

**SYNTHESIS, CHARACTERIZATION, AND ELECTROCHEMICAL STUDY OF
SCHIFF BASE AS A CORROSION INHIBITOR FOR MILD STEEL IN H₂SO₄
MEDIUM**

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ABSTRACT

2-Methoxy-5-(pyridine-2-yliminomethyl)-phenol (MPP) was synthesized and its inhibiting action on the corrosion of mild steel in 0.5 M H₂SO₄ was examined by different corrosion methods, such as potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and linear polarization studies (LPR). The experimental results show that 2-Methoxy-5-(pyridine-2-yliminomethyl)-phenol (MPP) is an efficient corrosion inhibitor and the inhibition efficiency increases with increase in the inhibitor concentration. The inhibitor molecules were first adsorbed on the mild steel surface thereby blocking active sites available for acid attack.

Keywords: Schiff base, Mild steel, potentiodynamic polarization, EIS, LPR.

Introduction

Mild steel is widely used as structural material in automobiles, pipes and chemical industries [1]. Mild steel undergoes severe corrosion in pickling processes. Hydrochloric and sulphuric acids are widely used for pickling and de-scaling of mild steel [2–4]. Different organic compounds have been reported as effective corrosion inhibitors during acidization in industrial cleaning processes [5–7]. It is well known that heterocyclic compounds, containing electronegative functional groups, pi-electrons and heteroatoms like sulphur, nitrogen and oxygen as well as aromatic rings in their structures, often show good corrosion inhibitive ability in acid media [8–11]. Recently more emphasis is being paid in the investigation of Schiff bases as corrosion inhibitors in acidic media due to their enhanced inhibiting action and ease of their synthesis from relatively cheap raw materials. The objective of this present investigation is to determine the corrosion inhibition efficiency of 2-Methoxy-5-(pyridine-2-yliminomethyl)-phenol as a novel inhibitor for the corrosion of mild steel in 0.5 M H₂SO₄ and to calculate the surface parameters of the synthesized inhibitor. The inhibition efficiency was determined using three different techniques: viz linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements.

Materials and experimental methods

Material preparations

Mild steel specimens of the following chemical composition (wt. %) were used in the experiments: C – 0.21; Si – 0.38; P – 0.09; Mn – 0.05; S – 0.05; Al – 0.01; and balance was Fe. Before the measurements, the surface of mild steel was mechanically abraded using different grades of sand papers, which ended up with the 1000 grade. Then, the electrode was cleaned by washing with distilled water, acetone, distilled water, respectively, and immersed into the test solution quickly. After washing with each cleaning agent, the surface was dried with a filter paper.

Synthesis of MPP

The Schiff base was synthesized from the condensation reaction of 2-Amino pyrimidine with 4-methoxy 3-Hydroxy Benzaldehyde in methanol. The molecular structure of synthesized Schiff base has been given in Fig. 1.0. 2-Aminopyrimidine was purchased from Fuluka, all the other chemicals were purchased from Merck and used without further purification. After completion of the synthesis procedure, the reacted mixture was filtered, organic solvent was removed and compound was characterised.

Electrochemical measurements

The potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) measurements were carried out using a CHI 760c A.C. Electrochemical Analyzer under computer control. A double-wall one compartment cell with a three-electrode configuration was used. The auxiliary electrode was a platinum sheet with 2 cm² surface area. The reference electrode was "calomel" (Hg₂Cl₂). The working electrode was immersed in test solution for 4 h to establish a steady state open circuit potential (E_{ocp}). After measuring the E_{ocp} , the electrochemical measurements were performed. The EIS experiments were conducted in the frequency range of 100 kHz–0.003 Hz at open circuit potential. The amplitude was 0.005 V. The cathodic polarization curves were obtained in the potential ranges from E_{ocp} to 1.0 V (Hg₂Cl₂) with a scan rate of 0.001 V s⁻¹ and the anodic polarization curves were obtained in the potential ranges from E_{ocp} to 0.0 V (Hg₂Cl₂) with a scan rate of 0.001 V s⁻¹. LPR measurements were carried out by recording the electrode potential ± 0.010 V around open circuit potential with 0.001 V s⁻¹ scan rate. The polarization resistance (R_p) was determined from the slope of the obtained current–potential curves. To determine the potential of zero charge of the Mild steel, the impedance of the Mild steel was determined at different potentials in the absence and presence of MPP. After different immersion time, electrochemical measurements were performed under un-stirring conditions. In the hydrogen gas evolution measurements, a burette filled with 0.5 M H₂SO₄ solution was placed over the working electrode.

RESULTS AND DISCUSSION

Characterization of MPP

Synthesis of 2-Methoxy-5-(pyridine-2-yliminomethyl)-phenol by condensation of 2-Amino-pyrimidine (0.2500 m mol) with 4-methoxy 3-Hydroxy Benzaldehyde (0.2014 mmol) in methanol was carried out for 10 hours and solid product was then characterised with ¹H NMR and FT-IR (KBr). The azomethine $\delta(C=N)$ stretching vibration for MPP was found at 1620 cm⁻¹. The band at 2820 cm⁻¹ was due to the C–H bond stretching. The ¹H NMR spectrum of MPP in CDCl₃ showed no resonance peak at δ 7.21 ppm assignable to C–H proton. One singlet of three protons at δ 3.91 ppm, Aromatic protons appear as a doublet and triplet in Figure 2 at δ 6.91 ppm, 6.93 ppm, 7.32 ppm, 7.81 ppm and δ 6.71 ppm, 7.62 ppm range respectively.

Potentiodynamic polarization measurements

The potentiodynamic polarization curves of mild steel in 0.5 M H₂SO₄ with and without various concentrations of MPP is shown in Fig. 3. The values of related electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), and inhibition efficiency (IE%) were calculated from these curves and are given in Table 1. The inhibition efficiency IE% was calculated from polarization measurements according to the relation:

$$EI \% = \frac{I_{corr_i} - I_{corr}}{I_{corr_i}} \times 100$$

Where I_{corr_i} and I_{corr} are the uninhibited and the inhibited corrosion current densities, respectively. The values of current densities were obtained by the extrapolation of the current-potential lines to the corresponding corrosion potentials as can be seen from Table 1. From Fig. 3, it can be observed, that the cathodic reaction of mild steel corrosion is significantly inhibited in the presence of the inhibitors. Moreover, the cathodic current-potential curves give rise to almost parallel Tafel lines. The adsorbed inhibitor molecules only block the active sites of hydrogen evolution on the metal surface. For anodic polarization curves, it is apparent that the Schiff's base inhibitors perform good inhibition ability between corrosion potential and -300 mV (vs. SCE). However, for potential more positive than -300 mV (vs. SCE), the presence of inhibitors do not alter the current vs potential characteristics obviously. This potential is usually defined as desorption potential [16]. This phenomenon is generally associated with the significant dissolution of the mild steel, which leads to desorption of the inhibitor molecules from the electrode surface. In this case, desorption rate of the inhibitors is higher than their adsorption rate [17,18]. Therefore, the studied MPP can be classified as cathodic inhibitors in 0.5 M H₂SO₄. Table 1 shows that the inhibition efficiency increases with increasing inhibitor concentration. This result indicates that MPP acts as an adsorption inhibitors, given that more molecules are adsorbed on the metal surface as the concentration increases, promoting wider surface coverage [19]. Table 1 also shows that the corrosion rate decreases when the inhibitor concentration increases.

Electrochemical impedance measurements

Electrochemical impedance spectroscopy (EIS) has been employed in order to investigate the surface layer created by inhibitors. The inhibition efficiency (IE%) using R_{ct} values were calculated from the equation.

$$EI \% = \left(1 - \frac{R_{ct}}{R_{ct}(i)} \right) \times 100$$

where $R_{ct}(i)$ and R_{ct} are the charge transfer resistance in absence and presence of optimum concentration of inhibitor. The values of phase shift, n (ranges from 0.821 to 0.899) were not changed significantly and its ongoing stability showed the charge transfer controlled dissolution mechanism of mild steel in 0.5 M H₂SO₄ with and without inhibitor. In table 2, the double layer capacitance (C_{dl}) values have been calculated from CPE parameter values Y and n by using the following equation.

$$C_{dl} = \frac{Y\omega^{n-1}}{\sin\left(n\left(\frac{\pi}{2}\right)\right)}$$

where ω is angular frequency ($\omega = 2\pi f_{\max}$) at which the imaginary part of the impedance (Z_{im}) is maximal and n is the phase shift, which can be used as a gauge of the heterogeneity or roughness of the mild steel surface.

The effect of inhibitor concentration on the impedance behaviour of mild steel in 0.5 M H_2SO_4 solution at 25 °C is investigated for the studied concentrations. The results for 10^{-3} to 10^{-6} M concentration are shown in Fig. 4. The Nyquist plots display a depressed semi-circle in the first quadrant, indicating that there is only one time constant corresponding to the charge transfer process [16,17]. Inhibition effect of the inhibitors can easily be observed from the low frequency impedance modulus [18]. From Fig. 4, the low frequency impedance modulus increase with increasing the concentration of the inhibitors, which demonstrates that the adsorption of the inhibitors improves corrosion resistance of mild steel in 0.5 M H_2SO_4 . In the phase angle plots of mild steel in 0.5 M H_2SO_4 in the presence and absence of the inhibitors, a phase peak close to 90° at the middle frequency range can be observed, indicating that there is merely one time constant related to the electrical double layer formation at surface-solution interface [19].

After the analysis of impedance results (table 2), we find that the charge-transfer resistance value, R_{ct} increases in inhibited system than in the uninhibited system. A large R_{ct} is associated with a slower corroding system, due to decrease in the active surface necessary for the corrosion reaction.

The decreased C_{dl} values can result from the increase of the thickness of the electrical double layer or the local dielectric constant which suggest the substitution of H_2O molecules (with higher dielectric constant) with inhibitor molecules (lower dielectric constant) leading to a protective film on electrode surface.

Linear polarization resistance

The inhibitory efficiency of MPP on the mild steel in 0.5 M H_2SO_4 solution was also studied with the help of LPR technique. The R_p values were calculated from the slope of the current-potential curves and the data obtained are given in Table 2 with corresponding inhibition efficiencies. As it can be observed from Table 2, the agreement between the inhibition efficiencies obtained from LPR and EIS methods are quite well. The increase in concentration of the inhibitor results in higher R_p values, which suggests the enhancement of adsorption of MPP molecules on the mild steel surface and blocking the surface against the corrosive attack more efficiently [20].

Conclusion

Inhibitive performance of MPP in 0.5M H_2SO_4 solution on mild steel was investigated in this study using EIS, potentiodynamic polarization and liner polarization method. Following conclusions can be drawn from above mentioned investigation;

1. The potentiodynamic polarization curves indicate that MPP acts as mixed type of inhibitor.
2. The impedance results indicate that the value of polarization resistance increased and double layer capacitance decreased. This result can be attributed to the increase of the thickness of electrical double layer.
3. The percentage inhibition efficiency of MPP obtained from EIS and potentiodynamic polarization are in good agreement with one another.

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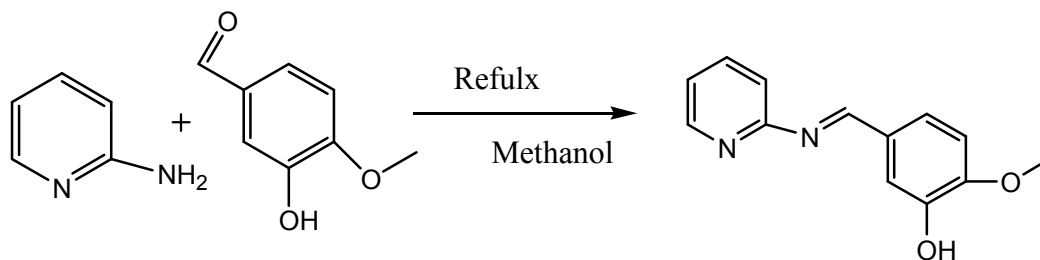


Fig.1. Scheme

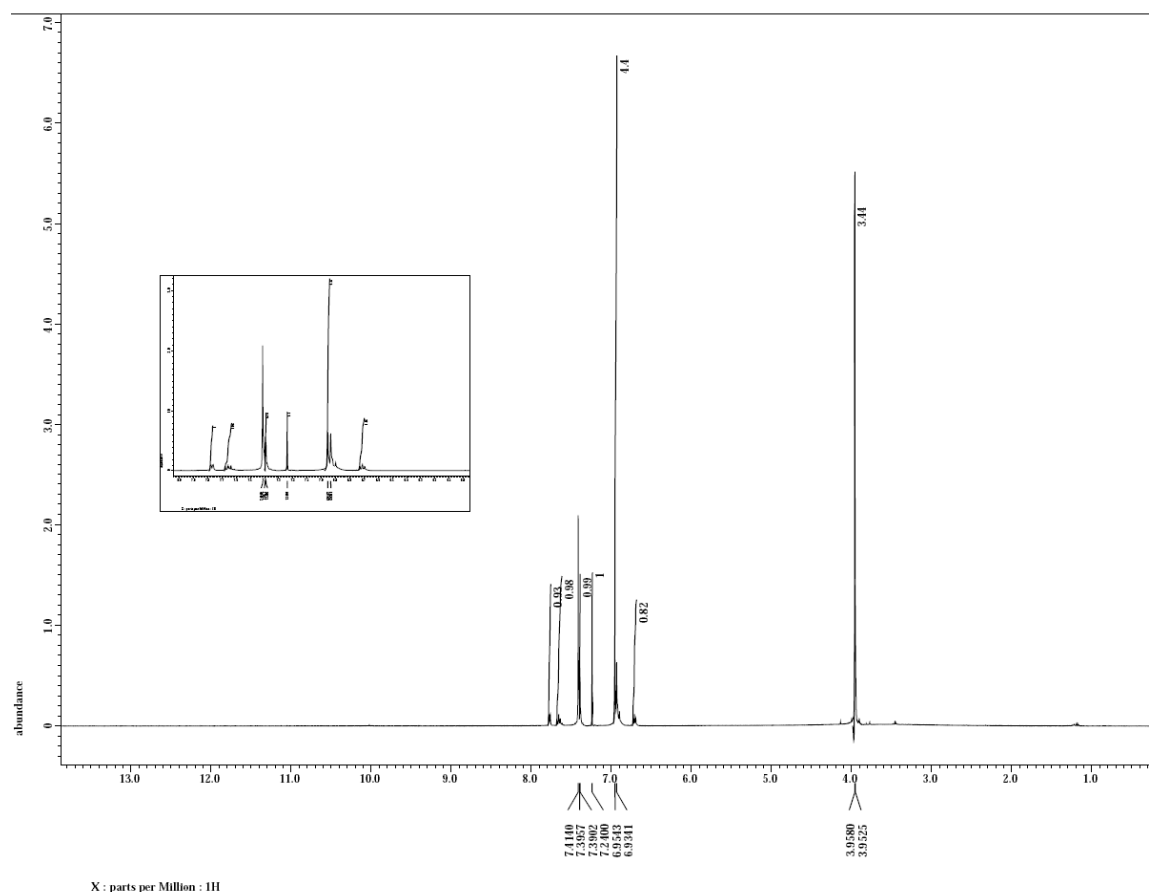


Fig. 2. The ¹H NMR spectrum of 2-Methoxy-5-(pyridine-2-yliminomethyl)-phenol.

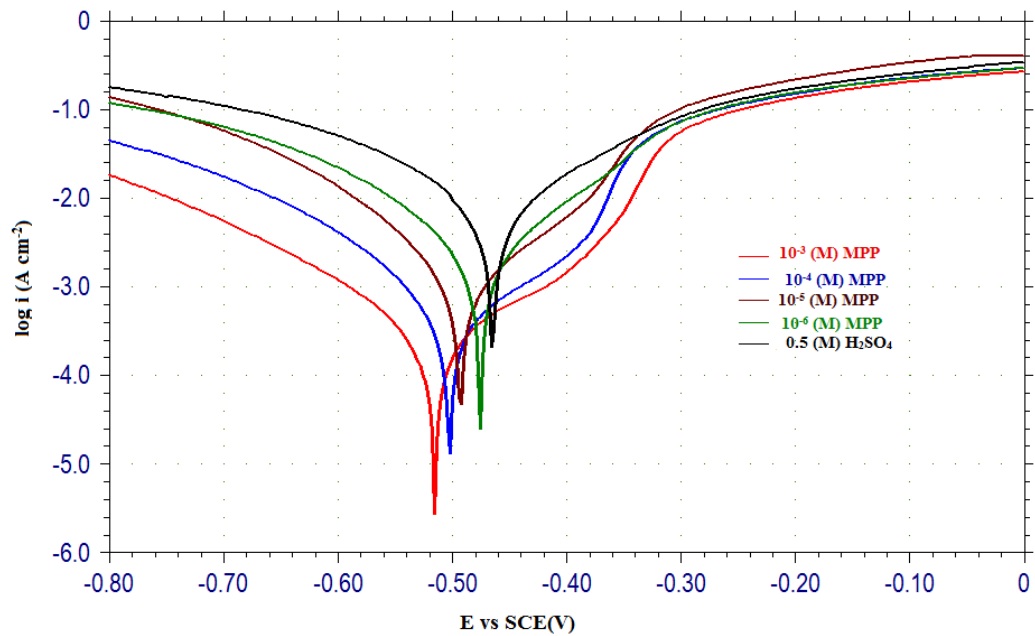


Fig. 3. Anodic and cathodic polarization curves for mild steel obtained at 25 °C in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations of inhibitor MPP at 298 K.

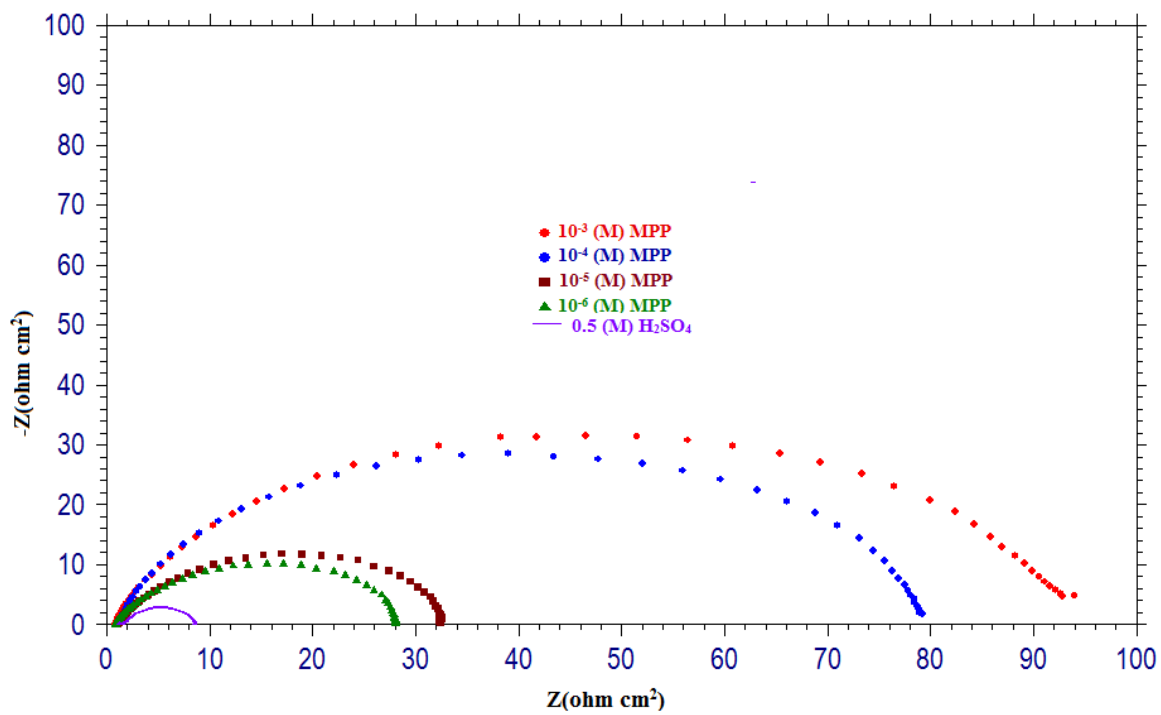


Fig. 4. Nyquist plots for mild steel in 0.5 M H₂SO₄ in absence and presence of different concentrations of inhibitor MPP at 298 K.

Table 1. Electrochemical parameters determined from polarization measurements in 0.5 M H₂SO₄ solution in the absence and presence of various concentrations of MPP at 298 K.

Conc. (M)	E _{corr} (mV _{SCE})	b _a (mV/dec)	b _c (mV/dec)	I _{corr} (μA/cm ²)	IE%
blank	465	71.59	60.89	8.805	-
10 ⁻⁶	476	90.31	80.92	2.342	73.10
10 ⁻⁵	493	93.33	97.67	1.562	82.26
10 ⁻⁴	503	98.89	110.54	0.4915	94.41
10 ⁻³	516	99.65	120.76	0.3048	96.53

Table 2. Fitting results of EIS data for mild steel in 0.5 M H₂SO₄ solution without and with various concentrations of MPP at 298 K.

Conc ⁿ mol / L	Rs (□ cm ²)	Y ₀ (10 ⁻⁶ □ ⁻¹ cm ⁻²)	n	R _{ct} (□ cm ²)	Cdl (□ cm ²)	IE%	LPR R _p (□cm ²)	IE%
Blank	1.1	158	0.750	6.713	1990	-	4	-
10 ⁻⁶	1.0	67	0.821	28.447	442	78.51	15.61	75.11
10 ⁻⁵	1.3	45	0.867	36.781	336	83.33	22.31	81.18
10 ⁻⁴	1.2	38	0.873	81.778	235	92.59	37.12	89.18
10 ⁻³	1.0	33	0.899	102.363	192	94.61	51.43	92.15

Received on March 2, 2014.