Inhibitory power of *N*,*N*'-(1,4-phenylene)bis(1-(4nitrophenyl)methanimine) and the effect of the addition of potassium iodide on the corrosion inhibition of XC70 steel in HCl medium: Theoretical and experimental studies

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Abstract

The inhibitory efficacy of N,N'-(1,4-phenylene)bis(1-(4-nitrophenyl)methanimine) (PNM) and its synergistic effect with KI on corrosion of XC70 steel in 1.0 M HCl solution have been studied by electrochemical impedance spectroscopy and potentiodynamic polarization measurements. The results show that the percentage of inhibition of XC70 steel in 1.0 M HCl solution increases with the increase of the concentration of PNM and reaches 84% at $1.0 \cdot 10^{-4}$ M PNM as an optimal concentration of this inhibitor. It was found that the percentage of inhibition of XC70 steel increases with the addition of KI to the optimal concentration of PNM in 1.0 M HCl solution, reaching 94% with a concentration of 7.5 mM of KI. This inhibitor N,N'-(1,4phenylene)bis(1-(4-nitrophenyl)methanimine) (PNM) may form a film which acts as a barrier decreasing the contact area between the XC70 surface and the HCl solution. PNM acts as cathodic inhibitor in HCl solution without modifying the mechanism of hydrogen evolution. From the EIS examination, we notice that with an increase in the concentration of PNM, the double layer capacitance decreased, but the charge transfer resistance increased. Thermodynamic parameters of activation and adsorption were calculated and explained. The sign of the free energy of adsorption implies that the adsorption process is spontaneous. The surface morphology of XC70 was examined by employing the SEM technique. Finally, the quantum chemical parameters were calculated by the Density Functional Theory (DFT) method and a Monte Carlo simulation was used to find the equilibrium configurations of the inhibitor/Fe(110) adsorption systems in the presence of water molecules. The results obtained by all the methods are in good harmony.

Received: March 6, 2022. Published: March 29, 2022

doi: <u>10.17675/2305-6894-2022-11-1-26</u>

Keywords: carbon steel, N,N'-(1,4-phenylene)bis(1-(4-nitrophenyl)methanimine), potassium iodide, XC70 steel, HCl, DFT and Monte Carlo simulation.

1. Introduction

Pipelines are a relatively safe way to transport oil and natural gas compared to other modes of transportation, but harmful corrosion problems can occur [1]. Corrosion in oil fields occurs at all stages, from down hole wells to surface equipment and processing facilities [2]. In addition, corrosive solutions (HCl and H_2SO_4) especially the former, are widely used for industrial acid cleaning, acidification of oil wells [3]. It is also noted that XC70 steel is widely used for pipelines and is prone to corrosion due to its chemical instability in acidic media [4–7]. As a result, the search for adequate effective, economical and above all ecological means of preventing and protecting pipelines against acid corrosion remains the objective of many researchers [8, 9]. The use of corrosion inhibitors, in particular non-toxic substances, added in the aqueous solution, constitutes the best means of protection against corrosion in many industrial systems, in particular in the petroleum industry [10]. Organic inhibitors, especially amino-based, are widely used in petroleum refining processes [11]. In addition, heterocyclic compounds containing heteroatoms such as oxygen, nitrogen and sulfur are widely used [12, 13].

Several literatures indicate that Schiff base compounds have aroused great interest to researchers because of their good corrosion inhibition in acidic media [14, 15]. In addition, certain theoretical and experimental studies have contributed to the definition and determination of their different properties [16, 17]. Shetty [18] recommended the use of compounds containing nitrogen as good corrosion inhibitors in hydrochloric acid media. With reference to some studies by Jamil *et al.*, they tested two Schiff base compounds with a quinoxalene moiety as acid corrosion inhibitors for mild steel. They found that the compounds were effective in inhibiting steel corrosion, and this inhibition is related to certain physical and chemical parameters present in the molecules of these compounds [19]. Another report on certain Schiff bases also documented inhibition efficiency greater than 90% at 300 ppm [20].

Currently, considerable efforts have been devoted to corrosion inhibitors have included ease of synthesis from readily available precursors and high efficiency at very low concentrations [21–23]. Several studies have demonstrated that organic compounds with the addition of halide salts, especially potassium iodide (KI) have a synergistic effect and

enhance the corrosion inhibition of the organic compounds [24, 25]. Despite the studies that have been done on corrosion inhibitors, which are ubiquitous in various industrial applications, in particular the petroleum sector, more new studies still need to be carried out. In this work, the adsorption and the corrosion inhibition effect of PNM in the absence and the presence of iodide ions for the dissolution of XC70 steel in 1.0 M HCl solution was studied using electrochemical potentiodynamic polarization and electrochemical spectroscopy impedance (EIS) techniques. Several factors are studied such as, inhibitor concentration, iodide ions concentration and temperature, in order to find the best conditions for the corrosion inhibitor was determined. The effect of iodide ions on the adsorption of PNM molecules on the surface of XC70 steel and the corrosion inhibition efficiency of PNM on XC70 steel and the molecular structure of PNM has been illustrated via molecular dynamics simulation (MD) and quantum chemical calculations.

2. Experimental

2.1. Metal specimen

The working electrode was a carbon steel XC70 grade (with a surface area of 0.36 cm²). The chemical composition of this steel (wt.%): 0.1038 C, 0.1261 Si, 0.0320 Al, 0.0021 S, 0.971 Mn, 0.0100 Cu, 0.1261 Si, 0.0021 P, 0.0100 Cr, 0.005 Mo, 0.0050 Ni, 0.0500 Co, 0.0100 Cu, 0.0419 Nb, 0.0025 V, 0.0500 W, 0.0050 Sn and 98.7 Fe. Before each test, the working electrode underwent mechanical stripping and polishing with an abrasive paper of different particle sizes (180, 320, 600, 800, 1000, 1200 and 2500). Then, it was rinsed with distilled water, acetone and dried at room temperature. Its surface became smooth and shiny.

2.2. Solution

The 1.0 M HCl solution was prepared by diluting of a reagent grade HCl (37%). The inhibitor N,N'-(1,4-phenylene)bis(1-(4-nitrophenyl)methanimine) (PNM) (Scheme 1) was synthesized according to the published procedure [26, 27]. The range of concentrations used for the PNM inhibitor is $(5 \cdot 10^{-6} - 1.0 \cdot 10^{-4})$ M. For study the influence of potassium iodide (KI) on the inhibitory efficacy of PNM, different concentrations of KI were added to a solution containing $1.0 \cdot 10^{-4}$ M of PNM inhibitor in a solution of 1.0 M HCl. All experiments were performed in aerated solution.



Scheme 1. Molecular structure of N, N'-(1,4-phenylene)bis(1-(4-nitrophenyl)methanimine).

2.3. Electrochemical investigations

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves were recorded using a PGZ 301 Potentiostat Galvanostat, VOLTALAB 40 RADIOME brand, driven by "VoltaSer4" software and connected to a computer. The experiments were performed in a thermostatic cell. A platinum plate was used as counter-electrode (EC) and a silver silver-chloride electrode (Ag/AgCl/KCl) was used as a reference electrode (RE). The work electrode (WE) was a soft XC70 quality steel. All tests were carried out at room temperature. Before recording the polarization curves, the freshly polished electrode was immersed in the working solution at the open circuit potential for 60 minutes until a stable state is reached. The impedance spectroscopy measurements were carried out in the frequency range (10^5-10 Hz) at the open circuit potential with superposition of a sinusoidal alternative signal of low amplitude, 10 mV peak crest. The intensity-potential curves are plotted in potentiodynamic mode. After recording the cathodic branch, the open circuit potential was then restored before determining the anodic branch. The potential applied to the sample varied from -600 to -300 mV vs (Ag/AgCl/KCl) with a scanning speed equal to 2 mV·s⁻¹, which allows tests in quasi-stationary conditions.

2.4. Surface analysis

The surface morphology of the steel specimens immersed in 1.0 M HCl solution without and with the inhibitor PNM as well as with KI was studied using scanning electron microscopy (SEM), (Neoscope JCM-5000). The immersion time of the electrodes for SEM analysis was 24 hr's.

2.5. Density functional theory (DFT) calculations

To study the effect of the molecular structure of the PNM inhibitor on the mechanism and its corrosion inhibition efficiency on XC70 steel, quantum calculations were carried out, using the Gaussian version 9.0 [28]. All calculations were performed with complete geometric optimization using the B3LYP hybrid functional level with a higher base set rated 6-31G (d, P) [29–31]. Some quantum chemistry parameters were calculated through the values of the energies of the HOMO and the LUMO using the following formulas [32]:

Ionization energy (*I*):

$$I = -E_{\text{HOMO}} \tag{1}$$

Electronic affinity (A):

$$A = -E_{\rm LUMO} \tag{2}$$

Energy Gap (ΔE_{GAP}):

$$\Delta E_{\rm GAP} = E_{\rm LUMO} - E_{\rm HOMO} \tag{3}$$

Global Hardness (η) :

$$\eta = \frac{E_{\rm LUMO} - E_{\rm HOMO}}{2} \tag{4}$$

Absolute Electronegativity (χ):

$$\chi = \frac{(I+A)}{2} \tag{5}$$

Chemical Softness (σ):

$$\sigma = \frac{1}{\eta} \tag{6}$$

Electrophilicity Index (ω):

$$\omega = \frac{\chi^2}{2\eta} \tag{7}$$

The number of transferred electrons (ΔN) was calculated using the following equation:

$$\Delta N = \frac{\chi_{\rm Fe} - \chi_{\rm Inh}}{2(\eta_{\rm Fe} - \eta_{\rm Inh})}$$
(8)

where χ_{Fe} and χ_{Inh} are the absolute electronegativity's of iron and inhibitor, respectively; η_{Fe} and η_{Inh} are the absolute hardness's of iron and the inhibitor, respectively. The theoretical χ value of 7.0 eV·mol⁻¹ and η value of zero eV·mol⁻¹ for iron were used from the literature [32].

2.6. Molecular dynamic simulations (MDS)

The SDMs were performed using Biovia Materials Studio 8.0 software, marketed by Accelrys Inc. USA [33, 34]. A dimensional simulation box $17.38 \times 17.38 \times 27.16$, is used for simulations of the molecular dynamics of the interaction between the studied inhibitor molecule and the surface Fe (110). Periodic conditions were used in the three directions and the movement equations were incorporated into the canonical NVT assembly. The Fe plate and the iodine plate containing the studied inhibitor and a vacuum layer were included in the simulation box. We used a temperature of 298 K controlled by the nose method using the compass force field.

3. Results and Discussion

3.1. Results of the potentiodynamic studies

The polarization curves obtained for XC70 steel in 1.0 M HCl solution in the absence and in the presence of various concentrations of PNM are shown in Figure 1.

The corrosion potential (E_{corr}), the values of the corrosion current densities (i_{corr}), the surface coverage (θ) and the values of inhibition efficiency *EI* (%) that determined for different concentrations of PNM in 1.0 M HCl solution are summarized in Table 1.

The inhibitory efficacy (*EI* (%)) and the surface coverage (θ) are defined as follows:

$$EI(\%) = \frac{i_{\rm corr} - i_{\rm corr(Inh)}}{i_{\rm corr}} \cdot 100$$
(9)

$$\theta = \frac{i_{\rm corr} - i_{\rm corr(Inh)}}{i_{\rm corr}} \tag{10}$$

where $i_{\text{corr}(\text{Inh})}$ are the values of the current densities of the XC70 steel in 1.0 M HCl without and with the inhibitor which determined by extrapolation of the Tafel lines, respectively. This equation is valid under the hypothesis of a blocking mechanism of the active cities by the inhibitor.



Figure 1. Tafel curves of corrosion of XC70 steel in 1.0 M HCl without and with different concentrations of PNM at 293 K.

Figure 1 shows the cathodic and anodic polarization curves of XC70 steel in 1.0 M HCl with and without various concentrations of PNM at 293 K. We can see that as the concentration of PNM increases, the corrosion current density of the anode branch and cathode branch decreases significantly. Moreover, the polarization curves of the cathodic branch show an almost parallel trend, show that the addition of PNM does not modify the mechanism of hydrogen evolution and the reduction of hydrogen ions on the surface of mild steel is done mainly by a charge transfer mechanism [36]. This can be attributed to the fact that the inhibitor molecule coats the surface of the steel, thereby reducing the area of active

sites for the reaction, while the mechanism of evolution of the hydrogen by charge transfer remains unchanged [37].

С (М)	-Ecorr (mV vs. Ag/AgCl)	i _{corr} (mA/cm ²)	EI (%)	θ
Blank	425	0.94	_	_
5.10^{-6}	460	0.33	65	0.65
5.10^{-5}	466	0.18	81	0.81
10^{-4}	467	0.16	83	0.83

Table 1. Electrochemical parameters of corrosion of XC70 steel in 1.0 M HCl solution in the absence and in the presence of various concentrations of PNM.

Table 1 shows that when the concentration of PNM increases, the E_{corr} shifts slightly towards the cathodic direction. The amplitude of motion is less than 85 mV, and the i_{corr} values of the anodic and cathodic branches are significantly reduced, so PNM is a mixed-type inhibitor [38].

The experimental results confirm that PNM is an effective mixed inhibitor (EI=65%) at low concentration ($5.0 \cdot 10^{-6}$ M) and reaches 84% at a concentration of $1.0 \cdot 10^{-4}$ M. These good inhibition efficiencies may be attributed to the adsorption of PNM molecules on the surface of XC70 steel [39]. Based on the results reported in the literature, the high molecular flatness of the heterocyclic compound PNM, the presence of electron donor groups and aromatic rings are responsible for the good performance of this inhibitor [40]. In addition, the nitrogen atom of imine and nitro groups, the oxygen atom of nitro groups with their sp² and free p electron pair, respectively and the p orbitals (π bonds) of aryl rings are suitable anchoring sites. This is how the blocking of active sites on the steel surface decreases the corrosion rate [41].

3.2. Results of the electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy studies of XC70 steel in 1.0 M HCl solution in the absence and in the presence of various concentrations of PNM is illustrated in Figure 2.

It is observed that all the Nyquist plots obtained are semi-circular and that their diameters are affected by the change in the inhibitor concentration. The impedance of the XC70 steel electrode in the HCl medium and in the presence of PNM increases with the concentration. This fact is due to the increase in the surface coverage (θ) of the steel surface by inhibitor molecules and therefore implies an increase in the rate of inhibition [42].

It should be noted that the change in concentration of PNM inhibitor did not alter the shape of the impedance curves, suggesting that same inhibition mechanism is involved. The semicircles obtained are represented in the Nyquist (real) Z plot, which is often due to a frequency dispersion resulting from the inhomogeneity and/or the roughness of the metal

surface [16]. The mild steel/solution interface in the absence and in the presence of the inhibitor is represented by the equivalent electrical circuit (Figure 3).



Figure 2. Nyquist diagrams of corrosion of XC70 steel in 1.0 M HCl solution without and with different concentrations of PNM at 293 K.

It is clear that the corrosion inhibition efficiency increases significantly upon the addition of PNM inhibitor.



Figure 3. Electrochemical equivalent circuit used for simulation of the impedance spectra.

The circuit consists of the electrolytic resistance (R_s), the charge transfer resistance (R_{ct}) and the constant phase element (*CPE*) [43]. The *CPE* parameter replaces the double layer capacitance (C_{dl}) in order to give a more precise fit to the experimental results [43]. It is recommended to use the *CPE* instead of the pure capacitor to model the frequency dispersion generally related to the heterogeneity of the surface caused by corrosion in an acidic media.

Bode's diagrams (Figure 4) indicate the existence of an equivalent circuit containing a single element of constant phase in the metal/solution interface. The increase in absolute impedance at low frequencies in the Bode's diagrams confirms that protection is better at higher concentrations of the inhibitor. The observation of a single phase peak in the central frequency range shows the existence of a single constant, linked to the electrical double layer [44].



Figure 4. Bode's (a) phase angle and (b) curves of corrosion of XC70 steel in 1.0 M HCl solution without and with different concentrations of PNM at 293 K.

The electrochemical characteristics obtained by (EIS) from the Nyquist diagrams are given in Table 2. The values of the load transfer resistance (R_{ct}) are calculated from the difference in impedance at lower and higher frequencies [44]. The values of the double layer capacitance (C_{dl}) are obtained from the following equation:

$$f\left(-Z_{\max}\right) = \frac{1}{2\pi C_{\rm dl}R_{\rm ct}} \tag{11}$$

The inhibition efficiency is calculated from equation:

$$EI(\%) = \frac{R_{\rm ct(Inh)} - R_{\rm ct}}{R_{\rm ct(Inh)}} \cdot 100$$
(12)

where R_{ct} and $R_{ct(Inh)}$ are the values of the load transfer resistance of XC70 steel in 1.0 M HCl solution without and with PNM, respectively.

Table 2. Electrochemical impedance parameters for XC70 steel in 1.0 M HCl solution in the absence and in the presence of different concentrations of PNM.

С (М)	Rs (Ohm/cm ²)	<i>CPE-T</i> ·10 ⁴	CPE-P	R _{ct} (Ohm/cm ²)	C _{dl} (µF/cm²)	EI (%)
Blank	2.6	17.4	0.74	22	590	—
5.10^{-6}	0.65	4.3	0.79	57	155	61
10^{-5}	1	3.6	0.80	74	153	70
5.10^{-5}	1	3.5	0.78	99	128	78
10^{-4}	1	2.9	0.76	136	105	84

The values of C_{dl} in Table 2, indicate that increasing the PNM concentration results in a decrease in C_{dl} values and an increase in the rate of effectiveness of the inhibitor [44]. Aljourani *et al.* [45] interpreted the decrease in C_{dl} through a decrease in the local dielectric constant and/or an increase in the thickness of the electric double layer, resulting from the adsorption of PNM molecules on the metal surface by replacing water molecules with inhibitor molecules at the electrode surface as follows:

$$Org_{sol} + xH_2O_{ads} \leftrightarrow Org_{ads} + xH_2O_{sol}$$

where Org_{sol} and Org_{ads} represent organic molecules in solution and another one that adsorbed on the metal surface, respectively. H₂O_{ads} is the water molecule adsorbed on the metal surface and *x* is the ratio, *i.e.* the number of molecules of water replaced by one molecule of an organic inhibitor. In addition, the inhibitor molecules can reduce the capacity by increasing the thickness of the double layer according to the Helmholtz model [46]. These results clearly indicate that the corrosion of XC70 steel in 1.0 M HCl solution is controlled by a charge transfer process [44, 47].

Nevertheless, the results that obtained in 1.0 M HCl solution from the electrochemical Tafel plots are in consistent with these results (EIS). The determined inhibition efficiency values are close and evolve in the same way. To confirm this observation, the inhibition efficiency (*EI*%) was plotted against the concentration of PNM as shown in Figure 5. This figure shows that the values of inhibition efficiency are almost the same in both techniques.



Figure 5. Variation of inhibition efficiencies (*EI*%) with different concentrations of PNM for electrochemical Tafel plots and EIS techniques.

3.3. Adsorption isotherm

The interaction between inhibitors and the steel surface can be described by the adsorption isotherm. Two main types of interactions govern adsorption.

Physisorption involves electrostatic forces between the ionic charges or dipoles on the adsorbed species and the electric charge at the metal/solution interface. In this case, the heat of adsorption is low, and therefore, this type of adsorption is stable at low temperature [58].

Chemisorption involves charge sharing or charge transfer from inhibitor molecules to positive sites on the metal surface inducing coordination binding. Chemical adsorption has much stronger adsorption energy than physical adsorption. Therefore, these bonds are more stable at higher temperatures [49].

In addition, solvent molecules (H₂O) can also be adsorbed at the metal/solution interface. Thus, the adsorption of organic inhibitor molecules in aqueous solution can be considered as a process of quasi-substitution between organic compounds in aqueous phase (Org_{sol}) and water molecules on the surface of the electrode (H₂O_{ads}) [45, 50]. The adsorption isotherm provides basic information on the interaction between the inhibitor and the XC70 steel surface. A linear relationship between the degree of surface coverage (θ) and the inhibitor concentration (*C*) must be verified. To identify the type of adsorption corresponding to this inhibitor, different types of isotherms were tested: Langmuir, Temkin and Frumkin. The Langmuir adsorption isotherm was found to be the most appropriate for the adjustment of the experimental results (R^2 closest to unity) using the following equation:



Figure 6. Langmuir presentation of PNM inhibitor for XC70 steel in 1.0 M HCl solution at 293 K.

The thermodynamic parameters derived from this adsorption isotherm for the studied PNM inhibitor provide information on the type of adsorption that occurred in the inhibition process.

The equilibrium constant of the adsorption value ($K_{ads}=5.5 \cdot 10^5 \text{ M}^{-1}$) was determined from the intercepts of the straight line (C_{inh}/θ) axis.

The value of Gibbs free energy (ΔG_{ads}^0) for the inhibitor is calculated from the equation:

$$\Delta G_{\rm ads}^0 = -RT \ln(55.55K_{\rm ads})$$

where *R* is the universal gas constant, *T* the thermodynamic temperature and the value 55.55 is the concentration of water in solution expressed in mol/l.

Indeed, the high value of K_{ads} (5.5 · 10⁵ M⁻¹) reflects the strong adsorption of PNM [51]. The Gibbs free energy of adsorption is equal to -42.7 kJ/mol and the negative value of ΔG_{ads}^0 indicates that the PNM inhibitor is spontaneously adsorbed on the XC70 steel surface in the form of a neutral molecule by chemisorption [52].

3.4. Quantum calculation methods

To understand the relationship between the molecular structure of the inhibitor and its corrosion inhibition behavior, a density functional theory was carried out and all quantum chemistry calculations were performed by acquiring a full geometric optimization. The quantum chemical parameters calculated in the aqueous phase are presented respectively in the Table 3.

Quantum chemical parameters	Aqueous phase	
E _{tot} (eV)	-3511	
$E_{ m HOMO}~(m eV)$	-6.022	
$E_{ m LUMO}~(m eV)$	-3.00	
$\Delta E_{ m GAP} (m eV)$	-3.022	
μ (Debye)	2.00	
η (eV)	1.5	
$\sigma (eV^{-1})$	0.67	
χ (eV)	4.50	
ω (eV)	7.00	
ΔN	0.83	

Table 3. The calculated quantum chemical parameters for the studied PNM inhibitor in the aqueous phase obtained using the DFT method at the B3LYP/6-31G(d,p) basis set.

The frontier orbitals (highest occupied molecular orbital - HOMO) and (lowest unoccupied molecular orbital - LUMO) of a chemical species are very important parameters to define the reactivity of a corrosion inhibitor.

As can be seen in Figure 7, the location of the HOMO density is distributed over the entire PNM molecule except for the nitrogen atoms of the nitro groups, on the other hand LUMO is distributed over the entire molecule. This confirms the tendency of PNM to transfer and accept electrons [53]. This further, supports the experimental results.



Figure 7. Optimized structure and the HOMO and LUMO of PNM in aqueous phase using DFT/B3LYP/6-31G(d,p) given by the B3LYP/6-31(d.p).

 $E_{\rm HOMO}$ is a quantum chemical parameter that is generally related to the electron contributing capacity of the molecule. The high value of $E_{\rm HOMO}$ provides the ability of the molecule to share electrons with the appropriate acceptor molecule which has the low empty molecular orbital [54]. Therefore, $E_{\rm LUMO}$ implies the ability of the inhibitor molecule to accept electrons from an electron-rich species, which implies that the inhibition efficiency of the tested inhibitor should increase with decreasing values of $E_{\rm LUMO}$ [55]. $E_{\rm HOMO}$ and $E_{\rm LUMO}$ values were found to be negative, indicating that the ligand was stable [56].

The energy difference (ΔE) between E_{HOMO} and E_{LUMO} is an important factor to determine the chemical reactivity and the chemical stability of a molecule [56]. The ΔE explains the charge transfer interaction within the molecule. If the value of the energy difference is large, this implies a low reactivity of a chemical species. If the value is low, the inhibition efficiency is good, because the energy to remove an electron from the last occupied orbital to give it to the unoccupied d orbitals of the metal will be low [57].

Overall electronegativity (χ) is also considered a crucial reactivity descriptor that helps to assess the ability of a molecule to attract electrons to it in a covalent bond [58]. The higher the electronegativity value of the molecule, the more the atoms in the molecule will attract the electrons of the bond. This will lead to a decrease in the inhibition efficiency of the molecule [59]. A small value of electronegativity means a high efficiency of the inhibitor.

One of the ways to measure molecular stability and reactivity is absolute hardness, η , and softness σ , where a hard molecule has a fairly large energy gap and a soft molecule has a small energy gap. Soft molecules are more reactive than hard molecules because, they easily donate electrons to the receptor. In a simple transfer of electrons from the adsorption

molecule, the transfer takes place from the part where the σ value of the molecule is the highest [60]. Therefore, soft base inhibitors are most effective for corrosion inhibition of metals [61].

According to the principle of minimum electrophilicity, the lower the electrophilicity of a compound, the higher its stability [56].

According to Lukovits, if $\Delta N < 3.6$, the inhibition efficiency of the organic inhibitor increases with the increase of the electron donating capacity at the metal surface [62].

Another important electronic parameter is the dipole moment, its product of the uniformly distributed charge on the atoms and the distance between the two bonded atoms. High dipole moment values are reported to facilitate adsorption and hence inhibition by influencing the transport process through the adsorbed layer. The efficiency of inhibition increases with dipole moment values [63].



Figure 8. (a) Mulliken charges (b) MEP and (c) Contour maps of (ESP) of PNM obtained in the aqueous phase using DFT at the B3LYP/6-31G (d.p) basis set.

Other descriptors related to electrostatic potential, namely molecular electrostatic potential (MEP) and MEP contour, have also been studied for a better understanding of electrophilic attack sites and nucleophilic reactions. Moreover, Mulliken atomic charges are one of the important parameters used for the study of electronic charges on the atoms of the molecule. Figure 8(a,b,c) show the optimized molecular structure with Mulliken charges,

molecular electrostatic potential (MEP), and molecular electrostatic potential contour of PNM. Accordingly, atoms bearing negative Mulliken charges like N, O and some of the C atoms are considered as electron donor sites. These atoms interact with the iron on the surface of XC70 steel to form coordinate bonds. It has been noticed that these atoms facilitate the adsorption on the surface of the metal [64]. The MEP map was evaluated using different colors, in which the red and yellow colors represented the negative regions [65, 66]. In Figure 8(b), the most electrostatic potential, indicated by the red and yellow colors, can be seen concentrated around the NO₂ group and C=N cluster suggesting a huge electron deficit and hence, a possible center of electrophilic active regions. Figure 8(c) shows that the MEP contour of the PNM molecule is distributed on the nitrogen atoms of the imine functional groups suggesting that these atoms are adsorbed in a planar manner on the metal surface [23].

3.5. Study of the effect of potassium iodide

The addition of the halide ions to the corrosive solution is a practical and common method to improve the inhibition efficiency an organic compound, particularly in an acidic media [67–70]. In this section, the inhibition efficiency of (PNM) in 1.0 M HCl solution was studied in the presence of I⁻ ions. The same experimental techniques were used in this part as in the previous parts of this study.

3.5.1. Results of the potentiodynamic studies

The potentiodynamic polarization curves of XC70 in 0.1 M HCl+10⁻⁴ M PNM containing different concentrations of KI at 298 K are presented in Figure 9.



Figure 9. Tafel curves of corrosion of XC70 steel in 1.0 M $HCl+10^{-4}$ M PNM solution without and with different concentrations of KI at 293 K.

The electrochemical parameters and the corrosion inhibition efficiency of XC70 steel in 1.0 M HCl solution containing $1.0 \cdot 10^{-4}$ M PNM without and with addition of different concentrations of KI are given in Table 4. note that the KI/inhibitor system gave the highest

inhibition efficiency value than the inhibitor system alone. This increase is all the more marked as the concentration of KI becomes higher. The maximum value of *EI*% reaches 92% at a concentration of 7.5 mM KI. This difference in efficiency is generally attributed to the strong adsorption of I⁻ ions at high concentration of KI [71].

С (М)	-Ecorr (mV vs. Ag/AgCl)	i _{corr} (mA/cm ²)	EI (%)	θ
Blank	425	0.94	_	_
PNM (10 ⁻⁴ M)	467	0.16	83	0.83
+2.5 mM KI	408	0.13	86	0.86
+5 mM KI	439	0.09	90	0.90
+7.5 mM KI	446	0.08	92	0.92

Table 4. Electrochemical parameters of corrosion of XC70 steel in $1.0 \text{ M HCl}+10^{-4} \text{ M PNM}$ solution without and with different concentrations of KI at 293 K.

3.5.2. Results of the electrochemical impedance spectroscopy (EIS).

The impedance diagrams (Figure 10) of XC70 steel in 1.0 M HCl solution containing $1.0 \cdot 10^{-4}$ M PNM in the absence and in the presence of different concentrations of KI are plotted under the same conditions as above. The results of this study are listed in Table 5. The impedance diagrams consist of a single loop corresponding to the load transfer resistance (R_{ct}). It was found that the values of (R_{ct}) increase with the addition of KI in the corrosive media containing $1.0 \cdot 10^{-4}$ M of the inhibitor (Table 5). The percentage of inhibition efficiency (EI%) also increases with increasing the KI concentration and reaches 94% for a concentration 7.5 mM KI.



Figure 10. Nyquist diagrams of corrosion of XC70 steel in 1.0 M HCl+ 10^{-4} M PNM solution without and with different concentrations of KI at 293 K.

С (М)	Rs (ohm/cm ²)	R _{ct} (Ohm/cm ²)	C _{dl} (µF/cm²)	EI (%)
Blank	2.6	22	590	_
PNM (10 ⁻⁴ M)	1	136	105	84
+2.5 mM KI	0.56	181	79	88
+5 mM KI	1	240	105	91
+7.5 mM KI	4.20	375	43	94

Table 5. Electrochemical impedance parameters for XC70 steel in $1.0 \text{ M HCl}+10^{-4} \text{ M PNM}$ solution without and with different concentrations of KI at 293 K.

The variation in the corrosion inhibition efficiency of PNM in the absence and in the presence of different concentrations of KI at 293 K are illustrated in Figure 11. Figure 11 reveals that the addition of KI improved the efficiency of inhibition, as shown (the percentage of inhibition efficiency (EI%) also increases with increasing the KI concentration and reaches 94% for a concentration 7.5 mM KI).



Figure 11. Variation of inhibition efficiencies (*EI*%) in 1.0 M HCl solution containing $1.0 \cdot 10^{-4}$ M PNM with different concentrations of KI.

This can be attributed to electrostatic interactions between base Schiff moles. Therefore, iodide ions improve the adsorption of inhibitor molecules on the steel surface and increase the compounds inhibition efficiency.

3.6. Scanning electron microscopy

The surface morphology of the carbon steel samples before and after immersion in uninhibited and inhibited 1.0 M HCl solution was assessed using SEM and the photomicrographs are shown in the Figure 12.



Figure 12. The surface morphology of the carbon steel samples before and after immersion in uninhibited and inhibited 1.0 M HCl (a) polished sample, (b) 0.1 M HCl, (c) 0.1 M HCl+ 10^{-4} M PNM and (d) 0.1 M HCl+ 10^{-4} M PNM+7.5 mM KI.

The surface morphology of the carbon steel electrode was studied by scanning electron microscopy, SEM. Figure 12 shows SEM images obtained on the steel surface before and after soaking in 1.0 M HCl with and without the addition of inhibitor for 24 h at 298 K. From Figure 12(a), it can be seen that the fresh carbon steel surface was homogeneous morphological structure. Nevertheless, after dipping, an extreme change in the surface condition is observed. In the absence of inhibitor Figure 12(b), the surface condition was severely damaged resulting from the attack of the corrosive solution. In the presence of 10^{-4} M PNM+7.5 mM KI in the hydrochloric acid electrolyte, the SEM image of the carbon steel surface is significantly unaffected by the corrosive medium, as shown in Figure 12(d). This indicates that PNM molecules impede the dissolution of carbon steel in the presence of KI better than in the presence of PNM alone Figure 12(c) by blocking active cites.

3.7. Molecular dynamic simulations study (MDS)

For more information on the interaction between the inhibitor molecule (PNM) and the iron surface. An MD simulation was done in an aqueous phase. The equilibrium configuration (top and side views) of the PNM/H₂O/Fe (1 1 0) and PNM/H₂O/iodide/Fe (1 1 0) adsorption system is shown in Figure 13.

Examination of this figure clearly shows that there are strong interactions between the inhibitor molecule studied and the Fe atoms. It is clear from (Figure 13) that the inhibitor was able to adsorb on the surface with a parallel orientation either in the absence or in the presence of KI with different forms. This mode of adsorption can be attributed to the strong interaction between the aromatic rings and the heteroatoms (N and O) of this exclusion and

the metal surface. These results confirm the difference in the protective film formed during the adsorption of the inhibitor molecule in the absence and in the presence of KI [72].



Figure 13. MD simulation of the PNM/H₂O/Fe (1 1 0) and PNM/H₂O/iodide/Fe (1 1 0) adsorption system.

Adsorption energy is a powerful tool to prove the inhibition efficiency of organic molecules. The Total energy, adsorption energy, rigid adsorption energy and Deformation energy of PNM in aqueous phase on the Fe surface in the absence and in the presence of KI were calculated as follows (Table 6).

Table 6. Molecular dynamics simulation results for the lowest adsorption configurations of PNM on the H_2O/Fe (110) interface in the absence and in the presence of KI in (kcal/mol).

	PNM/H ₂ O/Fe (1 1 0)	PNM/H ₂ O/iodide/Fe (1 1 0)
Total energy	-988.38	-3336
Adsorption energy	-977.33	-3651
Rigid adsorption energy	-1015	-3675
Deformation energy	38.08	24.16
dE _{ad} /dNi (PNM)	-182.34	-521.06
dEad/dNi(eau)	-19.92	-51.55

It is generally assumed that high negative adsorption energy indicates that the adsorption is most stable and strong [73–77].

After the analysis of the results, it was found that PNM exhibited a great interaction with the metallic surface in particular with the iodide/Fe(1 1 0) surface. The adsorption energy values were found to be equal to -977.33 Kcal/mol and -3651 Kcal/mol for the PNM/H₂O/Fe(1 1 0), PNM/H₂O/iodide/Fe(1 1 0) systems, respectively.

4. Conclusion

Based on the results obtained in this study, we have drawn the following conclusions:

- PNM showed that the inhibition efficiency increases with the increase of inhibitor concentration, and attains a maximum value at 10⁻⁴ M.
- A good agreement is obtained for the inhibition efficiency determined by EIS and polarization methods.
- Adsorption of PNM on XC70 surface in 1.0 M HCl obeyed to Langmuir adsorption isotherm and the values of ΔG_{ads}^0 revealed that the adsorption mechanism of this inhibitor is mainly dominated by chemical adsorption.
- Addition of iodide greatly helps PNM to higher corrosion inhibition of carbon steel in 1.0 M HCl.
- The SEM analysis showed that the presence of the inhibitor alone in the corrosive solution modifies the morphology of the surface of the XC70 corroded by HCl, the presence of KI improves it even more. The SEM figures proved the formation of a protective inhibiting layer against corrosion.
- DFT calculations, molecular dynamic simulations (MDS) are in excellent agreement with the experimental findings.

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