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The Influence of *Macro thiourea* Derivative on the Corrosion of Mild Steel in Marine Environment

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ABSTRACT

The influence of 1-O-Tolyl-3,3 diethyl thiourea (TDETU) on corrosion of mild steel in marine water (5% NaCl) has been studied using weight loss measurements and various electrochemical techniques. The compound inhibited the steel corrosion in salt water. Potentiodynamic polarization studies clearly indicated that TDETU behaved as a cathodic inhibitor. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition. A chemdraw 3D simulation technique used to run the quantum mechanical analysis and established correlation's between different types of descriptors and measured corrosion inhibition efficiency for the compound. The use of this method substantiates the inhibition efficiencies of the compounds determined by electrochemical methods. AFM studies confirmed that the adsorption of the inhibitor reduces surface roughness on mild steel.

Key words : Corrosion inhibitor, Thio compounds, Impedance measurements, AFM.

INTRODUCTION

Mild steel is a significant category of materials due to their wide range of industrial applications. It is used in many industries due to its excellent mechanical properties. These are used in industries as pipelines for petroleum industries, storage tanks, shipment vessels and chemical batteries [1] in seashore, the salt water may cause damage to the steel components due to their corrosive nature. Various methods are used to decrease the corrosion rate of metals in salt water, among the different methods use of inhibitors is most commonly suggested [2,3]. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion[4-7]. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives have been proved as potential corrosion inhibitors. While extensive investigations have been carried out on inhibitor properties of thiourea, due attention has not yet been paid to a systematic study of inhibitor action of thiourea derivatives. However, several substituted thiourea have been investigated as corrosion inhibitors[8]. Most of the effective organic inhibitors have heteroatoms such as O, N, S

containing multiple bonds in their molecules through which they can adsorb on the metal surface[9-12]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair determines the adsorption of these molecules on the metal surface. All the above studies reveal the one common observation that thiourea derivatives can be regarded as excellent corrosion inhibitors. The present paper describes a study of corrosion protection action of 1-O-Tolyl-3,3 diethyl thiourea (TDETU) on corrosion of mild steel in salt water (5% NaCl) using weight loss, gasometric measurements and various electrochemical techniques.

1-O-Tolyl-3,3 diethyl thiourea (TDETU) is an organic compound with π-electrons and heteroatom's S, N & O. The molecule is large enough (Melting point :135) and sufficiently planar to block more surface area due to adsorption on mild steel. These factors favour the interaction of TDETU with the metal. As far as we know no concrete report has been published so for TDETU in salt water (5% NaCl). The optimized structure of the TDETU is shown in the figure.1. Different concentrations of inhibitor were prepared, and their inhibition efficiency in 5% salt water was investigated.

EXPERIMENTAL

Mild steel specimens of compositions, C = 0.08%, P = 0.07%, Si = O%, S = O%,

Mn = 0.41% and Fe remainder, and of size 4 x 1 x 0.020 cm were used for weight loss, gasometric and AFM studies. A mild steel cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of 0.283 cm^2 was used for potentiodynamic polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier[13]. Both cathodic and anodic polarisation curves were recorded in 5% NaCl potentiodynamically (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, Hg/Hg_2Cl /5%NaCl were used as auxiliary and reference electrodes, respectively. Double layer capacitance (Cdl) and charge transfer resistance values (R,) were obtained using AC impedance measurements as described in an earlier publication[10]. The surface morphology of the inhibitor was analyzed by AFM using Nanosurf easy surf 2 (Switzerland).

RESULTS AND DISCUSSION

Weight loss and Gasometric measurements

Table 1 gives the values of inhibition efficiency for different concentrations of 1-O-Tolyl-3,3 diethyl thiourea (TDETU)for the corrosion of mild steel in 5% NaCl obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of mild steel effectively in salt water. The inhibition of corrosion of brought about by TDETU can be due to the following interactions:

1. The interaction between the lone pairs of electrons of the sulfur atom of the organic molecule and the positively charged metal surface[14].
2. The interactions between lone pairs of electrons of the nitrogen atoms and the positively charged metal surface[15].
3. The presence of tolyl and two –C2H5 groups in the molecule which shows inductive (+I) effect may increase the electro density on the sulfur atom that leads to better performance than the unsubstituted thiourea[16].

It is found that there is exceptionally strong conformity between the values of inhibition

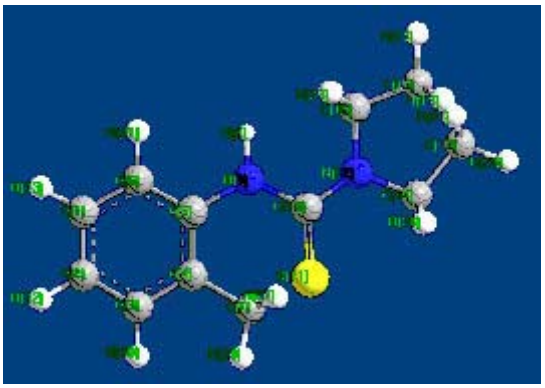

Fig. 1: Optimized structure of 1-O-Tolyl-3,3 diethyl thiourea

efficiency obtained by weight loss and gasometric methods.

Potentiodynamic polarization studies

Table 2 gives values of corrosion kinetic parameters such as Tafel slopes (ba and bc), corrosion current (Icorr) and corrosion potential (Ecorr) and efficiency obtained from potentiodynamic polarization curves for mild steel in 5% NaCl containing different concentrations of inhibitor.

It can be seen from this table that values of Tafel slopes and Icorr are extremely much similar to those reported earlier[16-17]. Further it is ascertained that increasing concentrations of TDETU enhances the values of both ba and bc, but the values of bc are enhanced to a greater extent. So the inhibition of corrosion of mild steel in both acids is under cathodic control. The Values of corrosion potential is shifted to less negative values in the presence of different concentrations of compound. This can be ascribed to the formation of closely adherent adsorbed film on the metal surface. The presence of increasing concentrations of TDETU retards I_{corr} values in both the acids.

Impedance measurements

Corrosion inhibition of mild steel in 5% NaCl solution with and without inhibitor was investigated by electrochemical impedance spectroscopy measurements are presented in Table 3. It can also be seen in the table that the values of the charge transfer resistance (R_t) is found to increase with the increase in concentration of compound in 5% NaCl solution whereas values of double layer capacitance (C_{dl}) are brought down by increasing concentrations of inhibitor . This can

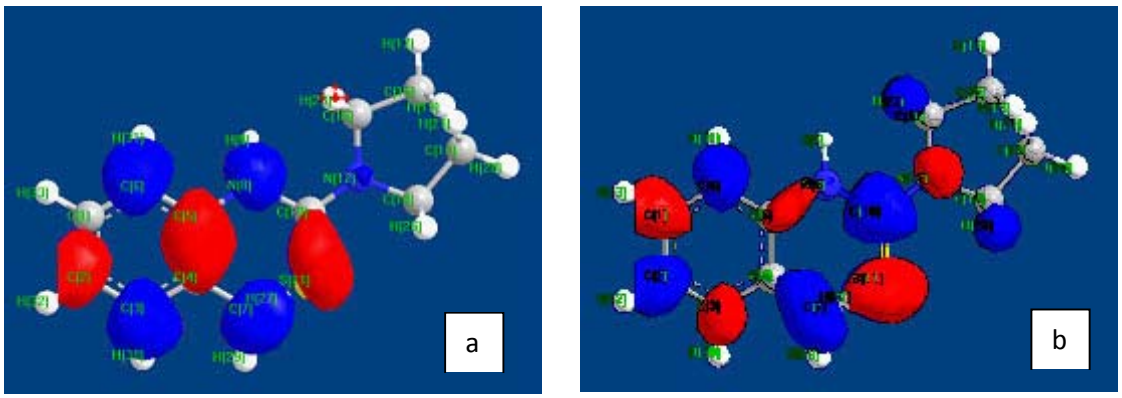

Fig. 2: Quantum parameters for TDMTU (a) Highly occupied molecular orbital (b) Lowest unoccupied molecular orbital

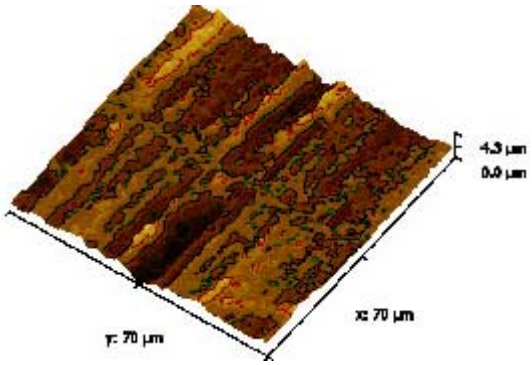

Fig. 3: AFM study of Mild Steel in 5% NaCl

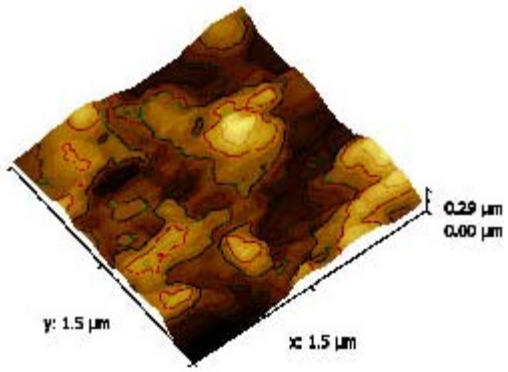

Fig. 4: AFM studies of Mild Steel in 5% NaCl + 150 ppm inhibitor

Table 1: Values of inhibition efficiency for the corrosion of mild steel in 5%NaCl in the presence of different concentrations of O-Tolyl-3,3 diethyl thiourea (TDETU) obtained from weight loss and gasometric measurements

Concentration of Inhibitor (ppm)	Inhibition efficiency (%)	
	Weight loss Studies	Gasometric measurements
Blank	-	-
50	70	70.4
100	83	82.6
150	93.2	93.0

be attributed to increasing adsorption of the compound on the metal surface with an increase in its concentration. Similar observation has been made earlier by Harikumar and Lane[18-19] for the corrosion inhibition of mild steel by Ampicilin drug.

Quantum mechanical studies

The computed quantum chemical parameters like energy of highest occupied molecular orbital (EHOMO), energy of lowest unoccupied molecular orbital (ELUMO), LUMO-HOMO, energy gap (DE), dipole moment (μ), are summarized in Table 4. From Fig. 2(a) and 2(b) , it can be observed that HOMO and LUMO energy orbitals were strongly localized on tolyl moiety and

Table 2: Corrosion kinetic parameters of mild steel in 5%NaCl in the presence of different concentrations of 1-O-Tolyl-3,3 dimethyl thiourea obtained from potentiodynamic polarization studies

Con. TDMTU	E_{corr} (mV vs SCE)	I_{corr} (μA cm^{-2})	βa (mV dec^{-1})	βc (mV dec^{-1})	IE (%)	Ø
Blank	-379.12	559.57	84.0	135.3	-	
50 PPM	-366.18	170.37	70.2	122.0	69.04	0.69
100 PPM	-352.82	90.67	66.6	131.3	83.07	0.83
150 PPM	-345.43	45.45	81.0	118.6	91.87	0.92

Table 3: Impedance parameters for the corrosion of mild steel in 5%NaCl in the presence of different concentrations of 1-O-Tolyl-3,3 dimethyl thiourea

Concentrationm of Inhibitor (ppm)	5%NaCl	
	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) μF.cm^{-2}
Blank	30	172
50	80	117
100	115	71
150	100	62

Table 4: Quantum mechanical parameters for TDETU on the corrosion of steel in salt water

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment(Debye)
1-O-Tolyl-3,3 Diethyl thiourea	0.247604	-6.82439	7.071994	3.94

almost nil, on diethyl moiety indicating that the tolyl moiety posses strong adsorption centres[20-23] consolidating the opinion of several researchers that p electrons and hetero atoms are responsible for inhibition activity[24].

According to Tang *et al.,*[25], when a molecule possess similar frontier orbitals, its inhibition efficiency can be correlated to the energy levels of HOMO and LUMO and the difference between them. It has been enormously claimed that, higher the value of E_{HOMO}, greater is the ease for an inhibitor to donate electrons to unoccupied d orbital of metal atom.In addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the LUMO"HOMO energy gap decreased and the efficiency of inhibitor improved and higher is the inhibition efficiency. The gap between HOMO–LUMO energy levels of molecules was another prominent parameter that needs to be considered. Smaller the value of ΔE of an inhibitor, higher is the inhibition efficiency of that inhibitor. It has been reported that, large values of the dipole moment will enhance corrosion inhibition[26-28].

Atomic force Microscopic studies

AFM images of mild steel exposed for 3 hours in 5% NaCl solutions in absence and presence of 150 PPM of TDETU are shown in Fig. 3 - 4 The roughness of mild steel coupons in 5% NaCl in absence and presence of the TDETU are 4300 nm and 290 nm, respectively .This indicates that the addition of the compound reduced the surface roughness. This confirms that the corrosion inhibition on mild steel occurs through adsorption of TDETU on it.

CONCLUSIONS

1. 1-O-Tolyl-3,3 diethyl thiourea inhibits the corrosion of mild steel effectively in 5%NaCl .
2. The inhibition of corrosion of mild steel in salt water , by the compound is under cathodic control.
3. R_t and C_{dl} values obtained from impedance measurements confirm the better performance of the compound.
4. The quantum chemical parameters substantiate the inhibition efficiency of TDETU determined by electrochemical methods.
5. AFM studies confirm that corrosion inhibition of mild steel in 5%NaCl is due to adsorption of the extract on it.

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