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Performance characteristics of 1, 3-diorthotolyl thiourea on the corrosion of mild steel in 5% NaCl

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Abstract

The Inhibition of mild steel corrosion in 5% NaCl solution using 1, 3-diorthotolyl thiourea (DOTU) has been reported by weight loss, electrochemical polarization technique, impedance method and quantum mechanical measurement. It was found that the compound effectively reduces the steel dissolution in the salt water medium. It was also noticed that the mere adsorption of the compound on metal surface follows Temkin's adsorption isotherm. The inhibition efficiency (IE) increases as the inhibitor concentration is increased. Quantum mechanical studies confirm the adsorption of protective layer of inhibitor on mild steel surface.

Keywords Corrosion, quantum, inhibition, impedance

Introduction

Mild steel is used in industries as pipelines for petroleum transportation, storage tanks, submarines and battery containers [1] in seashore. Since mild steel is prone to corrosion, brine water may cause damage to the steel parts. Numerous methods have been adapted to retard the corrosion of steel in salt water media. However, the use of inhibitors is most commonly employed. The derivatives of thiourea were reported as

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corrosion inhibitors[2-4] due to the presence of hetero atoms like O, N, S along with lone pair of electrons in the molecules which help the adsorption of compounds on the steel [5-8]. The present paper discusses the influence of 1, 3-diorthotolyl thiourea (DOTU) on the dissolution of mild steel in brine water using weight loss, gasometric measurements and various electrochemical techniques.

1, 3-diorthotolyl thiourea (DOTU) is an organic compound with localized electrons and heteroatom's S, N & O. The molecule is large in size (Melting point: 162) and planar structure which favour its adsorption on mild steel surface. As far as we know no concrete report has been published so for DOTU in brine water .The structure of the DOTU is given in the figure.1. DOTU with various concentrations were prepared and their inhibition efficiencies in brine water were evaluated.

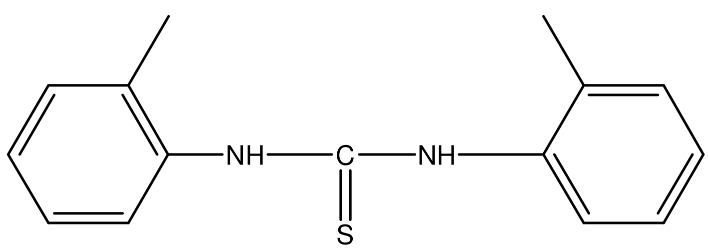

Figure 1. Structure of 1, 3-diorthotolyl thiourea (DOTU)

Experimental

Mild steel specimens of compositions, C = 0.09%, P = 0.06%, Si = nil, S = nil, Mn = 0.43% and balance being Fe .The surface area exposed was 4 x 1 x 0.020 cm for weight loss and gasometric studies. The weight loss study was performed at room temperature for 5 hours in 5% NaCl. The inhibition efficiency (IE %) was determined by the following equation,

$$\text{Inhibition Efficiency (\%)} = (W - W_i / W) \times 100$$

Where W & Wi are the weight loss values in the absence and presence of the inhibitor. A mild steel cylindrical rod of the above composition of elements with surface area of 0.3 cm2 was taken for potentiodynamic polarisation and A.C impedance measurements.

The inhibitor was screened by a weight loss method as reported in earlier publications [9]. Both cathodic and anodic polarisation curves were recorded in brine water (5% NaCl) using EG&G Princeton Applied research model: 7310 with platinum foil (3 cm^2 surface area) and Hg/Hg_2Cl_2/5%NaCl as counter and reference electrodes respectively. The Nyquist plots were recorded for various concentrations of the inhibition reaction and the corresponding double layer capacitance (Cdl) and charge transfer resistance values (Rt) were measured.

Results and Discussion

Weight loss and Gasometric measurements

The inhibition efficiencies obtained from weight loss and gasometric studies for various concentrations of DOTU for the corrosion of mild steel in brine water is presented in table 1 . It is found that the compound retards the corrosion of mild steel efficiently in 5% NaCl. This can be ascribed to the the presence of two tolyl and two –CH_3 groups in ortho position of the inhibitor molecule exerted inductive (+I) effect which may increase the electron density on sulfur atom that leads to better performance than thiourea.

It has been observed that the values of inhibition efficiency obtained from weight loss and gasometric methods are consistent with each other.

Potentiodynamic polarization studies

Table 2 indicates the corrosion kinetic factors like Tafel slopes (b_a and b_c) , corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency measured from potentiodynamic polarization curves for mild steel in the presence and absence of various concentrations of DOTU .

The values of b_a, b_c and I_{corr} obtained for the present system resemble the investigations already made by Soriaga [11], Reeta [12] and Mathavan [13]. Further it was observed that increasing concentrations of DOTU raise the values of both b_a and b_c, but the values of b_c are increased to better extent indicative of cathodic control reaction. Hence the inhibition of corrosion of mild steel in salt water involves the retardation chlorine gas evolution which in turn diminishes aluminium oxidation. Values of E_{corr} are shifted to high positive directions in the presence of different concentrations of DOTU. This can be due to the formation of closely adherent adsorbed layer of inhibitor on aluminium surface. The results of potentiodynamic polarization for the corrosion of mild steel in brine water are given in figure 2.

Impedance measurements

The Nyquist plots for the corrosion of mild steel with and without the presence of inhibitors are given in figure 3. The capacitive circles at low frequency end represent aluminium oxidation and evolution of chlorine gas while at high frequency end correspond to the formation of inhibitive layer [14-17] . For all concentrations limit of DOTU, large capacitive circles at higher frequency range followed by small capacitive loops at lower frequency range were visualized. The diameter of the circles increased with enhance in DOTU concentrations. Also the values of Rt have been increased with increase in concentrations of compound in brine water solution whereas values of Cdl are brought down considerably. This can be attributed to the effective adsorption of the compound on the aluminium surface as described earlier [18].

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SEM studies

SEM photos taken for mild steel surface immersed in brine water for 5hrs without and with 150 ppm of DOTU are given in figures 4 & 5.The specimen surface (figure 4) was damaged to a greater extent due to the attack of chloride ions in the absence of the inhibitor . Figure 5 indicates that a strong layer of compound has formed on the specimen's exposed area. Also the plot of Log c Vs ϕ gave a straight line (Figure 6) confirming that the adsorption of inhibitor on mild steel surface follows Temkin's adsorption isotherm.

Quantum mechanical calculations

The quantum mechanical factors like energy of highly occupied molecular orbitals (HOMO),Lowest un occupied molecular orbitals, energy gap(ΔE), and dipole moment (μ), calculated from structure of DOTU are given in table 5. These values confirm that DOTU inhibit the corrosion of mild steel in 5% NaCl. It has been proved that if ΔE values are > 8 and μ > 4 debye , the inhibition efficiency of the compound will be more than 90% [19]. The distribution of orbital's is greater in LUMO (Figure 7) than HOMO (Figure 8) established that there is a strong interaction between the compound and vacant d- orbital's of iron metal. The high electron density Mullikan's charges for C(1), C(2), C(3), C(4), C(7), S(11), C(15), C(17), C(18) and C(29) justifying that adsorption of the inhibitor on mild steel surface could take place through the above atoms. Apart from the above reasons, other adsorption sites such as tolyl moiety with delocalized π – electrons in the six membered ring and thionyl group have contributed for the successful adsorption of DOTU on metal surface.

Conclusions

1. Di-ortho tolyl thiourea brings down the corrosion of mild steel effectively in salt water water.

2. The corrosion kinetic parameters indicated that the compound behaved as cathodic inhibitor.

3. Nyquist plots confirmed the impressive performance of the compound in reducing the dissolution of steel in 5% NaCl.

4. The adsorption of the inhibitor on steel surface obeyed Temkin's adsorption isotherm which is further justified from SEM images and quantum mechanical values.

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Table 1. Values of inhibition efficiencies in brine water for the corrosion of mild steel with and without the presence of different concentrations of di ortho tolyl thiourea obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (ppm)	Inhibition efficiency (%)	
	Weight loss Studies	Gasometric measurements
Blank	---	---
20	74	73.7
40	86.7	86.0

60	93.4	93.0

Table 2: Corrosion kinetic parameters of mild steel in brine water in the presence of different concentrations of DOTU .

Con. DOTU	Ecorr (mV vs SCE)	Icorr (μA cm-2)	ba (mV dec-1)	bc (mV dec-1)	IE (%)	θ
Blank	-388.32	562.47	84.0	138.3	-	-
20 PPM	-332.23	152.32	69.3	127.2	73.80	0.74
40 PPM	-270.82	79.12	56.7	104.2	85.93	0.86
60 PPM	-235.83	43.45	44.0	72.0	92.27	0.92

Table 3.Impedance values for the corrosion of mild steel in brine water in the presence of different concentrations of DOTU .

Concentration of Inhibitor (ppm)	Brine water solution	
	Charge Transfer resistance (Rct) Ohm.cm^2	Double layer capacitance (Cdl) $\mu F.cm^{-2}$
Blank	47	162
20	114	75
40	158	48
60	166	36

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

C	**-0.067**	**C(1)**
C	**-0.078**	**C(2)**
C	**-0.058**	**C(3)**

C	**-0.090**	**C(4)**
C	0.116	C(5)
C	0.028	C(6)
C	**-0.205**	**C(7)**
N	0.065	N(8)
H	0.098	H(9)
C	0.234	C(10)
S	**-0.452**	**(11)**
N	0.054	(12)
H	0.099	(13)
C	0.124	C(14)
C	**-0.093**	**(15)**
C	-0.057	(16)

C	**-0.076**	**')**
C	**-0.072**	**C(18)**
C	0.039	)
C	**-0.155**	**C(20)**
H	0.053	H(21)
H	0.050	(22)
H	0.052	(23)
H	0.089	H(24)
H	0.053	(25)
H	0.040	(26)
H	0.025	(27)
H	0.027	(29)
H	0.027	(29)

	0.026	(30)
H	0.027	(31)
H	0.027	(32)
H	0.025	(33)
H	0.026	(34)

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Table 5: Quantum mechanical parameters for DOTU on the corrosion of steel in salt water.

Inhibitor	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
DI ORTHO TOLYL THIOUREA	-1.01570	-9.523417	8.507717	4.3

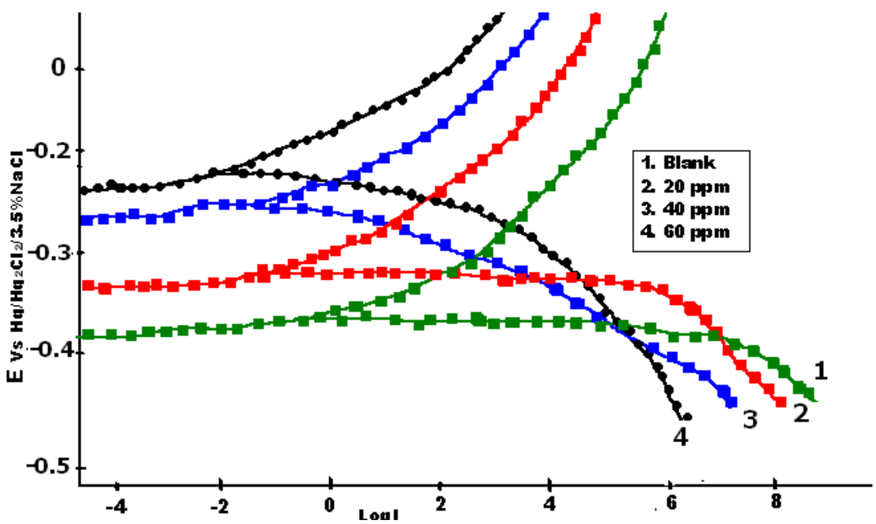

Figure 2. Potentiodynamic polarization plot for mild steel in brine water with different concentrations of DOTU.

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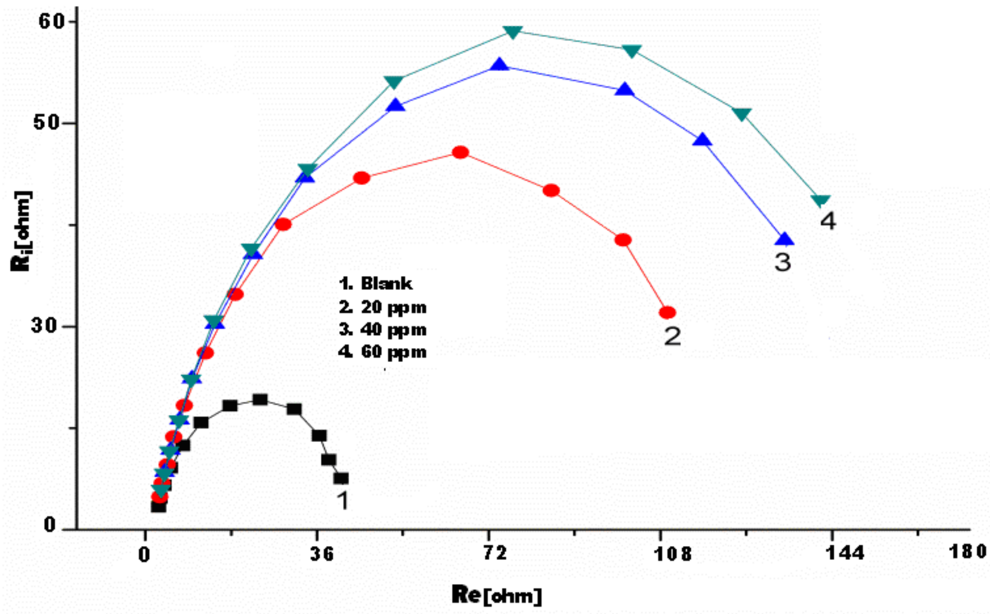

Figure 3. Impedance curves for the corrosion of mild steel in brine water in the presence and absence of inhibitor.

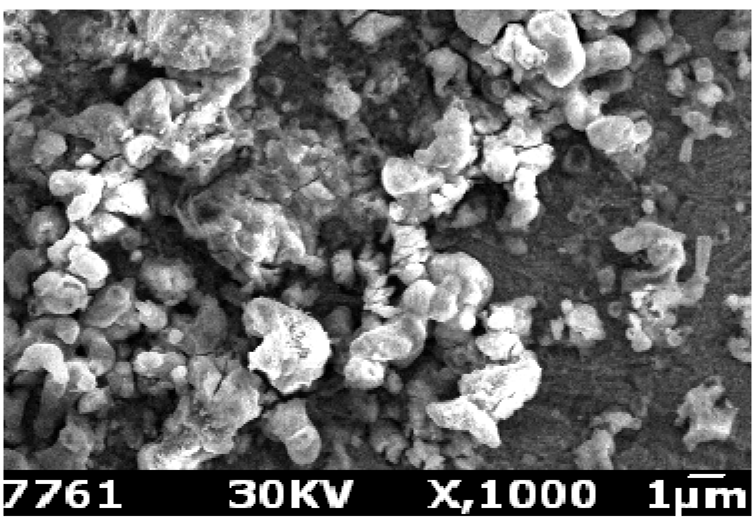

Figure 4. SEM images of mild steel in brine water

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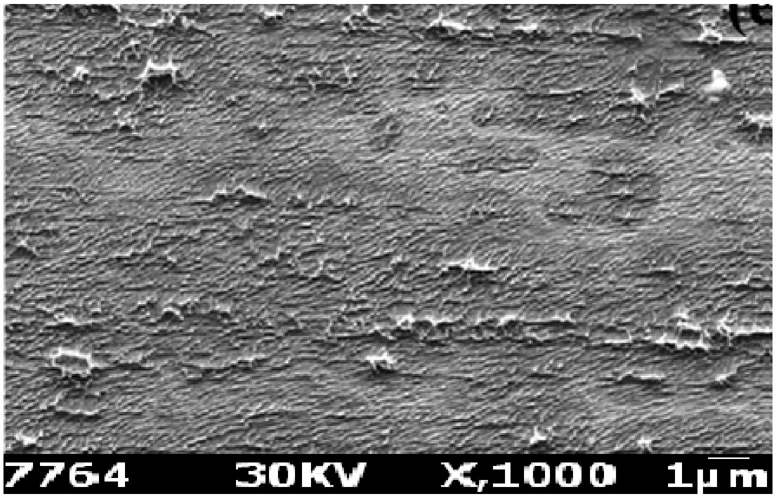

Figure 5. SEM images of mild steel in the presence of DOTU (60 ppm).

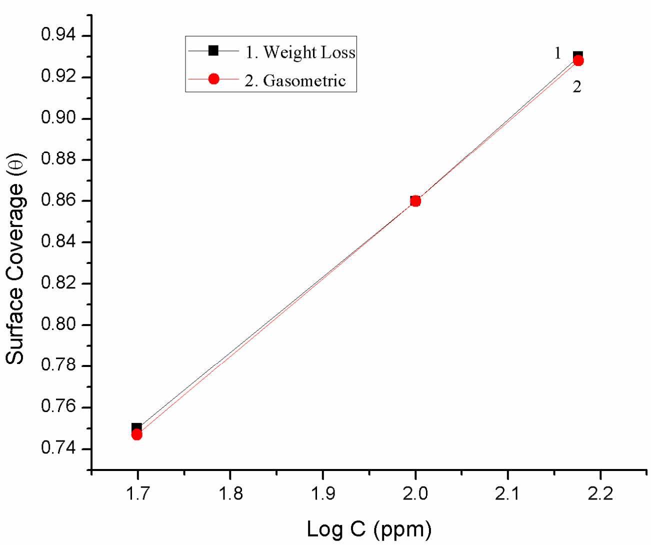

Figure 6.Temkin's adsorption isotherm for DOTU

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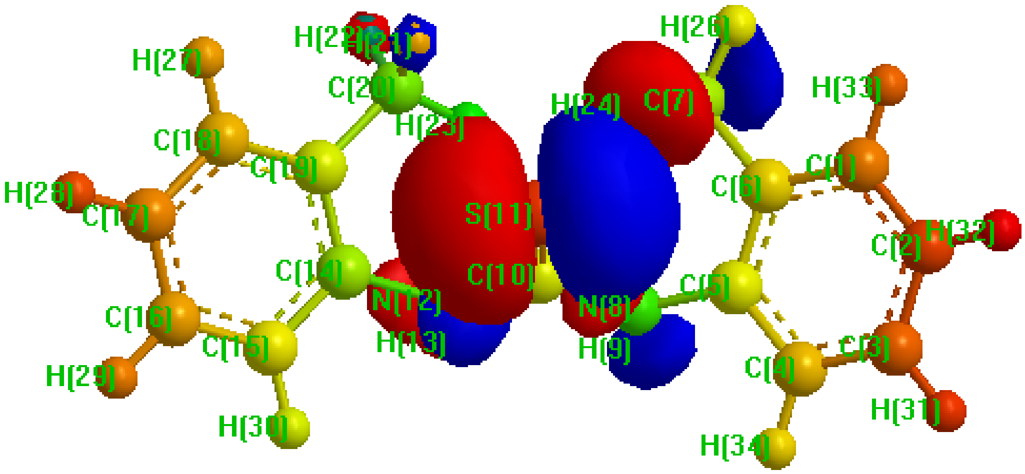

Figure 7. Highly occupied molecular orbital structure for DOTU

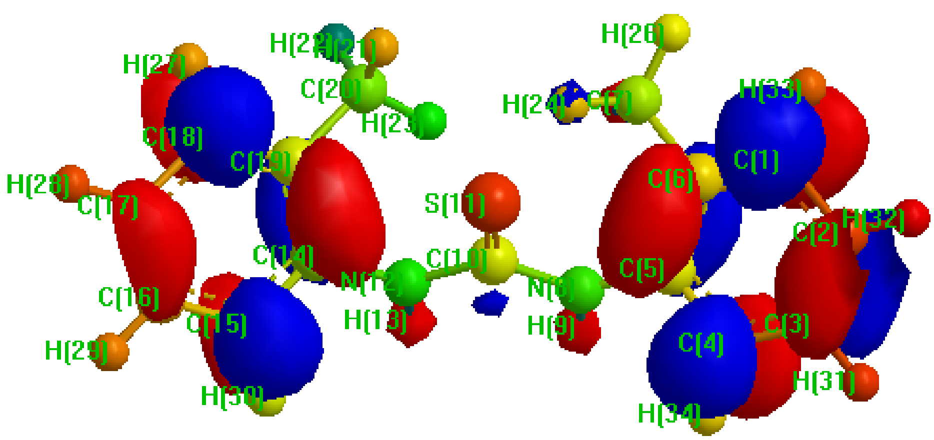

Figure 8. Lowest unoccupied molecular orbital for DOTU.