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Studies on the reduced dissolution of stainless steel in industry environment- A laboratory approach

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Abstract: The reduction of dissolution of Stainless less steel 304 could be achieved by using 1,1-Diallyl-3-(2,3-dimethyl-6-quinoxalinyl) thiourea (DDQT) as inhibitor in 5M Na_2SO_4. The computational quantum mechanical analysis for inhibition performance of the compound has been studied using values of E_{HOMO}, E_{LUMO}, ΔE and dipole moment, mass loss, gasometric and electrochemical studies. Potential-Current Curves manifested that the inhibitor follows mixed type of inhibition in industry environment. The adsorption of inhibitor on SS 304 surface obeyed Temkin's adsorption isotherm.
Keywords : Corrosion, potential, impedance, inhibition.

1.Introduction

Stainless steel 304 is an important category of metals due to its excellent mechanical properties. It is widely used under different conditions in chemical and allied industries in handling acidic, alkaline and salt solutions. Stainless steel is used in auromobile industries industries as bus bars, pipelines for petroleum industries, storage tanks, reaction vessel and chemical batteries [1]. When SS 304 is exposed to an industry environment containing sulphate ions that causes damage to the substrate, because of their corrosive nature. Several methods were used to decrease the corrosion of metals in acidic medium, but the use of inhibitors is most commonly used [6-10].

Organic compounds are widely used as corrosion inhibitors for steel in acidic media [11-16]. The rate of corrosion decreases by adsorption of organic inhibitors on the metal surface. The inhibitors block the active sites by displacing water molecules and form a compact barrier film on the metal surface. The most of the organic inhibitors are toxic, highly expensive and non environment friendly. Research activities in recent times are geared towards developing the cheap, non-toxic drugs as environment friendly corrosion inhibitors [17-18].

The aim of this work is to investigate the corrosion protection efficiency of 1,1-Diallyl-3-(2,3-dimethyl-6-quinoxalinyl)thiourea (DDQT). for stainless steel corrosion in 5M Na_2SO_4. The molecular weight of the compound is 312.4. The authors came to know that exceedingly few reports are available by using this compound as corrosion inhibitor in 0.1M H_2SO_4 [19]. No concrete report is available for the use these compounds as corrosion inhibitors in 5M Na_2SO_4. From the literature the higher concentration of Na_2SO_4 acts as descaling chemical for stainless steel used as cathodes for anodizing , battery electrodes in the presence of sulphur containing organic compounds. Use of this inhibitor in 5M Na_2SO_4 will reduce the metal loss in acid medium. The compound is large enough and sufficiently planar to block more surface area on the stainless steel. The inhibition efficiency was calculated using weight loss measurement, potentiodynamic polarization studies, impedance techniques, and quantum mechanical methods. A definite correlation exists between

different types of descriptors and measured corrosion inhibition efficiency for 1,1-Diallyl-3-(2,3-dimethyl-6-quinoxalinyl) thiourea using chemical and electrochemical techniques.

2. Experimental

Stainless steel 304 specimens of the following composition was widely used. C= 0.08% , Si = O%, Ni = 8%, Cr = 18% and Fe= balance with exposed area of 4 x 1 x 0.020 cm were used for weight loss and gasometry measurements. A stainless steel cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of 0.3 cm^2 was used for potential-current plots and EIS measurements.

The compound was mainly monitored by aweight loss studies as reported by Madhavan et al [9]. cathodic and anodic potential- current curves were recorded galvano statically (1 mA s^{-1}) using corrosion measurement system BAS Model: 1OOA computerised electrochemical analyser (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil of 4 cm^2, $Hg/Hg_2Cl_2/KCl_{(satd)}$ was used as auxiliary and reference electrodes, respectively. Double layer capacitance (Cdl) and charge transfer resistance values (R,) were obtained using EIS measurements. A special computational program has been used to interpret theoretical values of E_{HOMO}, E_{LUMO}, ΔE and dipole moment of DDQT in 5M Na_2SO_4.

3. Results and Discussion

3.1 Weight loss and Gasometric measurements

Table 1 indicates the results of inhibition efficiency for various concentrations of DDQT for the corrosion of SS 304 in 5M Na_2SO_4 determined from weight loss and gasometric measurements. It is perceived that the inhibitor checks the dissolution of stainless steel in 5M Na_2SO_4. Also, the coverage of the SS 304 by the inhibitor is extensively more, giving rise to greater values of inhibition effect for all concentrations of the inhibitor used. The structure of the compound is given in Figure 1.

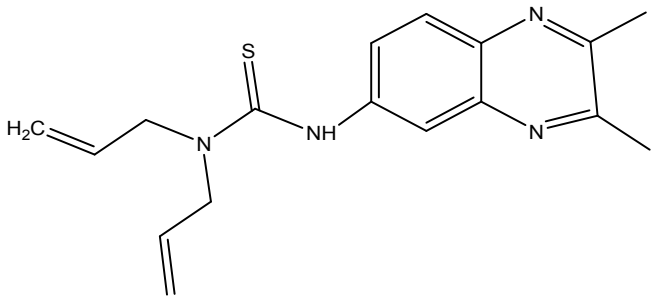

Figure 1.Structure of 1,1-Diallyl-3-(2,3-dimethyl-6-quinoxalinyl)thiourea

Table 1. Values of inhibition efficiency for the corrosion of mild steel in 5M Na_2SO_4 in the presence of different concentrations of DDQT obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (mM)	Inhibition Efficiency	
	Weight loss Studies	Gasometric measurements
10	52	51.7
50	61	60.6
90	82	82.6
130	98	97.8

The retardation on the dissolution of SS 304 in acid medium favoured by DDQT were involving the following interactions:

1. The interaction between the lone pairs of electrons of the Sulphur and nitrogen atoms of the thiouurea group of DDQT and the positively charged metal surface [10].
2. The interactions between delocalized electrons of the nitrogen atoms in the quinolino moiety and the positively charged metal surface of the green inhibitor [11].

It is found that there is a very good agreement between the values of inhibition efficiency obtained by mass loss and gasometric studies.

3.2 Potential-Current plots

Table 2(a) and 2(b) gave the results of potential-current curves such as Tafel slopes (b_a and b_c), corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency obtained from galvanostatic polarization studies for SS 304 in 5M Na_2SO_4 containing several concentrations of DDQT. It can be envisioned from this table that outcomes of Tafel slopes and I_{corr} are very much similar to those reported previously [12,13.] Further it is proven that increasing concentrations of DDQT increases the values of b_a and b_c in irregular fashion alleviating that the inhibition of corrosion of SS 304 in 5M Na_2SO_4 follows mixed type. Values of E_{corr} is shifted to positive direction in the presence of different concentrations of inhibitor. This can be accredited to the establishment of firmly adsorbed inhibitor layer on the steel surface. The presence of increasing quantity of inhibitor molecule ominously impedes I_{corr} values in the acids. It can also be found that most of the values of inhibition efficiency obtained by weight loss and potential-curve studies agree very well.

Table 2. Corrosion kinetic parameters of SS 304 in 5M Na_2SO_4 in the presence of different concentrations of DDQT obtained from galvanostaic polarization studies.

Concentration of Inhibitor (mM)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} $\mu A\ cm^{-2}$	Inhibition efficiency (%)
		b_a	b_c		
Blank	-1060	167	141	550	---
10	-1058	114	132	264	52
50	-1059	123	141	215.6	60.8
90	-1055	99	126	101.2	81.6
130	-1053	115	137	11	98

3.3 Impedance studies

The results of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) acquired from EIS measurements are shown in table 4.It can be noticed from the table that the values of R_t is perceived to increase with enhancement of DDQT concentrations in 5M Na_2SO_4. It is observed that values of C_{dl} are lowered by increasing concentrations of DDQT in 5M Na_2SO_4. This can be attributed to the strong adsorption of the thiourea compound on the surface of SS 304 with increase in its amount to the electrolyte containing sulphate ions.

A plot of surface coverage (ø) versus log C gave a straight line signifying that the adsorption of DDQT on SS 304 surface in in 5M Na_2SO_4 observes Temkin's adsorption isotherm [16]. This is main evidence to corrosion inhibition by this compound, as a result of its adsorption on the surface of SS 304.

3.4 Quantum chemical studies:

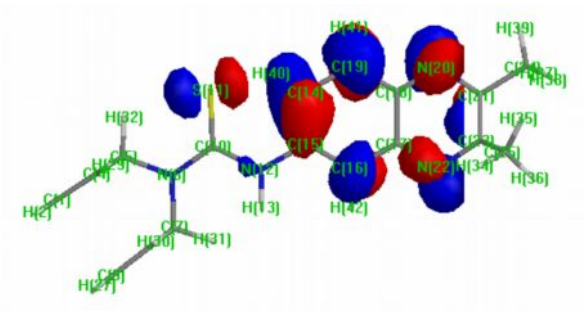

Fig. 2. Highly Occupied MO's of DDQT

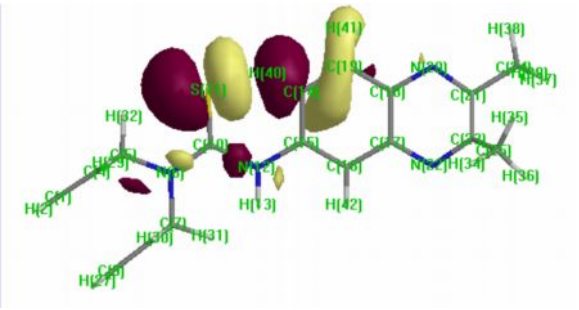

Fig.3.Lowest unoccupied MO's of DDQT

The computed quantum chemical indices such as energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), LUMO- HOMO, energy gap (ΔE), dipole moment (μ), are summarized in Table 2. From figure 2 and 3 , it can be observed that HOMO and LUMO energy orbital's were strongly distributed on amino groups and and pyran-diol for HOMO and LUMO structures establishing that the 1,1-Diallyl-3-(2,3-dimethyl-6-quinoxalinyl)thiourea (DDQT) posses good adsorption centers [19–20] and this is in agreement with publications of molecular orbital studies confronting that π electrons and N atoms are liable for inhibition activity.

Table 3.Impedance parameters for the corrosion of Stainless steel 304 in 5M Na_2SO_4 in the presence of different concentrations of DDQT.

Concentration of Inhibitor (mM)	5M Na_2SO_4	
	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) µF.cm^{-2}
Blank	20	155
10	33	74.55
50	44	60.76
90	120.1	28.36
130	82.5	3.72

Table 4: Quantum chemical parameters for DDQT

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
DDQT	-6.044	-7.726	1.682	3.563

According to Hari Kumar et al [21], when a molecule has similar distribution of electronic orbital's, its inhibition performance could be associated with the energy values of HOMO and LUMO and the difference in values between them. It has been widely stated that, higher the value of E_{HOMO}, larger is the easiness for an inhibitor to release electrons to vacant d orbital of Iron atom and higher is its adsorption. Also, lower E_{LUMO}

values, favour obtaining capacity of electrons by the inhibitor from Fe atom to form feedback bonds. Hence the gap between HOMO–LUMO energy levels of molecules was dignified as an vital data. Smaller the value of ΔE of an inhibitor, greater is the inhibition efficiency of that compound. It is further claimed that, large values of dipole moment will noticeably elevate the adsorption of the compound on stainless surface [22-24].

4. Conclusions

1. 1-Diallyl-3-(2,3-dimethyl-6-quinoxalinyl) retards the dissolution of the corrosion of SS 304 in 5M Na_2SO_4.
2. The inhibition of corrosion of stainless steel by the compound falls under mixed Type.
3. R_t and C_{dl} values studied from impedance measurements prove the impressive performance of the inhibitor.
4. The adsorption of the compound on SS 304 surface follows Temkin's adsorption isotherm.

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