Research Article

Monitoring the Interaction of Two Heterocyclic Compounds on Carbon Steel by Electrochemical Polarization, Noise, and Quantum Chemical Studies

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A heterocyclic phenylhydrazone 2-[(*E*)-(2-phenylhydrazinylidene)methyl]pyridine (P2APH) and its reduced form 2-[(2-phenylhydrazinyl)methyl]pyridine (RP2APH) were synthesized, characterized, and subjected to corrosion inhibition investigation on carbon steel (CS) in 1M HCl using gravimetric, polarization, electrochemical noise, quantum chemical, and surface studies. P2APH showed more inhibition capacity than RP2PPH. But RP2PPH was very stable in acid medium and showed pronounced corrosion inhibition efficacy for days. Energy of HOMO and LUMO, their difference, number of electrons transferred, electronegativity, chemical hardness, and so forth were evaluated by quantum chemical studies. Agreeable correlation was observed between the results of quantum chemical calculations and other corrosion monitoring techniques.

1. Introduction

Acid corrosion is a serious problem in many metal industries. Metal surface cleaning processes like pickling and descaling will escalate the rate of corrosion appreciably since these practices consume large amount of acids. In oil industry, acidizing of oil wells with strong acids enhances the rate of corrosion of oil pipes. Generally HCl or H₂SO₄ is used for the above industrial purposes. The only solution to combat corrosion in these circumstances is the application of corrosion inhibitors [1–6]. Investigation of corrosion inhibition response of various molecules is very much alive in contemporary research. Many organic molecules possessing aromatic rings and heterocyclic atoms act as corrosion inhibitors in acidic media [7–10]. Structure and geometry of a molecule have a definite role in preventing the corrosion of metal in acid medium. Sometimes inhibitor molecules react with the aggressive medium and this leads to alteration in the inhibition response. For instance, the corrosion inhibition behaviour of Schiff base *N,N'*-bis(salicylidene)-1,2-ethylenediamine (Salen), mixture

of its parent compounds, and reduced form of Salen on carbon steel in 1M HCl solution was studied by da Silva et al. [11] using corrosion potential measurements, polarization studies, EIS, and spectrophotometric measurements. Results obtained in the presence of Salen were similar to those obtained in the presence of the parent mixture, implying that in acid medium the Salen molecule undergoes hydrolysis, regenerating its precursor molecules. Reduced Salen exhibited more inhibition efficiency than Salen.

To explore the mechanism of corrosion inhibition, contemporary investigators rely on computational quantum chemical and molecular simulation techniques [12–18]. Industries are ever in search of soluble, highly stable, economical, and potential corrosion inhibitors. In the present course of study, we synthesized two highly water soluble heterocyclic compounds derived from pyridine-2-aldehyde. This article reveals the corrosion inhibition behaviour of two heterocyclic molecules on carbon steel in HCl medium, which was explored by gravimetric, electrochemical, quantum chemical, and surface analytical techniques.

2. Materials and Method

2.1. Synthesis and Characterization. The phenylhydrazone (P2APH) was synthesized by the condensation of equimolar mixtures of pyridine-2-aldehyde and phenylhydrazine hydrochloride in ethanol medium under reflux condition for 4 h. The mixture was cooled in ice and the precipitated pale yellow coloured solid was filtered, washed with ethanol-water (1:1) mixture, and dried [19].

5 mmol of P2APH was dissolved in ethanol-water mixture (1:1). The mixture was cooled in ice bath and ethanolic solution of NaBH₄ (1 g in 10 mL) was added dropwise with constant stirring until the yellow colour of the reaction mixture disappeared. This mixture was kept for 10 h and the precipitated product (RP2APH) was filtered, washed with small quantities of water-ethanol mixture (1:1), and dried [20].

The products were characterized by elemental (Vario EL III Element Analyzer) analysis and mass (Shimadzu, QP 2010 GCMS), nmr (Bruker Avance III HD, dms_o-d₆ solvent), and IR (Shimadzu Affinity-1, KBr pellet method) spectroscopic analyses.

2.2. Metal Specimen and Corrosive Medium. Carbon steel coupons were abraded (1 × 1 × 0.15 cm) with various grades of SiC papers (120, 400, 600, 800, 1000, and 1200), washed with soap solution, and degreased by acetone. The approx. composition of the steel specimen was determined by EDAX technique (0.58% C, 0.07% Mn, 0.02% P, 0.015% S, 0.02% Si, and Fe the rest, Hitachi SU6600 model SEM). A stock solution of P2APH and RP2APH (1.0 mM) in 1 M HCl was prepared and diluted with 1 M HCl solution to get aggressive solutions in different concentrations (0.2-1.0 mM).

2.3. Gravimetric Studies. The metal specimens were immersed in the aggressive medium for 4 days at 29 ± 0.2°C with periodical evaluation of the corrosion rate. The rate of corrosion [21, 22] was determined by

$$v = \frac{KW}{DSt}, \quad (1)$$

where v = corrosion rate (mm^y), W = weight loss (g), S = surface area of metal specimen (cm²), t = time of treatment (h), D = density of specimen (gcm⁻³), and K = a constant (8.76×10^4).

The inhibition efficiency ($\eta_w\%$) was obtained [21] by the following equation:

$$\eta_w\% = \frac{v - v'}{v} \times 100, \quad (2)$$

where v & v' are the corrosion rate of the metal specimen in the absence and presence of the inhibitor, respectively.

2.4. Electrochemical Corrosion Studies. Three-electrode system was used for polarization studies in which saturated calomel electrode (SCE) acted as reference electrode. Platinum and metal specimen (both having 1 cm² area) acted as

counter and working electrodes, respectively. The working electrode was allowed to contact with the aggressive solution to attain steady-state open-circuit potential (OCP). Each metal specimen was immersed in the aggressive medium for a period of 30 min prior to the experiment at 29°C. Polarization studies were carried out in the potential range +250 to -250 mV with a sweep rate of 1 mV/s [23-26]. The inhibition efficiencies were calculated from the corrosion current densities using the following equation:

$$\eta_{pol}\% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100. \quad (3)$$

Electrochemical noise (ECN) experiments were performed in a three-electrode cell assembly, which consisted of two carbon steel electrodes (1 cm²) and SCE. All ECN analyses were conducted for a period of 1200 s [27, 28]. Ivium Compactstate electrochemical system controlled by iviumsoft software was employed for the electrochemical investigations.

2.5. Surface Morphological Studies. SEM analyses were conducted using Hitachi SU6600 model scanning electron microscope. Analysis of surface film deposited on CS was done by IR spectroscopy.

3. Results and Discussion

3.1. Structure of Molecules. The structures of molecules were confirmed by CHN and spectroscopic techniques. The results are summarized as follows. P2APH: CHN, found: (calc.), C%; 72.69 (73.09), H%; 4.98 (5.58), N%; 21.08 (21.32). Mass spectrum; M⁺ peak m/z = 196.75 (base peak) ([C₁₂H₁₁N₃]⁺), ¹Hnmr; 8.17δ(s) (CH=N), 12.08(s) (NH), ¹³Cnmr; 148.97 ppm (C-2 pyr), 143.35 ppm (C-1 ph), 144.41 ppm (CH=N).

RP2APH: CHN, found: (calc.), C%; 71.69 (72.36), H%; 6.66 (6.53), N%; 20.87 (21.11). Mass spectrum; M⁺ peak m/z = 198.84 (base peak) ([C₁₂H₁₃N₃]⁺), ¹Hnmr; 6.8(t) (CH₂), 8.5δ(d) (NH-1), 10.67δ(d) (NH-2), ¹³Cnmr; 111.39 ppm (CH₂), 153.78 ppm (C-2 pyr), 148.18 ppm (C-1 ph). The structures and optimized geometries of molecules P2APH and RP2APH are given in Figure 1.

3.2. Gravimetric Corrosion Inhibition Studies. The corrosion inhibition efficiencies of two molecules for 24 h at (29 ± 0.1°C) are listed in Table 1. Both molecules displayed very high inhibition efficiency on CS surface. For a period of 24 h, the P2APH molecule showed little bit higher inhibition efficiency than its reduced form RP2APH at all concentrations. This can be attributed to the presence of strongly coordinating azomethine linkage in P2APH and the complete planar geometry of the molecule. Figure 2 represents the variation of corrosion inhibition efficiency with time for the molecules at 1.0 mM. The plot reveals that decrease of $\eta_w\%$ for P2APH was very much steeper than that of RP2APH as the days went on. This may be due to the slow hydrolysis of P2APH molecules in acidic medium. The azomethine linkage (C=N) present in the molecule is susceptible to hydrolysis [11]. The

FIGURE 1: Structure of P2APH and RP2APH and their optimized geometries.

TABLE 1: Gravimetric corrosion inhibition efficiencies ($\eta_w\%$) of P2APH and RP2APH on CS in 1 M HCl for 24 h at $29 \pm 0.2^\circ\text{C}$.

C (mM)	P2APH	RP2APH
0.2	92.14	91.64
0.4	92.98	91.91
0.6	94.42	92.57
0.8	94.82	93.80
1.0	95.50	95.40

reduced form of this molecule (RP2APH) is free from the azomethine linkage and is not vulnerable to hydrolysis and showed higher inhibition efficiency for days. The stability of the inhibitor in the aggressive medium is very important if it is to be recommended for a long time use. From the results of gravimetric corrosion studies one can reach into the conclusion that RP2APH molecule acts as very good corrosion inhibitor for a long time.

To get a more insight into the mechanism of corrosion, adsorption isotherms were plotted. Among the various isotherm models tried, the most suitable one was selected with the help of correlation coefficient. The most fit isotherm model for P2APH and RP2APH on CS in 1 M HCl was Langmuir adsorption isotherm equation (4). Isotherm plots having correlation coefficients close to one are given in Figure 3.

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C, \quad (4)$$

where C is the concentration of the inhibitor, θ is the fractional surface coverage, and K_{ads} is the adsorption equilibrium constant [1]. Standard free energy of adsorption (ΔG_{ads}^0) is related to equilibrium constant of adsorption (K_{ads}) by the following equation:

$$\Delta G_{\text{ads}}^0 = -RT \ln (55.5 K_{\text{ads}}), \quad (5)$$

where 55.5 is the molar concentration of water, R is the universal gas constant, and T is the temperature in Kelvin. Both molecules exhibited free energies of adsorption approximately 38.0 kJ/mol, which established that both the molecules interact with the metal surface by strong chemical forces [29].

3.3. Polarization Studies. To get an idea about the electrokinetic reactions and the involvement of molecules in the process polarization studies have been performed. Table 2 provides the Tafel polarization parameters of CS in the presence and absence of the inhibiting molecules. Figures 4(a) and 4(b)

FIGURE 2: Variation of corrosion inhibition efficiencies ($\eta_w\%$) of 1.0 mM P2APH and RP2APH with time on CS in 1 M HCl.

show the Tafel polarization curves for metal specimens in 1 M HCl with and without P2APH and RP2APH. The corrosion current density of the metal specimens markedly decreased with the concentration of inhibitors. A significant reduction of the active surface area of the metal specimen exposed to the corrosive medium occurs due to the increase of the thickness of the adsorbed layer with concentration [14]. The notable rise in $\eta_{\text{pol}}\%$ was observed by these inhibitors with concentration. At 1.0 mM concentration, P2APH displayed 92.3% inhibition efficiency. Since the cathodic slopes of Tafel lines (Figure 4) were deviated more than anodic slopes, one can assume that these two molecules delay the metal corrosion by inhibiting the cathodic process of corrosion more. In other words, the hydrogen evolution process was considerably hindered by both molecules compared to the oxidation of Fe into Fe^{2+} .

3.4. Electrochemical Noise Studies. Electrochemical noise experiments were performed with identical CS electrodes and reference electrode (SCE) immersed in the test solution (1 M HCl) in the presence and absence of P2APH and RP2APH for a period of 1200 s at $29 \pm 0.2^\circ\text{C}$. Figure 5 represents the current noise for blank metal specimen and metal treated with acid in the presence of 1.0 mM P2APH and RP2APH. From the noise data it is understandable that the mean values of the current noise follow the order blank > RP2APH > P2APH, which reveals that the protective power of the molecules is in the order P2APH > RP2APH. The ratio of standard deviation of potential noise to the standard deviation of current noise gave the noise resistance R_n [30]. The noise resistance for

TABLE 2: Potentiodynamic polarization parameters of CS in the presence and absence of P2APH and RP2APH in 1 M HCl at $29 \pm 0.2^\circ\text{C}$ for immersion period of 30 min.

C (mM)	P2APH					RP2APH				
	$-E_{\text{corr}}$ (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-b_c$ (mV/dec)	b_a (mV/dec)	$\eta_{\text{pol}\%}$	$-E_{\text{corr}}$ (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-b_c$ (mV/dec)	b_a (mV/dec)	$\eta_{\text{pol}\%}$
0	531	639.31	102	152	—	531	639.31	102	152	—
0.2	511	383.20	110	137	40.03	433	375.61	126	161	41.22
0.4	497	219.93	85	123	66.68	517	249.71	122	175	60.92
0.6	488	108.08	67	126	83.08	511	206.93	94	162	67.62
0.8	501	55.67	52	126	91.23	509	105.76	119	168	83.45
1.0	484	49.40	112	136	92.27	512	77.55	146	167	87.86

FIGURE 3: Langmuir adsorption isotherm for (a) P2APH and (b) RP2APH on CS in 1 M HCl for 24 h.

FIGURE 4: Tafel lines for CS in the absence and presence of (a) P2APH and (b) RP2APH in 1 M HCl at $29 \pm 0.2^\circ\text{C}$.

FIGURE 5: Current noise for CS in the absence and presence of P2APH and RP2APH (1.0 mM) in 1 M HCl $29 \pm 0.2^\circ\text{C}$.

the blank metal specimen was 2.8, which was increased appreciably by the addition of inhibitors. CS treated with P2APH and RP2APH displayed noise resistances 4.22 and 3.92, respectively, which obviously reflects the involvement of molecules in the metal dissolution process.

The frequency domain analysis of noise data gave the Power spectral density (PSD) of various systems (Figure 6). The advantage of PSD is that it is independent of time and the signal statistics do not alter with time [31–33]. Fast Fourier Transformation (FFT) was adopted to convert time dependent noise data into PSD plots using ivium software. The frequency response of the noise signals can be monitored with the help of PDS plots. To improve the spectral resolution, Burg introduced maximum entropy method (MEM) for short time records [34]. Mathematically this method makes some assumptions about unmeasured data which are consistent with the existing data [35]. The red lines shown in the FFT spectrum of various CS specimens depicts MEM curves.

Current and potential noise for the blank specimen were comparatively higher than the specimens treated with inhibiting molecules. The magnitude of noise was significantly lowered with the frequency. Higher amplitude of potential noise signal is an indication of appreciable localized metallic corrosion [36]. On analyzing the PSD plots and MEM curves, it is clear that the magnitude of potential noise values is very much higher for blank metal specimen than the specimens immersed in acid in the presence of P2APH and RP2APH (1.0 mM). This is the indication of the considerable localized corrosion on CS surface in the absence of inhibitors. At all frequencies potential noise and current noise of CS treated with P2APH are lower than those of specimen treated with RP2APH, suggesting that the former molecule inhibits well the dissolution of CS in 1 M HCl.

The slope of the PSD plot is important parameter which depicts the response of the inhibiting molecules on the metal surface. A considerable change in the magnitude of slope of a PSD plot is a measure of the vulnerability for the metal dissolution [37]. Though the slopes of the PSD_v curves almost remain unchanged for CS treated with 1.0 mM P2APH and RP2APH, significant change in the slopes of PSD_i plots was noticed. Slopes of PSD_i spectral curves of CS specimen treated with 1.0 mM inhibitor molecules roughly changed to zero from -0.19 . This result establishes that carbon steel in the presence of P2APH and RP2APH is less vulnerable to corrosion in 1 M HCl.

3.5. IR Spectral Studies. The surface film deposited on the CS specimen treated with 1.0 mM inhibitor in the aggressive medium for 24 h was removed mechanically and analyzed using IR spectroscopy. Figures 7(a) and 7(b) denote the overlay IR spectra of the P2APH and RP2APH and their surface film spectra on CS surface, respectively. The phenylhydrazone P2APH displayed a peak at 3330 cm^{-1} which was due to the stretching vibration of N-H group. This peak in the surface film spectrum shifted to higher frequency (3420 cm^{-1}) with very strong absorption. When we consider the structure of P2APH, the ample chance for the intramolecular hydrogen bonding between the heterocyclic nitrogen atom and N-H group is very obvious. The enhancement of N-H stretching frequency in the surface film spectrum may be due to the rupturing of hydrogen bond during the adsorption of molecule on CS surface through the N-atom of the pyridine ring which will lead to the free vibration of N-H bond. The $\text{CH}=\text{N}$ stretching frequency appearing at 1600 cm^{-1} in the IR spectrum of P2APH changed to 1620 cm^{-1} in the spectrum of surface film. This is due to the interaction of this group with the surface metal atoms. The C-N(pyr) stretching vibration of P2APH was also shifted from 1540 cm^{-1} to 1520 cm^{-1} in surface film spectrum which is a clear indication of the interaction of the compound with metal atoms through pyridine nitrogen. Strong absorption below 900 cm^{-1} in the spectrum of surface film can be attributed to the formation of metal-nitrogen and metal-carbon bonds. Due to the lack of complete coplanarity of RP2APH, it is difficult to propose intramolecular hydrogen bonding. The N-H stretching frequency appearing at 3400 cm^{-1} in the spectrum of RP2APH is not appreciably altered in the spectrum of surface film. The peak observed at 1580 cm^{-1} was changed to 1600 cm^{-1} in the IR spectrum of surface film, which can be attributed to the interaction of pyridine nitrogen with Fe atoms. Below 1000 cm^{-1} , the spectrum of surface film of RP2APH exhibited very intense IR absorption indicating the formation of strong Fe-N and Fe-C bonds.

3.6. SEM Studies. Surface morphology of the metal surfaces was evaluated with the aid of SEM. All micrographs were recorded at a magnification of 200x. Figures 8(a)–8(d), respectively, show the magnified surface images of bare metal, metal immersed in acid, and metal treated with acid in the presence of P2APH and RP2APH (1.0 mM) for

FIGURE 6: Power spectral density (current and voltage) of CS (a) and blank (b) in presence of P2APH and (c) RP2APH (1.0 mM) in 1 M HCl.

FIGURE 7: IR spectrum of (a) P2APH and surface film on CS; (b) RP2APH and surface film on CS.

FIGURE 8: SEM images of (a) bare metal; (b) CS treated with 1.0 M HCl; (c) with P2APH (1.0 mM); (d) with RP2APH (1.0 mM) for 24 h.

24 h. The textures of all surface images showed considerable differences. The pits and cracks appearing in the SEM image of the bare metal specimen were due to the polishing effects. The micrograph of blank specimen appeared to be very rough due to severe corrosion. Comparatively smoother images were displayed by metal specimens immersed in HCl in the presence of P2APH (1.0 mM) and RP2APH (1.0 mM). This can be attributed to the prevention of CS acid corrosion in acid by the adsorption of molecules.

3.7. Quantum Chemical Calculations. The corrosion inhibition response of organic molecules can be correlated with the energy of frontier molecular orbitals. The donor-acceptor interactions (HSAB concept) between the filled molecular orbitals of the inhibitor molecules and the vacant d-orbitals of Fe atoms on the surface are very important in the prevention of metal dissolution. High value of E_{HOMO} and the lowest value of $E_{\text{LUMO}} - E_{\text{HOMO}}$ (ΔE) are the important quantum chemical parameters which facilitate the strong binding of the molecules on the metal surface [34, 38]. Optimization of geometry of molecules and quantum chemical calculations were performed by DFT method using GAMMES software. A combination of Beck's three-parameter exchange functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP) was employed in DFT calculations [34]. Estimated quantum mechanical parameters like E_{HOMO} , E_{LUMO} , and ΔE for P2APH and RP2APH are provided in Table 3. The HOMO and LUMO of the molecules are P2APH and RP2APH represented in Figure 9. Approximate HSAB parameters like electronegativity (χ) and chemical hardness (η) of the

molecules were evaluated by the following equations [39] and are also reported in Table 3:

$$\chi \approx -\frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}), \quad (6)$$

$$\eta \approx \frac{1}{2}(E_{\text{HOMO}} - E_{\text{LUMO}}).$$

The E_{HOMO} values of the two molecules were almost the same, but the energy separation between HOMO and LUMO was considerably lower for P2APH than RP2APH, which indicate that P2APH is a finer inhibitor than RP2APH. The energy required to render electrons from HOMO of P2APH to the vacant d-orbitals of Fe is low compared to that of RP2APH. Lowest value of E_{LUMO} is an indication of the higher probability of the molecule to accept electrons from the metal surface. On comparing the E_{LUMO} values of the two molecules, it is obvious that P2APH molecule possesses very low value than RP2APH. This originates a strong backdonation of electrons from the filled orbital of Fe to the unoccupied molecular orbital of P2APH. Quantum chemical parameters provide a room for the calculation of number of electrons transferred (ΔN) from donor to acceptor molecules. As an approximation, the chemical hardness of Fe bulk metal is assumed as zero and the approximate electronegativity of bulk Fe is taken as 7 eV [39]. Equation (7) gives the approximate quantity of electrons transferred from the inhibitor molecule to the Fe atoms.

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inhib}}}{2(\eta_{\text{Fe}} + \eta_{\text{inhib}})}. \quad (7)$$

TABLE 3: Quantum chemical parameters of P2APH and RP2APH.

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	χ	η	ΔN
P2APH	-3.4640	0.7429	4.2069	1.36055	2.10345	1.340524
RP2APH	-3.4613	1.4803	4.941	0.9905	2.4708	1.216104

FIGURE 9: HOMO and LUMO of P2APH and RP2APH.

The number of electrons transferred from the inhibitor to the acceptor atom is higher for P2APH than RP2APH, which suggests that P2APH can make a strong coordinate type interaction with the metal atoms.

Perturbation of electron cloud occurs in molecules during chemical reaction. Chemical hardness of a molecule is a measure of resistance against the polarization of electron cloud. Soft molecules generally have low value of chemical hardness, low HOMO-LUMO energy gap, and high polarizability [40]. They are also associated with high chemical reactivity. If we consider the interaction of Fe with two organic molecules as soft-soft type, it is evident that P2APH has a great tendency to adsorb on Fe surface and hence prevent the metal dissolution appreciably, since it possesses low value of chemical hardness than RP2APH.

4. Conclusions

- (1) P2APH and its reduced form RP2APH were very effective corrosion inhibitors for CS in HCl medium.
- (2) All corrosion monitoring studies revealed that inhibition efficiency of P2APH is greater than that of RP2APH at all concentrations, which may be attributed to the presence of azomethine linkage present in P2APH.
- (3) Gravimetric corrosion studies showed that the prolonged corrosion inhibition efficiency of molecules follows the order RP2APH > P2APH.
- (4) Two molecules obeyed Langmuir adsorption isotherm on CS surface during the inhibition process.

- (5) The inhibitors delay the process of corrosion by hindering the cathodic process mainly.
- (6) The participation of P2APH and RP2APH in preventing the localized corrosion on CS in HCl was verified by electrochemical noise studies.
- (7) Quantum chemical studies differentiated the protective power of molecules.
- (8) Surface analysis using SEM and IR clearly portrayed the anticorrosive mechanism of inhibitors.

Competing Interests

The authors declare that they have no competing interests.

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