Interaction of two heterocyclic Schiff bases derived from 2-acetyl pyridine on mild steel in hydrochloric acid: Physicochemical and corrosion inhibition investigations

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CHRONICLE	ABSTRACT
	Two heterocyclic Schiff bases namely (E)-2-(1-(2-phenylhydrazono)ethyl)pyridine (or 2-acetyl pyridine phenyl hydrazone) (2APPH) and (E)-2-(1-triazylidineethyl)pyridine (or 2-acetyl pyridine semicarbazone) (2APSC) were synthesized, characterized and their corrosion inhibition behaviour as well as mechanism of inhibition were investigated by different techniques. Structural characterization includes NMR, Mass, IR and UV-visible spectroscopy and elemental analysis. Corrosion inhibition behaviour of aforesaid compounds on mild steel in 1M hydrochloric acid was examined by electrochemical methods including potentiodynamic polarization analysis and electrochemical impedance spectroscopic techniques. The mechanism of corrosion inhibition was explored and supplemented by adsorption and surface morphological studies. Quantum mechanical investigations on corrosion behaviour of compounds were also conducted and satisfying correlation was noticed between the results of corrosion measurement methods and quantum mechanical evaluations.

1. Introduction

The study of Schiff bases was considered as predominant research area to prevent the metal corrosion, since it is an important threat which can affect directly or indirectly on the economy[1-4]. Corrosion is the deterioration of metals and alloys by chemical or electrochemical means. Corrosion is considered as a universal phenomenon, omnipresent and omnipotent. In industrial fields, de-scaling, pickling etc. commonly employed for the metal surface cleaning, demands enormous amount of HCl and leads to metal disintegration. Many organic compounds containing azomethine (C=N) linkage act as corrosion inhibitor in acid media[5-10]. Schiff bases are organic compounds containing azomethine linkage and have many applications in corrosion science. The hetero atoms present in these molecules are responsible for the corrosion inhibition property for mild steel (MS), aluminium, copper and zinc in acid media[11-18].

The present investigation was done to examine the corrosion inhibition efficiency and mechanism of two novel heterocyclic Schiff base molecules derived from 2-acetyl pyridine on MS in 1M HCl solution. The experimental study was performed by different corrosion monitoring methods such as electrochemical investigations including polarization analysis and electrochemical impedance

spectroscopic method. The corrosion inhibition mechanism of the compounds was confirmed by adsorption studies and surface morphological analysis. Quantum mechanical investigations on corrosion inhibition using Gammess software were also performed.

2. Results and Discussion

2.1. Physicochemical discussions

2APPH: Elemental analytical data calculated: C, 73.9; H, 6.16; N, 19.90%. Found: C, 73.6; H, 6.12; N, 19%. Melting point: 220°C. The ^{1}Hnmr spectrum of the Schiff base 2APPH exhibited nine clear peaks. The methyl protons displayed a peak at 2.42δ. A weak broad peak exhibited at 10.48 δ was due to the NH proton and the broadness of the peak can be explained by the effects of H-bonding and quadrupole broadening. The peaks appeared in the range 7.78- 8.72 δ were assigned to the pyridine ring aromatic protons. In the ^{13}Cnmr spectrum a peak appeared at 12.1ppm assigned to methyl carbon atom and all 10 different type sp^2 hybridized carbon atoms on aromatic ring exhibited their signals in the range 114-149ppm. Mass: Base peak at 211 (M$^+$). The clear signals appeared at m/z 196, 194 and 106 were assigned due to the fragments $[C_{12}H_{10}N_3]^+$, $[C_{12}H_8N_3]^+$ and $[C_6H_6N_2]^+$ respectively. IR: 1606 cm^{-1} (C=N), 3343 cm^{-1} (-N-H). UV-vis: 28901cm^{-1} (n→π^*), 32680cm^{-1} (π→ π^*) and 39216cm^{-1} (π→π^*).

2APSC: Elemental analytical data calculated: C, 53.93; H, 5.61; N, 31.46. Found: C, 53.46; H, 5.45; N, 31.39. Melting point: 200°C. The eight distinct non equivalent protons of 2APSC exhibited eight clear peaks on ^{1}Hnmr spectrum. The three protons on sp^3 hybridized carbon atom (CH$_3$) showed its characteristic peak at 2.31δ. A broad peak observed at 3.9 δ is assigned to the NH$_2$ protons and the broadness of the peak can be explained by the effects of H-bonding and quadrupole broadening. The NH proton exhibited a peak at 10.167 δ and the peaks appeared in the range 7.91- 8.80 δ were assigned to the aromatic protons. A very weak peak appeared at 6.18 δ can be assigned to the –OH proton, which generates by the mechanism of tautomerism. In the ^{13}Cnmr spectrum the peaks appeared at 12.02ppm and 156ppm were displayed by methyl carbon atom and carbonyl carbon atom respectively. Mass: m/z at 178 (M$^+$). The base peak observed at m/z 134 is assigned to the fragment $[C_7H_8N_3]^+$, which was generated the removal of amide group from the molecular ion. The clear signals appeared at m/z 106, 78 and 51 were assigned due to the fragments $[C_7H_8N]^+$, $[C_5H_4N]^+$ and $[C_4H_3]^+$ respectively. IR: 1608 cm^{-1} (C=N), 3176 cm^{-1} (-N-H). UV-vis: 29142cm^{-1} (n→π^*), 34013 cm^{-1} (π→ π^*) and 39370cm^{-1} (π→π^*).

2.2. Corrosion Inhibition Studies

2.2.1. Gravimetric studies

Weight loss analysis of mild steel was performed by immersing metal coupons of 1 cm^2 area in 1 M HCl solution for 24hrs without and with the prepared Schiff bases at different concentrations. The percentage of inhibition of the prepared Schiff bases 2APPH and 2APSC are recorded in the table 1. From the analytical studies conducted it is evident that there is a significant increase in the corrosion inhibition efficiency with the introduction of Schiff bases in different concentrations in the corroding 1M HCl solution for the mild steel examined. Thus the prepared Schiff bases under study have the capacity to efficiently inhibit metallic disintegration of mild steel in the acidic medium even at very low concentration. The inhibiting Schiff bases 2APPH and 2APSC exhibited more than 80 percent inhibition efficiency at all examined concentrations as evident from the experimental results. However, inhibitor 2APPH performed marginally higher efficiency at all concentrations and a maximum inhibition efficiency of 95.64% was achieved at 1mM concentration.

Table 1. Inhibition efficiency of mild steel in the presence and absence of 2APPH and 2APSC in 1M HCl for 24hrs

Schiff base	Con (mM)				
	0.2	0.4	0.6	0.8	1
2APPH	88.99	91.43	94.31	95.09	95.64
2APSC	81.12	86.98	89.23	91.64	94.71

2.2.2 Electrochemical Impedance Spectroscopic studies (EIS)

The corrosion behaviour of MS in 1 M HCl without and with inhibitor was examined using impedance spectroscopic analysis at 30^0C. **Fig. 1** and **Fig. 2** represent the Nyquist plots and Bode plots of two Schiff bases 2APPH and 2APSC respectively. The impedance parameters including double layer capacitance (C_{dl}), solution resistance (R_s) and percentage of inhibition efficiency ($\eta_{EIS\%}$) were evaluated from the values of charge transfer resistance (R_{ct}) and tabulated in **Table 1**. At both higher and lower frequencies the capacitance loop intercepts the real axis. These intercepts at the high frequency end represents the solution resistance (R_s) and at the lower frequency end represent the sum of R_s and R_{ct}. The difference between these intercepts can be calculated to find out R_{ct} which is the measurement of the electron transfer that takes place on the exposed metallic surface under analysis and is inversely proportional to the corrosion rate of the surface.

The study of impedance behaviour was carried out by electric models which helped to evaluate numerical measurements for the chemical and physical properties of the corresponding electrochemical system under investigation. The equivalent circuit that exactly fit to the EIS curves generally consisted of a double solution resistance R_s, charge transfer resistance R_{ct} and double layer capacitance C_{dl} (Figure 3). Generally, all the Nyquist plots were observed in semicircles and showed some irregularities which can be ascribed to the non-homogeneous nature or roughness of the metal surface. From the **Table 2**, it was observed that along with the increasing of the inhibitor concentration, C_{dl} values were decreased and R_{ct} values were increased in the case of both inhibitors. The variation in R_{ct} values can be explained by the adsorption process by which the inhibition mechanism takes place. As the inhibitor concentration increases there would be a considerable increase in the amount of adsorption process. It is due to the prevention of the charge transfer of the metal atoms on the metallic surface and solution by adsorbed molecules resulting in raising the charge transfer resistance with increasing inhibitor concentration. The lowering of C_{dl} values with increase in the inhibitor concentration can be associated with the reduction of local dielectric constant values and rise in the thickness of electrical double layer. These observations testify the inhibitor action at the solution–metal interface.

Table 2. Electrochemical impedance parameters of MS corrosion with and without Schiff bases 2APPH and 2APSC in 1M HCl

Schiff base	C(mM)	$R_{ct}(\Omega cm^2)$	C_{dl}	$\eta_{EIS\%}$
	0	59.7	98.9	
2APPH	0.2	342	94.1	82.54
	0.4	359	77.9	83.30
	0.6	395	77.6	84.88
	0.8	445	66.9	86.58
	1	826	54.5	92.70
2APSC	0.2	231	102	74
	0.4	267	85.2	77.64
	0.6	317	84.7	81.16
	0.8	413	82.4	85.54
	1	470	81.6	87.29

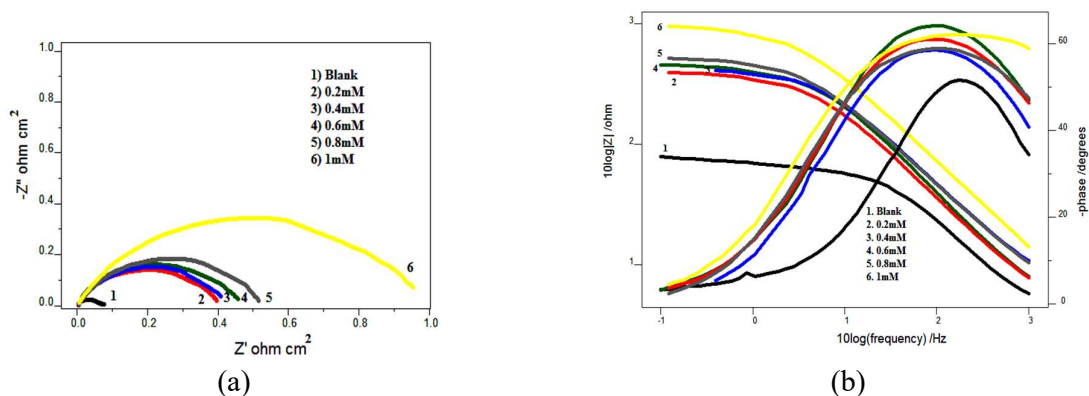(a)   (b)

Fig. 1. a) Nyquist plots and **b)** Bode plots of MS corrosion with and without 2APPH in 1M HCl

(a)   (b)
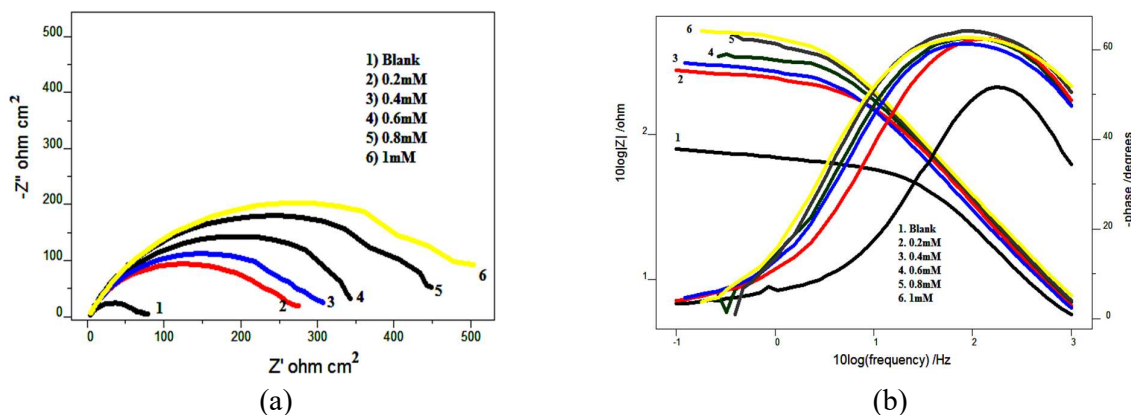
Fig. 2. a) Nyquist plots and **b)** Bode plots of MS corrosion with and without 2APSC in 1M HCl
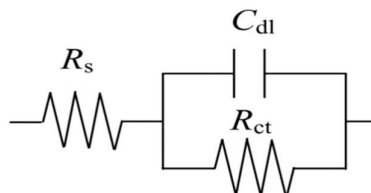

Fig. 3. Equivalent circuit for EIS measurements

From the data it is obvious that both Schiff bases 2APPH and 2APSC act as potential corrosion inhibitors in hydrochloric acid media. Both of them exhibited above 70% efficiency of corrosion inhibition and a maximum efficiency of inhibition, 92.7% was obtained for 2APPH at concentration of 1mM. The efficiency of inhibition of the two Schiff bases derived from 2-acetyl pyridine obeys the order 2APPH > 2APSC.

2.2.3   *Potentiodynamic polarization studies*

Tafel extrapolation analysis and linear polarization studies were conducted to establish the impact of Schiff base compounds towards the polarization of metal specimens by the determination of polarization resistance, corrosion current density and the percentage of inhibition efficiencies. Tafel polarization curves and linear polarization curves obtained for the different concentrations are represented in the **Fig. 3** and **Fig. 4.** The corrosion parameters -corrosion potential (E_{corr}), corrosion

current density (I_{corr}), polarization resistance (R_p) and inhibition efficiency percentage (η_{pol} %) are listed in **Table 3**.

Table 3. Polarization data for MS corrosion with and without inhibitors 2APPH and 2APSC in 1M HCl

Schiff Bases	Con (mM)	E_{corr} (mV/SCE)	I_{corr} ($\mu A/cm^2$)	b_a (mV/dec)	$-b_c$ (mV/dec)	η_{pol}%	R_p (ohm)	η_{Rp} %
				Tafel Data			**Polarization Data**	
2APPH	0	-498	360	122	150	-	83.23	-
	0.2	-458	110.8	86	188	69	232	64
	0.4	-425	103.9	75	166	71	215.4	61
	0.6	-455	87	81	191	76	282.8	70
	0.8	-460	66.4	72	164	82	327.8	75
	1	-450	34.4	61	143	90	542.8	85
2APSC	0	-498	360	122	150	-	83.23	-
	0.2	-456	66.6	71	163	82	321.6	74
	0.4	-451	56.2	64	155	84.3	351.8	76
	0.6	-460	55	66	144	84.7	358.4	76.7
	0.8	-453	54.2	67	150	84.9	370.4	77.5
	1	-448	53.2	62	162	85.2	367.7	77.7

(a)   (b)
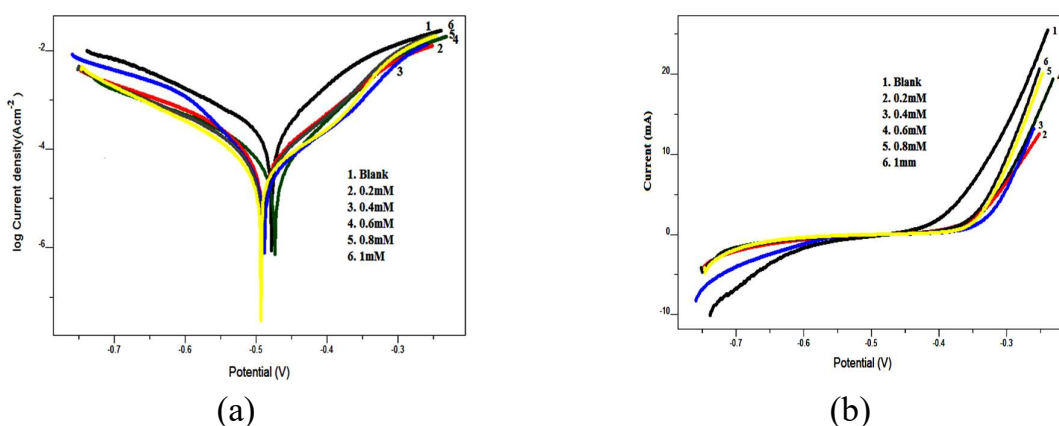
Fig. 3. a) Tafel plots and **b)**linear polarization curves for MS corrosion with and without of 2APPHin 1M HCl

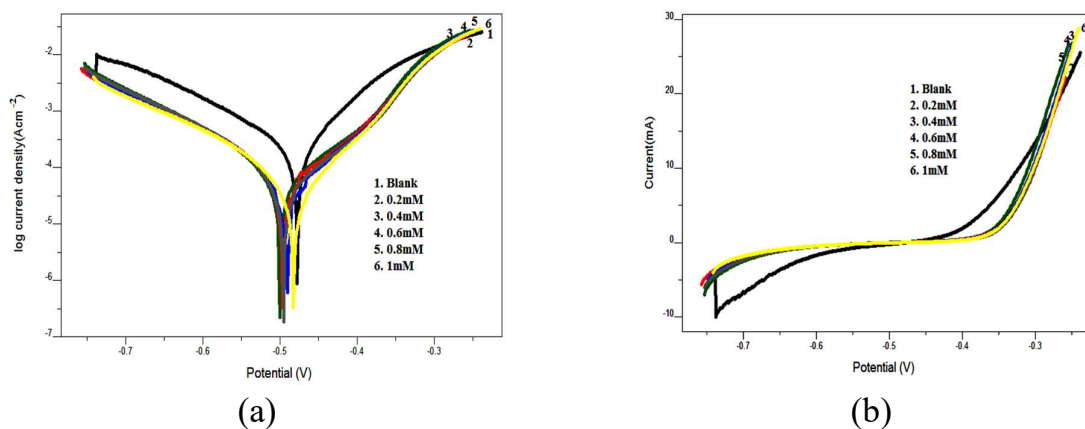(a)   (b)

Fig. 4. a) Tafel plots and **b)**linear polarization curves for MS corrosion with and without of 2APSC in 1M HCl

Tafel data analysis elucidates that the values obtained for corrosion current density (I_{corr}) were significantly decreased and high inhibition efficiencies were obtained in presence of both inhibitors in

1M HCl even at low concentrations. A closer examination clarified that the Schiff base 2APPH displayed more efficiency on MS surface as compared to 2APSC and a maximum inhibition efficiency of 85% achieved by 2APPH at 1 mM concentration. This is also congruent with the data obtained in gravimetric analysis and EIS measurements. In the cases of both Schiff bases 2APPH and 2APSC the cathodic slopes exhibited predominant changes than the anodic slopes which is a clear evidence for relatively higher adsorption of these Schiff bases on the cathodic sites. Furthermore, the E_{corr} value was not altered (>85) with respect to E_{corr} of blank experiment with the appreciable change in anodic or cathodic slopes in both the Schiff bases suggesting that in 1M HCl they are mixed type inhibitors for MS.

2.2.4 Adsorption studies

The mechanism of adsorption of the Schiff base under study represented in figure 6 and their surface modifications can be described by invoking suitable adsorption isotherms in which the commonly used ones are Langmuir, Temkin, Frumkin and Freundlich isotherms[19-23]. Evaluation of adsorption parameters is done by selecting the best fit isotherm model assisted by the correlation coefficient (R^2). **Fig. 5** represents the adsorption isotherms for the compounds 2APPH and 2APSC in 1M HCl. The adsorption behaviour of both 2APPH and 2APSC on MS specimens in 1M HCl were obtained from Langmuir adsorption isotherm and it can be expressed as

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \,,$$

where C is the concentration of inhibitor, θ is the fractional surface coverage and K_{ads} is the value of adsorption equilibrium constant. This adsorption equilibrium constant, K_{ads} mainly depends on the standard free energy of adsorption ΔG^0_{ads}, by the following relationship,

$$\Delta G^0_{ads} = -RT \ln(55.5 \, K_{ads})$$

where 55.5 is the molar concentration of water, R is the ideal gas constant and T is the temperature in Kelvin.
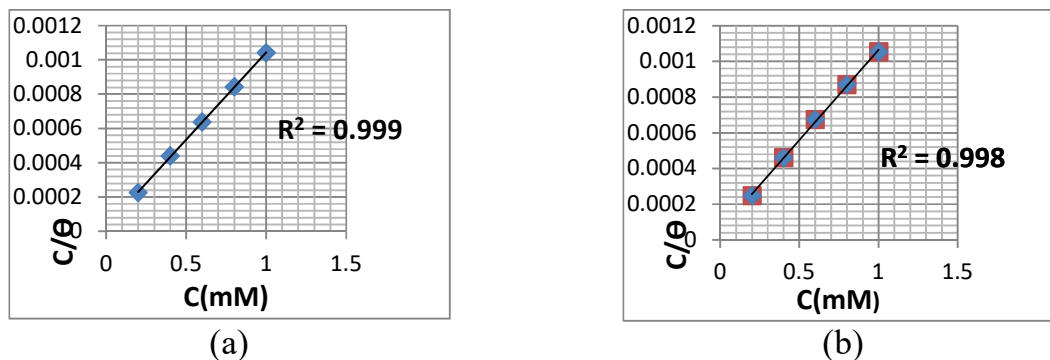
Fig. 5. Langmuir adsorption isotherms for **a)** 2APPH and **b)** 2APSC on MS in 1M HCl

The adsorption equilibrium constant K_{ads} represents the measurement of the adsorption taking place on the corresponding surface. The Schiff base 2APPH has K_{ads} value 33333, which is comparatively higher than K_{ads} value 20000 of 2APSC. It implies that the efficacy of adsorption of 2APPH is greater than that of 2APSC. The ΔG^0_{ads} values obtained for 2APPH and 2APSC are -36.13 and -34.85 KJ/mol respectively. The ΔG^0_{ads} values up to -20kJ mol^{-1} indicates clearly the electrostatic attraction or physisorption between a charged molecule and a charged metal surface whereas those more negative than -40kJ mol^{-1} indicates the strong adsorption of the inhibitors on metallic surface through strong co-ordinate bonds or chemisorption.

Fig. 6. Corrosion inhibition mechanism of Schiff base molecules on MS surface

2.2.5   Surface morphological studies

   To verify the inhibition mechanism of investigated Schiff base compounds on the MS surface, morphological studies were conducted by taking SEM images of steel surfaces[24,25].   represents the SEM images of bare sample, metal immersed in 1M HCl, and metal immersed in 1M HCl containing 1M 2APPH. On close examination of figures it was evident that the MS su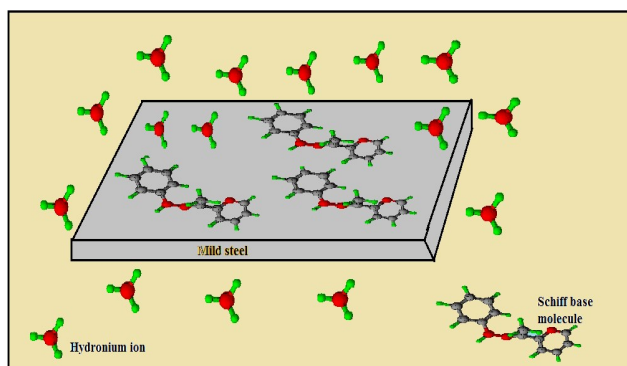rface was highly corroded in blank HCl solution. Small cracks and pits on the bare metal surface generated by the surface polishing were totally disappeared on the metal surface dipped in acid solution in the absence of Schiff base due to the intensive corrosion. The comparison of figures established that the surface damaging was appreciably decreased in the presence of 2APPH, which indicates that the corrosion tendency was considerably suppressed due to the formation of a protective film of 2APPH through adsorption.

(a)   (b)   (c)
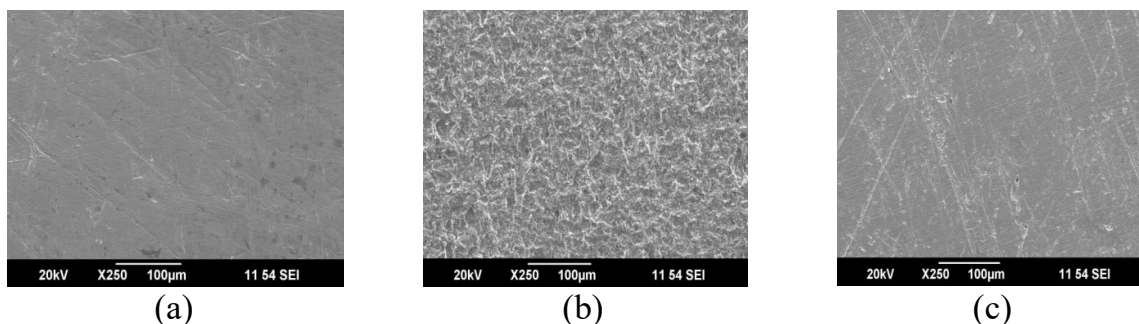
Fig. 7. a) bare sample **b)** metal immersed in 1M HCl **c)** metal immersed in 1M HCl containing 1M 2APPH

2.2.6   Quantum mechanical analysis

   The corrosion inhibition efficacy of Schiff base inhibitors can be correlated with the frontier molecular orbital energies. The HSAB concept (donor-acceptor interaction) between the vacant orbitals of Fe atoms and the filled molecular orbitals of the inhibitor compounds has an important role in the prevention mechanism of metal disintegration. The lowest $E_{\text{LUMO}} - E_{\text{HOMO}}$ (ΔE) value of inhibitors is the essential quantum mechanical parameter which helps them to bind on the metal surface strongly. Quantum mechanical evaluations were carried out using DFT method by GAMMES software. Calculated quantum mechanical parameters like E_{HOMO}, E_{LUMO}, ΔE, electronegativity (χ), hardness (η) and number of transferred electrons (ΔN) for the investigated inhibitors are tabulated in table 4. The HOMO and LUMO pictures of the inhibitors are represented in the figures 8 and 9 respectively. The ΔE between HOMO and LUMO is comparably low for 2APPH than 2APSC, which imply that 2APPH have predominant inhibition efficiency. These data indicate that the energy required to move electrons from HOMO of 2APPH to the vacant orbitals of Fe is very low. The ΔN values corresponding to the electron transfer from donor to acceptors are also evaluated from these quantum mechanical parameters

which provide the information about interaction with the metal atoms. Optimized structures of compounds, established quantum mechanically, are represented in the figure 10. The calculations are conducted using following equations,

$$\chi \approx -1/2 \ (E_{HOMO} + E_{LUMO}) \qquad\qquad \eta \approx 1/2 \ (E_{HOMO} - E_{LUMO})$$

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

Table 4. Quantum mechanical parameters of the Schiff base inhibitors on MS

Inhibitor	E_{HOMO}(eV)	E_{LUMO}(eV)	ΔE (eV)	χ	η	ΔN
2APPH	-3.2653	1.0612	4.3265	1.1020	2.1632	1.36
2APSC	-3.5919	1.1156	4.7075	102381	2.3537	1.22

(a)   (b)

Fig. 8. HOMO of **a)** 2APPH **b)** 2APSC

(a)   (b)

Fig. 9. LOMO of **a)** 2APPH **b)** 2APSC

(a)   (b)

Fig. 10. Optimized structures of **a)** 2APPH **b)** 2APSC

3. Conclusion

Both studied Schiff bases 2APPH and 2APSC displayed predominant corrosion inhibition efficiency on MS in 1M HCl medium. According to the electrochemical analysis, corrosion inhibition efficiency of the studied compounds followed the order 2APSC < 2APPH. The higher efficiency of 2APPH was explained by the presence of two aromatic ring systems in the molecule. Both compounds obeyed Langmuir adsorption isotherm on MS surface. Surface morphological analysis revealed that the studied compounds form a protective barrier on MS surface and resist the metallic disintegration appreciably. Quantum mechanical investigations using Gammess software was also established that 2APPH possesses relatively higher corrosion inhibition capacity.

4. Experimental analysis

4.1. Synthesis

Heterocyclic hydrazones were synthesized by the condensation reaction of equimolar amounts of 2-acetylpyridine and amino compounds such as phenyl hydrazine and semicarbazide in ethanol medium. The resulting solutions were concentrated and the separated crystals were collected and washed with ethanol. Recrystallization from methanol gave the desired products. The products were characterized by elemental (Vario EL III Element Analyzer) analysis, mass (Shimadzu,QP 2010 GCMS), nmr (Bruker Avance III HD, CDCl3 solvent), IR (Shimadzu affinity-1, KBr pellet method) and UV spectroscopic analyses

2-acetyl pyridine   Phenyl hydrazine   2APPH

2-acetyl pyridine   Semicarbazide   2APSC

4.2. Physicochemical Investigations

C H N analysis: Carbon, hydrogen and nitrogen percentage of the Schiff bases were measured by microanalysis using Elementar make Vario EL III model CHN analyzer. Infrared spectra: The infrared spectra of the Schiff base compounds were recorded by KBr pellet method in the range of 4000-400cm^{-1} on Shimadzu model FT-IR Spectrometer (Model IR affinity-1). The infrared spectra contain the characteristic stretching frequencies which help to predict the functional groups present in the compounds. Electronic spectra: The electronic spectra of the Schiff bases were recorded on a Shimadzu UV-Visible-1800 Spectrophotometer with DMSO as solvent. The obtained data gives additional evidence for the molecular structure of Schiff bases. Mass spectra: The mass spectral studies were carried out only after the removal of the impurities present in trace amount by chromatographic method. Mass spectra were recorded using Gcms Qp-2010 plus model. NMR spectra: ^{1}Hnmr and ^{13}Cnmr studies of the compounds were recorded in CDCl$_3$ and DMSO solvent using Bruker Avance lll, 400MHz model.

4.3. Gravimetrical measurements

The gravimetric measurements were carried out using ASTM standard method. Mild steel metal specimens of approximate composition C,0.42%; Mn,0.05%; P,0.01%; S,0.016%; Si,0.025% and rest

Fe were used for the studies. The weight loss happened for the metal specimens were calculated for 24 hours. A blank measurement was also taken without inhibitor addition. From weight loss measurements corrosion rate and percentage of corrosion inhibition efficiency was determined. The corrosion rate and the inhibition efficiency of compounds were calculated using Eq. (1) and Eq. (2), respectively.

$$\text{Rate of corrosion W} = \frac{\text{K} \times \text{wt. loss in grams}}{\text{Area in sq. cm} \times \text{time in Hrs} \times \text{Density}}, \tag{1}$$

where 'K' = 87600 (This is a factor used to convert cm/hour into mm/year), density of MS specimen = 7.88g/cc and the density of Cu = 8.76g/cc

Percentage of inhibition or the inhibition efficiency (η) is given by

$$\text{Inhibition efficiency } \eta = \frac{W - W'}{W} \times 100, \tag{2}$$

where W & W' are the corrosion rate of the MS specimen with and without the inhibitor respectively.

4.4. Electrochemical measurements

The steel samples used for the electrochemical studies were abraded with different grades of silicon carbide paper, washed and dried. Different inhibitor solutions were prepared in the concentrations range of 0.2–1.0mM in 1M HCl medium. Electrochemical studies were carried out using three electrode cell assembly consisting of MS as working electrode (exposed area 1cm^2), platinum electrode as counter electrode (1cm^2) and saturated calomel electrode (SCE) as reference electrode at 30^{0}C. For acid corrosion the working area of metal specimens were exposed to the electrolyte for 30 min prior to the experiment. Ivium Compact state electrochemical system together with Iviumsoft software package was used to perform the experiments.

4.4.1 Electrochemical Impedance Spectroscopic studies (EIS)

EIS measurements are were taken at constant potential in the frequency range from 1KHz to 100 mHz with amplitude of 10 mV as excitation signal[26-28]. The percentage of inhibition calculated by the following equation,

$$\eta_{EIS} \% = \frac{R_{ct} - R'_{ct}}{R_{ct}} \times 100$$

where R_{ct} and R'_{ct} are the charge transfer resistances of working electrode in the presence and absence of inhibitor, respectively.

4.4.2. Potentiodynamic Polarization studies

A potential range of +250 to -250 mV with a sweep rate of 1mV/s was used for the study[29]. Slope analysis of Tafel curves gave the corrosion current densities and the inhibition efficiency was calculated by the following equation

$$\eta_{pol} \% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100,$$

where Icorr and I'corr are corrosion current densities of the exposed area of steel rebar in the absence and presence of inhibitor respectively.

4.5. Surface Morphological analysis

The analysis of changes observed in the surface morphology of the metal surface helps to explain the inhibition mechanism by which the Schiff bases decrease the corrosion rate. This was carried out by recording scanning electron micrographs (SEM) of the surfaces of bare metal, metal immersed in

acid solution (48 h) and metal immersed in inhibitor solution (24 h). It was taken by the model JEOL model JSM-6390LV in the resolution value 2.00 x.

4.6. Quantum Mechanical evaluations

GAMMES software and DFT method were used for the determination of optimized geometry of compounds and quantum chemical evaluations. A combination of Lee–Yang–Parr nonlocal correlation functional (B3LYP) and Beck's three parameter exchange functional was employed in DFT method[30-32].

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