

# Inhibitory Effect of Some Methylxanthines on Copper Corrosion in 1M HNO<sub>3</sub>: Experimental, DFT and QSPR Studies

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## ABSTRACT

Inhibition corrosion of metals by using organic compounds has become an unavoidable means. So, in this work, the effect of methylxanthines on copper corrosion inhibition in 1M HNO<sub>3</sub> was investigated by mass loss measurements and by two theoretical approaches: Density Functional Theory (DFT) and Quantitative Structure Property Relationship (QSPR.) Quantum chemical calculations based on DFT at the B3LYP/6-31G(d) level permit to establish a correlation between the quantum chemical parameters and the experimental inhibition efficiency (IE %). It was found that inhibition efficiencies increase with increasing temperature and immersion time. In addition, the QSPR approach was used to find the best set of parameters for each molecule. This set of parameters make it possible to characterize the inhibition performance of the tested molecules solution significantly. The theoretical calculations are consistent with the experimental results.

Keywords: Methylxanthines, Mass loss measurements, DFT, QSPR, Copper corrosion

## INTRODUCTION

In recent years, environmental protection has become a battle for every country. One of the solutions of this protection is the use of biodegradable, non-toxic and eco-compatible compounds. The fight against corrosion of metals has been oriented for some time towards the use of organic and inorganic inhibitors. The choice of these inhibitors often does not comply with the rules set by the new directives concerning environmental protection. Indeed, the use of inorganic compounds, such as chromate, dichromate, nitrite, etc. has recently been questioned because of the many negative effects they have caused in the environment [1-4]. Thus, the development of new corrosion inhibitors from natural sources and of a non-toxic type has been considered more important and more desirable [5]. This is why the search for non-toxic organic molecules for the inhibition of metal corrosion has led several researchers to focus on pharmaceutical molecules. Thus, several classes of molecules including antibiotics [6-8], antifungals [9-11], analgesics [12], vitamins [13, 14] have been used as corrosion inhibitors for metals such as steel, copper and aluminium. The inhibition efficiency of organic molecules is generally attributed to their interactions with the metal through the phenomenon of adsorption [15, 16]. The adsorption of an inhibitor on a metal surface depends on the nature of the interface, the type of interactions between the molecule and the metal, the number and type of adsorption sites and the charge distribution within the molecule [17-18]. It is generally

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accepted that the chemical adsorption process involves electron transfer or sharing between the inhibitor molecules and the unsaturated "d" orbitals of the metal surface, thereby forming covalent or dative bonds, respectively [19-21]. The electron transfer takes place with the orbitals of organic molecules having weakly bonded electrons and generally containing heteroatoms (S, P, O, N). Interactions between the molecules and the metal can also take place through the multiple (double or triple) bonds contained in these molecules. The inhibition of corrosion of copper in acidic environments by organic compounds has been the subject of considerable research as copper is used in many fields such as telecommunications, transport, architecture, conventional energy, sanitary, cooling, electronics, electricity and renewable energy [22-26].

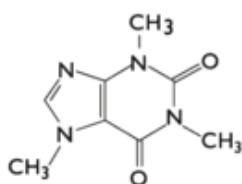
Currently, computer software has paved the way for the use of quantum chemical methods in the search for corrosion inhibitors [27-33]. In addition, the results of quantum chemical calculations could be obtained without laboratory measurements, thus saving time and equipment, alleviating safety and disposal concerns. These methods, based on the Density Functional Theory (DFT), permit to establish the correlation between the experimental inhibition efficiency and the descriptive parameters of the molecules (highest occupied molecular orbital energy ( $E_{\text{HOMO}}$ ), lowest unoccupied molecular orbital energy ( $E_{\text{LUMO}}$ ), energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness ( $S$ ), electrophilicity index ( $\omega$ )) or to establish a mathematical relationship between these different entities. QSPR approach allows to predict the effectiveness of the inhibitor because it can be used to find the optimal group of parameters that could predict the structure and the aptitude of a molecule to be an inhibitor [34].

The aim of this work is to study the inhibition properties of some methylxanthines such as caffeine, theobromine and theophylline for the copper corrosion in nitric acid solution and to establish a mathematical relationship between the experimental and calculated inhibition efficiency of each compound studied.

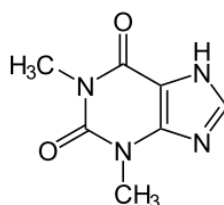
## EXPERIMENT

### Chemicals and instrumentation

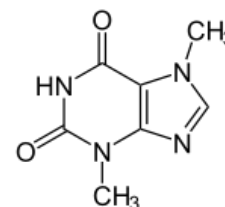
In this work we use three molecules which are caffeine, theophylline and theobromine. Their structures are given in Figure 1. These organic compounds have been synthesized in SIGMA-ALDRICH Laboratory.



1, 3, 7-triméthylxanthine  
or Caffeine



1, 3-diméthylxanthine  
or Theophylline



3, 7-diméthylxanthine  
or Theobromine

**Figure 1.** Chemical structure of the investigated inhibitors

Analytical grade 65% nitric acid solution from Merck was used to prepare the corrosive aqueous solution. Acetone solution from EUCLID was used to clean the copper samples. An analytical balance (CONTECH) (precision:  $\pm 0,1$  mg) was used to weigh the copper samples.

## Mass loss measurements

This method consists of measuring the mass loss undergone by a copper sample in form of rod measuring 10 mm in length and 2,2 mm of diameter (95% purity) immersed in the corrosive medium (50mL of 1M HNO<sub>3</sub>) with or without the tested compounds for 1h, 1h30 and 2h. The samples were polished successively with fine grade emery papers, with grains ranging from 150 to 600, cleaned with acetone, washed with double distilled water and dried in moisture free desiccator. The samples were weighed before and after each test. Tests were carried out at temperatures ranging from 298 K to 328 K. The temperature was controlled by a thermostat water bath SELECTA (FRIGITHERM) and a proofer (ASTEL) for drying copper samples. The corrosion rate (W) was calculated according to the equation below:

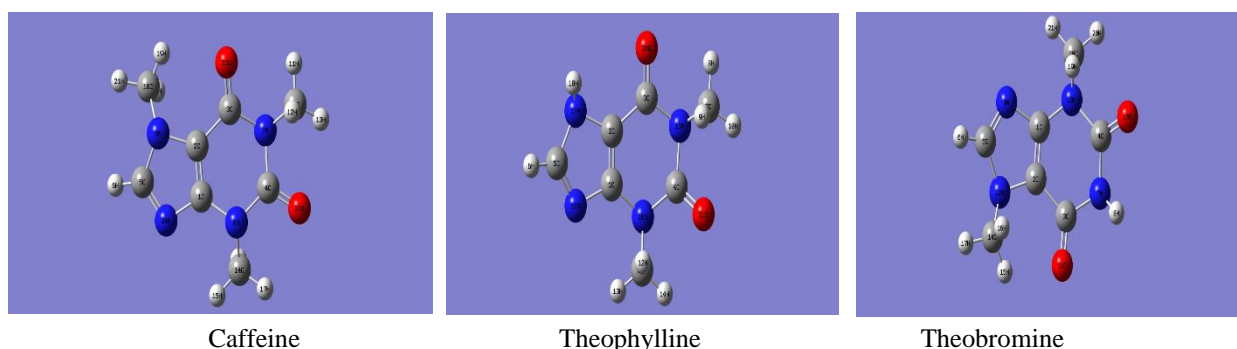
$$W = \frac{\Delta m}{S_{e.t}} = \frac{m_1 - m_2}{S_{e.t}} \quad (1)$$

$$IE(\%) = \frac{W_0 - W}{W_0} * 100 = \theta * 100 \quad (2)$$

$\Delta m$  : is the mass loss (g) ;  $m_1$  and  $m_2$  are respectively, the weight (g) before and after immersion in the solution test;  $t$  : the immersion time (h) ;  $S_e$  : the total surface of sample (cm<sup>2</sup>) ;  $w_0$  and  $w$  ; are respectively the corrosion rates of copper in the absence and presence of each molecule

## Quantum chemical and QSPR approach

The quantum chemical method used in this work has become a very powerful tool for studying the corrosion inhibition of metals in aggressive solutions. Indeed, the calculations from this method allow to establish a correlation between inhibition efficiency and the quantum chemical parameters of molecules that can be used for the pre-selection of new inhibitor which are, at the moment being, essentially derived from empirical knowledge. All calculations were performed using DFT (Density Functional Theory) method which differs from ab initio methods based on the Hartree-Fock equations by the notion of electronic density  $\rho(r)$  [35]. The full geometry optimization of the molecules (figure 2) was carried out at B3LYP/6-31 G(d) level of theory, using Gaussian 03 W [36]



**Figure 2.** Optimized structure of studied molecules obtained by B3LYP/6-31G(d)

DFT This theory includes in its formalism most of the electronic correlation compared to other methods.

In this work QSPR approach is based on the quantum chemical parameters determined in the DFT method. This model has been used by some authors to correlate inhibition efficiency with molecular descriptors, with satisfactory results [37-39]. This prediction is based on the

assumption that there is a linear relationship between a dependent variable  $y$  (property) and a series of  $n$  independent variables (descriptors). The objective is to obtain an equation of the form:

$$y = a_0 + a_1x_1 + a_2x_2 + \dots + a_ix_i + \dots + a_nx_n \quad (1)$$

$x_1$  to  $x_n$  represent the specific descriptor, while  $a_1$  to  $a_n$  the coefficient of those descriptors;  $a_0$  is the intercept of this equation.

The validation of QSPR model is done with the statistical indicators in order to unambiguously find the best set of parameters. These indicators are determined from the equations expressed below.

The Sum of Square Errors (SSE) :

$$SSE = \sum_{i=1}^N (IE_{\text{exp}} - IE_{\text{calc}})^2 \quad (2)$$

The Root Mean Square Error (RMSE) :

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (IE_{\text{exp}} - IE_{\text{calc}})^2}{N}} \quad (3)$$

The Mean Percent Deviation (MPD):

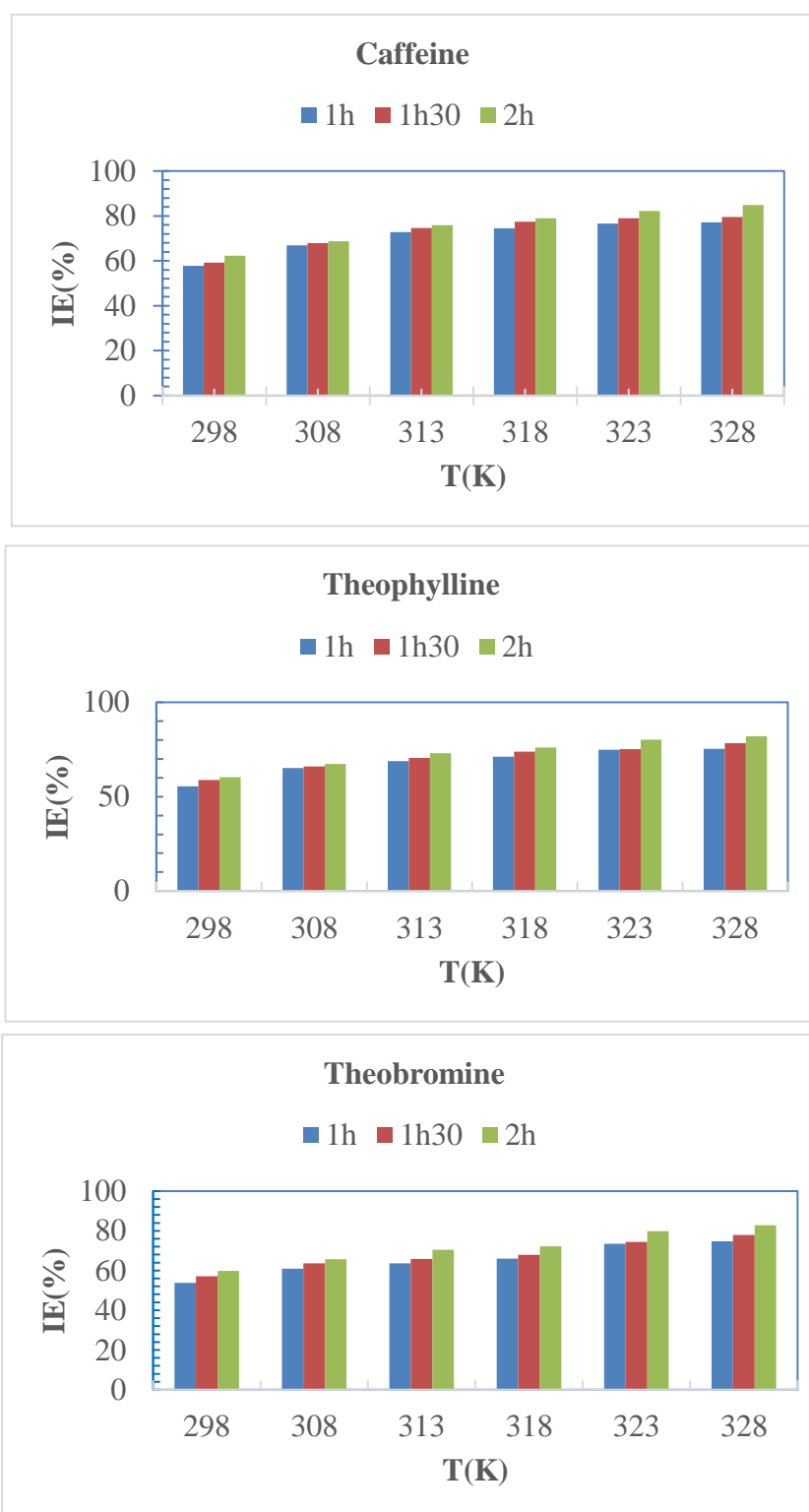
$$MPD = \frac{1}{N} \sum_{i=1}^N \left| \frac{(IE_{\text{exp}} - IE_{\text{calc}})}{IE_{\text{exp}}} \right| \quad (4)$$

After validation, the findings can be used to predict the activity of untested compounds

## RESULT AND DISCUSSION

### Effect of temperature and immersion time

The following figures show the evolution of inhibition efficiency and immersion time at molecules tested concentration of 5mM.



**Figure 3.** Variation of inhibition efficiency with temperature and immersion time for each inhibitor

The analysis of the different figures indicates that the inhibition efficiency of methylxanthines increases with the immersion time for the different temperatures chosen. The corrosion rate is therefore attenuated by the presence of caffeine, theophylline and theobromine in the nitric acid solution, which means that these molecules bind on the copper surface, creating a protective barrier that will isolate the metal from the aggressive environment. Indeed, the increase in temperature promotes an exchange of electrons between the inhibitors and the copper surface, which will participate in the formation of covalent bonds (protective barrier). These bonds are the basis for the reduction of the corrosion process. This means that these compounds can be used to protect metal installations over a long period of time. This type of inhibitors, whose effectiveness depends on temperature and immersion time, is recommended for industrial companies.

### 3.2 Relationships between experimental inhibition efficiency and quantum chemical parameters

The values of quantum chemical parameters derived from DFT method and the inhibition efficiencies determined by mass loss measurements at 328 K with the 5mM concentration of each molecule are listed in Table 1.

**Table 1.** Quantum chemical parameters and experimental inhibition efficiencies

	Caffeine	Theophylline	theobromine
Inhibition efficiency IE (%)	77,21	75,32	74,68
$E_{LUMO}$ (eV)	-1.251	-0.920	-0.897
$E_{HOMO}$ (eV)	-6.304	-6.071	-6.042
Energy gap $\Delta E$ (eV)	5.053	5.151	5.145
Dipole moment $\mu$ (D)	4.071	3.544	4.339
Ionization energy I (eV)	6.304	6.071	6.042
Electron affinity A (eV)	1.251	0.920	0.897
Electronegativity $\chi$ (eV)	3.777	3.495	3.4669
Hardness $\eta$ (eV)	2.526	2.575	2.572
Softness $\sigma$ (eV) <sup>-1</sup>	0.396	0.388	0.389
Fraction of electron transferred $\Delta N$	0.238	0.292	0.294
Electrophilicity index $\omega$	2.823	2.371	2.339

According to Koopmans' study [40], Electron affinity (A) and Ionization potential (I) are related respectively to  $E_{LUMO}$  and  $E_{HOMO}$  through the equation:

$$A = -E_{LUMO} \quad (5)$$

$$I = -E_{HOMO} \quad (6)$$

$\chi$ ,  $\eta$  and  $S$  can be expressed in function of I and A or  $E_{LUMO}$  and  $E_{HOMO}$  as [39]:

$$\chi = \frac{I+A}{2} = -\frac{E_{LUMO} + E_{HOMO}}{2} \quad (7)$$

$$\eta = \frac{I-A}{2} = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (8)$$

$$\sigma = \frac{1}{\eta} = \frac{2}{I-A} \quad (9)$$

$E_{LUMO}$  is a parameter which indicates the ability of a molecule to accept electrons [41]. So, the lower the value of  $E_{LUMO}$  in our case, the more probable the molecules would accept electrons.  $E_{LUMO}$  values are following order: Caffeine < Theophylline < theobromine. This result shows that caffeine would accept more electrons from copper than other molecules, thus it could have best performance as corrosion inhibitor. This is in good agreement with the experimental data where caffeine is more efficient than theophylline and theobromine.

$E_{HOMO}$  is a chemical indicator which often associated with the electron donating ability of a molecule, and a higher  $E_{HOMO}$  value indicates higher tendency of the molecule to donate electron(s) to an electron deficient species [42]. In our study  $E_{HOMO}$  values of the molecules are high, and it is observed that these value increases in the following order: theobromine > theophylline > caffeine, which does not correlate with experimentally determined inhibition efficiency.

Energy gap ( $\Delta E = E_{LUMO} - E_{HOMO}$ ) is an important reactivity parameter for organic molecules [43]. Indeed, molecules with a high value of  $\Delta E$  have a low reactivity towards other chemical species, while molecules with low values of  $\Delta E$  have a high reactivity. The data reported in Table 1 show that caffeine with the lowest value of  $\Delta E$  would therefore be more reactive than the other two compounds. This means that caffeine adsorbs more easily to the surface of copper, resulting in strong inhibition, hence its high inhibition efficiency. This result is consistent with experimental observation, showing that caffeine is the most effective corrosion inhibitor.

The dipole moment ( $\mu$ ) is another parameter of the electronic distribution in a molecule and is the measure of polarity of a polar covalent bond. According to some authors [44, 45] the dipole moment increases with increase in the inhibition efficiencies of the inhibitors, other authors [46, 47] have shown that dipole moment decreases with increase in the inhibition efficiencies of the inhibitors. So in general, there is no significant relationship between the dipole moment values and inhibition efficiencies.

The ionization potential ( $I$ ) and the electronic affinity ( $A$ ) are also reactivity parameters. The high value of Electron affinity ( $A$ ) when compared to values in the literature [48, 49], indicate the capacity of the molecules to accept electrons. The electron-accepting behavior of these molecules shows their good inhibition performance.

Electronegativity ( $\chi$ ) is a chemical parameter that describes the ability of a molecule to attract electron towards itself in a covalent bond [50]. In this study, the electronegativity values of the molecules are lower than copper (4,98), this indicates that copper attracts more electrons from the different molecules, which strengthens its surface in the formation of a protective layer.

The hardness ( $\eta$ ) and softness ( $\sigma$ ) allow to measure the reactivity and molecular stability. A hard molecule has a large energy gap and a soft molecule has a small energy gap. [51]. Soft molecules are more reactive than hard ones because they could easily offer electrons to an acceptor. In the inhibition process, the inhibitor acts as a Lewis base while the metal acts as a Lewis acid [52]. The values recorded in Table 1 indicate that caffeine has the least value of global hardness (2,526 eV) and the highest value of global softness (0,396 eV) so, it is expected to have the highest inhibition which correlate well within the experimentally determined inhibition efficiency values efficiency

The fraction of transferred electrons ( $\Delta N$ ) from the inhibitor molecule to the metal surface can be calculated using the following [53]:

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})} \quad (10)$$

Where  $\chi_{Cu}$  and  $\eta_{Cu}$ ,  $\chi_{inh}$  and  $\eta_{inh}$  denote the electronegativity and hardness of copper and the inhibitor molecule respectively. We use the theoretical value of  $\chi_{Cu} = 4,98 \text{ eV}$  [54], and  $\eta_{Cu} = 0$  [55], for the calculation of the number of transferred electrons.

The fraction of transferred electrons ( $\Delta N$ ) values recorded in table 1 show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [56]. If  $\Delta N < 3,6$ , the inhibition efficiency increases by increasing electron donating ability of the inhibitors to the metal surface. These values are following order: theobromine > theophylline > caffeine which does not confirm the order obtained for the experimental inhibition efficiencies. Normally, the highest fraction of electrons transferred is associated with the best inhibitor, while the least fraction is associated with the inhibitor that has the least inhibition efficiency. In our study theobromine has the highest value of  $\Delta N$  is not the best inhibitor.

Chemical potential ( $\mu_p$ ) can be expressed as a function of the ionization potential I and the electron affinity A:

$$\mu_p = -\frac{I+A}{2} \quad (11)$$

The global electrophilicity index ( $\omega$ ), introduced by Parr [57], calculated using the electronic chemical potential and chemical hardness is given by:

$$\omega = \frac{\mu_p^2}{2\eta} \quad (12)$$

The values of this index in the table follow the trend: caffeine > theophylline > theobromine. Thus, caffeine exhibits the highest value of electrophilicity which confirms its highest capacity to accept electrons. In general, all three inhibitors have high  $\omega$  values, which means that these compounds could accept electrons from copper ( $\text{Cu}^{2+}$ ).

### Quantitative Structure Property Relationship investigation

In this investigation, Quantitative Structure Property Relationship (QSPR) has been used to correlate the molecule quantum chemical parameters with experimental inhibition efficiencies. Thus, for this study, the relevant parameters that will theoretically evaluate the inhibition efficiency have been selected for each molecule studied. This selection is based on the mathematical relationship proposed by Lukovits et al. in the non-linear model (LKP) in order to study the interaction of corrosion inhibitors with metal surface in acidic solutions. This non-linear model [58] is based on the Langmuir adsorption isotherm which is given by relationship:

$$\text{IE}_{theor}(\%) = \frac{[Ax_j+B]C_i}{1+[Ax_j+B]C_i} * 100 \quad (13)$$

Where A and B are real constants determined by solving the system of simultaneous equations obtained with the different values of the inhibitor concentration  $C_i$ .  $x_j$  is a quantum or reactivity chemical parameter characteristic for the molecule (j).



Using four inhibitors concentrations, which are  $100\mu M$ ,  $500\mu M$ ,  $1000\mu M$  and  $5000\mu M$ . We tested sets of three parameters ( $x_1, x_2, x_3$ ). In this case, the equation becoming:

$$IE_{theor}(\%) = \frac{[Ax_1+Bx_2+Dx_3+E]C_i}{1+[Ax_1+Bx_2+Dx_3+E]C_i} * 100 \quad (14)$$

This equation permit to have a system of four equations with four unknowns A, B, D and E. It is thus a question of finding for the molecule the set of coefficients A, B, D and E which make it possible to obtain the value of the inhibition efficiency closest to the experimental value. The calculations were carried out using the EXCEL software.

The experimental inhibition efficiencies for the molecules tested at 298K are collected in Table 2. The real constants determined are listed in Table 2-4.

**Table 2.** Inhibition efficiencies at T= 298 K for different concentrations of molecules studied

	IE(%)		
concentration	Caffeine	Theophylline	Theobromine
$100\mu M$	26,55	25,17	24,55
$500\mu M$	34,64	33,71	32,64
$1000\mu M$	42,68	40,43	39,64
$5000\mu M$	57,74	55,41	53,74

**Table 3.** Real constants A, B, D and E for the sets of quantum chemical parameters of caffeine

Set of Parameters	A	B	D	E
$(\Delta E, \omega, \Delta N)$	5752,47643	-2,8654 $10^{12}$	-1,3416X $10^{13}$	1,1282X $10^{13}$
$(E_{LUMO}, \mu, \eta)$	-2700,99478	8,3848X $10^{11}$	2,5595X $10^{12}$	9,8787X $10^{12}$
$(E_{HOMO}, \Delta E, \chi)$	-3268,96151	1331,96079	1,2544X $10^{12}$	-4,7379X $10^{12}$
$(E_{HOMO}, \mu, \Delta E)$	228,021147	-1,6035X $10^{11}$	8,0173X $10^{11}$	-3,3984X $10^{12}$
$(\sigma, \Delta N, \omega,)$	-435,209752	7,4717X $10^{13}$	-9,2829X $10^{11}$	-1,5162X $10^{13}$
$(\omega, \Delta E, \Delta N)$	-6,6865X $10^{10}$	4,4827X $10^{10}$	-1,5862X $10^{11}$	0,00302053

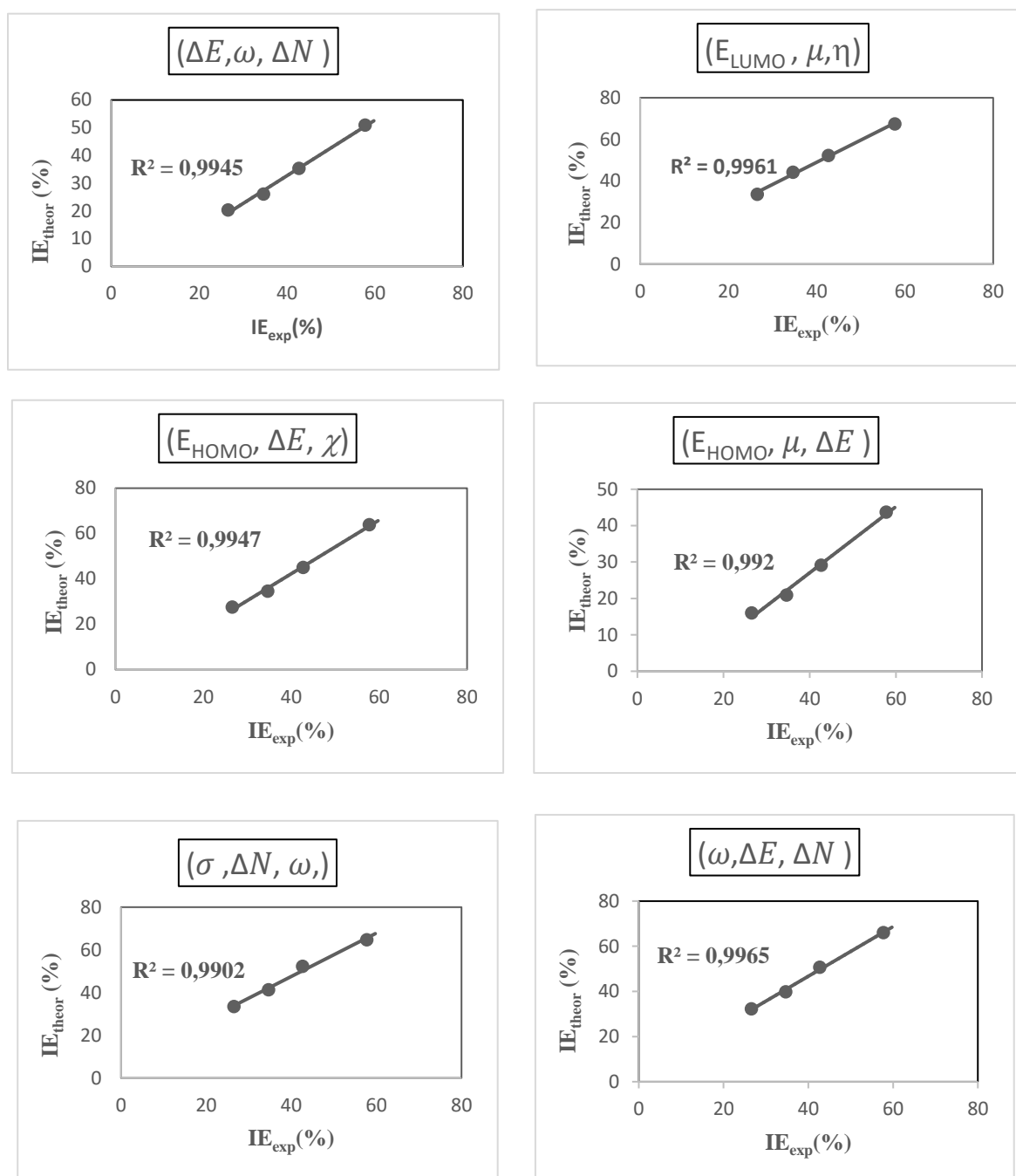
**Table 4.** Real constants A, B, D and E for the sets of quantum chemical parameters of Theophylline

Set of Parameters	A	B	D	E
$(\Delta E, \omega, \Delta N)$	3888,86622	-17779,0666	6915,17702	20103,3887
$(E_{LUMO}, \mu, \eta)$	-3,0921X $10^{13}$	1273,6219	-3,05133475	-2,8447X $10^{13}$
$(E_{HOMO}, \Delta E, \chi)$	9230,87438	602,225458	-2315,23206	61030,3134
$(E_{HOMO}, \mu, \Delta E)$	10468,3507	-2840,10684	8554,19188	29556,0557
$(\sigma, \Delta N, \omega,)$	-1420,05328	1435,61916	-10468,3504	24952,2413
$(\omega, \Delta E, \Delta N)$	-8583,82136	917,117757	-3523,76429	16657,1082

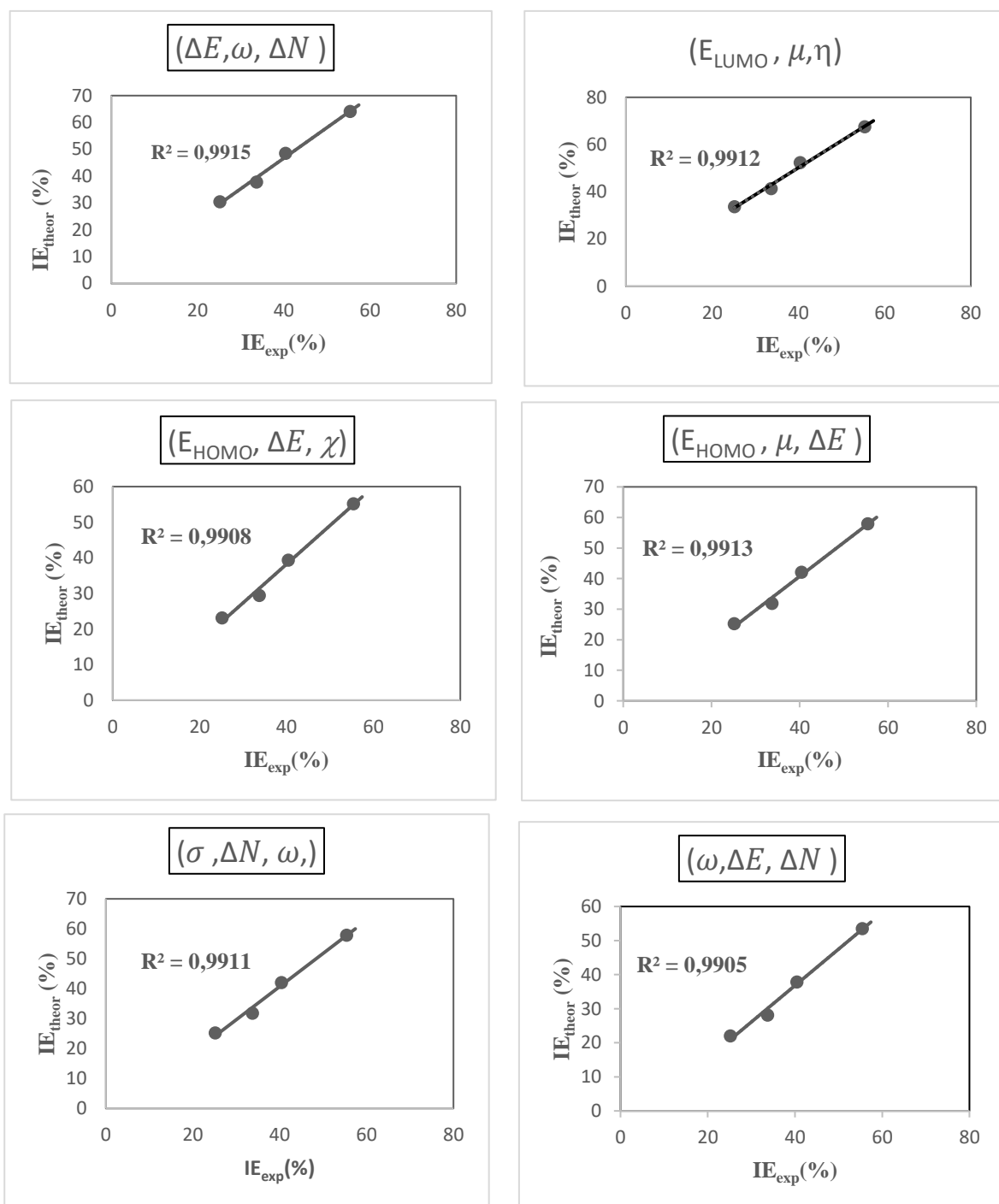
**Table 5.** Real constants A, B, D and E for the sets of quantum chemical parameters of Theobromine

Set of Parameters	A	B	D	E
$(\Delta E, \omega, \Delta N)$	4248,60784	-9417,63756	573,970067	0,02182353
$(E_{\text{LUMO}}, \mu, \eta)$	-6,6638X 12	4958,78493	-1281,9283	-5,9774X 10 <sup>12</sup>
$(E_{\text{HOMO}}, \Delta E, \chi)$	-5082,48244	-2,5033X 10 <sup>12</sup>	-422,851501	1,2879X 10 <sup>13</sup>
$(E_{\text{HOMO}}, \mu, \Delta E)$	52566,0942	-925,844105	-1883,48813	331312,128
$(\sigma, \Delta N, \omega,)$	4,1278X 10 <sup>13</sup>	360,812399	92,5887118	-1,6057X 10 <sup>13</sup>
$(\omega, \Delta E, \Delta N)$	1,85X 10 <sup>12</sup>	-4,4047X 10 <sup>11</sup>	-5,2856X10 <sup>11</sup>	-1,9055X 10 <sup>12</sup>

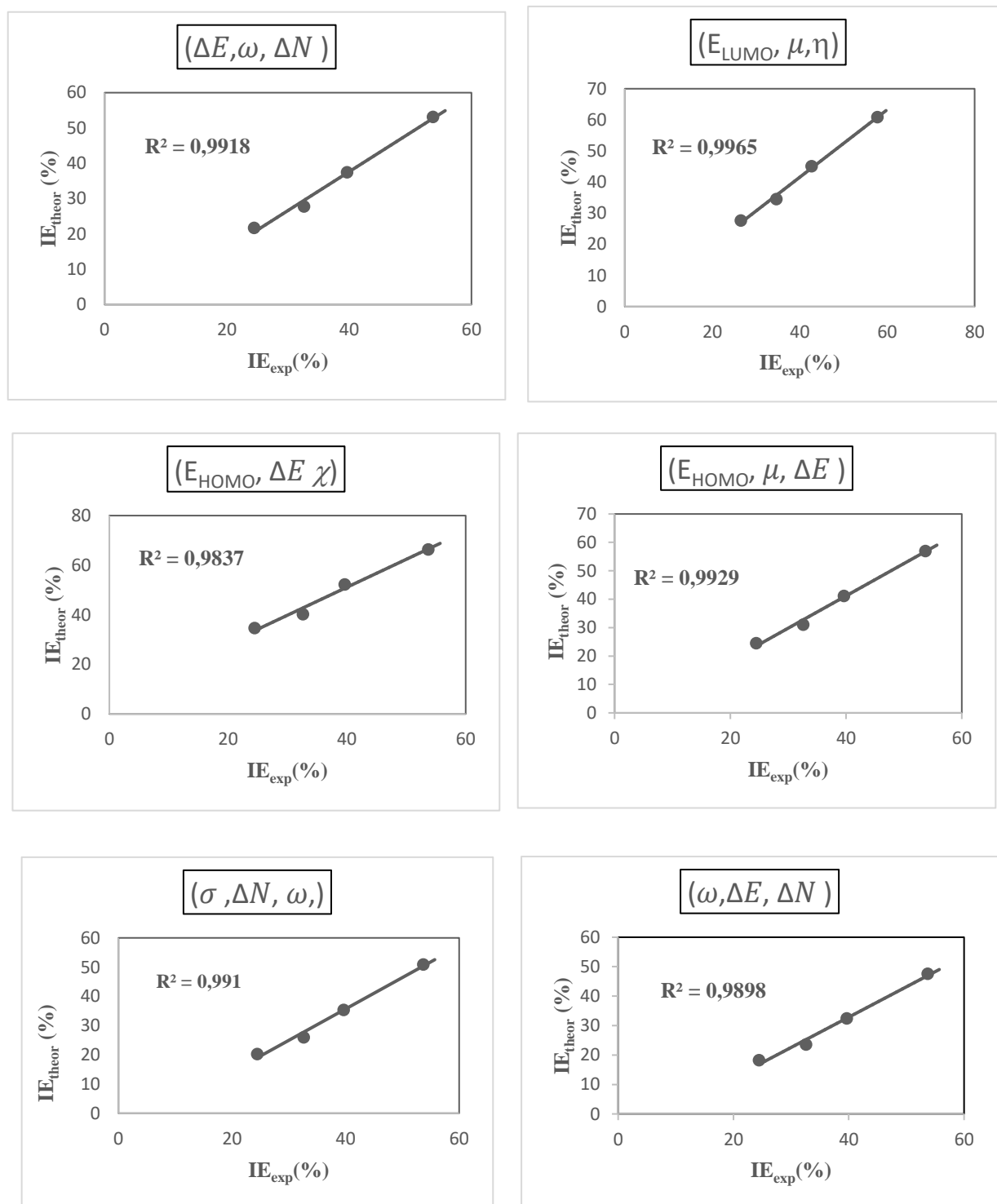
The calculated versus experimental inhibitor efficiencies for caffeine, theophylline and theobromine are represented in Figure 4-6.



**Figure 4.** Variation of experimental inhibition efficiency ( $IE_{exp}$ ) of caffeine with the theoretical inhibition efficiencies ( $IE_{Theor}$ ) for different set of parameters



**Figure 5.** Variation of experimental inhibition efficiency ( $IE_{exp}$ ) of Theophylline with the theoretical inhibition efficiencies ( $IE_{Theor}$ ). for different set of parameters



**Figure 6.** Variation of experimental inhibition efficiency ( $IE_{exp}$ ) of Theobromine with the theoretical inhibition efficiencies ( $IE_{Theor}$ ). for different set of parameters

Observing the Figures 4-6, we can see that the correlation coefficients are all close to unity. It is evident that there is a strong relationship between the theoretical and experimental inhibition efficiencies, which might help in planning of new effective inhibitor molecules. In order to find the best set of parameters for each molecule, we have calculated the statistical indicators. The different values of these indicators are shown in Tables 6-8.

**Table 6.** Correlation coefficients ( $R^2$ ) and statistical indicators for the selected set of caffeine

Set of Parameters	Caffeine			
	$R^2$	SSE	RMSE	MPD
$(\Delta E, \omega, \Delta N)$	0,9945	215,2302	7,3353	0,7773
$(E_{LUMO}, \mu, \eta)$	0,9961	328,7226	9,0653	0,9380
<b><math>(E_{HOMO}, \Delta E \chi)</math></b>	<b>0,9947</b>	<b>42,9497</b>	<b>3,3147</b>	<b>0,2036</b>
$(E_{HOMO}, \mu, \Delta E)$	0,9920	682,4444	13,0618	1,3563
$(\sigma, \Delta N, \omega)$	0,9902	232,9634	7,6316	0,7991
$(\omega, \Delta E, \Delta N)$	0,9965	189,2886	6,8791	0,6899

**Table 7.** Correlation coefficients ( $R^2$ ) and statistical indicators for the selected set of theophylline

Set of Parameters	Theophylline			
	$R^2$	SSE	RMSE	MPD
$(\Delta E, \omega, \Delta N)$	0,9915	183,5099	6,7732	0,6829
$(E_{LUMO}, \mu, \eta)$	0,9912	415,1134	10,1872	1,0735
$(E_{HOMO}, \Delta E \chi)$	0,9908	23,2423	2,4223	0,2376
<b><math>(E_{HOMO}, \mu, \Delta E)</math></b>	<b>0,9913</b>	<b>6,4688</b>	<b>1,2717</b>	<b>0,1076</b>
$(\sigma, \Delta N, \omega)$	0,9911	12,4265	1,7626	0,1439
$(\omega, \Delta E, \Delta N)$	0,9905	51,4021	3,5848	0,3888

**Table 8.** correlation coefficients ( $R^2$ ) and statistical indicators for the selected set of theobromine

Set of Parameters	Theobromine			
	$R^2$	SSE	RMSE	MPD
$(\Delta E, \omega, \Delta N)$	0,9918	36,169	3,0069	0,3272
$(E_{LUMO}, \mu, \eta)$	0,9965	93,4533	4,8336	0,4554
$(E_{HOMO}, \Delta E \chi)$	0,9837	483,4807	10,9941	1,2065
<b><math>(E_{HOMO}, \mu, \Delta E)</math></b>	<b>0,9929</b>	<b>15,8297</b>	<b>1,9893</b>	<b>0,1510</b>
$(\sigma, \Delta N, \omega)$	0,9910	87,7538	4,6838	0,5356
$(\omega, \Delta E, \Delta N)$	0,9898	212,9521	7,2964	0,8337

Analyzing the different values of the statistical indicators recorded in the tables 6-8, it appears that the best set of parameters for caffeine is  $(E_{HOMO}, \Delta E \chi)$  for theophylline is  $(E_{HOMO}, \mu, \Delta E)$  and for theobromine is  $(E_{HOMO}, \mu, \Delta E)$ . Indeed the values of the statistical indicators of these sets of parameters are the lowest. These sets of parameters thus obtained

can be used to calculate the theoretical inhibition efficiency of the compounds tested. Therefore QSPR approach is one of the theoretical methods that is sufficient to predict the effectiveness of inhibitors.

## CONCLUSION

This study shows that caffeine, theophylline and theobromine are good corrosion inhibitors. Their inhibition efficiency is temperature and immersion time dependent. It was also noted that some quantum chemical parameters are not sufficient in correlating the inhibitive ability of methyloxanthine with their experimental inhibition efficiency, while others allow a good correlation to be established between these entities. QSPR model has shown that there is a strong correlation between inhibition efficiency and quantum chemical parameters. Thus, for each compound tested in 1M HNO<sub>3</sub>, the best set of parameters to calculate the theoretical inhibition efficiency was found from the correlation coefficients and statistical indicators. Overall, there is good agreement between the experimental data and the theoretical results

## Declaration of Competing Interest

Conflict of interests: The authors declare that they have no conflict of interest. Author contributions: All authors contributed equally to this work.

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