at 850 and 738 cm^{-1} assigned to the out of plane C-H vibrations are shifted to 835 and 715 cm^{-1} , respectively. Reference has been made to the fact that these bands (out of plane vibrations) move to lower wavenumbers on coordination [78]. All the informations indicate clearly towards adsorption of Phen molecules on the cast iron surface, similar conclusions have been made by many other researchers [79-80].

3.6 Inhibition mechanism

The adsorption process of organic molecules on a metal surface depends on their chemical structure, the distribution charge in the molecule, the aggressive medium and the topography of the metal surface. Therefore, on the basis of the experimental results, FTIR in particular which indicates the presence of most functional groups of Phen on the adsorbed layer, a corrosion inhibition mechanism could be proposed:

In HCl solution, Phenanthroline may exist in the protonated form in equilibrium with its molecular form, thus, two modes of adsorption could be envisaged. According to the literature, generally ferrous alloys carry an excess positive charge in acid solution, thus, the acidic anions (Cl^-) specifically adsorbed on the metal surface create an excess negative charge which favors the adsorption of Phen-H^+ , by involving electrostatic forces.

In addition to the physical adsorption, the neutral Phen may be adsorbed on the metal surface through chemical adsorption by sharing electrons on the basis of donor-acceptor between the π -electrons of the phenanthroline ring and the vacant d-orbital of iron surface atoms. The molecular structure of Phen-H^+ remains almost unchanged with respect to its neutral form, it can be stated that when Phen-H^+ is adsorbed on the metal surface, the coordination bond can also be formed by partial transference of electrons from the polar Nitrogen atom to the metal surface.

4. Conclusions

The corrosion inhibition effect of Phenanthroline on the corrosion of ductile iron in 1 M HCl was investigated using electrochemical and theoretical calculations. On the basis of the results of these studies, the following conclusions can be drawn:

- Analysis of the polarization curves showed that Phenanthroline acts as a mixed-type inhibitor; its inhibition efficiency increases with the concentration up to a limit value obtained at the optimum concentration.
- The adsorption of Phen molecules on the metal surface obeys the Langmuir adsorption isotherm model.
- The high negative adsorption free energy value and the inhibition efficiency maintained at high temperatures indicate that Phen adsorption on the cast

iron surface could be of mixed type where both physisorption and chemisorption contribute to the whole process.

- SEM and AFM micrographs have shown that the cast iron surface damage is greatly reduced in the presence of Phenanthroline which forms a protective layer. The Phen adsorption on the cast iron surface was confirmed by FTIR analysis.

- The Fukui indices analysis of inhibitor molecules has successfully described the nucleophilic and electrophilic sites responsible for the donation and acceptance of electrons.

- In summary, it is concluded that the results obtained from the analysis of chemical quantum data corroborate those achieved by electrochemical measurements.

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