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Experimental and theoretical studies on the inhibition of corrosion of mild steel by some Schiff bases in 0.1M HCl solution

Yiheyis B. Zemede and Ephrem G. Demissie*

Department of Chemistry, College of Natural and Computational Science, Hramaya University, Ethiopia

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ABSTRACT

*Four schiff bases, namely 4-((thiophene-2-yl) methyleneamino) phenyl sulphonamide (**I**), N,N'-bis((thiophene-2 yl)methylene)benzene-1,2-diamine (**II**), (2E)-2-((5-((E)-(2-hydroxyphenylimino) methyl)thiophene-2-yl)methyleneamino) phenol (**III**) and 2-(5-methoxy-2-hydroxy benzylidene amino) phenol(**IV**) were synthesized. The chemical structures of the products were confirmed by FT-IR, ^{1}H NMR, UV-Vis, mass spectral and elemental analyses techniques. Corrosion inhibition of the schiff bases were evaluated using weight loss and quantum chemical methods in a 0.1MHCl solution for mild steel. The Schiff bases had exhibited a good inhibitory action against corrosion of mild steel in the medium investigated. For further confirmation of the result, the values of inhibition efficiency obtained from weight loss measurements were correlated with theoretical values obtained through DFT calculations. The results were in a good agreement with the order of inhibition efficiency of the Schiff bases obtained from experimental results.*

Keywords: Schiff bases, Corrosion inhibition, weight loss measurement, quantum chemical parameters

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INTRODUCTION

Aggressive acid solutions are widely used for industrial applications such as pickling of metals and steel, processes which are normally accompanied by considerable dissolution and consumption of the metal. To control metal dissolution as well as consumption during these processes corrosion inhibitors are commonly used [1]. Compounds with functional groups containing hetero-atoms, which can donate lone pairs of electrons are found to be particularly useful as inhibitors of metal corrosion [2,3].

In this regards Schiff bases, since they at least contain an azomethine-N, are well-known organic inhibitors of various metal corrosion in acid media [4, 5]. The greatest advantage of Schiff base compounds as corrosion inhibitors is that they can be conveniently and easily synthesized from relatively cheap material [4]. Study revealed that the inhibition efficiency of Schiff bases is much greater than that of the corresponding amines and aldehydes [6]. The azomethine linkage, –HC=N– , which enriches the electron cloud in the back bone of the Schiff bases is responsible for their inhibition efficiency, which can be altered depending upon the type of substituent present on the aromatic rings. However, studies on the use of schiff base compounds as corrosion inhibitors are few in the literature. In addition, a perusal of literature reveals that corrosion inhibition efficiency of the Schiff bases we synthesized have not been reported earlier using quantum chemical calculations.

In view of the above point, we report herein the synthesis of four Schiff bases by condensing sulphanilimide, o-aminopehenol and o-pheneylediamne with 2-Hydroxy-5-Methoxybenzaldehyde, 2-thiophenecarboxaldehyde and

2,5-thiophenedicarboxaldehyde in the presence of glacial acetic acid (Scheme1). All the synthesized Schiff bases have been characterized on the basis of their elemental analysis, FT-IR, ^{1}HNMR, MS-EI and UV-Vis spectral data. The effect of the schiff bases on the corrosion behavior of mild steel in a 0.1MHCl solution was studied by weight loss method and based on theoretical studies using chemical reactivity descriptors such as energy of highest occupied molecular orbital (EHOMO), energy of lowest unoccupied molecular orbital (ELUMO), energy gap (ΔE), dipole moment (μ), electronegativity (χ), global hardness (η), softness (σ), the fraction of electrons transferred (ΔN) and chemical potential (μ)

MATERIALS AND METHODS

Materials and Analytical Methods

All chemicals used in this investigation were of analytical reagent grade (AR) and of highest purity available and hence used as received. The Schiff base components were purchased from Sigma Aldrich and Alfa. Melting points were recorded in open capillaries in Stuart Melting point, SMP10, apparatus. IR spectra of the compounds were recorded using KBr pellets on FT-IR spectrometer Perkin-Elmer Infrared model 337. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. ^{1}H NMR spectra of the Schiff bases in $CDCl_3$/ DMSO-d_6 were recorded on a BRUKER AVANCE III 500 MHz FT NMR Spectrometer. The EI mass spectra of the Schiff bases were recorded on GC-MASS spectrometer. Elemental analyses were performed on a CHN-Analyser: PERKIN-ELMER CHN-2400 analytical instrument.

Synthesis of Schiff bases

i) 4-((thiophene-2-yl) methyleneamino) phenyl sulphonamide (I)

Sulfanilamide (1.84 g, 0.0107 mole) dissolved in a 40ml of mixture of THF/EtOH in a ratio of 1:4,v/v was mixed with 2-thiophenecarboxaldehyde (1 ml,0.0107 mole) dissolved in 30ml of a mixture of same solvent. To this solution 2.5 ml of glacial acetic acid was added. The reaction mixture was refluxed on oil bath at 75^{o}C for 6hrs with continuous stirring. The progress of the reaction was monitored by TLC**.** The mixture was cooled and poured into ice-cooled water to precipitate Schiff base. The resulting colored precipitate was filtered and dried in vacuum oven at 80^{o}C. The dried solid product was recrystallized twice from hot ethanol and then dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The product isolated as Shiny yellow powder in 92% yield. The melting point of the product was found to be 217^{o}C.

IR (KBr cm^{-1}) **:** 3290 (υ(N-H);-NH_2), 1607 (υ(C=N)), 1335 (υ_{asym}(S=O)), 1314(υ_{sym}(S=O)), 1153(υ(C-N); aromatic),846 (υ(C-S-C)*asym),* 821(,υ(C-S-C)*sym*); **Uv-Vis** (Acetonitrile, nm): 269, 328; **^{1}HNMR (DMSO-D$_6$)**: δ=10.3 (s, 2H, NH_2), 8.82 (s, 1H,CH=N), 7.255-7.895 (m,7H, aromatic); MS [EI] m/z 267 [M+1]; **Elemental analysis (CHN):** ($C_{11}H_{10}O_2N_2S_2$) Found (Calc.) (%), C 49.52(49.56), H 3.77(3.75), N 10.48 (10.51).

ii) N,N'-bis((thiophene-2-yl)methylene)benzene-1,2-diamine(II)

The title schiff base was synthesized from o-phenylenediamine (4g, 0.037 mole) and 2-thiophenecarboxyaldehyde (8.3g, 0.07398 mole) by the Similar procedure employed for synthesis of **I**, except that the reaction mixture was refluxed at 85 ^{o}C for two extended hours. The product isolated as yellow powder in 73% yield. The melting point of the product was found to be 150 ^{o}C.

IR(KBr cm^{-1}) **:** 1600 (υ (C=N)), 851 (υ(C-S-C)*asym),* 834(υ(C-S-C)*sym*), 733 (υ(C-S)); **Uv-Vis**(DMF, nm): 242, 291,349; **^{1}HNMR**($CDCl_3$): δ= 8.7 (s, 1H,CH=N), 6.8-7.5 (m,10H, aromatic); **MS [EI]** m/z 297[M+1]. **Elemental analysis (CHN):** ($C_{16}H_{12}N_2S_2$) Found (Calc.) (%), C 64.78(64.83), H 3.96(4.05), N 9.37(9.45).

iii) (2E)-2-((5-((E)-(2-hydroxyphenylimino) methyl) thiophene-2-yl)methyleneamino) phenol (III)

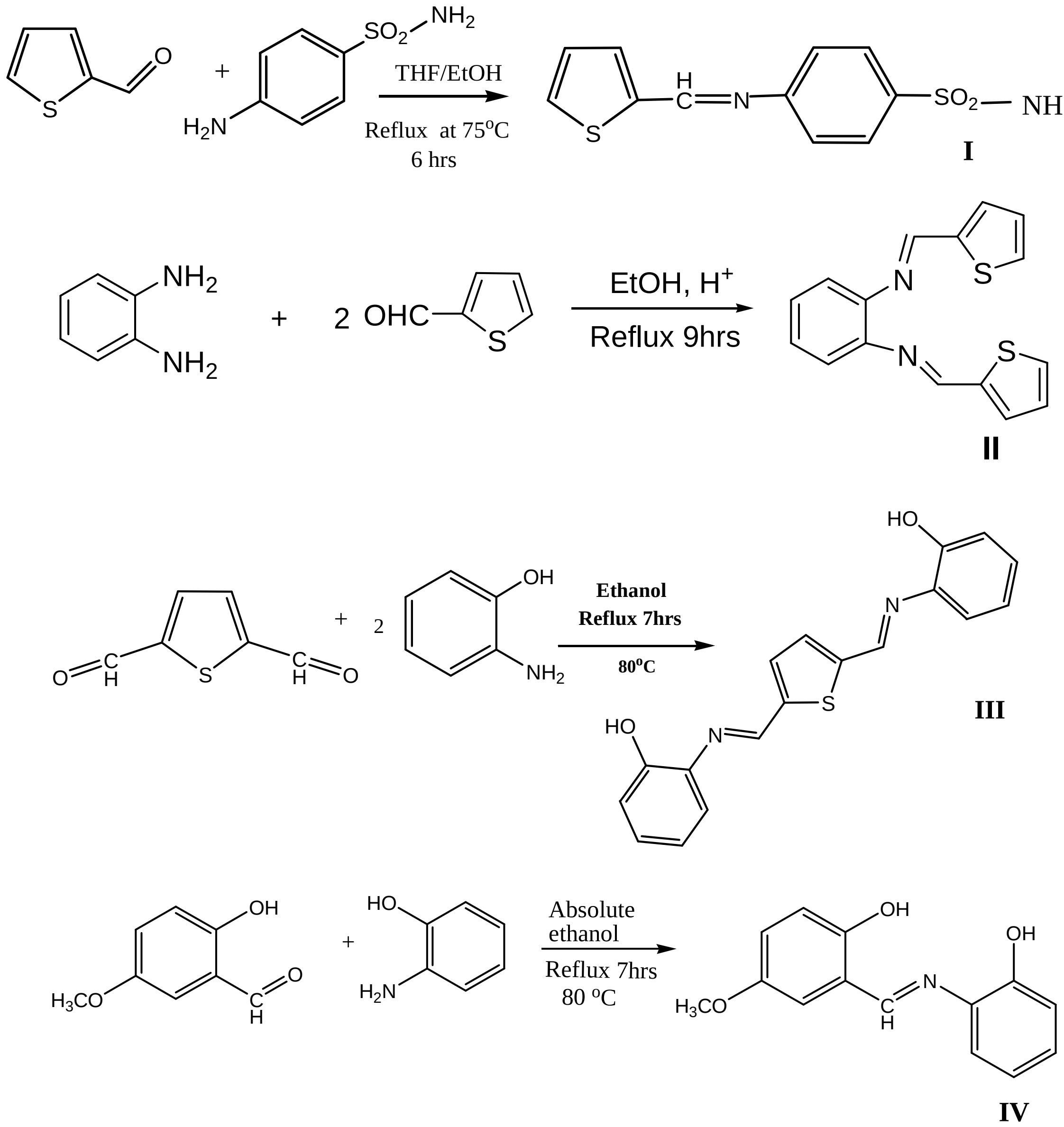
Similar procedure was used to synthesize the title schiff base from o-Aminophenol (0.1454 g, 0.0014 mole) and 2,5-Thiophenedicarboxaldehyde (0.0993gm,0.0007 mole), except that the solid product was precipitated out on cooling of the resulting reddish clear solution at room temperature. The product isolated as Golden yellow powder in 97% yield. The melting point of the product was found to be 189^{o}C.

IR (KBr cm^{-1}) **:** 3357 (υ(O-H)), 1612 (ν(C=N)), 1456 (ν(C–O) phenolic), 2698(ν(OH)), 820,807 (ν(C-S-C) (asym, sym)), 744 (ν(C-S)), 1152 (ν(C-N) aromatic); **Uv-Vis**(Acetonitrile, nm): 228, 268, 329 ; **^{1}HNMR** (DMSO-D$_6$) : δ= 13.08 (s, 1H,OH), 8.593(s, 1H,CH=N), 6.87-7.367 (m,10H, Aromatic); MS [EI] m/z 323 [M+1]: **Elemental analysis (CHN):** ($C_{18}H_{14}O_2N_2S$) Found (Calc.) (%), C 66.89 (66.99), H4.33 (4.34), N8.71(8.68).

iv) 2-(5-methoxy-2-hydroxybenzylideneamino) phenol (IV)

The title schiff base was synthesized from o-Aminophenol (0.874 g, 0.0080 mole) dissolved in a 30ml of absolute ethanol and 2-Hydroxy-5-Methoxybenzaldehyde (1.22gm,0.0080 mole) dissolved in 30ml of same solvent by the similar procedure employed for synthesis of **I**. The product isolated as reddish powder in 97% yield. The melting point of the product was found to be 157°C.

IR (KBr cm^{-1}) **:** 3444 (υ(O-H)), 1627 (υ(C=N)), 1517 (υ(C–O) phenolic), 2700 (υ(OH)), 1140,1040 (υ (C-O-C) (asym, sym)), 1222 (υ(C-N)), 2985-2830 (υ (C-H) -CH_3) ,737 (δ (C-H) aromatic); **Uv-Vis (**DMSO, nm**):** 238, 270, 370; **^{1}HNMR (DMF-D$_6$): δ** =12.678ppm (s,1H,OH), 8.689 (s,1H, CH=N), 6.945-7.447(m, 7H, 7ArH). MS [EI] m/z 244 [M+1]: **Elemental analysis (CHN): (**$C_{14}H_{13}O_3N$) Found (Calc.) (%) C 69.08 (69.06), H 5.35(5.34), N 5.75(5.75)



Scheme 1 Synthetic route for the new Schiff bases (I-IV)

Gravimetric measurements

Aggressive solution (0.1M HCl) was prepared by dilution of reagent grade 37% HCl with double distilled water. Inhibitor solutions with concentrations of 400 and 800ppm were employed for inhibition studies and were prepared by dissolving the required amount of the schiff bases in 80 ml of 0.1 M HCl by stirring at room temperature. 80 ml of 0.1 M HCl without inhibitor was used as blank test solution.

In the weight loss experiment, beakers of 100ml capacity were labeled 1 to 9, each containing 0.1M of HCl solution. The first beaker was reserved as blank while each of the remaining beakers contained the schiff bases at concentrations of 800 and 400 ppm. All placed at room temperature. Mild steel coupons having 1 × 1 × 0.1 cm size were abraded with emery paper and washed with ethanol, acetone, distilled water then dried and weighed. The area of the mild steel coupons was measured. The coupons were immersed in hanging position in the experimental solutions with the help of glass hooks for two days. The weights of the specimens were noted before immersion. After immersion time of 48 hours, the specimens were removed, polished with emery papers, washed in distilled water, degreased with acetone, dried in oven, and reweighed. Duplicate experiments were conducted at same time and average values were taken. From the initial and final weights of the specimens, the loss of weights was calculated, ΔW, as follows:

$$\Delta W = \frac{m1 - m2}{A} \qquad (1)$$

where $m1$ is the mass of the specimen before corrosion, $m2$ the mass of the specimen after corrosion, and A the exposed area of the specimen.

The corrosion rate (in mmy^{-1}) was computed from the following equation [7]

$$CR = \frac{87.6 \times W}{DAt} \qquad (2)$$

where W is the weight loss in mg, D is the density of the specimen (7.85 $\mathrm{g/cm}^3$), A is the surface area of specimen (cm^2) and t is the time of exposure of the sample in hours .

The efficiency of the inhibitor (%IE) was computed using the following equation [8]:

$$\%IE = \frac{\Delta W1 - \Delta W2}{\Delta W1} \times 100 \qquad (3)$$

Where $\Delta W1$ is the weight loss without inhibitor and $\Delta W2$ is the weight loss with inhibitor.

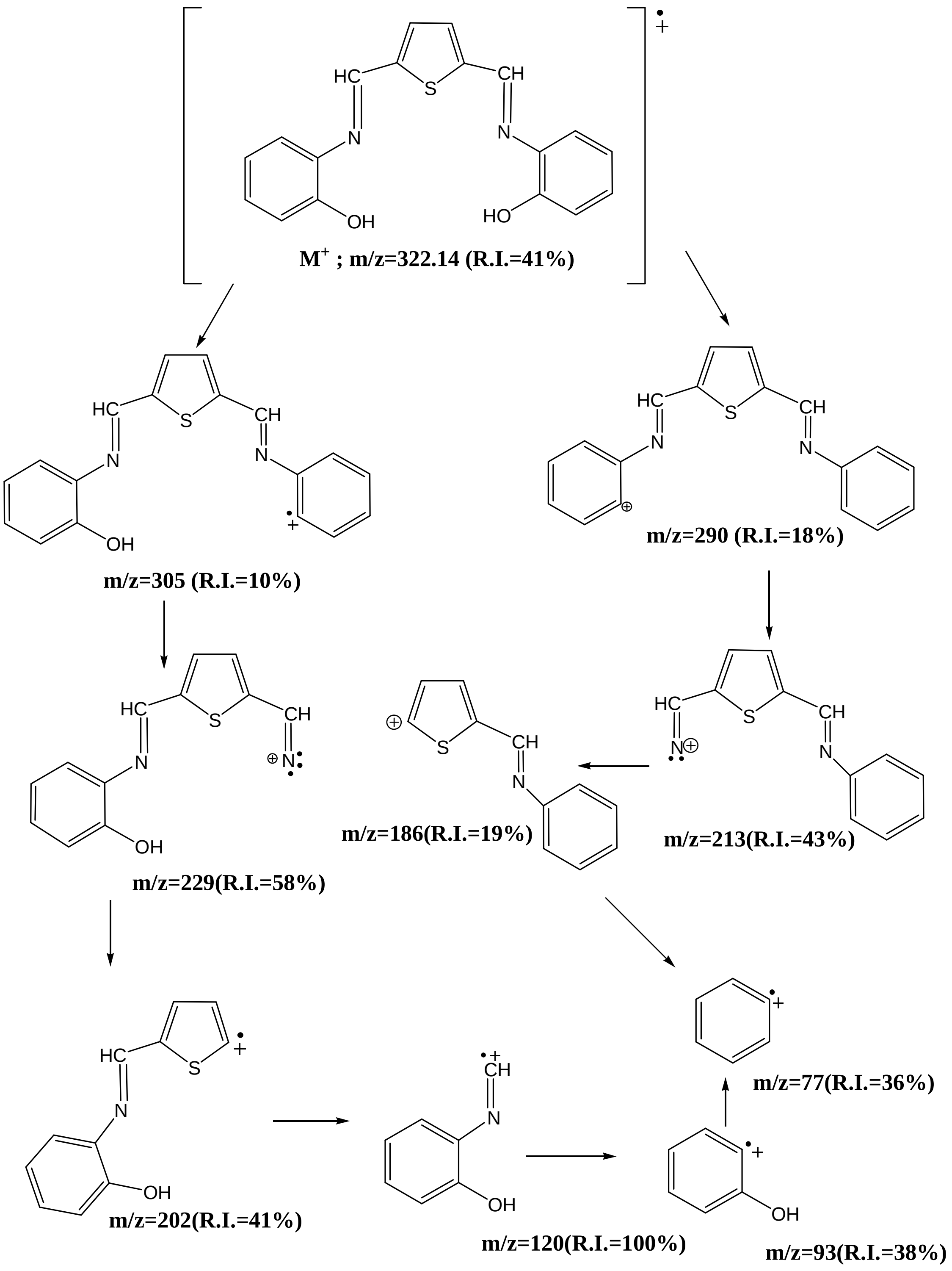
Computational Details

Quantum chemical calculations are carried out with Gaussian 09 packages at the DFT levels with the hybrid B3LYP exchange-correlation functional and the split-valence 6-31G(d,p) basis set. . Among quantum chemical methods for evaluation of corrosion inhibitors, density functional theory (DFT) has shown significant promise and appears to be adequate for pointing out the changes in electronic structure responsible for inhibitory action [9].

RESULTS AND DISCUSION

Characterization of the Schiff Bases (I-IV)

The route for the synthesis of Schiff bases (I-IV) and their structures is illustrated in Scheme 1. The synthesized Schiff bases were checked by comparing the TLC with the starting materials, which resulted in a single spot different from the starting materials. The Synthesis achieved in high yields**.** The structures of all synthesized compounds in Scheme 1 were confirmed on the basis of elemental analyses, IR, Uv-Vis, ^{1}H NMR and mass spectral data.



Scheme 2 Suggested mass fragmentation of Schiff base III

IR studies of each compound confirms the formation of -C=N- bonds as well as lack of -C=O- from original aldehydic compounds. The IR spectra of compounds I-IV showed absorption bands in the range of 1600-1627cm^{-1} due to -C=N- stretching. The bands in the range 1456-1517 and 3357-3480 cm^{-1} were due to C-O and O-H stretch, respectively, for compounds of III and IV. The spectra of the Schiff bases of **III** and **IV** exhibited a band in the range 3290-2560 cm^{-1} due to intramolecularly hydrogen bonded vibration (O-H---N)[10,11]. In the IR spectrum of **I**, N–H stretching and N-H bending vibrations were observed at 3290 and 1579 cm^{-1}, respectively. These values are in agreement with those observed for similar compounds [12,13]. In addition, **I** exhibited two bands at 1335 and 1314 cm^{-1} due to υ_{asym}(S=O) and υ_{sym}(S=O) stretching vibration of -SO_2- moiety, respectively. Similarly Schiff bases **I, II** and **III** exhibited two bands at 846,851 and 820, and 821,834 and 807 cm^{-1} due to υ(C-S-C) asymmetric and υ(C-S-C) symmetric stretching vibration of thiophene moiety, respectively.

The ^{1}H NMR spectra of compounds I-IV showed singlet in the range of 8.59-899 ppm which was due to the presence of azomethine,–CH=N-, proton [14]. The signal at13.08 and 12.678 ppm were due to the resonance hydroxyl groups of III and IV, respectively. The down field signal of OH group could be attribute to the contribution of the OH group to the intramolecular and intermolecular hydrogen bonding [15,16]. In addition to this, multiple signals lying in range 7.757-7.895, 6.8-7.5, 6.87-7.367 and 6.945-7.447 ppm were attributed to resonance of aromatic protons of schiff bases of I, II,III and IV, respectively [17,18].

The mass spectra of the schiff bases confirmed the structure of the Schiff bases as indicated by the peak corresponding to their molecular masses. The spectra showed a signal with m/z ratio of 266.35 (R.I.100%, base peak), 296.4379 (R.I.51%), 322.41 and 243.27 (R.I.100%, base peak) which are same as the calculated formula m/z= 266.35, 296.44, 322.14 and 243.12 for Schiff bases of I, II, III and IV, respectively. The m/z ratio of 266.35, 296.43, 322.41 and 243.27 confirm their molecular formulas are $C_{11}H_{10}N_2O_2S_2$, $C_{16}H_{12}N_2S_2$, $C_{18}H_{14}O_2N_2S$ and $C_{14}H_{13}O_3N$, respectively. It is observed that, the molecular ion peaks are in good agreement with their suggested empirical formula as indicated from elemental analyses. As representative example, the fragmentation of **III** obtained from the rupture of different bonds inside the molecule is shown in scheme **2**. The fragment was in good agreement with the proposed formula of the Schiff base. Similarly the spectral values for all the compounds and C, H, N analyses are given in the experimental part. The elemental analysis of the prepared Schiff bases is consistent with the calculated result from the empirical formula of the compounds. The melting points are sharp, which indicate the purity of the prepared Schiff bases.

The effect of Schiff Bases (I-IV) on acid Corrosion of Mild Steel

In order to study the effect of the synthesized Schiff bases on corrosion of mild steel in 0.1 M HCl, gravimetric measurements of mild steel was carried out in absence and presence of 800 and 400 ppm of the compounds in the same solution at room temperature. The percentage inhibition efficiency and corrosion rate calculated from the weight loss results for 48 h are given in Table 1.

Table 1: The weight loss, percentage inhibition efficiency and corrosion rate obtained for a mild steel coupon immersed in 400 and 800ppm of 0.1MHCl solutions of Schiff bases (I-IV) at RT for 48 h duration

Inhibitor	Inhibitor concentration (ppm)	Weight loss ($mgcm^{-2}$)	IE (%)	CR (mmy^{-1})
Blank	-	470	-	109.27
I	400	229.22	51.23	53.29
	800	183.91	60.87	42.76
II	400	159.80	66.00	37.15
	800	126.57	73.07	29.43
III	400	148.52	68.4	34.53
	800	111.39	76.3	25.90
IV	400	141.0	70.0	32.78
	800	100.11	78.7	23.27

It can be seen from the data that the Schiff bases synthesized in this study exhibited good corrosion inhibition efficiency against corrosion of mild steel in a 0.1MHCl solution. This might be due to coordination by the donor-acceptor interactions between the unshared electron pairs of donor atoms of the schifff base and metals in the steel [19,20]. The order of inhibition efficiency is **IV>III>II>I**. The higher in inhibition efficiency of **IV** compared to **III** was due to the effect of additional –OCH_3 substituent group on the aromatic ring. The methoxy and hydroxyl groups exhibit an inductive effect that results in changing the electron density and activate the aromatic ring, which may impart better absorptivity to the inhibitor. The effect would result in improved adsorption of the chemisorptions type through the aromatic ring and confer better protection than the others. The poor inhibition effect of **I** was rather due to the sulfonamide substituent that deactivates the aromatic ring. Further in the case of **III** and **IV**, the presence of –OH groups in the ortho position would facilitate the formation of chelates that stabilize the interaction between the

Schiff bases and the metals. The inhibition efficiency increased with increased concentration of the compounds. This suggests corrosion inhibition is a result of adsorption of inhibitor on the metal surface and the compounds acts as adsorption inhibitors. The inhibition efficiency of the Schiff bases was better at higher concentration. This might be due to larger coverage of the steel with inhibitor molecules [21].

Thus, among all the compounds synthesized in this study, III and IV could be best used as corrosion inhibitors to protect and control metals deployed whenever aggressive acid solutions are used in industry for cleaning, descaling and pickling of steel structures, processes which are normally accompanied by considerable dissolution as well as consumption of the metal.

Theoretical Calculation

Global chemical reactivity

The researchers are often encouraged to use theoretical data in their studies not only to support their experimental results but also to find the efficient way to minimize the chemical expenditures [22]. The major thrust of quantum chemical research is study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities [23,24]. Among quantum chemical methods for evaluation of corrosion inhibitors, density functional theory (DFT) has shown significant promise and appears to be adequate for pointing out the changes in electronic structure responsible for inhibitory action [23,25]

According to Koopman's theorem [26], the energies of the HOMO and the LUMO of the inhibitor molecule are related to the ionization potential and the electron affinity respectively according to equations 4 and 5. The calculated quantum chemical indices values of E_{HOMO}, E_{LUMO}, dipole moment and energy gap of the investigated inhibitor from Gaussian 09 using DFT/B3LYP given in Table 2.

$$I = -E_{HOMO} \tag{4}$$

$$A = -E_{LUMO} \tag{5}$$

Table 2: Global chemical reactivity indices for schiff bases I-IV calculated using B3LYP/6-31G (d,p) in aqueous solution

Parameters	I	II	III	IV
E_{HOMO}	-0.22873	-0.20049	-0.19837	-0.19464
E_{LUMO}	-0.07767	-0.07823	-0.07925	-0.08002
Energy gap (ΔE)	0.15106	0.12226	0.11912	0.11462
Dipole Moment (D)	4.73880	2.32310	3.87780	0.66520
Ionization Energy (I)	0.22873	0.20049	0.19837	0.19464
Electron Affinity (A)	0.07767	0.06123	0.07925	0.08002
Global Hardness (η)	0.07553	0.06113	0.05956	0.05731
Electronegativity (χ)	0.15320	0.13936	0.13881	0.13733
Chemical potential (μ)	-0.15320	-0.13086	-0.13881	-0.13733
Global Softness (S)	13.23977	16.35858	16.78979	17.44896
Transferred electrons fractions (ΔN)	0.18324	0.18533	0.18546	0.18571

According to the frontier molecular orbital theory of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species (Figure 1) [27]. The deeper reason is that the shapes of the HOMO and LUMO resemble features in the total electron density, which determines the reactivity. The energy of highest occupied molecular orbital measures the tendency of the inhibitor to donate the electron. The adsorption of the inhibitor on the metal surface can occur on the basis of donor–acceptor interactions between the π-electrons of the heterocyclic compound and the vacant d-orbital of the metal surface atoms [28]. As can be seen from table 2, the E_{HOMO} of these heterocyclic compounds increased in the following order: I<II<III<IV. With increasing the energy of E_{HOMO} of the inhibitor the electrons can jump easily to the metal surface, which in turn enhancing the adsorption of the inhibitor on mild steel and therefore has better inhibition efficiency [29]. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower value of E_{LUMO}, the more probable the molecule accepts electrons [30]. The E_{HOMO} values show that Schiff Base IV has the lowest energy compared to other Schiff bases. In this study, it is experimentally shown that Schiff Base IV decelerates the corrosion rate. This result is also supported by the calculated quantum chemical parameters i.e., the highest E_{HOMO} and the lowest E_{LUMO} were found for Schiff Base IV which has best inhibition efficiency compared to

others. In addition, the smaller values of the energy gap (ΔE) will provide good inhibition efficiencies, because the excitation energy to remove an electron from the last occupied orbital will be low [31]. The ΔE decreased in the following order: I>II>III>IV. Survey of the literature reveals that several irregularities appeared in the case of the correlation of dipole moment and Inhibition efficiency [32, 33,]. In our theoretical calculation we observed a result as the dipole moment decreases the inhibition efficiency increases. Schiff Base I has the lowest inhibition efficiency among the inhibitors, which may be explained that too higher value of dipole moment will prevent the accumulation of inhibitor molecules in mild steel surface [34].

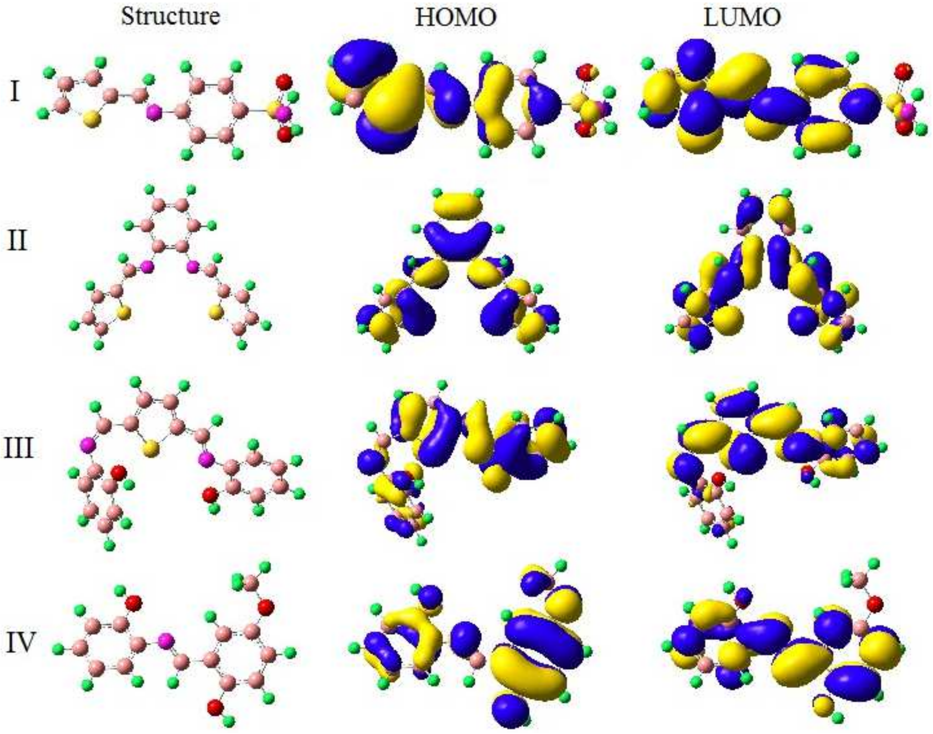


Figure 1: Optimized structure and HOMO-LUMO of sciff bases (I-IV)

Parr et al. established the basic relationship between the electronic chemical potential μ and electronegativity χ with the average arithmetic sum of the ionization potential (I) and electron affinity (A) as can been seen in eqn. (6) [35].

$$-\mu = \chi = \frac{I+A}{2} = \frac{-(E_{HOMO} + E_{LUMO})}{2} \qquad (6)$$

Electronegativity is a measure of how hospitable an atom or a group of atom in a molecule is to the access of electronic charge. With lowest electonegativity and highest chemical potential, a heterocyclic compound has best inhibition efficiency. It can be clearly seen from Table 2 that the inhibition efficiency based on the $E_{HOMO,}$ energy gap and the dipole moment for the Schiff bases compounds followed the order of I<II<III<IV. This was in a good agreement with the experimentally determined inhibition efficiency values.

Absolute hardness and softness are also important properties to measure the global chemical reactivity and molecular stability. Global softness (σ) is the reciprocal of global hardness, which again can be approximated in terms of ionization potential (I) and the electron affinity (A) of the inhibitor molecule using the following equation (7) [36,37].

$$\sigma = \frac{1}{\eta} = \frac{2}{I-A} \qquad (7)$$

It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [38]. As can be seen clearly from Table 2, Schiff Base IV with lowest hardness (highest softness) value signifies high reactivity toward mild steel and corresponds to the highest inhibition efficiency.

According to Pearson theory [39], the number of electrons transferred (ΔN) can be calculated depending on the quantum chemical method as shown below.

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \qquad (8)$$

where χ (Fe) and χ (inhibitor) denotes the absolute electronegativity of iron and the inhibitor molecule, respectively; η (Fe) and η (inhibitor) denotes the absolute hardness of iron and the inhibitor molecule respectively. ΔN shows inhibition efficiency resulting from electrons transferred from the inhibitor molecule to the iron atom [31]. According to Lukovits et al.[40] , if the value of ΔN is less than 3.6, the efficiency of inhibition increases with increasing electron-donating ability of the inhibitor at the metal surface. In this study, it can be seen from Table 2 that the ability to donate electrons to the metal surface (ΔN) follows the order I<II<III<IV, which is in good agreement with the order of inhibition efficiency of these inhibitors obtained from experimental results.

Local chemical reactivity (Fukui functions)

The local reactivity of the molecules was analyzed through an evaluation of the Fukui function was introduced by Parr and Yang [41]. This function used as a measurement of changes in electron density that accompanies chemical reactions; indicative of the reactive regions, that is, the nucleophilic and electrophilic behavior of the molecule [42]. The change in electron density is the nucleophilic $f^{+}(r)$ and electrophilic $f^{-}(r)$ Fukui functions, which can be calculated using the finite difference approximation as equations 9 and 10.

$$f^{+}(r) = q_{N+1} - q_N \qquad (9)$$

$$f^{-}(r) = q_N - q_{N-1} \qquad (10)$$

Where q_N , q_{N+1} and q_{N-1} are the electronic population of the atom in neutral, anionic and cationic systems. The values of Fukui functions for a nucleophilic and electrophilic attack of the Schiff base compounds were shown in Table 3-6 (only for the nitrogen, sulphur, oxygen and carbon atoms). For nucleophilic attack, the most reactive site of Schiff base I is on the S7, O9 and C14 atom, Schiff base II is on the C5, C6, S14 and S20 atom, Schiff base III is on C5, C12, C17 and O22 atom and Schiff base IV is on C6 and C8 atom. For electrophilic attack, the most reactive site of Schiff base I is on the S15 and N17 atom, Schiff base II is on C9, S17, C15 and S20 atoms, Schiff base III is on N15 and C23 atoms and Schiff base IV is on C10 and N1120 atom. As can be seen from Figure 1 the electron density distributions of HOMO and LUMO on each inhibitor are basically consistent with the atoms that exhibit greatest values of nucleophilic and electrophilic Fukui functions, which demonstrate that these active atoms will play a significant role in the interaction with the iron surface.

Table 3 Fukui function for Schiff base I calculated from Mulliken atomic charges

Atom No.	f_k^-	f_k^+
C1	0.05692	0.0217
C2	-0.00495	0.00915
C3	0.02013	0.03522
C4	-0.02849	0.02248
C5	0.0234	0.03402
C6	0.009	0.01331
S7	0.05948	**0.04728**
O8	0.0262	0.03315
O9	0.03266	**0.04298**
N10	-0.00651	0.00336
C11	-0.0261	-0.00268
C12	0.0365	0.03731
C13	-0.00123	0.01142
C14	0.03352	**0.04334**
S15	**0.1268**	0.12107
C16	0.06587	0.02629
N17	**0.0886**	0.01709

Table 4 Fukui function for Schiff base II calculated from Mulliken atomic charges

Atom No	f_k^-	f_k^+
C1	0.00068	0.02125
C2	0.01809	0.01707
C3	0.01809	0.01707
C4	0.00074	0.02123
C5	-0.00056	**0.04137**
C6	-0.00048	**0.04129**
N7	0.03869	0.00306
N8	0.03873	0.00300
C9	**0.04762**	0.01735
C10	-0.01847	-0.00944
C11	0.02907	0.02687
C12	-0.00027	0.00670
C13	0.02719	0.02759
S14	**0.07615**	**0.06385**
C15	**0.04762**	0.01735
C16	-0.01847	-0.00944
C17	0.02907	0.02687
C18	-0.00027	0.00670
C19	0.02719	0.02759
S20	**0.07614**	**0.06386**

Table 5 Fukui function for Schiff base III calculated from Mulliken atomic charges

Atom No	f_k^-	f_k^+
C1	0.04069	0.02692
C2	-0.1047	0.08321
C3	0.02368	0.02352
C4	0.00982	0.01005
C5	0.01397	**0.02106**
C6	-0.0099	0.01004
O7	0.03269	0.04177
N8	0.1825	0.01036
C9	0.00483	-5.6E-4
C10	0.01129	0.02945
C11	0.01008	0.00984
C12	-0.00598	**0.02171**
S13	0.11663	0.01726
C14	0.04259	0.01125
N15	**0.06969**	-0.01011
C16	-0.03501	0.01123
C17	0.02461	**0.02215**
C18	0.00669	0.00848
C19	0.01893	0.01548
C20	-2.9E-4	0.00247
C21	0.02239	0.01866
O22	0.00274	**0.02026**
C23	**0.06596**	0.01702

Table 6 Fukui function for Schiff base IV calculated from Mulliken atomic charges

Atom No	f_k^-	f_k^+
C1	-2.49E-4	-0.05061
O2	0.00309	0.0607
O3	0.00342	0.07015
C4	-0.00182	0.07204
C5	-0.00309	0.03667
C6	-8.09E-4	**0.08026**
C7	8.1E-5	0.03201
C8	-0.00279	**0.08599**
C9	-0.01419	-0.01197
C10	**0.00996**	0.10277
N11	**0.03845**	0.07672
O12	0.00603	0.05675
C13	0.00268	0.02741
C14	0.00543	0.05105
C15	-6.75E-4	0.01122
C16	0.01476	0.04743
C17	-0.03571	0.01912
C18	0.00384	0.06671

CONCLUSION

In the present work, four Schiff bases were synthesized and characterized by analytical and spectral techniques. The compounds were evaluated for their corrosion inhibition behavior against corrosion of mild steel. The experimental result was supported by quantum chemical method. In conclusion, from the corrosion inhibition study, it was observed that both electron donating and electron withdrawing groups of the compounds influenced the efficiency and activity of the compounds. The Schiff bases synthesized in this study exhibited different corrosion inhibition efficiency against mild steel in a 0.1MHCl solution. The order was IV>III>II>I. Among all the compounds tested Schiff base IV being more efficient to protect metal deployed whenever aggressive acid solutions are used in industries for pickling of metals and steel and hence fabrication of such Schiff bases is highly beneficial in this regard.

REFERENCES

[1] W. D. Collins, R. E. Weyers, and I. L. Al-Qadi, **1993**, *Corrosion*, 49(1), 74-78
[2] N. A. Negm, and S. M. I. Morsy, *Journal of Surfactants and Detergents*, **2005**, 8(3), 283-287
[3] K. C. Emregul, A. A. Akay, and O. Atakol, *Material Chemistry and Physics*, **2005**, 93(2), 325 329
[4] H. Hosseini, F. L. Stijn, B. Mertens, M. Ghorbani, and M. R. Arshadi, *Materials Chemistry and Physics*, **2003**, 78(3), 800-808
[5] Y.A. Balaban, S. Kandemir, G. Bereket, and Y. Erk, *Material Chemistry and Physics*, **2004**, 85(2-3), 420-426
[6] Y. K. Agrawal, , J. D. Talati, M.D. Shah, M.N. Desai, and N. K. Shah, *Corrosion Science*, 2004, 46(5), 633-641
[7] J. I. Bhat and V. Alva, *Indian J. Chem. Techno*, **2009**, 16, 228–233
[8] I.A. Akpan and N.O. Offiong, *Chem. Mater. Res*., **2012**, 2, 40–47.
[9] Y. Yamamoto, H. Nishihara, and K. Aramaki, *Journal of the Electrochemical Society*, **1993**, 140(2), 436–443
[10] G. Mohamed, M. Omar and A. Ibrahim, *European Journal of Medicinal Chemistry*, **2009**, 44, 4801-4812
[11] S.A. Abdel-Latif, H.B. Hassib and Y.M. Issa, *Spectrochimica Acta A*, **2007**, 67, 950–957
[12] J. Balsells, L. Mejorado, M. Phillips, F. Ortega, G. Aguirre, R. Somanathan and P.J.Walsh, *Tetrahedron: Asymmetry*, **1998**, 9, 4135-4142
[13] U.K. Singh, S.N. Pandeya, S.K. Sethia, A. Pandey, A. Singh, A. Garg and P. Kumar, *International Journal of Pharmaceutical Science and Drug Research*, **2010**, 2, 216-228
[14] M.A. Redayan, *Journal of Baghdad for Science*, **2012**, 9, 532-540
[15] V.P. Daniel, B. Murukan, B. SindhuKumari and K. Mohanan, *Spectrochimica Acta A*, **2008**, 70, 403–410
[16] H. Naeimi, J. Safari and A. Heidarnezhad, *Dyes Pigments*, **2007**, 73, 251- 253
[17] G. Mohamed, M. Omar and A. Ibrahim, *Spectrochimica Acta A*, **2010**, 75, 678–685
[18] P. Bamfield, *Journals of American Chemical Society*, **1976**, 98, 804-808.
[19] K.S. Jacob and G. Parameswaran, *Corrosion Science*, **2010**, 52, 224-228
[20] H. Shokry, M. Yuasa, I. Sekine, R.M. Issa, H.Y. El-Baradie and G.K. Gomma, *Corrosion Science*, **1998**, 39, 2173-2186
[21] M. Mahdavian and M. Attar, *Corrosion Science*, **2009**, 51, 409- 414
[22] K.F. Khaled, *Corrosion Science*, **2010**, 52, 3225–3234
[23] E. G. Demissie, S. B. Kassa, G. W. Woyessa, *International Journal of Scientific & Engineering Research*, **2014**, 5(6), 304-312
[24] M. Sahin, G. Gece, F. Karci, S. Bilgic, *Journal of Applied Electrochemistry*, **2008**, 38, 809-815,
[25] P. M. Niamien, H. A. Kouassi, A. Trokourey, F. K. Essy, D. Sissouma, and Y. Bokra, *Materials Science*, **2012**, 1-15,.
[26] O. E. Nnabuk , I. I. Benedict, *Journal of Molecular Model*, **2011**, 359–376
[27] K. Fukui, Springer-Verlag, New York, **1975**
[28] A.Zarrouk, H. Zarrok, R. Salghi, B. Hammouti1, S.S. Al-Deyab, R. Touzani, M. Bouachrine, I. Warad, T. B. Hadda, *International Journal of Electrochemistry Science*, **2012**, 7, 6353–6364
[29] F. Bentis, M. Traisnel, H. Vezin, H.F. Hildebrand, M. Lagrenée, *Corrosion Science*, **2004**, 46, 2781–279.
[30] V.S. Sastri, J.R. Perumareddi, *Corrosion*, **1997**, 53, 617–621
[31] K.F. Khaled, *Corrosion Science*, **2010**, 52, 3225–3234
[32] Y. Feng, S. Chen, Q. Guo, Y. Zhang and G. Liu, *Journal of Electroanalytical Chemistry*, **2007**, 602, 115-122
[33] L. M. Rodríguez-Valdez, A. Martínez-Villafañe, and D. Glossman-Mitnik, *Journal of molecular Structure: THEOCHEM*, **2005**, 713(1–3), 65–70
[34] Jia-jun Fu, Su-ning Li, Ying Wang, Xiao-dong Liu, Lu-de Lu, *Journal of Material Science*, **2011**, 46, 3550–3559
[35] S. G. Sagdinc and Y. S. Kara, *Protection of Metals and Physical Chemistry of Surfaces*, **2014**, 50(1), 111–116
[36] G. Gokhan, *Corrosion Science*, **2008**, 50, 2961–2992
[37] A.M.Charles, *Journal of Chemical Science*, **2011**, 123, 727–731
[38] M. Yadav, Debasis Behera, R. R. Sinha and P. N. Yadav, *Acta Metallurgica Sinica. (English Letter)*, **2014**, 27(1), 37–46
[39] R.G. Pearson, *Inorganic Chemistry*, **1988**, 27, 734-740
[40] I. Lukovits, E. Kálmán, and F. Zucchi, *Corrosion*, **2000**, 57(1), 3–8
[41] R.G. Parr and W. Yang, *Journal of the American Chemical Society*, **1984**, 106, 4049-4050
[42] C. Lee, W. Yang and R.G. Parr, *Journal of Molecular Structure (THEOCHEM)*, **1988**, 163, 305-312