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The Quantum Chemical Calculations of Serine, Therionine and Glutamine

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An examination of quantum chemical and corrosion inhibition studies for three serine (Ser), therionine (Thr) and glutamine (Glu) which had been tested as corrosion safe inhibitors for cold rolled steel (CRS) in 1.0 M HCl solutions at different temperatures (283-333 K) were made to see if any clear links exist between them. The Genetic Function Approximation Method has been used for QSAR study. The correlation between inhibition efficiency and descriptor variables obtained from the quantum chemical calculation using B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p), MP2/6-311G(d,p), and CBS-APNO methods.

Keywords: Corrosion inhibition, Serine, Therionine, Glutamine, Genetic Function Approximation Method

1. INTRODUCTION

There are several quantum-chemistry studies performed in order to relate the inhibition efficiency to the molecular properties of the different types of compounds. Rodrı´guez-Valdez et al. [1] investigated computational simulations of the molecular structure and corrosion properties of amidoethyl, aminoethyl and hydroxyethyl imidazolines inhibitors and found hydroxyethyl, aminoethyl and amidoethyl imidazolines in both, gaseous phase and solvent phase, indicated that all inhibitor systems have a very similar capacity for charge donation, since the values of E_{HOMO} presented a small

difference between them [1]. Ma et al. [2] revealed that the inhibition efficiency has certain relationship to highest occupied molecular orbital (HOMO) energy and the combined energy between the pyridine–pyrazole inhibitor molecules and the iron atom. Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides [3] thiosemicarbazones [4], hydrazine carbodithioic acid derivatives [5], bipyrazole derivatives [6], schiff base corrosion inhibitors [7], piperidine and these derivatives [8] triazole Schiff bases [9], Aminic nitrogen-bearing polydentate Schiff base compounds [10], have been performed.

The quantitative structure-activity relationship (QSAR) methods were developed by Hansch and Fujita [11], and they have been successfully applied to many drug and corrosion inhibition efficiency and molecular structure El Ashry et al. [12]. Studied QSAR of lauric hydrazide and its salts as corrosion inhibitors by using the quantum chemical and topological descriptors. Lebrini et al. [13] obtained a significant correlation between inhibition efficiency and quantum chemical parameters using semi-empirical quantitative structure-activity relationships (QSAR) approach for 3,5-bis(n-pyridyl)-4-amino-1,2,4-triazoles as corrosion inhibitors for mild steel in perchloric acid.

There are also quantitative structure–activity relation (QSAR) studies to derive equations for the theoretical inhibition efficiency [14-16].

In this paper, a detailed quantum chemical study have been performed for the Ser, Thr, and Glu molecules used as inhibitor using the, density functional, theory (DFT), MP2 and CBS-APNO methods. The highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{HOMO} and E_{LUMO} (ΔE), dipole moments (DM), molecular volume (MV), sum of the total negative charge (TNC), global hardness (η), softness (σ), chemical potential (μ), electronegativity (χ), sum of electronic and zero-point Energies (SEZPE) have been calculated.

2. THEORETICAL CONSIDERATIONS

Full geometrical optimizations of the Ser, Thr, and Glu molecules were performed by using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee-Yang-Parr non-local correlation functional (B3LYP) [17-19] with 6-311G(d,p), 6-311++G(2d,2p) basis sets, by using MP2 (Moller-Plesset) with 6-311G(d,p) basis set for neutral and protonated forms in the gas phase and in the presence of water, and CBS-APNO methods for only neutral form in the gas phase, implemented in Gaussian 03 (Revision D.01) package [20]. Moller-Plesset (MP) perturbation theory [21] adding higher excitations to Hartree–Fock theory as a non-iteration correction, drawing upon techniques from the area of mathematical physics known as much body perturbation theory.

2.1. Statistical analysis of the data

In this study, the inhibition efficiencies of three tested compounds, with four methods using four different phases, are examined based on eleven descriptors. For this purpose, the most widely used approach called QSAR is conducted to predict the regression model which helps estimate the

inhibition efficiencies of three compounds. Before running QSAR approach, we employed Genetic Function Approximation (GFA) method [22] in order to select a regression model or models that have the ability of predicting the inhibition efficiency of the studied molecules. Therefore, the calculated model with descriptor variables can be used. The eleven descriptors which are symbolically represented as E_{HOMO}, E_{LUMO}, ΔE, DM, MV, TNC, η, σ, χ, μ and SEZPE. Also, the four phases are neutral, neutral in the presence of water, protonated and the protonated in the presence of water.

First of all, the correlations among the eleven descriptors are calculated to remove some variables which have co-linearity problems. We used a correlation measure called Spearman Correlation since the number of observations for each method is just three. Thus, Pearson Correlation measure cannot be used. We cannot give all calculations pertinent to correlation since many tables are needed. However, we just give one of them in order to show how the number of descriptors are reduced when co-linearity among them are exist. Also, throughout the analysis, SPSS 17 and Mat Lab 7.9 are used to conduct all statistical analysis.

3. RESULTS AND DISCUSSION

3.1. Theoretical studies

Table 1. The calculated quantum chemical parameters for the non-protonated compounds using B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p), MP2/6-311G(d,p), and CBS-APNO methods

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	DM (D)	MV (cm^3/mol)	TNC (e)	η (eV)	σ (eV^{-1})	χ (eV)	μ (eV)	SEZPE (eV)
B3LYP/6-311G (d,p)											
Ser	-6.92	-0.06	6.86	0.365	82.083	-1.642	3.430	0.292	-3.490	3.490	-10856.311
Thr	-6.78	0.07	6.85	2.408	76.329	-1.859	3.425	0.292	-3.355	3.355	-11925.848
Glu	-6.91	-0.16	6.75	4.757	103.684	-2.468	3.375	0.296	-3.535	3.535	-14469.749
Regression for WL (283 K)	0.059	0.472	0.982	0.929	0.837	0.998	0.982	0.954	0.274	0.274	0.993
B3LYP/6-311++G (2d,2p)											
Ser	-7.20	-0.53	6.67	0.391	73.987	-1.739	3.335	0.300	-3.865	3.865	-10857.136
Thr	-7.03	-0.56	6.47	2.575	100.168	-1.990	3.235	0.309	-3.795	3.795	-11926.659
Glu	-7.15	-0.67	6.48	4.336	118.993	-2.088	3.240	0.309	-3.910	3.910	-14470.695
Regression for WL (283 K)	0.00	0.999	0.408	0.868	0.840	0.720	0.408	0.452	0.423	0.423	0.993
MP2/6-311G (d,p)											
Ser	-11.16	3.98	15.14	0.649	81.202	-1.162	7.570	0.132	-3.590	3.590	-10828.020
Thr	-11.03	3.80	14.83	2.721	89.202	-1.983	7.415	0.135	-3.615	3.615	-11894.086
Glu	-11.19	3.67	14.86	5.039	117.243	-2.176	7.430	0.135	-3.760	3.760	-14430.866
Regression for WL (283 K)	0.218	0.846	0.366	0.925	1.000	0.631	0.366	0.452	0.994	0.994	0.993
CBS-APNO											
Ser	-11.26	0.97	12.22	-0.412	-	-1.825	6.111	0.164	-5.144	5.144	-10795.112
Thr	-11.13	0.90	12.04	-1.186	-	-1.983	6.018	0.166	-5.113	5.113	-11856.944
Glu	-11.29	0.72	12.01	-2.381	-	-2.176	6.005	0.167	-5.281	5.281	-14385.536
Regression for WL (283 K)	0.218	0.996	0.584	0.965	-	0.937	0.564	0.770	0.856	0.856	0.994

Table 2. The calculated quantum chemical parameters for the non-protonated compounds in the presence of water using B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p) and MP2/6-311G(d,p) methods

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	DM (D)	MV (cm^3/mol)	TNC (e)	η (eV)	σ (eV^{-1})	χ (eV)	μ (eV)	SEZPE (eV)
B3LYP/6-311G (d,p)											
Ser	-6.80	0.02	6.82	0.424	77.667	-1.855	3.410	0.293	-3.390	3.390	-10857.170
Thr	-6.74	0.17	6.91	3.499	96.149	-2.062	3.455	0.289	-3.285	3.285	-11926.665
Glu	-6.81	0.03	6.84	6.803	100.674	-2.715	3.420	0.292	-3.390	3.390	-14470.781
Regression for WL (283 K)	0.182	0.061	0.009	0.919	0.637	0.999	0.009	0.004	0.092	0.092	0.993
B3LYP/6-311++G (2d,2p)											
Ser	-7.06	-0.41	6.65	0.563	74.154	-2.025	3.325	0.301	-3.735	3.735	-10858.033
Thr	-6.98	-0.31	6.67	3.899	109.412	-2.297	3.335	0.300	-3.645	3.645	-11927.517
Glu	-7.04	-0.38	6.66	6.537	118.674	-2.472	3.330	0.300	-3.710	3.710	-14471.790
Regression for WL (283 K)	0.004	0.000	0.045	0.864	0.648	0.823	0.045	0.452	0.001	0.001	0.993
MP2/6-311G (d,p)											
Ser	-11.15	3.95	15.10	0.642	71.770	-2.189	7.550	0.132	-3.600	3.600	-10828.856
Thr	-11.02	3.75	14.77	3.836	107.731	-2.353	7.385	0.135	-3.635	3.635	-11894.875
Glu	-11.18	3.57	14.75	6.580	101.766	-2.708	7.375	0.136	-3.805	3.805	-14431.764
Regression for WL (283 K)	0.218	0.889	0.503	0.880	0.302	0.99	0.503	0.690	0.997	0.997	0.993

Table 3. The calculated quantum chemical parameters for the protonated compounds using B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p), and MP2/6-311G(d,p) methods

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	DM (D)	MV (cm^3/mol)	TNC (e)	η (eV)	σ (eV^{-1})	χ (eV)	μ (eV)	SEZPE (eV)
B3LYP/6-311G (d,p)											
Ser	-12.18	-5.19	6.99	5.814	62.373	-1.439	3.495	0.286	-8.685	8.685	-10865.643
Thr	-12.55	-4.96	7.59	3.429	99.865	-1.777	3.795	0.264	-8.755	8.755	-11935.579
Glu	-10.38	-4.95	5.43	5.781	90.856	-2.384	2.715	0.368	-7.665	7.665	-14479.321
Regression for WL (283 K)	0.866	0.489	0.781	0.085	0.234	0.978	0.781	0.836	0.928	0.928	0.993
B3LYP/6-311++G (2d,2p)											
Ser	-12.38	-5.38	7.00	5.632	70.169	-1.464	3.500	0.286	-8.880	8.880	-10866.299
Thr	-12.67	-5.20	7.47	3.623	81.076	-1.906	3.735	0.268	-8.935	8.935	-11936.221
Glu	-10.55	-5.18	5.37	5.819	110.403	-1.957	2.685	0.372	-7.865	7.865	-14480.102
Regression for WL (283 K)	0.888	0.543	0.826	0.141	0.997	0.546	0.826	0.864	0.934	0.934	0.993
MP2/6-311G (d,p)											
Ser	-16.97	-1.71	15.26	6.301	91.428	-1.452	7.630	0.131	-9.340	9.340	-10837.355
Thr	-16.97	-1.20	15.77	3.650	76.725	-1.789	7.885	0.127	-9.085	9.085	-11903.807
Glu	-14.35	-1.38	12.97	6.579	102.459	-2.385	6.485	0.154	-7.865	7.865	-14440.442
Regression for WL (283 K)	0.954	0.139	0.858	0.148	0.465	0.977	0.858	0.881	0.997	0.997	0.993

Table 4. The calculated quantum chemical parameters for the protonated compounds in the presence of water using B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p) and MP2/6-311G(d,p) methods

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	DM (D)	MV (cm^3/mol)	TNC (e)	η (eV)	σ (eV^{-1})	χ (eV)	μ (eV)	SEZPE (eV)
B3LYP/6-311G (d,p)											
Ser	-7.97	-0.77	7.20	7.782	68.812	-1.635	3.600	0.278	-4.370	4.370	-10869.145
Thr	-8.16	-0.63	7.53	4.487	97.914	-1.919	3.765	0.266	-4.395	4.395	-11938.697
Glu	-7.34	-0.62	6.72	7.920	125.876	-2.562	3.360	0.298	-3.980	3.980	-14482.824
Regression for WL (283 K)	0.820	0.512	0.651	0.114	0.900	0.992	0.651	0.686	0.929	0.929	0.993
B3LYP/6-311++G (2d,2p)											
Ser	-8.23	-1.08	7.15	8.108	78.449	-1.651	3.575	0.280	-4.655	4.655	-10869.850
Thr	-12.46	-5.20	7.26	4.943	95.078	-2.160	3.630	0.275	-8.830	8.830	-11939.450
Glu	-10.35	-5.26	5.09	8.141	90.861	-2.254	2.545	0.393	-7.805	7.805	-14483.705
Regression for WL (283 K)	0.045	0.465	0.934	0.098	0.222	0.597	0.934	0.938	0.229	0.229	0.993
MP2/6-311G (d,p)											
Ser	-16.91	-1.94	14.97	8.059	83.220	-1.635	7.485	0.134	-9.425	9.425	-10840.872
Thr	-16.78	-1.34	15.44	4.763	76.446	-1.931	7.720	0.130	-9.060	9.060	-11907.001
Glu	-14.22	-1.59	12.63	8.507	111.199	-2.567	6.315	0.158	-7.905	7.905	-14443.955
Regression for WL (283 K)	0.970	0.093	0.868	0.165	0.849	0.989	0.868	0.884	0.999	0.999	0.993

According to Fukui's frontier orbital approximation, interactions between frontier molecular orbital (MO) only, HOMO and LUMO of both reactants are frequently considered, since the inverse dependence of stabilization energy on orbital energy differences ensures that terms involving the frontier MO will be larger than others. So, HOMO and LUMO orbitals may be used to predict the adsorption centers of the inhibitor molecule (Tables 1-4).

HOMO and LUMO orbitals and total electron density of three amino acids which are serine (Ser), therionine (Thr) and glutamine (Glu) obtained from the quantum chemical calculations for gase phase were given in Fig. 1. The quantum chemical properties in gas and water phase were calculated with B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p), MP2/6-311G(d,p) and CBS-APNO methods for neutral and protonated forms of the studied amino acids and were also given in Tables 1-4. There is no relationship found for E_{HOMO} and experimental I_{Tafel}(%) at gas and water phase for neutral molecules. But excellent correlations obtained for prototaned forms in gas and water phase (95% at gas phase and 97% at water phase). While the E_{HOMO} increases, experimental inhibition efficiency increases at MP2/6-311g(d,p) method in water phase for protonated forms. The HOMO energies decreased with protanation, meaning that the protonated forms make more ionic characterized bond with metal.

While the E_{HOMO}- I_{Tafel}(%) relation is better in protonated forms, E_{LUMO}- I_{Tafel}(%) relation is better in neutral forms. The best regressions were found to be 99.9%, 99.6% and 84.6% at B3LYP/6-311++G(2d,2p), CBS-APNO and MP2/6-311G(d,p) methods for E_{LUMO}- I_{Tafel}(%) relationship at gas phase for neutral molecules, respectively.

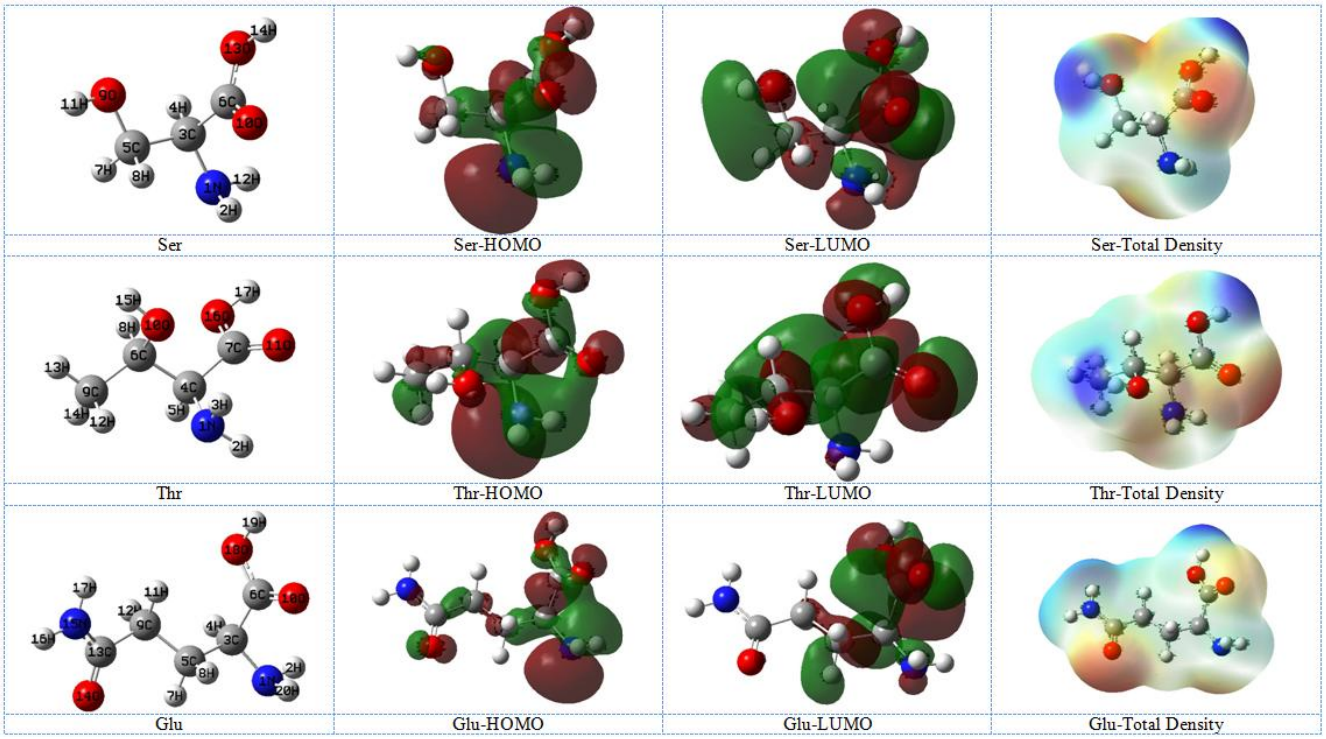

Figure 1. The optimized molecular structures, HOMO, LUMO and total density of the non-protonated inhibitor molecules using B3LYP/6-311G(d,p)

The HOMO-LUMO energy gap (ΔE) is effective on chemical reactivity. So there must be a relationship with corrosion inhibition mechanism. The higher correlation was found 98.2% at B3LYP/6-311g(d,p) method for neutral molecules at the gas phase. The correlations were changed between 78.1% -85.8% for protonated molecules at gas phase for all studied methods. The chemical potential (μ) and hardness (η) are defined as follows [21, 23]:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v \quad (1)$$

$$\eta_S = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v = \frac{1}{2}\left[\frac{\partial \mu}{\partial N}\right] \quad (2)$$

Following Koopmans' theorem, the chemical potential and hardness values can be approximated in terms of the energies of the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}):

$$\mu = \left(\frac{E_{LUMO} + E_{HOMO}}{2}\right) \quad (3)$$

$$\eta = \left(\frac{E_{LUMO} - E_{HOMO}}{2}\right) \quad (4)$$

The inverse of the hardness is expressed as the global softness (σ),

$$\sigma = \left(\frac{1}{\eta}\right) \quad (5)$$

When the hardness (η) values decrease, the inhibition values increases at B3LYP/6-311g(d,p) method with 98% regression values for neutral molecules at gas phase. This regression value decreased in water phase to 0%. The opposite trend was obtained for softness comparing with hardness, namely

inhibition efficiency increases with softness. The best regression value obtained (95%) at same method and same phase for neutral molecule. The highest correlations were obtained at MP2 method as 99.9% for chemical potential and electronegativity relations with experimental inhibition efficiency for protonated forms at water phase. For the dipole moment (DM), lower values of (DM) will favor accumulation of the inhibitor in the surface layer [24].

The dipole moment – *I*(%) relations were found to be higher than 86.4% for neutral molecules at gas and water phase at all methods. These regression values decrased at protanated molecules. The molecular volume is related with experimental inhibition efficiency. We observed good relationship with molecular volume and experimental inhibition efficiencies at all methods for neutral molecules. The lowest correlation is 83.7% at B3LYP/6-311g(d,p) method and the highest regression value is 99.9% at MP2/6-311g(d,p) method for gas phase neutral compounds. These correlations decreased with solvation at all methods. The best regression values were obtained at B3LYP/6-311++G (2d,2p) method in gas phase for protonated forms.

Total negative charge (TNC) of the molecules shared with metal ion in inhibition process. The calculation results were shown that inhibition increases with increasing TNC values at all methods at gas and water phase for neutral and protonated amino acids. Adding diffuse functions to calculation parameter were decreased the regression values. The corrected electronic energies (SEZPE) regressions are 99% at all methods for neutral and protonated forms at both phases.

3.2. Quantitative structure–activity relation (QSAR) study

Table 5. The correlations (Spearman) among eleven descriptor variables

	E_{HOMO}	E_{LUMO}	ΔE	DM	MV	TNC	η	σ	χ	μ	SEZPE
E_{HOMO}	1	.87	.37	.02	-.61	.20	.37	-.44	.95	-.95	.17
E_{LUMO}		1	.78	-.47	-.92	.66	.78	-.83	.98	-.98	.63
ΔE			1	-.93	-.96	.99	1*	-.99	.63	-.63	.98
DM				1	.78	-.97	-.92	.89	-.28	.28	-.98
MV					1	-.89	-.96	.98	-.82	.82	-.88
TNC						1	.98	-.97	.49	-.49	.99*
η							1	-.99	.63	-.63	.97
σ								1	-.69	.69	-.96
χ									1	-1*	.46
μ										1	-.46
SEZPE											1

The entries below the diagonal are the same as the entries above the diagonal
"*" denotes that the correlation between variables is significant at 0.05.

As stated before, the number of observations for each method is very few. Therefore, instead of using Pearson Correlation measure, Spearman Correlation measure is suitable. The correlations are computed and given for the method called B3LYP/6-311G(d,p) in Table 5. As it is observed from Table 5, the correlations among the descriptors show that Δ*E* and η have correlations with the value of

1. Similar observations can be made for this table and also the ones we do not provide here. We compute correlations in order to remove variables that show co-linearity. Thus, before running GFA, some descriptors are removed based on the correlation measure.

3.2.1. Genetic Function Approximation

Due to the non-linearity and co-linearity existed among descriptor variables, using linear regression or non-linear regression does not generate satisfactory results in the studies of QSAR. Recently, a new statistical method called GFA based on Genetic Algorithm is introduced in order to pick a model or models which are expected to produce better predictions when compared to just a single regression model. Genetic Algorithm is a search methodology that is a non-conventional optimization method used for either minimization or maximization. This method is inspired by genetics and evolution and uses the operations that are called such as selection, crossover and mutation. GFA which is a statistical tool constructing various types of models using strings, that is the power of terms and splines, based on the data aim at determining functional relationship that fits the available data using fitness function whose error is expected as small as possible. Those strings called populations are used by GFA in order to generate models.

When GFA is compared with other available models in the study of QSAR, it has some advantages that should be mentioned. Instead of being forced to use a single model in the prediction of inhibition efficiency, GFA is a method that generates a single model from the various types of models. Also, it does not face the overfitting problem. In this study, we found the model that is generated by GFA is as follows:

$$-4.984E_{HOMO} + 2.214E_{LUMO} + 1.717\sigma + 81.928MV + 7.432\Delta E$$

By using the model obtained by GFA, QSAR study is conducted between the inhibition efficiencies of the compounds and the model given above. Therefore, the method called B3LYP/6-311G (d,p) with R^2=0.96 is found.

4. CONCLUSIONS

In order to study the relationship between quantum chemical and corrosion inhibition for serine, therionine and glutamine were carried out to see if any clear relations exist between them. Quantum chemical descriptors such as E_{HOMO}, E_{LUMO}, the energy gap between E_{HOMO} and E_{LUMO}, dipole moments, molecular volume, sum of the total negative charge, global hardness, softness, chemical potential, electronegativity, sum of electronic and zero-point energies were calculated. The results show that inhibition increases with increasing total negative charge values of the molecules at all studied methods. It was also observed a good relationship with molecular volume and experimental inhibition efficiencies for neutral molecules. Correlation coefficients of the neutral compounds, calculated with B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p) and MP2/6-311G(d,p), were found as 0.837, 0.840 and 1.00, respectively, in gas phase. A new statistical method called Genetic Algorithm was introduced and R^2=0.96 with B3LYP/6-311G(d,p) was found as the best model among the other models generated by GFA.

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