Research Journal of Chemical Sciences E-ISSN 2231-606X
Vol. 6(3), 16-19, March (2016) Res. J. Chem. Sci.

The Effect of 1, 3, 5-trimethyl-2, 6-diphenyl piperidin-4-one oxime on the Electrochemical Behaviour of Mild Steel in HCl Medium

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Available online at: www.isca.in, www.isca.me
Received 27th October 2015, revised 5th January 2016, accepted 12th March 2016

Abstract

Corrosion inhibitive performance of synthesized heterocyclic compound namely 1, 3, 5-trimethyl-2, 6-diphenyl piperidin-4-one oxime (TPO) was tested by weight loss study, electrochemical methods and SEM studies in 1M hydrochloric acid (HCl) medium against mild steel (MS). The weight loss studies were conducted at three different temperatures such as 30^{o}C, 40^{o}C and 50^{o}C for various concentrations (0, 25, 50,100, 200 and 300 ppm) for 2h duration. The study revealed that the inhibition efficiency had positive correlation with enhancing TPO concentration and negative correlation with raising temperature. TPO adsorbs physically over mild steel surface obeying Temkin's isotherm. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current (i_{corr}) and Tafel slopes (b_a and b_c) were determined using Tafel plot. The results showed that TPO decreases corrosion current significantly and behaves as mixed mode inhibitor. AC impedance measurement as determined by Nyquist plot were utilized to calculate the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) whose results tribute each other. SEM studies revealed the film forming ability of TPO in HCl medium.

Keywords: 1, 3, 5-trimethyl-2, 6-diphenyl piperidin-4-one oxime, Temkin's isotherm, Polarization, Impedance and SEM.

Introduction

Mild Steel (MS) an excellent fabricating material undergo rapid corrosion in acid environments. Generally, hydrochloric acid (HCl) 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, 5-trimethyl-2, 6-diphenyl piperidin-4-one oxime (TPO) on MS in 1M HCl is investigated.

Materials and Methods

Materials: 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.

The precursor ketones viz., 1, 3, 5-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, 5-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.

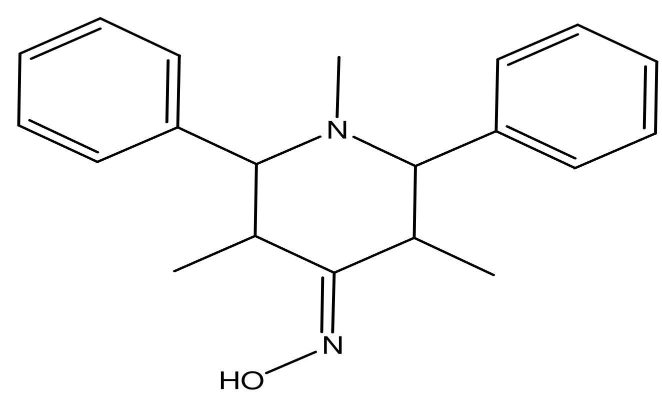

Figure-1
Structure of 1, 3, 5-trimethyl-2, 6-diphenyl piperidin-4-one oxime (TPO)

Electrochemical studies: MS coupons were immersed in pure 1M HCl containing various concentrations of TPO for 2h time interval at temperatures 30–50^{o}C. The percentage inhibition efficiency (IE) and rate of corrosion (CR) were calculated using Equations-1, 2 and 3.

$$\theta = \frac{W0 - Wi}{W0} \quad (1)$$

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

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

Where: W_o – Weight loss without TPO. W_i – Weight loss with different concentrations of TPO.

Polarization and impedance studies: Potentiodynamically, the polarization curves were recorded using computerized CH 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 HCl with and without different concentrations of TPO. IE was calculated using R_{ct} as follows:

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

Where: R_{cto}–Charge transfer resistance in absence of TPO. R_{cti} – Charge transfer resistance in presence of various concentrations of TPO.

SEM Analysis: SEM provides a supported the protective film onto the mild steel surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of mild steel, the SEM micrographs of the surface are examined.

The SEM micrographs of polished mild steel surface show the smooth surface of the metal. This show the absence of any corrosion products or inhibitors complex formed on the metal surface.

Results and Discussion

The calculated values of IE and CR for TPO inhibition for MS dissolution in HCl 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 HCl solution with different concentrations of TPO showed that the 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 obtained in the presence and absence of various concentrations of TPO in 1M HCl contained dispersion 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 (Table-2).

Table-1
Weight loss measurements for the mild steel dissolution immersed in 1M HCl 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	-	5.24
25	44.6	0.76	39.0	2.22	32.4	3.52
50	50.2	0.68	45.4	1.99	40.6	3.10
100	65.1	0.48	54.4	1.65	47.6	2.73
150	70.7	0.38	66.0	1.23	58.2	2.13
200	80.6	0.24	74.2	0.93	64.8	1.83
300	90.2	0.13	79.3	0.74	72.1	1.44

Table-2
Electrochemical parameters calculated for the various concentrations of TPO

Concentration of inhibitor (ppm)	$-E_{corr}$ mV	i_{corr} ($\mu A\ cm^{-2}$)	$-\beta_a$ $mV\ dec^{-1}$	$-\beta_c$ $mV\ dec^{-1}$	R_{ct} $\Omega\ cm^2$	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

SEM micrographs are shown in Figures-2 and 3 for MS specimen exposed to 1M HCl and MS exposed to 300 ppm of TPO in 1M HCl respectively. Figure-2 displayed the surface of MS, which were damaged in presence of 1M HCl Figure-3 showed the surface protection ability exhibited by TPO.

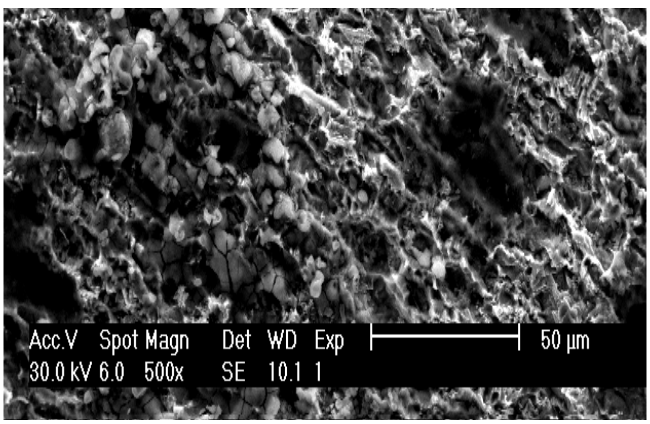

Figure-3
SEM analysis of MS surface exposed to 1M HCl

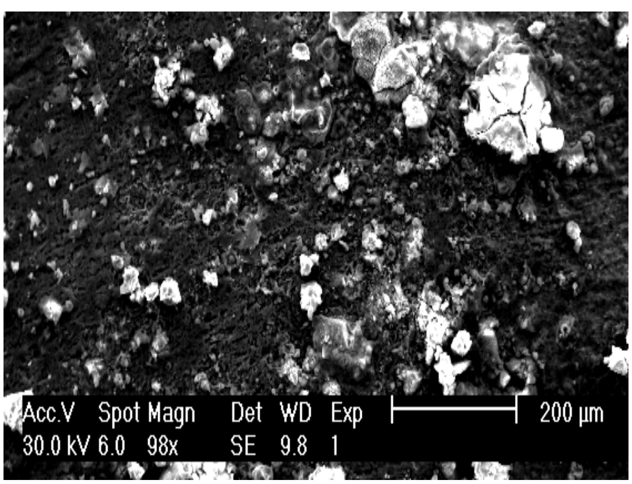

Figure-4
SEM picture of MS surface exposed to 1M HCl

Conclusion

TPO decreases the corrosion rate of MS in HCl 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.

Acknowledgements

Authorities of GAC, Trichirappalli and AGAC, Karaikudi are thanked for their help and encouragement.

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