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SHORT COMMUNICATION

THEORETICAL STUDY ON THE STRUCTURAL EFFECT OF SOME ORGANIC COMPOUNDS AS CORROSION INHIBITORS ON MILD STEEL IN ACID MEDIA

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ABSTRACT. A quantitative structure property relationship (QSPR) analysis of some organic compounds (imines or Schiff bases) is studied. The corrosion inhibition efficiencies of these imines have been studied by using AM1 (Austin model 1) Hamiltonian SCF-MO method and QSPR analysis. One of the most promising semi-empirical methods for predicating geometries and electronic properties is AM1. The geometry of all compounds **1-11** was optimized and all data obtained for building the multiple regression model. The proposed equations were applied to predict the corrosion inhibition efficiency of some related structures to select molecules of possible activity from a presumable library of compounds was obtained from the regression coefficients for the model.

KEY WORDS: Corrosion inhibition, Schiff base, Mild steel, QSPR, AM1

INTRODUCTION

Mild steel is an important metal regarding to its wide applications in industry in various mechanical and structural purposes. It is widely used in engineering fabrications like bridge, buildings, steam engine parts and automobiles etc. It is much prone to corrosion while in use by different corrosion agents like acids, HCl and H_2SO_4 (have been used for drilling operations, picking baths and in decaling processes) which are most common and dangerous [1]. Most organic compounds employed as metal corrosion inhibitors, protect the metal by forming a chelate on the metal surfaces. The efficiency of the inhibitor depends on the stability of the chelate formed. On the other hand, the effectiveness of an organic compound as an inhibitor depends on the structure of the inhibitor. Organic compounds containing one or more N, O, S and P atoms with lone pair electrons can inhibit the corrosion of metal in aqueous acid solutions [2-4]. The inhibitor molecules should have centers capable of forming bonds with the metal ions surface by electron transfer. The metal ion acts as an electrophile and organic compound with N, O, S and P atoms with lone pairs have nucleophilic centers and readily available for sharing. With the mechanism of inhibition being based on the adsorption of the organic molecules to the metal surface, a qualitative account of the relative inhibition efficiencies of **1-11** molecules include in Scheme 1 can be given. Literature reports on the adsorption of Schiff bases on metal surfaces consistently indicate that the prevailing mechanism is chemisorption. A chemical adsorption between the Schiff bases and the steel surface is most likely to be due to Lewis-type, acid/base interaction. Here, neutral metal atoms would be expected to act as Lewis acids as they have empty atomic orbital of suitable energy, whereas, Schiff bases, as the name implies, would donate electron pairs through the functional groups. The appropriate sites to donate electrons are –CH=N– groups and less importantly, aromatic rings. Phenolic –OH would be too ineffective in donating electrons in a strongly acidic medium, because phenolic –OH groups are, "hard bases", π-electron systems "soft bases" and the neutral metal atoms, "soft acids". Soft acid-soft base interaction is more favored than "soft-hard" alternative.

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On the other hand the choice of effective inhibitors has been mostly done by using the empirical knowledge based on their macroscopically physico-chemical properties and electron donating ability. At this time the development of theoretical calculations emphasized the scientific approaches involved in the section of inhibitors by correlating the experimental data with quantum chemical properties [5-7].

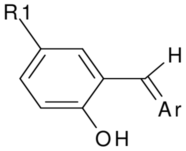
In the present study the reactions between the electronic property of **1-11** compounds and inhibition efficiency on the corrosion of mild steel have been discussed. A powerful tool to help this work is chemometrics, which uses statistical and mathematical methods to extract maximum of information from a data set. The complex interactive processes in the environment are per multidimensional because of its usefulness. By the use chemometric methods quantitative structure-activity and structure-property relationships (QSAR/QSPR) describe how a given physicochemical property varies as a function of molecular descriptors and describe the chemical structure of the molecule [8].

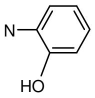
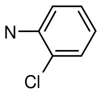
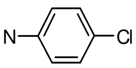
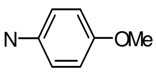
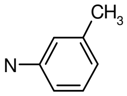
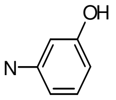
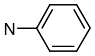
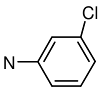
QSAR and QSPR modelling were used in many works for estimate properties such as boiling point and toxicity of chemicals [9, 10].

METHOD OF CALCULATIONS

In this work (AM1) semi-empirical SCF-MO method [11] was employed in the MOPAC 7.00 program [12] for the characterization of the electronic structure of the various bi- and tri-dentate Schiff base molecules **1-11** [Scheme 1], and in addition the reaction between the corrosion inhibition effect by these organic compounds and the geometric properties for all compounds has been discussed by some equations. All quantum theoretical calculations were starting without any geometry constraints for full geometry optimizations. The following quantum chemical indices were considered: the energy of the highest occupied molecular orbital (E_{HOMO}), the lowest unoccupied molecular orbital (E_{LUMO}), the band gap energy (ΔE), the dipole moment (μ), the length of C=N (D1), the length of O-H group (D2), the net charge on the nitrogen atom in the imine group (σ_N), the net charge on the oxygen atom in the hydroxyl group (σ_O), the ionization potential (Ip), the volume of compound (V) and the experimental inhibition of compounds (η %) (Table 1).

In order to study QSPR, quantum chemical calculations have been applied to the **1-11** imino compounds to select corrosion inhibitors [Scheme 1]. The corresponding structures have been optimized and the energies and coefficients of their molecular orbital have been calculated using the semi-empirical AM1 method in the MOPAC 7.0 program. AM1 is a semi-empirical method based on the neglect of differential diatomic overlap integral approximating. All calculations were performed on a Pentium IV, 2.8 GHz computer. The geometry of the molecules under investigation was determined by optimization all geometrical variables. Consequently, highest occupied molecular orbital energy (HOMO), lowest unoccupied molecular orbital energy (LUMO), band gap (ΔH), C=N bond length (D_1), O-H bond length (D_2), the net charge density on nitrogen atom in imin group (σ_N), the net charge density on oxygen atom in hydroxyl group (σ_O), ionization potential (**IP**) and the volume of molecule (V) for **1-11** compounds were obtained. Table 1 shows some quantum chemical parameters of **1-11** compounds in the gas phase by using AM1 semi-empirical calculations.



Compound	Ar	R1	%*	Ref.
1		H	93	13 (a)
2		H	94.8	13 (b)
3		H	94.1	13 (b)
4		H	92.2	13 (c)
5		H	99.9	13 (d)
6	N-NH-SO_2-CH_2-CH_3	Br	69	13 (e)
7		H	94	13 (d)
8	N-NH-SO_2-CH_2-CH_3	Cl	70	13 (e)
9		H	91.3	13 (b)
10		H	92	13 (f)
11		H	99.96	13 (d)

*. % = %η.

Scheme 1. Chemical structures of **1-11** Schiff base compounds having experimental corrosion inhibition efficiency.

Table 1. Some calculated electronic parameters for **1-11** Schiff base compounds by AM1 semi-empirical method.

Compd.	E_{HOMO}	E_{LUMO}	ΔE	μ	D_1	D_2	σ_N	σ_O	IP	V	η %
1	-8.6358	-0.5675	8.0582	2.967	1.2924	2.8838	-0.2060	-0.2578	8.63	656.57	93
2	-8.8198	-0.8433	7.9765	1.336	1.2896	2.1422	-0.2292	-0.2578	8.81	673.29	94.8
3	-8.8365	-0.9140	7.9225	2.150	1.2924	2.8842	-0.2084	-0.2558	8.83	682.20	94.1
4	-8.5302	-0.6669	7.8633	3.426	1.2918	2.8831	-0.1973	-0.2576	8.53	716.45	92.2
5	-8.7452	-0.6863	8.0589	2.024	1.2918	2.8818	-0.2054	-0.2574	8.74	693.26	99.9
6	-9.0917	-0.4667	8.6250	0.650	1.3067	3.0283	-0.2441	-0.093	9.09	734.01	69
7	-8.8277	-0.7793	8.0484	3.280	1.2779	2.7460	-0.2086	-0.2558	8.82	660.48	94
8	-9.0397	-0.4498	8.5899	0.705	1.3067	4.4316	-0.0378	-0.2453	9.03	717.72	70
9	-8.7740	-0.7124	8.0616	2.151	1.2918	2.8848	-0.2006	-0.2552	8.77	638.22	91.3
10	-8.6029	-0.5212	8.0817	2.409	1.2919	2.8822	-0.1751	-0.2577	8.60	713.24	92
11	8.9107	-0.8820	8.0287	3.120	1.2922	2.8848	-0.2086	-0.2552	8.91	682.89	99.9

RESULTS AND DISCUSSION

The quantitative structure activity relationships (QSAR) of some Schiff base compounds **1**-**11** (Scheme 1) as inhibitors for corrosion of steel in acidic medium have been done with AM1 semi-empirical method. The experimental values of the corrosion inhibition efficiency (η %) of **1**-**11** inhibitor molecules were obtained from literatures [13]. Conformation searching of the inhibitor molecules has been performed. Following equation was obtained, if a first-order regression analysis was made of relationship between corrosion inhibition efficiency (η %) and the calculated electronic parameters (Table 1).

$$\eta\ \% = 85.6167 - 28200\ (E_{HOMO}) + 78.6989\ (E_{LUMO}) - 102.7043\ (\Delta E) - 53.6560\ (\mu) + 139.5888\ (D_1) + 0.8195\ (D_2) - 1.8582\ (\sigma_N) - 25.7874\ (\sigma_O) - 130.1397\ (IP) - 11.5779\ (V) \qquad (1)$$

where, R = 1, max error = 1.7053×10^{-13}, min error = 0, mean error = 3.3589×10^{-14}, (R = correlation).

Eq. (1) and Table 1 show that the investigated compounds have very similar chemical structure and therefore the differences in their inhibitive properties are due to their different electronic molecular structure. Table 1 shows that the increasing in the negative charges of N (σ_N) and O (σ_O) atoms, act as active center in adsorption process, and decrease in E_{HOMO} values cause the significant increase in inhibitive action of studied compounds. It is known that in the chemical adsorption an increase in E_{HOMO} cause the significant increase in inhibition efficiency of organic compounds. The negative sign of the coefficient of E_{HOMO} can be concluded that the adsorption of these Schiff bases on the mild steel surface has no chemical mechanism and it may be physical. Physical adsorption results from electrostatic interaction between the charged centers of molecules and charged metal surface which results in a dipole interaction of molecule and metal surface. So, the positive sign of the coefficients μ suggest that these Schiff bases can be adsorbed on mild steel surface by physical mechanism. Eq. (1) can also show that forming of the feedback bond of the eleven kinds of Schiff bases, with Fe atoms in mild steel plays a role in inhibiting the mild steel corrosion in acid solutions, and the main aspect of the forming of feedback bonds is ability to offer electrons of the inhibitors.

On the other hand the substituent group with conjugated system, to the benzene ring will improve corrosion inhibition efficiency of these compounds (see Scheme 1 and Table 1). In all these compounds (Scheme 1) the nitrogen atom in –CH=N– group stands in sp^2 hybrid, and has one π-molecular orbital (π-MO), and p_z-atomic orbital (p_z-AO) can interact with the π-MO of the C atom in benzene ring to form p-π conjugation system. Owing to the conjugation system, π-electron is easily translated to d-orbital of metal atom (Fe atoms in mild steel) along to π-system. For this reason, electron-releasing substituent or conjugation system on N atom in the –CH=N– group will strengthen remarkably chemical adsorption of the N atom on the metal surface. The electron-releasing substituent or conjugation system obviously strengthens the interaction between the N and Fe atom. Therefore, it can be predicted that inhibition efficiency is improved in the following order: compound **11** >> **5** > **2** > **3** > **7** > **1** > **4** > **10** > **9** > **8** > **6**.

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