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http://heteroletters.org

ISSN: 2231 – 3087(print)
ISSN: 2230 – 9632 (Online)
Coden HLEEAI
Vol. 4: (2), 2014, 287-293

SYNTHESIS, CHARACTERIZATION AND INVESTIGATION OF SCHIFF BASE AS A CORROSION INHIBITOR FOR MILD STEEL IN H_2SO_4 MEDIUM

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Abstract:
The corrosion behaviour of mild steel (MS) in 0.5 M H_2SO_4 was studied by using (4-methoxy-6-methyl-pyrimidin-2-yl)-(1-pyridin-2-yl-ethylidene)-amine (MMPPE) as an inhibitor by using the conventional potentiodynamic polarization studies, linear polarization studies (LPR) and electrochemical impedance spectroscopy studies (EIS). The results showed that MMPPE possesses excellent inhibition effect towards mild steel corrosion. The inhibitor molecules were first adsorbed on the mild steel surface thereby blocking the active sites available for acid attack.

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

Introduction

Nitrogen-containing heterocyclic organic compounds have been found to be effective corrosion inhibitors. Lately, at industrial level, these were in to use not only due to their efficiency but also due to their safety. These are also valid as well for other organic compounds which act as corrosion inhibitors for metals and alloys. In this respect, there is a special emphasis on natural compounds which are nontoxic and ecologically friendly. Different types of organic compounds have been reported to act as inhibitors of corrosion [1–6]. In acidic environments, organic compounds with more than one hetero-atom containing pi-electrons exhibit high inhibiting properties by providing electrons which interact with metal surface [7]. It has been reported that Schiff bases show more inhibition efficiency than corresponding amines and carbonyl compounds [8]. 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 (4-methoxy-6-methyl-pyrimidin-2-yl)-(1-pyridin-2-yl-ethylidene)-amine as a novel inhibitor for the corrosion of carbon steel in 0.5 M H_2SO_4 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.

Material preparation and experimental methods
Material preparation

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. A pre-treatment was carried out prior to each experiment, in which specimen surface was mechanically polished with 340, 400, 600, 800, 1000 and 1200 grades of emery paper, rinsed with distilled water, degreased in ethanol and dried at room temperature before use.

Synthesis of MMPPE

The Schiff base was synthesized from the condensation reaction of 2-Amino-4-methoxy-6-methyl pyrimidine with 2-Acetyl Pyridine in methanol.The molecular structure of synthesized Schiff base has been given in Fig. 1.0. 2-Amino-4-methoxy-6-methyl pyrimidine waspurchased 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 cm^2 surface area. The reference electrode was "calomel"(Hg_2Cl_2,). 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 (Hg_2Cl_2) with a scan rate of 0.001 V s^{-1} and the anodic polarization curves were obtained in the potential ranges from Eocp to 0.0 V (Hg_2Cl_2) 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 (Rp) 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 MMPPE. 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 H_2SO_4 solution was placed over the working electrode.

RESULTS AND DISCUSSION
Characterization of MMPPE

Synthesis of (4- methoxy-6-methyl-pyrimidin-2-yl)-(1-pyridin-2-yl-ethylidene)-amine by condensation of 2-Amino-4-methoxy-6-methyl pyrimidine (0.2500 m mol) with 2 acetyl pyridine (0.2014 mml) in methanol was carried out for 20 hours and solid product was then characterised with ^1H NMR and FT-IR(KBr).The azomethine ν(C=N) stretching vibration for MMPPE was found at 1627 cm^{-1}. The band at 2830 cm^{-1} was due to the C—H bond stretching. The^1H NMR spectrum of MMPPE in D_2O showed no resonance peak at δ 6.11 ppm assignable to C—H proton.Threesinglets of three protons at δ 2.6 ppm, δ 3.80 and δ 2.0 were attributed to the methyl protons, which are chemically and magnetically equivalent.

Aromatic protons appear as a doublet and triplet in Figure 2 at δ 8.5 - 8.8 ppm and δ 8.1 – 8.6 ppm range respectively.

Potentiodynamic polarization measurements

Tafel polarization curves of mild steel in 0.5M H_2SO_4 solution with various concentrations of MMPPE are 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:

$$EI\% = \frac{Icorr_i - Icorr}{Icorr_i} \times 100$$

where $Icorr_i$ 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, 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. This means that the addition of the inhibitors does not modify the mechanism of hydrogen evolution, and the inhibitive molecules only block the active sites of hydrogen evolution by adsorption on the metal surface. According to the polarization curves, the presence of the inhibitors promotes a decrease in the anodic current densities and a slight shift of E_{corr} in the cathodic direction. These results indicate that the addition of the inhibitors in the corrosive solution reduces the anodic dissolution of steel and slows the cathodic evolution of hydrogen [9,10]. Therefore, the studied MMPPE can be classified as cathodic inhibitors in 0.5 M H_2SO_4. Table 1 show that the inhibition efficiency increases with increasing inhibitor concentration. This result indicates that MMPPE act as an adsorption inhibitors, given that more molecules are adsorbed on the metal surface as the concentration increases, promoting wider surface coverage [11]. 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 Rct values were calculated from the equation.

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

Where Rct(i) and Rct are the charge transfer resistance in absence and presence of optimum concentration of inhibitor. The values of phase shift, n(ranges from 0.811 to 0.97) were not changes significantly and its ongoing stability showed the charge transfer controlled dissolution mechanism of mild steel in 0.5 M H_2SO_4 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 studied concentrations and only their present results of 10^{-6} M 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 [12, 13]. Inhibition effect of the inhibitors can easily be observed from the low frequency impedance modulus [14]. From Fig. 4, the low frequency impedance modulus increase with increasing the concentration of the inhibitors, which demonstrates that the adsorptions of the inhibitors improve 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, only a phase peak close to 90°C 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 [15].

After the analysis of impedance results (table 2), we find that the charge-transfer resistance value, R_{ct} increases in inhibited system then 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 increases 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.

Conclusion

Inhibitive performance of MMPPE in 0.5M H_2SO_4 solution on mild steel was investigated in this study using EIS, potentiodynamic polarization and liner polarization method. It comes down to the following conclusion:

a. The potentiodynamic polarization curves indicated that MMPPE act as mixed type of inhibitor.
b. 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.
c. The percentage inhibition efficiency of MMPPE obtained from EIS and potentiodynamic polarization are in good agreement with one another.

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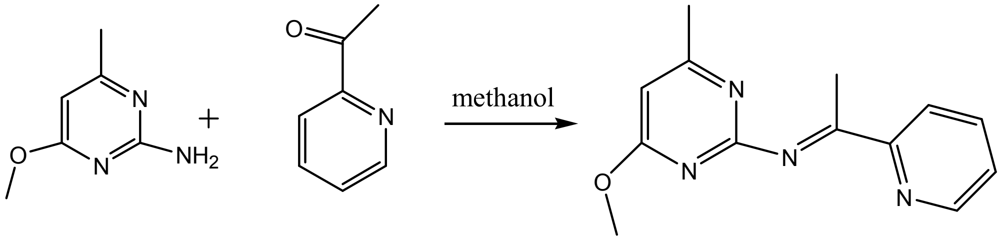

Fig.1. Scheme

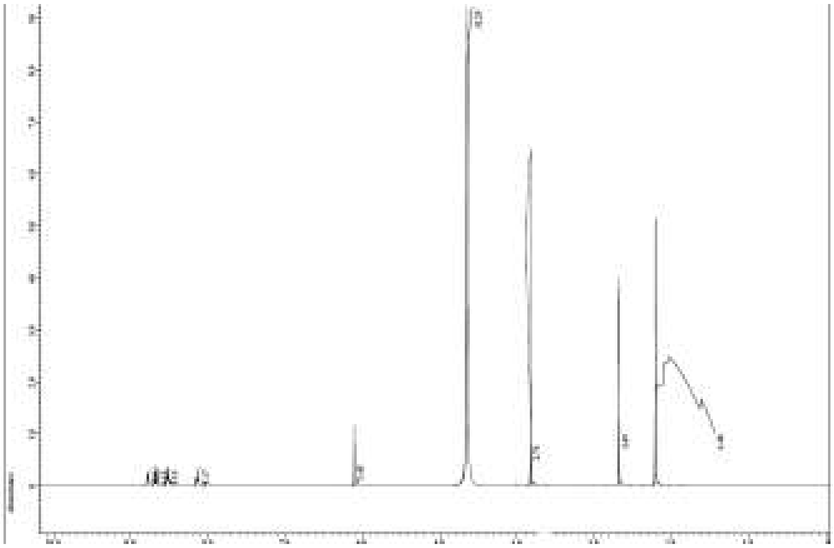

Fig. 2. The ^{1}H NMR spectrum of (4- methoxy-6-methyl-pyrimidin-2-yl)-(1-pyridin-2-yl-ethylidene)-amine

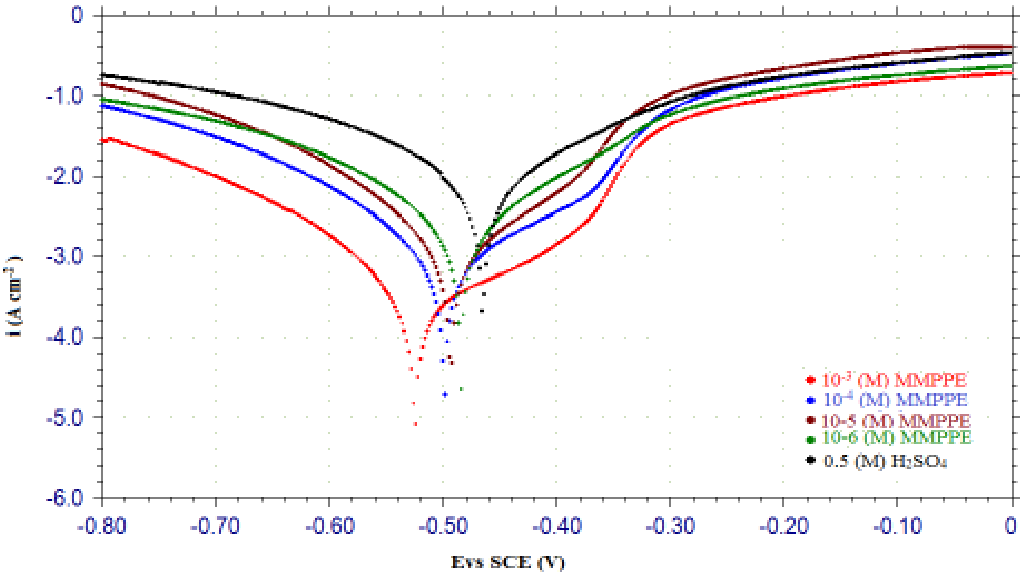

Fig.3. Anodic and cathodic polarization curves for mild steel obtained at 25 ^{0}C in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of inhibitor MMPPE.

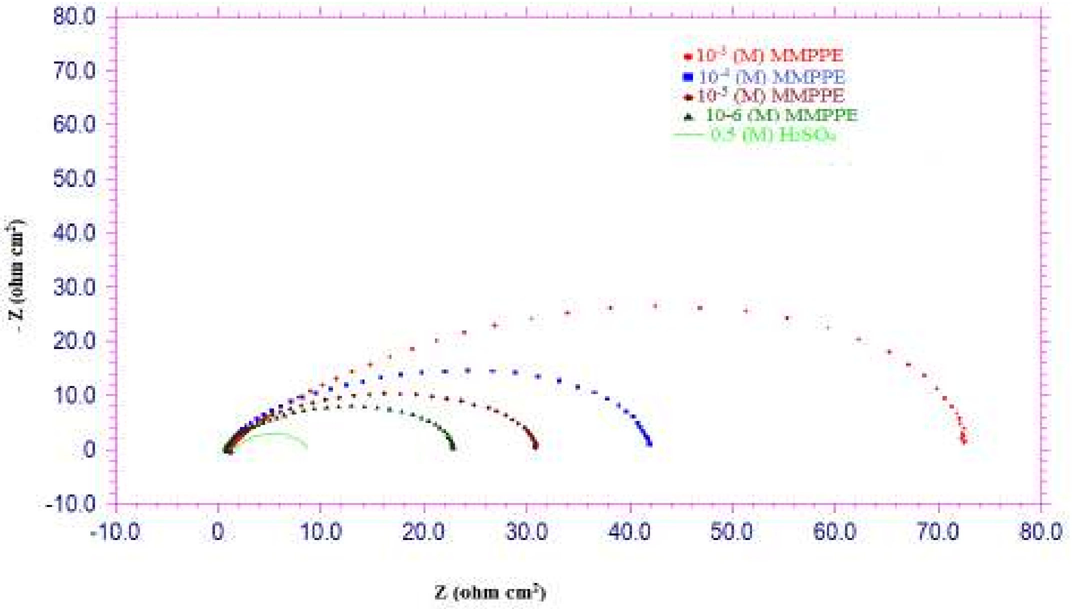

Fig. 4. Nyquist plots for mild steel in 0.5 M H_2SO_4 in absence and presence of different concentrations of inhibitor MMPPE.

Table1. Electrochemical parameters determined from polarization measurements in 0.5 M H_2SO_4 solution in the absence and presence of various concentrations of MMPPE 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}	484	80.21	78.92	2.421	72.10
10^{-5}	493	83.33	87.67	1.183	86.56
10^{-4}	499	90.89	120.54	0.9861	88.80
10^{-3}	525	97.45	125.76	0.3303	96.24

Table2. Fitting results of EIS data for mild steel in 0.5 M H_2SO_4 solution without and with various concentrations of MMPPE at 298 K.

Conc. mol / L	Rs (Ω cm^2)	Y_0 (10^{-6} Ω^{-1} cm^{-2})	n	R_{ct} (Ω cm^2)	Cdl (Ω cm^2)	IE%	LPR	
							R_p(Ωcm^2)	IE%
Blank	1.1	158	0.750	6.713	1990	-	4	-
10^{-6}	1.0	50	0.811	76.43	210	78.34	10.01	79.10
10^{-5}	1.3	35	0.855	44.34	137	81.55	20.21	83.33
10^{-4}	1.2	27	0.870	34.23	120	86.32	35.1	88.57
10^{-3}	1.0	22	0.897	29.56	110	92.11	45.7	91.77

Received on February14, 2014.