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Study of corrosion inhibition of mild steel in sulphuric acid medium by 1,3,3-trimethyl-2,6-diphenyl piperidin-4-one oxime

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ABSTRACT

Surface protecting ability of 1, 3, 3-trimethyl -2, 6-diphenyl piperidin-4-one oxime (TPO) against mild steel (MS) in 1M sulphuric acid medium has been investigated by weight loss study, electrochemical methods, SEM and theoretical studies. The weight loss studies were conducted at four different temperatures such as 30°C, 40°C and 50°C for various concentrations of (0, 50, 100, 200, 300 400 and 500 ppm) for 2h duration. The study showed that inhibition efficiency increased with increase of TPO concentration and decreased with increase of temperature. It was found that inhibition was due to adsorption of TPO on the MS surface obeying Temkin's adsorption isotherm. The calculated values of free energy of adsorption (ΔG_{ads}) support physisorption mechanism. Electrochemical data for corrosion processes such as corrosion potential(E_{corr}), corrosion current(i_{corr}) and Tafel slopes (b_a& b_c) were determined using Tafel plot, which showed that increase in concentration of TPO decreases corrosion current and behaves 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 complimenting each other. SEM studies revealed the surface protecting ability of TPO in H_2SO_4 medium. Quantum chemical studies illustrated that the corrosion inhibition efficiency of TPO is due to the electrons of phenyl ring.

Key words: 1, 3, 3-trimethyl -2,6-diphenyl-piperidin-4-one oxime, Corrosion inhibition, Polarization, Impedance, SEM and Quantum chemical studies.

INTRODUCTION

Mild Steel (MS) is a renowned fabricating material which undergoes 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, 3, 3-trimethyl -2,6-diphenyl-piperidin-4-one oxime (TPO) 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.

2.2 Preparation of TPO:
The precursor ketones viz., 1, 3, 3-trimethyl -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, 3, 3-trimethyl -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 TPO for 2h time interval at temperatures 30, 40 and 50^{o}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 TPO.
W_i – Weight loss with different concentrations of TPO.

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 TPO. 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 TPO. IE was calculated using R_{ct} as follows

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

where R_{cto} – charge transfer resistance in absence of TPO.
R_{cti} – charge transfer resistance in presence of various concentration of TPO.

2.5 SEM Analysis:
SEM micrographs were taken using computerized electron microscope of make 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 TPO 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 TPO concentration. Increase of IE with increase of TPO 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. Decrease of IE with increase of temperature supports physisorption process [6] . The calculated free energy of adsorption (< 40 kJ/mol) showed that adsorption of TPO on MS surface obeys physisorption mechanism [7]. The increase CR with increase of temperature also supports physisorption mechanism [8].

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

SEM micrographs are shown in Figures 4 & 5 for MS specimen exposed to 1M H_2SO_4 and MS exposed to 300 ppm of TPO in 1M H_2SO_4 respectively. Figure 4 displayed the surface of MS, which were damaged in presence of 1M H_2SO_4. Figure 5 showed the surface protection ability exhibited by TPO.

Quantum studies done for TPO with its E_{HOMO} is shown in Figure 6. E_{HOMO} of TPO is -8.9696 eV and that of its E_{LUMO} is 0.3283 eV. The high E_{HOMO} value of TPO indicates the good inhibiting nature of TPO. Moreover energy diagram of HOMO revealed that the protection of TPO 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.

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

Concentration ppm	303K		313K		323K	
	IE	CR	IE	CR	IE	CR
0	-	1.42	-	3.65	-	5.26
50	43.2	0.79	38.2	2.20	32.7	3.54
100	52.9	0.69	45.6	1.99	40.8	3.11
200	65.4	0.49	54.8	1.65	47.6	2.76
300	71.7	0.38	66.2	1.33	58.9	2.16
400	81.6	0.26	74.5	0.82	64.8	1.85
500	91.5	0.15	79.9	0.69	72.5	1.45

Table 2: Electrochemical parameters of various concentrations TPO 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**	**-**
50	**480.7**	**992**	**70**	**78**	**8.2**	**39.0**
100	**477.8**	**828**	**99**	**83**	**12.5**	**60.0**
200	**478.7**	**400**	**88**	**67**	**20.3**	**75.4**
300	**477.8**	**286**	**73**	**77**	**34.5**	**85.5**
400	**483**	**100**	**45**	**88**	**42.0**	**86.3**
500	**477.9**	**152**	**67**	**85**	**48.0**	**89.5**

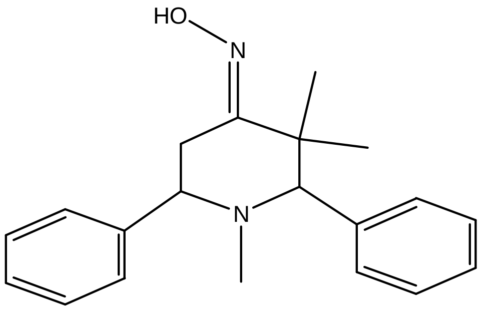
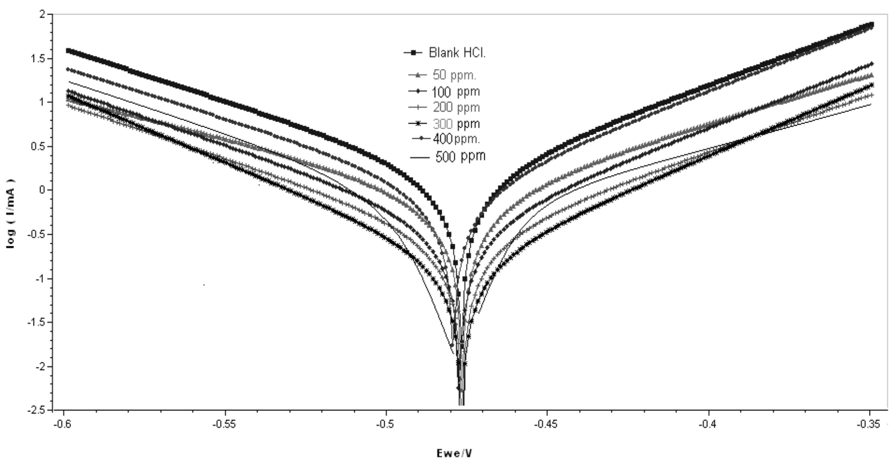


Figure 1: Structure of 1, 3, 3-trimethyl -2, 6-diphenyl piperidin-4-one oxime (TPO)



-Figure 2: Tafel curves in presence and absence of various concentration of TPO

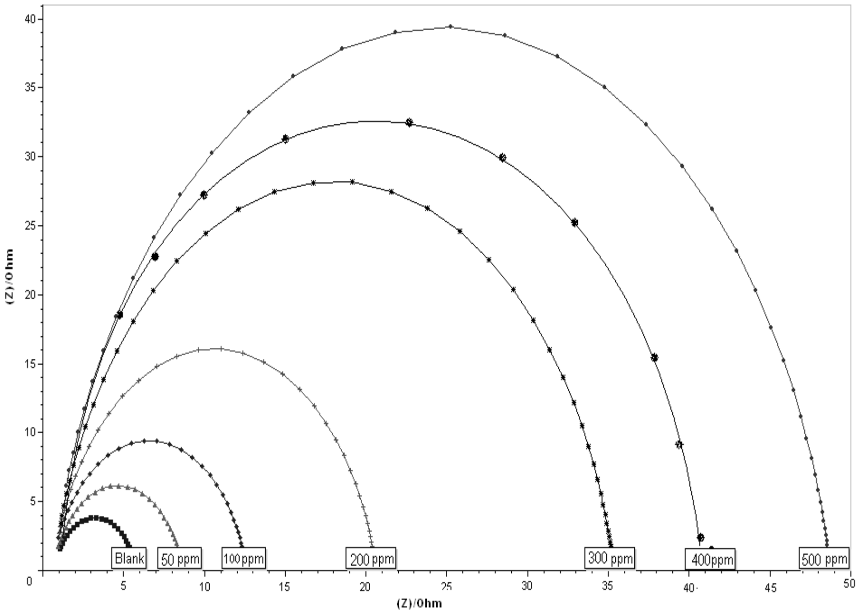


Figure 3: Nyquist plot for pure 1M H_2SO_4 and different concentration of TPO

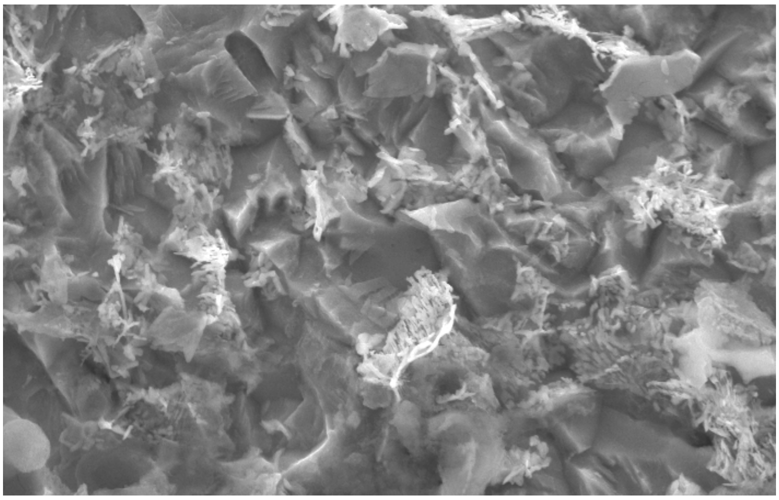


Figure 4: SEM picture of MS surface exposed to 1M H_2SO_4

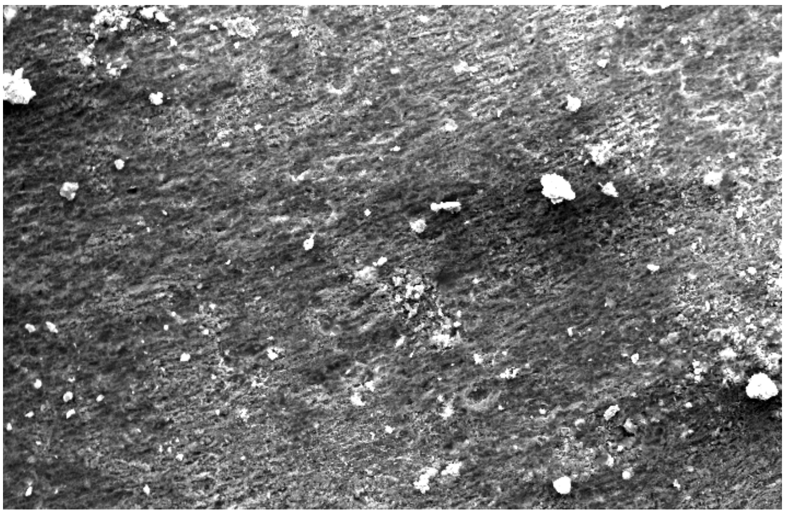


Figure 5: SEM analysis of MS surface exposed to TPO in H_2SO_4

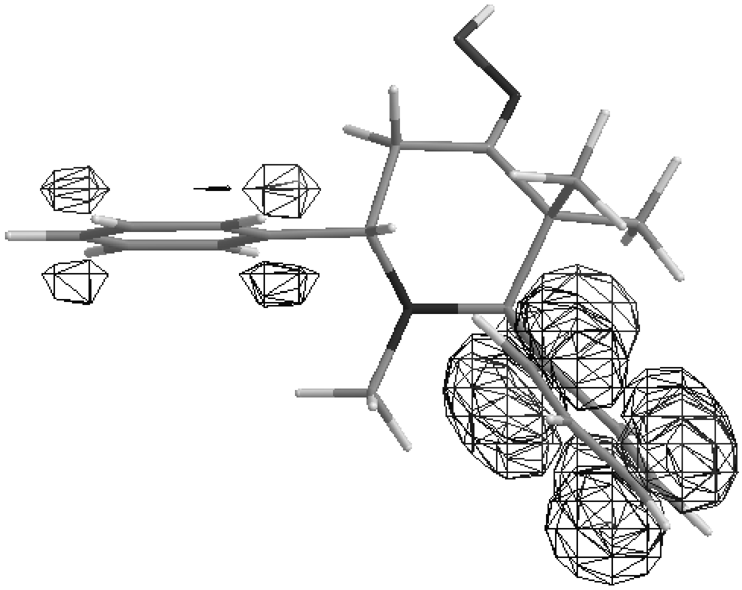


Figure 6: HOMO surface of TPO

CONCLUSION

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

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REFERENCES

[1] Senthilkumar A N, Tharini K, Sethuraman M G *Surf Rev Lett.* **2009** 16 1 141.
[2] Senthilkumar A N, Tharini K, Sethuraman M G *Acta Phys. Chim. Sin.* **2012,** 28 ,2, 399.
[3] Senthilkumar A N, Tharini K, Sethuraman M G *J.Mater.Engg & Perform.* **2011 ,**26, 2, 969.
[4] Stoyanova, A E, Sokolova, E I, Raicheva, S N *Corros,* **1997**, 39,9, 1595.
[5] Baliah V, Noller C R *J. Am. Chem. Soc*. **1948,** 70, 3853.
[6] Senthilkumar A N, Sethuraman M G *Corr. Rev*. **2008,** 26,1, 23.
[7] Ashassi-Sorkhabi H, Majidi M R, Seyyedi K *App.Sur.Sci* **2004** ,225,176.
[8] Ebenso E E , Okafor P C, Ekpe U f *Anti.Corros.Met.* Mat **2003 ,**50, 6, 414.
[9] Yurt A, Balaban A, Ustun Kandemir S, Bereket G, Erk B *Mat.Chem.Phy* **2004,** 85, 420.