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Graphical abstract

Corrosion inhibition of carbon steel pipelines by some novel

Schiff base during acidizing treatment of oil wells studied by

electrochemical and quantum chemical methods

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Corrosion inhibition of carbon steel pipelines by some novel Schiff base compounds during acidizing treatment of oil wells studied by electrochemical and quantum chemical methods <u>Hany M. Abd El-Lateef</u>^{*}, Ahmed M. Abu-Dief and Mounir A. A. Mohamed

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Abstract

Three novel Schiff bases compounds were prepared and their structures were characterized by X-ray, ¹³C-NMR, ¹H-NMR, mass, UV-Vis, FT-IR, spectral data and elemental analyses. The corrosion inhibition of the investigated inhibitors towards carbon steel in 15% HCl was investigated by using electrochemical measurements (EIS, LPR corrosion rate and Tafel plots), SEM, EDX and quantum chemical methods. The results showed that, the inhibitors are efficient mixed type corrosion inhibitors, and their inhibition performance increased with the rise of inhibitor concentration and temperature. The adsorption of the inhibitors on steel surface was found to obey Langmuir's adsorption isotherm and chemisorption. Quantum chemical calculations provide good support to empirical results.

Keywords: Carbon steel alloy; Corrosion inhibition; Schiff base compounds; EIS; SEM; Quantum chemical calculations

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<u>1. Introduction</u>

The electrochemical properties of carbon steel are the subject of many studies due to its wide applications in industry such as heat exchange and boiler systems, construction material for chemical reactors, storage tanks, and oil and gas transport pipelines [1-4]. Hydrochloric acid solution is extensively used in industrial-cleaning processes, such as: industrial acid cleaning, acid pickling, oil well acidizing, acid descaling and in petrochemical processes [5]. In petroleum industry, 15% HCl is generally used for acidizing treatment because it leaves no insoluble products after the handling. The use of HCl leads to destructive effects on the metal surface. The corrosion protection of the equipments and vessels is one of chief concerns of the maintenance and design engineers. The use of organic molecules as corrosion inhibitors to decrease the corrosion rate processes has been the focus of very many efforts within the chemical process industry especially in acidic environments [6-8].

Schiff base (imines) are organic compounds containing azomethine group (– CH=N–) which resulted from condensation of a primary amine with a carbonyl compounds (aldehyde or ketone) [9]. Due to the presence of the azomethine group, sulphur and/or oxygen atoms and electronegative nitrogen in the molecule, Schiff bases compounds should be good corrosion inhibitors. The action of such compounds depends on the specific interaction between the metal surface and the functional groups. So it is very important to clarify the interactions between metal surfaces and the inhibitor molecules in order to find new and efficient corrosion inhibitors [10-12]. Many Schiff bases had been investigated as efficient corrosion inhibitors for carbon steel [13], zinc [14], aluminium [15], aluminium alloys [16] and copper [17] in acidic media. These compounds generally become effective by adsorption on metal surfaces. The adsorption species help to protect metals from aggressive medium which causes

decomposition of the metal **[18]**. Abd El-Lateef **[3]** studied the corrosion behavior of carbon steel in hydrochloric acid solution with and without two Schiff bases namely Sodium 3-[{[1-carboxy-3- (methylthio) propyl] imino} methyl]-4hydroxybenzenesulfonate and Sodium 3-{[(1-carboxy-2-phenylethyl) imino] methyl}-4-hydroxybenzenesulfonate synthesized based on amino acids and found that, these compounds had excellent inhibition efficiency **[3]**.

Temperature has significant effectiveness on the process of metal corrosion [19]. Temperature variation supplies the possibility to obtain the thermodynamic adsorption and kinetic corrosion parameters [20], and the obtained results can help to deduce the type of adsorption of the inhibitor on the metal surface.

Nowadays, the choice of effective inhibitors has been mostly achieved by using the experimental information based on their electron donating ability and macroscopically physicochemical properties. At this time the expansion of theoretical calculations emphasized the scientific approaches involved in the branch of inhibitors by correlating the empirical data with quantum chemical properties [21, 22]. Thus, the purpose of the present work is to investigate the inhibition effect of three novel Schiff bases on the corrosion of carbon steel pipelines during acidizing treatment (15% HCl) in petroleum industry using electrochemical techniques. The effects of inhibitor concentration, temperature and immersion time were investigated. In order to examine the relation between the structure of studied Schiff bases and the inhibition efficiency, some quantum chemical indices such as E_{HOMO} and E_{LUMO} , ΔE , charge density of adsorption centers and dipole moment have also been calculated.

2. Experimental Details

2.1. Chemical composition of carbon steel C1018 alloy

Carbon steel C1018 (which is representative of a pipeline material) used for electrochemical measurements and immersion tests has the following composition (wt%): C 0.18 %, Si 0.17 %, Mn 0.70 %, S 0.03 %, Ni 0.01 %, Cr 0.01 % and Fe balance. The data was provided by European Corrosion Supplies Ltd. The cylindrical shaped working electrode has a diameter of 0.5 cm, length of 3.0 cm and 4.55 cm² exposed area to fluid.

2.2. Synthesis of the investigated inhibitors

Starting materials (2-amino-4, 6-dimethylpyridine, 3, 5-dimethylaniline, 3methoxy-4-nitroaniline, Tripropylamine, 2-hydroxynaphthaldehyde and 5bromosalicylaldehyde) were purchased from Sigma-Aldrich and all manipulations and used directly without further purification in the preparation of the investigated inhibitors.

Synthesis of 4-bromo-2-{(Z)-[(3, 5-dimethylphenyl) imino]methyl }phenol (HA-1)

HA-1 was synthesized by the condensation between 5-dimethylaniline (1.9 ml, 5 mmol) in 30 ml of dry ethanol treated with (1.1 g, 5 mmol) of 5bromosalicylaldehyde under vigorous stirring at 80 °C for 2 h. Then, the reaction mixture was left standing at room temperature to cool. The yellow crystals were collected and washed several times with ethanol to get pure product. The obtained crystal was used for X-ray single crystal measurements.

Synthesis of 1-{(Z)-[(4, 6-dimethylpyridin-2-yl)imino]methyl}naphthalen-2-ol (HA-2)

The title inhibitor was obtained in a high yield (92 %) by reflux condensation of equimolar of 2-amino-4, 6-dimethylpyridine and 2-hydroxynaphthaldehyde in

ethanol. The reaction mixture was refluxed for 2 h, cooled by keeping overnight to obtain yellow colored crystals filtered, washed, and dried (cf. Fig. 1).

<<Figure 1>>

Synthesis of 1-{(Z)-[(2-methoxy-4-nitrophenyl)imino]methyl}naphthalen-2-ol (HA-3)

The investigated inhibitor was synthesized by condensation of 3-methoxy-4nitroaniline with 2-hydroxynaphthaldehyde in ethanol. Drops of tripropylamine were added as a catalyst. The obtained mixture was refluxed for 3 h. The obtained yellow solution left at room temperature over night. Then the obtained yellow crystals were recrystallized from commercial ethanol.

2.3. Identification of the synthesized inhibitors

2.3.1. Crystal structure determination of the investigated inhibitors

X-ray crystal determination: single crystal of the investigated compounds suitable for X-ray diffraction was obtained by slow evaporation method. The diffraction data from a selected single crystal was collected at room temperature on Oxford Diffraction Xcalibur Gemini S diffractometer equipped with Copper k_{α} radiation source for the investigated inhibitors. The structures were solved by direct methods and refined on F₂ by full-matrix least-squares procedures using the SHELXL-97 program. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP [23-25].

2.3.2. Melting points and spectral measurements

Melting points for the prepared inhibitors were carried out on a melting point apparatus, Cimarec 3 Thermolque. C, H and N analyses were performed with a Perkin-Elmer 2400 series II analyzer. Infrared spectra (4000-400 cm⁻¹) were recorded

from KBr pellets on a Bruker IFS-125 FT-IR spectrophotometer. NMR spectra were measured and recorded in the Central Lab., Chemistry Department, Faculty of Science, Sohag University at 25 °C on a multinuclear FT-NMR spectrometer Bruker ARX400 at 400.1 (¹H) and 100.6 (¹³C and dept) MHz. The ¹H and ¹³C chemical shifts δ are given in ppm. Mass spectra were performed on a Shimadzu GCeMS-QP 1000 mass spectrometer at 70 eV. Absorption spectra were recorded with 1 nm resolution for all cases on JASCO UV–Visible spectrophotometer.

HA-1 data

Yield: 95%. Melting: 130 °C. IR (cm⁻¹): 3258 m,3052 m, 2913 m, 1640 s, 1558 m, 1499 s, 1391 s, 1205 m, 1161 m, 739 m, 628 m. Elemental analysis calculation for HA-1 ($C_{30}H_{28}N_2O_2Br_2$): C, 59.21; H, 4.60; N, 4.60 %, Found: C, 59.57; H, 4.49; N, 4.72 %. ¹H NMR (400 MHz, DMSO-d₆): δ 13.21 (s, 1H, OH), 8.91 (s, 1H,=CH), 7.85-6.43 (m, 6H, CH aromatic), 2.31(S, 6H, 2 CH3) (Fig. S1a; Supporting data); ¹³CNMR (400 MHz, DMSO-d₆): δ 161.99, 159.91, 148.09, 139.15, 135.82, 134.46, 129.22, 121.63, 119.54, 119.5, 110.92;21.32 (Fig. S1b; Supporting data); ESI MS (M/Z): 304.1(M⁺).

HA-2 data

Yield: 92 %. Melting: 170 °C. IR (cm⁻¹): 3346 m, 3076 m, 2918 m, 2866 m, 1612 s, 1536 s, 1432 s, 1392 m, 12 s, 829 m, 753 w. Elemental analysis calculation for HA-2 ($C_{18}H_{16}N_2O$): C, 78.17; H, 5.79; N, 10.13%, Found: C, 77.93; H, 5.65; N, 9.98 %. ¹H NMR (400 MHz, DMSO-d₆): δ 15.2 (s, 1H, OH), 9.79 (s, 1H,=CH), 8.24-6.83 (m, 8H, CH aromatic), 2.2 (S, 3H, CH₃), 2.12 (S, 3H, CH₃) (**Fig. S2a; Supporting data**); ¹³CNMR (400 MHz, DMSO-d₆): δ 157.94, 150.82, 150.63, 139.52, 136.11, 135.26,134.88, 129.73, 129.12, 124.94, 124.26, 122.32, 119.95, 113.03, 112.66, 106.18, 24.22, 21.05(**Fig. S2b; Supporting data**); ESI MS (M/Z): 276.30 (M⁺).

HA-3 data

Yield: 87 %. Melting: 210 °C. IR (cm⁻¹): 3379 m, 3056 m, 2936 m, 2841 m, 1622s, 1526s, 1329 s, 1267 s, 1075 s, 842 m, 735 w. Elemental analysis calculation for HA-3 ($C_{18}H_{16}N_2O_5$): C, 66.85; H, 4.95; N, 8.67%, Found: C, 66.64; H, 5.05; N, 8.81 %. ¹H NMR (400 MHz, DMSO-d₆): δ 15.5 (s, 1H, OH), 9.5 (s, 1H,=CH), 8.46-6.78 (m, 10H, CH aromatic), 4.1(S, 3H, OCH₃) (Fig. S3a; Supporting data); ¹³CNMR (400 MHz, DMSO-d₆): δ 179.43, 150.48, 150.08, 144.95, 140.17, 136.86, 133.95, 126.84, 125.28, 124.58, 120.95, 117.58, 117.42, 109.64, 107.38, 57.33(Fig. S3b; Supporting data); ESI MS (M/Z): 323.10(M⁺).

2.4. Test solution and inhibitors

The aggressive solution 15% HCl which is generally used for acidizing treatment was prepared by dilution of AR grade (BDH) HCl (Assay 37 %, density 1.017 g/ml at 25 °C). The concentration range of inhibitors employed was 0.01 to 1.0 mM. All Schiff bases inhibitors were dissolved in 15% HCl solution. Figure 2 shows the chemical and optimized structures of the inhibitors HA-1, HA-2 and HA-3.

<<Figure 2>>

2.5. Corrosion Measurements

All the electrochemical measurements under unstirred conditions were performed at atmospheric pressure in a one liter glass cell which consisted of a in a three electrode cell, A carbon steel C1018 specimen was used as the working electrode (This electrode was used for one time), a platinum wire and a saturated calomel electrode (SCE) served as counter and the reference electrodes, respectively. All electrochemical measurements were carried out using VersaSTAT4 potentiostat/galvanostat.

A stabilization time of 60 minutes was allowed before each run were completed and this time was deemed to be sufficient to attain a stable open circuit potential (E_{ocp}). Polarization measurements were carried out at potential ±250 mV vs. the corrosion potential (E_{corr}) at a sweep rate of 1 mV s⁻¹ at 45 and 60 °C.

Electrochemical impedance spectroscopy (EIS) measurements were performed with a phase-sensitive amplifier (Model-5208) driven by using Versa-STAT4 potentiostat/galvanostat with a frequency response analyzer (FRA) contained in a single unit and connected computer system. The EIS measurements were conducted at open circuit potential, after 1 h of immersion in the test solution in the frequency range from 100 kHz to 0.5 Hz. The amplitude of the voltage perturbation was 10 mV RMS. Parameters such as the double-layer capacitance (C_{dl}), the solution resistance (R_s) and the resistances of charge transfer (R_{ct}) were obtained from the EIS study by fitting the experimental data to the equivalent model circuit using the fit and simulation tool of the Z-View software.

The immersion tests were performed by using the linear polarization resistance (LPR) corrosion rate method implicated evaluating the corrosion of carbon steel in 15%HCl solution at 45 °C as described in Abd El-Lateef [3]. Fresh solution and fresh specimens were used in each experiment and three measurements were performed to ensure the reliability and reproducibility of the data.

2.6. Surface characterization by SEM/EDX

In order to get insight into the changes on surface of corrosive samples before and after introducing of inhibitors, the substrates were initially immersed in the corrosive solution (15% HCl) in the absence and presence of 1.0 mM HA-1 and HA-3 for 24 h at 45 °C, respectively, then taken out from the test solutions, cleaned with bidistilled water and acetone, and dried with air. The morphology of the tested samples was observed by using energy dispersive spectroscopy (EDX) on the scanning electron microscope (SEM) (SEM/EDX) (JEOL, model 5300). The tested samples obtained from LPR corrosion rate measurements were used in investigations.

2.7. Quantum chemical calculations

MOPAC2000 with WinMOPAC 2.0 as a graphic interface was used to carry out the quantum chemical calculations [26, 28]. At the beginning, structure the starting material was optimized with the eigenvector-following routine (EF) [28] using the semi-empirical PM3 method [29]. Quantum chemical calculations were performed using Gaussian-09 software package at B3LYP/6-31G (d, p) basis set [30]. The quantum chemical indices calculated included, the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), the dipole moment (μ), the absolute hardness (η), the electronic energy (E_e), core-core repulsion (C-CR), heat of formation (H_f) and ionization potential (IP).

3. Results and discussions

3.1. Structural conformation for the investigated compounds

3.1.1. FT-IR and molecular electronic spectra

Infrared spectra for the investigated inhibitors system were recorded in the range of $400 - 4000 \text{ cm}^{-1}$. A broad hydroxyl (-OH) peak is observed within the region 3258-3379 cm⁻¹. The broadening of these bands and the low frequency could be attributed to the formation of strong hydrogen bonding (O-H....N) in the solid state **[31].** The peaks appear within the regions 3052-3076 cm⁻¹ and 2913-2936 cm⁻¹ refer to aromatic and aliphatic –CH respectively. Moreover, the strong peaks lie within the region 1612-1640 cm⁻¹, could be rationalized to v(C=N) stretching indicating that condensation between aldehyde and amine has taken place, resulting in the formation

of the desired the investigated inhibitor compounds [32]. The appearance of bands within the range of 1205- 1292 cm⁻¹ for, respectively are mainly due to the bending of C-O bond.

The molecular electronic spectra of HA-1 inhibitor and its complex with Fe(II) was carried out in ethanol at room temperature at concentration 1.0 mM for each compound. The investigated HA-1 inhibitor has an absorption bands in ultraviolet region (200–400 nm), these bands extends over to higher wavelength region due to conjugation. (cf. Fig. 3). The spectrum of the investigated HA-1 exhibits band at 379 nm were observed and assigned to $n \rightarrow \pi^*$ transitions originating from the imine or amide group of the Schiff base ligand [33]. These bands disappeared via complexation and new band attributed to the donation of the lone pair of electrons of the nitrogen atoms of the Schiff base to metal ion (M \rightarrow N) appear [34]. Moreover, the appearance of bands at 443 nm in HA-1 inhibitor due to extra conjugation between the amine and aldehyde ring [8]. Furthermore, the [Fe-HA-1] complex show additional band at 480 nm due to d-d transition [32-34].

3.1.2. ¹H, ¹³CNMR spectra and elemental analalysis for the prepared compounds

Data are reported along with the possible assignments in experimental. The ¹HNMR spectra of the prepared Schiff bases inhibitors showed the characteristic NMR signals. Signals of phenolic proton are appeared at 15.50-13.20 ppm. The characteristic proton of azomethine appeared at 9.5-8.91 ppm. The signals in the range of 7.80-6.70 ppm are characteristic to the aromatic protons. The ¹³CNMR spectra of the free ligand (nap) have showed a peak at 179.00-157.94 ppm due to characteristic azomethine carbon. The signals at 150-106 ppm may be attributed to phenyl aromatic carbons and 57-21.05 for aliphatic carbon.

The micro analytical data for the prepared inhibitors are in a good agreement with calculated values. This confirmed the proposed structures of the prepared inhibitors (cf. Fig. 2)

<<Figure 3>>

3.1.3. X-ray crystallographic

The molecular structures and the packing arrangements of the molecules with hydrogen bonds of compounds HA-1, HA-2 and HA-3 are presented in Figure 4. The crystal data and structure refinement of investigated synthesized inhibitors are given in Table 1. Some selected geometrical parameters (bond lengths and bond angles) are listed in Table 2. Compounds HA-1 crystallized in the orthorhombic $Pn2_1a$ space groups and the determined unit cell parameters are a = 21.8290 (3) Å, b = 16.9484 (3) Å, c = 7.11447 (13) Å, $\alpha = \beta = \gamma = 90$ and V= 2632.11 (7) Å³. The ORTEP diagram of the HA-1 compound with atomic labeling scheme in Figure 4 showed that, the molecule form a dimer sustained by N-H...N hydrogen bonds. The crystal structure is settled by intermolecular C-H...N interactions. The compound HA-2 crystallizes in monoclinic crystal system with the space group $P2_1$. The unit cell parameters are a = 8.8848(2) Å, b = 6.3713(1) Å, c = 12.6507(2) Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 94.429^{\circ}$ and V = 713.99(2) Å³. Furthermore, the planarity of molecule is stabilized by a strong intramolecular hydrogen bond. The compound HA-3 (Fig.4) crystallizes in triclinic crystal system with the space group P-1. Summary of the crystallographic data and refinement parameters is given in Table 1. The important interatomic distances and angles are listed in Table 2. The crystal structure is stabilized by intermolecular C-H...N interactions. The packing diagram is given in the Fig. 4b.

The molecular structures of compounds HA-1, HA-2 and HA-3 consist of an electronic π -system from the hydroxy-aldehyde derived fragment connected to an

aromatic aniline ring. The bond distances from N to C (-C=N-) were found to be 1.286 (7) Å, 1.327(4) Å and 1.332(3) Å for compounds HA-1 (N1—C7), HA-2 (N1—C11) and HA-3 (N1—C11), respectively. Bond angles C7—N1—C8, 119.3(4) °; C11—N1—C12, 123.8(3) ° and C11—N1—C12, 127.02 (17) ° were also found for compounds HA-1, HA-2 and HA-3, respectively. The bond distances and angles are in accordance with the normal ranges previously reported for other Schiff bases derived from cinnamaldehyde [**35**].

<<Figure 4>>

<<Table 1>>

<<Table 2>>

3.2. Potentiodynamic polarization measurements

3.2.1. Effect of inhibitor dose

In order to estimate the inhibition ability of the investigated Schiff base compounds for carbon steel pipelines, polarization measurements were carried out on in 15% HCl solution in the absence and presence of the studied inhibitors at concentrations range 0.01-1.0 mM. Figure **5** shows the polarization curves of carbon steel in the test solution containing different dose of inhibitors HA-1, HA-2 and HA-3 at 45 °C. It is clear that from Fig. **5**, introduction of inhibitors to the system causes a significantly minimize in the rate of corrosion, i.e. shifts the cathodic curves to more negative potentials and the anodic curves to more positive potentials. This may be ascribed to adsorption of the inhibitors over the metal surface [**36**]. The pertinent Tafel indices such as the corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_{a} , β_{c}) and corrosion current densities (I_{corr}) were obtained by extrapolating the

polarization curve. The surface coverage (θ) and the inhibition efficiency (P %) can be calculated using Eq. (1) [1-4] :

$$P\% = \theta \times 100 = \left(1 - \frac{I_{inh}}{I_{uninh}}\right) \times 100 \tag{1}$$

where $I_{\text{uninh.}}$ and $I_{\text{inh.}}$ are the corrosion current densities in the free solution and the presence of inhibitors, respectively. An assessment of Table **3** shows that, with increasing the concentration of inhibitors, the corrosion current density (I_{corr}) decreased and the inhibition efficiency (P%) increased for carbon steel at studied temperatures. The high P% value suggested a full coverage of the studied steel surface with adsorbed inhibitor molecules. The above results indicated that retardation of the samples corrosion processes at cathodic and anodic reaction sites occurred, and the results were attributed to the adsorption of these sites by inhibitor molecules [1-4].

However, the addition of inhibitors shifted the corrosion potential E_{corr} , with respect to the blank, but this shift is not more than 85 mV (maximum ΔE_{corr} = -29 mV). According to Riggs [37], the classification of compounds as anodic or cathodic inhibitors is feasible when the potential displacement is at least 85 mV in relation to that measured for the free inhibitor system, it may be concluded that, these inhibitors molecule should be considered as a mixed-type inhibitors. Also with the addition of HA-1, HA-2 and HA-3 inhibitors both β_a and β_c values almost unchanged with respect to blank, indicating that, the hydrogen evolution mechanism do not modify by the addition of inhibitors to HCl solution, but acts as an adsorptive inhibitors [38]. On the other hand, the anodic Tafel slopes (β_a) are also found to be smaller than the respective cathodic Tafel slopes (β_c). The θ value found to be near unity (θ =0.96, Table 3), indicates almost a whole coverage of the steel surface with the adsorbed inhibitor molecules. Categorically, when the inhibitor has high θ value is considered

as a perfect physical barrier shielding the corroding steel surface from the aggressive solution. Correspondingly, *P*% increases with the inhibitor concentration. *P*% for 1.0 mM inhibitor reaches up to a maximum of 96.2% for HA-3, 91.6% for HA-2 and 89.2 % for HA-1. The results revealed that the investigated inhibitors had inhibition effectiveness on C1018 steel at studied temperatures, and *P*% follows the order: HA-3 > HA-2 > HA-1.

<<Figure 5>>

<<Table 3>>

3.2.2. Effect of temperature

The influence of the reaction temperature on the potentiodynamic polarization curves in the absence and presence of 1.0 mM of HA-1 for C1018 carbon steel in 15 % HCl is represented in Fig. 6. There is a clear acceleration of both the cathodic and anodic reactions with an increase in temperature. As it is observed from the polarization parameters (Table 3), for carbon steel, the corrosion current densities increased with the increase of temperature in 15% HCl solution without and with 1.0 mM of the investigated inhibitors. These results could be attributed to the acceleration of all the processes during the corrosion, such as electrochemical, chemical, transport with increase in temperature [39]. It is noted that from Table 3, the inhibition efficiency and surface coverage degree increased with the rise of temperature, indicating chemical adsorption of the Schiff base molecule on the metal surface [40].

To clarify the effect of temperature on the inhibition characteristics of the inhibitors, the apparent activation energies (E_a) of the corrosion process in the absence and presence of 1.0 mM of studied inhibitors at 45 °C and 60 °C were determined from the condensed Arrhenius equation as follows [41]:

$$\log \frac{I_{corr(2)}}{I_{corr(1)}} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
(2)

where $I_{corr(1)}$ and $I_{corr(2)}$ are the corrosion current densities at temperatures T_1 (45 °C) and T_2 (60 °C), respectively, and R is molar gas constant. The calculated E_a value of carbon steel in the absence of inhibitors was 45.49 kJ/mol. However, in the presence of 1.0 mM of HA-1, HA-2 and HA-3 inhibitors, the E_a values were decreased to 25.11, 24.87 and 21.71 kJ/mol, respectively. The decrease in activation energy after the addition of inhibitors could be interpreted as a chemical adsorption of the inhibitors on the steel surface [42].

The heat of adsorption was evaluated from the surface coverage and temperature, as follows [43]:

$$\Delta H_{ads} = 2.303 R \left[\log \left(\frac{\theta_2}{1 - \theta_2} \right) - \log \left(\frac{\theta_1}{1 - \theta_1} \right) \right] \left(\frac{T_1 T_2}{T_2 - T_1} \right)$$
(3)

where θ_1 and θ_2 are the values of surface coverage at temperatures T_1 (45 °C) and T_2 (60 °C), respectively. The calculated values of the heat of adsorption for the carbon steel were 22.31, 22.69 and 25.36 kJ/mol in 15% HCl in the presence of 1.0 mM of HA-1, HA-2 and HA-3 inhibitors, respectively. The obtained positive values indicated that, the adsorption of the inhibitors on the metal surface was endothermic, and the results were in a good agreement with the phenomenon of the proposed chemisorption mechanism **[44]**.

<<Figure 6>>

3.3. Electrochemical impedance spectroscopy (EIS) measurements

To further study the corrosion inhibition of the investigated Schiff base inhibitors, EIS measurements were carried out at 45 °C. The EIS plots of carbon steel

in 15% HCl solution in the absence and presence of various concentrations of inhibitors are shown in Figs. **7-9**.

Nyquist plots of carbon steel immersed in 15% HCl solution without and with different concentrations of inhibitors HA-1, HA-2 and HA-3 are presented in Figs. 7a, 8a and 9a, respectively. The impedance spectra of all samples exhibit a single depressed capacitive loop, which indicates that the corrosion of carbon steel is mainly controlled by double layer behavior and charge transfer process [45]. Thus, the corrosion inhibition mechanism is almost the same in the presence of studied inhibitors [46]. The diameter of capacitive loop increases significantly when the Schiff base compounds are added into the aggressive solution, which proves that HA-1, HA-2 and HA-3 inhibitors can significantly inhibits the corrosion of carbon steel in 15% HCl solution [47]. The charge transfer resistance values (R_{ct}) were determined from the difference between impedance values at the higher and lower frequencies [48]. In order to obtain a more accurate and representative fit, the double layer capacitance (C_{dl}) was replaced by the constant phase element (*CPE*). According to the EIS data, the inhibition efficiency (P%) and the double-layer capacitance (C_{dl}) were calculated from charge transfer resistance (R_{ct}) and *CPE* parameters (Y_0 and n) using the following equations [3]:

$$C_{dl} = (Y_0 R_{ct}^{1-n})^{\frac{1}{n}}$$
(4)

$$P\% = \frac{R_{ct} - R_{ct(0)}}{R_{ct}} \times 100$$
(5)

where Y_0 is *CPE* constant and *n* is CPE exponent (represents the deviation from the ideal behavior and it lies between 0 and 1). $R_{ct(0)}$ and R_{ct} are the charge transfer resistance values without and with inhibitor, respectively.

The corresponding phase angle and Bode impedance magnitude plots recorded for carbon steel electrode in 15% HCl solution with addition of various inhibitors dose at its E_{corr} are shown in Figs. 7b, c, 8b,c and 9b,c. As seen from Figs. 7b, 8b and 9b, the Bode plots refer to the existence of an equivalent circuit containing a single constant phase element in the interface of steel/acid. In addition, at low frequencies in Bode plot the increase of absolute impedance confirms the higher protection with the increasing of inhibitors concentration, which is related to the adsorption of HA-1, HA-2 and HA-3 compounds on the surface of carbon steel [49]. In the phase angle plots (Figs. 7c, 8c and 9c), increasing the concentration of HA-1, HA-2 and HA-3 inhibitors in 15% HCl results in more negative values of phase angle indicating superior inhibitive performance due to more inhibitor molecules adsorbed on carbon steel surface at higher concentrations The maximum values in phase angle plots in the presence of investigated inhibitors approach towards -90°, which indicates that there is solely one time constant related to the electrical double layer formation at the surface- solution interface [50]. The linear region of the log(f) - log |Z| plots should have a slope (α) of unity for the ideal capacitors. The values of α are calculated from the log (f)-log |Z| plots and are given in Table 4. As shown in Table 4, α values range from -0.68 to -0.78, -0.70 to -0.81 and -0.73 to -0.85 for HA-1, HA-2 and HA-3, respectively, this could be related to the non-ideal structure of the metal/solution interface. In this case, a differential capacitance should be formed at the interface rather than an ideal capacitor.

Figure **10 a** and **b** shows the comparison of the simulated spectrum and the experimental EIS data, using the Z-View impedance fitting software for carbon steel samples immersed in 15% HCl without and with of 1.0 mM of HA-1 inhibitor. A good fit was obtained with the model used for all experimental data. The equivalent

circuit used in the present study is shown in Fig. **10 a** and **b** (Inset)). In this equivalent circuit, R_s , R_{ct} and CPE are the solution resistance, the charge transfer resistance and the constant phase element (instead of C_{dl}), respectively. The values of impedance parameters are determined by using the equivalent circuit software Z-view and listed in Table **4**.

As observed in Table **4**, the C_{dl} values decrease while R_{ct} values increase with increasing inhibitors concentration. The highest R_{ct} (130.7, 151.5 and 296.6 Ω cm² for HA-1, HA-2 and HA-3, respectively) have been found at optimum concentration 1.0 mM. This behavior was the result of an increase in the surface coverage by the inhibitor molecules, indicating that the exposed area decreased. The R_{ct} obtained in the presence of the HA-3 is bigger than that in the presence of the other compounds HA-1 and HA-2. The decrease in C_{dl} values may be considered in term of Helmholtz model [51]:

$$C_{dl} = \varepsilon_0 \varepsilon \frac{A}{d} \tag{6}$$

where ε_0 , ε , *d* and *A* are the permittivity of air, the local dielectric constant, the thickness of the film and the surface area of the electrode, respectively.

In fact, the decrease in the C_{dl} can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecules act by adsorption at the steel substrate/solution interface [52]. The addition of the synthesized inhibitors provides lower C_{dl} values, probably as a consequence of substitution of water molecules by the synthesized Schiff base compounds at the electrode surface. The value of C_{dl} is decreased from 128.4 µF cm⁻² in the blank solution to 12.1, 8.5 and 5.3 µF cm⁻² by addition of 1.0 mM of HA-1, HA-2 and HA-3, respectively, as a result of the effective adsorption of the studied inhibitors.

As listed in Table **4**, the values of inhibition efficiency (*P*%) increase with the concentration of these Schiff base inhibitors up to 90.51 % for HA-1, 91.81 % for HA-2 and 95.82% for HA-3, when concentration reaches 1.0 mM. These results again confirm that, the investigated Schiff bases compounds exhibit efficient inhibitive performance for carbon steel in the chosen strong acid solution (15% HCl) and *P*% values follows the order: HA-3 > HA-2 > HA-1. This result is in good agreement with obtained data from the potentiodynamic polarization studies that, 1.0 mM of the inhibitors (HA-1, HA-2 and HA-3) was the optimum concentration and HA-3 is a better corrosion inhibitor in 15% HCl solution.

<<Figure 7>> <<Figure 8>> <<Figure 9>> <<Figure 10>> <<Table 4>>

3.4. Effect of immersion times

It is well known that, the inhibition efficiency ability of organic inhibitor molecules depends on immersion time in the aggressive media. LPR corrosion rate measurements was employed to investigate the effect of exposure time on the corrosion behavior of carbon steel in 15% HCl containing 1.0 mM of HA1-, HA-2 and HA-3, respectively. Figure **11a** shows the variation of corrosion rate (CR) results with immersion time in 15% HCl in the absence and presence of 1.0 mM of HA1-, HA-2 and HA-3 at 45 °C. Inspection of the figure reveals that, the corrosion rate increases with increasing immersion time from 1 to 24 h in 15% HCl solution free

inhibitors. However, in the presence of 1.0 mM of the under testing Schiff base inhibitors the corrosion rate decrease until 2 h of exposure and after that remain stable (from 2 to 24 h). Figure **11b** show that inhibition efficiency of the investigated inhibitors was increased with increasing immersion time until 2 h which may be attributed to the formation of strong inhibitor layer which prevents the attack of corrosive media on the metal surface. However, the results show a stabilization of the inhibition efficiency from 2 h to 24 h of immersion. According to this study, it was found that the studied Schiff base compounds are very effective inhibitors for carbon steel in 15%HCl solution because after an immersion time of 24 h, the power of protection already achieved 88.7, 92.5 and 94.4% for HA1-, HA-2 and HA-3, respectively. Notwithstanding, these compounds can provide good protection to the carbon steel substrate even after 24 h exposure to this highly corrosive media (15%HCl). The results of LPR corrosion rate measurements also indicated that the inhibition efficiency (P%) of the inhibitor HA-3 was greater than that of the other inhibitor.

<<Figure 11>>

3.5. Adsorption isotherm

The adsorption of organic inhibitor on the carbon steel surface has been widely investigated by classical adsorption isotherms. The adsorption isotherm could provide useful information for the mechanism of inhibiting effect **[43, 53]**. The type of the adsorption isotherm is determined from the inhibitor concentration and the surface coverage.

The experimental data obtained from EIS measurements at 45 °C were supplied on different adsorption isotherm equations including Frumkin, Langmuir, Temkin, Freundlich and Flory–Huggins isotherms and found to fit the Langmuir isotherm (Fig. **12**) which may be formulated as:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$
⁽⁷⁾

where C_{inh} , K_{ads} and θ are the inhibitor concentration, the adsorption–desorption equilibrium constant and the surface coverage, respectively. A linear relation can be found between C_{inh}/θ and C_{inh} with regression coefficients (R^2) 0.9988, 0.9996 and 0.9993 for inhibitors HA-1, HA-2 and HA-3, respectively. The K_{ads} values were determined from the intercepts of the lines in Fig. 12. The value of K_{ads} was found to be 5.31×10^5 , 8.64×10^5 and 12.40×10^5 mol⁻¹ l for HA-1, HA-2 and HA-3, respectively. K_{ads} value represents the binding force of the inhibitor molecules adsorb onto the metal surface, and the large value of K_{ads} reflects strong adsorption ability of the inhibitor molecules onto the metal surface [43, 54]. The investigated Schiff base inhibitors give larger K_{ads} values at 45 °C, imply more efficient adsorption and hence better inhibition efficiency. In addition, HA-3 inhibitor had larger K_{ads} values at the studied temperature; the results meant that the adsorption ability of this inhibitor onto steel surface was stronger than that of HA-1 and HA-2 compounds. The K_{ads} value is possess of the standard free energy of adsorption (ΔG_{ads}^o) by the following equation

$$K_{ads} = \frac{1}{55.5} \exp(-\frac{\Delta G_{ads}^o}{RT})$$
(8)

where 55.5 is the concentration of water in solution expressed in mol/L, R is molar gas constant, T is the corresponding temperature.

The calculated values of ΔG_{ads}^{o} for the investigated compounds HA-1, HA-2 and HA-3 were -45.43, -46.74 and -47.71 kJ mol⁻¹, respectively. The obtained negative values indicated that, the inhibitors strongly adsorbed onto the metal surface

at 45 °C. In general, when the absolute value of ΔG_{ads}° is lower than 20 kJ mol⁻¹ indicates physisorption, while it is related to chemisorption when the value is 40 kJ mol⁻¹ or larger [55]. In our study, it is noted that the absolute values of ΔG_{ads}° for carbon steel were larger than 40 kJ mol⁻¹ at the studied temperature, indicating that the adsorption mechanism of inhibitors onto steel surface were chemical adsorption at 45 °C.

<<Figure 12>>

3.6 . Surface morphological observation and analysis

3.6.1. SEM analysis

The surface morphologies of carbon steel surfaces exposed and unexposed to 15% HCl solutions in the absence and presence of 1.0 mM of HA-1 and HA-3 after 24 h of immersion were observed by the SEM examination presented in Fig. 13. It can be seen from Fig. 13a that the steel specimen before immersion looks like smooth and appears some abrading scratches on the surface. After immersion 15% HCl solution with no inhibitor, displayed a very rough metal surface covered with thick porous oxide layer due to severe corrosion (Fig. 13b). In presence of the inhibitors (Fig. 13c, d), much less damage and smooth surfaces are observed. Among HA-1 and HA-3, the presence of HA-3 as corrosion inhibitor results into comparatively cleaner and smother surface. This elucidates a good adsorption and corrosion inhibition potentiality of HA-3 compare to HA-1. These results also approved that, the formation of the adsorbed layer of inhibitor provided the protective property against corrosion, resulting in excellent corrosion inhibition.

<<Figure 13>>

3.6.2. Energy dispersive analysis of X-Rays (EDX) Studies

In order to determine the elements present on the carbon steel surface after 24 h of exposure in the uninhibited and inhibited 15% HCl, the EDX spectra were used. A comparable elemental distribution of blank carbon steel, with and without studied Schiff base inhibitors analyzed by (% weight) is shown in Table 5. Before the corrosion test, the characteristic peaks are related to the metals which are present in the carbon steel alloy (Table 5). In the absence of inhibitors, the data exhibits the distinctive peaks which are regarding to Fe, Mn, P, S, Ni, Cr, Cl and oxygen elements. This indicated that the passive film contained Fe₂O₃ and/or FeCl₃. The EDX spectrum of carbon steel immersed in the 15% HCl containing 1.0 mM of HA-1 and HA-3 inhibitors shows the additional peaks, demonstrating the existence of C and N (owing to the carbon and nitrogen atoms of Schiff base inhibitors). These finding shows that the carbon and nitrogen atoms covered the steel surface. In addition, the intensity of O signals is reduced from 34.4% to 12.4% and 11.7% and the intensity of Fe signal is increased from 43.45% to 71.54% and 72.41% (Table 5) in the presence of 1.0 mM of HA-1 and HA-3 inhibitors, respectively. This result demonstrated that, the adsorption of inhibitor molecule on carbon steel surface leads to a decrease of metal oxide layer.

<<Table 5>>

2.7. Quantum Chemical Studies

In order to confirm the correlation between and inhibition efficiency of the investigated Schiff base inhibitors and electronic structure quantum chemical calculations were performed. In this study, the relationship between quantum chemical indices and inhibition efficiency was inspected. The distribution of lowest unoccupied molecular orbitals (E_{LUMO}) and highest occupied molecular orbitals (E_{HOMO}) of HA-1, HA-2 and HA-3 models are shown in Fig. **14**. It is obvious from

this figure that the HOMO and LUMO orbitals are distributed on oxygen, nitrogen atoms and phenyl ring. Table **6** shows the values of some quantum chemical parameters including E_{LUMO} , E_{HOMO} , the total electronic energy of the molecules (E_e), the energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), dipole moment (μ), core-core repulsion (C-CR), absolute hardness (η), ionization potential (*IP*) and heat of formation (H_f).

 E_{HOMO} and E_{LUMO} are significant parameters for the prediction of the reactivity of inhibitor species. The E_{HOMO} is often associated with the electron donating ability of a molecule [56-58]. According to Eddy and Ebenso [59], increasing values of E_{HOMO} facilitate the adsorption of the inhibitor. It is evident that from Table 6, the E_{HOMO} for the investigated imines decreases in the order; (HA-3> HA-2>HA-1), which is in agreement with the experimental results of inhibition efficiency (*P*%). In addition, the lower the E_{LUMO} , as the ΔE decreased and the *P*% improved [60]. Inspection of the data in Table 6 reveals ΔE value obeys the order of HA-3< HA-2< HA-1, which is in completely accordance with the order of inhibition efficiency (*P*%) of HA-3 > HA-2 > HA-1. Thus, there is a good correlation between ΔE and *P*%.

The dipole moment (μ) is a suitable index for the prediction of the trend of a corrosion inhibition process. μ is related to the distribution of electron in a molecule and is measure of polarity in a bond [58]. The large value of dipole moment probably increases the inhibitor adsorption through electronic force [61]. In Table 6, HA-3 has higher μ value that that of the other, which suggests that the better inhibitive behavior of HA-3 would be arisen from intermolecular electrostatic force to some extent. The dipole moment of the investigated inhibitors are 3.922, 2.23 and 7.01 Debye for HA-1, HA-2 and HA-3, respectively, which is higher than that of H₂O (μ = 1.88 Debye). Accordingly, the adsorption of Schiff base molecules can be considered as a quasi

substitution method between the inhibitor molecule and water molecules at the electrode surface.

Absolute hardness (η) is important parameter to measure the reactivity and molecular stability. A hard molecule has a large energy gap and vice versa [62]. In our present study HA-3 with low hardness value 3.34 eV compared with other compounds have a low energy gap and highest inhibition efficiency. The core-core repulsion energy (C-CR) is a quantum chemical index that may have excellent correlation with inhibition efficiency. El Ashry *et al.* [63] reported that, the inhibition efficiency of some Schiff bases increased with decreasing value of core-core repulsion energy. Similarly, the inhibition efficiencies of the investigated inhibitors were found to increase with decreasing values of C-CR.

The electronic energy of the molecule (E_e), heat of formation (H_f), and ionization potential were also calculated. These indices have been found to be useful in expecting the direction of a corrosion inhibition reaction for some systems **[64]**. From the results in Table **6**, it is evident that, the ionization potentials (*IP*) increased in the same order of inhibition efficiency (HA-3 > HA-2 > HA-1). This is because *IP* is directly related with the E_{HOMO} . High electronic energy of the molecule indicates high stability and chemical inertness and small value indicates high reactivity of the atoms and molecules **[65]**. The low E_e (-21721.9 eV) of HA-3 enumerates its better inhibition efficiency. It was obvious that HA-2 had a heat of formation (H_f) (21062. kJ mol⁻¹) than did of the other compounds.

In order to ascertain the adsorption sites of inhibitor atomic charges in the molecule are considered. Based on the MOPAC calculations using AM1 method, the atomic charge distributions of the HA-1 compound were calculated. Net atomic charge distribution on monomer and dimer of HA-1 molecule and are given in Fig.

15. From the Figure, it could be observed that the oxygen and nitrogen atoms play an important role in the adsorption process of molecule on carbon steel surface. The results reveal that, the most negative charge in the studied compound is resident in the nitrogen and oxygen atoms. As seen from Fig. **15**, all non-hydrogen atomic charge distributions of the dimer structure are decreased according to the secondary dipole-dipole interaction forces. The charges of nitrogen are -0.154 and -0.118 for monomer and dimer HA-1 molecule, respectively and oxygen charges are -0.249 and -0.231 for monomer and dimer HA-1 molecule, respectively. It was found that, the charge decreased in the case of dimer, this due to the monomer molecule consumed a part from charge to form a dimer. This explains why the HA-1 compound has the less adsorption and subsequently lower inhibition efficiency. This observation is consistent with the data obtained from experimental investigations.

<<Figure 14>>

<< Figure 15>>

<<Table 6>>

3.8. Inhibition mechanism and potential of zero charge (PZC)

In general, the mechanism of corrosion inhibition in acid solution is the adsorption of the inhibitor onto the metal surface. The adsorption process of organic compounds onto the metal surface is influenced by the type of aggressive media, the nature and charge of the metal and the charge or dipole moment of the inhibitor molecule. Generally, due to the complex nature of adsorption, it is not possible to foresee a single adsorption mechanism [66]. The charge on the metal surface can be determined from the position of corrosion potential (E_{corr}) in regard to the respective

zero charge potential (E_{PZC}). Antropove [67] suggests a special scale of potential, the initial value of which is E_{PZC} . Then the potential ϕ on this scale will be the difference between E_{corr} and E_{PZC} [3]:

$$\phi = E_{\rm corr} - E_{\rm PZC} \tag{9}$$

If the $E_{PZC} > E_{corr}$ of the metal in a given electrolyte, the metal surface is negatively charged, then the adsorption of cations will be most likely. For $E_{PZC} < E_{corr}$, the metal surface is positively charged, the adsorption of anions is most likely. EIS measurements were used to gain more information about the surface charge of the carbon steel. The E_{PZC} of the steel electrode in the investigated acid solution containing 1.0 mM of inhibitors HA-1, HA-2 and HA-3 was found to be -0.591, -0.601 and -0.599 V (SCE), respectively. From Table 3, it was observed that, the $E_{\rm corr}$ of carbon steel in 15% HCl solution with addition of 1.0 mM of HA-1, HA-2 and HA-3 are -0.514, -0.545 and -0.555 V (SCE), respectively. It can be said that ϕ potential is positive at the open circuit potential after 1 h of exposure time ($\phi = +0.077, +0.056$ and +0.044 V (SCE) for HA-1, HA-2 and HA-3, respectively). From the above result, Cl^{-} ions in aqueous HCl solution first adsorbed at the steel/acid interface at the E_{corr} through electrostatic attraction force due to the excess positive charge at this interface. After this first adsorption step, the carbon steel surface becomes negatively charged. Among the studied Schiff base inhibitors HA-1, HA-2 and HA-3 molecules exist as protonated through -OH and nitrogen atoms (-C=N-) in HCl solution and it is in equilibrium with the corresponding molecular form. Hence, the positively charged of cationic forms of molecule has been formed an electrostatic bond with the Cl⁻ ions already adsorbed on carbon steel surface. Accordingly, the adsorption of HA-2 molecule on steel surface can be proposed as in Fig. 16.

In addition to the physical adsorption, these molecules are also adsorbed through the chemisorption mechanism that may be formed between the lone pair electrons of the unprotonated 4-bromo-2-{(Z)-[(3, 5-dimethylphenyl) imino] methyl}phenol, 1-{(Z)-[(4,6 dimethylpyridin-2-yl)imino]methyl}naphthalen-2-ol and 1-{(Z)-[(2-methoxy-4-nitrophenyl)imino]methyl}naphthalen-2-ol and the unoccupied d-orbital in the Fe surface to form a coordinate type of a bond which enhanced the combination strength between the inhibitor molecule and metal surface. [Fe(II)-HA-1] complex was characterized by UV/vis spectrophotometric method as shown in Fig. 3. From UV/vis spectra obtained, one can observe that, HA-1 compound exhibits two maxima at about 379 and 443 nm. While the Fe(II) ions do not show any absorption maxima. But the [Fe(II)-HA-1] complex does exhibit one absorption maximum at about 480 nm. The shift in band maximum from 443 nm to 480 nm, suggesting the interaction between organic molecule and Fe(II) ions in the solution. Abboud et al. **[68]** has reported that change in position of the absorbance maximum and change in absorbance value indicate the formation of a complex between two species in solution. The stoichiometries of the titled inhibitors were measured by applying a continuous variation method [8] (Fig. 17). The results suggested the possible formation of 1:2 complex (Fe (II): Schiff base) as in Fig. 18.

Among the Schiff base investigated inhibitors, the corrosion inhibition efficiency follows the order: HA-3 > HA-2> HA-1. The higher protection ability even at low concentrations were probably due to the presence of aromatic rings and -OH, -C=N- groups. Lower values of *P*% of HA-1 inhibitor compared to those of HA-3 and HA-2 inhibitors may be due to the presence of that compound in the dimer form (as discussed in Section **3.7** by using the quantum chemically calculated charge density values). Otherwise, the highest inhibition efficiency of HA-2 and HA-3 inhibitors

may be attributed to the presence of naphthalene ring and unshared electron pairs presenting on N- hetero-atoms in HA-2 compound which interact with the vacant d-orbital of iron atoms (Fig. **16**).

<<Figure 16>>

<< Figure 17>>

<<Figure 18>>

4. Conclusions

Three new Schiff base inhibitors HA-1, HA-2 and HA-3 were synthesized and their molecular structure has been confirmed with support of X-ray single crystal, ¹³CNMR, ¹HNMR, mass, UV-Vis, FTIR spectra and elemental analyses. The corrosion inhibition ability of these inhibitors on of carbon steel in 15 % HCl was investigated by electrochemical and quantum chemical methods. From the overall results and discussions, the main conclusions are as follows:

- **1.** The inhibition efficiency increases with the increase in the inhibitor dose and temperature, and attains a maximum value at 1.0 mM.
- **2.** The results indicate a stabilization of the inhibition efficiency from 2 h to 24 h of immersion.
- **3.** The compounds acted as a mixed type inhibitors controlling both cathodic and anodic reactions.
- **4.** Among the Schiff base investigated inhibitors, the corrosion inhibition efficiency follows the order: HA-3> HA-2> HA-1. The inhibition effectiveness was attributed to the adsorption of the inhibitors onto steel

surface by chemisorption. The adsorption model of the inhibitors obeyed Langmuir adsorption isotherm.

- **5.** The charge on the metal surface was evaluated by PZC analysis and a probable mechanism has been proposed.
- **6.** The SEM micrographs approved that, the formation of the adsorbed inhibitor layer provided the protective property against corrosion.
- 7. A good correlation was found between the inhibition efficiency and the quantum chemical parameters (E_{LUMO} , gap energy (ΔE) and dipole moment (μ)).

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Appendix A. Supplementary material

Figure S1: (a) ¹H-NMR and (b) ¹³C-NMR spectra of 4-bromo-2- $\{(Z)-[(3, 5$ dimethylphenyl) imino]methyl }phenol (compound HA-1), <u>Figure S2</u>: (a) ¹H-NMR ¹³C-NMR and **(b)** spectra of $1-\{(Z)-[(4,$ 6-dimethylpyridin-2yl)imino]methyl}naphthalen-2-ol (compound HA-2) and Figure S3: (a) ¹H-NMR ¹³C-NMR spectra 1-{(Z)-[(2-methoxy-4-nitrophenyl) and **(b)** of imino]methyl}naphthalen-2-ol (compound HA-3).

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<u>Table 1:</u>

| Compounds | HA-1 | HA-2 | HA-3 |
|------------------------------|--|--|--|
| Empirical formula | $\underline{C_{15}H_{14}BrNO \cdot C_{15}H_{14}BrNO}$ | $C_{18}H_{16} N_2O$ | $C_{18} H_{14} N_2 O_4 \! \cdot H_2 O$ |
| Formula weight | 608.34 | 276.33 | 339.44 |
| Temperature/K | 100.0 | 293.0 | 293.0 |
| Crystal system | Orthorhombic | <u>Monoclini</u> c | <u>Triclinic</u> |
| Space group | <u>Pn2₁a</u> | <u>P2</u> 1 | P-1 |
| a/Å | <u>21.8290 (3)</u> | 8.8848(2) | 7.2885(4) |
| $b/{ m \AA}$ | <u>16.9484 (3)</u> | 6.3713(1) | 8.8646(5) |
| $c/{ m \AA}$ | <u>7.11447 (13)</u> | 12.6507(2) | 14.0050(8) |
| α/° | 90.00 | 90 | 95.660 |
| β/° | 90.00 | 94.429(2) | 100.258 |
| $\gamma/^{\circ}$ | 90.00 | 90 | 112.670 |
| Volume/Å ³ | <u>2632.11 (7)</u> | 713.99(2) | <u>807.54 (9)</u> |
| Z | 4 | 2 | 2 |
| $ ho_{calc} mg/mm^3$ | 1.533 | 1.285 | 1.369 |
| F(000) | 1228 | 292 | 355 |
| Crystal size/mm ³ | $\underline{0.54} \times \underline{0.19} \times \underline{0.13}$ | $\underline{0.78}\times\underline{0.51}\times\underline{0.38}$ | $\underline{0.32} \times \underline{0.17} \times \underline{0.10}$ |
| 20 range for data collection | 4. 84 to70.6° | 3.84 to 70.15° | 5.47 to 70.7° |
| Reflections collected | 12770 | 5753 | 11870 |
| Independent reflections | 2533[Rint= 0.11] | 2091[Rint= 0.019] | 3088 [Rint=0.034] |
| Data/restraints/parameters | 2583/1/326 | 2014/1/195 | 3033/0/223 |

Table 2:

 \mathbf{Y}

| HA-1 | | HA-2 | | НА-3 | |
|--------------------|----------|------------|----------|-------------|------------|
| Bond lengths (Å) | | | | | |
| Br2—C20 | 1.893(5) | C1—C11 | 1.393(5) | N1—C11 | 1.332(3) |
| Br1 —C5 | 1.912(6) | C1—C12 | 1.447(4) | N1—C12 | 1.396(2) |
| O1 —C2 | 1.351(6) | C1—C9 | 1.455(4) | C1—C11 | 1.392(3) |
| N1 —C7 | 1.286(7) | O1—C2 | 1.265(4) | O1—C2 | 1.268(2) |
| N1 —C8 | 1.425(6) | N2—C16 | 1.379(5) | O2—C18 | 1.428(3) |
| C2 —C3 | 1.388(6) | N2—C12 | 1.394(4) | C15—N2 | 1.457(3) |
| C2 —C1 | 1.397(7) | C13—C12 | 1.326(4) | N2—O3 | 1.216(3) |
| C5—C6 | 1.365(7) | N1—C11 | 1.327(4) | N2—O4 | 1.221(3) |
| C22—N2 | 1.284(6) | N1—C12 | 1.418(4) | C5—C6 | 1.364 (3) |
| N2 —C23 | 1.418(6) | C6—C7 | 1.383(7) | C7—C6 | 1.394(3) |
| Bond angles (°) | | | | | |
| C7—N1—C8 | 119.3(4) | C11—C1—C2 | 119.4(3) | C11—N1—C12 | 127.02(17) |
| O1—C2—C3 | 118.4(4) | C11—C1—C9 | 120.4(3) | C11—C1—C2 | 119.26(18) |
| O1—C2—C1 | 121.5(4) | C2—C1—C9 | 120.1(3) | C11—C1—C9 | 121.03(17) |
| C3—C2—C1 | 120.1(5) | C16—N2—C12 | 117.2(3) | O2—C13— C14 | 125.29(18) |
| C21—C20— Br2 | 119.4(4) | O1 —C2— C3 | 120.4(3) | O2—C13—C12 | 114.63(18) |
| N2—C22—C16 | 122.0(4) | 01—C2—C1 | 122.1(3) | C17—C12—N1 | 124.08(18) |
| N1—C7—C1 | 121.3(4) | C11—N1—C12 | 123.8(3) | N1—C12—C13 | 116.32(17) |
| C24—C23—N2 | 122.9(4) | N2—C12—N1 | 117.6(3) | O3—N2—O4 | 122.5(2) |

Table 3:

| T/ °C | Systems | I _{corr} / mAcm ⁻² | E _{corr} / mV (vs. SCE) | $\beta_{\rm a}/$ mV dec ⁻¹ | -β _c / mV dec ⁻¹ | θ | P/ % |
|-------|-----------------------|--|-------------------------------------|---------------------------------------|---|-------|------|
| 45 | 15 % HCl | 93.75±9.1 | -531±4 | 90 | 180 | | |
| | 15% HCl+0.01 mM HA-1 | 59.84±5.2 | -537±3 | 94 | 179 | 0.361 | 36.1 |
| | 15% HCl+0.05 mM HA-1 | 42.18±4.7 | -552±5 | 92 | 190 | 0.552 | 55.2 |
| | 15% HCl+0. 10 mM HA-1 | 31.25±4.1 | -560±4 | 87 | 193 | 0.666 | 66.6 |
| | 15% HCl+0.50 mM HA-1 | 21.86±2.6 | -518±3 | 93 | 170 | 0.766 | 76.6 |
| | 15% HCl+1.00 mM HA-1 | 10.12±1.8 | -514±4 | 97 | 185 | 0.892 | 89.2 |
| 60 | 15 % HCl | 203.50±16.4 | -520±5 | 92 | 185 | | |
| | 15% HCl+1.00 mM HA-1 | 15.46 ±1.1 | -524±4 | 89 | 176 | 0.924 | 92.4 |
| 45 | 15 % HCl | 93.75±9.1 | -531±4 | 90 | 180 | | |
| | 15% HCl+0.01 mM HA-2 | 52.49±4.9 | -533±3 | 95 | 175 | 0.441 | 44.1 |
| | 15% HCl+0.05 mM HA-2 | 38.51±3.3 | -542±6 | 86 | 171 | 0.589 | 58.9 |
| | 15% HCl+0. 10 mM HA-2 | 27.81±2.6 | -524±5 | 94 | 177 | 0.703 | 70.3 |
| | 15% HCl+0.50 mM HA-2 | 16.13±1.5 | -548±6 | 97 | 181 | 0.827 | 82.7 |
| | 15% HCl+1.00 mM HA-2 | 7.83±0.80 | -545±4 | 93 | 186 | 0.916 | 91.6 |
| 60 | 15 % HCl | 203.50±16.4 | -520±5 | 92 | 185 | | |
| | 15% HCl+1.00 mM HA-2 | 12.01 ±1.0 | -529±6 | 91 | 187 | 0.941 | 94.1 |
| 45 | 15 % HCl | 93.75±9.1 | -531±4 | 90 | 180 | | |
| | 15% HCl+0.01 mM HA-3 | 48.94±4.4 | -535±4 | 98 | 177 | 0.477 | 47.7 |
| | 15% HCl+0.05 mM HA-3 | 34.14±3.1 | -519±6 | 92 | 181 | 0.635 | 63.5 |
| | 15% HCl+0. 10 mM HA-3 | 22.12±2.3 | -529±3 | 94 | 187 | 0.764 | 76.4 |
| | 15% HCl+0.50 mM HA-3 | 11.94±1.1 | -540±3 | 97 | 185 | 0.872 | 87.2 |
| | 15% HCl+1.00 mM HA-3 | 3.51±0.5 | -555±6 | 96 | 171 | 0.962 | 96.2 |
| 60 | 15 % HCl | 203.50±16.4 | -520±5 | 92 | 185 | | |
| | 15% HCl+1.00 mM HA-3 | 5.08± 0.4 | -549 ± 4 | 95 | 183 | 0.975 | 97.5 |

Table 4:

| | СРЕ | | | | | | | | |
|--------------------|---------------------------|------------------------------------|------------------------------|--|---|-------|-------|-------|-------|
| Inhibitors code | C _{inh.} / mM | $R_{\rm s}/\Omega$ cm ² | $R_{\rm ct}/\Omega{ m cm}^2$ | C _{dl} / μF cm ⁻² | $\frac{Y_0}{\mu\Omega^{-1} \text{ s}^{\text{n}} \text{ cm}^{-1}}$ | п | α | θ | P/ % |
| Absence | 0 | 0.50 | 12.4±1.1 | 128.4 | 3.757 | 0.768 | | | |
| | 0.01 | 0.55 | 17.5±1.5 | 90.9 | 1.552 | 0.862 | -0.78 | 0.291 | 29.14 |
| | 0.05 | 0.61 | 28.8±2.6 | 55.2 | 0.945 | 0.874 | -0.76 | 0.569 | 56.94 |
| HA-1 | 0.1 | 0.66 | 40.1±3.7 | 39.7 | 0.652 | 0.885 | -0.73 | 0.690 | 69.07 |
| | 0.5 | 0.89 | 65.1±5.9 | 24.4 | 0.337 | 0.897 | -0.71 | 0.809 | 80.95 |
| | 1.0 | 1.25 | 130.7±10.9 | 12.1 | 0.181 | 0.906 | -0.68 | 0.905 | 90.51 |
| HA-2 | 0.01 | 0.61 | 20.7±1.7 | 76.9 | 1.192 | 0.878 | -0.81 | 0.400 | 40.09 |
| | 0.05 | 0.64 | 32.8±2.5 | 48.5 | 0.720 | 0.868 | -0.79 | 0.621 | 62.19 |
| | 0.1 | 0.71 | 51.6±4.8 | 30.8 | 0.495 | 0.888 | -0.77 | 0.759 | 75.96 |
| | 0.5 | 0.82 | 90.7± 7.5 | 17.5 | 0.247 | 0.895 | -0.74 | 0.863 | 86.32 |
| | 1.0 | 1.01 | 151.5±12.3 | 8.5 | 0.135 | 0.919 | -0.70 | 0.918 | 91.81 |
| | 0.01 | 0.53 | 26.3±2.2 | 60.5 | 0.922 | 0.893 | -0.85 | 0.528 | 52.85 |
| | 0.05 | 0.64 | 39.6±3.3 | 40.2 | 0.562 | 0.904 | -0.82 | 0.686 | 68.68 |
| HA-3 | 0.1 | 0.72 | 56.1±5.4 | 28.3 | 0.382 | 0.897 | -0.79 | 0.778 | 77.89 |
| | 0.5 | 0.84 | 109.2±8.6 | 14.5 | 0.202 | 0.932 | -0.76 | 0.886 | 88.64 |
| | 1.0 | 0.99 | 296.6±22.7 | 5.3 | 0.112 | 0.957 | -0.73 | 0.958 | 95.82 |
| | | | | | | | | | |

Table 5:

| Test | Samples | Elements (wt. %) | | | | | | | | | |
|---------------------|--|------------------|------|------|------|------|-------|------|-------|------|-------|
| | Pres | С | Si | Ni | Mn | S | 0 | Cr | Fe | Ν | Cl |
| Before corrosion | Carbon steel | 0.18 | 0.17 | 0.01 | 0.70 | 0.03 | - | 0.01 | 98.9 | - | - |
| | Carbon steel immersed in 15 % HCl | 0.16 | 0.14 | 0.01 | 0.52 | 0.02 | 34.40 | | 43.45 | - | 21.30 |
| fter corrosion | Carbon steel immersed in 15 % HCl+1.0 mM HA-1 | 4.37 | 0.09 | - | 0.43 | W AL | 12.40 | - | 71.54 | 6.40 | 4.77 |
| V | Carbon steel immersed in 15 % HCl+1.0 mM HA-3 | 6.87 | 0.01 | | 0.11 | - | 11.70 | - | 72.41 | 3.78 | 5.12 |
| | | | | | | | | | | | |

<u> Table 6:</u>

| Quantum chemical | HA-1 | HA-2 | HA-3 |
|---------------------------------------|----------|----------|----------|
| parameters | Model | Model | Model |
| u/ Dobyo | 3 022 | 2.23 | 7.01 |
| μ/ Debye | 3.922 | 2.23 | 7.01 |
| $E_{ m HOMO}$ / eV | -8.609 | -8.774 | -8.911 |
| $E_{ m LUMO}$ / eV | -0.410 | -0.600 | -1.190 |
| $\Delta E/ \mathrm{eV}$ | 8.199 | 8.174 | 7.721 |
| η/ eV | 3.87 | 3.54 | 3.34 |
| IP/ eV | 8.609 | 8.774 | 8.911 |
| H _f / kJ mol ⁻¹ | 172.58 | 210.62 | 76.66 |
| $E_{\rm e}/{\rm eV}$ | -49823.9 | -27990.2 | -21721.9 |
| C-CR/ eV | 43837.70 | 23802.40 | 18464.31 |



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| | ACCEL LED WIANOSCALL |
|---------------|--|
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| | Curve fitting of the corrosion data obtained from EIS measurements for carbon steel in |
| Figure 12 | 15% HCl containing various concentrations of inhibitors (a) HA-1, (b) HA-2 and (c) HA- |
| | 3 according to Langmuir adsorption isotherm model at 45 °C. |
| Figuro 13 | SEM images of carbon steel surfaces (a) before immersion and after immersion for 24 h |
| Figure 15 | in 15% HCl having (b) no inhibitor, (c) 1.0 mM HA-1 and (d) 1.0 mM HA-3. |
| Figure 14 | Frontier molecular orbital density distributions of the synthesized Schiff bases (a) HA-1, |
| rigure 14 | (b) HA-2 and (c) HA-3. |
| Figure 15 | Net atomic charge distribution on (a) monomer and (b) dimer of HA-1 molecule. |
| F ' 1(| Schematic representation of the mode of adsorption and inhibition mechanism of HA-2 |
| Figure 16 | onto the carbon steel surface. |
| Figuro 17 | Continuous variation plots for the prepared complexes in aqueous-alcoholic mixture at |
| Figure 17 | $[Fe^{2+}] = [L] = 1.0 \text{ mM} \text{ and } 298 \text{ K}.$ |
| Figure 18 | The suggested structures for the complexes which formed on the steel surface (a) [Fe |
| i igui e io | $(HA-1)_2$] and (b) [Fe $(HA-2)_2$]. |
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<u>Figure 1</u>

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<u>Figure 4</u>

<u>Figure 6</u>

<u>Figure 8</u>

<u>Figure 9</u>

<u>Figure 14</u>

<u>Figure 16</u>

Highlights

- The synthesized imines are good inhibitors for the corrosion of 15% HCl.
- Schiff base compounds were found to be mixed-type inhibitors.
- The adsorption of the inhibitors on steel surface obeyed Langmuir isotherm.
- The SEM and EDX analyses support the polarization and EIS data.
- Excellent correlation exists between inhibition efficiency and quantum chemical parameters.