

Computational Simulation of the Molecular Structure of Benzimidazole and Substituted Benzimidazoles as Corrosion Inhibitors for Brass in Perchloric Acid

Musa El Balla Mohamed^{1,*}, Kamal K. Taha²

^{1,2} Department of Chemistry, College of Applied and Industrial Sciences,
University of Bahri, Khartoum State, Khartoum, Sudan

*e-mail address: musa.elballa@gmail.com

*Telephone number: 00249923023519, Fax: 00249-85294191

ABSTRACT

The density functional theory (DFT) at the B3LYP/6-31G* /6-31+g(d) basis sets level and semi-empirical AM1 methods were performed on four Benzimidazole (BZL) and substituted benzimidazole namely 2-aminobenzimidazole (ABZL), 2-mercaptobenzimidazole (MBZL) and 2-phenylbenzimidazole (PhBZL) as corrosion inhibitors for (70/30) brass in M HClO₄, to investigate the correlation between its molecular structure and the corresponding inhibition efficiency (%IE). Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), charge on the reactive center, hardness (η) and the total energy have been calculated. A good correlation between the theoretical data and the experimental results was found.

Keywords: Benzimidazoles, Brass Corrosion, Density Functional Theory (DFT), AM1 Method

{ **Citation:** Musa El Balla Mohamed, Kamal K. Taha. Computational simulation of the molecular structure of benzimidazole and substituted benzimidazoles as corrosion inhibitors for brass in perchloric acid. American Journal of Research Communication, 2015, 3(4): 143-152} www.usa-journals.com, ISSN: 2325-4076.

1. INTRODUCTION

Imidazoles have been used as corrosion inhibitors for copper⁽¹⁻⁷⁾, zinc⁽⁸⁾, steel^(9,10) and brass⁽¹¹⁻¹³⁾ in different environments. Their inhibition is due to their complexation ability^(14,15) especially with transition metals⁽¹⁶⁻¹⁹⁾.

In acidic medium these organics are protonated at the azole nitrogen (=N-) and subsequently chemisorbed on the metal surfaces through coordinate type of linkage involving the lone pair of electron on the imino nitrogen^(20,21).

The inhibition performance of four Benzimidazoles derivatives as corrosion inhibitors in HCl mild steel corrosions ⁽²²⁾, including 2-mercaptobenzimidazole, 2-amidobenzimidazole, 2-methylbenzimidazole, and benzimidazole, was theoretically evaluated using quantum chemistry calculations and molecular dynamics simulations, and the corrosion inhibition mechanism was analyzed ⁽²²⁾.

Quantum chemical SCF calculations of some parameters of benzimidazoles were correlated with their inhibition efficiency in case of steel in aqueous acidic medium using the semi-empirical AM1 and B3LYP/6-31G* as a higher level of theory ⁽²³⁾.

Experimental means are useful in explaining the inhibition mechanism but they are often expensive and time consuming. Advance in computer hardware and software and in theoretical chemistry have brought high-performance computing and graphical tools within the reach of many academic and industrial laboratories. Recently more corrosion publications contain substantial quantum chemical calculations ⁽²⁴⁾. Such calculations are usually used to explore the electronic properties of the inhibitors, the effect of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, the difference between highest occupied molecular orbital and lowest unoccupied molecular orbital energies ($E_{LUMO}-E_{HOMO}$), charge on the reactive center, dipole moments, global hardness and total energies had to be investigated to achieve the appropriate correlation ^(25, 26).

In our previous quantum chemical calculation using density functional theory (DFT) methods B3LYP/6-31G*, RHF/6-31G* and semi-empirical method (AM1) in gas phase on Some thiocarbamides ⁽²⁷⁾ and on sulfur containing amino acids ⁽²⁸⁾ as corrosion inhibitors for Brass in acidic media, a good correlation between experimental and theoretical have been obtained by these methods.

The inhibitor efficiency (%P) was calculated experimentally of Benzimidazole (BZL) and substituted benzimidazole namely 2-aminobenzimidazole (ABZL), 2-mercaptobenzimidazole (MBZL) and 2-phenylbenzimidazole (PhBZL) for Brass in Perchloric acid using weight loss, Tafel extrapolation and electrochemical impedance spectroscopy (EIS) method ⁽²⁹⁾. Results obtained showed that the percentage inhibition (%P) was found to be in the order PhBZL > MBZL > ABZL > BZL ⁽²⁹⁾.

The aim of this work is to extend these investigations in order to discuss the relationship between quantum chemical calculations and experimental inhibition efficiencies of these substituted benzimidazole by Am1, B3LYP/6-31G* and B3LYP/6-31+g(d) from these data, by determining quantum chemical parameters such as the energies of the highest occupied molecular orbital (E_{HOMO}) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO} , charge on the reactive center, dipole moments and global hardness.

2. METHODS OF CALCULATIONS

Firstly theoretical calculations were carried out by using AM1 semi-empirical methods in MOPAC2007 program, implemented on an Intel Pentium (R) 1.86 GB personal computer. Initial estimates for the geometries of all the structures were obtained by molecular mechanics program (ACD11) for Widows, followed by full optimization of all geometrical variables (bond lengths, bond angles and dihedral angles), without any symmetry constraint, using AM1 semi-empirical methods in gas phase. The structures obtained from AM1 calculations were fully re-optimized by using Density functional theory (DFT) methods to estimate the quantum chemical parameters. Calculations at the DFT level were performed with basic sets 6-31+g(d) and 6-31G* respectively. For this purpose the Gaussian 03 Quantum Chemistry Program with complete geometry optimization was used.

3. RESULTS AND DISCUSSION

The chemical structures of the compounds under investigation are presented in figure 1. The optimized molecular structures of the studied molecules using B3LYP/6-31G* methods are shown in figure 2.

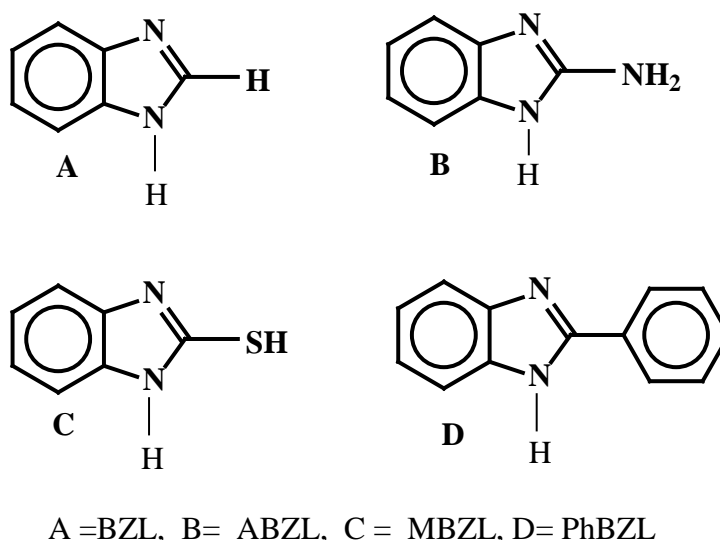


Figure 1. The structure of Benzimidazole and substituted benzimidazoles.

The calculated quantum chemical indices E_{HOMO} , E_{LUMO} , $E_{\text{L}}-E_{\text{H}}$, global hardness, total energies, dipole moment and inhibition efficiencies obtained from the experimental measurements are given in table 1, Mulliken atomic charges on nitrogen, sulphur and carbon atoms are shown in table 2. It has been proven that local electron densities or

charges are important, in many chemical reactions and physicochemical properties of compounds⁽³⁰⁾. Inhibition action of organic molecules can be explained by the adsorption on metal surface. Since the surface of the brass is positively charged in acidic solution⁽³¹⁾, table 2 show that all nitrogen, sulphur and most of the carbon atoms of benzimidazoles carry the negative charges, this indicate that these atoms are the negative charge centers which could offer electrons to the brass surface to form a coordination type of bond.

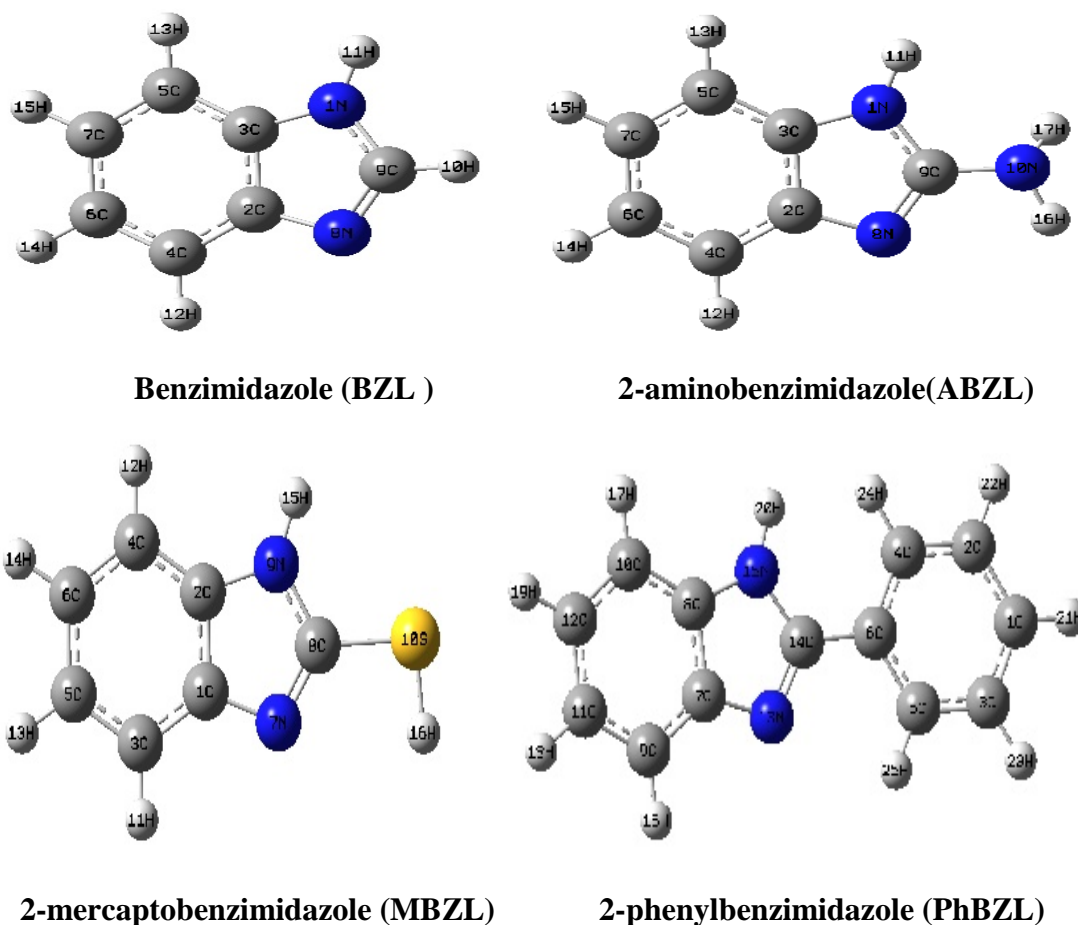


Figure 2. The optimized structures of Benzimidazoles (1-4) by B3LYP/6-31G*.

Table 1. AM1, B3LYP/6-31G* and B3LYP /6-31+g(d) data for Benzimidazoles (1-4)

Inhibitor	E _{LUMO} (eV)	E _{HOMO} (eV)	E _L -E _H (eV)	Hardness eV	Dipole Moment (D)	Total energy eV	% Inhibition in 0.1M HClO ₄
AM1							
1 BZL	0.058	-8.996	9.054	4.527	3.138	-1391.2	68.9
2 ABZL	0.058	-8.580	8.638	4.319	2.805	-1612.1	84.9
3 MBZL	-0.124	-8.516	8.392	4.196	1.912	-1585.7	87.1
4 PhBZL	-0.207	-8.492	8.285	4.142	3.016	-2214.1	89.2
B ₃ LYP/6-31G*							
1 BZL	-0.3409	-6.0668	5.7259	2.8629	3.441	-10336.4	68.9
2 ABZL	0.0952	-5.4473	5.5425	2.7712	3.748	-11842.8	84.9
3 MBZL	-0.3553	-5.8334	5.4781	2.7390	2.194	-21171.3	87.1
4 PhBZL	-1.1703	-5.6995	4.5292	2.2646	3.086	-16623.8	89.2
B ₃ LYP/6-31+g(d)							
1 BZL	-0.8451	-6.6116	5.7675	2.8837	3.395	-10318.1	68.9
2 ABZL	-0.5112	-5.7902	5.2790	2.6395	3.841	-11843.3	84.9
3 MBZL	-0.8570	-6.0951	5.2381	2.6190	2.398	-21171.8	87.1
4 PhBZL	-1.5447	-6.0067	4.4620	2.2310	3.159	-16624.4	89.2

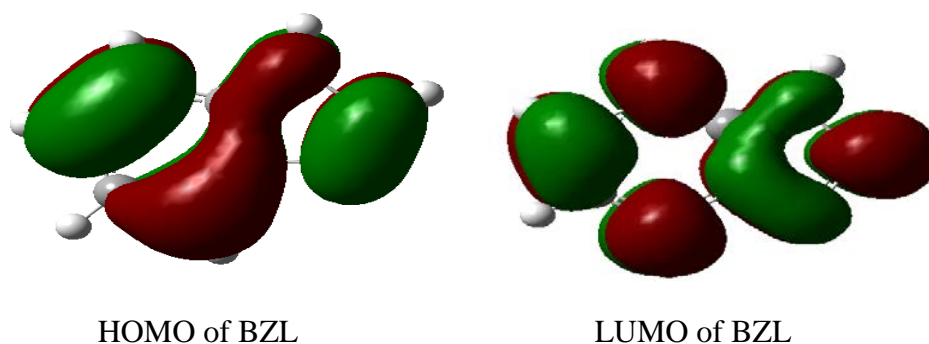
% Inhibition are taken from reference (29)

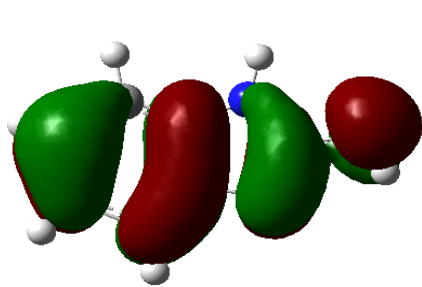
Table 2. Mulliken atomic charges of Benzimidazoles (1-4) by B3LYP/6-31G*

Benzimidazole	2-aminobenzimidazole	2-mercaptobenzimidazole	2-phenylbenzimidazole
1 N -0.678	1 N -0.728	1 C 0.220	1 C -0.123
2 C 0.224	2 C 0.245	2 C 0.347	2 C -0.135
3 C 0.339	3 C 0.341	3 C -0.174	3 C -0.135
4 C -0.174	4 C -0.194	4 C -0.166	4 C -0.183
5 C -0.168	5 C -0.180	5 C -0.141	5 C -0.163
6 C -0.143	6 C -0.141	6 C -0.148	6 C 0.123
7 C -0.149	7 C -0.152	7 N -0.504	7 C 0.248
8 N -0.490	8 N -0.555	8 C 0.296	8 C 0.362
9 C 0.227	9 C 0.650	9 N -0.704	9 C -0.182
	10 N -0.781	10 S -0.022	10 C -0.175
			11 C -0.143
			12 C -0.148
			13 N -0.572
			14 C 0.469
			15 N -0.775

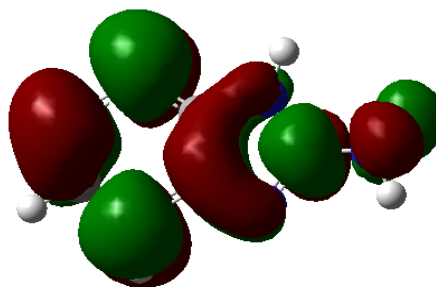
Another important point to be considered in the energy level terms is gap between the HOMO and LUMO energies for the studied molecules (1-4). Cherry *et al.*⁽³²⁾ have used the concept of LUMO-HOMO energy gap in developing theoretical models which is capable of explaining the structure and conformation barriers in many molecular systems qualitatively. Low absolute values of the energy band gap (ΔE) gives good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low⁽²⁵⁾. According to the data in table 1, there is a good correlation in LUMO-HOMO energy gap by these methods in gas phase, it can be seen that phenylbenzimidazole (PhBZL) is best inhibitor and has smallest LUMO- HOMO gap i.e (8.285 eV), (4.529 eV) and (4.462 eV) by AM1, B3LYP / 6-31G* and B3LYP/6-31+g(d) respectively, but the benzimidazole (BZL), which is least inhibitor and has highest LUMO- HOMO gap i.e (9.054 eV), (5.725 eV) and (5.767 eV) by AM1, B3LYP / 6-31G* and B3LYP/6-31+g(d) respectively. Thus the difference between the LUMO-HOMO of the PhBZL and LUMO- HOMO of BZL by B3LYP/6-31+g(d) method is of 1.205 eV caused an inhibition increase to 20.3%. As can be seen from table 1 for all methods of calculations, the inhibition efficiencies increases as the E_L-E_H values decrease, which indicates the stability of formed complexes between benzimidazoles and brass in perchloric acid media, i.e the order of inhibition efficiencies as follows: PhBZL> MBZL> ABZL>BZL as can be obtained from experimental data⁽²⁹⁾. This indicates that the best correlations between experimental and calculated inhibition efficiencies were obtained by using AM1, B3LYP / 6-31G* and B3LYP/6-31+g(d) in gas phase for benzimidazoles, correlations are almost in the same order. Correlation coefficients greater than 60% were well accepted in quantum chemical calculations of corrosion studies⁽³³⁾.

Figure 3. Frontier molecular orbital diagrams of Benzimidazoles (1-4) by the B3LYP/6-31G* model chemistry.

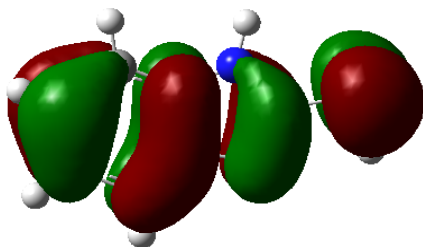




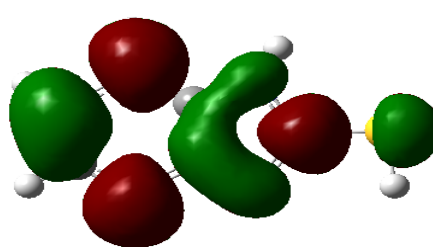
HOMO of ABZL



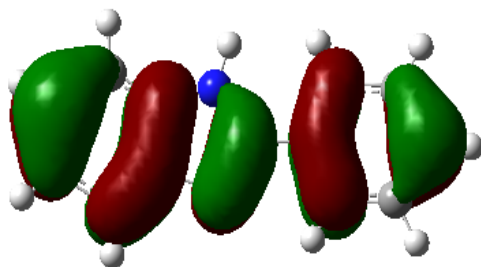
LUMO of ABZL



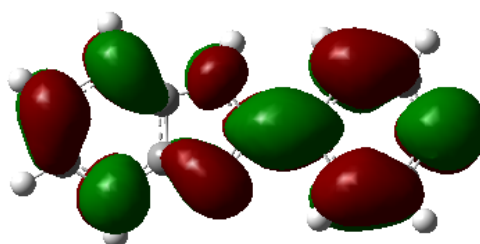
HOMO of MBZL



LUMO of MBZL



HOMO of PhBZL



LUMO of PhBZL

High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer, low LUMO energy indicates the ability of the molecules to accept electrons⁽²⁴⁾. The results obtained by AM1 method in gas phase, (table 1) show that PhBZL has highest HOMO energy ($E_{\text{HOMO}} = -8.492$ eV) and lowest LUMO energy ($E_{\text{LUMO}} = -0.207$ eV) among these inhibitors. Whereas the BZL has low E_{HOMO} ($E_{\text{HOMO}} = -8.996$ eV) and high E_{LUMO} ($E_{\text{LUMO}} = 0.058$ eV). The same results can be shown by B3LYP/6-31G* methods in table 1. Figure 3 shows the shapes of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the compounds under investigations. From these figures it can be concluded

that the compounds adsorbed on the mild brass surface by using the Benzimidazoles moiety which contains the heteroatom Nitrogens and Sulphur and aromatic rings.

Quantum chemical calculation reveals that the substitution of hydrogen atom in BZL by primary amines in ABZL, results in a great increase of HOMO energy level (and a decrease of energy of the gap $E_{\text{LUMO}} - E_{\text{HOMO}}$) obviously. The same effect can be seen in substitution of hydrogen atom in BZL by -SH in MBZL and by phenyl group in PhBZL. The increase of inhibition efficiency due to $\text{NH}_2/\text{SH}/\text{C}_6\text{H}_5$ substitution should arise from the increase of HOMO level energy, low LUMO energy and low ΔE implying the ability of PhBZL to offer free electrons to the metal surface. The relatively high inhibitor efficiency of PhBZL when compared to that of ABZL and MBZL may be attributed to the presence of the bulkier phenyl group in PhBZL. The phenyl group while contributing to stronger binding through its π -system also provides greater surface coverage by virtue of its size. C_6H_5 which is an phenyl group is an electron donor, which has π -orbital able to overlap with the metal d-orbital resulting in stronger adsorption with brass. BZL has the lowest E_{HOMO} value, also the lowest inhibition efficiency. Thus, the order of inhibition efficiency is $\text{PhBZL} > \text{MBZL} > \text{ABZL} > \text{BZL}$, as can be deduced above, which agreed with experimental ones.

Another property calculated for these molecules is the global hardness η , calculated as $\Delta E/2$, which is parameter that gives important information about the reactive behavior of the molecule, and can be defined under the principle of chemical hardness and softness (HSAB)⁽³⁴⁾, as can be seen in table 1, the PhBZL exhibits the minimum hardness value, whereas the BZL presents the maximum value of hardness this indicate that PhBZL is potential corrosion inhibitor over the other.

4. CONCLUSIONS

Through AM1 semi-empirical, B3LYP /6-31G* and B3LYP/6-31+g(d) quantum chemical calculations a correlation between parameters related to structure of some Bezoamidazoles derivatives and their ability to inhibit the corrosion process could be established.

The inhibition efficiency of Bezoamidazoles and its derivatives obtained experimentally increase with the increased in E_{HOMO} , and decreased in E_{LUMO} and decreased in the energy of the gap (ΔE). PhBZL has the highest inhibition efficiency because it had low (ΔE) values, and it was most capable of offering electrons. BZL has the high (ΔE) values, also the lowest inhibition efficiency. Thus, the order of inhibition efficiency is $\text{PhBZL} > \text{ABZL} > \text{MBZL} > \text{BZL}$.

Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

REFERENCES

- (1) Gi Xue, Xue-Ying Huang, Jian Dong and Jungfeng Zhang. The formation of anticorrosion on copper surface from 2-mercaptobenzimidazole, *J. Electroanal. Chem.*, (1991)310, 139-148.
- (2) G. Lewis, , The corrosion inhibition of copper by benzimidazole, *Corr. Sci.*, (1982) 22 579 - 584.
- (3) F. X. Perrin and J. Pagatti, , Characterization and mechanism of direct film formation on a Cu electrode through electro-oxidation of 2-mercaptobenzimidazole, *Corr. Sci.*, (1998)40, 1647-1662..
- (4) E. Stupnisek-Lisac, A. Loncaric Bozic and I. Cafuk, , Low-toxicity copper corrosion inhibitors *Corrosion*, (1998) 54, pp. 713 - 720.
- (5) Carron K T, Lewis M L, Dong J., Surface-enhanced raman scattering and cyclic voltammetry studies of synergetic effects in the corrosion inhibition of copper by polybenzimidazole and mercaptobenzimidazole at high temperature, *J Mater Sci*, (1993) 28, pp. 4099~4103.
- (6) Gi Xue, Jianfu Ding, W. Peiyi and Gending Ji, , The formation of a compact film on a copper electrode from benzimidazole solution, *J. Electroanal. Chem.*, (1989) 270. pp. 163 - 173.
- (7) R. Gasparac, C.R. Martin and E. Stupnisek-Lisac, In situ studies of imidazole and its derivatives as copper corrosion inhibitors - I. Activation energies and thermodynamics of adsorption, *J. Electrochem. Soc.*, (2000) 147, pp. 548.
- (8) E. Stupnisek-Lisac, D. Kasunic and J. Vorkapic-Furac, Imidazole derivatives as corrosion inhibitors for zinc in hydrochloric acid, *Corrosion*, (1995) 51, pp. 767-772.
- (9) Lin Wang, , Corrosion and Inhibition of 316L stainless steel in neutral medium, *Corr. Sci.*, (2001)43, pp. 2281.
- (10) F. Khaled, The inhibition of benzimidazole derivatives on corrosion of iron in 1 M HCl solutions, *Electrochimica Acta*, (2003) 48, pp. 2493_ 2503.
- (11) A. Popova, and M. Christov, Evaluation of impedance measurements on mild steel corrosion in acid media in the presence of heterocyclic compounds, *Corrosion Science*, (2006) 48 (10), pp. 3208-3221.
- (12) N.K. Patel, S.C. Makwana and M.M.Patel, , Action of benzimidazoles on the corrosion of 63/37 brass in NaOH, *Corr. Sci.*, (1974) 14 pp. 91-94.
- (13) S.K. Bag, S.B. Chakraborty, A. Roy and S.R. Chaudhuri, 2-aminobenzimidazole as corrosion inhibitor for 70/30 brass in ammonia, *B. Corrosion J.*, (1996) 31, pp. 207 – 212.
- (14) Badawy W. A., El-Agamy S. S. and Azab A. S., The electrochemical behaviour of leaded brass in neutral Cl^- and SO_4^{2-} media, *Corrosion Sci.*, (1995) 37 pp. 1969 – 1975.
- (15) N Papish, E. T.; Taylor, M. T.;;* Jernigan, F. E.;;* Rodig, M. J.;;* Shawhan, R. R.;;* Yap, G. P. A.; Jové, F. A., Synthesis of Zinc, Copper, Nickel, Cobalt and Iron Complexes Using Tris(pyrazolyl)methane Sulfonate Ligands: A Structural Model for N,N,O Binding in Metalloenzymes, *Inorganic Chemistry*, (2006) 45, pp. 2242-2250.

- (16) Chang-Tong Yang and Jagadese J. Vittal, Synthesis and structural behavior of ternary copper(II) complexes containing reduced Schiff base *N*-(2-hydroxybenzyl)-4-aminobutyric acid and 1,10-phenanthroline, *Inorganica Chimica Acta*, (2003) 344, pp. 65 - 76.
- (17) Xue G, Shi GQ, Ding JF, Zhang WM, Chen RS, Complex-induced coupling effect: adhesion of some polymers to copper metal promoted by benzimidazole, *J. Adhesion Sci. Tech.*, 1990, 4. pp. 723.
- (18) Xue G, Zhang JF, Shi GQ, Wu PY, Spectroscopic studies on the polymerization of benzimidazole with metallic copper, *J. Chem. Soc., Perkin Trans* (1989)11, pp. 33-36.
- (19) Xue G, Zhang JF, Huang XY, Shi GQ, Chemical reaction of metallic copper with imidazole *J. Chem. Soc., Dalton Trans.*, (1988) 1487.
- (20) J. Bukowska, A. Kudelski, K. Jackowska, The use of surface enhanced Raman scattering (SERS) to probe the interaction of imidazole with the silver electrode surface. *J. Electroanal. Chem.*, (1991) 309, pp.251-261.
- (21) Jacinto Morales Roque, T. Pandiyan, J. Cruz and E. García-Ochoa, DFT and electrochemical studies of tris(benzimidazole-2-ylmethyl)amine as an efficient corrosion inhibitor for carbon steel surface, *Corrosion Science* (2008), 50, pp. 614-624.
- (22) ZHANG Jun, ZHAO Wei-Min, GUO Wen-Yue¹, WANG Yong, LI Zhong-Pu, *Acta Phys. Chim. Sin.*, 2008, 24(7) : 1239-1244.
- (23) Ashry, El Sayed H. El; Nemr, Ahmed El; Essawy, Samy A.; Ragab, Safaa. *Progress in Organic Coatings* vol. 61 issue 1 January, 2008. p. 11-20.
- (24) Gece, G. *Corros. Sci.*, 2008, 50, 2981.
- (25) Bereket, G.; Ogretir, C. and Yurt, A.; *J.Mol. Struct.(THEOCHEM)* 2001, 571,139.
- (26) Bereket, G.; Ogretir, C. and Hur, E.; *J.Mol. Struct.(THEOCHEM)* 2002, 578, 79.
- (27) Musa E. Mohamed, Kamal K. Taha., *Nature and Science*, 10(3)2012, 55-60
- (28) Musa E. Mohamed, Kamal K. Taha., *Researcher* 2012;4(11)92-97
- (29) Taha, K.K., B.S. sheshadri and M.F. Ahmed, 2008. Benzimidazole and substituted benzimidazoles as corrosion inhibitors for brass in perchloric acid. *Ind. Res. J.*, 6: 25-49
- (30) Karelson, M. and Lobanov, V.S.; *Chem. Rev.*1996, 96, 1027
- (31) Taha, K. K., Ph. D thesis, Corrosion Inhibition of Brass in perchloric acid, Bangalore University, 2002.
- (32) Cherry, W.; fpiotis, N. and Thatcher, W.; *Acc. Chem. Res.*; 1977, 16,167.
- (33) Goliak, V. and Bedoglavov, S. *Proceeding of seventh International Corrosion Symposium*, Yildiz Teknik Uni Istanbul, 2000.
- (34) Pearson, R.G.; *J. Am. Chem. Soc.*1963, 85, 353