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Electrochemical evaluation of 1-methyl-2,6-diphenyl-piperidin-4-one oxime as corrosion inhibitor for mild steel immersed in an sulphuric acid medium

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ABSTRACT

A novel corrosion inhibitor namely 1-methyl-2, 6-diphenyl piperidin-4-one oxime (MDPO) has been synthesized and its inhibitive performance towards the corrosion of mild steel in 1M sulphuric acid(H_2SO_4) was tested by weight loss study, electrochemical methods, SEM and theoretical studies. The weight loss studies were conducted at three different temperatures such as 30°C, 40°C and 50°C for various concentrations (0, 25, 50,100, 200 and 300 ppm) for 2h duration. The study revealed that inhibition efficiency increases with increase of MDPO concentration and decreases with increase of temperature. It was studied that MDPO adsorbs over alloy surface obeying Temkin's isotherm. The calculated values of free energy of adsorption (ΔG_{ads}) support physisorption mechanism. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current (i_{corr}) and Tafel slopes (b_a& b_c) were determined using Tafel plot. The results showed that increase in concentration of MDPO decreases corrosion current and behave as mixed mode inhibitor. AC impedance measurement as determined by Nyquist plot revealed that charge transfer resistance increases with increase of concentration, whereas double layer capacitance decreases with increase of concentration tribute each other. SEM studies revealed the film forming ability of MDPO in H_2SO_4 medium. Quantum chemical studies exemplified that the electrons present in the phenyl ring of MDPO assist largely in the corrosion control process.

Key words: 1-methyl-2,6-diphenyl-piperidin-4-one oxime, Polarization, Impedance, SEM and Quantum chemical studies.

INTRODUCTION

Mild Steel (MS) an excellent fabricating material undergo rapid corrosion in acid environments. Generally, sulphuric acid (H_2SO_4) is employed for industrial operations such as acid pickling, industrial cleaning, acid descaling and oil well acidizing which in turn creates corrosion of fabricated alloy. One of the important methods of protection of metals and alloys against corrosion is the use of inhibitors. Many organic compounds are recognized as effective inhibitors because they have hetero atoms such as N, O and S which form co-ordinate bond with metal or alloys owing to their free electron pairs. Compounds with π electrons also exhibit inhibitive character due to interaction between metal and alloy with π orbitals [1-4]. In the present study, the inhibition property of 1-methyl-2, 6-diphenyl piperidin-4-one oxime (MDPO) on MS in 1M H_2SO_4 is investigated.

MATERIALS AND METHODS

2.1 Sample Preparation:

MS specimens of following composition C – 0.13%, P – 0.032%, Si – 0.014%,S – 0.025%, Mn –0.48% and Fe remainder were mechanically cut into specification of 4X1X0.2 cm, cleaned and scrubbed with emery paper to expose clean shining surface and degreased with acetone.

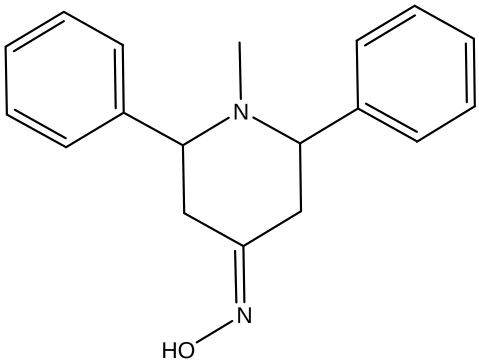

Figure 1: Structure of 1-methyl-2, 6-diphenyl piperidin-4-one oxime (MDPO)

2.2 Preparation of MDPO:
The precursor ketones viz., 1-methyl -2, 6-diphenyl piperidin-4-one were prepared by the method of Baliah et al [5]. Then that ketone was treated with filtrate formed from hydroxyl amine hydrochloride and sodium acetate in ethanol and refluxed for 4h and finally poured into water. The products viz., 1-methyl-3-ethyl-2, 6-diphenyl piperidin-4-one oxime was re-crystallized from ethanol and duly characterized using ^{1}H and ^{13}C NMR spectra and their structures are depicted in Figure 1.

2.3 Weight loss method :
MS coupons were immersed in pure 1M H_2SO_4 containing various concentrations of MDPO for 2h time interval at temperatures 30 – 50°C. The percentage inhibition efficiency (IE) and rate of corrosion (CR) were calculated using equations 1, 2 &3.

$$\theta = \frac{W_0 - W_i}{W_0} \quad (1)$$

$$IE = \theta \times 100 \quad (2)$$

$$CR = \frac{\text{Weight loss in mg}}{\text{Surface area in cm}^2 \times \text{immersion period in h}} \quad (3)$$

where W_o – Weight loss without MDPO.
W_i – Weight loss with different concentrations of MDPO.

2.4 Polarisation and impedance studies :
Potentiodynamically, the polarization curves were recorded using computerized CHi 604 c model. In this set up Pt electrode, calomel electrode and MS specimens were used as auxiliary, reference and working electrodes respectively which were immersed in the presence and absence of MDPO. Impedance studies were carried out in the frequency range of 10 KHz to 10 mHz for MS in 1M H_2SO_4 with and without different concentrations of MDPO. IE was calculated using R_{ct} as follows

$$IE = \frac{1 - R_{cto}}{R_{cti}} \times 100 \quad (4)$$

Where R_{cto} – Charge transfer resistance in absence of MDPO.

R_{cti} – Charge transfer resistance in presence of various concentrations of MDPO.

2.5 SEM Analysis:
SEM micrographs were taken using computerized electron microscope (Philips XL series).

2.6 Quantum chemical studies:
The quantum chemical study was done using Dewar's LCAO – SCF – MO semi empirical method, AM1 in the commercially available computer package program in an Intel Pentium duo core processor computer.

RESULTS AND DISCUSSION

The calculated values of IE and CR for MDPO inhibition for MS dissolution in H_2SO_4 medium is depicted in Table 1. From the table it is clear that IE increases with increase of MDPO concentration. Increase of IE with increase of

MDPO concentration showed that the corrosion is controlled by adsorption process. Several adsorption isotherms were tested with the experimental results and the Temkin's isotherm was found to be the best. A representative graph is given in Figure 2. Decrease of IE with increase of temperature supports physisorption process (6). The calculated free energy of adsorption (< 40 kJ/mol) showed that adsorption of MDPO on MS surface obeys physisorption mechanism [7]. The increase CR with increase of temperature also supports physisorption mechanism [8].

Table 1: Weight loss measurements for the mild steel dissolution immersed in 1M H_2SO_4 and in different concentrations of MDPO at various temperatures

Concentration ppm	303K		323K	
	IE	CR	IE	CR
0	-	1.42	-	5.26
25	45.2	0.78	32.7	3.54
50	50.9	0.69	40.8	3.11
100	65.4	0.49	47.6	2.76
150	71.7	0.4	58.9	2.16
200	81.6	0.26	64.8	1.85
300	90.5	0.14	72.5	1.45

Table 2: Electrochemical parameters of various concentrations MDPO for the corrosion process of mild steel immersed in 1M H_2SO_4

Concentration of inhibitor (ppm)	$-E_{corr}$ mV	i_{corr} (μA cm^{-2})	$-ß_a$ mV dec^{-1}	$-ß_c$ mV dec^{-1}	R_{ct} Ω cm^2	IE% using R_{ct}
Blank	478.2	1600	65	100	5.0	-
25	480.7	992	70	78	8.2	39.0
50	477.8	828	99	83	12.5	60.0
150	478.7	400	88	67	20.3	75.4
200	477.8	286	73	77	34.5	85.5
300	477.9	152	67	85	48.0	89.5

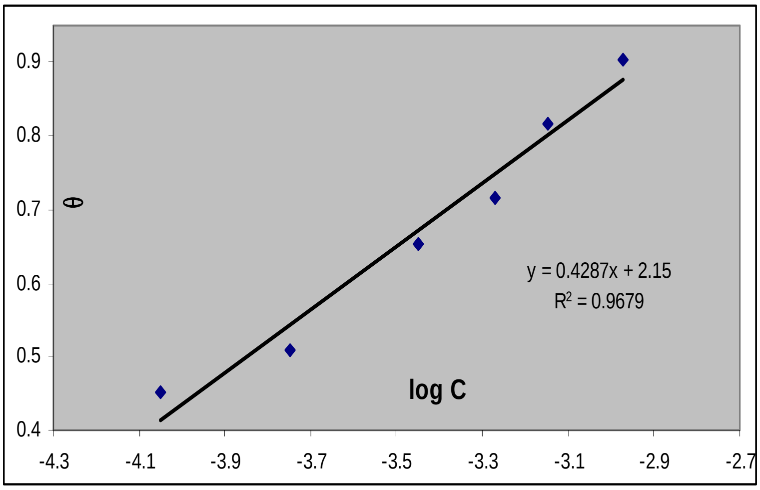

Figure2: Temkin's isotherm for adsorption of MDPO on MS surface at 30°C for 2h duration

Tafel polarization curves of MS in 1M H_2SO_4 solution with different concentrations of MDPO are shown in Figure 3. Increase in concentration of MDPO causes shifting of corrosion potential on both the directions indicating mixed mode inhibiting action of MDPO. No particular trend was observed from Tafel constants, which is suggestive of mixed mode inhibition. i_{corr} values decreased with increase of MDPO concentration (Table 2) which indicates the corrosion controlling property of MDPO. Nyquist plot in the presence and absence of various concentrations of MDPO in 1M H_2SO_4 is shown in Figure 4. The dispersion obtained in Nyquist plot was due to the dispersive capacitive loop and the in homogeneities on the electrode surface [9]. R_{ct} increases with increase of MDPO concentration whereas C_{dl} decreases with increase of MDPO concentration indicating the protection efficiency of MDPO.

SEM micrographs are shown in Figures 5 & 6 for MS specimen exposed to 1M H_2SO_4 and MS exposed to 300 ppm of MDPO in 1M H_2SO_4 respectively. Figure 5 displayed the surface of MS, which were damaged in presence of 1M H_2SO_4. Figure 6 showed the surface protection ability exhibited by MDPO.

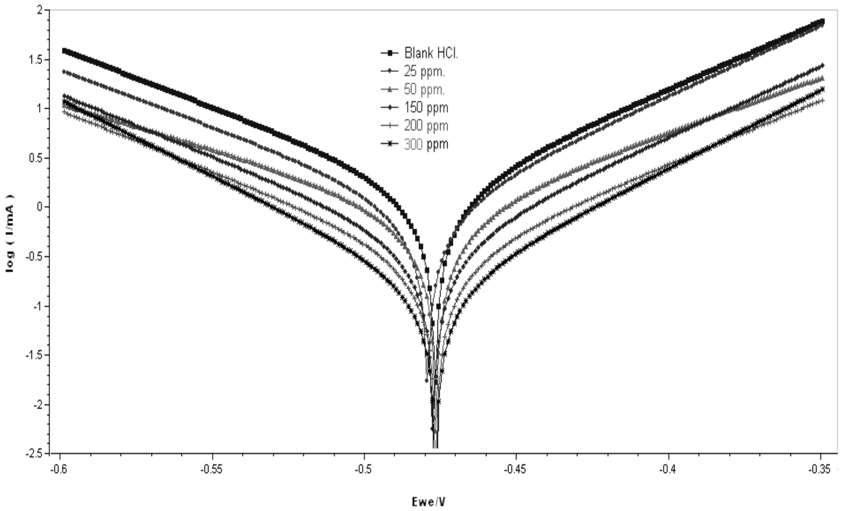

Figure 3: Tafel curves in presence and absence of various concentration of MDPO

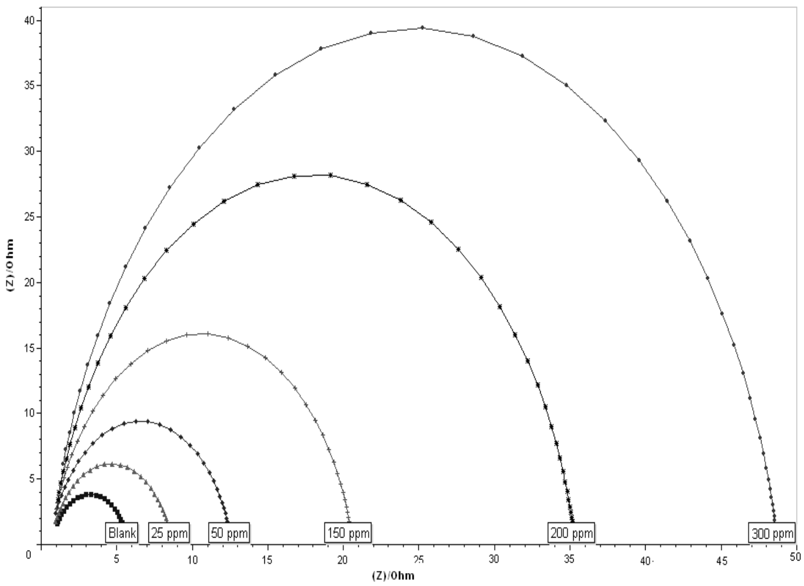

Figure 4: Nyquist plot for pure 1M H_2SO_4 and different concentration of MDPO

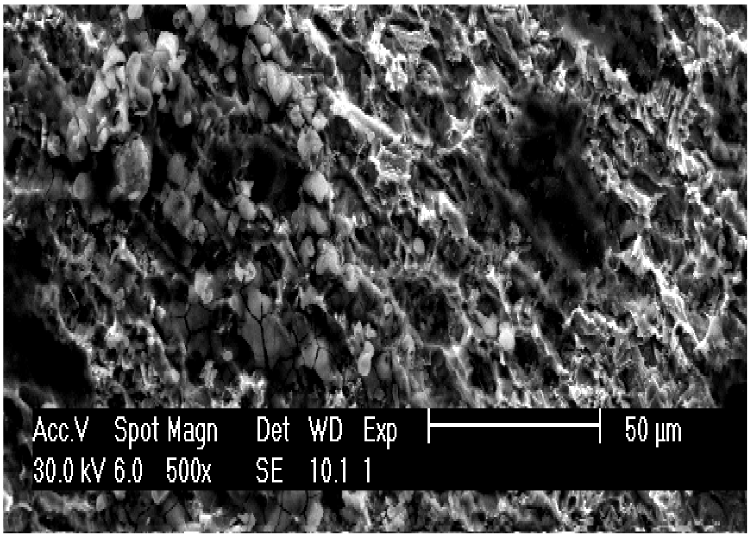

Figure 5: SEM analysis of MS surface exposed to 1M H_2SO_4

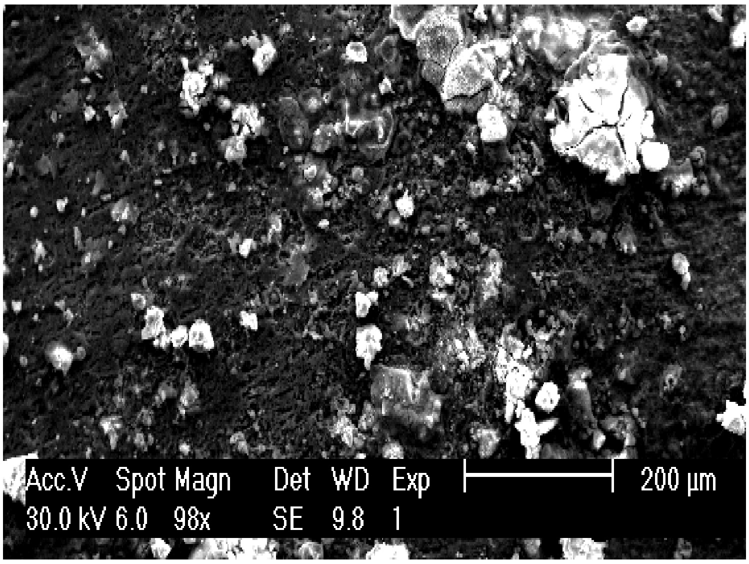

Figure 6: SEM picture of MS surface exposed to 1M H_2SO_4

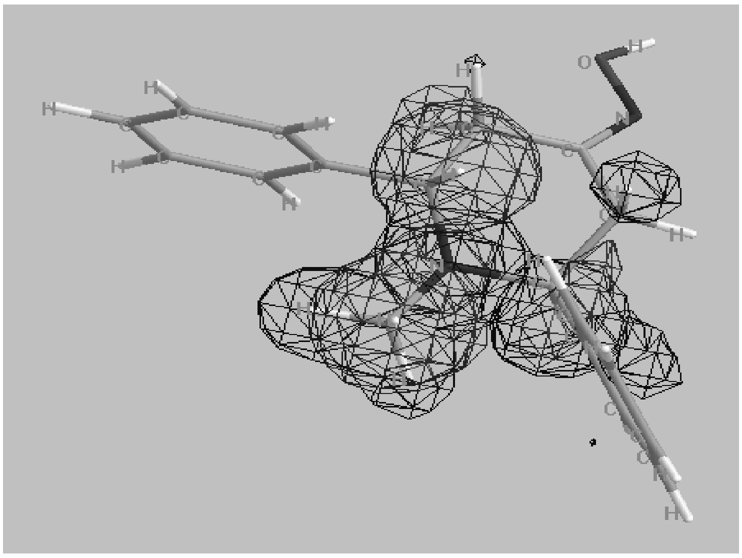

Figure 7: HOMO surface of MDPO

Quantum studies done for MDPO with its E_{HOMO} is shown in Figure 7. E_{HOMO} of MDPO is -9.027791 eV and that of its E_{LUMO} is 0.284891 eV. The high E_{HOMO} value of MDPO indicates the good inhibiting nature of MDPO. Moreover energy diagram of HOMO revealed that the protection of MDPO is due to π electrons present in the benzene ring of the molecule and lone pair of electrons present on N atom attached to the ring.

CONCLUSION

MDPO decreases the corrosion rate of MS in H_2SO_4 medium in a concentration dependent manner. Adsorption of MDPO on MS Surface obeys Temkin's adsorption isotherm. E_{corr}, b_a and b_c values have not been shifted to particular direction indicating MDPO as mixed mode indicator. Decrease of i_{corr} with increase of concentration showed MDPO as a good inhibitor. The values of R_{ct} increase with increase of MDPO concentration showed MDPO as good inhibitor. SEM revealed surface film forming ability of MDPO. Quantum chemical studies showed that the π electrons electrons present in phenyl ring are responsible for inhibiting ability of MDPO.

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