Correlation of Electronic Structure of Some Nitrogen Sulfur Derivatives with Corrosion Inhibition Performance

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Abstract: In this paper a correlation between performance of corrosion inhibitors and quantum chemical, thermodynamic parameters has been made. The Quantum chemical calculations were done using semi-empirical method (PM3). The Inhibition efficiency (IE) is predicted for some Nitrogen Sulfur compounds. The electronic parameters entering our model are the energy of the highest occupied molecular orbital E_{HOMO}, the lowest unoccupied molecular orbital E_{LUMO} and the dipole moment. All of these parameters relate to IE, so their cumulative index is correlated with IE obtained from experiments. Our method predicts IE of selected compounds with good accuracy. This approach can be useful in design and analysis of high performance inhibitors.

Keywords: Metals, organic compounds, computational techniques, corrosion.

1. INTRODUCTION

Corrosion is a complex phenomenon occurring at the atomic and electronic scales, and no theory exist to predict corrosion inhibition efficiency (IE). The usual approach is to conduct numerical experiments to find some fundamental electronic parameters and correlate performance of corrosion inhibitors (IE) with these parameters [1-10]. In this method the quantum chemical parameters like energy of highest occupied molecular orbital E_{HOMO}, lowest unoccupied molecular orbital E_{LUMO}, and dipole moment μ are correlated with inhibitor performance data obtained from experiments.

2. THEORY

The working of a typical quantum mechanical code is depicted in Fig. (**1**). In the present study we have used semi-empirical self-consistent field (SCF) [11], linear combination of atomic orbitals (LCAO) method for calculation of the electronic parameters. This method is used to solve the time-independent Schrdinger equation for a multi-electron molecule as described in the Born-Oppenheimer approximation. Due to iterative nature of solution procedure, the method is also known as "self-consistent field method". The solutions obtained from this method are more accurate than that of *abinitio* Hartree Fock (HF) theory, but it involves some parameters to be adjusted from experimental data so it is termed as *semiempirical* theory. We have used neglect of diatomic differential overlap(NDDO) formalism, [12] to simplify the HF Hamiltonian.

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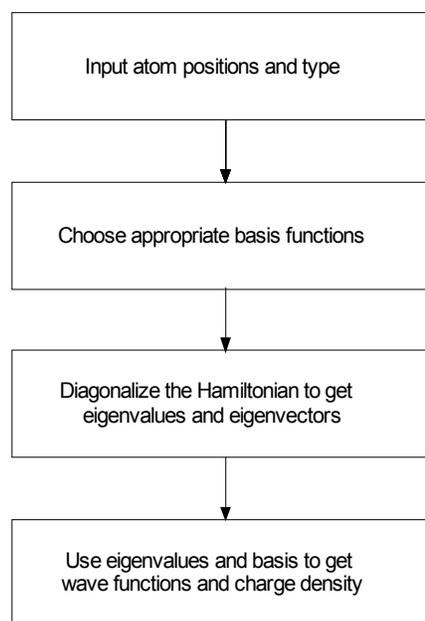

Fig. (1). Working of a typical quantum mechanical code.

3. NUMERICAL EXPERIMENTS

SAR (structure activity relationships) is usually a relationship between quantum parameters and IE. The quantum chemical parameters of relevance depend on the kind of phenomena we are trying to model. In predicting IE the variables of interest could be E_{HOMO}, E_{LUMO}, dipole moment, hydrophobicity, partition coefficient etc. Using some of these parameters we have obtained simple equations that predicts the IE of Thiourea and benzothiazole derivatives.

Table 1.   Electronic Parameters of Thiourea and Comparison of Predicted IE with Experimental IE

Parameters	PTU	TTU	DPTU	DTTU
E_{HOMO} (eV)	-8.56388	-8.52734	-8.55589	-8.36387
E_{LUMO} (eV)	-0.70435	-0.69864	-0.91041	-0.89114
ΔE (eV)	7.85953	7.8287	7.64548	7.47273
μ (Debye)	5.557	5.82	5.899	6.095
Total Energy (eV)	-1462.04	-1611.67	-2234.02	-2533.33
Predicted IE %	90.2	90.4	93.0	95.3
Experimental IE %	90.00	90.23	93.71	94.86
% Error in Predicted IE	0.22	0.19	0.76	0.60

Table 2.   Electronic Parameters of Benzothiazoles and Comparison of Predicted IE with Experimental IE

Parameters	AMEBT	AMOBT	ABT	ACLBT
E_{HOMO} (eV)	-8.98715	-8.65633	-8.54094	-5.97644
E_{LUMO} (eV)	-1.79222	-0.49553	-0.38654	-3.29323
ΔE (eV)	7.19493	8.1608	8.1544	2.68321
μ (Debye)	2.209	2.112	1.66	2.014
Total Energy (eV)	-1577.61528	-1873.43338	-1431.42759	-1723.18161
Predicted IE %	80	-	90	94
Experimental IE %	85	90	94	99
% Error in Predicted IE	5.27	-	4.56	5.63

The calculations are based on Parametrized Model 3 (PM3) [13]. This method is suitable for analyzing closely resembling molecules that are subject of our correlation studies. We have used a software package MOPAC 2007 which is a freely available electronic structure code [14]. The structure is first optimized and the simulations are conducted to calculate the electronic parameters.

The output of MOPAC program reports values such as ionization potential, eigenvalues, dipole moment etc. According to Koopmans theorem [15] ionization potential is negative of eigenvalue of the highest occupied molecular orbital (HOMO). This value is used to compute the energy of lowest unoccupied molecular orbital (LUMO) from the MOPAC results.

Experimental details of inhibition characteristics of Thiourea and benzothiazole based inhibitors can be found from work by M.A. Quraishi *et al.* [16, 17], the efficiency were determined by weight loss method [18] using the relation

$$IE(\%) = \frac{W_0 - W_i}{W_0} \times 100 \qquad (1)$$

where, W_0 and W_i are the values of corrosion weight loss of mild steel in uninhibited and inhibited solutions, respectively.

Four Thiourea derivatives: phenyl thiourea (PTU), tolyl thiourea (TTU), diphenyl thiourea (DPTU) and dilolyl thiourea (DPTU) and three benzothiazole derivatives: 2-

aminobenzothiazole (ABT), 2-amino-6-chloro benzothiazole (ACLBT), 2-amino-6-methyl benzothiazole (AMEBT) are selected and studied for corrosion of mild steel by weight loss and potentiodynamic polarization methods. All of these compounds have shown very good inhibition efficiency (IE). IE of these compounds has been found to vary with the concentration of the compounds, solution temperature, immersion time and concentration of the acid solution. IE at optimal conditions is obtained from experimental results and is tabulated as Experimental IE in Tables **1** and **2**.

RESULTS AND DISCUSSION

The Thiourea and benzothiazole derivatives studied are given in Fig. (**2**). The Thiourea derivatives are selected based on the fact that presence of electron on phenyl and nitrogen and readily polarizable sulfur atoms is likely to induce greater adsorption of the compound on the surface leading to higher efficiency. This could be correlated to Dipole moment.

The high value of E_{HOMO} suggests electron donating ability of molecule while low value of E_{LUMO} suggests electron accepting ability of molecule, so energy gap between HOMO and LUMO energies explains the electron transfer mechanisms occurring at the metal surface.

For Thiourea derivatives it can be seen from Fig. (**3**) to Fig. (**7**) that IE correlates well to energy gap $\Delta = E_{HOMO} - E_{LUMO}$, and the combined equation of regression is:

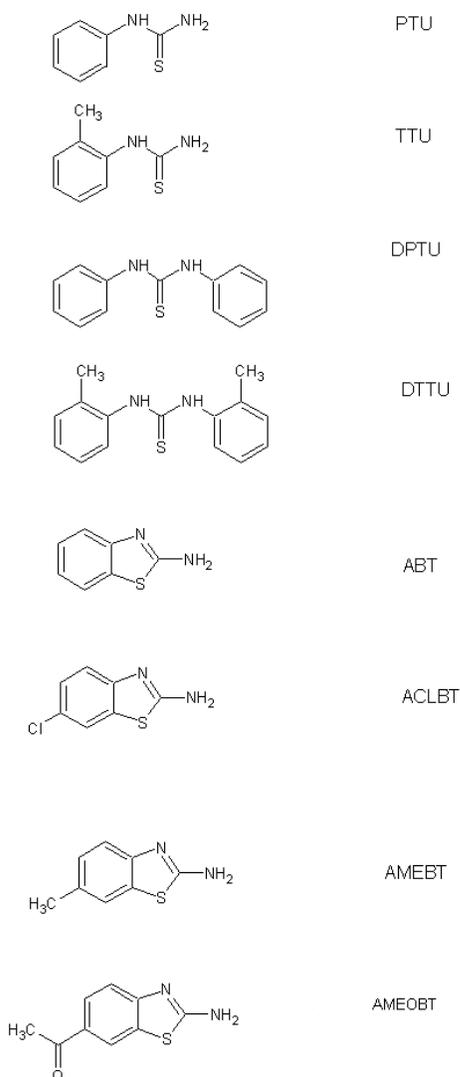$$IE = 209.6 + 14.48759\Delta - 0.99649\mu, \qquad (2)$$

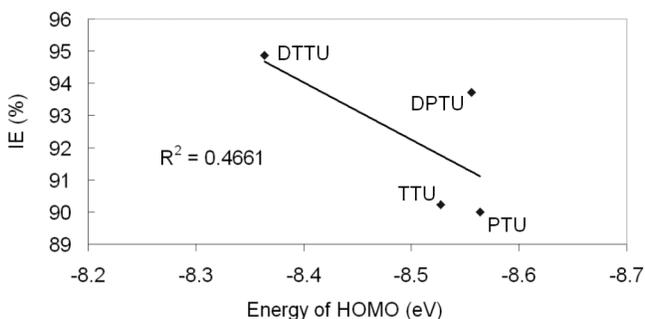**Fig. (2).** Chemical structures of selected compounds.
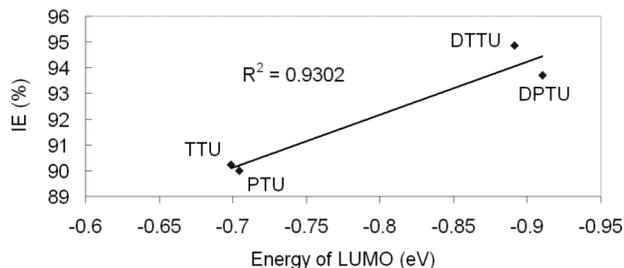

Fig. (3). HOMO energy versus IE of thiourea.

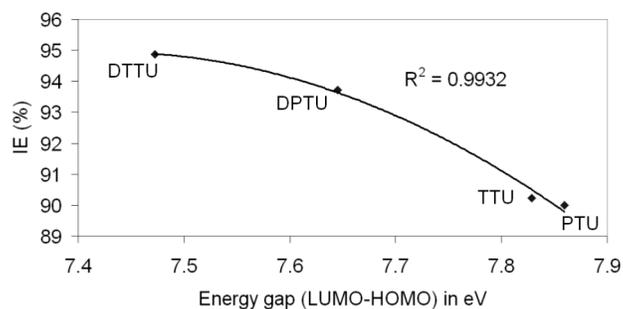**Fig. (4).** LUMO energy versus IE of thiourea.

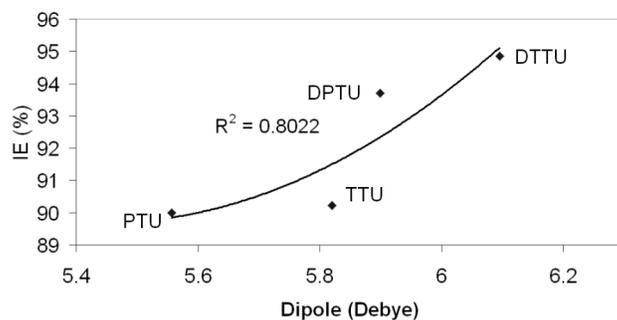**Fig. (5).** Energy gap versus IE of thiourea.

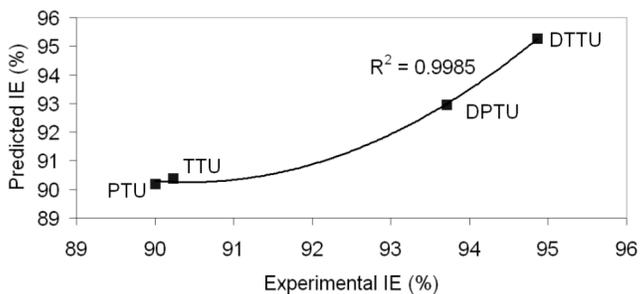**Fig. (6).** Dipole versus IE of thiourea.

Fig. (7). Predicted versus experimental versus IE of thiourea.

For benzothiazoles Fig. (**8**) to Fig. (**12**) depicts variation of key parameters and the curve fit equation is:

$$IE = \frac{(0.59727E_{HOMO} + 0.851E_{LUMO} + 2.662\mu)}{(1 + 0.59727E_{HOMO} + 0.851E_{LUMO} + 2.662\mu)}, \quad (3)$$
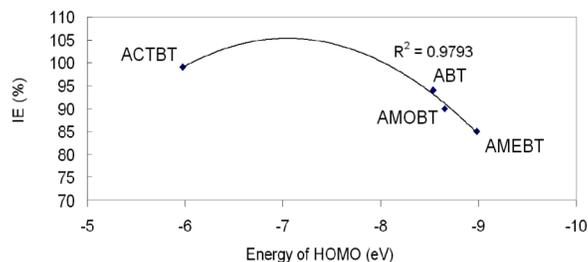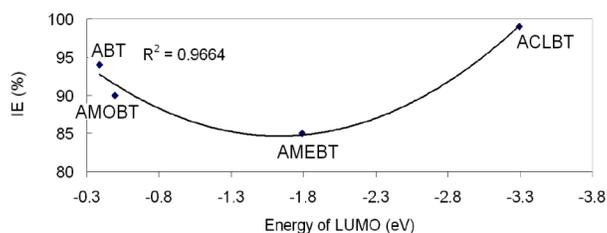

Fig. (8). HOMO energy versus IE of benzothiazole.
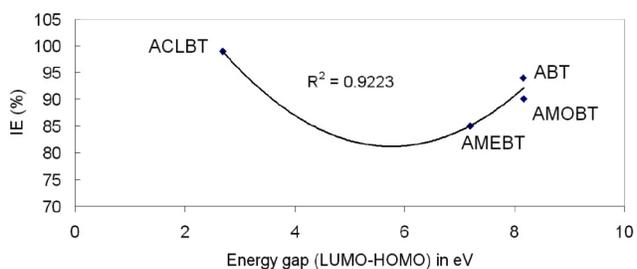

Fig. (9). LUMO energy versus IE of benzothiazole.

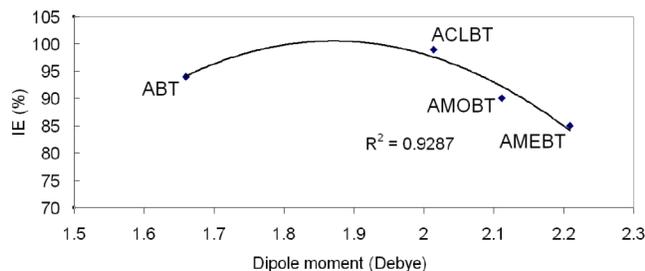**Fig. (10).** Energy gap versus IE of benzothiazole.

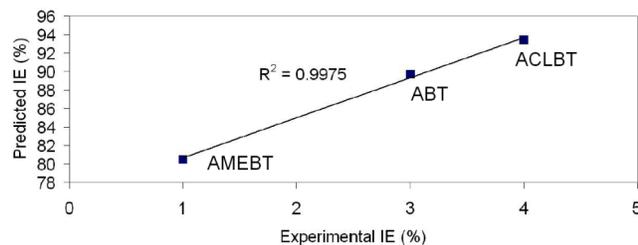**Fig. (11).** Dipole versus IE of benzothiazole.

Fig. (12). Predicted versus experimental versus IE of benzothiazole.

In Thiourea correlations coefficient of energy gap, Δ is large which suggests that it has most influence on IE and it is the parameter to be optimized at the design stage for maximizing efficiency of Thiourea. The results of Benzothiazoles were fitted into a nonlinear equations and a cumulative effect of these parameters is responsible for IE.

Table 3.   Electronic Correlations of Thiourea Derivatives

Correlations	Empirical Equation	R^2
1. IE versus E_{HOMO}	IE = 17.847 E_{HOMO}+ 243.95	0.4661
2. IE versus E_{LUMO}	IE = -20.525 E_{LUMO}+ 75.756	0.9302
3. IE versus ΔE	IE = -27.659ΔE^2 + 410.91ΔE -1431.2	0.9932
4. IE versus μ	IE = 12.742μ^2 -138.69μ + 467.07	0.8022

The significant quantum chemical parameters of interest are calculated and are tabulated in Tables **1** and **2**. The effect of individual parameters on IE is studied, results and equations are tabulated in Tables **3** and **4**. From the curve fitting we have predicted that the efficiencies are in the order:

PTU < TTU < DPTU < DTTU

AMEBT < ABT < ACLBT

These results could be useful in making further modification to these compounds, as our equations can predict IE of compounds belonging to this family.

Table 4.   Electronic Correlations of Benzothazoles Derivatives

Correlations	Empirical Equation	R^2
1. IE versus E_{HOMO}	IE = -5.4688 E_{HOMO}^2 -77.092 E_{HOMO} -166.4	0.9793
2. IE versus E_{LUMO}	IE = 5.2134 E_{LUMO}^2 + 17.02 E_{LUMO}+ 98.555	0.9664
3. IE versus ΔE	IE = 1.8898ΔE^2 -21.767 ΔE + 143.8	0.9223
4. IE versus μ	IE = -144.27μ^2 + 539.95μ 404.65	0.9287

CONCLUSIONS

Corrosion inhibition efficiency correlates directly with the electronic and thermodynamic parameters. This correlation provides a powerful means of designing inhibitors. Our numerical experiments clearly show that inhibition is highly dependent on cumulative index consisting of quantum chemical parameters. The SAR are typically used to correlate properties with some fundamental parameters, with a library of functional group choices this procedure can be automated and the structure with optimum properties can be designed.

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