International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.7, pp 1048-1058, 2017

Theoretical study for several synthesized compound as a corrosion inhibitors

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Abstract : Semi-empirical method (PM3) using Gaussian03and Gaussian view03and (MOPAC) computational packages was carried out to achievedQuantum chemistry calculations for geometrical complete optimization of number synthesized inhibitors.The calculated quantum parameters were:(E_{HOMO}) the energy of highest occupied molecular orbital,(E_{LUMO})the energy, oflowest,unoccupied,molecular orbital,, (ΔE) = (E_{LUMO}) – (E_{HOMO}) is Energy gap,(X) is ,the Electronegativity, (μ) is the dipole moment, (δ)=1/(γ) is Softness, (γ) is hardness, ,(π) = - X is chemical potential,,ΔN= No. of electron transferand(M_g) is molecularvolume.The research study the effect of synthesis organic inhibitors:[N – Phenyl-N\-(4-aminobenzene)thiourea], N – Phenyl-N\-(4-methyl benzene)thiourea, N-Phenyl-N\-(4 -amino-5-methyl benzene)thiourea, N-Phenyl-N\-(3-aceto benzene) thiourea, N-Phenyl-N\-(2,3-Dimethyl benzene)thiourea, N-Phenyl-N\-(4-bromo benzene)thiourea, N-Phenyl-N\-(4-Cloro benzene)thiourea, N,N\-Diphenylthiourea and thiourea as acorrosion inhibitors. The inhibition efficiency P% of these compounds wereexamined by Semi–empirical method and the experimental P% results were compared with variation of (ΔE), (E_{HOMO}) , (μ) , (E_{LUMO}), ΔN and the nature of the inhibitor. It is clear from the results that P% increased with the increase of inhibitor (I) ionization potential and (A) electron affinity,from Polarization measurement, the inhibition type by these inhibitors were like mixed type inhibitors because corrosion potential stays the same before and after adding these inhibitors. Theaction of studied organic compounds wasanalyzed through PM3 Quantum chemical methods, to compare the P% of compounds with experimental P%.There is excellentconsistency between theoretical and experimental data, where the correlation factor (R^2)reach to 0.9950 for relationbetween the highest occupied molecular orbital (E_{HOMO}), (μ) the dipole moment, (I) is inhibitor ionization potentialandexperimental P% for synthesize compound that used in the study.

Keywords : Gaussian program package,Corrosion inhibitors,Optimization,Inhibition efficiency, PM3.

Introduction

In particularcorrosion and corrosion inhibition of iron,steeland iron alloys[1], have got a great attention in various media [2-6] with various types of inhibitors and becomes of interest due to its excellent, properties and low cost its used as materials, in several industries [7], despite its, corrosion resistance,carbon steel used in engineering material,itis used in industries applications, production of petroleum and refining, the equipment construction and metal- processing [8]. The efficiency of corrosion inhibition is relatedwith, adsorption properties.,The studies of adsorption , report that organic inhibitors ,depends on stateand nature of surface[9],

the kind of corrosive medium, on the chemical structure of the inhibitor [10,11] and some properties with physic -chemical sortof molecule concerningwith functional group**,** the effects of donor atoms and the electronic density of; supposed adsorption is depend on d-orbital's of a surface atoms that possible interaction withπ-orbital's of the inhibitor, which do better and greateradsorptionmoleculesof inhibitoron the Carbon, Steel, leading to a corrosion protecting film formation [12,13,14**].**Quantum mechanical calculations have been used to investigate the experimental results and tostudy the mechanism of the reaction togate chemical parameters.This is benefitway to research themechanism of the reactionof inhibitors molecules onCarbon Steel surface[9]**.** The structural and electronic data of the inhibitorscan be obtained using theoretical calculations [9,15].In our research weintend to study theinhibition of organic corrosion on Carbon Steelwith (1M) H_2SO_4solutions by organic inhibiters as corrosion inhibitors using Theoretical study[16], to compare theexperimental results with the theoretical ones.The adsorption ofinhibitor on carbon Steel as surface ,in H_2SO_4 solution follows Langmuir isotherm for these compounds [17]. Quantum calculations ofchemical parameters for these compounds were calculated, so as to study the technical, of corrosioninhibition [18].In presentwork we study many organic compounds were applied asorganic corrosion inhibitors on Carbon steel as surface in H_2SO_4(1M) solution[19], then theoretical data (γ , ΔN, μ, δ, I,X, ΔE,H, A) were measured and companied with experimental data to explain each parameter effected on[20].The effect of inhibiting of these compounds, is explained,generally by formation of a chemicaland/or physicaladsorption on the Carbon, Steel surface [9,21]. The adsorption process depend on the structures of organic compounds, steric factor,aromaticity and the functional groups [9,22]. The adsorption of surfactant changes the corrosion resisting property of a metal. For that reason, the relation wasstudying between,inhibition corrosion and adsorptionare important[23-28].High inhibition efficiency of Surfactants inhibitors corrosion have advantages such as, low price and easy production[29].

1. Chemistry of corrosion

Corrosion process is transformation metals from the state which is stable to energetic state [30,31].The obtained metals from their compounds naturally by the lossenergy in big amounts. These metals can regarded as stablemetastate and it will to miss energy by returning to formed moreor less than original states[32]. All reactionsnatureof corrosion areelectrochemical on surface at anodic sites inthe iron,for instancegoes ferrous ions (Fe^{2+})to solution**,** this is in anodic reaction.Iron atoms(Fe) are oxidation to ferrous ions (Fe^{2+}) and release electrons. This degradationwill go on if the liberated electrons can prosper to a site on surface metal, where cathodicreaction allowable. Theelectrons respond atcathodeby lectrolyte and are themselves taken away toward metal. Depending on Faraday's Lawsthe rates incathodeand anodeequivalent reactions necessarily,resolved by the go offoverallelectrons from anodesto cathodes called"corrosion current",I_{corr}go offelectrolyteaccording to the conductivity and ionic conductance of electrolyte.Corrosion operate way by reactions if electrochemical in corrosion iron(Fe) are[31,33]:

The reaction inanode: $Fe \rightarrow Fe^{2+} + 2e$---------- 1

The reaction incathode[31]:$2H^+ + 2e \rightarrow H_2$----------2

2. Corrosion inhibitors

Great efforts had beenemployed in the past years to discover excellent corrosion inhibitors of organic sources[34]**.** In alkaloids,nitrogen-base materials,acidic medium, and their derivatives[31], Compounds which contain sulphurare used as inhibitors[35].TheInhibitors prevent or decrease according toreactionof metal with the midst. In surface of metalthe adsorption of ions /molecules the corrosion rate reduce,growingor lesseningtheanodic reaction and /or cathodeinterplay**,**the emanation rate of reactors will decreasedof metal surface, and electrical resistance will decreasedin the surface metal.When choosing an inhibitor many factors are needed to be considered including the amount and the cost, safety to the species of environment**.**The suitable corrosion inhibitors must follow some aspects including environmental andstructural considerations**.**Structural kind which belong to the organic inhibitors are pertain to the construction,the characteristicof compound like, the functional collection, electron concentration at the giver atom, p-orbitalcharacter**,** and molecule electronic structure.The element related for building up which associate to the transaction of inhibitorsare[31,36]:

The chain length,size ofmolecule [31], Bonding, the conjugate aromaticsystem, the bond strength to the substrate, the ability of cross-linking, and the environmentSolubility [37].

3. Quantum Chemical Calculations

Calculations were done by using Semi–empirical methods(PM3) [38] , by using a Gaussian03, Gaussian view03 set programs package and (MOPAC) computational packages[39],to investigate the influence energy of molecular orbital HOMO ,LUMO and calculated molecular parameters include, electro negativity,electron affinity,the hardness and softness of global, the potential of ionization, etc.[9],these following parameters are in Koopmans' theorem defined[40,41]. Electronic negativity(χ) is the power of measured of a group or an electron of atoms pulltowards intoelectrons dependent to Koopmans's theorem, it maybedefined by the subsequent equation[9,42]:

$\chi \cong -½ (E_{HOMO} + E_{LUMO})$---------- 3

Where the energies of (HOMO) defined as E_{HOMO},and the energy of (LUMO)defined as E_{LUMO}.TheGlobal hardness is (η),resistance measures of atom to a charge transportationand it is determinedby thefollowing equation[9,43]:

$\eta \cong -½ (E_{HOMO} - E_{LUMO})$---------- 4

(σ) is the Global softness which describes the capacity of group of atoms or an atom which received electrons and it is determined by the followingequation[43]:

$\sigma = 1/\eta \cong -2/(E_{HOMO} - E_{LUMO})$----------5

The global hardness values is (η), Global electrophilicity index is defined byusing the and chemical hardness(ω), and electro negativityparameters through the followingequation[43];

$\omega = \chi^2/2\eta$---------- 6

The increased value of (ω)is a good as electrophile while it describes good nucleophile as small value of elecrophilicity**.** Electronic affinity (E_A) is related to E_{LUMO} through the following equation[9]:

$A \cong - E_{LUMO}$----------7

(I)is the ionization potential related to the E_{HOMO} through the equation:

$I \cong - E_{HOMO}$---------- 8

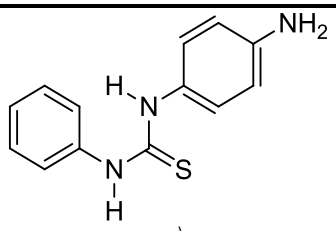
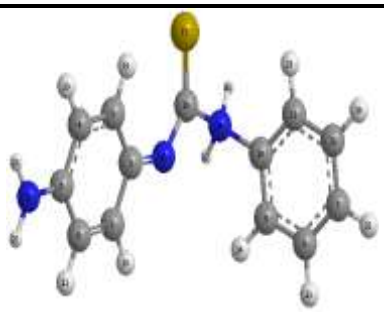
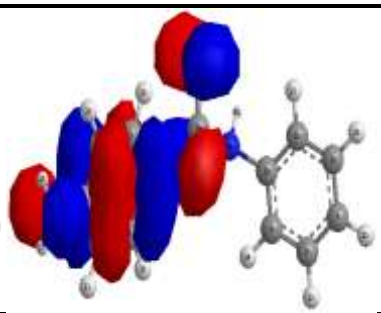
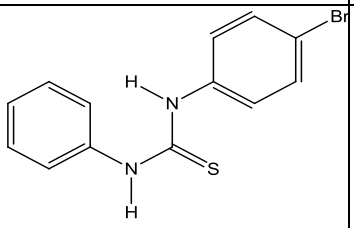
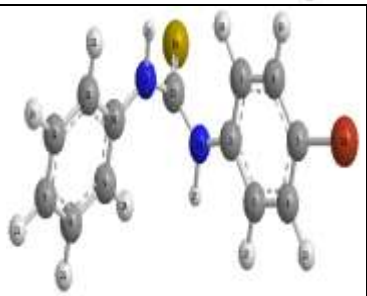
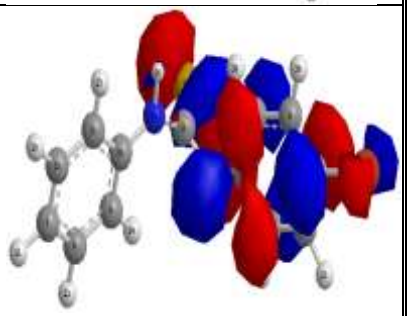
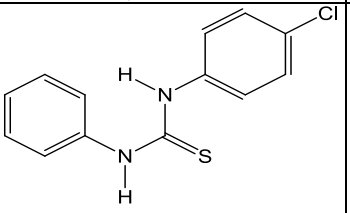
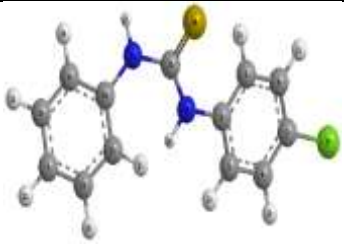
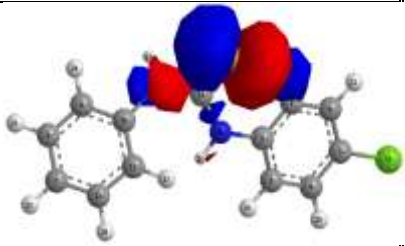
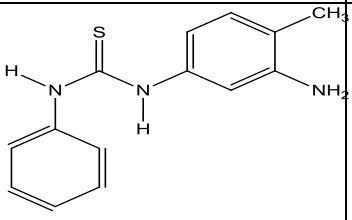
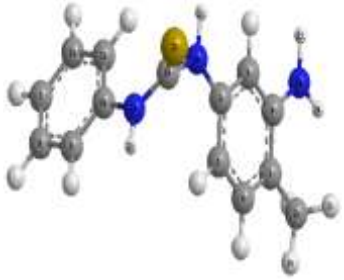
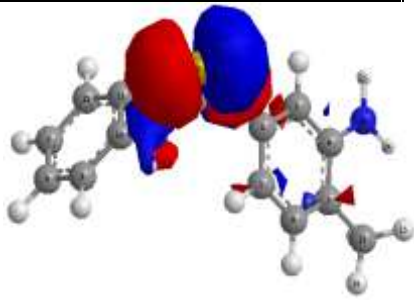
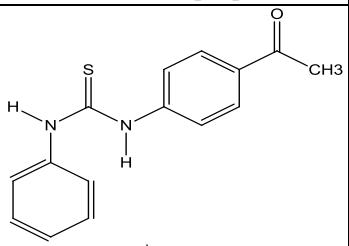
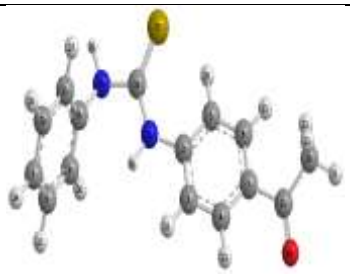
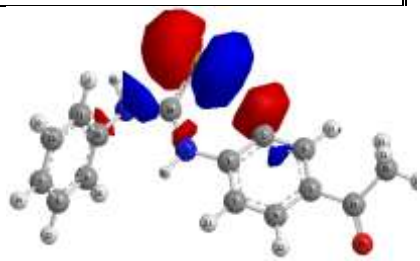
The number of change the electrons transferred is determined by the subsequent equation[9]:

$\Delta N = \chi_{Fe} - \chi_{inh} / 2(\eta_{Fe} + \eta_{inh})$ ---------9

The χ_{Fe},χ_{inh}determined by exhibit the unequivocalelectro negativityfrom iron, and the molecule of inhibitor severally; η_{Fe} is the unbounded hardness of iron,and η_{inh} is the unbounded hardness of inhibitor**.** The values of $\chi_{Fe}$is 7eVmol^{-1}, and $\eta_{Fe}$are taken as 0 eVmol^{-1} respectively [9,44].

4. Result and discussions

The quantum mechanical calculations have been performed by Gaussian03 program[45].The study performed on to establish the nature of the stationary surface was optimized geometries [9],To study the relationship betweencorrosion efficiency inhibition and electronic properties of the molecules,This method has been implemented [47].The chemical optimized structuresof studied compounds are noticeable in Fig 1. [46].The interaction between HOMO and LUMObecause ofelectrontransition oftheof reacting atoms.The tendency ofelectrondonation by a molecule measures the energyE_{HOMO}. A higher energy values (E_{HOMO}) indicate a better tendency to the donation of the electron, of the (E_{HOMO})the adsorption increasing valueon carbon steel inhibitor is better inhibition efficiency.The molecule ability indicates by $E_{LUMO}$to accept electrons**,**with HOMO increasing and decreasing of LUMO. Ability ofbinding of inhibitor to metal surface increases [47].

1	 N-Phenyl-N\-(4-amino benzene) thiourea[48].		
2	 N-Phenyl-N\-(4-bromo benzene) thiourea[48].		
3	 N-Phenyl-N\-(4-Cloro benzene) thiourea[48].		
4	 N-Phenyl-N\-(4-amino-5-methyl benzene) thiourea[48]		
5	 N-Phenyl-N\-(3-aceto benzene) thiourea[49].		

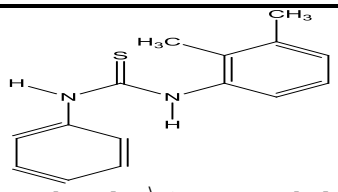
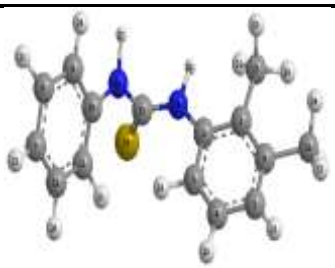
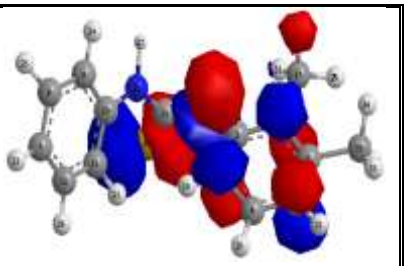
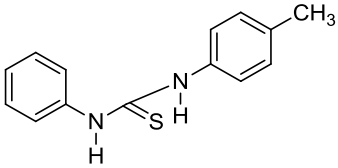
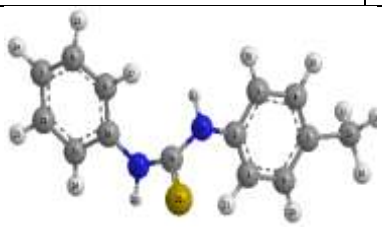
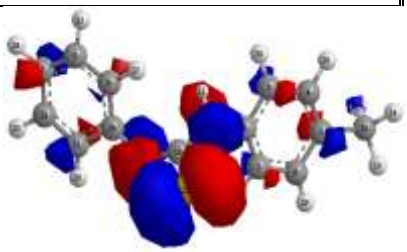
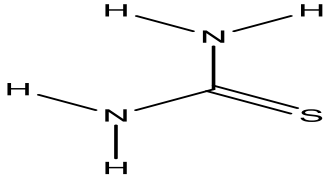
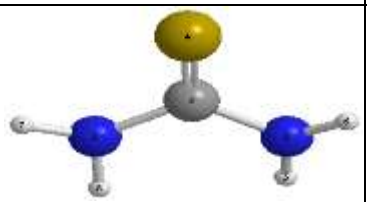
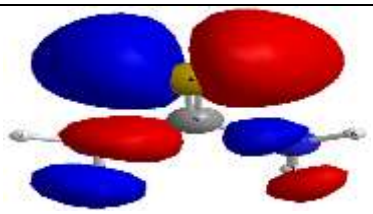
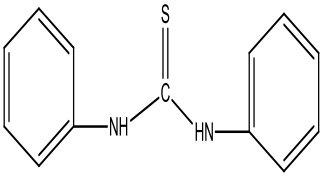
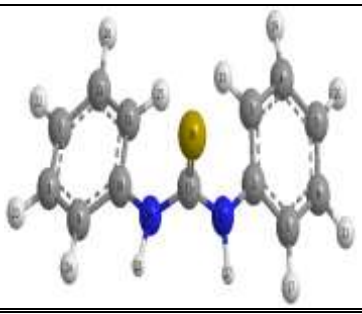
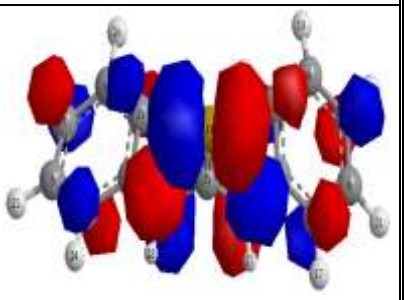
6	 N-Phenyl-N\-(2,3-Dimethyl benzene) thiourea[49]		
7	 N-Phenyl-N\-(4-methyl benzene) thiourea		
8	 Thiourea		
9	 Diphenylthiourea		

Figure1:Equilibrium geometry oforganic inhibiters and the structures of obtained molecular, HOMOand LUMO of organic inhibitors[50].

Fig.1 Shows the molecular modeling as quantumchemical method technique, the binding properties of studied molecules was calculated .There is two advantages with using theoretical study; firstly, the variation fragments and substituent's can be characterized directly, secondly, the mechanism of action can be known from chemical reactivity for studied compounds[52]. The main quantum parameterswhich can be extracted were[51,52]:

4.1. Atomic Charges

Obviously the molecule has an electric charges take place in electrostatic interactions. The charges or electron densities responsible for physico-chemical properties and chemical reactions of compounds [51].Atomic charges have been employed widely to measures of the kind of intermolecular interactions as chemical reactivity. The computation of charge classification in molecule can be studied by Mullikan analysis to understanding reactivity[51,53], the structure of molecule [54], and to described the polarity of the molecules[51].

4.2. Molecular orbital

The general parametersin quantum computation (E_{HOMO}) and (E_{LUMO}). The HOMO is(highest Molecular orbitalenergy) because it is containing electrons called an electron donor orbital [55]. The(lowest orbital energy) orbital LUMO is the orbital has chamber to approve electrons could act asan electron acceptor [51].

The ionization potential belong to the E_{HOMO}[55], electron affinity pertain to the E_{LUMO}, the difference between the energylevels called theenergy gap, it is important in stability [56]. A large value in energy gap for the molecules leads to high stability in chemical reactions for molecules [57,58].

4.3. Dipole moment (μ)

A quantity described the di-pole moment and the polarity of polar contribute bond of the molecule [59].

4.4. Energy

The overall energyof a systematic is includingpotential, and internal kinetic energy[9]. The settled state energy of molecule is smallest value of the overall energy[60,61], the overall energy of scheme effects from electrons in staticpotential[62].

Table 1:Quantum chemical descriptors for inhibitor calculated using Semi–empirical method (PM3) by Gaussian03program package.

	corrosion inhibitors	%P	H_f(kcal /mol	μ(D)	Etotal(kcal/mol	HOMO(eV)	LUMO(eV)	ΔE(eV)
1	N-Phenyl-N\-(4-amino benzene) thiourea	59.440	89.999	3.838	-19.331	-4.775	-1.032	3.743
2	N-Phenyl-N\-(4-bromo benzene) thiourea	74.500	81.001	3.200	-16.051	-6.921	-1.321	5.600
3	N-Phenyl-N\-(4-Cloro benzene) thiourea	82.940	76.012	4.373	-15.432	-9.035	-2.155	6.880
4	N-Phenyl-N\-(4-amino-5-methyl benzene) thiourea	91.900	69.001	5.400	-18.439	-9.389	-0.973	8.416
5	N-Phenyl-N\-(3-aceto benzene) thiourea	93.600	65.001	5.630	-12.021	-8.328	-0.720	7.608
6	N-Phenyl-N\-(2,3-Dimethyl benzene) thiourea	93.900	67.101	5.1859	-14.560	-9.322	-1.096	8.226
7	N-Phenyl-N\-(4-methyl benzene) thiourea	94.000	64.998	3.275	-18.648	-8.276	0.164	8.440
8	Thiourea	94*	25.989	5.777	-21.550	-8.968	6.940	15.908
9	Diphenylthiourea	74*	90.0565	3.464	-6.967	-7.502	0.258	7.760

*calculated values from the linear relation [%P ,E_{HOMO}, ΔN, I,ΔE, μ].

Table 2:The calculated quantum chemical parameters using Semi–empirical method (PM3) by Gaussian03 program package.

	corrosion inhibitors	I= - E_{HOMO}(eV)	A= - E_{LUMO} (eV)	X = I+A/2 (eV)[9]	Ɣ=I – A/2[9] (eV)	$\Delta N=\chi_{Fe}-\chi_{inh}/2(\eta_{Fe}+\eta_{inh})$ [9](electron)
1	N-Phenyl-N\-(4-amino benzene) thiourea	4.775	1.032	2.9035	1.871	1.094
2	N-Phenyl-N\-(4-bromo benzene) thiourea	6.921	1.329	4.125	2.796	0.514
3	N-Phenyl-N\-(4-Cloro benzene) thiourea	9.035	2.155	5.595	3.440	0.204
4	N-Phenyl-N\-(4-amino-5-methyl benzene) thiourea	9.389	0.973	5.181	4.208	0.216
5	N-Phenyl-N\-(3-aceto benzene) thiourea	8.328	0.720	4.524	3.804	0.325
6	N-Phenyl-N\-(2,3-Dimethyl benzene) thiourea	**9.322**	**1.096**	**5.209**	**4.113**	**0.217**
7	N-Phenyl-N\-(4-methyl benzene) thiourea	**8.276**	-0.164	4.056	4.220	**0.348**
8	Thiourea	**8.968**	**-6.940**	1.014	7.954	0.376
9	Diphenylthiourea	**7.502**	**-0.258**	3.622	3.880	0.435

Table 3: The calculated the (inhibitory efficiencies) %P of (Thiourea)and (DiphenylThiourea) by liner equation.

Calculated data	%P (Thiourea)	%P (DiphenylThiourea)
μ	96.731	51.066
ΔE	155.150	91.360
E_{HOMO}	82.425	79.597
H_f	37.000	58.940
I	99.762	85.645
ΔN	93.211	79.000
Mean	94.027	74.260

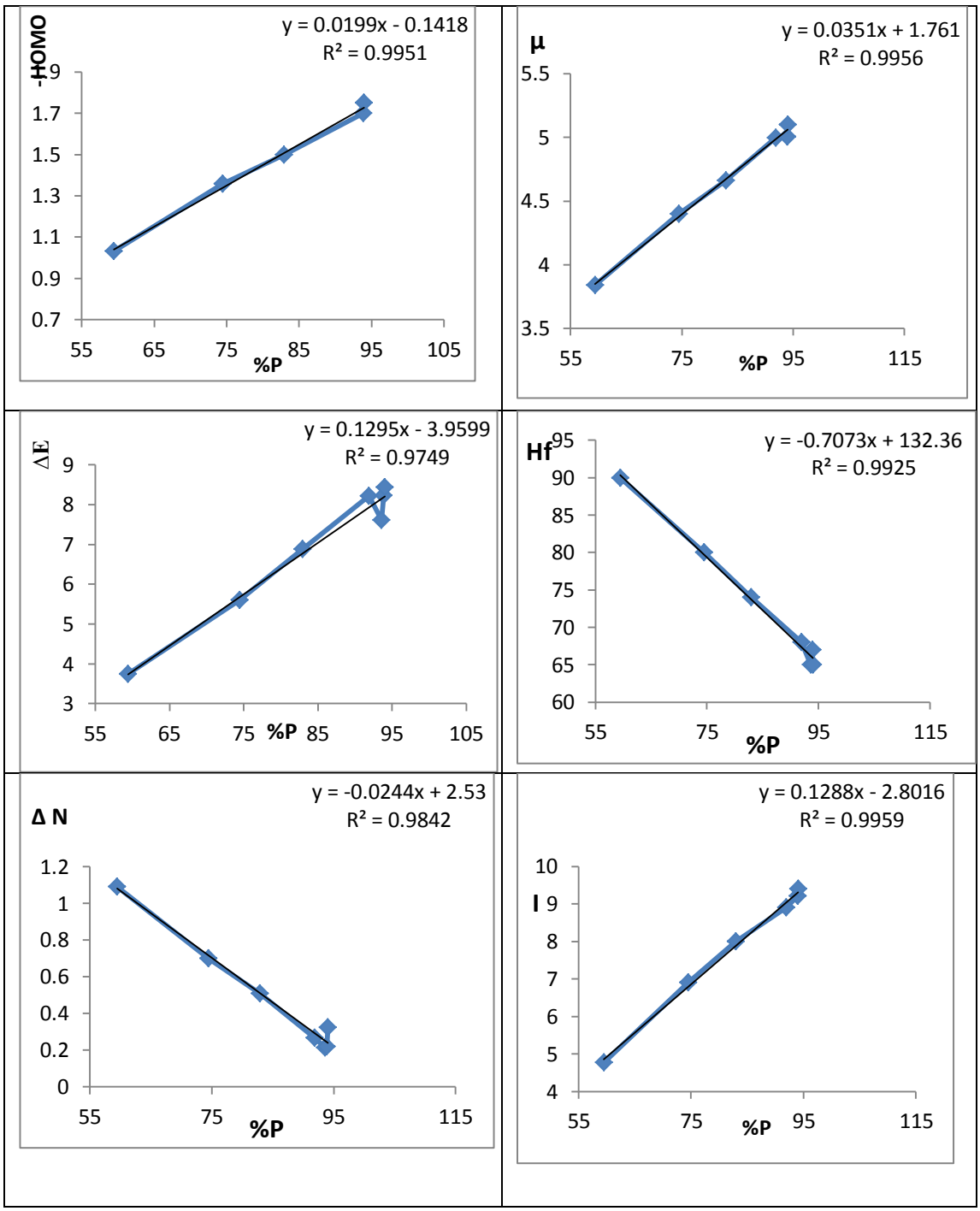


Figure 2:Correlation between the E_{HOMO} , μ,H_f, ΔE,I,ΔN and the inhibitory efficiencies ofcorrosion inhibiters.

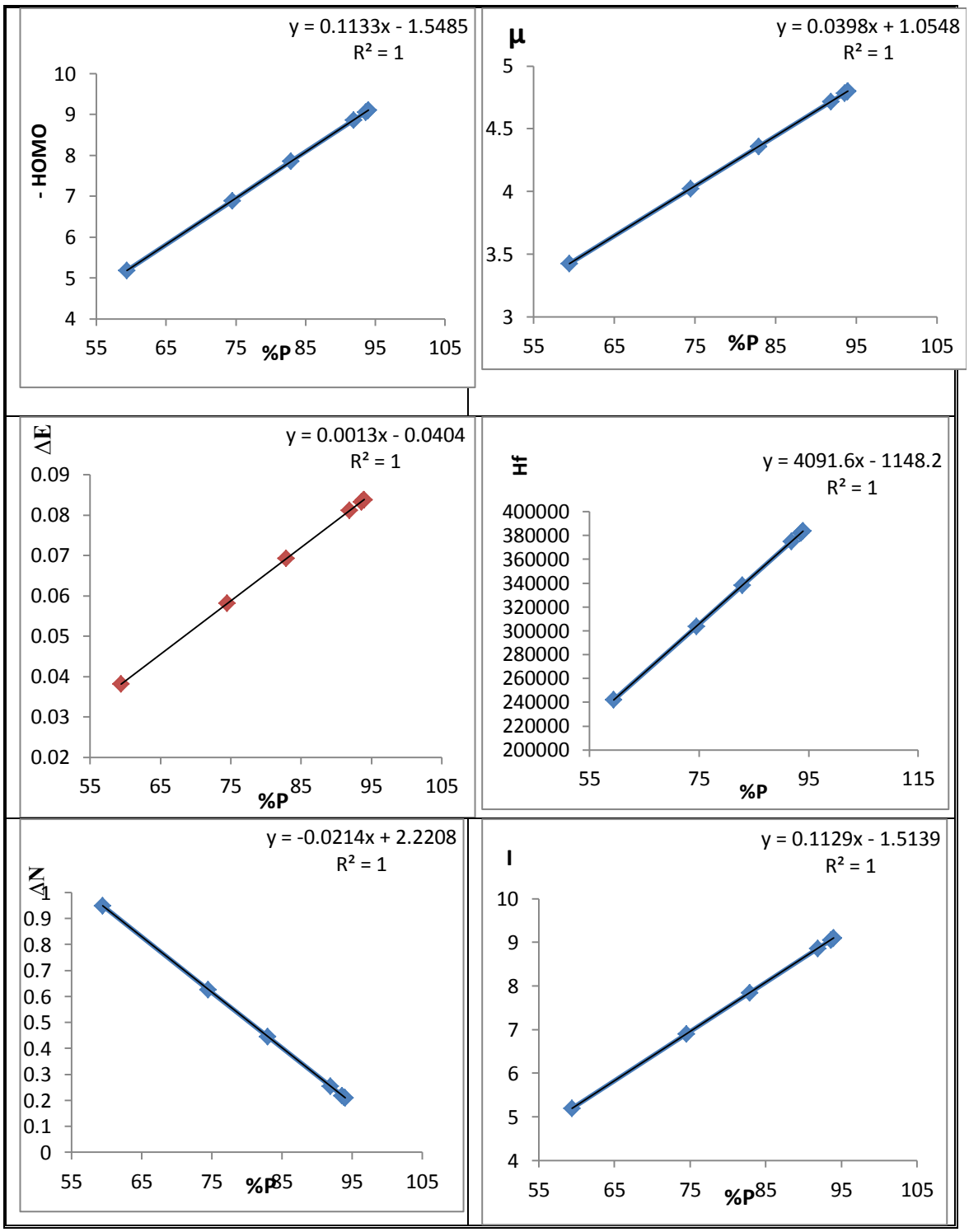


Figure 3:Correlation between the E_{HOMO} ,μ,H_f, ΔE,I,ΔN (calculated with thestatical method)and the inhibitory efficiencies ofcorrosion inhibiters.

Using Gaussian 03 the molecular were plotted, the quantum chemical parameters were performed by Semi–empirical method (PM3)[63] using Gaussian03 and (MOPAC) computational packages[64]. Thequantum chemical parameters were studied[65]: (E_{HOMO}), (E_{LUMO}) and (μ). (X), (γ), (δ) =1/(γ) , (π)= - X, and ΔN[66].

The correlation between the efficiencies inhibition and quantum parameters of some organic inhibiters was studiedbySemi empirical method (PM3)[63] using a Gaussian03 program package and (MOPAC) computational packages.The inhibition efficiencies of the inhibitor are related to (μ), E_{HOMO} and E_{LUMO}, it is

increased with increase in E_{HOMO} values[63].The results show that HOMO, LUMO and partial charges has an influence on the properties of the inhibitors [67]. The results show that species have less charge density which have less electron donor were protonated,Which interact with metal surface by chemisorptions mechanism [68]. Table 2. Shows ΔN values for inhibition efficiency resulting from electron donation[68].The experimental efficiencies inhibition correlate strongly with ΔN values[68,69].

5. Conclusions

Quantum calculation methods very useful fordetermination of the molecular constitute onlike reactivity and electronic construction[70]. ΔN values are the number of electrons departing the givertoreceiver molecule[71]. The most significantparameter is dipole moment that used to describe the polarity of a polar contribute bond [72].The consequent of charge on atoms is defined as the farness between two atomsbonde. Theoretical studycalculation give us the relation that the dipole moment is well linked with inhibition corrosion efficiency Indeed,Theincreasing of dipole momentwith the inhibition efficiency increases[73]. From the obtained results and by using the Semi empirical method (PM3) calculations, the inhibition efficiency of some organic molecules [18].that leads to the following conclusions. The inhibition efficiency of some organic inhibiters as acorrosion inhibiterscorrelated to molecular building,the dipole moments exhibitexcellent relation with inhibition corrosion efficiency, The correlations that we obtained and theoretical data agree well with the reported experimental data [73].

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