

UDC 627.257:621.3.035.221.727:621.315.617.1

**QUANTUM CHEMICAL MODELING OF ADSORPTION OF THIOUREA
DERIVATIVES, THAT USED AS INHIBITORS OF MICROBIOLOGICAL CORROSION
ON THE IRON OF ST3S GRADE OF STEEL**

**ПРОДУКТЫ КОНДЕНСАЦИИ ТИОМОЧЕВИНЫ И ЯНТАРНОЙ И КРОТОНОВОЙ
КИСЛОТ (УРЕИДЫ) КАК ИНГИБИТОРЫ МИКРОБИОЛОГИЧЕСКОЙ КОРРОЗИИ
СТАЛИ: МОДЕЛИРОВАНИЕ АДСОРБЦИИ**

©Sikachina A.

SPIN-code: 8133-3363, ORCID: 0000-0002-0695-1750

Immanuel Kant Baltic Federal University

Kaliningrad, Russia, sikachina@list.ru

©Сикачина А. А.

SPIN-код: 8133-3363, ORCID: 0000-0002-0695-1750

Балтийский федеральный университет им. И. Канта

г. Калининград, Россия, sikachina@list.ru

Abstract. In the published work, the process of adsorption of organic derivatives of thiourea and dicarboxylic acids (thiourea class) modeled with semi-empirical ZINDO / 1, on iron (97% in steel St3, Poland) is presented. The structures of “thiourea” for the study were chosen so that the sequential complication of the molecular structure could be traced. Such an approach, as will be shown below, reflects with high accuracy the process of protection against corrosion with bacterial content by chemisorption of an organic compound on the metal surface with the formation of a complex compound. In the course of the study, the following compositions were obtained and analyzed: the compositions of the complexes obtained, global and local electro-filter values, a graph showing the dependence of the local electrophilicity of an arbitrary heteroatom taken by the author. The graph shows the equations of the obtained lines.

Аннотация. В публикуемой работе представлен смоделированный посредством полуэмпирического ZINDO/1 процесс адсорбции органических производных тиомочевины и дикарбоновых кислот (класса уреидов), на железе (имеющегося в стали Ст3 в количестве 97%). Структуры уреидов для исследования были выбраны так, чтобы прослеживалось последовательное усложнение молекулярной структуры. Такой подход, как будет показано далее, с высокой точностью отражает процесс защиты от коррозии с бактериальным контентом путем хемосорбции органического соединения на поверхности металла с образованием комплексного соединения. В процессе исследования были получены и проанализированы: составы полученных комплексов, глобальных и локальных величин электрофильности, график, отображающий зависимость локальной электрофильности произвольно взятого автором гетероатома. На графике показаны уравнения полученных прямых.

Keywords: thiourea derivatives, ureids, corrosion rate, sulfate-reducing bacteria, hydrogen sulfide corrosion, chemical adsorption, St3 steel, iron, partial effective charges, global electrophilicity of the molecule, complex substances.

Ключевые слова: уреиды, органические производные дикарбоновых кислот, скорость коррозии, сульфатредуцирующие бактерии, сероводородная коррозия, химическая адсорбция, сталь Ст3, железо, парциальные эффективные заряды, глобальная электрофильность молекулы, комплексные соединения.

The economic and environmental damage from corrosion in industry is associated with high metal intensity of equipment and the presence of highly aggressive media [1–4]. An effective method of protection in such environments is the use of corrosion inhibitors [5–6], the synthesis of new forms of which is continuously expanding, [7], as the requirements of industrial companies are tightened to high efficiency at low concentrations (100 ... 200 mg / L). This research is a contribution to the development of the search for organic compounds that can act as corrosion inhibitors, which is currently being conducted not so much through screening, but also by involving more and more aspects of the numerical experiment, the most recent of which is the quantum chemical modeling of the adsorption of an organic compound on a metal [7–11]. The author attempts to achieve this by searching for a relationship between the protective effect of corrosion and the values of the quantum chemical descriptors of adsorption complexes resulting from the donor-acceptor interaction of the organic compound with iron atoms, which provides a predictive basis for preliminary studies of the organic compound as a corrosion inhibitor.

A large amount of data on the inhibition of corrosion with the help of the derivatives of thiourea (U Y) is not present. In a number of works it is proposed to use thiourea and its derivatives as inhibitors of acid and hydrogen sulfide corrosion of steel [12–13]. In aqueous media, thiourea at a concentration of 0.03 ... 5.0 mmol / L slows down the cathodic reaction (at lower thiourea concentrations) and anode (at higher thiourea concentrations) on carbon steel. However, it was shown in [14] that the introduction of thiourea into acidic chloride media can cause an increase in the flux of hydrogen diffusion into carbon steel, which can lead to hydrogen brittleness of the metal.

Effective corrosion inhibitors added to gasolines and distillate fuels are mixed salts of carboxylic acids. Corrosion slows the formation of rust by adding an oil-soluble inhibitor, the lithium salt of alkyl- or alkenylsuccinic acid, to lubricating oils. As magnesium-soluble inhibitors, magnesium salts of organic acids have also been studied [15].

Methods

A variety of microbiological corrosion system

In the article investigated the heterogeneous thermodynamic system of closed type “St3S/breeding ground of Postgate “B” class + *Desulfovibrio desulfuricans* cells”. Samples of steel were parameters 20×50×1 mm. Samples of steel were taken from one batch, which guaranteed them the same chemical composition [16].

Using organic inhibitors and their method of application in the corrosion system

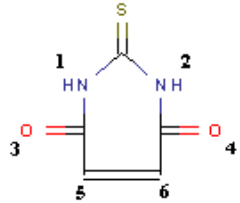
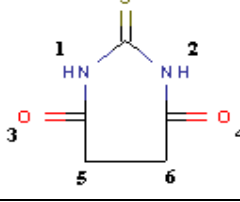
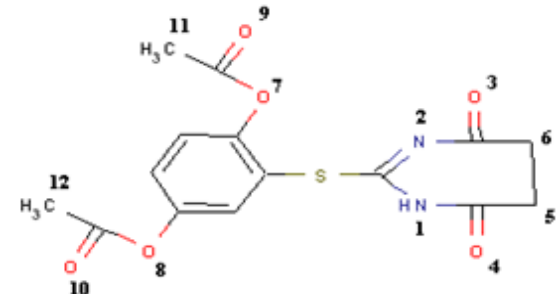
3 representatives of the “thiourea” class were selected. 3 representatives act as inhibitors of hydrogen sulfide corrosion, added at a concentration of 1, 2, 10 mmol / L contained in a closed system (this is a tube with a volume of 0.9 L) Liquid sterile de-oxygenated medium Postgate “B” (Table 1).

The protective effect against corrosion

The protective effect against microbiological corrosion (Z%) was published in [17–18], calculated by gravimetric method, mentioned in many works, including [19–22], therefore the inhibitory effect of these compounds has been proven. According to [22], the above structure was a structural series of molecules.

Table 1.

THE STRUCTURES OF THE MOLECULES OF THE INVESTIGATED INHIBITORS AND THE NUMBERING OF THE ASSUMED ADSORPTION CENTERS

Abbreviation of inhibitor	Structural formulas with numbered (according to the author, not according to IUPAC) assumed adsorption centers	Preferred IUPAC name of inhibitor	Molecular weight
U1		2-sulfanylidene-2,3,4,7-tetrahydro-1H-1,3-diazepine-4,7-dione	157.1
U2		2-sulfanylidene-1,3-diazepane-4,7-dione	236.3
U3		4-(acetyloxy)-3-[(4,7-dioxo-4,5,6,7-tetrahydro-1H-1,3-diazepin-2-yl)sulfanyl]phenyl acetate	213.2

The technology of quantum chemical calculations

The quantum chemical experiment was carried out with HyperChem 8.0.7, using the built-in visualization tools.

The scientific novelty of the study is the application of a more informative approximation of the donor–acceptor interaction of the U Y with iron atoms $a\text{Fe}^0 + \text{U Y} = \text{Fe}_a \leftarrow [\text{U Y}]$ (the support and the base were the Lewis representations, from which it follows that the U Y is the Lewis base, and the iron atom is Lewis acid). The calculation was performed using HyperChem 8.0.7. Software, empirically, the limit was set by the number of iron atoms: number a , when out of $(a + b)$ given by HyperChem-user iron atoms carrying zero charge number b . The plane of neutral iron atoms specified by HyperChem-user was 1.2 Å (angstroms) away from the U Y plane with the expectation that the program produced fewer iterations, which provides the necessary accuracy. Then it was assumed that the U Y donor possibilities are exhausted. Equation electrophilic $a\text{Fe}^0 + \text{U Y} = [\text{U Y}] \rightarrow \text{Fe}_a$ reaction, where iron atoms are acceptors, which are charged negatively. Finding the values of quantum chemical descriptors held level theory MM+, OPLS / PM3 / ZINDO / 1 [14, 16, 23]. OPLS most accurately reflects non-covalent interactions, while the two-dimensional structure given by the researcher, consisting of a molecule of the inhibitor and iron atoms lying in one plane, turns into a three-dimensional one. Mesomeric effect was taken into account, which is manifested in different parts of the investigated U Y. In the following controlled descriptors of electronic structure: charges on heteroatoms (by Mulliken) will be calculated as Σq , i. e. charges on the same arrangement of atoms will be summarized as a result of a high degree of symmetry of the test running, the energy frontier orbitals, the resulting composition $[\text{U Y}] \rightarrow \text{Fe}_a$, where the U Y acts as a ligand. Based on these characteristics will be calculated from the data file. *out*: the charge density on the iron (1 atom of Fe), global and local electrophilicity, consider the complex structure. Along the length of “Fe-heteroatom” bond taken into account within the 2.50 Å.

Software was computed: charges on heteroatoms through the analysis of Mulliken populations, the energy of boundary orbitals (the author did not set the goal of mapping and reviewing software-calculated content). Of these, global and local electrophilicity values of both “thiourea” and thiourea complexes based on “thiourea” (ω , ω) were derived. Local electrophilicity, calculated due to the symmetry of compounds, with preliminary summation of charges on symmetrically located heteroatoms, but also you will see the values of local electrophilicities in terms of 1 heteroatom, on the basis of which comparisons will be made (Figure 1–3).

Results and discussion

Properties of the general molecular structure

The simplest formulas for “thiourea” and obtained iron complexes, and shortened encodings and global electrophilicity too are shown in Table 2.

Table 2.

DESCRIPTORS OF AN INTEGRAL MOLECULE

Code of inhibitor iron complexes	Formulas of iron complexes	Global electrophilicity	Code of inhibitor	Formulas of inhibitor	Global electrophilicity
Fe _a ← [U1]	Fe ₉ ← C ₄ H ₄ O ₂ N ₂ S	3.450	U1	C ₄ H ₄ O ₂ N ₂ S	1.863
Fe _a ← [U2]	Fe ₈ ← C ₄ H ₆ O ₂ N ₂ S	1.959	U2	C ₄ H ₆ O ₂ N ₂ S	1.767
Fe _a ← [U3]	Fe ₁₄ ← C ₁₄ H ₁₄ O ₆ N ₂ S	1.857	U3	C ₁₄ H ₁₄ O ₆ N ₂ S	1.972

The donor properties of heteroatoms are reflected by the global and local electrophilicity values. From the presented Figures, it is obvious that the magnitude of the global electrophilicity (ω) of the U Y under consideration falls in the series U3–U1–U2. There is a drop in the number of electrons that can be attached to the metal surface, the number of multiple bonds decreases, which explains why the number of adsorbed iron atoms decreases with decreasing number of conjugated bonds. ω decreases in the series U1–U2–U3.

The protective effect, manifested by iron complexes of “thiourea”, decreases in the series Fe₁₄ ← [U3], Fe₈ ← [U2], Fe₉ ← [U1]. On the one hand, the high protective effect of Fe₁₄ ← [U3] is due to the large number of iron atoms reacted with the large molecule U3. On the other hand, in the series of iron complexes Fe₁₄ ← [U3], Fe₈ ← [U2], Fe₉ ← [U1], the Fukui function (FF) falls, characterizing the change in global electrophilicity (this is $U_3FF_{\omega} = 1.587$, $U_2FF_{\omega} = 0.192$, $U_1FF_{\omega} = -0.115$, respectively). This illustrates the strength of donor–acceptor “Fe-heteroatom”, since the largest value of FF_ω shows the highest strength of donor–acceptor bonds.

Values of local electrophilicity of heteroatoms of molecular structure

The adsorption process directly depends on the local electrophilicity. The Figures 1–3 reflects the local electrophilicity values due to the total charges on the symmetrically arranged atoms of the thiourea fragment ($\Sigma_U \Delta q_E$) and the hydroquinone fragment ($\Sigma_H \Delta q_E$), where E is any heteroatom.

The change in the magnitude of local electrophilicity during complexation (angles with the abscissa axis)

It is obvious from the Figures 1–3 that the more the values of the local electrophilicity of different heteroatoms differ from each other (in the iron complex or in the initial substance) and the smaller the change in these values during the chemisorption, the larger is the Z% value.

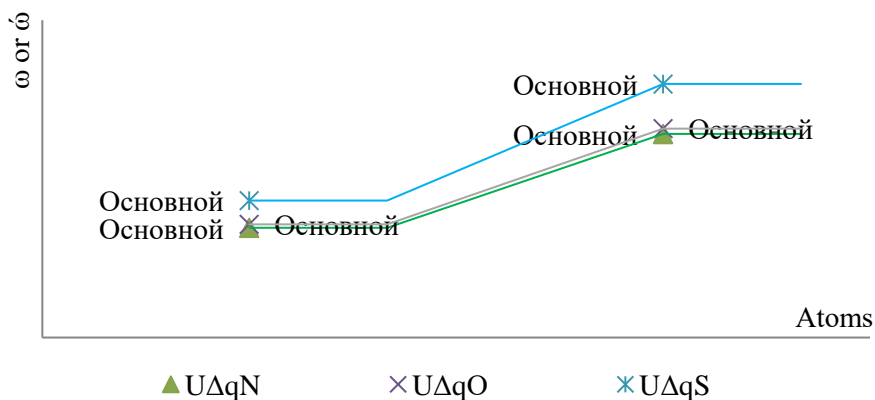


Figure 1. Values of local electrophilicity of heteroatoms in $C_4H_4O_2N_2S$ (from the left side) and in $Fe_9 \leftarrow C_4H_4O_2N_2S$ (from the right side) and its changes in the chemisorption process

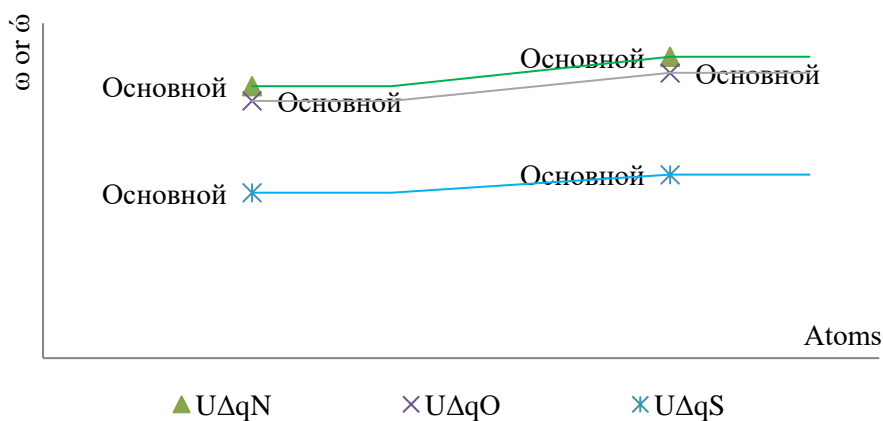


Figure 2. Values of local electrophilicity of heteroatoms in $C_4H_6O_2N_2S$ (from the left side) and in $Fe_8 \leftarrow C_4H_6O_2N_2S$ (from the right side) and its changes in the chemisorption process

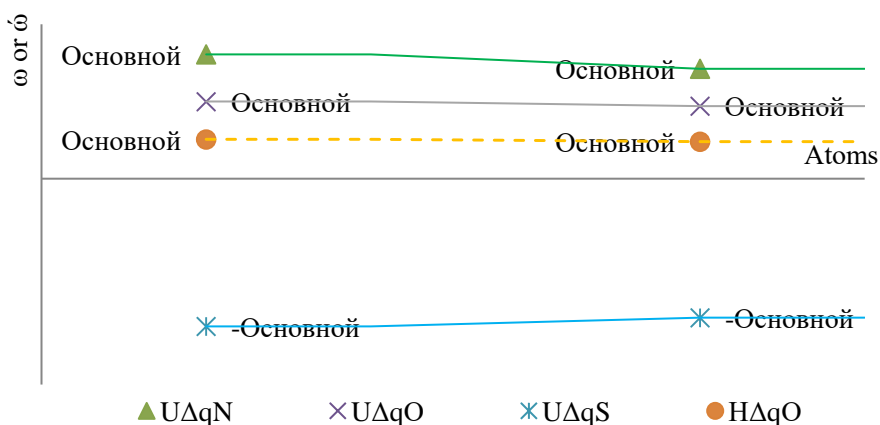


Figure 3. Values of local electrophilicity of heteroatoms in $C_{14}H_{14}O_6N_2S$ (from the left side) and in $Fe_{14} \leftarrow C_{14}H_{14}O_6N_2S$ (from the right side) and its changes in the chemisorption process

Values of local electrophilicity

Two phenomena contribute to the value of the index of local electrophilicity (Figures 1–3): the thiourea structure and the depth of the electron density transition along the “*Fe-heteroatom*” bonds, which is determined by the value of the Fukui function, which all the more strongly the thiourea heteroatom performs a donor activity on a specific iron atom, increasing the charge on the heteroatom. Thus, in U1, the distribution of local electrophilicity values is $\omega_U\Delta q_S$ — $\omega_U\Delta q_O$ — $\omega_U\Delta q_N$.

The volume of sulfur can take electrons from the metal thickness, promoting its ionization (short Fe–S bonds), so the maximum protective effect at the highest concentration does not exceed 43%.

Therefore, the main adsorption centers are oxygen and nitrogen atoms. This can be explained by the presence of mesomeric effect in the whole chain (by the benzene principle), and a large electron density flows from the whole molecule to oxygen atoms. Further, from the oxygen atoms of the ketogroups, the electron density is doped to the metal (the value of FF is the highest, therefore, $\omega_{\Sigma_U}\Delta q_O$ is high).

In the structurally similar to U2 (and also in U3 including the substituent bonded through the sulfur bridge) the following: $\omega_U\Delta q_N$ — $\omega_U\Delta q_O$ — $\omega_U\Delta q_S$. The electrophilicity of sulfur is lowered, and the protective effect reaches 54%. In U2, unlike U1, ${}_5C-{}_6C$ bond is single, and the mesomeric effect can manifest only on a part of the molecule. Then the critical value in the process of chemisorption has a nitrogen atom as less electronegative, therefore the highest value of $\omega_U\Delta q_N$ is high, since the value of the Fukui function is large in connection with the strong donation of the electron density to the iron atom. In U3, the decrease in the magnitude of the local electrophilicity of the sulfur atom is expressed most sharply: the sulfur atom donates its electron density and facilitates the outflow of the latter from the thiourea fragment to the hydroquinone fragment. The same applies to the atoms ${}_7O$ and ${}_8O$. The values of the local electrophilicity indices are extremely low ($\omega_U\Delta q_S = -0.574$ and $\omega_{\Sigma_H}\Delta q_O = 0.305$) — their participation in the $aFe^0 + U Y = Fe_a \leftarrow [U Y]$ reaction is indirect through the mutual influence of atoms in the molecule.

There is also a tendency towards enolization, while a less electronegative nitrogen atom better densifies the electron density on the metal orbital, and on the oxygen atom there can be some positive charge that contributes to the electro-sorption on the metal. This inclination is higher on U2 than on U1.

Analyzing the values of local electrophilicity, in the molecule U3, most likely, the electron density flows from the substituent (hydroquinone fragment) to the main chain (thiourea), since the calculated $\omega_{\Sigma_H}\Delta q_O$ is strongly reduced. This can be the result of two simultaneous reactions: the first is $aFe^0 + U Y = Fe_a \leftarrow [U Y]$, and the second is the non-covalent interaction of the substituent with the iron atoms.

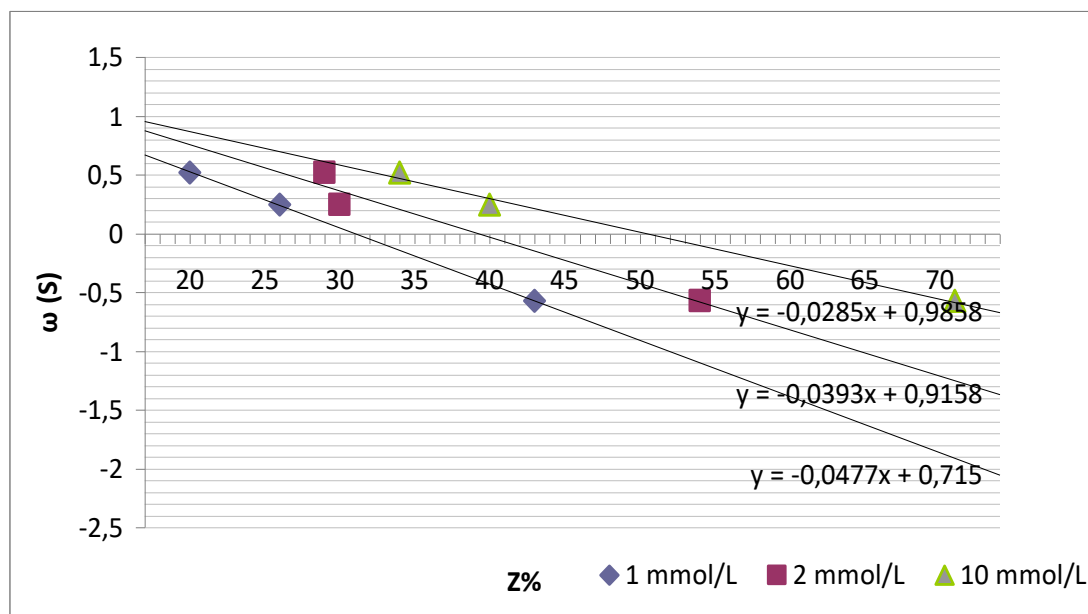


Figure 4. Graphical dependence of the type “ $\Sigma U \Delta q_E$ — Z%” and the corresponding equations of the computer-generated trend lines

Graphic dependence of the protective effect against corrosion on the heteroatom parameter

The relationship between the local electrophilicity of the sulfur atom ($\omega_U \Delta q_S$ or shorter than ω (S)) and Z% is as follows

If the graphical dependence were parallel, it would mean that there is no chemisorption component in the effect of inhibiting microbiological corrosion.

According to Figure 4 (with linear trend lines generated by the computer, with the applied equations of such), the protective effect of corrosion grows the more, the lower $\omega_U \Delta q_S$. This phenomenon manifests itself starting with Z% = 20 at the lowest taken concentration and ending at Z% = 31, etc. Electrophilicity, while this should decrease (which proves the participation of this atom in the process of chemisorption). The smaller the concentration of the inhibitor, the stronger the local electrophilicity of the sulfur atom will decrease, which is the key to manifesting a high protective effect. In case of occurrence of Z% = 31%, 41%, 51% $\omega_U \Delta q_S$ is a zero value. This obviously occurs because the sulfur atom is practically not involved in connection with iron atoms at the indicated Z% values. After Z% = 31%, 41%, 51%, the further increment of Z% can be only when the nucleophilicity of the sulfur atom increases, i. e. the decisive role in the mission of inhibitor protection begins to have electrosorption.

The structures of adsorption complexes, on which the inhibitory properties depend

The structure of the donor and acceptor complexes (by the example of donor and acceptor bonds) is shown in Tables 3–5.

Table 3.

LENGTHS OF DONOR AND ACCEPTOR BONDS IN $FE_9 \leftarrow C_4H_4O_2N_2S$

<i>The charge of a particular iron atom</i>	<i>Name of bonds with heteroatom</i>	<i>quantum chemically calculated length relationships, Å</i>
-0.350	Fe- ₃ O	2.43
	Fe- ₁ N	2.31
-0.235	Fe- ₃ O	2.14
-0.235	Fe- ₅ C	2.49
	Fe- ₆ C	2.41
-0.364	Fe- ₄ O	2.38
-0.517	Fe- ₁ N	2.25
	Fe- ₂ N	2.39
-0.271	Fe- ₄ O	2.34
-0.364	Fe- ₄ O	2.38
	Fe- ₂ N	2.45
-0.334	Fe-S	2.50
	Fe- ₂ N	2.50
-0.154	Fe-S	2.50

Table 4.

LENGTHS OF DONOR AND ACCEPTOR BONDS IN $FE_8 \leftarrow C_4H_6O_2N_2S$

<i>The charge of a particular iron atom</i>	<i>Name of bonds with heteroatom</i>	<i>quantum chemically calculated length relationships, Å</i>
-0.427	Fe-S	2.50
	Fe- ₁ N	2.47
	Fe- ₃ O	2.38
-0.244	Fe- ₁ N	2.50
-0.234	Fe- ₃ O	2.20
-0.258	Fe- ₅ C	2.40
	Fe- ₆ C	2.42
-0.465	Fe- ₂ N	2.34
	Fe- ₃ O	2.38
-0.319	Fe- ₄ O	2.16
-0.469	Fe- ₂ N	2.50
	Fe- ₁ N	2.25
	Fe- ₆ C	2.40
-0.390	Fe- ₂ N	2.40
	Fe-S	2.48

Table 5.

LENGTHS OF DONOR AND ACCEPTOR BONDS IN $Fe_{14} \leftarrow C_{14}H_{14}O_6N_2S$

<i>The charge of a particular iron atom</i>	<i>Name of bonds with heteroatom</i>	<i>quantum chemically calculated length relationships, A</i>
-0.347	Fe- ₄ O	2.17
	Fe- ₂ N	2.29
-0.495	Fe- ₂ N	2.41
	Fe- ₆ C	2.41
-0.436	Fe- ₆ C	2.50
	Fe- ₄ O	2.15
-0.393	Fe- ₃ O	2.28
	Fe- ₆ C	2.41
	Fe- ₅ C	2.50
-0.359	Fe- ₃ O	2.29
-0.594	Fe- ₂ N	2.39
	Fe- ₁₀ O	2.36
-0.534	Fe- ₁₀ O	2.45
	Fe- ₃ O	2.50
	Fe- ₁ N	2.47
-0.282	Fe- ₁₀ O	2.50
	Fe- ₁₂ CH ₃	2.46
-0.416	Fe- ₁₂ CH ₃	2.46
	Fe- ₈ O	2.26
-0.691	Fe- ₁₁ CH ₃	2.45
-0.451	Fe- ₇ O	2.26
	Fe- ₁₁ CH ₃	2.42
-0.436	Fe- ₆ C	2.50
	Fe- ₄ O	2.15
-0.504	Fe- ₉ O	2.21
-0.651	Fe-A	2.25
-0.691	Fe-A	2.46

In the structure of $Fe_9 \leftarrow C_4H_4O_2N_2S$ it is obvious that the iron atom has a coordination number in the range I ... II (Table 3). The coordination numbers seem to correlate with charges: when the charge on an iron atom is greater than -0.334, there are the highest coordination numbers. The bonds of the iron atom with the amide-fragment, formed with both ₈O and ₁N are the shortest. Dentativity for oxygen atoms of keto groups is V. Dentativity for nitrogen atom is V, for sulfur atom and carbon is II. Therefore, the main adsorption center is a nitrogen atom and an oxygen atom of keto groups.

In the structure of $Fe_8 \leftarrow C_4H_6O_2N_2S$ it is obvious that the iron atom has a coordination number in the range I ... III (Table 4). The coordination numbers seem to correlate with charges: when charged on an iron atom greater than -0.469, there are the highest coordination numbers. The bonds of iron atoms with oxygen of the keto groups of the thiourea ring are the shortest (2.16 ... 2.20 Å). Dentativity in oxygen atoms of keto groups is IV. Dentativity at the nitrogen atom is equal to VI, for the atom of sulfur is II and for the atom of carbon is III. Therefore, the main adsorption center is a nitrogen atom.

In the structure of $Fe_{14} \leftarrow C_{14}H_{14}O_6N_2S$ it is obvious that the iron atom has a coordination number in the range I ... III (Table 5). The coordination numbers seem to correlate with charges: when charged with an iron atom larger than -0.416, there are the highest coordination numbers. The bonds of the iron atoms with the oxygen of the keto groups of the thiourea ring (2.15 ... 2.29 Å) and oxygen atoms of the acetyl fragment (2.21 ... 2.26 Å) are the shortest. The dentativity in oxygen atoms of the keto groups of the thiourea ring is equal to V, for oxygen atoms of the keto groups of acetyl are IV,

for phenolic oxygen atoms is II (due to the electron density donation to the benzene ring, therefore, the carbon atom of the benzene ring ($\gamma_{\text{or } 8} \text{O-C}$ bond) has value of dentativity V). The dentativity with respect to the nitrogen atom is IV. The dentativity by methyl groups is IV, the dentativity by ${}^5\text{C}$ and ${}^6\text{C}$ is V. The electron density of the sulfur atom, unlike that of sulfur atoms U1 and U2, is extremely strongly delocalized on [(4,7-dioxo-4,5,6,7-tetrahydro-1H-1,3-diazepin-2-yl) sulfanyl] and 4-(acetyloxy)-3- ... phenyl rings, so this atom does not directly participate in the formation of Fe-S bonds. The presence of a large number of adsorption centers causes a very high Z%.

Atoms ${}^5\text{C}$ and ${}^6\text{C}$ in the U1 ... U3 have dentativity II ... V (the highest is in U2 and U3, where the bond is ${}^5\text{C}-{}^6\text{C}$), since the hydrogen atoms at them have acidic properties (the effect of carboxyl groups, together with the electronegativity of the nitrogen atoms in the thiourea molecule, which are condensation products of thiourea and succinic acid (U2 and U3)) and, under the action of bases, are capable of producing an anionic center. The basic (that is nucleophilic agent) from the “Postgate B + sulfatereduction bacteria environment” system will be able to eliminate the H-atoms.

Conclusion

Application of article approach, such as lack of hydration molecules, the use of pure iron atoms cluster instead of steel, neglect of participation in the adsorption of molecular hydrogen sulphide and its ions, semi-empirical methods of calculation and modeling obviously do not impose the print on the accuracy and predictive ability of the author improved cluster modeling theory. This enhancement allows you to get more information about protection of inhibitors of metal than the traditional and generally accepted theory. Including the correlation method used in [17] and earlier (with respect to sulfonamides) in [18].

The improved method of quantum chemical modeling provides a much more comprehensive set of data that can serve as an effective tool for forecasting. Because iron complexes is not seen as superficial, and as an independent organic compound (or rather, the adduct) with well-defined chemical composition, is similar to π -complexes may be calculated as the actual value of the electronic tags last structure and function of Fukui. This represents a great promise, because currently the selection of microbial corrosion inhibitors increasingly performed quantum-chemical methods of prediction [24], not a screening method [25–26].

Perhaps from such data (most likely from the graphical dependencies of the protective effect against corrosion or the rate of corrosion), in the near future a detailed card file will be created that covers all classes of organic compounds, which will leave a trial and error method in the past, because in the synthesis of a new inhibitor, the corrosion inhibitory action changes (often for the better) with a very slight “structural adjustment” of the molecule of the already known inhibitor.

There is no doubt that a significant role in shaping improvements quantum chemical modeling belongs to the tremendous development of the power of new versions of quantum chemical programs, as well as the full development of visual imaging software. As soon as supercomputers are increasingly becoming an essential attribute of any area of the economy, all of the above approach will be less needed along with an increase in the level of quantum-chemical theory.

Competing interests

The author declares that they have no competing interests.

References:

1. Yurt, A., Duran, B., & Dal, H. (2014). An experimental and theoretical investigation on adsorption properties of some diphenolic Schiff bases as corrosion inhibitors at acidic solution/mild steel interface. *Arabian Journal of Chemistry*, 7, (5), 732-740. doi:10.1016/j.arabjc.2010.12.010
2. Dasami, P. M., Parameswari, K., & Chitra, S. (1915). Inhibition of Mild Steel Corrosion in 1M H₂SO₄ Medium by Benzimidazole Mannich bases. *Oriental Journal of Chemistry*, 31 (1), 185-191. doi:10.13005/ojc/310120

3. Karthik, D., Tamilvendan, D., & Prabhu, G. V. (2014). Study on the inhibition of mild steel corrosion by 1,3-bis-(morpholin-4-yl-phenyl-methyl)-thiourea in hydrochloric acid medium. *Journal of Saudi Chemical Society*, 18, (6), 835-844. doi:10.1016/j.jscs.2011.10.009
4. Gupta, M., Mishra, J., & Pitre, K. S. (2013). Corrosion and Inhibition Effects of Mild Steel in Hydrochloric Acid Solutions Containing Organophosphonic Acid. *International Journal of Corrosion*, ID 582982, 5. doi:10.1155/2013/582982
5. Sathiq, M. A., Nasser, A. J. A. & Sirajudeen, P. M. (2011). Adsorption and Corrosion Inhibition Effect of N-(1-Morpholinobenzyl)urea on Mild Steel in Acidic Medium. *E-Journal of Chemistry*, 8, (2), 621-628. doi:10.1155/2011/892548
6. Scendo, M. & Uznanska, J. (2011). Inhibition Effect of 1-Butyl-4-Methylpyridinium Tetrafluoroborate on the Corrosion of Copper in Phosphate Solutions. *International Journal of Corrosion*, ID 761418, 12. doi:10.1155/2011/761418
7. Raphael, V. P., Shanmughan, Sh. K., & Kakkassery, J. Th. Monitoring the Interaction of Two Heterocyclic Compounds on Carbon Steel by Electrochemical Polarization, Noise, and Quantum Chemical Studies. *International Journal of Corrosion*, ID 4204532, 10. doi:10.1155/2016/4204532
8. Khaled, K. F., & El-Maghraby, A. (2014). Experimental, Monte Carlo and molecular dynamics simulations to investigate corrosion inhibition of mild steel in hydrochloric acid solutions. *Arabian Journal of Chemistry*, 7, (3), 319-326
9. Khodaei-Tehrani, M., & Niazi, A. (2015). Quantum chemical studies on the corrosion inhibition of some heterocyclic bases on mild steel in acidic medium. *Oriental Journal of Chemistry*, 31, (1). doi:10.13005/ojc/310150
10. Guo, L., Ren, X., Zhou, Y., Xu, Sh., Gong, Yu., & Zhang, Sh. (2017). Theoretical evaluation of the corrosion inhibition performance of 1,3-thiazole and its amino derivatives. *Arabian Journal of Chemistry*, 10, (1), 121-130. doi:10.1016/j.arabjc.2015.01.005
11. Karthikaiselvi, R., & Subhashini, S. (2014). Study of adsorption properties and inhibition of mild steel corrosion in hydrochloric acid media by water soluble composite poly (vinyl alcohol-*o*-methoxy aniline). *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 16, 74-82. doi:10.1016/j.jaubas.2013.06.002
12. Cardoso, S. P., Gomes, J. A. C. P., Borges, L. E. P., & Hollauer, E. (2007). Predictive QSPR analysis of corrosion inhibitors for super 13% Cr steel in hydrochloric acid. *Brazilian Journal of Chemical Engineering*, 24, (4), 547-559. doi:10.1590/S0104-66322007000400008
13. Prabhu, G. V., Karthik, D., & Tamilvendan, D. (2014). Study on the inhibition of mild steel corrosion by 1,3-bis-(morpholin-4-yl-phenyl-methyl)-thiourea in hydrochloric acid medium. *Journal of Saudi Chemical Society*, 18, (6), 835-844. doi:10.1016/j.jscs.2011.10.009
14. Geethamani, P., & Kasthuri, P. K. (2015). Adsorption and corrosion inhibition of mild steel in acidic media by expired pharmaceutical drug. *Cogent Chemistry*, 1, 1091558. doi:10.1080/23312009.2015.1091558
15. Ghareba, S., Kwan, S., Omanovic, S. (2015). Inhibition of carbon steel corrosion by 11-aminoundecanoic acid. *J. Electrochem. Sci. Eng.*, 5, (3), 157-172. doi:10.5599/jese.242
16. Nasser, A. J. A., & Sathiq, M. A. (2017). Comparative study of *N*-[(4-methoxyphenyl)(morpholin-4-yl)methyl]acetamide (MMPA) and *N*-[morpholin-4-yl(phenyl)methyl]acetamide (MPA) as corrosion inhibitors for mild steel in sulfuric acid solution. *Arabian Journal of Chemistry*, 10, (1), 261-273. doi:10.1016/j.arabjc.2012.07.032
17. Beloglazov, G. S., Sikachina, A. A., & Beloglazov, S. M. (2014). Modelling macroscopic properties of organic species on the basis of quantum chemical analysis (on an example of inhibiting efficiency of “thiourea” and acetylides against corrosion). *Solid State Phenomena*, 225, 7-12. doi:10.4028/www.scientific.net/SSP.225
18. Kolesnikova, N. V. (2004). Vliyanie proizvodnykh sulfanilamidov i ureidov na elektroosazhdenie splava Ni-Mn, ego korroziyu v prisutstvii sulfatredutsiruyushchikh bakterii i mitselialnykh gribov i absorbciiyu vodoroda. Avtoreferat kand. him. Nauk. Kaliningrad, 2004. 7 p.

19. Anbarasi, K. (2016). Electrochemical and Corrosion Inhibition Studies of Cucurbita Maxima. *Oriental Journal of Chemistry*, 32, (4), 2139-2145. doi:10.13005/ojc/320443
20. Pradityana, A., Sulistijono, Shahab, A., Noerochim, L., & Susanti, D. (2016). Inhibition of Corrosion of Carbon Steel in 3.5% NaCl Solution by Myrmecodia Pendans Extract. *International Journal of Corrosion*, ID 6058286, 6. doi:10.1155/2016/6058286
21. Awe, F. E., Idris, S. O., Abdulwahab, M., & Oguzie, E. E. (2015). Theoretical and experimental inhibitive properties of mild steel in HCl by ethanolic extract of Boscia senegalensis. *Cogent Chemistry*, 1, 1112676
22. El-Shamy, O. A. A. (2017). Semiempirical Theoretical Studies of 1,3-Benzodioxole Derivatives as Corrosion Inhibitors. *International Journal of Corrosion*, ID 8915967, 10. doi:10.1155/2017/8915967
23. Laarej, K., Bouachrine, M., Radi, S., Kertit, S., & Hammouti, B. (2010). Quantum Chemical Studies on the Inhibiting Effect of Bipyrazoles on Steel Corrosion in HCl. *E-Journal of Chemistry*, 7, 2, 419-424. doi:10.1155/2010/273206
24. Shukla, H. S., Haldar, N., & Udaybhanu, G. (2012). Binary Mixtures of Nonyl Phenol with Alkyl Substituted Anilines as Corrosion Inhibitors for Mild Steel in Acidic Medium. *E-Journal of Chemistry*, 9, (1), 149-160. doi:10.1155/2012/278496
25. Bouhrira, K., Ouahiba, F., Zerouali, D., Hammouti, B., Zertoubi, M., & Benchat, N. (2010). The Inhibitive Effect of 2-Phenyl-3-nitroso-imidazo [1, 2-a]pyridine on the Corrosion of Steel in 0.5 M HCl Acid Solution. *E-Journal of Chemistry*, 7, (1), 35-42. doi:10.1155/2010/525606
26. Nwankwo, H. U., Ateba, C. N., Olasunkanmi, L. O., Adekunle, A. S., Isabirye, D. A., Onwudiwe, D. C., & Ebenso, E. E. (2016). Synthesis, Characterization, Antimicrobial Studies and Corrosion Inhibition Potential of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane: Experimental and Quantum Chemical Studies. *Materials*, 9, (2), 107. doi:10.3390/ma9020107

Список литературы:

1. Yurt A., Duran B., Dal H. An experimental and theoretical investigation on adsorption properties of some diphenolic Schiff bases as corrosion inhibitors at acidic solution/mild steel interface // *Arabian Journal of Chemistry*. 2014. V. 7. №5. P. 732–740. DOI: 10.1016/j.arabjc.2010.12.010.
2. Dasami P. M., Parameswari K., Chitra S. Inhibition of Mild Steel Corrosion in 1M H₂SO₄ Medium by Benzimidazole Mannich bases // *Oriental Journal of Chemistry*. 2015. V. 31. №1. P. 185-191. DOI: 10.13005/ojc/310120.
3. Karthik D., Tamilvendan D., Prabhu G. V. Study on the inhibition of mild steel corrosion by 1,3-bis-(morpholin-4-yl-phenyl-methyl)-thiourea in hydrochloric acid medium // *Journal of Saudi Chemical Society*. 2014. V. 18. №6. P. 835–844. DOI: 10.1016/j.jscs.2011.10.009.
4. Gupta M., Mishra J., Pitre K. S. Corrosion and Inhibition Effects of Mild Steel in Hydrochloric Acid Solutions Containing Organophosphonic Acid // *International Journal of Corrosion*. 2013. ID 582982. 5 p. DOI: 10.1155/2013/582982.
5. Sathiq M. A., Nasser A. J. A., Sirajudeen P. M. Adsorption and Corrosion Inhibition Effect of N-(1-Morpholinobenzyl)urea on Mild Steel in Acidic Medium // *E-Journal of Chemistry*. 2011. V. 8. №2. P. 621-628. DOI: 10.1155/2011/892548.
6. Scendo M., Uznanska J. Inhibition Effect of 1-Butyl-4-Methylpyridinium Tetrafluoroborate on the Corrosion of Copper in Phosphate Solutions // *International Journal of Corrosion*. 2011. ID 761418. 12 p. DOI: 10.1155/2011/761418.
7. Raphael V. P., Shanmughan Sh. K., Kakkassery J. Th. Monitoring the Interaction of Two Heterocyclic Compounds on Carbon Steel by Electrochemical Polarization, Noise, and Quantum Chemical Studies // *International Journal of Corrosion*. 2016. ID 4204532. 10 p. DOI: 10.1155/2016/4204532.

8. Khaled K. F., El-Maghraby A. Experimental, Monte Carlo and molecular dynamics simulations to investigate corrosion inhibition of mild steel in hydrochloric acid solutions // *Arabian Journal of Chemistry*. 2014. V. 7. №3. P. 319-326.
9. Khodaei-Tehrani M., Niazi A. Quantum chemical studies on the corrosion inhibition of some heterocyclic bases on mild steel in acidic medium // *Oriental Journal of Chemistry*. 2015. V. 31. №1. DOI: 10.13005/ojc/310150.
10. Guo L., Ren X., Zhou Y., Xu Sh., Gong Yu., Zhang Sh. Theoretical evaluation of the corrosion inhibition performance of 1,3-thiazole and its amino derivatives // *Arabian Journal of Chemistry*. 2017. V. 10. №1. P. 121-130. DOI: 10.1016/j.arabjc.2015.01.005.
11. Karthikaiselvi R., Subhashini S. Study of adsorption properties and inhibition of mild steel corrosion in hydrochloric acid media by water soluble composite poly (vinyl alcohol-*o*-methoxy aniline) // *Journal of the Association of Arab Universities for Basic and Applied Sciences*. 2014. V. 16. P. 74-82. DOI: 10.1016/j.jaubas.2013.06.002.
12. Cardoso S. P., Gomes J. A. C. P., Borges L. E. P., Hollauer E. Predictive QSPR analysis of corrosion inhibitors for super 13% Cr steel in hydrochloric acid // *Brazilian Journal of Chemical Engineering*. 2007. V. 24. №4. P. 547-559. DOI: 10.1590/S0104-66322007000400008.
13. Prabhu G. V., Karthik D., Tamilvendan D. Study on the inhibition of mild steel corrosion by 1,3-bis-(morpholin-4-yl-phenyl-methyl)-thiourea in hydrochloric acid medium // *Journal of Saudi Chemical Society*. 2014. V. 18. №6. P. 835-844. DOI: 10.1016/j.jscs.2011.10.009.
14. Geethamani P., Kasthuri P. K. Adsorption and corrosion inhibition of mild steel in acidic media by expired pharmaceutical drug // *Cogent Chemistry*. 2015. V. 1. 1091558. DOI: 10.1080/23312009.2015.1091558.
15. Ghareba S., Kwan S., Omanovic S. Inhibition of carbon steel corrosion by 11-aminoundecanoic acid // *J. Electrochem. Sci. Eng.* 2015. V. 5. №3. P. 157-172. DOI: 10.5599/jese.242.
16. Nasser A. J. A., Sathiq M. A. Comparative study of *N*-[(4-methoxyphenyl) (morpholin-4-yl)methyl]acetamide (MMPA) and *N*-[morpholin-4-yl(phenyl)methyl]acetamide (MPA) as corrosion inhibitors for mild steel in sulfuric acid solution // *Arabian Journal of Chemistry*. 2017. V. 10. №1. P. 261-273. DOI: 10.1016/j.arabjc.2012.07.032.
17. Beloglazov G. S., Sikachina A. A., Beloglazov S. M. Modelling macroscopic properties of organic species on the basis of quantum chemical analysis (on an example of inhibiting efficiency of “thiourea” and acetylides against corrosion) // *Solid State Phenomena*. 2014. V. 225. P. 7-12. DOI: 10.4028/www.scientific.net/SSP.225.
18. Колесникова Н. В. Влияние производных сульфаниламидов и уреидов на электроосаждение сплава Ni-Mn, его коррозию в присутствии сульфатредуцирующих бактерий и мицелиальных грибов и абсорбцию водорода: автореф. дис. ... канд. хим. наук. Калининград, 2004. 17 с.
19. Anbarasi K. Electrochemical and Corrosion Inhibition Studies of Cucurbita Maxima // *Oriental Journal of Chemistry*. 2016. V. 32. №4. P. 2139-2145. DOI: 10.13005/ojc/320443.
20. Pradityana A., Sulistijono, Shahab A., Noerochim L., Susanti D. Inhibition of Corrosion of Carbon Steel in 3.5% NaCl Solution by Myrmecodia Pendans Extract // *International Journal of Corrosion*. ID 6058286. 6 p. DOI: 10.1155/2016/6058286.
21. Awe F. E., Idris S. O., Abdulwahab M., Oguzie E. E. (2015). Theoretical and experimental inhibitive properties of mild steel in HCl by ethanolic extract of *Boscia senegalensis* // *Cogent Chemistry*. 2015 V. 1). 1112676.
22. El-Shamy O. A. A. Semiempirical Theoretical Studies of 1,3-Benzodioxole Derivatives as Corrosion Inhibitors // *International Journal of Corrosion*. 2017. ID 8915967. 10 p. DOI: 10.1155/2017/8915967.

23. Laarej K., Bouachrine M., Radi S., Kertit S., Hammouti B. Quantum Chemical Studies on the Inhibiting Effect of Bipyrazoles on Steel Corrosion in HCl // *E-Journal of Chemistry*. 2017. V. 7. №2. P. 419-424. DOI: 10.1155/2010/273206.

24. Shukla H. S., Haldar N., Udaybhanu G. Binary Mixtures of Nonyl Phenol with Alkyl Substituted Anilines as Corrosion Inhibitors for Mild Steel in Acidic Medium // *E-Journal of Chemistry*. 2012. V. 9. №1. P. 149-160. DOI: 10.1155/2012/278496.

25. Bouhrira K., Ouahiba F., Zerouali D., Hammouti B., Zertoubi M., Benchat N. The Inhibitive Effect of 2-Phenyl-3-nitroso-imidazo [1, 2-a]pyridine on the Corrosion of Steel in 0.5 M HCl Acid Solution // *E-Journal of Chemistry*. 2010. V. 7. №1. P. 35-42. DOI: 10.1155/2010/525606.

26. Nwankwo H. U., Ateba C. N., Olasunkanmi L. O., Adekunle A. S., Isabirye D. A., Onwudiwe D. C., Ebenso E. E. Synthesis, Characterization, Antimicrobial Studies and Corrosion Inhibition Potential of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane: Experimental and Quantum Chemical Studies // *Materials*. 2016. V. 9. №2. DOI: 10.3390/ma9020107.

*Работа поступила
в редакцию 19.06.2017 г.*

*Принята к публикации
22.06.2017 г.*

Cite as (APA):

Sikachina, A. (2017). Quantum chemical modeling of adsorption of thiourea derivatives, that used as inhibitors of microbiological corrosion on the iron of St3s grade of steel. *Bulletin of Science and Practice*, (7), 8-21

Ссылка для цитирования:

Sikachina A. Quantum chemical modeling of adsorption of thiourea derivatives, that used as inhibitors of microbiological corrosion on the iron of St3s grade of steel // *Бюллетень науки и практики*. Электрон. журн. 2017. №7 (20). С. 8-21. Режим доступа: <http://www.bulletennauki.com/sikachina-a-a> (дата обращения 15.07.2017).