

Mathematical and Quantum Chemical Studies for The Corrosion Inhibition of Steel in HCL Acid

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ABSTRACT - The application of empirical and quantum chemical models on the corrosion inhibition of steel in hydrochloric acid in presence of phenylthiourea (PTU) as corrosion inhibitor have been modeled. Two mathematical models were used, third order polynomial model and Arrhenius type equation model. Levenberg-Marquardt method was used to evaluate the coefficients of two Models. Two models were suitable to represent the corrosion rate data at different conditions. The correlation coefficient of third order model was 0.973, while for the Arrhenius type model was 0.919. The structure of inhibitor was optimized by ArgusLab 4.0.1 package. The quantum chemical parameters (E_{HOMO} , E_{LUMO} , ΔE , and dipole moment μ) were estimated by PM3-SCF method.

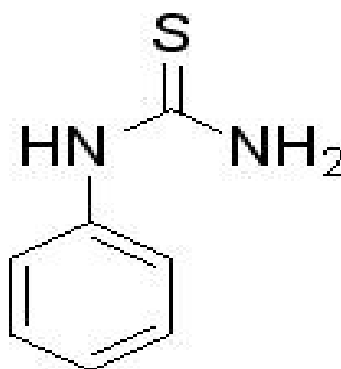
Keywords: - Quantum chemical, Corrosion inhibition, Hydrochloric acid, Carbon steel.

1- INTRODUCTION

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals and alloys. Steel has found wide application in a broad spectrum of industries and machinery; however, its tendency to corrosion. The corrosion of steel is a fundamental academic and industrial concern that has received a considerable amount of attention ⁽¹⁾. Using inhibitors is an important method of protecting materials against deterioration due to corrosion, especially in acidic media ⁽²⁾. Acid solutions are widely used in industry, some of the important fields of application being acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. As acidic media, HCl and H₂SO₄ are generally used in the treatment of steel and ferrous alloys. Because of the general aggression of acid solutions, inhibitors are commonly used to reduce the corrosive

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attack on metallic materials. Thiourea and its derivatives are widely used as acid inhibitors in industrial operations, such as pickling, descaling, cleaning, acidization of oil wells, to protect metals and alloys^(3,4). Extensive studies had been done on the effects of thiourea and some of its derivatives on the corrosion behavior of various metals and on the mechanism of inhibitive action. This kind of corrosion inhibitors acting as a protective film is superior to the amine-based inhibitors in acidic media and simultaneously acts on both anodic and cathodic areas. The organic substances belonging to this group contain mainly oxygen, sulfur, nitrogen atoms, which are strongly polar and facilitate the adsorption on the metal surface^(5,6). The use of organic compounds containing oxygen, sulphur and nitrogen to reduce corrosion attack on steel has been studied in some details⁽⁷⁻¹⁰⁾. Sulphur and nitrogen containing compounds are more effective as corrosion inhibitor in hydrochloric acid⁽¹¹⁾. The existing data show that most organic inhibitors get adsorbed on the metal surface by displacing water molecules and form a compact barrier film⁽¹²⁾. Due to availability of lone pairs and π electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal, forming a coordinate covalent bond⁽¹³⁾. The strength of the adsorption bond depends on the electron density on the donor atom of the functional group and also the polarisability of the group. Thiourea and its derivatives are widely used as acid inhibitors in industrial operations, such as pickling, descaling, cleaning, acidization of oil wells, to protect metals and alloys⁽¹⁴⁾. The corrosion inhibitor acts as a protective film and is superior to amine-based inhibitors in acidic media. This kind of inhibitor simultaneously acts in both anodic and cathodic areas. The organic substances belonging to this group contain mainly oxygen, sulfur, nitrogen atoms, and multiple bonds in the molecules that facilitate the adsorption on the metal surface⁽¹⁵⁾. Sulfur compounds, such as thiourea derivatives, are very effective corrosion inhibitors for steel in acidic conditions because of sulfur atom is easily protonated in acidic solution and a stronger electron donor than nitrogen. Therefore, sulfur atom is more strongly adsorbed to the metal surface⁽¹⁶⁾. The molecular structure of phenylthiourea (PTU) is shown as follows:



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Phenylthiourea (PTU) corrosion rate data were used in a present work ⁽¹⁷⁾. Al-Taie ⁽¹⁷⁾ studied the corrosion reaction of low carbon steel in 1, 3, and 5 M HCl, at 303, 313, 323, and 333 K, in presence of 0.00065, 0.005, and 0.0065 M Phenylthiourea (PTU) as a corrosion inhibitor at fixed speed of rotation for specimens of 600 rpm. These data were analyzed mathematically and chemically by using a software computer programs.

2- MATHEMATICAL STUDIES

The experimental corrosion rate results in inhibited HCl acid as a function of acid concentration, temperature and inhibitor concentration are given in Table 1. These data supplied by Chemical Engineering Department – Baghdad University from the experimental work of Al-Taie ⁽¹⁷⁾.

Many relationships can be suggested to correlate these variables. Third order polynomial model was used to represent these variables as follows;

$$Y = C_0 + C_1X_1 + C_2X_1^2 + C_3X_1^3 + C_4X_1X_2^2 + C_5X_1X_3^2 + C_6X_1X_2X_3 + C_7X_2 + C_8X_2^2 + C_9X_2^3 + C_{10}X_2X_3^2 + C_{11}X_3 + C_{12}X_3^2 + C_{13}X_3^3 + C_{14}X_3X_2^2 + C_{15}X_1X_2 + C_{16}X_1X_3 + C_{17}X_2X_3$$

.....(1)

Where; Y: Corrosion Rate ($\mu\text{A}\cdot\text{cm}^{-2}$)

X_1 : Inhibitor Concentration (M)

X_2 : Acid Concentration (M)

X_3 : Absolute Temperature (K)

And, $C_1, C_2, C_3, \dots, C_{17}$ are constants.

Equation (1) used as a first model (Model I) to represent the results. The corrosion rate results can be related to temperature by Arrhenius type equation, which expressed as follows:

$$\text{Corr.Rate} = A \exp\left(-\frac{E}{RT}\right) \quad \text{.....(2)}$$

It is known also, that the corrosion rate decreases as the inhibitor concentration increased and as acid concentration decreased, so;

$$\text{Corr.Rate} \propto \left(\frac{C_a^m}{C^n}\right) \quad \text{.....(3)}$$

Where C_a is acid concentration and C is inhibitor concentration, where both in M, and m, n are constants. So, it is suggested a new model to correlate the corrosion rate data

($\mu\text{A}\cdot\text{cm}^{-2}$), as a function of temperature (K), and inhibitor concentration (M), and acid concentration (M) through the following proposed equation;

$$\text{Corr.Rate} = \text{Cons} \tan t \left(\frac{C_a^m}{C^n} \right) \exp \left(-\frac{E}{RT} \right) \quad \dots(4)$$

Then, the second model (Model II) suggested in term of Y, X₁, X₂ and X₃ as in the first model is;

$$Y = C_o \left(\frac{X_2^{C_1}}{X_1^{C_2}} \right) \exp \left(-\frac{C_3}{X_3} \right) \quad \dots(5)$$

Where; C₁, C₂, C₃ are another constants.

Using non-linear least squares model estimation by STATISTICA 7 software. Levenberg-Marquardt method was used to evaluate the coefficients of Models I and II. These coefficients were shown in Table 2. Figures 1 and 2 shows the predicated corrosion rate which evaluated by the models against the observed values. From Table 2 and Figure 1 we can see that model I can represent the corrosion rate data with 0.973 correlation coefficient. Also Figures (3-11) shows the approach between the experimental corrosion rates and the modeled values. The coefficients of M₁ shows that the third order effect of variables were neglected, i.e. the values of C₂, C₃, C₁₀ and C₁₃ were all zero. Table 2, shows also the coefficients and correlations coefficient of model II. The constant C_o and C₃ in model II, can be compared with the values of A (frequency factor) and E/R (activation energy/gas constant) in Arrhenius equation respectively. The value of C_o is 3.727×10^9 which agrees with the order of experimental values of Al-Taie ⁽¹⁷⁾. The value of C₃ is 5.951×10^3 , and this represents the value of $\left(\frac{E}{2.303R} \right)$. This mean that E=55.361 kJ/mol., which agrees with the experimental average value (=66.587 kJ/mol) of Al-Taie ⁽¹⁷⁾.

3- QUANTUM CHEMICAL STUDIES

It is understood that computational methods have a potential application towards the design and development of organic corrosion inhibitors in corrosion field. Quantum chemical calculations have proved to be a very powerful tool for studying corrosion inhibition mechanism ⁽¹⁸⁾. Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity ⁽¹⁹⁾. Thus, a theoretical study was undertaken to observe its possible physical characters which could contribute to inhibition, and it has become a common practice to carry

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out quantum chemical calculations in corrosion inhibition studies. The study of corrosion processes and their inhibition by organic inhibitors is a very active field of research⁽²⁰⁾. Many researchers report that the inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and so on^(6,7). The inhibiting mechanism is generally explained by the formation of a physically and/or chemically adsorbed film on the metal surface^(21, 22). It is well known that organic compounds which act as inhibitors are rich in heteroatoms, such as sulphur, nitrogen, and oxygen^(23, 24). These compounds and their derivatives are excellent corrosion inhibitors in a wide range of media and are selected essentially from empirical knowledge based on their macroscopic physico-chemical properties. Recently, theoretical prediction of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations⁽²⁰⁾. In order to investigate the charge distribution of inhibitors molecule, quantum chemical calculations were performed by ArgusLab 4.0.1 package. The highest occupied molecular orbitals (HOMO), lowest unoccupied molecular orbital (LUMO) and dipole moment were calculated and presented in Figure 12, Table 3. It is confirmed that the more negative the atomic partial charges of the adsorbed centre are, the more easily the atom attracted to the metal surface. Table 3 show some of the key quantum chemical parameters were computed using the PM3-SCF method. These are mainly the energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals and total energy (E_{tot}). These quantum chemical parameters were obtained after geometric optimization with respect to the all nuclear coordinates. Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants⁽²⁰⁾. The HOMO–LUMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index.

A large HOMO–LUMO gap implies high stability for the molecule in chemical reactions. Moreover, the gap between the LUMO and HOMO energy levels of the molecules was another important factor that should be considered. Reportedly, excellent corrosion inhibitors are usually those organic compounds who are not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal. Quantum chemical parameters listed in Table 3 reveal that PTU has high HOMO and Low LUMO with high energy gap. In other hand, the dipole moment μ is the most widely used quantity to describe the polarity is the dipole moment of the molecule ⁽²⁰⁾. Dipole moment is the measure of polarity of a polar covalent bond. It is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments.

Charge-based parameters have been widely employed as chemical reactivity indices or as measures of weak intermolecular interactions there are many methods for estimating the partial charges. Mulliken population analysis ⁽²⁰⁾ is mostly used for the calculation of the charge distribution in a molecule. Furthermore, atomic charges are used for the description of the molecular polarity of molecules. The Mulliken charge distribution of PTU inhibitor was presented in Table 4 and Figure 12. It could be readily observed that nitrogen, sulfur and benzene cycle had higher charge density and may form the adsorption centers.

4- CONCLUSION

The two suggested models to represent the corrosion rate data of steel in HCl acid in presence of PTU as a corrosion inhibitor were very suitable at different conditions. This study also demonstrates that quantum chemistry is a powerful tool to study the fundamental, molecular-level processes related to corrosion inhibition. Quantum chemical calculations show that PTU can adsorbed as molecular species using sulfur, nitrogen and benzylic carbons as its active centers.

5- ACKNOWLEDGMENT

The author would like to thank University of Baghdad, Chemical Engineering Department for assistance and supplying the research data.

6- REFERENCES

1. F. Bentiss, M. Traisnel, M. Lagrenee, The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media, *Corros. Sci.* 42 (2000) 127–146.
2. G. TrabANELLI, Inhibitors an old remedy for a new challenge, *Corrosion* 47 (1991) 410–419.
3. C.B. Shen , D.Y.Han , Z.M. Ding, The inhibition effect of thiourea on bulk nanocrystallized ingot iron in acidic sulfate solution, *Material Chemsriy and Physics*, 109 (2008) 417-421.
4. B. Donnely, T.C. Downie, R. Grzeskourak, *Corros. Sci.* 14 (1974)597.
5. M.A. Quraishi, M.A.W. Khan, M. Ajmal, *Anti-Corros. Methods Mater.* 43 (1996) 5.
6. N.A. Andis, E. Khamis, A. Al-Mayouf, H. AboulEnein, *Corros. Prev. Control* 42 (1995) 135.
7. M. Elachauri, M.S. Hajji, S. Kertit, E.M. Salem, R. Coudert, Corrosion of iron in electrolytic anhydrous methanol solutions containing ferric chloride, *Corros. Sci.* 37 (1995) 823-381.
8. B. Mernari, H. Elattari, M. Traisnel, F. Bentiss, M. Lagrenee, Electrochemical and quantum chemical studies of 3,5-Di (n-Tolyl)-4-amino-1,2,4-triazole adsorption on mild steel in acidic media *Corrosion* 58 (2002) 399-407.
9. L. Wang, Evaluation of 2-mercaptobenzimidazole as corrosion inhibitor for mild steel in phosphoric acid, *Corros. Sci.* 43 (2001) 2281-2289.
10. M.E. Azhar, M. Mernari, M. Traisnel, F. Bentiss, M. Lagrenee, Corrosion inhibition of mild steel by the new class of inhibitors [2,5-bis(*n*-pyridyl)-1,3,4-thiadiazoles] in acidic media *Corros. Sci.* 43 (2001) 2229-2238.
11. F. Bentiss, M. Traisnel, M. Lagrenee, The substituted 1, 3, 4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media, *Corros. Sci.* 42 (2000) 127-146.
12. M.A. Quraishi, Sudhish Kumar Shukla, Poly (aniline-formaldehyde): A new and effective corrosion inhibitor for mild steel in hydrochloric acid, *Mater. Chem. Phys.* 113 (2009) 685–689
13. L.R. Chauhan and G. Gunasekaran, Corrosion inhibition of mild steel by plant extract in dilute HCl medium, *Corros. Sci.* 49 (2007) 1143–1161.
14. C.B. Shen, S.G. Wang, H.Y. Yang, K. Long, F.H. Wang, Corrosion and corrosion inhibition by thiourea of bulk nanocrystallized industrial pure iron in dilute HCl solution, *Corros. Sci.* 48 (2006) 1655–1665.

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15. M.A. Quraishi, M.A.W. Khan, M. Ajmal, Influence of some thiazole derivatives on the corrosion of mild steel in hydrochloric acid, *Anti-Corros. Methods Mater.* 43 (1996) 5-8.
16. S.A. Ali, M.T. Saeed, S.V. Rahman, The isoxazolidines: a new class of corrosion inhibitors of mild steel in acidic medium, *Corros. Sci.* 45 (2003) 253-266.
17. Al Taie, A. S, "*Ms.C Thesis*", university of Baghdad, College of Engineering, Department of Chemical Engineering (2004).
18. Leidheise, H., "The Corrosion of Copper, Tin, and their Alloys", (1971).
19. E. Kraka, D. Cremer, Computer design of anticancer drugs, *J. Am. Chem. Soc.* 122 (2000) 8245–8264.
20. G. Gece, The use of quantum chemical methods in corrosion inhibitor studies, *Corrosion Science* 50 (2008) 2981–2992.
21. F. Touhami, A. Aouniti, Y. Abed, B. Hammouti, S. Kertit, A. Ramdani, K. Elkacemi, Corrosion inhibition of armco iron in 1 M HCl media by new bipyrazolic derivatives, *Corros. Sci.* 42 (2000) 929–940.
22. L. Tang, X. Li, L. Li, G. Mu, G. Liu, Interfacial behavior of 4-(2-pyridylazo) resorcin between steel and hydrochloric acid, *Surf. Coat. Technol.* 201 (2006) 384–388.
23. M. Hosseini, S.F.L. Mertens, M. Ghorbani, M.R. Arshadi, Asymmetrical Schiff bases as inhibitors of mild steel corrosion in sulphuric acid media, *Mater. Chem. Phys.* 78 (2003) 800–808.
24. N.C. Subramanyam, B.S. Sheshardi, S.A. Mayanna, Thiourea and substituted thioureas as corrosion inhibitors for aluminium in sodium nitrite solution, *Corros. Sci.* 34 (1993) 563–571.

Table (1):- Corrosion Parameters at different conditions and fixed speed of rotation

HCl (M)	Temp (K)	0.00065 (M) PTU	0.005 (M) PTU	0.0065 (M) PTU
		i_{corr} ($\mu\text{A}/\text{cm}^2$)		
1	303	21.19	17.22	14.93
	313	65.98	50.16	42.93
	323	111.71	64.84	58.77
	333	199.35	109.24	92.3
3	303	91.55	51.46	46.5
	313	111.34	85.65	67.03
	323	903.89	576.15	379
	333	1088.58	876.04	527

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5	303	125.05	84.22	70.69
	313	399.23	289.9	229.39
	323	2022.95	1576.41	1182.42
	333	1840.71	1622.14	1354.15

Table (2):- Coefficients of models I and II with its correlation coefficients

Coefficients	Model I	Model II		
	Values	Correlation Coefficient	Values	Correlation Coefficient
C ₀	10400437		3.727×10 ⁹	
C ₁	6099774		-0.154	
C ₂	0		1.498	
C ₃	0		2.951×10 ³	
C ₄	2916			
C ₅	59			
C ₆	-616			
C ₇	-7351126			
C ₈	2869432	R=0. 973		R=0. 919
C ₉	-318848			
C ₁₀	0			
C ₁₁	-53003			
C ₁₂	167			
C ₁₃	0			
C ₁₄	1			
C ₁₅	165108			
C ₁₆	-37881			
C ₁₇	100			

Table (3):- Simulated and quantum chemical parameters for PTU inhibitor

E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	Dipole moment (debye)
-8.718	-0.415	8.302	5.12651209

Table (4):- Mulliken atomic charge density of PTU molecule

No	Atom	Charge	No	Atom	Charge	No	Atom	Charge
1	C	-0.2324	7	H	0.2013	13	C	0.1910
2	C	0.0919	8	H	0.1784	14	N	-0.5372
3	C	-0.2292	9	H	0.2013	15	S	-0.2831
4	C	-0.1523	10	H	0.2021	16	H	0.2909

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5	C	-0.2166	11	H	0.1975	17	H	0.3324
6	C	-0.1553	12	N	-0.4229	18	H	0.3421

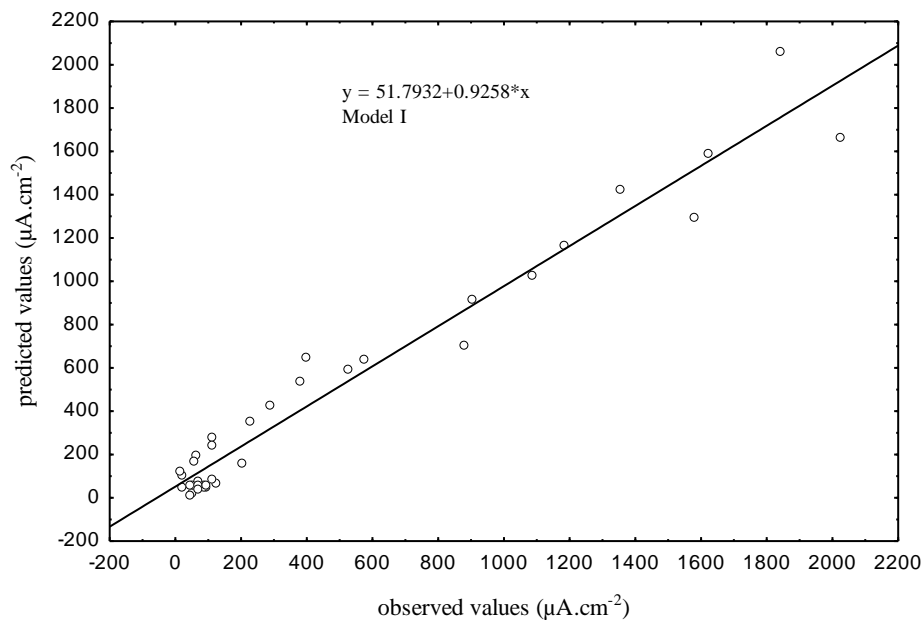


Fig. (1):- Predicated against observed corrosion rates at different conditions from model I

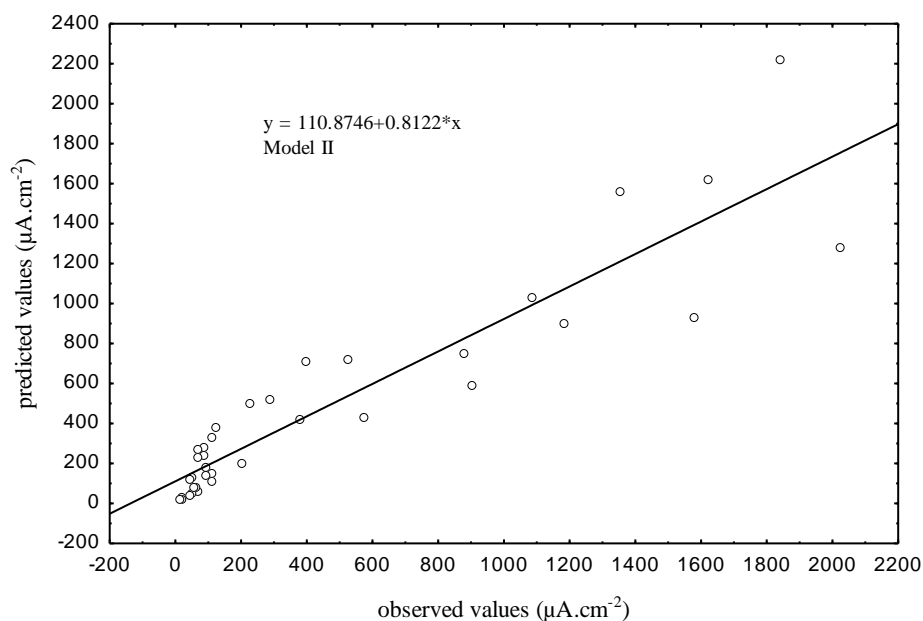


Fig. (2):- Predicated against observed corrosion rates at different conditions from model II

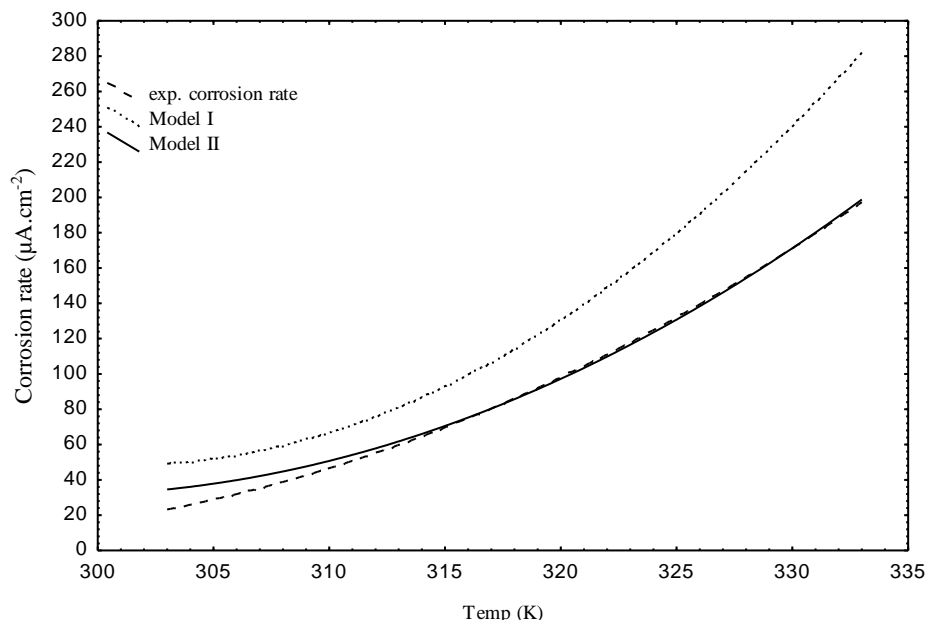


Fig. (3):- Experimental and model corrosion rates as a function of temperature at 0.00065M PTU and 1M HCL acid

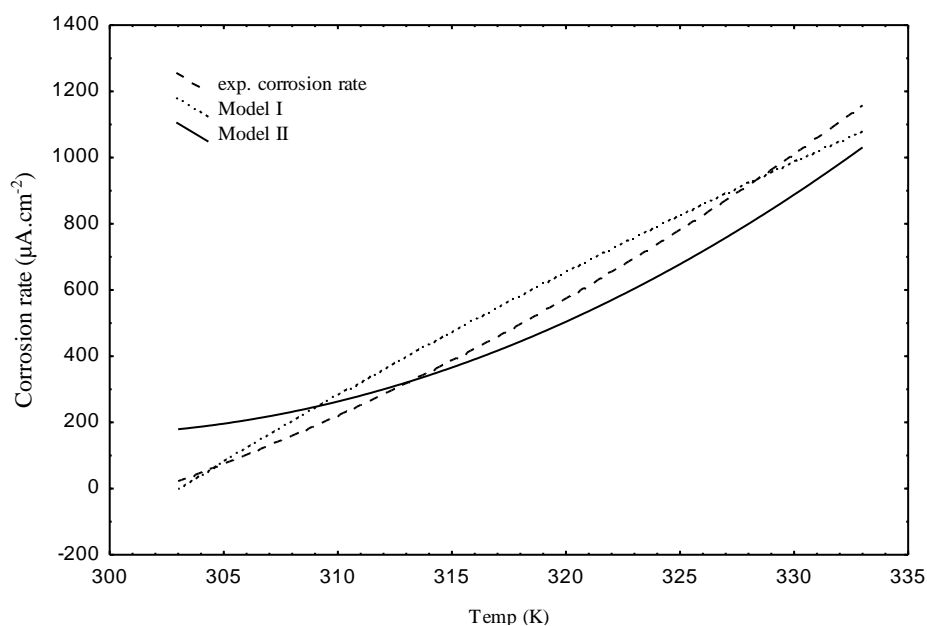


Fig. (4):- Experimental and model corrosion rates as a function of temperature at 0.00065M PTU and 3M HCL acid

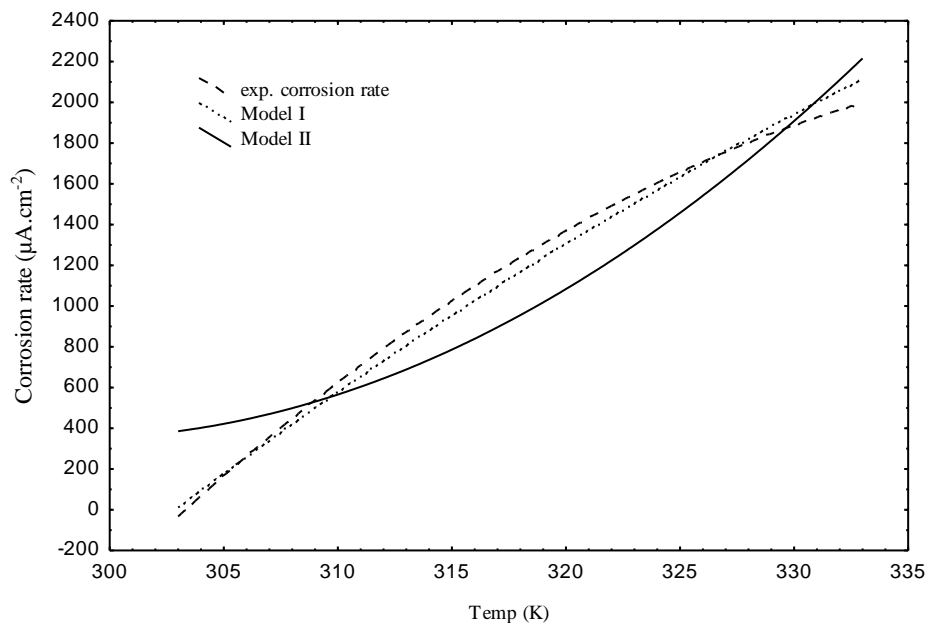


Fig. (5):- Experimental and model corrosion rates as a function of temperature at 0.00065M PTU and 5M HCL acid

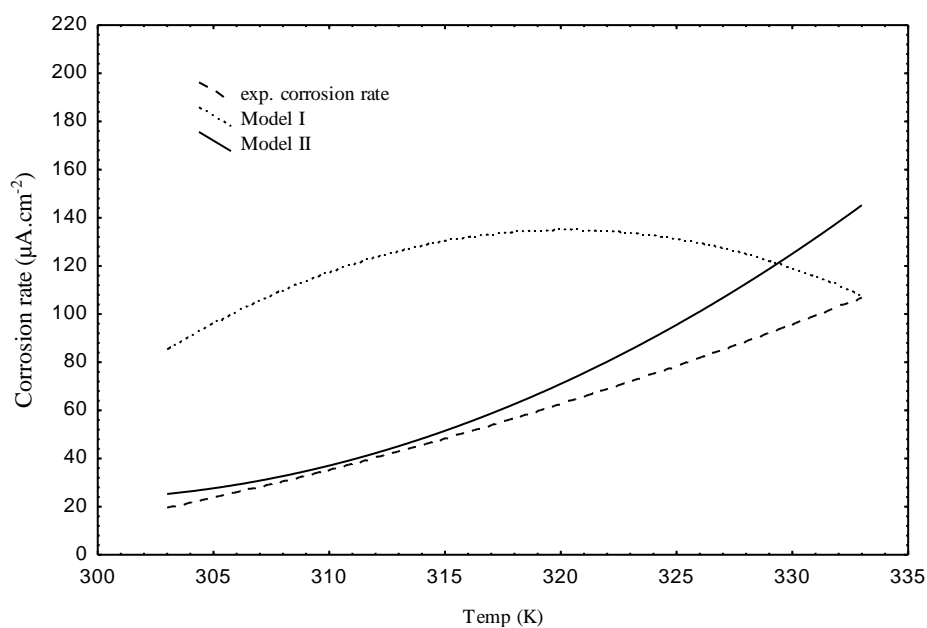


Fig. (6):- Experimental and model corrosion rates as a function of temperature at 0.005M PTU and 1M HCL acid

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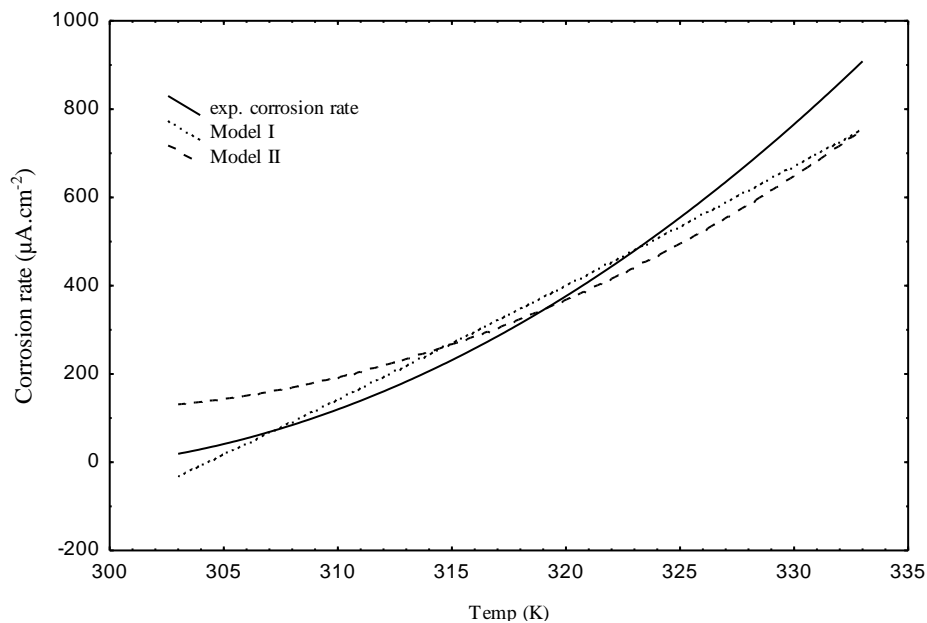


Fig. (7):- Experimental and model corrosion rates as a function of temperature at 0.005M PTU and 3M HCL acid

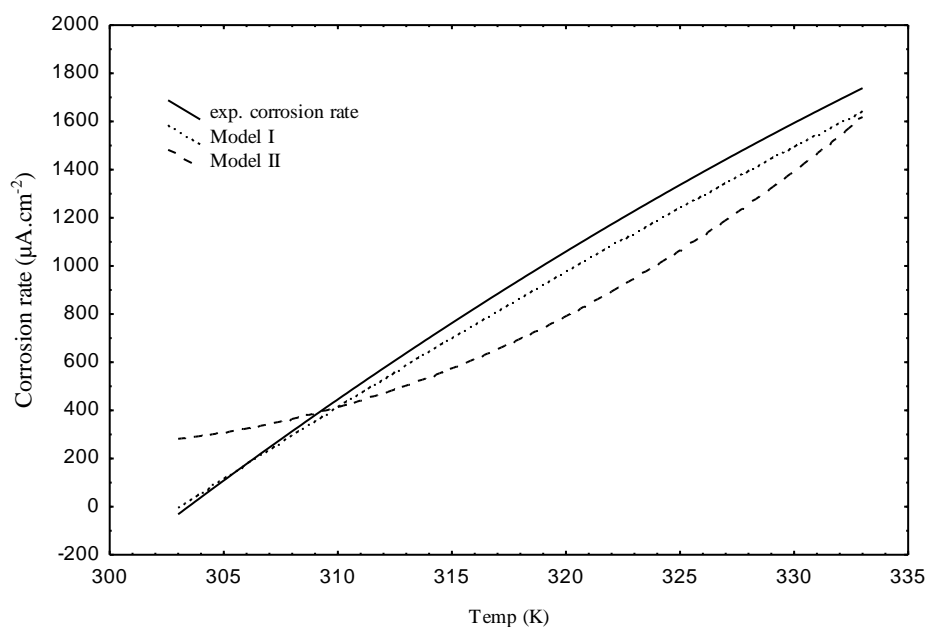


Fig. (8):- Experimental and model corrosion rates as a function of temperature at 0.005M PTU and 5M HCL acid

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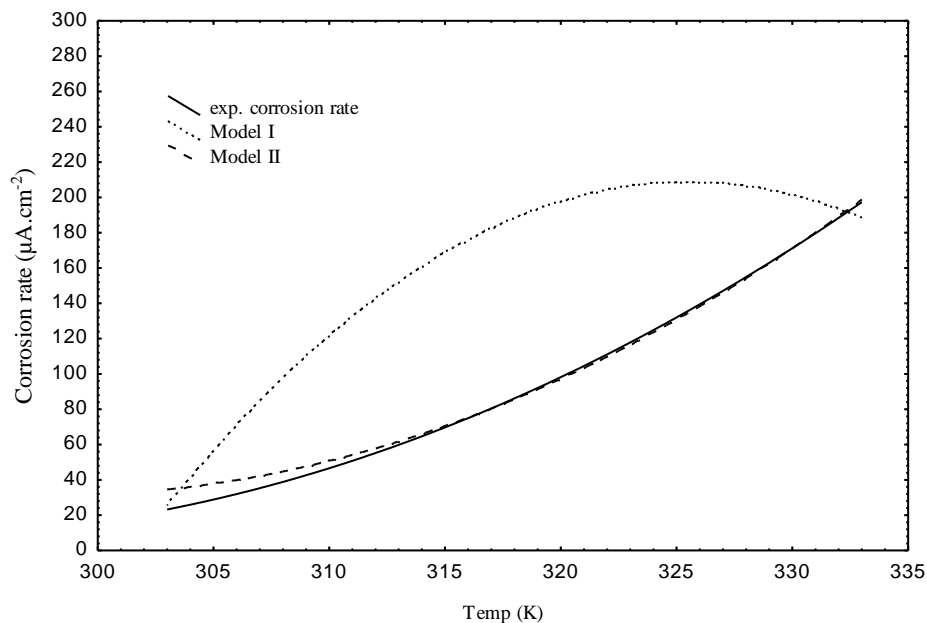


Fig. (9):- Experimental and model corrosion rates as a function of temperature at 0.0065M PTU and 1M HCL acid

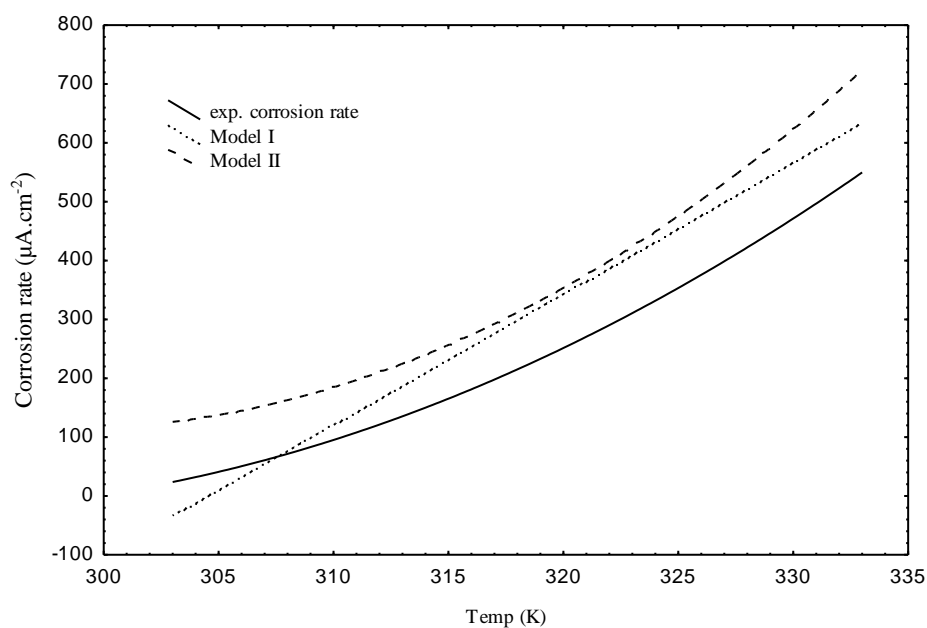


Fig. (10):- Experimental and model corrosion rates as a function of temperature at 0.0065M PTU and 3M HCL acid

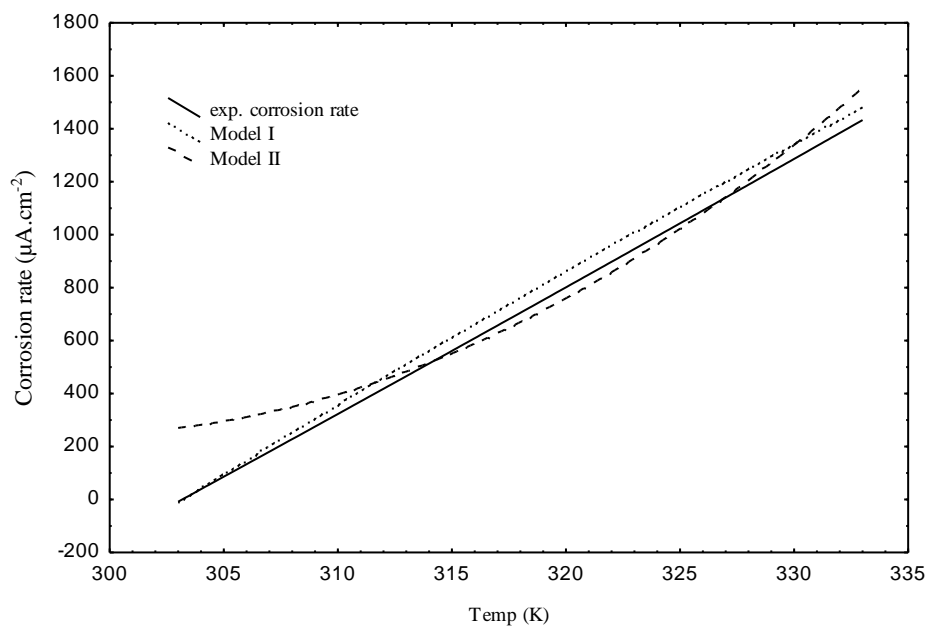
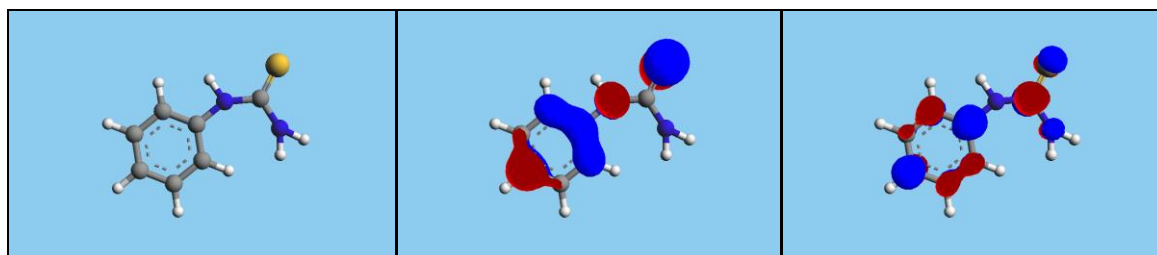


Fig. (11):- Experimental and model corrosion rates as a function of temperature at 0.0065M PTU and 5M HCL acid



a

b

c

Fig. (12):- (a) optimized geometry of PTU molecule
(b) HOMO energy density of PTU
(c) LUMO energy density of PTU.

دراسات رياضية وكمية لمنع تآكل الفولاذ في حامض الهيدروكلوريك

د. انيس عبدالله كاظم

مدرس

جامعه ديالى – كلية الهندسة

الخلاصة

تم تطبيق الموديلات الرياضية وموديلات الكيمياء الكمية على عملية تآكل الحديد الفولاذي في حامض الهيدروكلوريك بوجود الفينيل ثايويوريا كمادة مانعة للتآكل. تم اقتراح موديلين رياضيين لغرض تمثيل بيانات عملية التآكل. الموديل الأول هو متوالية من الدرجة الثالثة والموديل الثاني هو موديل يسلك نفس سلوك معادلة ارينيوس. تم استخدام برنامج حاسوبي لغرض إيجاد معاملات هذه الموديلات. ولقد وجد ان كلا الموديلين قادر على تمثيل بيانات عملية التآكل، حيث كان معامل ارتباط الموديل الأول ٠.٩٧٣ وللموديل الثاني هو ٠.٩١٩. تم أيضا إيجاد البنية المتألية للمثبط عن طريق استخدام برنامج حاسوبي مخصص لهذا الغرض ومن خلال هذا البرنامج أيضا تم إيجاد بعض المعاملات المهمة في الكيمياء الكمية.

الكلمات الدالة: كيمياء كمية , منع التآكل, حامض الهيدروكلوريك, فولاذ كاربوني.