

Electroanalytical Studies on the Interaction Of L-Serine-Based Schiff Base, HHDMP, with Copper in Sulphuric Acid

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Abstract Amino acids and its Schiff bases have been widely recognized as green corrosion inhibitors primarily due to its non-toxic nature and biodegradable properties. Considering its unique nature and significant contribution in corrosion chemistry, studies were undertaken with an objective to find out the inhibitory effect of L-serine based Schiff base HHDMP on copper in 0.5, 1.0 and 1.5 M of sulphuric acid at 303, 308 and 313 K. Various techniques such as weight loss method, electrochemical impedance spectroscopy, potentiodynamic polarization (Tafel), basic computational calculations and adsorption studies were employed in the present investigations. Results revealed that Schiff base HHDMP do offer attractive inhibition efficiency in all concentrations of sulphuric acid. The inhibition effect advanced with the increased concentration of the inhibitor. However, with the increased concentration, the inhibition efficiency showed decline trend. Such behaviour of the amino acid Schiff base HHDMP on copper in sulphuric acid may be due to surface adsorption of the inhibitor molecules on the metal, which contributes to decrease in the double-layer capacitance and increase in the polarization resistance.

Keywords Copper · HHDMP · EIS · Polarization · Weight loss

1 Introduction

Copper and its alloys have been used from prehistoric times, and the importance of the metal today is greater than ever before. It is one of the non-ferrous materials widely used in various industries owing to its combination of excellent workability, high thermal and electrical conductivity, and attractive mechanical properties over a wide range of temperature and high resistance to electromigration [1]. Although copper is a noble metal, resistant against corrosion in nearly neutral and alkaline solution, it undergoes severe corrosion in highly acidic solution [2–4]. It is, therefore, the protection of copper is of great interest, especially in acidic media possessing chloride and sulphate ions [5–8]. The use of inhibitor is one of the most practical methods to protect metals from corrosion, especially in aggressive media. Various types of organic compounds are widely used as corrosion inhibitors to protect metals from quality deterioration due to corrosion. The organic compounds containing nitrogen, oxygen and sulphur are known to be effective as corrosion inhibitors for copper [9–13]. Since most of the inhibitors available are toxic in nature, these should be replaced with environment friendly inhibitors. Recently, the research efforts are prioritized towards the development of green corrosion inhibitors with good inhibition efficiency as well as least impact to environmental pollution. The isolation and identification of efficient and eco-friendly corrosion inhibitors became highly necessary as an alternative to toxic corrosion inhibitors. Reports are available on the effect of different amino acids on corrosion behaviour of different metals, but information on the effect of amino acid derived Schiff bases is lacking. There are, therefore, studies undertaken to find out the effect of L-serine amino acid Schiff base on copper under various concentrations of sulphuric acid medium at temperatures of 303, 308 and 313 K.

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2 Materials and Methods

2.1 Inhibitor

Schiff base, HHDMP (Z-3-hydroxy-2-((2-hydroxy-4a,8a,-dihydronaphthalene-1-yl)methyleneamino)propanoic acid), (Fig. 1) was employed as inhibitor, and it was prepared as per the reported procedure [14]. HHDMP was prepared by dissolving 2-hydroxy-1-naphthaldehyde (10 m mol 1.72 g) in 100 ml methanol and then added to the amino acid L-serine (10 m mol) solution in methanol (50 ml) for the preparation of HHDMP. The mixture was refluxed for 3 h, and the solvent was removed on a rotary evaporator and the residue crystallized at room temperature. After a day, crystals were obtained and recrystallized from methanol/n-heptane and characterized by physico-chemical methods. HHDMP: $^1\text{H NMR}$ (DMSO- d_6 ; δ , ppm): 9.06 (s, HC = N), 4(q, C-H), 4(m, CH_2), 10.92(s, COOH), 6.90–8.05 (m, ArC-H) Infrared (KBr, cm^{-1}): $\nu(\text{C} = \text{N})$, 1630; $\nu(\text{COOH})$, 16384; $\nu(\text{C} = \text{O})$, 16334; $\nu(\text{O-H})$, 3306 s.

2.2 Medium

The medium was prepared from reagent grade sulphuric acid (E. Merck) and double-distilled water. All tests were performed in aerated medium at 303, 308 and 313 K under atmospheric pressure.

2.3 Materials

The copper specimens of dimension $8 \times 1.9 \text{ cm}^2$ were used in weight loss measurements (0–4 grit of 1200 mesh). Coupons of same size were used for electrochemical studies, but only 1 cm^2 area is exposed during each test. Before recording the measurements, the samples were polished using different grades of emery papers followed by washing with water and acetone as recommended by ASTM.

2.4 Weight Loss Measurements

The weight loss experiments were carried out according to the method described previously [15]. For weight loss studies, specimens of required dimension were cut and

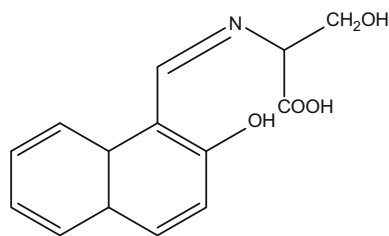


Fig. 1 Structure of HHDMP

Table 1 Inhibition efficiency (%) of HHDMP for copper at different time intervals

HHDMP (mgL^{-1})	% Inhibition efficiency with time in hours			
	24	48	72	96
Blank	—	—	—	—
50	68.21	66.36	62.58	59.63
100	72.36	69.36	67.71	64.78
150	74.89	71.61	70.86	68.89

cleaned in acid solutions and later polished with finer grades of emery paper to mirror bright finish. Beaker (250 ml) containing the solution was used for experimentation. After the stipulated exposure time, the specimens were removed from the test solution for washing initially with running tap water to remove the loosely adhering corroded particle and finally cleaned with a mixture of 20 % NaOH and 200 g/L Zinc dust followed by acetone (ASTM). Subsequently, the loss in weight was determined using analytical balance. The inhibition efficiency % IE was calculated using the equation

$$\% \text{ IE} = \frac{W_0 - W}{W_0} \times 100, \quad (1)$$

where W_0 and W represent weight losses in the uninhibited and inhibited solutions, respectively.

2.5 Electrochemical Measurements

Electrochemical tests were carried out in a conventional three-electrode configuration with platinum sheet (1 cm^2 surface area) as auxiliary electrode and saturated calomel electrode (SCE) as the reference. The working electrode was first immersed in the test solution for an hour to establish a steady-state OCP [87–88]. The electrochemical measurements were carried out with a Gill AC computer-controlled electrochemical workstation (ACM, U.K model no: 1475). The potentiodynamic polarization curves were obtained in the potential range from -250 to $+250 \text{ mV}$ with a sweep rate of 1 mV/s , and electrochemical impedance spectroscopy (EIS) measurements were carried out with amplitude of 5 mV ac sine wave with a frequency range of 0.1 – 10000 Hz .

2.6 Computational Studies

Various quantum chemical parameters of the inhibitor HHDMP (Z-3-hydroxy-2-((2-hydroxy-4a,8a,-dihydronaphthalene-1-yl)methyleneamino)propanoic acid) were calculated using B3LYP, which is a version of the DFT method that uses Becke's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms

Table 2 Data on electrochemical parameters of copper obtained from polarization curves in 1M_HSO₄

Temp (K)	HHDMP (ppm)	E _{corr} (mV)	β _a (mV dec ⁻¹)	β _c (mV dec ⁻¹)	I _{corr} (mA cm ⁻²)	CR (mils/yr)	(%IE)
303	Blank	-39.52	61.15	-184.44	0.0110	10.30	—
	50	-79.20	57.76	-110.72	0.0032	3.010	71.42
	100	-72.60	54.32	-62.13	0.0021	2.560	75.89
	150	-110.32	37.12	-56.45	0.0020	2.100	80.35
308	Blank	-52.20	43.77	-275.60	0.0090	11.26	—
	50	-80.65	56.29	-90.64	0.0032	3.25	68.68
	100	-110.25	45.97	-68.57	0.0024	2.60	71.74
	150	-84.87	64.45	-99.30	0.0025	2.23	74.74
313	Blank	-53.21	47.32	-396.42	0.0126	11.57	—
	50	-78.63	58.67	-144.30	0.0040	3.73	66.66
	100	-39.56	36.93	-50.42	0.0038	3.49	69.84
	150	-80.47	58.20	-92.04	0.0034	3.11	73.01

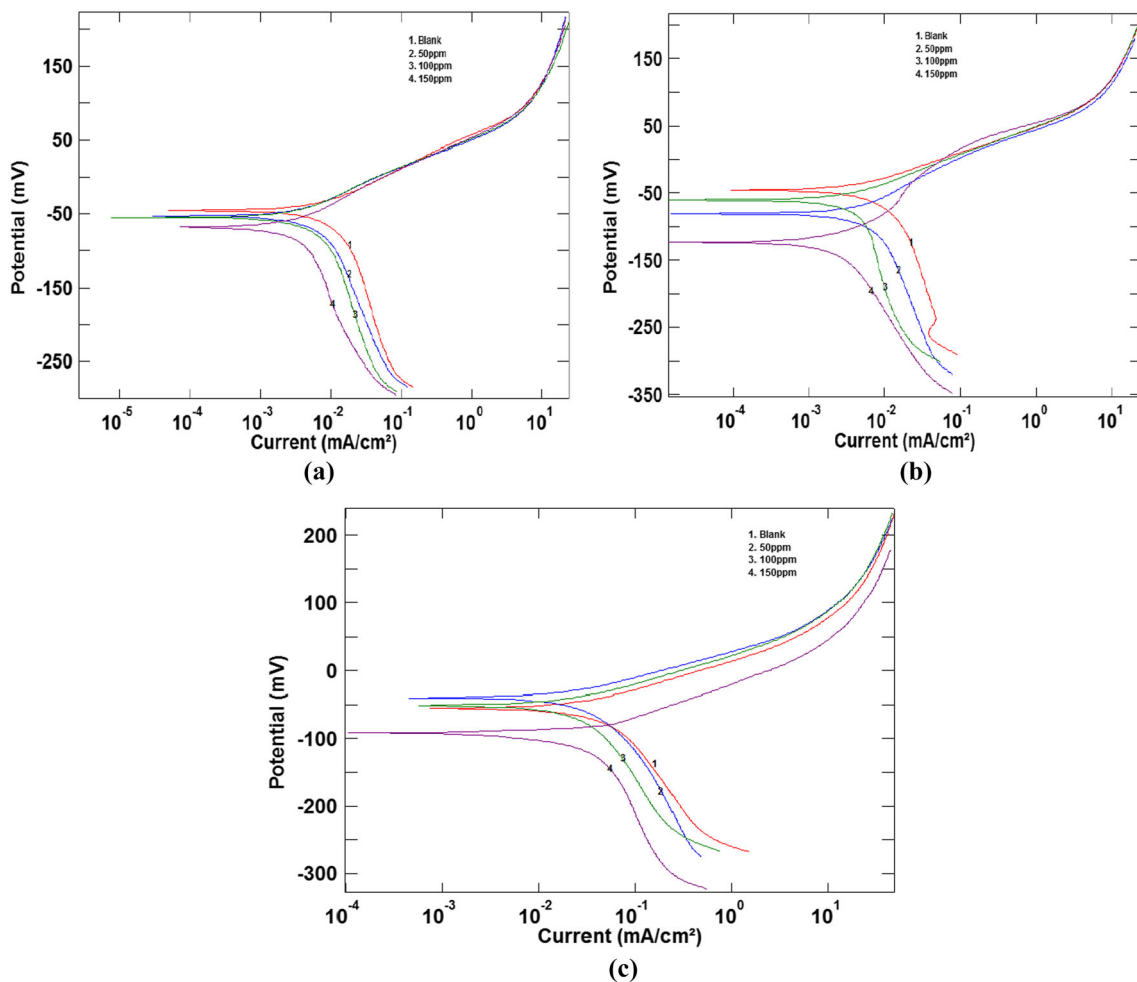


Fig. 2 Polarization curves for copper in 1 M sulphuric acid at 303, 308 and 313 K, respectively

associated with the gradient corrected correlation functional of Lee, Yang and Parr [16]. It was recognized specifically for systems containing transition metal atoms

[17, 18], and hence, B3LYP was used in the present study to carry out quantum calculations. Subsequently, full geometry optimization of the inhibitor was carried out at

Fig. 3 Plot of I_{corr} against inhibitor concentration in 1 M sulphuric acid at **a** 303 K, **b** 308 K and **c** 313 K

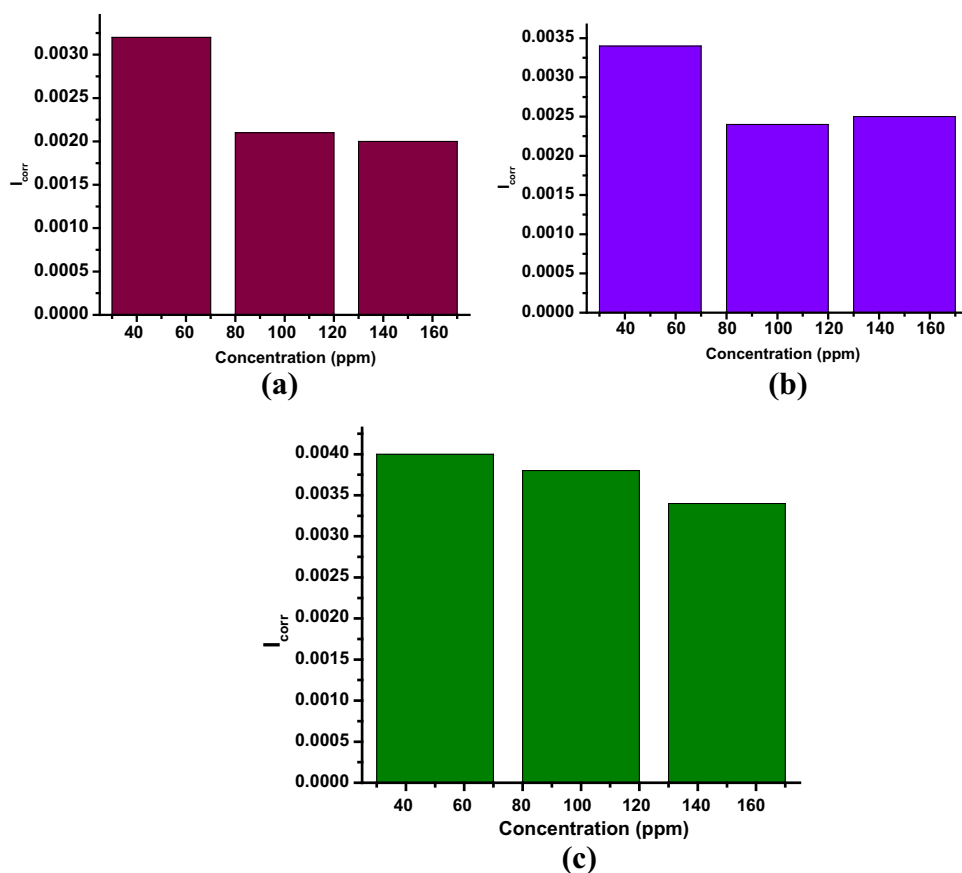


Table 3 AC impedance data on copper with HHDMP in 1 M H_2SO_4 at 303, 308 and 313 K

Temp (K)	HHDMP (ppm)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	I_{corr} (mA cm^{-2})	C.R (mils/yr)	(%IE)
303	Blank	493	409.10	0.052	48.38	—
	50	1533	315.30	0.017	15.58	68.84
	100	2588	261.60	0.010	9.23	80.95
	150	3273	234.00	0.008	7.52	85.98
308	Blank	442	1430.00	0.058	54.02	—
	50	1311	173.00	0.019	18.15	67.28
	100	1772	107.80	0.014	13.48	75.05
	150	2715	76.00	0.009	8.79	83.72
313	Blank	438	1105.00	0.060	54.96	—
	50	1298	318.20	0.020	19.36	66.00
	100	1715	54.22	0.015	13.93	74.40
	150	2512	29.13	0.010	9.51	82.50

the B3LYP/6-311 + G (d, P) level using the Gaussian 09W program package.

2.7 Scanning Electron Microscopy (SEM)

The surface morphology of copper in the absence and presence of the inhibitor HHDMP was studied using a Digital Microscope Imaging Scanning electron microscope model SU6600 (Serial No: HI-2102-0003) with an

accelerating voltage 20.0kv. Samples were attached on the top of an aluminium stopper by means of carbon conductive adhesive tape. All micrographs of the specimen were taken at the magnification of $\times 500$.

2.8 Atomic Force Microscope (AFM)

The copper strips having a size of $8 \times 1.9 \text{ cm}^2$ were immersed in 1.0 M H_2SO_4 with and without the inhibitor

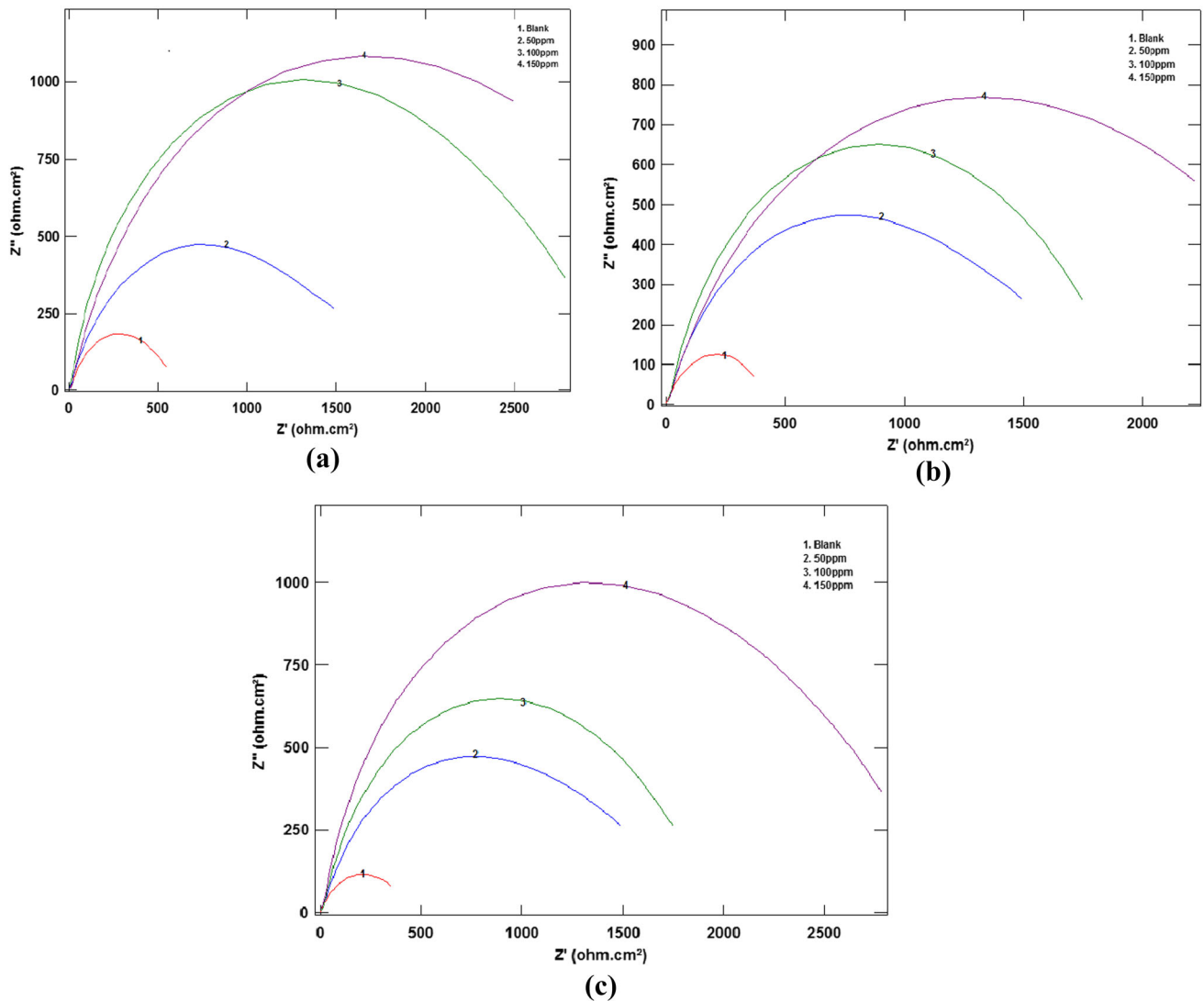


Fig. 4 Nyquist plots of copper in 1 M sulphuric acid solution at **a** 303 K, **b** 308 K and **c** 313 K

(150 ppm) at 303 K for 120 h. The specimens were cleaned after the treatment period with distilled water, dried and then used for atomic force microscopic studies.

3 Results and Discussion

3.1 Weight Loss Studies

The weight loss recorded on the sample specimen reflects on the inhibition efficiency. The weight loss under different intervals of time (24, 48, 72 and 96 h) in 1 M sulphuric acid at different concentrations of inhibitor HHDMP was studied, and the results are summarized in Table 1. Results revealed that the inhibition efficiency is high at 24 h interval irrespective of the concentrations of the inhibitors and subsequently the efficiency declined. The inhibition

efficiency increased with the increased concentrations of the inhibitor, however with the advancement of time interval inhibition efficiency decreased irrespective of the inhibitor concentrations. Similar observations were also reported in copper with Cysteine [19].

3.2 Potentiodynamic Polarization Studies

Potentiodynamic polarization behaviour of copper in 1 M sulphuric acid in the absence and presence of inhibitor HHDMP at 303, 308 and 313 K are presented in Table 2. Results indicated that the electrochemical parameters vary with the inhibitor concentration and temperature. Tafel polarization curves for copper in 1 M sulphuric acid in the absence and presence of different concentrations of HHDMP at 303, 308 and 313 K are presented in Fig. 2. The polarization results indicated that increase in the

Fig. 5 Plot of efficiency against concentration of the inhibitor in 1 M H₂SO₄ at **a** 303 K, **b** 308 K and **c** 313 K

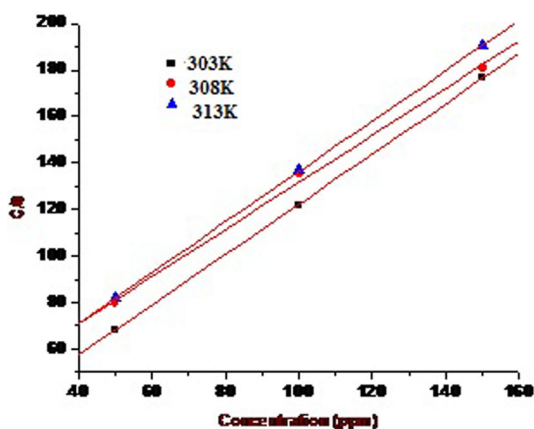
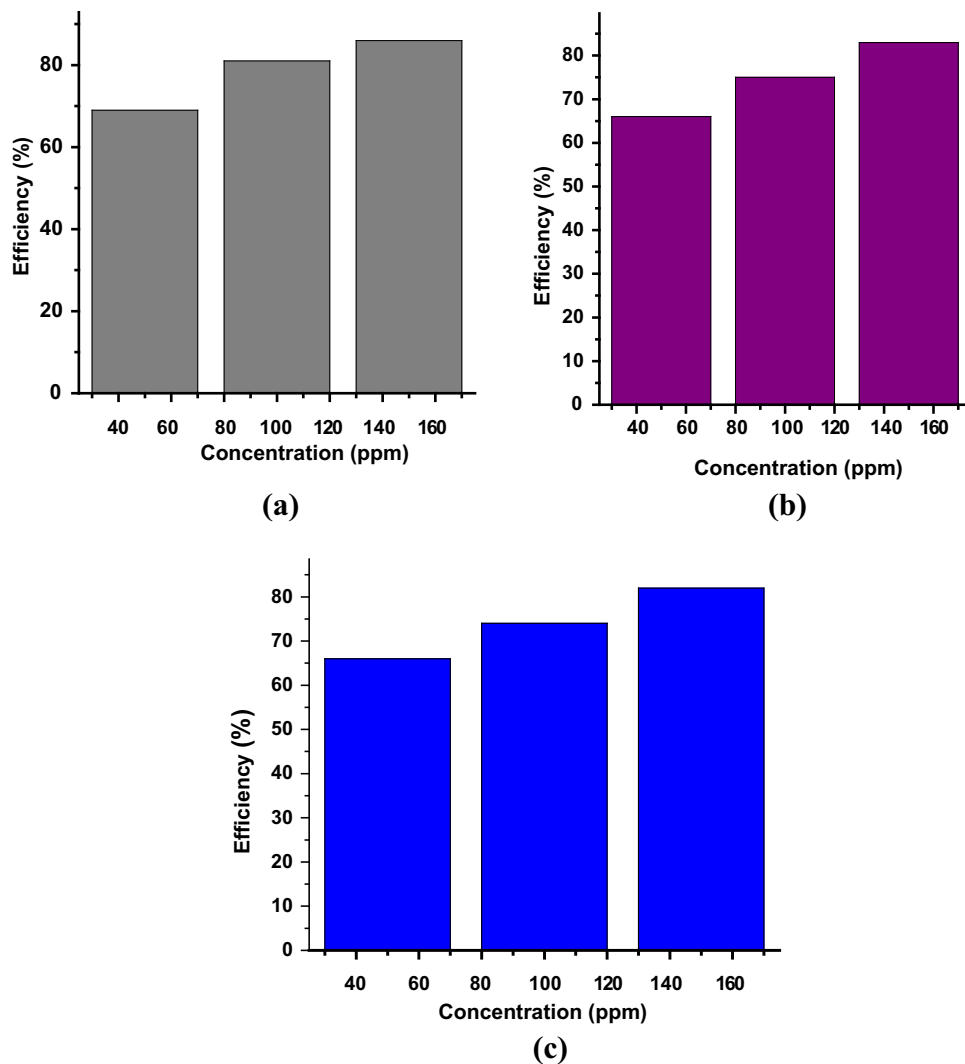


Fig. 6 Langmuir adsorption isotherm

inhibitor concentration changes both the cathodic and anodic current, and there is no definite trend in the shift of E_{corr} values. The displacement in E_{corr} value was less than

85 mV between blank acid solution and acid solution with the inhibitor, which confirms the mixed type behaviour of the inhibitor. Therefore, it is also clear that the values of electrochemical parameters like I_{corr} and corrosion rate decreased with the increase in concentration of the inhibitor. The decreasing trend of I_{corr} with the increase in inhibitor concentration in all the acid concentration is shown in Fig. 3. The corrosion inhibition efficiency was calculated using the equation

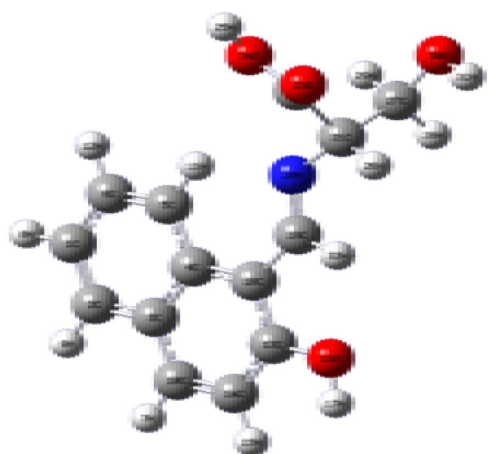
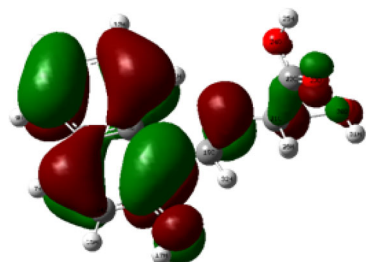
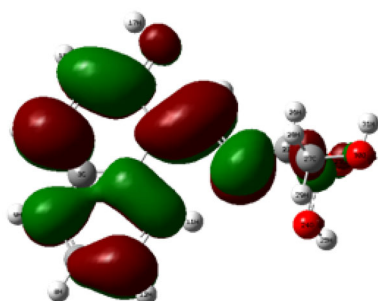
$$IE \% = \frac{I_{Corr^*} - I_{Corr}}{I_{Corr^*}} \times 100, \tag{2}$$

where I_{Corr*} and I_{corr} represent uninhibited and inhibited corrosion current densities.

The mechanism of corrosion inhibition involves the blocking of reaction sites by the inhibitor due to the adsorption of inhibitor molecule on the metal surfaces, and the surface adsorption increases by increase in the concentration of inhibitor [20]. The formation of a coating on

Table 4 Adsorption parameters of inhibitor (HHDMP) for corrosion of 1 M H₂SO₄ at 303, 308 and 313 K

Temperature (K)	$\Delta G_{\text{ads}}^{\circ}$ (kJ mol ⁻¹) & $K_{\text{ads}} \times 10^4$ (mol ⁻¹) HHDMP (ppm)					
	50		100		150	
303	-16.18	11.00	-16.19	11.12	-16.08	10.68
308	-16.06	10.59	-15.30	7.83	-15.50	8.49
313	-15.95	10.13	-15.17	7.42	-15.33	7.91

**Fig. 7** Optimized geometry of HHDMP**(a)** HOMO**(b)** LUMO**Fig. 8** a HOMO b LUMO of HHDMP

the surface of the metal as a result of adsorption of the inhibitor molecule gives a considerable protection against corrosion.

3.3 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is an efficient technique to study organic coatings on the metal as this technique does not disturb the double layer at the metal/solution interface and thus provides highly reliable results. The electrochemical parameters associated to impedance study at varying temperatures (303 K, 308 K, 313 K) are presented in Table 3. Results revealed that I_{corr} value showed decreasing trend with the increase in concentration of the inhibitor. Nyquist plots of copper in 1 M sulphuric acid solution at 303, 308 and 313 K containing various concentrations of HHDMP after 30 min of immersion are presented in Fig. 4. The plot of concentration of the inhibitor against efficiency is depicted in Fig. 5. The efficiency is found to be high at 150 ppm of inhibitor HHDMP. It further reveals that in uninhibited solution, Nyquist plot yields a slightly depressed semicircle, and it amply explains that the corrosion of the copper in the absence of inhibitor is mainly controlled by a charge transfer process. [21, 22]. The simplest circuit fit for these experimental data was a Randle's circuit consists of a solution resistance, R_s , in series to a parallel combination of resistor, R_{ct} , and a double-layer capacitor, C_{dl} . Here R_{ct} represents the charge transfer resistance and C_{dl} represents the electrode capacitance. It may be noted from Nyquist plots that R_{ct} values increased with inhibitor concentration, which can be attributed to the formation of a protective layer at the metal surface, and this layer acts as a barrier for the mass and the charge transfers. The inhibition efficiency was calculated using the equation

$$\text{IE} (\%) = \frac{R_{\text{ct}^*} - R_{\text{ct}}}{R_{\text{ct}^*}} \times 100, \quad (3)$$

where R_{ct^*} and R_{ct} represent the values of the charge transfer resistance observed in the presence and absence of HHDMP.

3.4 Adsorption Studies

The adsorption isotherm provides information pertaining to the interaction of inhibitor with metal surface [23]. Adsorption behaviour of the HHDMP in copper corrosion is presented in Table 3. Results revealed that corrosion behaviour varies with inhibitor concentrations. The surface

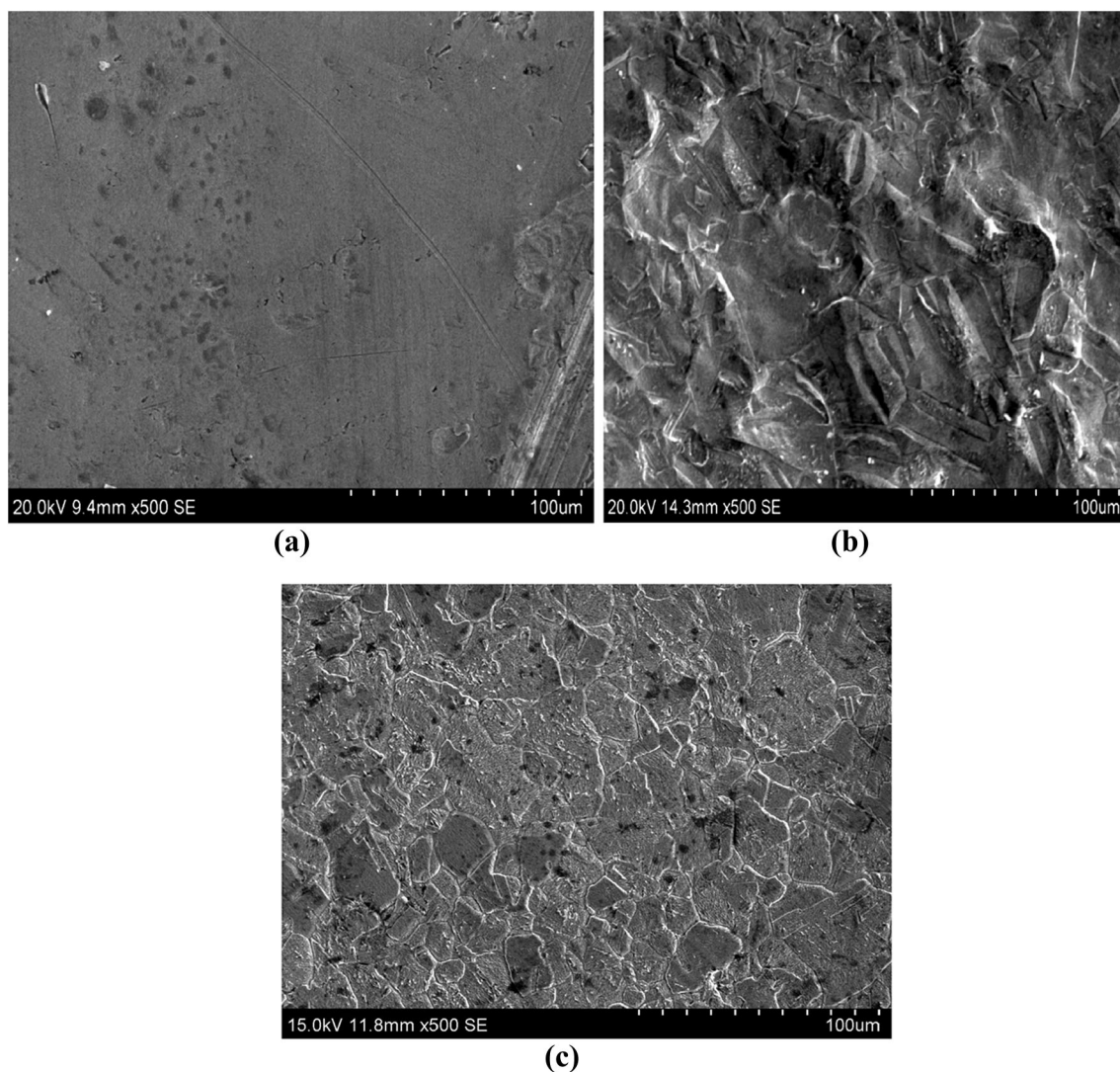


Fig. 9 The SEM images of **a** bare polished copper, **b** copper after immersion in 1 M sulphuric acid medium without inhibitor and **c** copper in the presence of 150 ppm of HHDMP after 24 h exposure

coverage values (θ) for different concentrations of inhibitor in 1 M sulphuric acid obtained from electrochemical measurements were used for the construction of adsorption isotherm. Using these data, different isotherms have been plotted to find out the most suitable adsorption isotherm. The plot C/θ versus C shows a straight line, providing that the adsorption of HHDMP on copper surface obeys Langmuir adsorption isotherm, and the same at 303, 308 and 313 K is shown in Fig. 6. The values of K_{ads} and ΔG_{ads}^0 of inhibitor HHDMP are presented in Table 4. The negative value of ΔG_{ads}^0 indicates the spontaneity of adsorption process and stability of the adsorbed layer on the copper surface. Generally, the values of ΔG_{ads}^0 around -20 kJ mol^{-1} or lower are consistent with physisorption, while those around -40 kJ mol^{-1} or higher value involve chemisorptions [24]. In this case, mode of adsorption involved is physisorption.

3.5 Computational Studies

Computational calculations of various quantum chemical parameters like energy of highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE), i.e., $E_{HOMO} - E_{LUMO}$, ionization potential, I which is $-E_{HOMO}$, electron affinity, A which is $-E_{LUMO}$, electro negativity, χ which is $(I + A)/2$ and hardness, η which is $(I - A)/2$ were calculated, and they optimized the geometry of the molecule using Gaussian 09 program package. The calculated values of quantum chemical parameters are E_{HOMO} (eV), E_{LUMO} (eV), ΔE (eV), I (eV), A (eV), χ (eV) and η (eV) which are found to be -5.72, -1.62, 03, 5.72, 1.62, 3.67 and 2.05, respectively. The optimized geometry of HHDMP is presented in Fig. 7. HOMO and LUMO of HHDMP are shown in Fig. 8. It is generally stated that the efficiency of

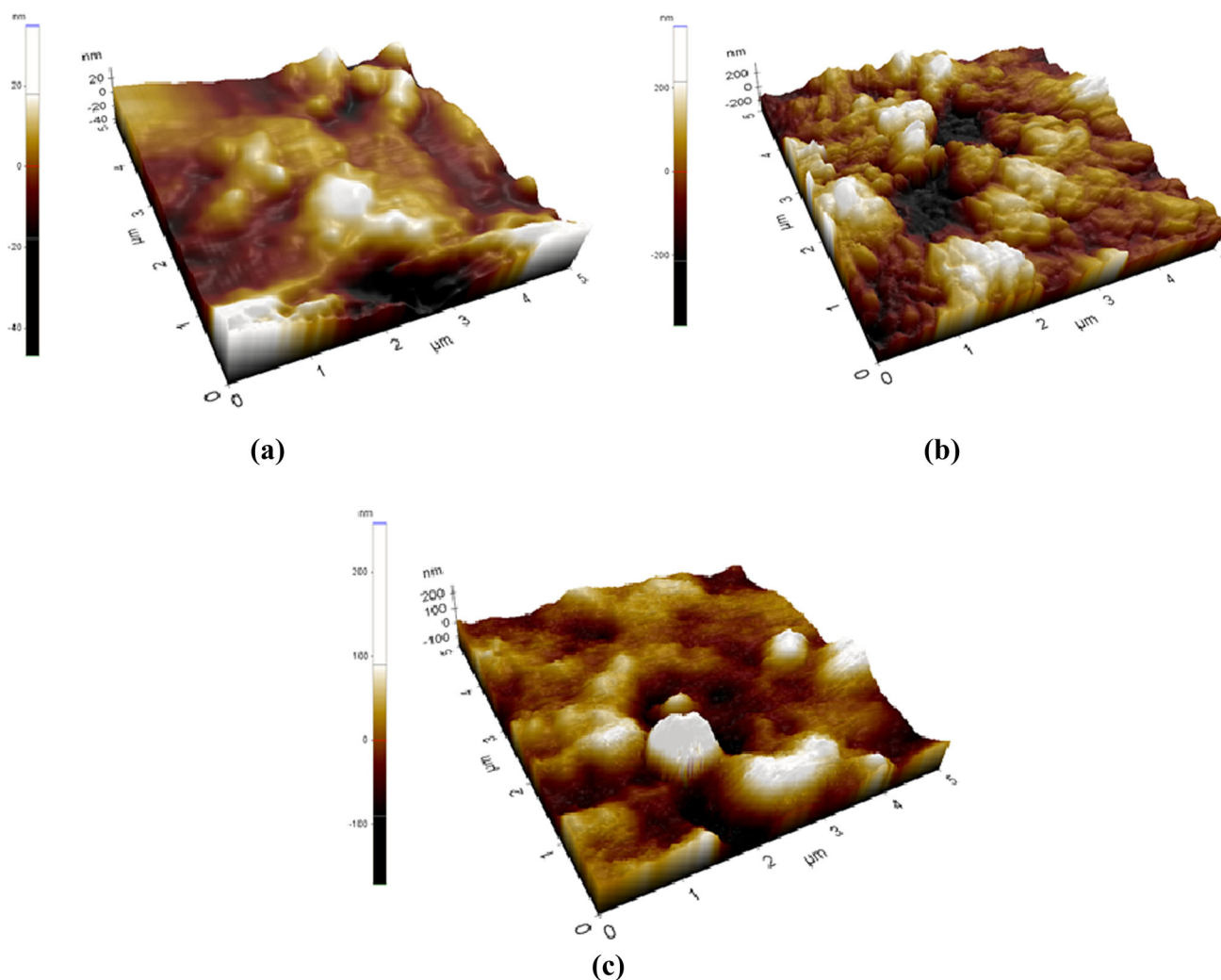


Fig. 10 AFM images of **a** copper, **b** copper in 1 M H_2SO_4 without inhibitor and **c** copper in the presence of 150 ppm of HHDMP after 24-h exposure

inhibitors increases with the decrease in energy gap, ΔE , increase in E_{HOMO} and decrease in E_{LUMO} . Higher E_{HOMO} value enhances the adsorption of inhibitor, thereby increasing the inhibition efficiency. The smaller the E_{LUMO} value, the greater will be the probability of molecules to accept electrons. The higher the ionization energy, the easier will be the removal of electrons from the molecule.

3.6 Scanning Electron Microscopy

SEM studies enable understand the effect of inhibitor molecules on the surface of copper [25–27]. The SEM images of a bare polished copper, copper after immersion in 1 M sulphuric acid without inhibitor and with inhibitor for a period of 24 h are shown in Fig. 9a–c, respectively. It also revealed that the metal surface was smooth and free from depressions in the case of copper immersed in

sulphuric acid containing HHDMP, whereas the surface is damaged in the case of copper immersed in sulphuric acid without inhibitor.

3.7 Atomic Force Microscope (AFM)

Atomic force micrographs were taken to study whether inhibition is due to the formation of a film on the metal surface through adsorption [28, 29]. The three-dimensional AFM images are shown in Fig. 10(a–c). It is evident from Fig. 10c there is much less damage on the surface of copper in the presence of HHDMP. The average roughnesses of polished copper (Fig. 10a) and copper exposed in 1 M H_2SO_4 without inhibitor (Fig. 10b) were calculated to be 6.84 and 84 nm, respectively. The copper surface exposed in free acid solution is getting cracked considerably due to the attack of ionic species (Fig. 10b), and the

same can be moderately controlled by the usage of 150 ppm of inhibitor where the average roughness was reduced to 33.72 nm.

4 Conclusions

- (1) The amino acid Schiff base HHDMP is a green corrosion inhibitor with fairly good efficiency.
- (2) As the concentration of the inhibitor increases, corrosion inhibition efficiency as well as charge transfer resistance increases.
- (3) The corrosion rate and double-layer capacitance decreased due to increased adsorption of the inhibitor.
- (4) The inhibitor molecule affects both the anodic and cathodic processes and hence acts as a mixed type inhibitor.
- (5) The adsorption of the inhibitor obeys Langmuir adsorption isotherm model.
- (6) HHDMP inhibits copper corrosion in 1 M H₂SO₄ even at fairly high temperature also.

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