Full Length Research Article

CORRELATION BETWEEN ELECTRONIC STRUCTURE AND CORROSION INHIBITION OF COPPER IN 3M NITRIC ACID SOLUTION BY SOME ACETOPHENONE AROYL HYDRAZONE DERIVATIVES

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ABSTRACT

Some acetophenone aroyl hydrazone derivatives have been studied by the inhibition of copper corrosion in 3M nitric acid solution. The structure of some acetophenone aroyl hydrazone derivatives were calculated by using the AM1 method of the quantum chemical program HyperChem 7.0. Results of the above calculation are coordinated with inhibitor efficiency (P) that is determined by experiment and both are applied to Statgraphics 4.0 software to carry out linear regression. Based on regression results, we draw a conclusion on the relation between electronic structure and corrosion inhibitor efficiency of some acetophenone aroyl hydrazone derivatives.

INTRODUCTION

Corrosion inhibitors are widely used in industry to reduce corrosion occurring to metals and alloys in contact with aggressive media including nitric acid solution (Sastri *et al.,* 1997) Different organic compounds are used in these applications, especially those that tend to adsorb at the interfaces. Surface-active agents containing nitrogen, sulfur or both give excellent inhibition of corrosion for metals in acidic medium (Hoang *et al.,* 2013*;* Growcock *et al.,* 1989; Lukovits *et al.,* 1995). Heterocyclic compounds play an important role in the inhibition process owing to their tendency to adsorb at interfaces. It is known that the corrosion inhibition efficiency of an organic compound depends not only on the characteristics of the environment in which it acts, the nature of the metal surface, electrochemical potential at the interface and temperature, but also on the structure of the inhibitor itself (Khaled *et al.,* 2012; Riggs *et al*., 1976). Quantitative relationships between parameters characterizing the chemical structure and corrosion inhibition efficiency of various types

of compounds have been the topics of several treatises (Hoang *et al.,* 2013*;* Lukovits *et al.,* 1995). Theoretical studies based on quantum chemical calculations can be helpful in selecting and designing possible corrosion inhibitor substances because these calculations can provide qualitative, semi-qualitative useful information to better understanding the undergoing inhibition processes and predict a number of molecular parameters directly correlated to the corrosion inhibitor efficiency of any chemical compound (Khaled *et al.,* 2003; Sastri 1998). Therefore, nitrogen containing compounds, have been studied theoretically as corrosion inhibitors on surface of metals (Lukovits *et al*., 2001). In this study, we report results obtained from theoretical calculations and mass loss experiments on the corrosion inhibition of copper in 3M nitric acid solution by some acetophenone aroyl hydrazone derivatives, and correlation between electronic structure and corrosion efficiency of hydrazone derivatives.

Study methods

Theoretical calculations were carried out using AM1 method attached in HyperChem 7.0 software (Riggs *et al*., 1976), to obtain quantum parameters of some derivatives of acetophenone aroyl hydrazone derivatives. The results

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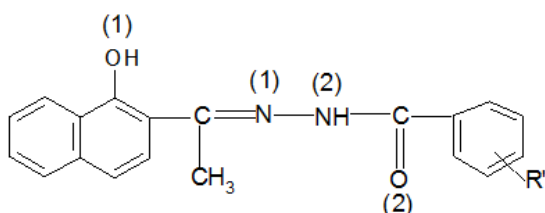
obtained from computational calculation and corrosion inhibition efficiency of copper in 3 M HNO$_3$ solution by acetophenone aroyl hydrazone derivatives, obtained from mass loss experiment were combined and used as input data for poly-variable regression method using Statgraphic 4.0 software (Sastri *et al.*, 1998).

RESULTS AND DISCUSSION

A series of acetophenone aroyl hydrazone derivatives, which have been studied, are shown as following:
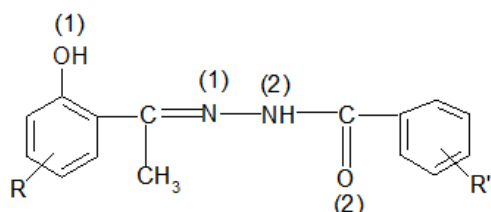
Where R is 4-CH$_3$ or 4-OH and R' is 3-CH$_3$, 4-CH$_3$, 2-OH or 4-OH, and

Where R' may be 2-OH or 4-OH

The quantum parameters of acetophenone aroyl hydrazone derivatives obtaibed from computational calculations are listed in Table 1 and Table 2. In general, inhibitor molecules can protect metal from the attact of oxidative species due to the adsorption of these melecules on surface of metal forming a satble barrier to protect metal surface (Hoang *et al.* 2013). Therefore, charge density on the adsorption sites (-NH, =N-, -OH and -CO) and E_{LUMO}, E_{HOMO} influence much on corrosion inhibition effeciency (Fouda *et al.*, 2003; Ju *et al.*, 2008; Zarrouk *et al.*, 2014). For these reasons, charge density on the adsorption sites, E_{LUMO} and E_{HOMO} were used as a basis in our study to evaluate the inhibition efficiency of derivatives. In order to get a good relationship between theoretical and experimental results, the effect of some other parameters such as S, V, E_H, E_{Total} and μ was also considerred in our computational calculations. The relationship between theoretical and experimental results was carried out by Stagraphic 4.0 software using poly-variable regression analysis. The linear function has the form as following:

$$\eta_{th} = \sum a_i x_i + \text{const}$$

Where: η_{th} *is the theoretical corrosion inhibition efficiency, a_i is regression coefficient and x_i is the parameter which affects to η_{th}.*

The regression analysis goals to find the best linear poly-variable function, where theoretical value of corrosion inhibition efficiency (η_{th}) is in good agreement with experimental value of corrosion inhibition efficiency of hydrazone derivatives. Every linear poly-variable functions used in our study all contain 8 different variables which are quantum parameters obtained from theoretical calculations and listed in Table 1 and Table 2.

Table 1. Total energy, E$_{total}$, of molecules (kcal/mol), hydrated energy, E$_H$, (kcal/mol), energy of the lowest unoccupied molecular orbital (E$_{LUMO}$/eV), energy of the highest occupied molecular orbital (E$_{HOMO}$/eV) and dipole moment (μ/D) of 10 hydrazone derivatives

Molecule	R	R'	E$_{total}$	E$_H$	E$_{HOMO}$	E$_{LUMO}$	μ
1	4-CH$_3$	4-CH$_3$	-80199.24	-8.30	-8.428	-0.579	5.792
2	4-CH$_3$	2-OH	-83993.03	-13.38	-8.339	-0.564	6.032
3	4-CH$_3$	4-OH	-83998.20	-16.38	-8.449	-0.589	6.359
4	4-OH	3-CH$_3$	-83997.98	-16.33	-8.457	-0.550	6.778
5	4-OH	4-CH$_3$	-83998.19	-16.28	-8.447	-0.591	7.176
6	4-OH	4-OH	-87797.14	-24.35	-8.469	-0.601	7.781
7	4-OH	2-CH$_3$	-83993.51	-16.47	-8.296	-0.622	6.487
8	4-OH	4-CH$_3$	-83996.63	-16.33	-8.301	-0.655	7.139
9	-	2-OH	-92837.07	-13.51	-7.968	-0.596	5.962
10	-	4-OH	-92842.25	-16.51	-8.058	-0.616	6.050

Table 2. Area, (S/Å^2) and volume, (V/Å^3) of molecules, charge density, (Z), on atoms and corrosion inhibition efficiency (η$_{exp}$/%), of 10 hydrazone derivatives with the concentration of 10^{-5} M, on Cu in 3.0 M HNO$_3$ solution

Molecule	R	R'	S	V	Z$_{N1}$	Z$_{N2}$	Z$_{O1}$	Z$_{O2}$	η
1	4-CH$_3$	4-CH$_3$	486.50	877.92	-0.066	-0.306	-0.259	-0.316	87.85
2	4-CH$_3$	2-OH	440.52	844.13	-0.062	-0.312	-0.260	-0.282	89.73
3	4-CH$_3$	4-OH	457.83	846.38	-0.066	-0.306	-0.259	-0.317	90.89
4	4-OH	3-CH$_3$	456.23	845.91	-0.071	-0.306	-0.254	-0.316	87.53
5	4-OH	4-CH$_3$	459.93	846.48	-0.070	-0.306	-0.254	-0.316	94.00
6	4-OH	4-OH	431.26	814.68	-0.070	-0.306	-0.254	-0.318	90.00
7	4-OH	2-CH$_3$	437.70	837.20	-0.058	-0.308	-0.259	-0.315	87.64
8	4-OH	4-CH$_3$	457.20	846.83	-0.059	-0.306	-0.259	-0.314	90.87
9	-	2-OH	431.57	916.40	-0.072	-0.311	-0.258	-0.284	87.68
10	-	4-OH	448.84	919.03	-0.076	-0.305	-0.257	-0.319	88.96

Z$_{N1}$, Z$_{N2}$, Z$_{O1}$, and Z$_{O2}$ are charge of N and O atom at the first and second positions, respectively.

η$_{exp}$ values were obtained from our experiments using mass lossmethod which is not presented here

Table 3. Values of η_{th} (%) obtained from theretical calculations using 7 different functions, η_{exp} (%) obtained from experiments and correlation coefficients

Molecule Function		1	2	3	4	5	6	7	8	9	10	R^2
1	η_{exp}	87.85	89.73	90.89	87.53	94.00	90.00	87.64	90.87	87.68	88.96	0.9713
	η_{th}	88.01	90.08	90.18	87.38	93.74	90.18	87.53	90.8	87.17	89.28	
2	η_{exp}	87.85	89.73	90.89	87.53	94.00	90.00	87.64	90.87	87.68	88.96	0.8495
	η_{th}	88.73	90.34	89.41	87.46	93.11	90.95	87.54	90.92	87.08	89.52	
3	η_{exp}	87.85	89.73	90.89	87.53	94.00	90.00	87.64	90.87	87.68	88.96	0.9935
	η_{th}	87.96	89.99	90.64	87.52	93.99	90.12	87.66	90.9	87.49	89.21	
4	η_{exp}	87.85	89.73	90.89	87.53	94.00	90.00	87.64	90.87	87.68	88.96	0.9918
	η_{th}	88.1	90.15	90.74	87.66	94.11	90.29	87.8	91.04	87.62	89.39	
5	η_{exp}	87.85	89.73	90.89	87.53	94.00	90.00	87.64	90.87	87.68	88.96	0.8380
	η_{th}	88.68	90.18	89.22	87.32	92.92	90.86	87.4	90.79	86.95	89.35	
6	η_{exp}	87.85	89.73	90.89	87.53	94.00	90.00	87.64	90.87	87.68	88.96	0.9230
	η_{th}	88.34	90.39	89.9	87.51	93.54	90.61	87.61	90.95	87.13	89.59	
7	η_{exp}	87.85	89.73	90.89	87.53	94.00	90.00	87.64	90.87	87.68	88.96	0.8165
	η_{th}	88.95	90.28	89.28	87.47	92.96	91.12	87.54	90.94	87.16	89.46	

Calculations gave 7 different linear functions with different coefficients and correlation coefficents as shown below:

(1) η_{th} depends on 8 factors including: E_{LUMO}, E_{HOMO}, Z_{N1}, Z_{N2}, Z_{O1}, Z_{O2}, S and E_{Total}.

η_{th} = 19874.4275 - 1373.1996E_{LUMO} + 428.6403E_{HOMO} - 24914.9384Z_{N1} + 42254.2687Z_{N2} - 17672.9575Z_{O1} + 5291.5943Z_{O2} - 7.9196S + 0.05905E_{Total}

(2) η_{th} depends on 8 factors including: E_{LUMO}, E_{HOMO}, Z_{N1}, Z_{N2}, Z_{O1}, Z_{O2}, S and μ

η_{th} = 3984.3766 - 522.3960E_{LUMO} - 105.0801E_{HOMO} + 509.4041Z_N^1 + 7985.3781Z_N^2 + 6359.7471Z_O^1 + 1665.5487Z_O^2 - 0.4890S - 33.7004μ

(3) η_{th} depends on 8 factors including: E_{LUMO}, E_{HOMO}, Z_{N1}, Z_{N2}, Z_{O1}, Z_{O2}, S and V

η_{th} = -2046.2676 - 123.4223E_{LUMO} + 100.3483E_{HOMO} - 2783.7135Z_{N1} - 7111.6298Z_{N2} - 1887.9686Z_{O1} - 766.3528Z_{O2} + 0.9743S - 0.7394V

(4) η_{th} depends on 8 factors including: E_{LUMO}, E_{HOMO}, Z_{N1}, Z_{N2}, Z_{O1}, Z_{O2}, V, E_{Total}

η_{th} = 356.9007 − 260.6229E_{LUMO} + 136.6663E_{HOMO} - 5218.5070Z_{N1} - 1705.5136Z_{N2} - 3625.3351Z_{O1} - 103.0779Z_{O2} - 0.6600V + 0.00648E_{Total}

(5) η_{th} depends on 8 factors including: E_{LUMO}, E_{HOMO}, Z_{N1}, Z_{N2}, Z_{O1}, Z_{O2}, μ and E_{Total}

η_{th} = 2867.7985 - 459.7930E_{LUMO} - 137.6347E_{HOMO} + 2120.4326Z_{N1} + 5587.9920Z_{N2} + 7775.4897Z_{O1} + 1398.1005Z_{O2} - 35.1785μ - 0.00379E_{Total}

(6) η_{th} depends on 8 factors including: E_{LUMO}, E_{HOMO}, Z_{N1}, Z_{N2}, Z_{O1}, Z_{O2}, V and μ

η_{th} = 2198.4091 - 412.3165E_{LUMO} - 36.7570E_{HOMO} - 615.6848Z_{N1} + 3300.3787Z_{N2} + 3900.8894Z_{O1} + 925.2613Z_{O2} - 0.2759V - 24.4509μ

(7) η_{th} depends on 8 factors including: E_{LUMO}, E_{HOMO}, Z_{N1}, Z_{N2}, Z_{O1}, Z_{O2}, μ and E_H

η_{th} = 2332.7926 - 416.8446E_{LUMO} - 70.2948E_{HOMO} + 481.8375Z_{N1} + 3684.7306Z_{N2} + 5427.4733Z_{O1} + 1140.0991Z_{O2} - 28.4149μ - 1.4766E_H

The values of ηth obtained from theoretical calculation are listed on Table 3 below:

As listed in the Table 3, all linear functions obtained from regression method have a relatively high value of correlation coefficient ranging from 0.8165 to 0.9935.

The relatively high value of correlation coefficient reveals that the corrosion inhibition efficiency of hydrazone derivatives is affected by all quantum parameters listed in Table 1 and Table 2 and these parameters affect to corrosion inhibition efficiency with different degrees. During calculation we noted that, EHOMO, ELUMO, charge density on N and O atoms, and area and volume of molecules affect to corrosion inhibition efficiency much more than other parameters do. The small value of these parameters makes an increase in correlation coefficient.

The effect of ELUMO and EHOMO on the efficiency via the difference of ELUMO and EHOMO, (ΔE). When value of ΔE is small, the inhibitor molecules are easy to reach the excited state, where the larger molecules will be adsorbed more powerfully than the smaller one and with the larger area and volume they cover better than small one and therefore they produce a higher corrosion corrosion efficiency. Beside the effect of EHOMO, ELUMO, charge density on N and O atoms, area and volume of molecules on inhibition efficiency, Etotal, EH and μ also affect to the inhibition efficiency with a lower degree. Though there is a correlation between electronic structure of hydrazone derivatives and their corrosion inhibition efficiency on copper metal in 3.0 M HNO3 solution, Further work must be done to calculate the adsorption energy of hydrazone derivatives on copper surface for explaining the clearer the mechanism of inhibition of hydrazone derivatives.

Conclusion

Several quantum parameters of hydrazone derivtive molecules were achieved from theoretical calculation using HyperChem 7.0 software. The effect of these parameters on corrosion inhibition efficiency was then studied by regression method with the help of Stagraphic 4.0 software. Amongst the obtained linear functions, the equation (3) is the best one which has the smallest deviation between corrosion inhibition efficiencies obtained from theoretical calculation and experiment work. The regression analysis shows that E_{LUMO}, E_{HOMO}, charge density on N and O atoms, area and volume of hydrazone derivative molcules affect strongly on corrosion inhibition efficiency of derivatives on copper surface. The obtained data could be used as a basis to synthesize hydrone derivatives which have high inhibition efficiency on metals.

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