Adsorpitivity and corrosion inhibtion performance of 2-(alkyloxy)-N,N,N-tris(2-hydroxyethyl)-2-oxo-ethanaminium chloride using DFT Approach

Elshafie A. M. Gad[1] Jabir H. Al-Fahemi[2]

Abstract: Density function theory (DFT) study on adsorpitivity and corrosion inhibtion performance of reported molecules 2-(alkyloxy)-N,N,N-tris(2-hydroxyethyl)-2-oxoethanaminium chloride (where R= C6, C12 and C18) on carbon steel (Type L-52) in 0.5 M H2SO4 solution. The relevancy of quantum chemical descriptors to the performance of these molecules as corrosion inhibitors was investigated. These descriptors were EHOMO; energy of the highest occupied molecular orbital, ELUMO; energy of the lowest unoccupied molecular orbital, ΔEgap; the energy gap, η; Global hardness, S; global softness, I: ionization potential, A: electron affinity, X: absolute electronegativity, ΔN; the fraction of electron transferred, ω; global electrophilicity index, ΔE Back-donation ; the back donation, f +, f - ; Fukui indices for local nucleophilic and electrophilic attacks and s+, s- local softness. The results of descriptors calculation pronounce that the theoretical approach comply with the reported experimental data.

Keywords: DFT, quantum chemical descriptors, Fukui function, local reactivity

— — — — — — — — — ◆ — — — — — — — — —

IJSER

---

[1] Elshafie A. M. Gad, Petrochemicals Department, Egyptian Petroleum Research Institute EPRI. Nasr City,11727 Cairo, Egypt. e-mail: eamgad_99@hotmail.com Mobile: +2 01001437396
[2] Jabir H. Al-Fahemi Chemistry Department, College of Applied Science, Umm Al-Qura University Makah, 21955 Saudi Arabia

1 Introduction

Various comprehensive studies were carried out to interpret quantum chemical parameters as tools for corrosion inhibition performance [1-5]. The inhibition performance has been found to be related to adsorptivity of some organic compounds [6-8]. Chemically adsorbed compounds that include hetero atoms, aromatic ring, π-electron, or long carbon chain are found to be effective corrosion inhibitors [9], which involve either a charge sharing or charge transfer between a solid metal surface and an inhibitor.

Corrosion inhibition performance of three flavonoids, namely apigenin, luteolin-3'-methyl ether and quercetin-3, 3'-dimethylether on copper was evaluated by density functional theory (DFT) [10]. Relationships between corrosion inhibition efficiency of five kinds of mercapto-triazole inhibitors and their molecular electronic properties have been theoretically studied [11]. Y. Karzazi et al. investigated two piperidin derivatives namely 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)penta-2,4-dien-1-one (piperine) and 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)pent-2-en-1-one (piperanine) as corrosion inhibitors for mild steel using DFT [12]. Density-functional theoretical results of structural, electronics, and characterization of simulated dimethylpyridino-1-4-η-cyclohexa-1,3-diene iron tricarbonyl complexes using infra-red, uv-visible and NMR spectroscopy was studied on the basic concepts of frontier orbitals (HOMO/LUMO), chemical potential, global chemical hardness as well as electrophilicity index [13]. Computational calculations were carried out to obtain information about the relationships between the molecular and electronic structures of quinoxaline derivatives as corrosion inhibitors in acidic media [14]. Experimental and quantum chemical studies were conducted by K. I. Alaoui et al, on corrosion inhibition performance of pyrazolic derivatives for mild steel in HCl [15]. Data obtained from quantum chemical calculations were correlated to the inhibitive effect of alloxazine [16].
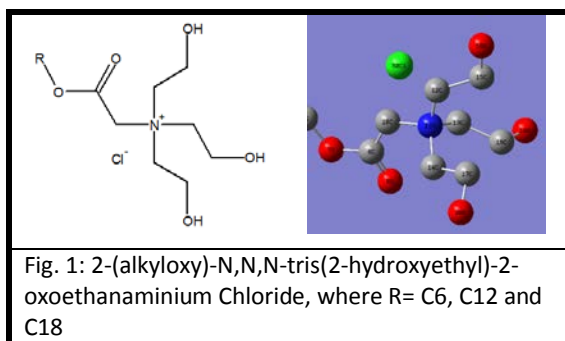
Inhibition effect of some cationic surfactants on the corrosion of carbon steel in H_2SO_4 media was studied previously [17]. These surfactants were 2-(hexyloxy)-N,N,N-tris(2-hydroxyethyl)-2-oxoethanaminium chloride; S_6, 2-(octyloxy)-N,N,N-tris(2-hydroxyethyl)-2-oxoethanaminium chloride; S_{12} and 2-(octadecyloxy)-N,N,N-tris(2-hydroxyethyl)-2-oxoethanaminium chloride; S_{18}, which were synthesized of as mentioned by Gad et al [18]. It was reported that inhibition efficiency of these cationic surfactants decreases in the following order: $S_{18} > S_{12} > S_6$,

The objective of this study is to discuss the dependence of inhibition efficiency of these compounds on quantum chemical descriptors such as E_{HOMO}; energy of the highest occupied molecular orbital, E_{LUMO}; energy of the lowest occupied molecular orbital, ΔE; the energy gap, η; global hardness, S; global softness, I: ionization potential, A: electron affinity, X: absolute electronegativity, ΔN; the fraction of electron transferred, ω; global electrophilicity index, ΔE $_{Back-donation}$; the back donation, f^+ and f^-; indices for local nucleophilic and electrophilic attacks and s+, s- local softness.

2 Computational methodology

ACD/ChemSktch version 11.02 (2008) was used to design the reported cationic surfactants[17]. Then geometrically optimized under no constraint using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) [19-21] with 6- 31G* basis set implemented in Gaussian 03 program package [22], using PC with processor Core i7 (8 CPU 1.7 GHz).

Fig. 1: 2-(alkyloxy)-N,N,N-tris(2-hydroxyethyl)-2-oxoethanaminium Chloride, where R= C6, C12 and C18

E_{HOMO}; energy of the highest occupied molecular orbital, and E_{LUMO}; energy of the lowest occupied molecular orbital were

calculated as listed in Table 1 and graphically represented in Fig. 2

The following parameters; Ionization potential (I), electron affinity (A), the electronegativity (χ), global hardness (η) and softness (S), can be explained in terms of the energy of the HOMO and the LUMO [23]

I: ionization potential = $- E_{HOMO}$ [1]

A: electron affinity = $- E_{LUMO}$ [2]

ΔE_{gap}; the energy gap (eV) = $E_{LUMO} - E_{HOMO}$ [3]

X: absolute electronegativity [24] $= \frac{I+A}{2}$ [4]

η; global hardness [25] $= \frac{I-A}{2}$ [5]

S; global softness [25] $= \frac{1}{\eta}$ [6]

ΔN; the fraction of electron transferred [26] $= \frac{X_{Fe} + x_{inh}}{2(\eta_{Fe} + \eta_{inh})}$ [7]

Where x_{Fe} and x_{inh} indicate the absolute electronegativity of Fe and the inhibitor molecule, respectively; η_{Fe} and η_{inh} indicate the absolute hardness of Fe and the inhibitor molecule, respectively

ω; global electrophilicity index [27] $= \frac{\mu^2}{2\eta}$ [8]

Where electronic chemical potential =- electronegativity; $\mu = -X$

$\Delta E_{Back-donation}$; the back donation [28] $= -\frac{\eta}{4}$ [9]

Electron charge distribution on the surfactant molecules were determined which can be used to calculate Fukui indices [29-30] (f^+ and f^-) for local nucleophilic and electrophilic attacks and $s+, s-$ local softness.

$f^+ = q_{N+1} - q_N$ (Nucleophilic attack)   [10]

$f^- = q_N - q_{N-1}$ (Electrophilic attack)   [11]

3 Results and discussion

Frontier molecule orbital density distributions of the investigated compounds: HOMO and LUMO are represented in Fig. 2. It shows that the electron density of the HOMO distributed over hydroxyl group where LUMO is mostly near the carbonyl group. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [31]. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feedback bond. According to the values of E_{HOMO} in Table 1, it is observed that E_{HOMO} increases in the following order; $S_6 > S_{12} > S_{18}$. The highest value of E_{HOMO} -0.13009 (eV) of the surfactant S_{18} indicates the better inhibition efficiency. Moreover, the tendency for the formation of a feedback bond would depend on the value of E_{LUMO}. The lower the E_{LUMO}, the easier is the acceptance of electrons from the d orbital of the metal [32]. Based on the values of E_{LUMO}, the order obtained for the decrease in E_{LUMO}: $S_{18} < S_{12} < S_6$.

The energy band gap (ΔE_{gap}), the difference of E_{LUMO} and E_{HOMO} is an indication to the reactivity of surfactant molecules towards adsorption on metallic surfaces. It has been reported [32] that the low ΔE_{gap} values indicate a good inhibition efficiency, because the energy for removing an electron from the highest occupied orbital will be low. According to the value of the energy gap as shown in Table 1, ΔE_{gap} decreases, in order $S_{18} < S_{12} < S_6$, the reactivity of the molecule increases leading to increase in inhibition efficiency of the molecule [33].

The ionization potential; I and the electron affinity; A, can be expressed as negative values of HOMO and LUMO as represented in equations (1) and (2), respectively. Ionization energy is a descriptor expressing the chemical reactivity of atoms and molecules. Higher values of ionization energy indicates higher stability and chemical inertness and vice versa smaller ionization energy indicates higher reactivity of the atoms and molecules [34]. Table 1 shows values of the ionization energy of the investigated molecules of surfactants. The low ionization

energy 0.13009 (eV) indicates the high inhibition efficiency of S_{18}.

Fig. 2: Graphical representation of FMO of studies cationic surfactants
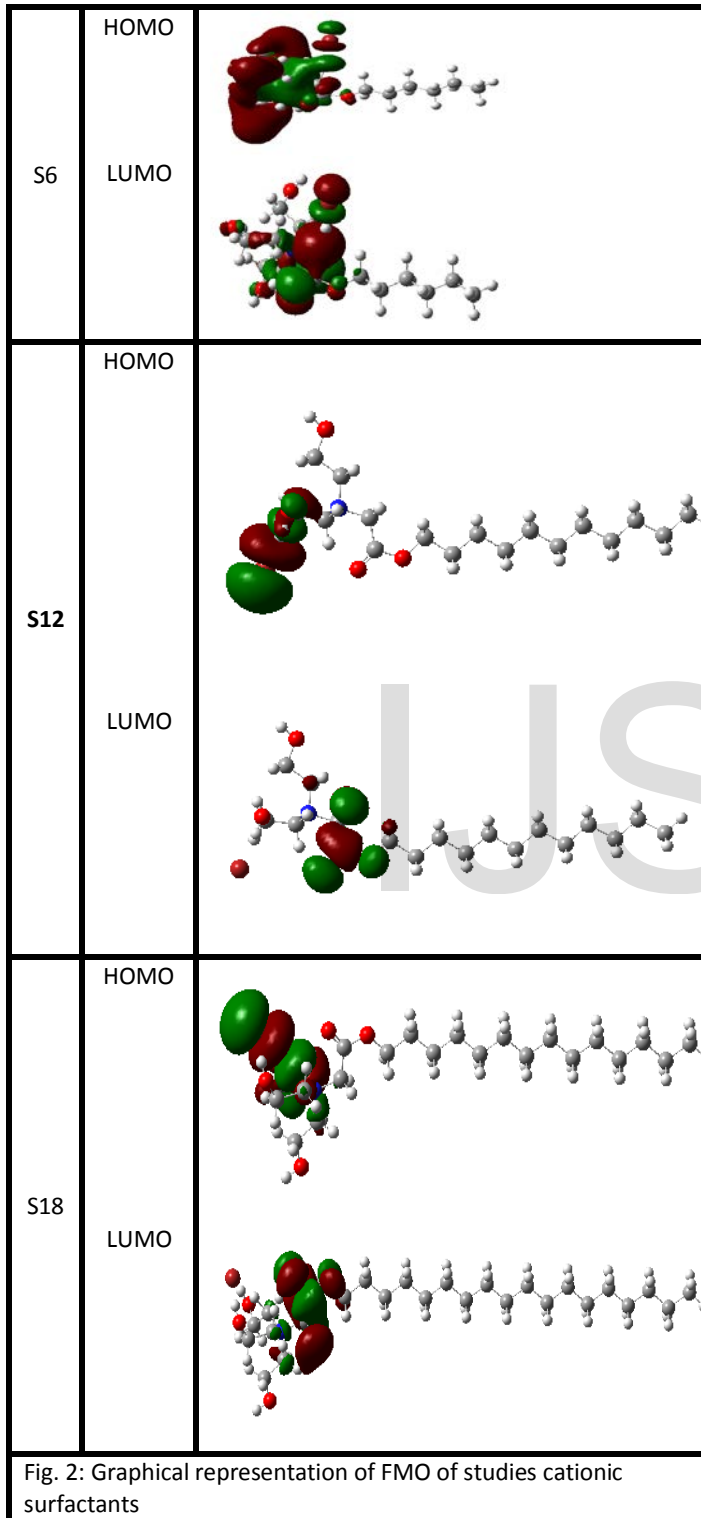
According to Sanderson's electronegativity equalization principle [35], S_6 with a high electronegativity quickly reaches equalization and hence low reactivity is expected which in turn

indicates low inhibition efficiency. Table 1 shows the order of electronegativity as S6 > S12 >S18. The electronic flow occurs from the molecule with the lower electronegativity (the surfactant inhibitor) to higher value (steel surface) for a reaction of two systems with different electronegativity, until the chemical potential becomes equalized. Thus the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated by applying the equation (7). Herewith this study, a theoretical value for the electronegativity of bulk iron was used $x_{Fe} = 1.83$ eV according to electronegativity of elements in periodic table and a global hardness of $\eta_{Fe} = 0$, by assuming that for a metallic bulk I = A, because they are softer than the neutral metallic atoms.

The values of the global hardness and global softness of the investigated surfactants; S_6, S_{12} and S_{18}, shown in Table 1 are important properties to measure stability and reactivity of molecules. It is clear that the chemical hardness indicates the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules. A hard molecule has a large energy gap however a soft molecule has a small energy gap [37-38]. Soft molecules are more reactive because the electrons can be easily released. Hence, in inhibitor with higher values of global softness S_{18} (22.33639 eV) (i.e., lower values of the global hardness (0.04477 eV) are pronounced to be better corrosion inhibitor.

According to the definition electrophilicity ω, it measures the tendency of chemical species to acquire electrons. The results of electrophilicity seen in Table 1 are in decreasing order; $S_6 > S_{12} > S_{18}$. A good, more reactive, nucleophile is characterized by low value of electronic chemical potential μ, and electrophilicity ω.

While two systems namely, metallic atoms as Fe and a surfactant as inhibitor are brought together, electrons will flow from lower electronegativity of (X_{inh}) inhibitor to higher value of (X_{Fe}) for iron, until the chemical potentials become equal. So, the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [39]. The calculated number of electrons

transferred (ΔN) from the inhibitor to the iron was also listed in Table.1. The values of ΔN show that the inhibition efficiency attributed to electron donation agrees with Lukovits's study [40]. The inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order; $S_{18} > S_{12} > S_6$. The results reveals that the ΔN value of the cationic surfactants S_{18} is greater which strongly correlates with the experimental inhibition efficiencies. ΔE $_{Back-donation}$ as values (Table 1) calculated using equation [9] are related to the global hardness which are arranged in the following order $S_{18} > S_{12} > S_6$ indicating that back-donation is favored for S_{18} to be a best inhibitor.

Calculated Mulliken atomic charge distribution are seen in Table 2 which is applied on equations [10[and [11] to calculate Fukui indices. The local reactivity of molecule is analyzed using condensed Fukui indices (Table 3). The f^+, measures the changes of density while the molecules receive electrons and it corresponds to reactivity with respect to nucleophilic attack. As vice versa, f^- denote to reactivity with respect to electrophilic attack or when the molecule loss electrons. The electrophilic and nucleophilic attacks of molecules S_6, S_{12} and S_{18} are listed in Table 3. For nucleophilic attack the most reactive site of S_6, S_{12} and S_{18} are C (10), N (11), O (18) O (19) and O (20) atoms and for electrophilic attack the most reactive site is C (8) and O (9). The local softness indices (Table 3) also explain the comparison between reactivity of similar atoms of each part of different molecules

Table 1: Calculated quantum chemical parameters of the investigated cationic surfactants

	S_6	S_{12}	S_{18}
E_{HOMO}	-0.18347	-0.14432	-0.13009
E_{LUMO}	-0.03689	-0.04033	-0.04055
ΔE_{Gap}	0.14658	0.10399	0.08954
I	0.18347	0.14432	0.13009
A	0.03689	0.04033	0.04055
X	0.11018	0.092325	0.08532
η	0.07329	0.051995	0.04477
S	13.64443	19.23262	22.33639
$\omega = \mu^2/2\eta$	0.082819	0.081969	0.081299
ΔN	0.332924	0.640975	0.822649

| ΔE $_{Back-}$ | -0.01832 | -0.013 | -0.01119 |

Table 2: Calculated Mulliken atomic charge distribution

		N	N+1	N-1
S6	7 O	-0.527	-0.481	-0.545
	8 C	0.619	0.655	0.596
	9 O	-0.571	-0.419	-0.601
	10 C	-0.230	-0.029	-0.197
	11 N	-0.624	-0.539	-0.584
	12 C	-0.222	-0.259	-0.230
	13 C	-0.252	-0.290	-0.250
	14 C	-0.237	-0.279	-0.243
	15 C	-0.145	-0.140	-0.146
	16 C	-0.135	-0.129	-0.140
	17 C	-0.138	-0.133	-0.142
	18 O	-0.552	-0.529	-0.569
	19 O	-0.553	-0.524	-0.570
	20 O	-0.550	-0.519	-0.570
	7 O	-0.490	-0.472	-0.542
	8 C	0.680	0.688	0.496
	9 O	-0.418	-0.436	-0.577
	10 C	-0.288	0.307	-0.269
	11 N	-0.585	-0.496	-0.586
	12 C	-0.188	-0.211	-0.153
	13 C	-0.264	-0.264	-0.237
	14 C	-0.264	-0.264	-0.236
	15 C	-0.149	-0.154	-0.156
	16 C	-0.155	-0.121	-0.164
	17 C	-0.155	-0.121	-0.164
	18 O	-0.576	-0.556	-0.582
	19 O	-0.581	-0.529	-0.594
	20 O	-0.581	-0.528	-0.594
S18	7 O	-0.492	-0.521	-0.539
	8 C	0.677	0.629	0.536
	9 O	-0.415	-0.406	-0.549
	10 C	-0.389	-0.345	-0.285
	11 N	-0.594	-0.559	-0.591
	12 C	-0.202	-0.263	-0.174
	13 C	-0.260	-0.422	-0.216
	14 C	-0.251	-0.313	-0.223
	15 C	-0.136	-0.179	-0.140
	16 C	-0.113	-0.184	-0.115
	17 C	-0.116	-0.182	-0.117
	18 O	-0.571	-0.535	-0.578
	19 O	-0.568	-0.521	-0.588
	20 O	-0.582	-0.557	-0.603

Table 3: Calculated Fukui indices and local softness for investigated compounds

	f^+	f^-	s^+	s^-
S6	0.046	0.018	0.623	0.241
	0.036	**0.023**	0.487	**0.316**
	0.152	**0.030**	2.072	**0.409**
	0.200	-0.033	**2.735**	-0.453
	0.085	-0.040	**1.156**	-0.543
	-0.037	0.008	-0.508	0.108
	-0.038	-0.002	-0.517	-0.026
	-0.042	0.006	-0.570	0.080
	0.005	0.001	0.066	0.012
	0.006	0.005	0.076	0.073
	0.005	0.004	0.066	0.051
	0.023	0.017	**0.315**	0.234
	0.029	0.017	**0.390**	0.234
	0.031	0.020	**0.418**	0.274
S12	0.018	0.052	0.360	1.043
	0.008	**0.184**	0.158	**3.677**
	-0.018	**0.159**	-0.361	**3.186**
	0.595	-0.019	**1.907**	-0.387
	0.090	0.001	**1.792**	0.025
	-0.023	-0.035	-0.454	-0.703
	0.000	-0.026	-0.007	-0.528
	0.000	-0.027	-0.009	-0.548
	-0.005	0.007	-0.109	0.143
	0.034	0.009	0.677	0.181
	0.034	0.009	0.677	0.186
	0.021	0.005	**0.413**	0.104
	0.052	0.014	**1.050**	0.270
	0.052	0.014	**1.047**	0.271
S18	-0.029	0.048	-0.601	0.974
	-0.049	**0.141**	-0.997	**2.880**
	0.009	**0.134**	0.192	**2.730**
	0.044	-0.104	**0.901**	-2.126
	0.035	-0.003	**0.710**	-0.061
	-0.061	-0.028	-1.239	-0.573
	-0.163	-0.044	-3.316	-0.899
	-0.062	-0.027	-1.275	-0.553
	-0.043	0.004	-0.877	0.083
	-0.071	0.003	-1.452	0.056
	-0.066	0.000	-1.344	0.009
	0.036	0.007	**0.740**	0.140
	0.047	0.020	**0.955**	0.403
	0.025	0.021	**0.513**	0.422

4 Conclusion

The results of quantum chemical calculations using DFT at the B3LYP- with 6- 31G* basis set level pronounces that the theoretical approach comply with the reported experimental data.

5 References

1. K. Efil , Y. Bekdemir, A DFT Study. Canadian Chemical Transactions Issue 1 (2015) 85-93
2. A. Zarrouk1, H. Zarrok, R. Salghi, B. Hammouti, S.S. Al-Deyab, R. Touzani1, M. Bouachrine, I. Warad, T. B. Hadda, Int. J. Electrochem. Sci., 7 (2012) 6353 – 6364
3. R.S. Oguike, O .Oni, Int. J. Res. Chem. Environ. Vol. 4 Issue 3 (2014) 177-186
4. K.F. Khaleda, Electrochimica Acta 55 (2010) 6523–6532.
5. S. Chen,*, S. Scheiner, T. Kar, U. Adhikari, Int. J. Electrochem. Sci., 7 (2012) 7128 – 7139.
6. H.L. Wang, RB Liu, J Xin. Corros Sci, 2004; 46:2455-2466.
7. S. Rengamati, S Muralidharan, M Anbu Kulamdainathan, S Venkatakrishna Iyer. J Appl Electrochem, 1994; 24:355.
8. E.E. Ebenso, Bull Electrochem, 2003; 19:209-216.
9. I. Dehri, M.Ozcan, Mater Chem Phys. (2006) 98:316
10. P.Udhayakala, T.V. Rajendiran and S. Gunasekaran, Journal of Chemical, Biological and Physical Sciences, 2(3) (2012) 1151-1165.
11. C. Shuangkou, S.Steve, K.Tapas, A. Upendra, Int. J. Electrochem. Sci., 7 (2012) 7128 – 7139
12. Y. Karzazi, M. E. Belghiti, A. Dafali and B. Hammouti, Journal of Chemical and Pharmaceutical Research, 6(4) (2014) 689-696
13. I.A. Adejoro T.I. Odiaka and O.F. Akinyele, Journal of Natural Sciences Research 4(1) (2014)38-45.
14. Z. El Adnani, M. Mcharfi, M. Sfaira, M. Benzakour, A.T. Benjelloun, M. Ebn Touhami, B. Hammouti , M. Taleb, Int. J. Electrochem. Sci., 7 (2012) 6738 – 6751
15. K. I. Alaoui, F. EHajjaji. M. Azaroual, M. Taleb, A. Chetouani, B Hammouti, F. Abrigach, M. Khoutoul, Y. Abboud, A. Aouniti and R. Touzani, Journal of Chemical and Pharmaceutical Research, 6(7) (2014) 63-81.
16. N.O. Obi-Egbedi, I.B. Obot, Corrosion Science 53 (2011) 263–275
17. O.A.Hazazi, M.Abdallah, E. A. M. Gad, Int. J. Electrochem. Sci., 9 (2014) 2237 – 2253.
18. E. A. M. Gad, Z Abdel-Hamid, D. A. Ismail and R. A. Al-adly, J Chem. Technol Biotechnol 74 (1999)345-348

19. A. Zarrouk, B. Hammouti, R. Touzani, S.S. Al-Deyab, M. Zertoubi, A. Dafali, S. Elkadiri, Int. J. Electrochem. Sci., 6 (2011) 4939.
20. A. D. Becke, J. Chem. Phys., 96 (1992) 9489.
21. A. D. Becke, J. Chem. Phys., 98 (1993) 1372.
22. C. Lee, W. Yang, R.G. Parr, Phys. ReV. B., 37 (1988) 785.
23. Wang H, Wang X, Wang H, Wang L, Liu A. J Mol Model 13(2007)147-153.
24. L. Pauling, The Nature of the Chemical Bond. Cornell University Press, Ithaca, New York; 1960.
25. P Senet, Chem. Phys. Lett. 1997,275, 527-532
26. R. G. Parr, L.Szentpaly, S. Liu, J. Am. Chem. Soc., 121 (1999) 1922.
27. R. G. Parr, L . Szentpaly, S . Liu. J Am Chem Soc, 1999; 121:1922-1924.
28. B. Gomez, N. V. Likhanova, M. A. Dominguez-Aguilar, R .Martinez-Palou, A. Vela, J. Gasquez. J Phy Chem, B 110 (2006) 8928-8934.
29. A. A. Siaka; N.O. Eddy; S. Idris, L. Magaji, Res.J. Appl. Sci., 6(7-120), (2011) 487-493.
30. Nnabuk O Eddy, Stanislav R. Stoyanov and Eno.E.Ebenso, Int. J .Electrochem. Sci., 5 (2010), 1127.

31. 28. A.Y. Musa, A. H. Kadhum, A. B. Mohamad, A.b. Rohoma, H. Mesmari, J. Mol. Struct., 969 (2010) 233.
32. M . Finsgara., A. Lesara, A. Kokalja, I. Miloseva, Electrochimica Acta, 53 (2008) 8287–8297
33. Y. Tang, X. Yang, W. Yang, Y. Chen, R. Wana, Corros. Sci., 52 (2010) 242–249
34. T. Chakraborty and D. C. Ghosh, Mol. Phys., 108(16), (2010) 2081.
35. P. Geerlings, F. De Proft, Int. J. Mol. Sci. 3 (2002) 276.
36. Z. El Adnani, M. Mcharfi, M. Sfaira, M. Benzakour, A. T., Benjelloun, M. E. Touhami, Int J Electrochem Sci, 7 (2012) 6738–51.
37. H Zarrok, SS Al-Deyab, A Zarrouk, R Salghi, B Hammouti, H Oudda, M Bouachrine, and F Bentiss, 7 (2012) 4047-4063.
38. Y Karzazi, M El Alaoui Belghiti, A Dafali and B Hammouti, Journal of Chemical and Pharmaceutical Research, 6(4) (2014) 689-696.
39. R.G. Pearson, Inorg.Chem., 27 (1988) 734.
40. I. Lukovits, E. Kalman and F. Zucchi, Corros., 57 (2001) 3.

IJSER