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Ethane-2- thioamido-4-amino-*N*-(5-methylisoxazol-3-yl)-benzene sulfonamide: A novel inhibitor for the corrosion of mild steel in 1N HCl

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Abstract

The corrosion of inhibition of mild steel has been monitored by Ethane-2- thioamido-4-amino-N-(5-methylisoxazol-3-yl)-benzene sulfonamide (ETAMBS) as an inhibitor in 1NHCl medium. The potentiodynamic polarization studies demonstrated the mixed mode of inhibitive action of the compound. The parameters like charge transfer resistance, double layer capacitance, surface uniformity and relaxation time derived from impedance analysis confirmed the effective performance of the inhibitor. The mode of adsorption of ETAMBS on mild steel surface was well demonstrated from quantum mechanical functions such as HOMO, LUMO, Hardness, softness, energy gap and dipole moment. The formation

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of protective film of the compound was proved by SEM images.

Keywords Corrosion, quantum, inhibition, impedance

Introduction

In industries, the corrosion of mild steel is an inevitable reaction in acidic media. Several thiourea derivatives have been reported as effective corrosion inhibitors for mild steel [1-5] . In recent years, the retardation of metal dissolution has been studied by using macro heterocyclic compounds or drug molecules. Eno etal [6] and Shukla [7] have studied the inhibitive actions of

sparflaxin and cefalexin on the corrosion of steel in acidic media. Harikumar and his co investigators [8-9] have reported the performances of cloxacillin and

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ampicillin drugs as corrosion inhibitors of mild steel in 1N HCl.

The careful study on literature confirms that no valid publication is existing for the use of Ethane-2-thioamido-4-amino-N-(5-methylisoxazol-3-yl)-benzene sulfonamide (ETAMBS) as an inhibitor for the corrosion mild steel in 1NHCl medium.

Experimental procedure

The mild steel specimens (98.7 % purity) of size 10mm^2 x 40 mm^2 were mechanically polished degreased with trichloro ethylene and then immersed in 1N HCl medium in the presence and absence of ETAMBS for weight loss and gasometric studies. The above specimens of size 10 mm^2 were employed as working electrodes, a platinum

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foil with surface area of 30 mm^2 and $Hg/Hg_2Cl_2/HCl_{(1N)}$ were used as counter and reference electrodes for potentiodynamic polarization and A.C impedance measurements using EG&G Princeton Applied research model-7310. Gaussian software was employed to calculate the quantum chemical parameters like HOMO, LUMO, Hardness, softness, energy gap ,electro negativity and dipole moment of the compound.

Results and discussion:

Weight loss and gasometric studies:

The results of weight loss and gasometric studies are given in table 1. It was observed that the dissolution of metal is minimized when the concentration of ETAMBS is increased. The maximum corrosion inhibition was

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noticed at the concentration of 10 ppm of inhibitor. The remarkable performance of inhibition is due to the adsorption of the compound on steel surface.

Potentiodynamic polarization measurements:

The polarization studies indicated that in the presence of ETAMBS the E_{corr} and
I_{corr} values have decreased as compared with blank (table 2). The anodic and cathodic Tafel slopes have been shifted to less negative directions equally. This confirms that the compounds behaved as mixed mode of inhibitor as it reduces the oxidation of Fe atom and evolution of hydrogen gas on the same extent (Figure 1). These

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results are in good conformity with weight loss and gasometric studies.

Impedance studies:

The nyquist graphs for the corrosion of mild steel in the presence and absence of different concentration of ETAMBS are given in table 3.From figure 2, it is cleared that perfect semicircles are obtained for the corrosion inhibition reaction indicating that the reaction follows charge transfer mode. The charge transfer resistance is found as high and it reaches maximum value at 10 ppm of ETAMBS ,where as double layer capacitance values is lessened with increased concentrations of inhibitor [10]. The factors like surface inhomogeneity or uniformity (n) and relaxation time (τ) played vital role for justification of performance of inhibitor. It has been proved that higher the surface uniformity, higher will be the

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inhibition and lesser will be the relaxation time for inhibitor.
The surface uniformity and relaxation time can be related as follows:

$$Z = 1 / C_{dl} [(-1/\tau)_{n}]^{-1}$$

It can be assumed that for 100% inhibition efficiency, the surface uniformity may be unity. The increased values of surface inhomogeneity (n) and reduced relaxation time values confirmed the role of inhibition of the compound.

Quantum mechanical calculations:

The quantum mechanical factors like energy of highly occupied molecular orbitals (HOMO),Lowest un occupied molecular orbitals, energy gap(ΔE), Hardness (η),softness (σ) , dipole moment (μ), electron affinity (A) and

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electronegativity (χ) calculated from optimized structure of ETAMBS (figure 3.a) are given in table 4. These values indicate that ETAMBS inhibit the corrosion of mild steel in 1N HCl. It has been well established fact that if ΔE values are > 8 and $\mu > 4$, then the inhibition efficiency of the compound will be above 90% [10]. The distribution of orbital's is higher in LUMO (Figure 3.c) than HOMO (Figure3.b) indicating that the interaction between the inhibitor and un occupied d- orbitlas of iron atom. The Mullikan's charges for C(1), S(3), C(6), C(8), C(9), C(10), C(11), O(13), O(14), N(15), N(18) and C(19) confirmed that adsorption of the compound on mild steel surface may take place through the above negatively charged atoms. Besides the above factors, other groups like sulphoxide, π - electrons in the five membered ring, -C=S group have significantly enhanced the adsorption on metal surface.

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SEM Analysis

The SEM photos for the corrosion of mild steel in 1N HCl is given in figure 4.a.The image evidently shows the formation of etched iron surface in acid medium. The formation of protective layer of the inhibitor on mild steel is clearly visible in Figure 4.b .

Conclusions:

1.The performance of a novel corrosion inhibitor Viz., Ethane-2- thioamido-4-amino-N-(5-methylisoxazol-3-yl)-benzene sulfonamide (ETAMBS) has been thoroughly screened by weight loss, gasometry and impedance measurements.

2. Potentiodynamic polarization results confirmed that the compound behaved as mixed type inhibitor.

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3. The adsorption of the inhibitor on steel surface is further justified from quantum mechanical factors and SEM images.

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Table 1. Values of inhibition efficiency obtained from weight loss and gasometric measurements with and without the presence of ETAMBS.

Concentration of Inhibitor (in ppm)	Inhibition efficiency (%) in 1N HCl	
	Weight loss studies	Gasometric studies
2	82	81.6
6	94	94.2
10	98.2	97.9

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Table 2 .Results of polarization measurements of mild steel in 1N HCl in the presence and absence of various concentrations of ETAMBS.

Concentration of Inhibitor (mM)	E_{corr} (mV)	Tafel slopes (m.V/ dec)		I_{corr} m.A /cm^2	Inhibition efficiency (%)
		b_a	b_c		
Blank	-520	65		120	2.64

2	-433	64		138	0.52

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80.3				
6	-347	78	141	0.17
93.6				
10	-285	85	140	0.05
98.1				

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Table 3.Nyquist parameters for the corrosion of mild steel in 1N HCl in the presence and absence of different concentrations of ETAMBS.

Concentration of Inhibitor (mM)	1N HCl			
	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) μF/cm^2	Surface uniformity (n)	Relaxation time (τ) in seconds
Blank	25	245		0.0708.
1	47	139	0.83	0.00121

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10	61	125	0.94	0.00011
50	77.8	114	0.98	0.00103

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Table 4. Mullikan's charges calculated from quantum mechanical studies

C	-0.178	**C(1)**
C	0.265	C(2)
S	**-0.245**	**S(3)**
N	0.107	N(4)

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C	-0.162	C(6)
C	0.150	C(7)
C	-0.152	C(8)
C	-0.035	C(9)
C	-0.204	C(10)
C	-0.027	C(11)

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S	2.533	S(12)
O	**-1.132**	**O(13)**
O	**-1.143**	**O(14)**
N	**-0.174**	**N(15)**
H	0.104	6)
C	0.202	C(17)

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N	**-0.268**	**8)**
C	**-0.170**	**C(19)**
C	0.062	0)
O	0.029	1)
H	0.056	2)
H	0.040	3)
H	0.067	4)
H	0.099	5)
H	0.026	6)

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H	0.026	7)
H	0.037	8)
H	0.023	9)
H	0.028	0)

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Table 5: Quantum mechanical studies of corrosion of mild steel in 1N HCl

Compound	E_{HOMO}(eV)	E_{LUMO}(eV)	Δ E (eV)	μ(Debye)	η	χ	σ
ETAMBS	-9.7142	-1.70437	8.0098	4.5	4.004	5.7092	0.2497

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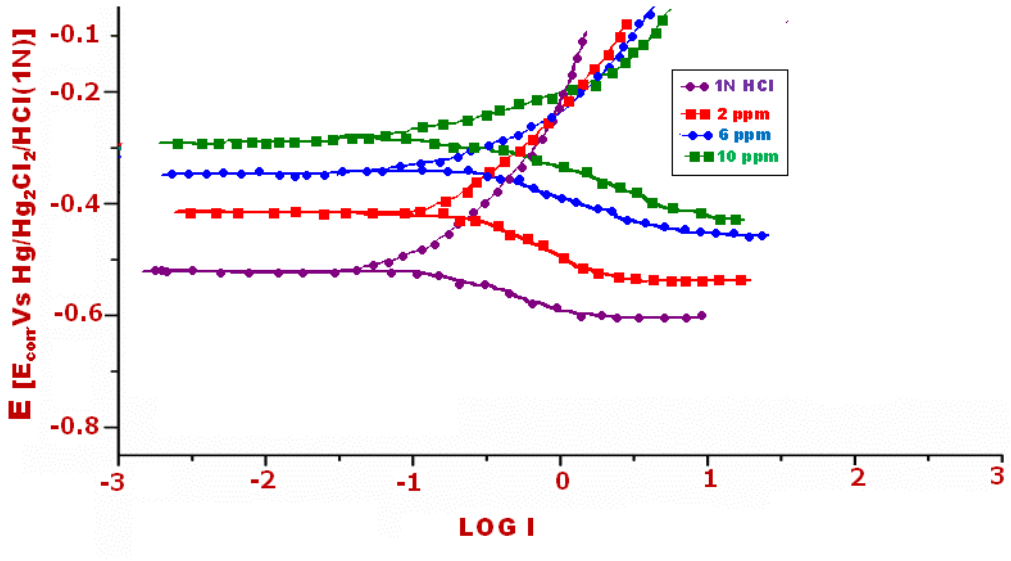

Figure 1: Tafel curves for the corrosion inhibition of mild steel in 1N HCl.

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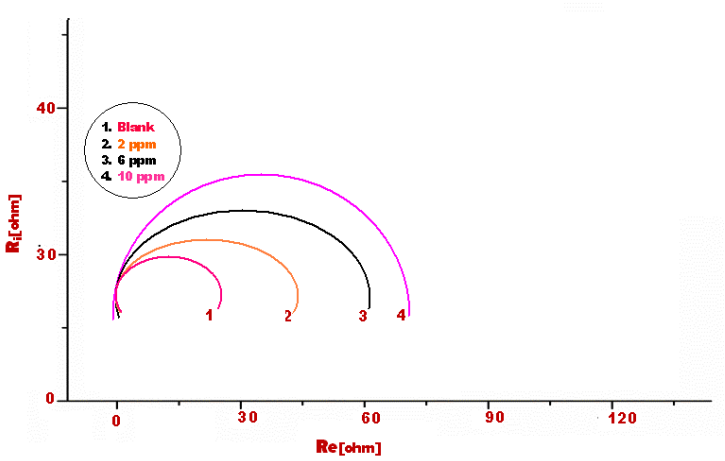

Figure 2. Nyquist plots for the corrosion inhibition of mild steel

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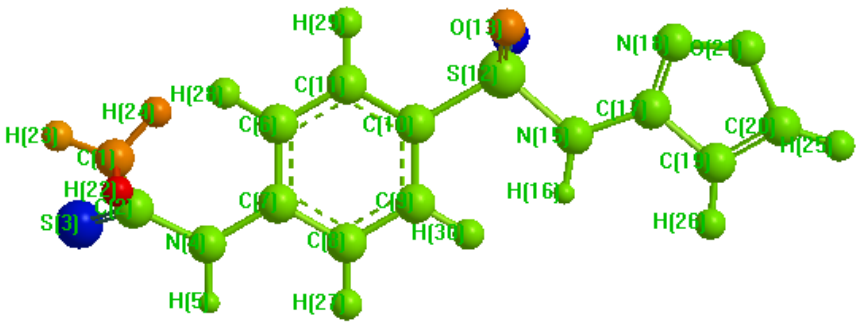

Figure 3 a.Optimized structure of ETAMS

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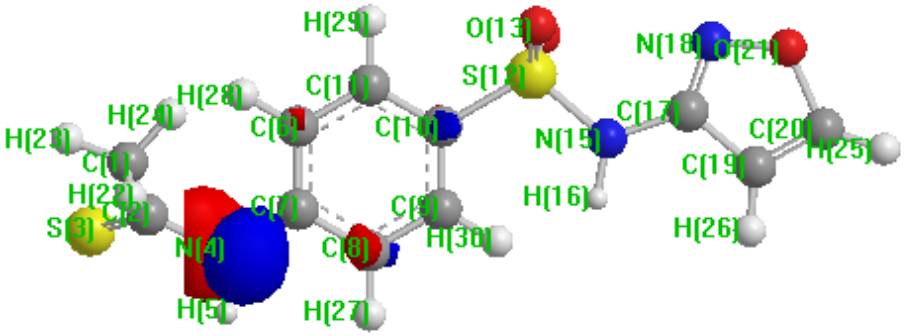

Figure 3.b. Highly occupied molecular orbital view of ETAMBS

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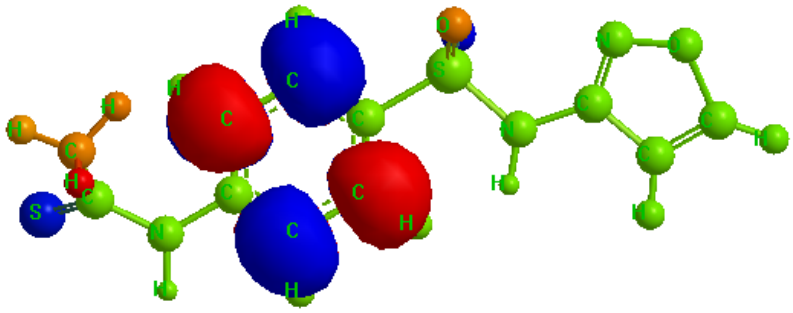
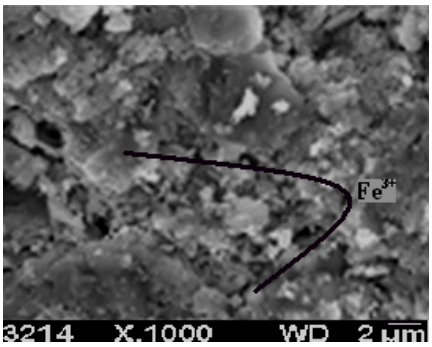


Figure 3.c. Lowest un- occupied molecular orbital view of ETAMBS



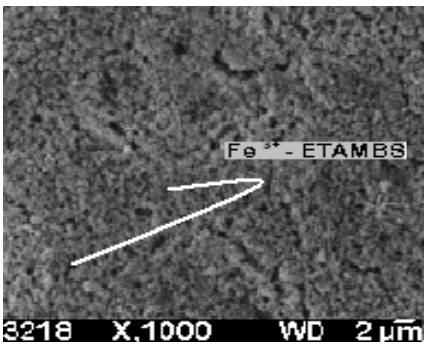


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Figure 4.a. SEM images for the etched iron surfaces in 1N HCl

Figure 4.b. SEM images for the corrosion mild steel with ETAMBS

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