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Quantum Mechanical Studies Of Thio Compunds On The Corrosion Inhibition Of Mild Steel In Acidic Media

P.A.Jeeva[1], S.Harikumar[2], S.Karthikeyan[3]*,

S.Narayanan[1], A.Mukherjee[3] , N.Chandrasekaran[3]

[1]School of Mechanical and Building Sciences,VIT niversity,Vellore,Tamilnadu,India
[2]School of Advanced Sciences, VIT University,Vellore,Tamilnadu,India
[3]Centre for Nanobiotechnology, VIT University,Vellore,Tamilnadu,India

Corres.author : skarthikeyanphd@yahoo.co.in

Abstract: The quantum mechanical approach is becoming more desirable tool for predicting the mechanism of inhibition by compounds. The inhibition efficiency of sulphur containing organic compounds is dependent on many basic molecular descriptors include: dipole moments, electronic parameters as E_{HOMO} (highest occupied molecular orbital energy); E_{LUMO} (lowest unoccupied molecular orbital energy); ΔE, energy gap (E_{LUMO} - E_{HOMO}).
A chemdraw 3D simulation technique was used to run the quantum mechanical analysis and established correlation's between different types of descriptors and measured corrosion inhibition efficiency for thiourea derivatives. The use of this method substantiates the inhibition efficiencies of the compounds determined by electrochemical methods.
Keywords: Corrosion inhibitors,Quantum mechanics,LUMO,HOMO.

Introduction:

Thiourea and its derivatives have been studied for more than four decades because they inhibit the corrosion of steels and are superior to amine-based inhibitors in acid media[1-3]. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are 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[4]. 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 [5-8]. 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. A good inhibitor should have the following two important requisites: (1) it should have very good inhibition efficiency and (2) it should bring down the hydrogen permeation current to a considerable extent.

The aim of the present study involves the quantum chemical adsorption of 1-O-Tolyl-3,3 dimethyl

thiourea, cyclohexyl thiourea and isopropyl thiourea using Chemdraw 3D simulation techniques to calculate the adsorption energy as well as the binding energy between the inhibitor molecule and the iron surface. The above compounds were reported as potential corrosion inhibitors for the corrosion of mild steel in acidic media as described elsewhere[15-16.] Also, the adsorption of the compound on mild steel surface obeyed Temkin's adsorption isotherm.

2. 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 measurements.

Many computational approaches exist for understanding the adsorption of the inhibitor molecules on the metal surface. These typically use quantum chemical calculation and molecular dynamics simulations to understand the inhibition mechanism of inhibitors on the metal surface was reported by S.E. Nataraja et al.[17] The thio compounds used in the present study were procured from Fluka, A.G, Switzerland.

The molecular structures of 1-O-Tolyl-3,3 dimethyl thioura (TDMTU), Cyclohexyl thiourea (CHTU) and isopropyl thiourea (ISPTU) optimized by Chemdraw 3D simulation technique are given in figure 1-3.

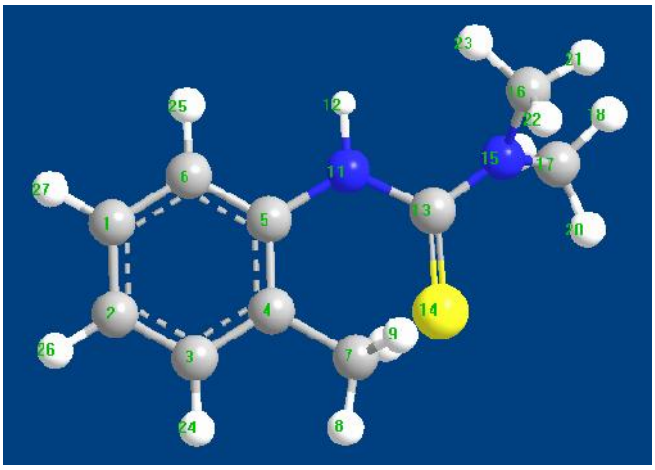

Figure 1.Structure of TDMTU

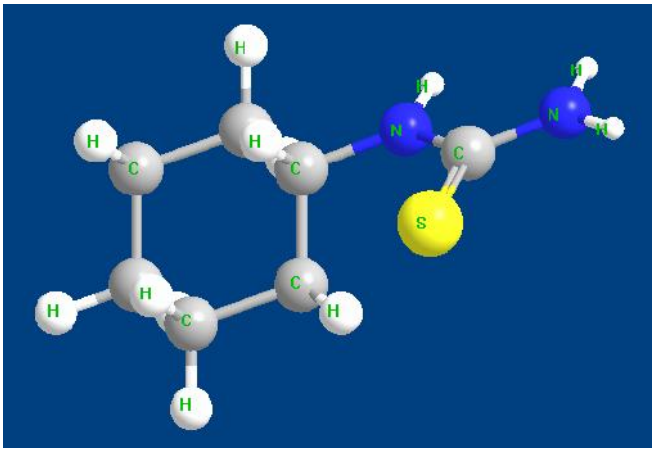

Figure 2.Structure of CHTU

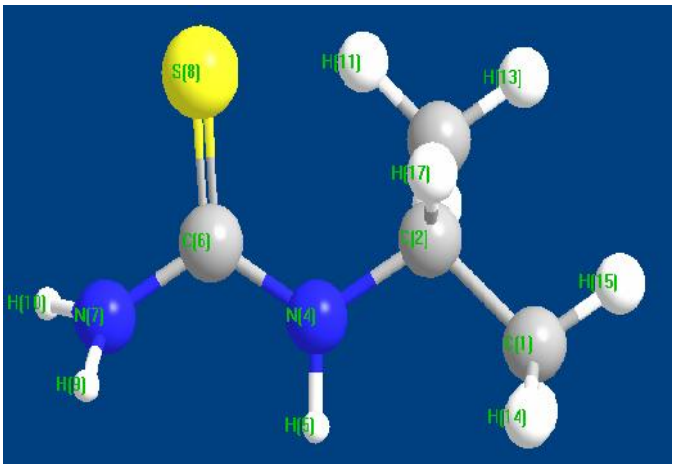

Figure 3.Structure of ISPT

Table 1. Values of inhibition efficiency for the corrosion of mild steel in 1M HCl in the presence of different concentrations of TDMTU,CHTU,ISPTU obtained from weight loss measurements.

Concentration of Inhibitor (mM)	Inhibition efficiency (%) in 1N HCL TDMTU	CHTU	ISPTU
	Weight loss Studies	Weight loss Studies	Weight loss studies
1	82	80	74
5	87	84.2	78
10	92	90.0	86
50	96	94.4	92
100	98	97.4	93

3. Results and discussion

Weight loss measurements

Table 1 gives the values of inhibition efficiency for different concentrations of TDMTU, CHTU,ISPTU for the corrosion of mild steel in 1N HCl obtained from weight loss measurements. It is found that the compound inhibits the corrosion of mild steel in HCL .

The inhibition of corrosion of brought about by these compounds 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 [9-10].

2.The interactions between lone pairs of electrons of the nitrogen atoms and the positively charged metal surface[11].

3.The presence of cyclohexyl group in CHTU which exhibits inductive (+I) effect may increase the electro density on the sulfur atom that leads to better performance than the unsubstituted thiourea [12] . Also The presence of tolyl and two $-CH_3$ groups in the molecule which shows inductive (+I) effect may increase the electro density on the sulfur atom that leads to better performance than CHTU and ISPTU. Even though the existence of isopropyl groups in ISPTU show inductive (+I) effect, it performance is comparatively less with other two compounds.

Quantum mechanical studies:

The computed quantum chemical parameters like 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 4, it can be observed that HOMO and LUMO energy orbital's were strongly localized on benzene moiety and almost nil, on dimethyl moiety indicating that the naphthalene moiety posses good adsorption centres [17–19] consolidating the opinion of several researchers that p electrons and hetero atoms are responsible for inhibition activity[20].

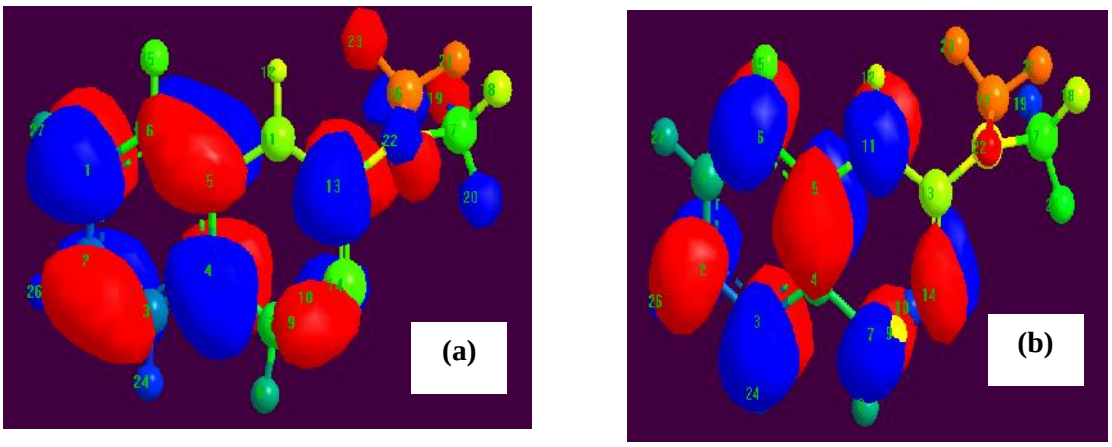

Figure 4 Quantum parameters for TDMTU (a) Highly occupied molecular orbital (b) Lowest unoccupied molecular orbital

Further, HOMO and LUMO distribution on thiourea moiety (Figure 5) is greater than cyclohexyl moiety and isopropyl moiety of CHTU and ISPTU, with a slight dominance of HOMO in thiourea moiety. According to Tang et al.[21], 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 greatly 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 and higher is the inhibition efficiency. Further lower the E_{LUMO}, easier is the acceptance of electrons from metal atom to form feedback bonds. The gap between HOMO–LUMO energy levels of molecules was another important 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 dipole moment will enhance corrosion inhibition [22-24].

The results are presented in table 2. Based on the above quantum studies it is evident that the adsorption of TDMTU is greater than CHTU and ISPTU and hence TDMTU could be good corrosion inhibitor for the mild steel corrosion in acidic media.

A plot of Ø (surface coverage) Vs log C, gives a straight line for all the compounds confirming that the adsorption by the compounds obey Temkins adsorption isotherm.

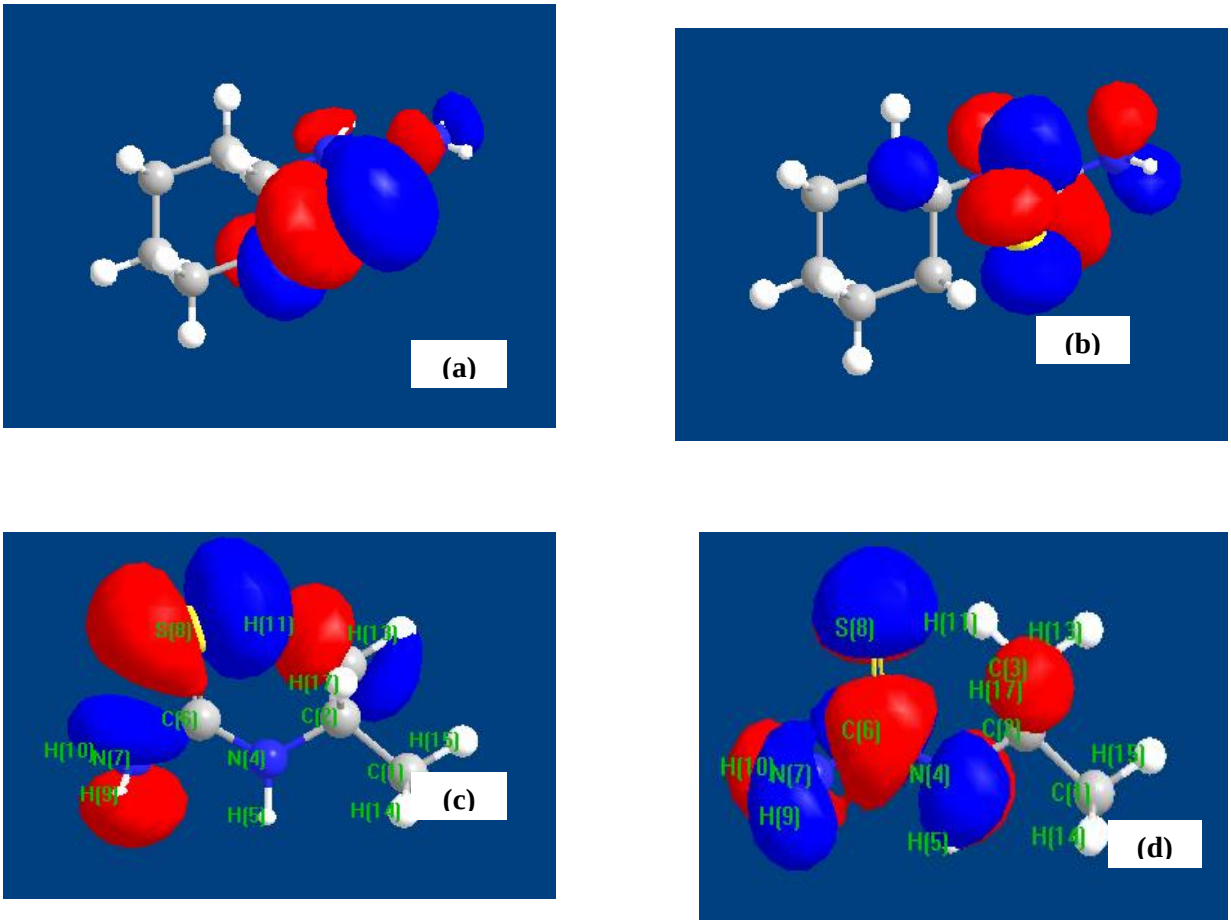

Figure 5 Quantum parameters for CHTU (a) Highly occupied molecular orbital (b) Lowest unoccupied molecular orbital (c) HOMO for ISPTU (d) LOMO for ISPTU

Table 2: Quantum mechanical parameters for the thio compounds

Compound	LUMO (eV)	HOMO (eV)	aE (Cal.Mol^{-1})	Dipole moment (Debye)
1-O-Tolyl-3,3 Dimethyl thiourea	-0.136245	-7.08069	6.944	1.9799
Cyclohexyl thiourea	0.597018	-8.13957	8.737	4.9493
Isopropyl thiourea	0.173069	-8.02091	8.914	4.8621

Conclusion:

An attempt has been made to utilize quantum mechanical approach using chemdraw-3D simulation technique for substantiating the corrosion inhibition properties of thiourea derivatives. The performance of inhibition by these compounds on the corrosion of mild steel follows the order:

TDMTU>CHTU>ISPTU.

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