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Adsoption and anticorrosion potential of N-Benyzl Piperidin-4-One oxime for corrosion of mild steel in 2m Hydrocholoric acid solution

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Abstract
N-benzyl piperidine -4- one oxime (BPOX) was tested as corrosion inhibitor for mild steel in 2M HCl solution using electrochemical and weight loss measurements. Results obtained showed that this compound has a good inhibiting properties for mild steel corrosion in acidic medium, with inhibition efficiencies values reach 77% at 300ppm. The inhibition was assumed to occur via adsorption of the BPOX molecules on metallic surface. Adsorption of inhibitor molecules on mild steel surface showed Temkin's adsorption isotherm fit in acidic media. Potentiodynamic polarization curves showed that the inhibition is a mixed nature. In addition, results obtained by weight loss and electrochemical measurements are in good agreement. Mechanism of physical adsorption is proposed from the apparent activation energy (Ea) and the thermodynamic parameters obtained. The adsorption of the BPOX on the mild steel surface is spontaneous.

Keywords: BPOX, weight loss, polarization, EIS, SEM, quantum chemical studies

1. Introduction

Acid solutions are commonly used for the removal of undesirable scale and rust in the metal working, cleaning of boilers and heat exchangers. Hydrochloric acids are most widely used for all these purposes. However, the strong corrosivity of hydrochloric acid needs to be controlled by an appropriate corrosion inhibitor [1]. The existing data show that most organic inhibitors act by adsorption on the metal surface. The adsorption of inhibitor occurs through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings. These compounds are adsorbed on the metallic surface block the active corrosion sites. The molecules that contain nitrogen and sulfur in their structures are of particular importance inhibitors. The reason is that these molecules provide excellent inhibition compared with compounds that contain only sulfur or nitrogen [2, 3]. The inhibition property of N-benzyl piperidine -4- one derivatives is attributed to their molecular structure. The planarity and pairs of free electrons in heteroatoms are important characteristics that determine the adsorption of these molecules on the metal surface. The strength of adsorbed layer is related to the functional groups connected to aromatic ring [4].The adsorption of organic compounds depends mainly on the electronic structure of the molecule and that the inhibition efficiency increases with the increase in the number of aromatic ring [5]. These compounds are adsorbed on the metallic surface and block the active corrosion sites. Adsorption behavior of organic molecules on the surface of metals depends on molecular structure of the organic compounds, surface charge density and zero charge potential of metals [6]. The aim of this work is to investigate the inhibiting influence of N-benzyl piperidin -4- one oxime on mild steel corrosion in 2M hydrochloric acid solution. This has been studied by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques.

2. Materials and Methods

2.1 Preparation of N-benzyl piperidin -4-one oxime

To the boiling solution of N-benzyl piperidin -4-one (0.01mol) in methanol (45ml) and few sodium acetate, hydroxylamine hydrochloride (0.01 mol) and the methanol solution were added by stirring. The reaction was refluxed for 4 hours on a water bath. After cooling,

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the solid product was filtered and recrystallized from methanol to get the corresponding oxime.

2.2 Weight loss method

The polished and weighed MS specimens of uniform size were suspended in 100 ml test solutions with and without the inhibitor at different concentrations for a period of 1hr and 2 hours. Then the specimens were washed, dried and weighed. The weight loss was calculated. From this data, inhibition efficiency (IE) was calculated from the following equation [7]

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

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

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

where Wo – Weight loss without BPOX.
W_i – Weight loss with different concentrations of BPOX.

2.3 Polarization 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 BPOX. Impedance studies were carried out in the frequency range of 10 KHz to 10 mHz for MS in 2M HCl with and without different concentrations of BPOX. IE was calculated using R_{ct} as follows

$$IE = 1 - \frac{Rcto}{Rcti} X 100 \longrightarrow (4)$$

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

2.4 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 B3LYP/6-31g(d) at DFT method in the method commercially available computer package program in an Intel Pentium duo core processor computer.

3. Results and Discussion

Table 1 shows calculated IE and CR values for BPOX inhibition for MS dissolution in acid medium. From the table it is clear that IE increases with increase of BPOX concentration. Increase of IE with increase of BPOX concentration revealed that process is under adsorption control. CR increases with increase of temperature indicating physisorption [8]. Several adsorption isotherms were assessed and the Temkin's adsorption isotherm was found to be the best (Figure 7). From the slopes and intercepts of plot, free energy of adsorption were calculated (< 40 kJ/mol) which showed that adsorption of BPOX on MS surface obeys physisorption mechanism [9].

Tafel polarization curves of MS in 2M HCl solution with different concentrations of BPOX are shown in Figure 5. Increase in concentration of BPOX causes slight shifting of corrosion potential on both the directions with variation in Tafel slopes indicating mixed mode inhibiting action of BPOX. i_{corr} values decreased with increase of BPOX concentration (Table 2) which indicates the corrosion controlling property of BPOX. Nyquist plot in the presence and absence of various concentrations of BPOX in 2M HCl is shown in Figure 6. The dispersion obtained in Nyquist plot was due to the dispersive capacitive loop and the in homogeneities on the electrode surface [10]. R_{ct} increases with increase of BPOX concentration whereas C_{dl} decreases with increase of BPOX concentration indicating the protection efficiency of BPOX.

SEM micrographs which were taken under 750x resolution is shown in Figures 8 and 9 for brightly polished MS surface, MS specimen exposed to 2M HCl respectively. Figure 9 explained surface protection efficiency exhibited by BPOX.

Quantum studies done for BPOX with its E_{HOMO} is shown in Figure 10b. E_{HOMO} of BPOX is -5.9724 eV and that of its E_{LUMO} is -0.0324 eV. The high E_{HOMO} values of BPOX indicates the good inhibiting nature of BPOX. Moreover energy diagram of HOMO revealed that the protection of BPOX 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. The adsorption of BPOX on MS can take place via following three ways [10] 1. Electrostatic attraction between charged BPOX and MS surface. 2. Interaction of uncharged electron pairs of BPOX on MS surface. 3. Interaction of π electrons of BPOX with MS. The third way would be the most probable mode for the protection efficiency of BPOX on MS surface as evidenced from computational studies.

Table 1: Calculated values of corrosion rate and inhibition efficiency for mild steel in 2 M HCl in the absence and presence of BPOX at 303K-333K

		303K		313K		323K		333K	
	Concentration	**IE**	**CR**	**IE**	**CR**	**IE**	**CR**	**IE**	**CR**
BPOX 1hr	25	71.88	0.24	62.66	0.27	63.75	0.3	59.13	0.32
	50	74.13	0.22	64.66	0.25	66.33	0.28	60.6	0.31
	100	74.61	0.21	67.33	0.23	67.33	0.27	63.13	0.29
	200	76.3	0.2	69.04	0.22	68	0.26	63.91	0.28
	300	77.51	0.19	70.28	0.21	68.75	0.26	64.52	0.28
BPOX 2hrs	25	73.2	0.29	68.2	0.33	51.76	0.42	40.37	0.5
	50	74.08	0.28	69	0.32	53.96	0.4	41.81	0.49
	100	74.57	0.28	69.31	0.31	54.78	0.4	43.46	0.47
	200	76.76	0.26	69.77	0.31	55.76	0.39	44.4	0.47
	300	76.07	0.25	71.21	0.29	56.82	0.38	45.6	0.46

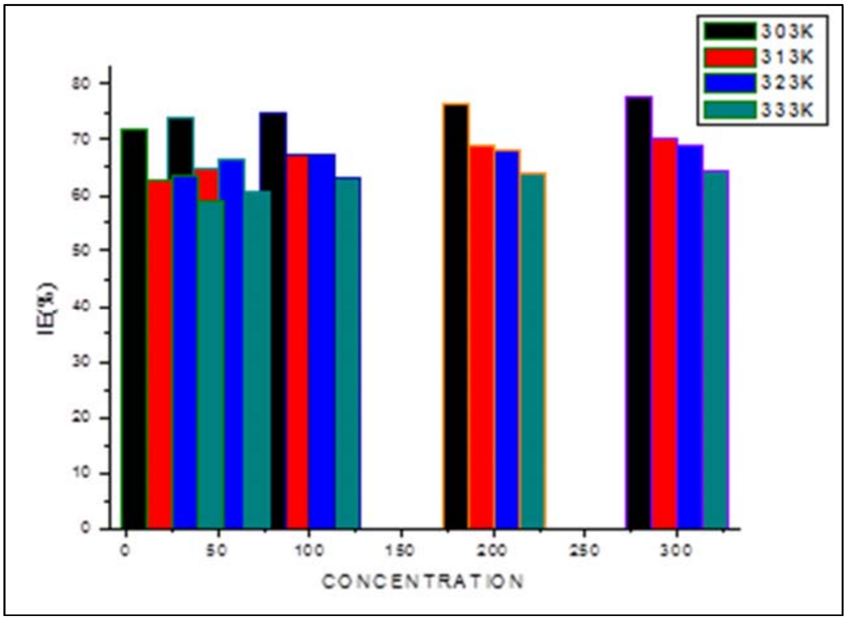

Fig 1: Plot of %Inhibition efficiency Vs concentration of BPOX at 1 hour duration

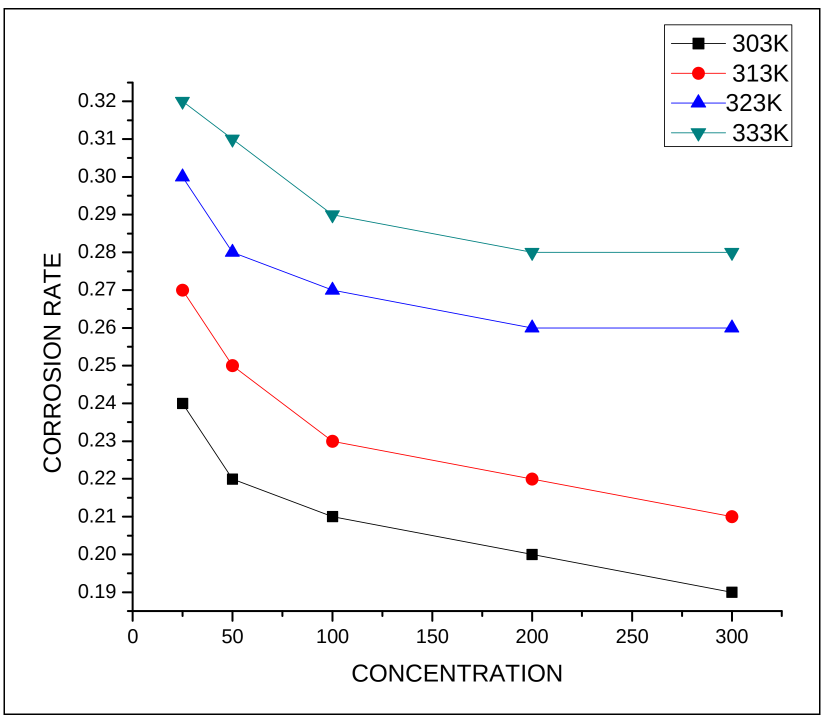

Fig 2: Plot of %corrosion rate Vs concentration of BPOX at 1 hour duration

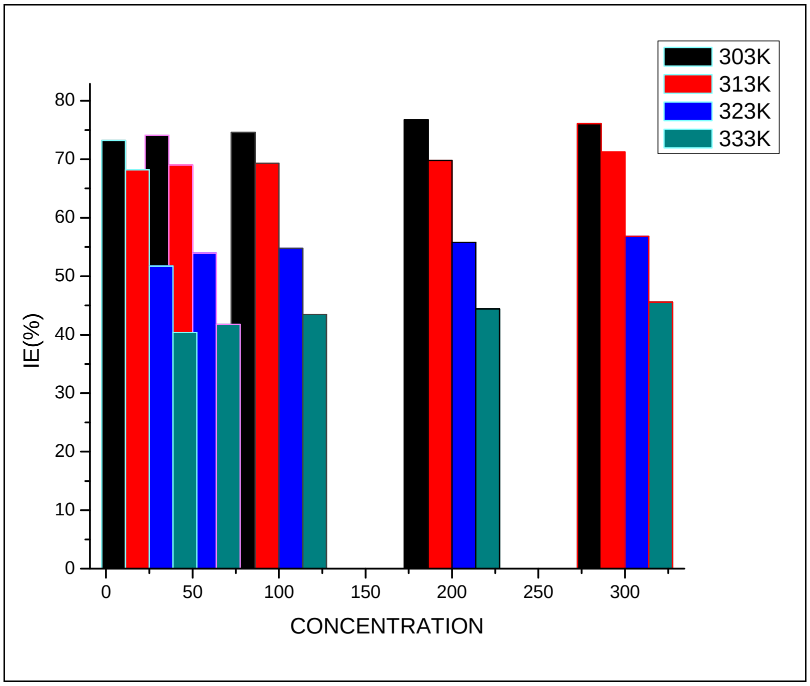

Fig 3: Plot of %Inhibition efficiency Vs concentration of BPOX at 2 hours duration

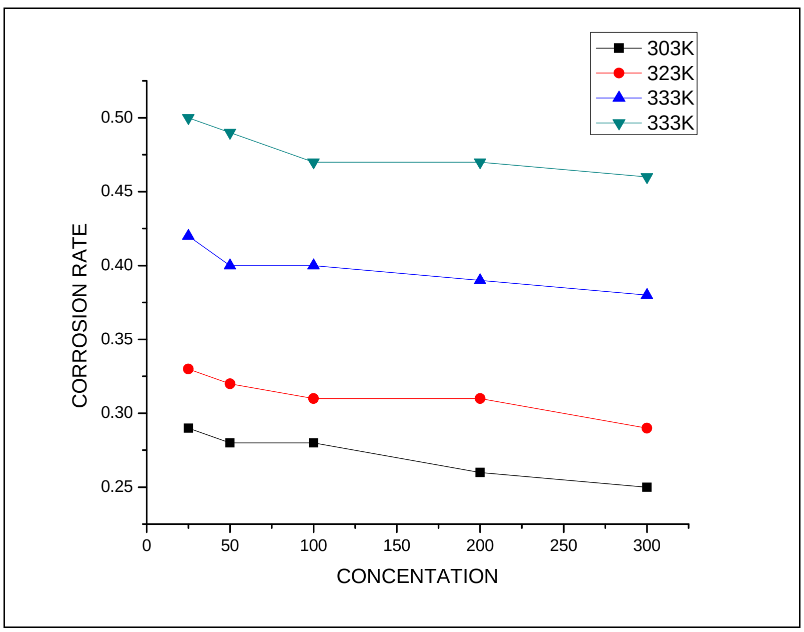

Fig 4: Plot of %corrosion rate Vs concentration of BPOX at 2 hours duration

Table 2: Tafel plot of Electrochemical parameters of BPOX in 2M HCl medium

S. No	Concentration of inhibitor (ppm)	$-E_{corr}$ Mv	I_{corr} μAcm^{-2}	$-b_a$ mV dec^{-1}	$-b_c$ mV dec^{-1}	C_{dl} $\mu F\ cm^{-2}$	R_{ct} $\Omega\ cm^2$	% of IE
1	Blank	0.4867	528.2	103	67	133.26	24.53	-
2	25	0.4661	407.8	80	43	128.23	31.51	22.15
3	50	0.4603	330.9	95	75	125.28	49.79	50.83
4	100	0.4541	281.9	35	82	123.58	80.39	69.54
5	200	0.4524	225.8	83	90	121.97	87.63	72.60
6	300	0.4512	203.2	58	45	120.42	101.32	75.89

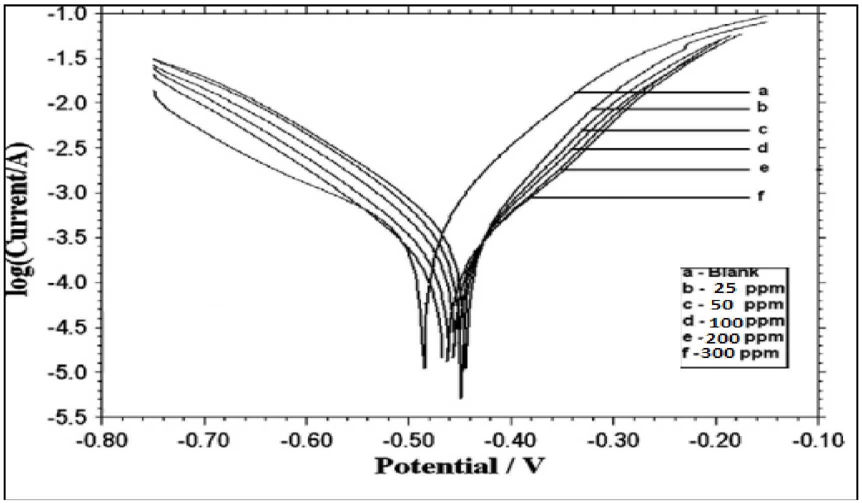

Fig 5: Tafel lines for mild steel corrosion in 2 M hydrochloric acid in the absence and presence of various concentration of BPOX inhibitor

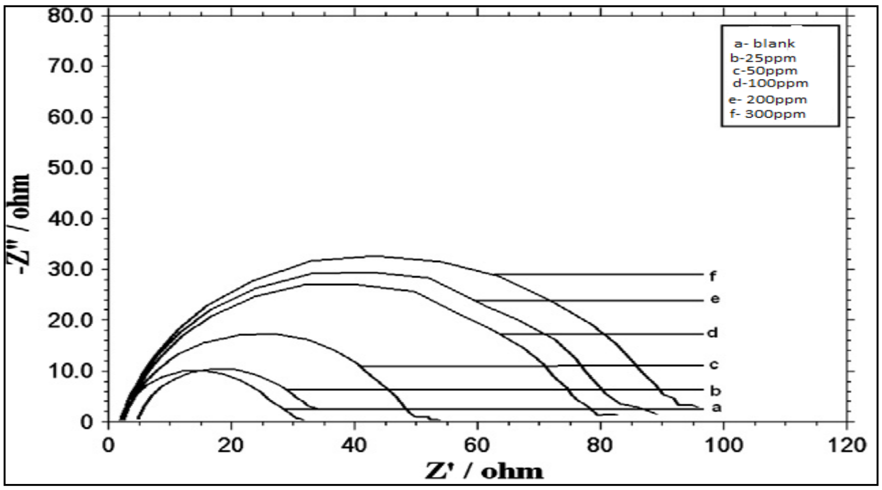

Fig 6: Nyquist plots for mild steel corrosion in 2 M hydrochloric acid in the absence and presence of various concentration of BPOX inhibitor

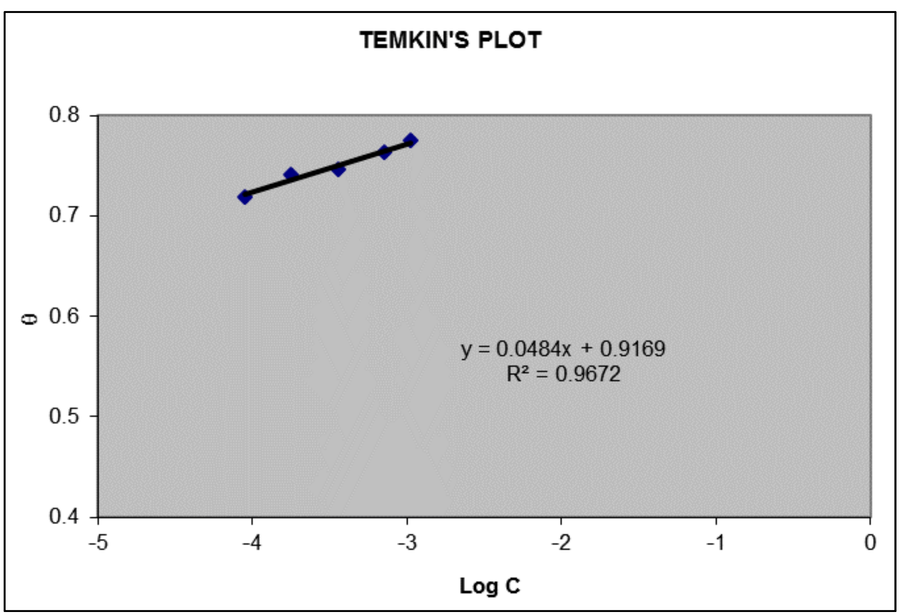

Fig 7: Temkin's plot for mild steel specimen exposed in 2M HCl medium in presence of BPOX at 303K

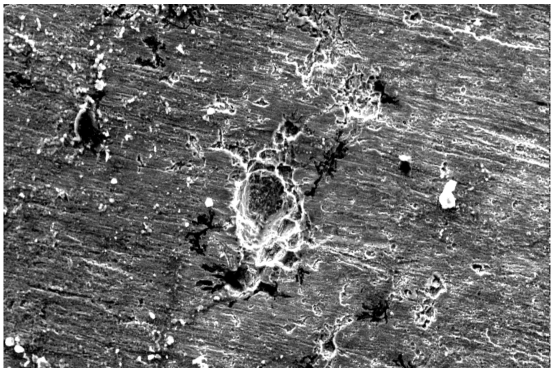

Fig 8: Micrograph of brightly polished MS exposed to 2M HCl

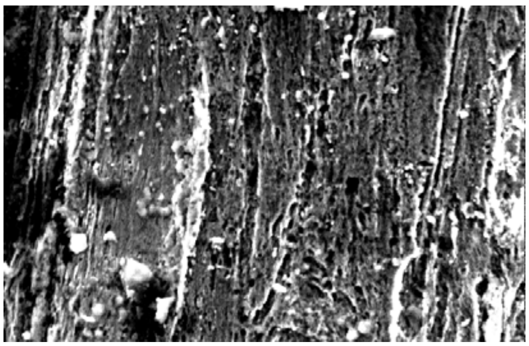

Fig 9: SEM analysis of MS surface exposed to BPOX in 2M HCl

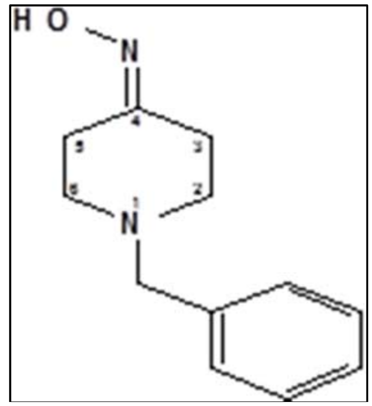

Fig 10a

N-benzyl piperidin -4-one Oxime

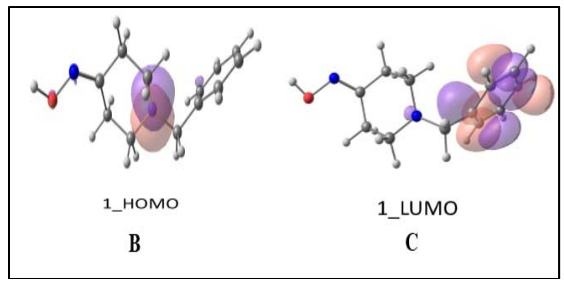

Fig 10B, C

Table 3: Calculated quantum chemical parameters of the studied inhibitor

Quantum parameters	N-benzyl piperdine -4-one oxime (BPOX)
E_{HOMO} (eV)	-5.9724
E_{LUMO} (eV)	-0.0324
ΔE gap (eV)	5.94
μ (debye)	0.77
I= $-E_{HOMO}$ (eV)	5.9724
A= $- E_{LUMO}$ (eV)	0.0324
$\chi = \frac{I+A}{2}$	3.0024
$\eta = \frac{I-A}{2}$	2.97
$\sigma = \frac{1}{\eta}$	0.3367
$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$	0.6729
TE(eV)	-17730.27

4. Conclusions

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

5. References

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