ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Corrosion Protection of Carbon Steel By Voltaren Drug in Acid Media and Theoretical Studies.

Ahlam Mohammed Farhan[1], Rasha abd Jasim[1], and Abdulkareem M. Ali[2]*.

[1]Department of Chemistry /College of Science of Women /University of Baghdad, Iraq, Baghdad.
[2]Department of Chemistry /College of Science /University of Baghdad, Iraq, Baghdad.

ABSTRACT

Recently, the metal carbon steel dissolution n 0.2N HCl solution is protected by using 2-(2-(2, 6-dichlorophenyl amino) phenyl) acetic acid using (EIS) measurements, potentiodynamic polarization, and (W.L). It is shown that these inhibitions are perfect corrosion inhibitiors for carbon steel protection. The adsorption of inhibitor of molecules on the carbon steel surface affects inhibitions activity were refer to the simple blocking . The results show that inhibitors play a mix- type inhibitor. The program of hyperchem-8 used in theoretical study of the voltaren drug the using molecular mechanics and semi-empirical calculation .The binding energy (ΔE_b), heat of formation (ΔH_F),and total energy ($\Delta E_{tot.}$) of the voltaren is calculated using PM3 method at 298K .The is calculated bond length and vibration spectra of drug complex used PM3.The theoretical data are compared with experimental result that same with those found experimentally.

Keywords: carbon steel, voltern drug, hydrochloric acid and theoretical studied, corrosion.

Corresponding author

ISSN: 0975-8585

INTRODUCTION

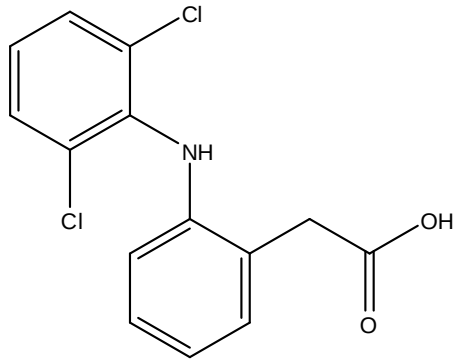
The corrosion of metals is a fundamental academic and processing concern that has received a big amount of care .The remove of rust and scale in several industrial processes by using acid solution are generally [1,2].The environmental chemicals with zero environmental impacts are best for corrosion prevention systems. The lessening corrosion rate of metals provides decreasing the dissolution of toxic metals from the composition into the environment and also a rising the lifetime of equipments lead to the saving of resources and economical benefits during the industrial applications. Organic molecules has been used corrosion inhibitor become increasingly popular; also it is the most practical methods for protecting metals against the corrosion [3-11].Corrosion inhibitors used is based on the following :

1-Drug molecular that contains sulfur, nitrogen and oxygen as active center

2-Drug can be easily purified and produced.

3-Drugs are important in biological reactions and reportedly environmentally friendly [12]. Forming protective barrier over the carbon steel surface and removing water molecule is due to the blocking of the active sites which decreases in the corrosion rate. The results that this compound interacts with the anodic and, or catholic reaction [13,14]. The voltaren drug is used as a corrosion inhibitor for carbon steel in acid media .The mathematical program is used automatically on a computer generally computational chemistry .The input field of computational chemistry is built around approximate solution .The solution is more accurate than any experiment that has yet been conducted but some of these solutions are very crude [15]. Molecular modeling could be synthesized in the laboratory and can be modeled with the hope that the particular molecular system and computational chemistry ,especially for species that are not easy ,dangerous ,not cheap or impossible to carry out experimentally .Molecular modeling is a simple method tat has properties of similar geometric bond distances, bond angles, electronic structures , chemical shifts, and frequencies .The best in predicating the vibration frequencies of transition and geometric properties and organ metallic complexes calculations by semi empirical PM3[16].This is further comfirmed with this study which also shows that PM3 calculations work perfectly as they predict closely the calculated properties with experimental result. The usefulness of the semi-empirical,PM3 is that it calculates and predicts the vibration modes [17].

Chemical Formula: $C_{14}H_{11}Cl_2NO_2$
Exact Mass: 295.02
Molecular Weight: 296.15
m/z: 295.02 (100.0%), 297.01 (63.9%), 296.02 (15.3%), 299.01 (10.3%), 298.02 (9.9%), 300.01 (1.6%), 297.02 (1.5%)
Elemental Analysis: C, 56.78; H, 3.74; Cl, 23.94; N, 4.73; O, 10.80



2-(2-(2,6-dichlorophenylamino)phenyl)acetic acid

ISSN: 0975-8585

This work is aims at to studying the inhibitive voltaren towards the corrosion of carbon steel in 0.2N hydrochloric acid at 25°C temperatures and at different concentrations of voltaren drug solution and studying potentiodynamic polarization measurements, weight loss, and open circuit potential.

EXPERIMENTAL WORK

Working specimens are of carbon steel with dimensions(6*6 cm).The metal specimens are placed in the phosphating bath at a depth of 10 cm blow the solution and also 10cm above the bottom of the solution in the carbon steel bath .The temperature is adjusted to 25°C using thermostat. Voltaren master (Pgz301,dynamic els voltammery). Corrosion cell consist of 3electrode a platinum foil auxiliary and asaturated calomel reference electrode (SCE) is used .The voltaren used is supplied by Samara Company .The aggressive 0.2N hydrochloric acid with distilled water ,using hyperchem-8 program which is known for its flexibility ,quality, and ease of use .It offers ten semi—empirical methods. Some of them have been devised specifically for the description of organic chemistry, generally good for predicting molecular geometry and energetic .PM3 calculations are more stable structure of voltaren drug to obtain the parameters ,such as bond angle properties ,bond length and FT-IR absorption are recorded and compared with experimental results [18,19].

RESUTS AND DISCUSSION

Potentiodynamic Polarization Measurements

The corrosion currents decrease due to the voltearen molecules adsorption at the cathodic site of the metal surface which increase inhibitor concentration , shift of corrosion potentials in the cathodic direction [20]. The addition of voltaren to the Hydrochloric acid solution to improve the corrosion the behavior of corrosion this and it forms a layer on metal surface. Thus, the process is considred a physical adsorption of active molecules [21]. Table (1) shows the corrosion protection (Ecorr), corresponding inhibitor efficiencies (I.E%) , (bc) cathodic Tafel slope values deduced from the polarization curves , (I corr) corrosion current densities, and (θ) surface coveage degree . Figure (1) shows that when there is an increase in the concentration there will be a decrease in the current which leads to the decrease of both the anodic and cathodic over potential of carbon steel.

Table 1: Polarization data of carbon steel in the absence and presence of different concentrations of voltaren in 0.2N HCl solution at 298K.

Inhibitor con.(p.p.m)	Icorr., µA/cm2	-Ecorr., mV	-bc, mV/decade	IE %	θ
Blank	913.25	515.3	195.7	0	0
10	550.95	498.1	102.6	46	0.46
100	576.90	494.1	119.8	42.4	0.42
200	382.97	495.7	78.1	62.0	0.62
300	373.50	487.7	92.6	62.80	0.62

ISSN: 0975-8585

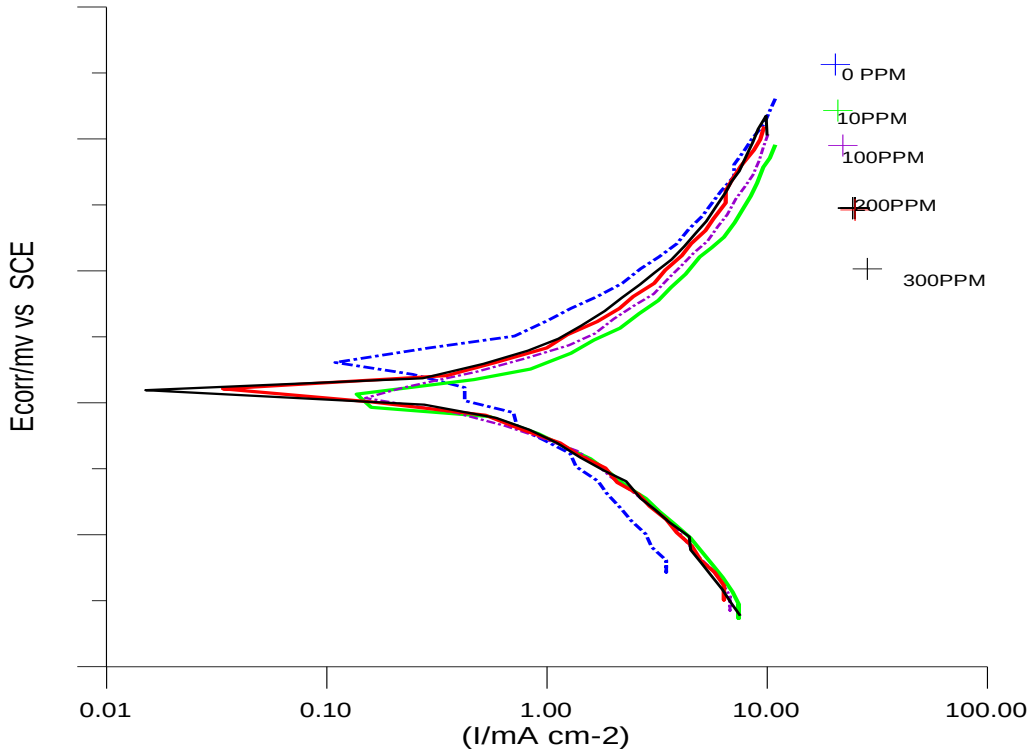


Fig 1: Potentidynamic Polarization curve of carbon steel with different concentrations of voltarean drug in 0.2N HCl at 25 °C

Effect of voltrean drug concentration

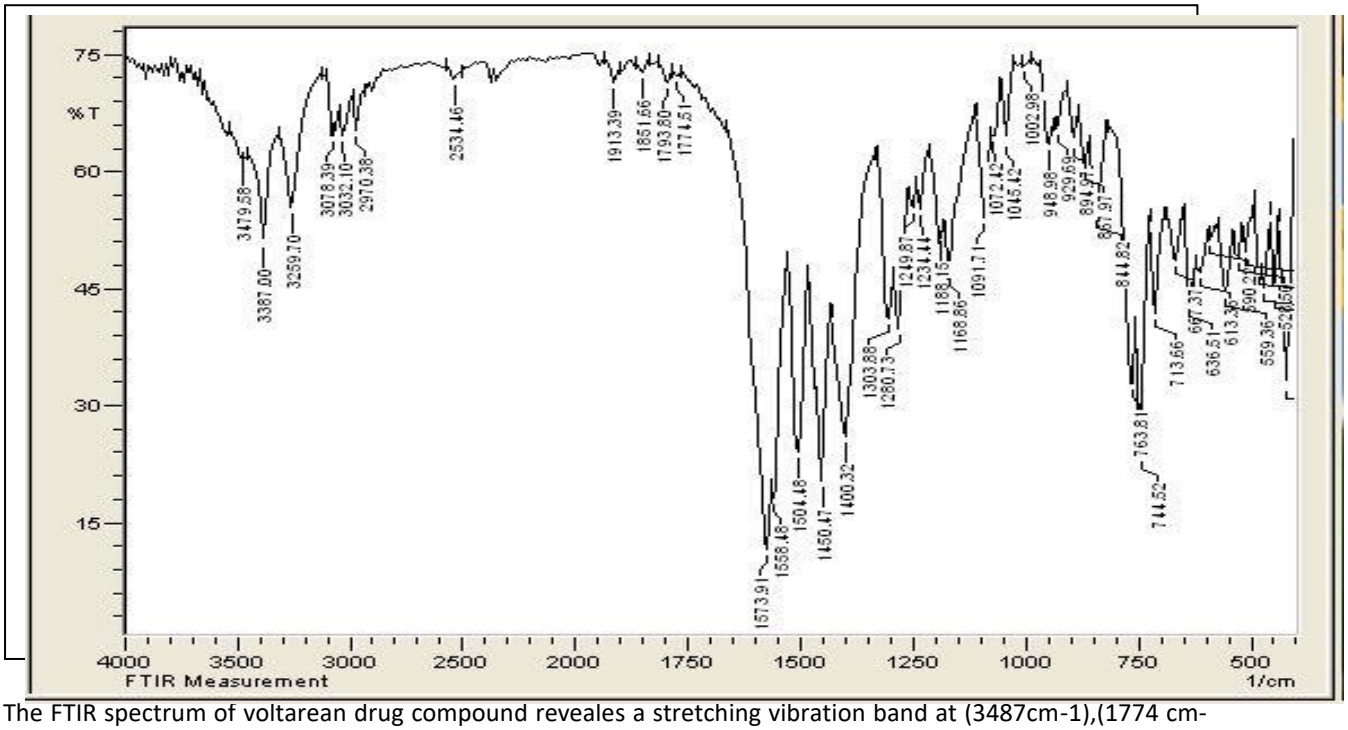
The addition of voltaren drug to carbon steel in 0.2 N hydrochloric acid at 298K temperatures decreases the corrosion rates as shown in Table(2).Table (2)shows these results decrease as the concentration of inhibitor is changed towards higher side revealing the fact that the adsorption of inhibitor and surface coverage metal increase with increasing the inhibitior concentration [22].

Table 2: shows the values of corrosion rates, inhibition efficiency (%IE) for carbon steel corrosion in without and with addition of different concentrations of voltaren in 0.2N hydrochloric acid solution at 298K.

Inhibitor con.(p.p.m)	Tempereature (K)	Corrosion Rate g/m2.d	%I.E
Blank	298	255	0
10		138	46
100		144	42
200		95.7	62
300		93.4	62.80

ISSN: 0975-8585

FT-IR Spectra



The FTIR spectrum of voltarean drug compound reveales a stretching vibration band at (3487cm-1),(1774 cm-1),(3033 cm-1) and 3259 cm-1),(OH),(C=O),(C-H),(C=C) and(NH) groups stretching vibrations respectively, as shown in Figure (2,3)and Table(3,4).

Figure 2: IR Spectrum of drug using hyperchem-8 program.'

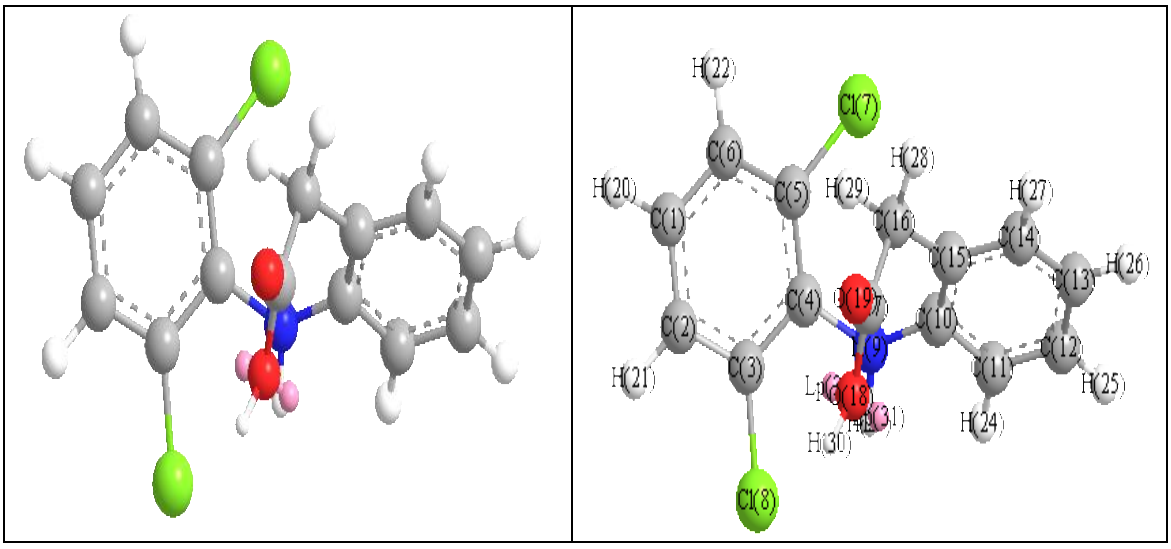


Figure 3: Serial number of atoms of compound

Table 3: Generate all bond length of compound.

Actual	Optimal	Atom
0.6	0.5987	O(18)-Lp(32)
0.6	0.6001	O(18)-Lp(31)
0.972	0.9702	O(18)-H(30)
1.113	1.1068	C(16)-H(29)
1.113	1.115	C16-H28

Table 4: Generate all bond angles of compound

Actual	Optimal	Atom
0.6	0.5987	O(18)-Lp(32)
0.6	0.6001	O(18)-Lp(31)
0.972	0.9702	O(18)-H(30)
1.113	1.1068	C 16-H 29
1.113	1.115	C 16-H28

1.1	1.103	C14-H27
1.1	1.1026	C13-H26
1.1	1.1012	C12-H25
1.1	1.103	C11-H24
1.05	1.0522	N9-H23
1.1	1.1023	C6-H22
1.1	1.1017	C2-H21)
1.1	1.1023	C1-H20
1.208	1.2089	C17-O19
1.338	1.345	C17-O19
1.509	1.5186	C16-C17
1.497	1.5169	C15-C17
1.42	1.4134	C15-C10)
1.42	1.4029	C15-C13)
1.42	1.395	C13-C14
1.42	1.3945	C12-C14)
1.42	1.3961	C11-C12
1.42	1.4043	C10-C11
1.462	1.4203	N9-C10
1.462	1.4179	C4-N9
1.719	1.7302	C3-CL8)
1.719	1.7324	C5-CL8)
1.42	1.3962	C6-C1
1.42	1.3972	C5-C6)
1.42	1.4097	C4-C5
1.42	1.4072	C3-C4
1.42	1.397	C2-C3)
1.42	1.3958	C1-C2

1.1	1.103	C14-H27
1.1	1.1026	C13-H26
1.1	1.1012	C(12)-H(25)
1.1	1.103	C11-H24
1.05	1.0522	N9-H23
1.1	1.1023	C6-H22
1.1	1.1017	C2-H21
1.1	1.1023	C1-H20
1.208	1.2089	C17-H19
1.338	1.345	C17-O18
1.509	1.5186	C16-C17
1.497	1.5169	C15-C16
1.42	1.4134	C15-C10
1.42	1.4029	C14-C15
1.42	1.395	C13-C14)
1.42	1.3945	C12-C13
1.42	1.3961	C11-C12
1.42	1.4043	C10-C11)
1.462	1.4203	N9-C10
1.462	1.4179	C4-N9
1.719	1.7302	C3-Cl 18
1.719	1.7324	C5-Cl15
1.42	1.3962	C6-C1
1.42	1.3972	C5-C6
1.42	1.4097	C4-C5
1.42	1.4072	C3-C4)
1.42	1.397	C2-C3
1.42	1.3958	C1-C2)
	115.125	Lp(32)-O(18)-Lp(31)
101	105.9321	Lp(32)-O(18)-H(30)
	110.1957	Lp(32)-O(18)-C(17)
101	105.6654	Lp(31)-O(18)-H(30)
	110.6051	Lp(31)-O(18)-C(17)
106.1	108.965	H(30)-O(18)-C(17)
122	121.2801	O(19)-C(17)-O(18)
122.5	126.2756	O(19)-C(17)-C(16)
107.1	112.3653	O(18)-C(17)-C(16)
109.4	104.206	H(29)-C(16)-H(28)
108.8	106.5141	H(29)-C(16)-C(17)

		109.41	113.1573	H(29)-C(16)-C(15)
		108.8	108.1677	H(28)-C(16)-C(17)
		109.41	110.0273	H(28)-C(16)-C(15)
		110.2	114.1758	C(17)-C(16)-C(15)
		121.4	117.9605	C(16)-C(15)-C(14)
		121.4	123.7962	C(16)-C(15)-C(10)
		120	117.8678	C(14)-C(15)-C(10)
		120	119.8962	H27-C14-C15C
		120	118.1123	H(27)-C(14)-C(13)
			121.9291	C15-C14-C13)
		120	120.1143	H26-C15-C15
		120	120.0499	H26-C13-C12
			119.7205	C14-C13-C12)
		120	120.4675	H25-C13-C12)
		120	120.2838	H25-C12-C13
			119.2472	C13-C12-C11)
		120	118.594	H24-C11-C12)
		120	120.3121	H24-C11-C10
			121.0515	C12-C11-C10
		120	119.6706	C15-C10-C11
		120	125.3967	C15-C11-N10
		120	114.52	C11-C10-N11
		118	112.4414	H23-N9-C10
		118	113.0229	H23-N9-C4
		124	134.4297	CC10-N10-C4
		120	120.8579	H22-C6-H5
		120	118.7032	H22-C6-C1)
			120.4288	C5-C6-C1
		118.8	117.6319	C7-C5-C1
		118.8	122.0104	CL7-C5-C1
		120	120.1594	C6-C5-C4
		120	124.4999	N9-C4-C5
		120	116.685	N9-C4-C3
		120	118.7303	C5-C4-C3
		118.8	120.8589	CL8-C3-C4)
		118.8	118.539	CL8-C3-C2
		120	120.4709	C4-C3-C2
		120	120.7868	H21-C3-C2
		120	119.0456	H21-C2-C1
			120.1659	C3-C2-C1
		120	120.1285	H(20)-C(1)-C(6)

ISSN: 0975-8585

		120	120.1028	H(20)-C(1)-C(2)

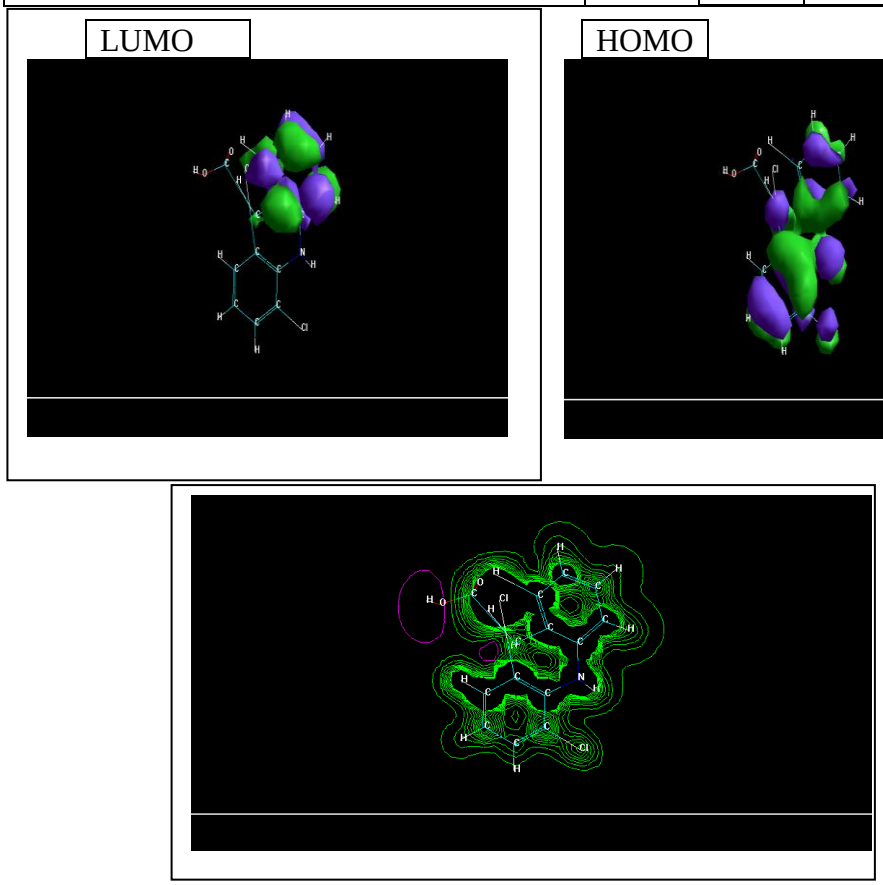
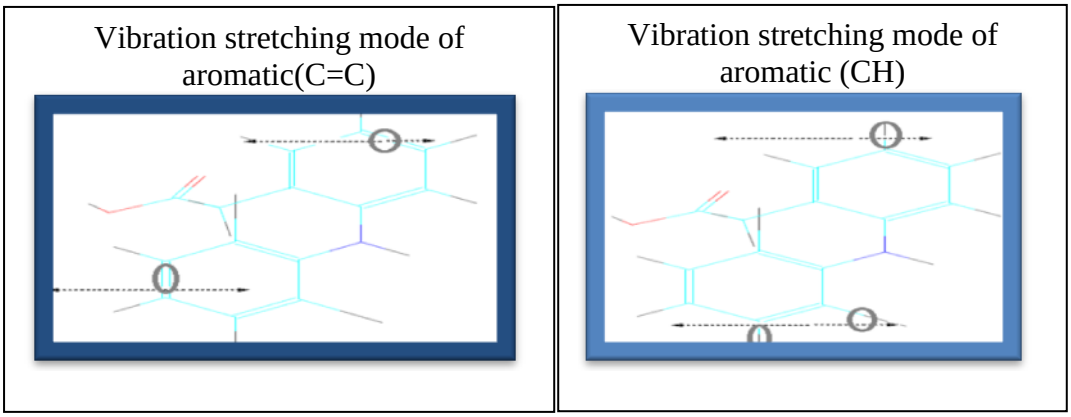


Figure 4: HOMO, LUMO & electrostatic potential for compound by Hyperchem-8.

Table 5: Conformation energetic in (Kcal. mol^{-1}), Homo and Lumo energy in (ev) and dipole moment in (debye) for Compound.

Compd.NO.	-ΔE_{tot}	-ΔH^{o}_{f}	-ΔE_{b}	- E_{Homo}	- E_{Lumo}	Dipole momen
	74107.13	106.96	3362.64	8.755858	1.723057	4.6662



ISSN: 0975-8585

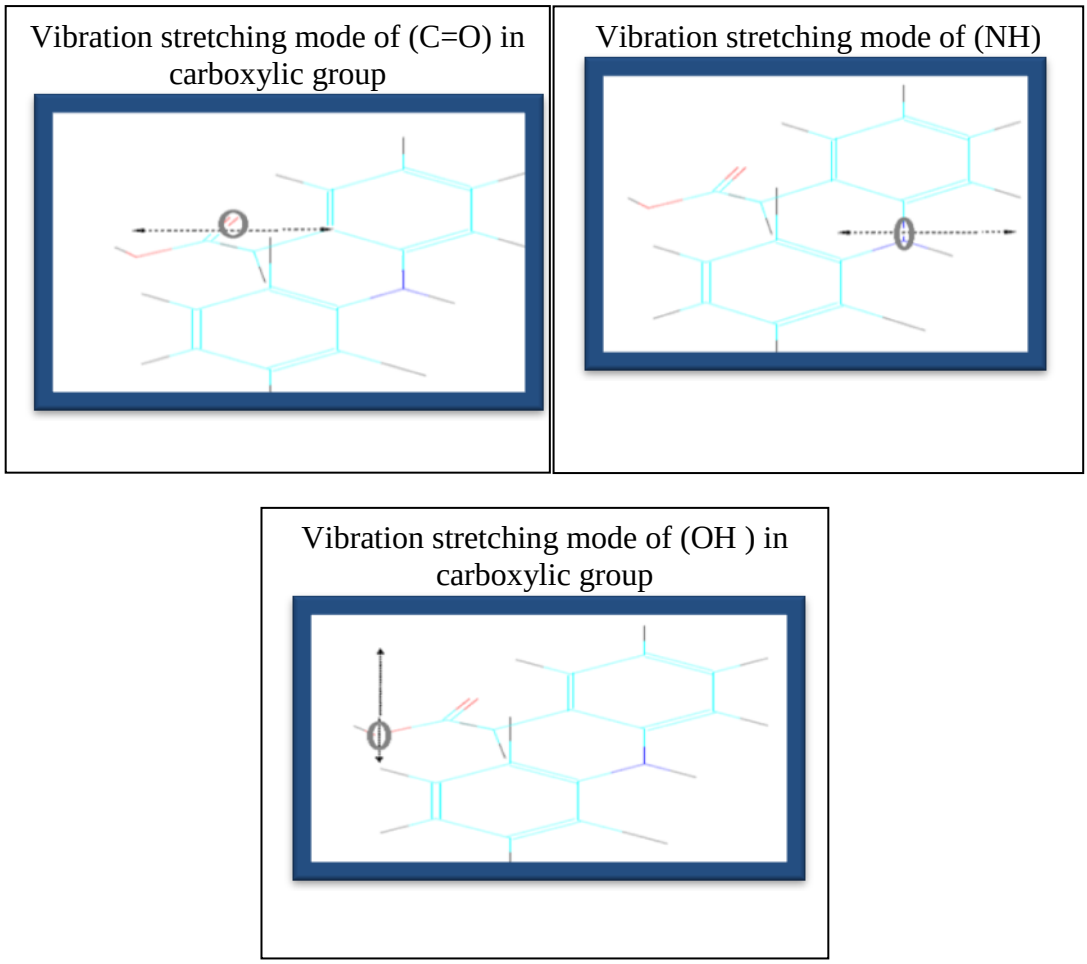


Figure 5: Show the Vibration stretching mode

Table 6: Comparison of experimental and theoretical vibrational Vibration stretching mode of aromatic

Comp. NO.	Frequency			Intensity
A1		Theoretical	experimental	
	OH (carboxlic group)	3484	3487	2.86254
	C=O (carboxlic group)	11780	1774	216
	C-H (aromatic ring)	3032	3033	13.72261
	C=C(aromatic ring)	1582	1573	46.87475
	NH	3233	3259	19.52369

Electronic Spectra

The electronic spectra of compound exhibit two bands. The first absorption band appears at 274 nm to intera ligand (n→π*) transition located on the group of (C=C) of olifinic rings . T he electronic spectra of compound shows the band at 210 nm that belong to ($\pi \rightarrow \pi$ *) of olifinic rings. As shown bellow in Figure (6) and Table(7).

ISSN: 0975-8585

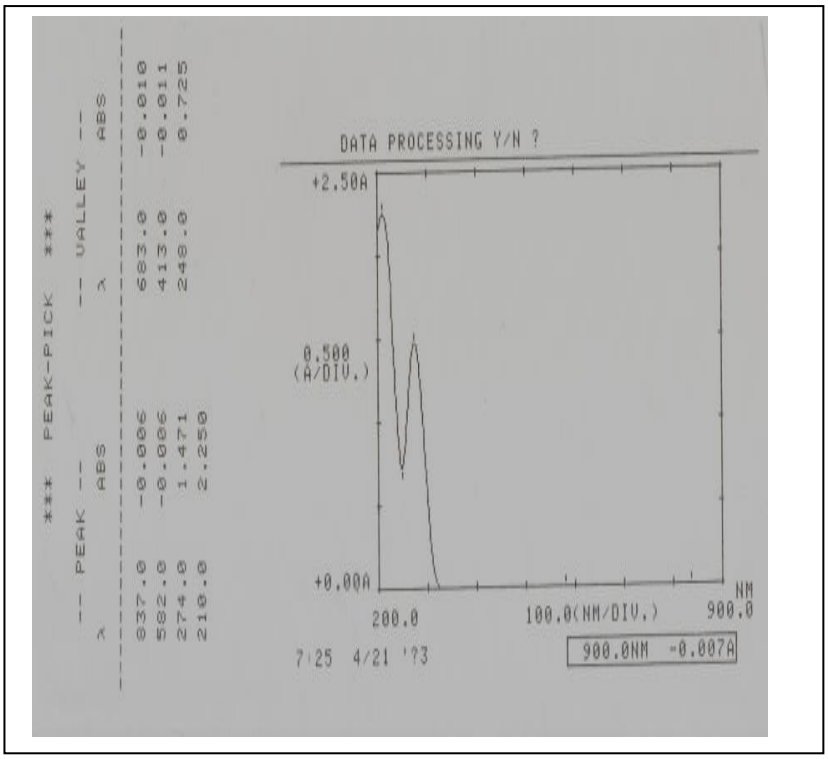


Figure 6: UV-Visible spectrum of compound

Table 7: Comparison of experimental and theoretical vibrational Vibration stretching mode of aromatic C=C (Olfinic)

Camped No.	Experimental Value of C=C (Olfinic)		Theoretical Value C=C (Olfinic)
2	π→π* (nm)	210	220
	n→π* (nm)	274.0	282

CONCLUSION

In this study, the metal carbon steel dissolution in 0.2N HCl solution is protected by using dichloro phenyl amino) phenyl) acetic acid -2,6)2-)2 using (EIS) electrochemical impedance spectroscopy measurements, potentiodynamic polarization, and (W.L) weight loss. It is shown that these corrosion inhibitors make carbon steel protection. The inhibition activity (voltaren drug) is blocking influence by the adsorption of inhibitor molecules on the carbon steel surface. We have tried to establish the characterization of the compounds voltaren by using PM3 Semi-empirical quantum mechanical calculations. The optimized geometries, dipole moments, geometric parameters, and vibrational frequencies are calculated and the data obtained from the calculated parameter are shown to have a good agreement with the experimental data. This agrees with the accuracy of computational results. The modeling and the calculations the opportunity to compile fundamental result on properties that cannot be calculated in the laboratory.

REFERENCES

[1] Al-Shafey, H. I. ; Abdel Hameed, R. S.; Ali, F. A. ; Aboul-Magd, A. S. and Salah, M. 2014 .Effect of Expired Drugs as Corrosion Inhibitors for Carbon Steel in 1M HCL Solution. Inter. J of Pharm. Scie., (26) 146-152.

[2] Al-Shafey, H.I.; El Azabawy, O.E and Ismail, E.A. 2011. Ethoxylated Melamine as Corrosion Inhibitor for Carbon Steel in 1M HCl. Dispersion Sci. and Tech. Journal 32, 995–1001.

[3] El-Haddad ,M. N. and Elattar , K. M. 2015. Synthesis, characterization and inhibition effect of new antipyrinyl derivatives on mild steel corrosion in acidic solution. Int J Ind Chem 13,3-5.

[4] El-Haddad , M .N. and Fouda, A.S. 2013. Inhibition effect and adsorp- tion behavior of new azo dye derivatives on corrosion of carbon steel in acid medium. J Sci Technol 34:1471–1480

[5] El-Haddad, M.N. and Fouda, A. S. 2013 Corrosion inhibition and ad- sorption behavior of some azo dye derivatives on carbon steel in acidic medium: synergistic effect of halide ions. Chem Eng Commun 200:1366–1393
[6] Abd El Maksoud ,S.S. 2002 Studies on the effect of pyra- nocoumarin derivatives on the corrosion of iron in 0. 5 M HCl. Corros Sci 44:803–813
[7] Abdallah, M. 2002 Rhodanine azosulpha drugs as corrosion in- hibitors for corrosion of 304 stainless steel in hydrochloric acid solution. Corros Sci 44:717–728
[8] Hu, J.; Zeng, D.; Zhang, Z.; Shi ,T.; Song, G. and Guo, X. 2013. 2-Hydroxy- 4-methoxy-acetophenone as an environment-friendly corrosion inhibitor for AZ91D magnesium alloy. Corros Sci 74:35–43
[9] Ghailane, T.; Balkhmima, R.A.; Ghailane, R.,;Souizi ,A.; Touir, R.; Ebn Touhami, M.;, Marakchi, K. and Komiha, N. 2013. Experimental and theoretical studies for mild steel corrosion inhibition in 1 M HCl by two new benzothiazine derivatives. Corros Sci 76:317–324
[10] Moretti, G.; Guidi, F. and Fabris, F. 2013. Corrosion inhibition of the mild steel in 0.5 M HCl by 2-butyl-hexahydropyrrolo[1,2- b][1,2]oxazole. Corros Sci 76:206–218
[11] Pournazari ,S.H.; Moayed, M.H. and Rahimizadeh, M. 2013.In situ in- hibitor synthesis from admixture of benzaldehyde and benzene- 1,2-diamine along with $FeCl_3$ catalyst as a new corrosion inhibitor for mild steel in 0.5 M sulphuric acid. Corros Sci 71:20–31.
[12] Fouda, A. S.; Abdallah, A. and Yousef , M. 2014. Corrosion Inhibition and Adsorption Properties of Cefixime on Carbon Steel in Acidic Medium. Chem Sci Rev Lett, 3(11S), 130-143 .
[13] Kumer ,S. H. and Karthikeyan ,S. 2012 .Inhibition of mild steel corrosion in hydrolic acid solution by cloxacillin. J. Mater. Enviro. Sci., 3(5) 925-934.
[14] Mahdi, A., S. 2014 AMOXICILLIN AS GREEN CORROSION INHIBITOR FOR CONCRETE REINFORCED STEEL IN SIMULATED CONCRETE PORE SOLUTION CONTAINING CHLORIDE.International Journal of Advanced Research in Engineering and Technology (IJARET), 5(6) 99-107.
[15] Abdel Hameed, R. S.; Ismail, E. A.; Abu- Nawwas, A. H. and AL-Shafey,H.,I. 2015. Expired Voltaren Drugs as Corrosion Inhibitor for Aluminium in Hydrochloric Acid . Int. J. Electrochem. Sci., (10) 2098 - 2109 .
[16] David, C. Y. 2001. Computational Chemistry- A practical guide for applying real world problems. Wiley-interscience. ISBN 0-471-33368-9.
[17] Warren, J. H. 2003. A guide to molecular mechanics and Quantum Chemical calculations in Spartan. Wavefunction, Inc. ISBN 1-890661-18-X.
[18] Topacli, C. and Topacli, A. 2003. Journal of Molecular Structure, 654:131-137.
[19] Stewart, J. 1996. Reviews in Computational Chemistry, K. B. Lipkowitz, D. B. Boyd (Eds.) . VCH Publishers, New York, (1) 9, 72-80.
[20] Cook, D.B. 1998. Hand Book of Computational Quantum Chemistry, Oxford Univ. Press, New York, pp. 14.
[21] Abdel Hameed, R. S.; Alshafey ,H. I. and , Abu-Nawwas ,A. H. 2014. Int. J. Electrochem. Sci., (9)6006.
[22] Naqvi, I. ; Saleemi, A. R. and Naveed, S.2011.Cefixime: A drug as Efficient Corrosion Inhibitor for Mild Steel in Acidic Media.Int. J. Electrochem. Sci., 6 146