Study on Corrosion Inhibition from Aspect of Quantum Chemistry

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Calculated ionization potential, electron affinity, electron density and bond order of some thiophene derivatives have been obtained and correlated with the inhibition of corrosion produced by these substances as evaluated by polarization curves. It is apparent that such quantities as the electron density or ionization potential play an important role. The calculation was carried out by the Extended Hückel method for the series of substituted thiophene derivatives.

Introduction

Organic substances utilized as corrosion inhibitors are selected and judged on the basis of their physico-chemical properties.[1-5] Relatively little attention has been paid to the quantitative evaluation of the internal and steric effect of these substances upon their inhibition efficiency. Vosta and Coworkers[6-7] have correlated some quantum chemical parameters of a series of structurally related compounds with their corrosion inhibition characteristics. Maitra[8] studied theoretically the corrosion inhibition of furoic acid, furan and furfurylamine and concluded that the corrosion inhibition mostly depends upon the energy of the highest occupied molecular orbitals. Lewis[9] reported that the corrosion inhibition of a group of heterocyclic compounds, was dependent on both the heats of formation and the geometries of molecules, and on several quantum parameters. This paper reports a correlation between some quantum chemical parameters[10] such as ionization potentials, bond orders, electron densities and electron affinities of thiophene and some of its derivatives with their corrosion inhibition characteristics.

Experimental

A cylindrical piece of iron (99.99% pure) mounted on teflon holder was used as the electrode. The electrode surface was polished successively with a fine grade emery paper (G 400) and degreased with acetone and dried. Twice distilled water was used. Thiophene, 2-acetylthiophene, 2-thiophenecarboxylic acid and 2-thiophenecarboxaldehyde were of AR grade and used as such.

The galvanostatic method used for steady state polarization studies consisted of a constant current generator and a potentiometer for measuring corrosion potentials. All experiments were carried out at $30 \pm 1°C$. Corrosion rates were measured in terms of log $i_{corr.}$ in 2N HNO_3 containing 0.5 ml inhibitor solution.

Method of Calculation

The Extended Hückel method,[11-12] was applied to calculate the electronic structure and reactivity indices of the molecules. The structural parameters of molecules utilized in the calculation are obtained from the work by Dewar *et al.*[13]

For H-atoms only 1s orbitals; for carbon and oxygen atoms

2s, $2p_x$, $2p_y$ and $2p_z$ orbitals; for the S-atoms, 3s, $3p_x$, $3p_y$, $3p_z$, $3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals were employed.

The ionization energies used to evaluate the coulomb integrals and the orbital exponents used to calculate resonance integrals[14] are given in Table 1.

Results and Discussion

The results obtained from the relation between inhibition characteristics and quantum chemical data show that log $i_{corr.}$ ($i_{corr.}$ is the corrosion current or the corrosion rate in mA cm^{-1}) mostly depends upon the energies of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). From Figure 1 it is evident that the inhibition efficiency increases with the increase of energy of the HOMO, that is, the increase of the ionization potential. It is further evident that the inhibition efficiency increases with the ease of ionization of the molecule, which means that the molecule acts as an electron donor when blocking the corrosion reaction. 2-thiophenecarboxaldehyde lies the first one followed by 2-acetylthiophene followed by 2-thiophenecarboxylic acid and finally by thiophene in corrosion inhibition[15,16] properties, indicating that electron density on the heterocyclic sulphur atom and the oxygen atom (from C = O) are the determining factors for the inhibition effect. Thiophene which contains only one centre of adsorption, is on one side difficult to reduce, but with regard to its stability which is evident even from its low ionization potential, it is the least effective inhibitor.

Figure 2 shows the molecular diagram of 2-thiophenecarboxaldehyde. The most interesting turned out to be the electron densities, in the sulphur heteroatom and oxygen from C = O inhibition centres, which related to the inhibition efficiency are shown in Table 1. The comparison indicates the

Table 1. The ionization energies and the exponents of the orbital

Atomic Orbital	Exponent	Ionization Energy eV
H (1s)	1.000	13.60
C (2s)	1.625	21.01
C (2p)	1.620	11.27
O (2s)	2.246	35.57
O (2p)	2.240	18.30
S (3s)	2.000	21.13
S (3p)	1.810	13.30
S (3d)	0.650	7.00

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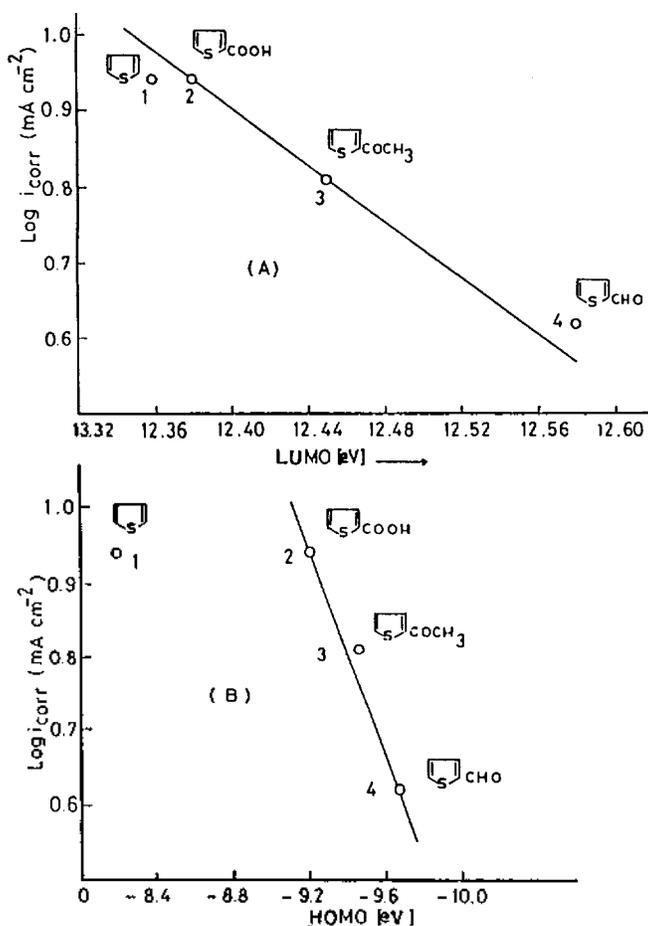
Figure 1. Correlation of LUMO (A) and HOMO (B) energies with log i_corr. 1) Thiophene; 2) 2-Acetylthiophene; 3) 2-Thiophenecarboxylic acid; 4) 2-Thiophenecarboxaldehyde.
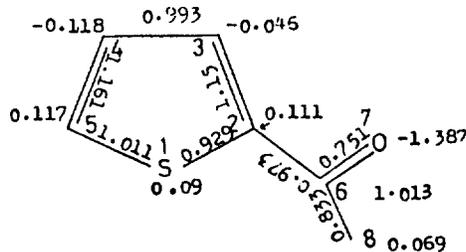
Figure 2. Molecular diagram of 2-Carboxaldehydethiophene.

fact that inhibitors with higher efficiency have been a higher electron density in the presumed inhibition centre. That means, from the point of view of the general chemical reactivity, that these centres are able to participate by their own electrons when forming a chemical bond between inhibitor and a metal. Also from the results it was shown that the bond order decreases with the increase of the inhibition in forming a chemical bond between inhibitor and a metal. Also from the results it is shown that the bond order decreases with the increase of the inhibition.

The presented quantum–chemical parameters, that means the electron densities and bond orders, belong to the so-called static indices of the chemical reactivity, because they characterize the reactivity of a substance by means of quantities in its basic state.

Table 2. Quantum Chemical Parameters of the Investigated Compounds

Inhibitor	log i_corr. (mA cm⁻¹)	S heteroatom O from (C=O)	electron density	HOMO energy (eV)	LUMO energy (eV)	% Inhibition.
Iron	1.1399	—	—	—	—	—
2-Thiophenecarboxaldehyde.	0.620	S O	+0.090 -1.387	-9.689	12.585	45.6
2-Acetylthiophene	0.807	S O	+0.060 -1.384	-9.473	12.444	29.2
2-Thiophenecarboxylic acid	0.940	S O	+0.035 -1.372	-9.217	12.388	17.5
Thiophene	0.940	S	-0.129	-8.168	12.362	17.5

Mechanism of Inhibition. The corrosion of iron in nitric acid solutions is an electrochemical process and its inhibition can take place by change in corrosion potential or increase in the polarization of the cathode or the anode or both. All inhibitors under consideration influence both the cathodic and anodic processes.[16] The order of inhibition efficiency of these inhibitors are in support of this mechanism.

The results obtained in Table 2 show that the inhibition by thiophene derivatives is due to adsorption on both cathodic and anodic areas. Introducing an electrophilic group such as -COOH, -COCH₃ and -CHO instead of hydrogen atom in thiophene, increases the inhibitor efficiency. This is due to the increase of positive charge of the sulphur heteroatom and negative charge of oxygen atom (Table 2). This reinforces its adsorption, on cathodic and anodic areas respectively, as result of the increased Coulombic interaction.[17] Therefore, one can expect an increase of its adsorption ability and its inhibitor efficiency as well. Also the results of electron affinities (Table 2) of the inhibitors used are in support of this mechanism.

Kaminski[18] studied the effect of various substituents in thiophene on the inhibitor efficiency and reported that these compounds are adsorbed on the metal surfaces via the electrons of the thiophene ring. The same mode of adsorption was assumed by Conway and Barradas[15] for pyridine on mercury in 1N HCl.

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Ortho-normalized Gaussian Type Orbitals

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Received August 26, 1985

The conventional Gaussian type orbitals (GTO's) were generalized to have a regular form which is similar to the conventional Slater type orbitals (STO's). They were also orthogonalized and orthonormalized to have the same number of radial nodes that the hydrogenic orbitals have.

Introduction

Gaussian functions of the type of the next Eq.(1) and their linear combinations were first proposed by S.F. Boys as basis set orbitals in the calculation of ab-initio molecular orbitals.[1-3]

$$r^P \exp(-ar_A^2) Y_l^{|m|}(\theta, \phi) \qquad (1)$$

where $Y_l^{|m|}(\theta,\phi)$ are spherical harmonics, and $a>0, P$ is integral, equal to or greater than 1, and is restricted to odd values for odd l, even values for even l. The virtue of these functions is the relatively simple closed analytic expression for the two-electron integrals in the three and four-centers cases, as well as for one and two-centers.

The Gaussian-type orbitals (GTO's) described in Eq.(1) do not contain same radial nodes that hydrogenic orbitals have. Therefore, author transformed Eq.(1) into the following form;

$$g_{nlm}(r) = N_r r^{n-1} e^{-ar^2} \qquad (2)$$

where N_r is the normalizing constant and $n, l,$ and m stand for the usual quantum number. Normalizing Eq.(2) leads to the following equation.

$$g_{nlm}(r) = \left(\frac{2^{n+1}}{1\cdot3\cdot5\cdots(2n-1)}\right)^{\frac{1}{2}} ((2a)^{2n+1}/\pi)^{\frac{1}{4}} r^{n-1} e^{-ar^2} \qquad (3)$$

where $g_{nlm}(r)$ stand for the radial GTO's.

The combination of Eq.(3) and the real spherical harmonics, $Y_{lm\delta}^{real}(\theta,\phi)$, yields equation (4)

$$g_{nlm\delta}(r, \theta, \phi) = (2^{n+1}/1\cdot3\cdot5\cdots(2n-1))^{\frac{1}{2}} ((2a)^{2n+1}/\pi)^{\frac{1}{4}}$$
$$r^{n-1} e^{-ar^2} Y_{lm\delta}^{real}(\theta, \phi) \qquad (4)$$

where δ denotes zero, cosine and sine combination which the complex spherical harmonics are transformed into the real spherical harmonics according to its value zero, 1 and -1.[4]

Eq.(4) is called to the generalized GTO's. The $g_{nlm\delta}(r,\theta,\phi)$ have the similar form with the Slater type orbitals (STO's) and are different only in the normalization constant and exponential term. $G_{nlm\delta}(r,\theta,\phi)$ do not have the radial nodes for the hydrogenic functions like STO's.[5,6]

Accordingly, author orthogonalize and normalize the $g_{nlm\delta}(r,\theta,\phi)$ as follows; one can consider atom as a vector space and its atomic orbitals (AO's) as the component vector in its vector space.[6] Putting g_k equal to $g_{nlm\delta}(r,\theta,\phi)$ in Eq.(4), we may obtain the next equation by using the Schmidt's orthorgonalizing process for vectors.[4,7]

$$g_1^\circ = g_1$$

$$g_2^\circ = g_2 - \frac{(g_1^\circ/g_2)}{(g_1^\circ/g_1^\circ)} g_1^\circ$$

$$g_3^\circ = g_3 - \frac{(g_2^\circ/g_3)}{(g_2^\circ/g_2^\circ)} g_2^\circ - \frac{(g_1^\circ/g_3)}{(g_1^\circ/g_1^\circ)} g_1^\circ$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$g_k^\circ = g_k - \frac{(g_{k-1}^\circ/g_k)}{(g_{k-1}^\circ/g_{k-1}^\circ)} g_{k-1}^\circ \cdots - \frac{(g_1^\circ/g_k)}{(g_1^\circ/g_1^\circ)} g_1^\circ \qquad (5)$$

where g_i° are the orthogonalized GTO, $g_{nlm\delta}^\circ(r,\theta,\phi)$ and (g_i°/g_k) denotes the dot product, overlap integral between g_i° and g_k.

Then, these g_k° can be normalized as follows;[8]

$$g_k^\oplus = g_k^\circ/(g_k^\circ/g_k^\circ) \qquad (6)$$

where $g_k^\oplus$ denotes orthonormalized GTO, $g_{nlm\delta}^\oplus(r,\theta,\phi)$.

Results and Discussion

The result calculated from Eq.(4) was listed in Table 1. Comparing $g_{nlm\delta}(r,\theta,\phi)$, in Table 1 with the conventional STO's