

Carbethoxythiazole Corrosion Inhibitor: As an Experimentally Model and DFT Theory

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Abstract: Inhibitor for mild steel derived from carbethoxythiazole namely 2-amino-4-methyl-5-carbethoxythiazole was synthesized and the chemical structure was elucidating by fourier transform in frared and nuclear magnetic resonance spectroscopies. The inhibition efficiency for 2-amino-4-methyl-5-carbethoxythiazole to inhibit the damage effects for mild steel of corrosion in 1 M hydrochloric acid solution was figured and was 82.5% regarding to weight loss technique. Scanning electron microscopy was used as a confirmation of ability of 2-Amino-4-Methyl-5-Carbethoxythiazole (AMC) to inhibit the corrosion of specimens of mild steel surface. The standard free energy of adsorption and adsorption equilibrium constant were calculated and the adsorption of 2-amino-4-methyl-5-carbethoxythiazole on surface of mild steel was obey adsorption isotherm of Langmuir. To proof the methodological findings, density function theory at the B3LYP/6-311+G** level of theory was used to calculate highest occupied with lowest unoccupied molecular orbitals energies and dipole moment.

Key words: Carbethoxythiazole, FT-IR, NMR, CHN, corrosion inhibitor, inhibit

INTRODUCTION

For the time being compounds of organic origin are quite significant due to pharmaceutical employments (Al-Majedy *et al.*, 2014; Naama *et al.*, 2013). Derivatives of thiazole were quite, significant compounds that related to biology. Many of these thiazles were proved as antimicrobial (Kadhum *et al.*, 2011; El-Agrody *et al.*, 2001; Rositica *et al.*, 2002), anti-inflammatory (Flasik *et al.*, 2009), anticoagulant (Kovalenko *et al.*, 2000), antiHIV (El-Saghier and Khodairy, 2000) and antitumor compounds. Corrosion inhibitors were impedance for metal surface in basic or/and acidic solutions and prevent corrosion through adsorbed molecules of inhibitor (Satyanarayana *et al.*, 2008; Garazd *et al.*, 2007; Smitha and Reddy, 2004; Kotali *et al.*, 2008; Nofal *et al.*, 2000) and make protect barrier to the metal surface (Kennedy and Thornes, 1997; Zabradnik, 1992; Heravi *et al.*, 2008). Many factors influenced the adsorption ability of inhibitor molecules on metal surface and that were the nature of surface and the type of electrolyte in addition to molecular structure of the utilized inhibitor (Kampranis *et al.*, 1999). Corrosion inhibitor may react chemically with the atoms of the metal surface and

formed a stable complex with coordination bonds between inhibitors and atoms of the metal that become film on the surface of metal (Wang and Ng, 2001). To increase our previous investigations on usable molecules (Mao *et al.*, 2002; Al-Amiery *et al.*, 2014a, b; Junaedi *et al.*, 2013; Obayes *et al.*, 2017; Kadhum *et al.*, 2013; Obayes *et al.*, 2014; Al-Azawi *et al.*, 2016; Issa *et al.*, 2016; Rubaye *et al.*, 2015), a synthesized thiazole namely 2-amino-4-methyl-5 carbethoxythiazole that was characterize by FT-IR and nuclear magnetic resonance NMR spectroscopies. The inhibition efficiency was figured according to weight loss technique and scanning electron microscopy. Moreover, DFT was used as theoretical calculations to associate the inhibitive characteristics with electronic structure.

MATERIALS AND METHODS

Purchase chemical compounds and solvents that employed in the investigation were utilized without extra purifications. Spectra of infra-red and nuclear magnetic resonance (with dimethylsulfoxied-d6 as solvent and TMS as internal standard) have been done utilizing of

FTIR-8300 Shimadzu spectrometer and 300 MHz bruker instrument, respectively. Carbon, hydrogen and nitrogen-elemental analysis have been done through 5500 Carlo Erba.

Synthesis of 2-Amino-4-Methyl-5-Carboxythiazole (AMC) as corrosion Inhibitor: A solution of ethanol (100 mL) that have ethyl 2-chloro-3-oxobutanoate (8.20 g, 0.05 mol) and thiourea (3.8 g, 0.05 mol) were under refluxed for 4.0 h, then cooled and concentrated NH_4OH has been add. Filtered dried and using ethanol as recrystallization solvent. M.P. 176°C . FT-IR in cm^{-1} : 3344.2 for amino group, 1708.8 for carbonyl, 2913.6 and 2943.9 for alkyl groups. The ^1H NMR: 1.58 (t, CH_3), 2.53 (s, CH_3), 3.98 (q, CH_2), 6.47 (s, NH). Elemental analysis: C, 44.93 (45.15), H, 5.87 (5.41), N, 14.81 (15.04).

Corrosion technique: Samples alloy of mild steel that employed in this study as an electrodes have been purchased from metal-samples-company. Elements percentage were as follows: 99.21, 0.21, 0.38, 0.09, 0.05 and 0.01 for iron, carbon, silicon, sulfur, manganese and aluminum, respectively.

Inhibition efficiency of 2-amino-4-methyl-5-carboxythiazole for mild steel surface with the area of 4.5 cm^2 . Cleaning was done regarding to methodology at reference (Mashelkar and Audi, 2006). The samples were suspension in hydrochloric acid 200 mL as corrosive acidic solution without/with the 2-amino-4-methyl-5-carboxythiazole at the concentrations 0.001, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.50 g/L for (1, 3, 5, 10, 24 and 72 h). The inhibition efficiency was figured based on Eq. 1:

$$\text{IE (\%)} = \left(1 - \frac{W_2}{W_1}\right) \times 100 \quad (1)$$

where, W_1/W_2 point to weight of MS in presence/absence 2-Amino-4-Methyl-5-Carboxythiazole (AMC).

Computational details: A geometrical optimization for 2-amino-4-methyl-5-carboxythiazole was performed utilizing density functional theory DFT. All calculations were carried out utilizing the Gaussian 09 program package with the B3LYP method at 6-311++G** basis set. The parameters such as energy gap (EHOMO-ELUMO), dipole moment (μ), Ionization potential ($I = -\text{EHOMO}$), Electron affinity ($A = -\text{ELUMO}$) and the inhibition efficiency (%) was calculated based on Al-Amiery (Obayes *et al.*, 2017), methodology (Eq. 2-4):

$$I_{\text{add}} \% = \frac{I_{\text{AMC}} - I_{\text{x-AMC}}}{I_{\text{AMC}}} \times 100\% \quad (2)$$

$$I_{\text{e}_{\text{add}}} \% = I_{\text{add}} \% \times I_{\text{e}_{\text{AMC}}} \% \quad (3)$$

$$I_{\text{e}_{\text{theory}}} \% = I_{\text{AMC}} \% \times I_{\text{e}_{\text{add}}} \% \quad (4)$$

Where:

$I_{\text{add}} \%$ = The percent change in the ionization potential of model x-AMC relative to that of AMC

$I_{\text{e}_{\text{add}}}$ and $I_{\text{e}_{\text{theory}}} \%$ = The corresponding additional and theoretical inhibition efficiencies, respectively

Electronegativity x and global hardness (η) depend on the values of I and A and could evaluated regarding to Eq. 5 and 6. Chemical Softness (S) could be estimated according to Eq. 7:

$$X = \frac{1+A}{2} \quad (5)$$

$$\eta = \frac{1-A}{2} \quad (6)$$

$$S = \frac{1}{\eta} \quad (7)$$

RESULTS AND DISCUSSION

Synthesis: The inhibitor 2-Amino-4-Methyl-5-Carboxythiazole (AMC) was synthesized in a good yield via. refluxation reaction of same molar ratio of ethyl 2-chloro-3-oxobutanoate and thiourea. The molecular formula of 2-amino-4-methyl-5-carboxythiazole has been elucidate. In infrared spectrum of 2-amino-4-methyl-5-carboxythiazole has a carbonyl absorption band for ester group that appeared for 2-amino-4-methyl-5-carboxythiazole also the amino group at 3344.2. The nuclear magnetic resonance spectrum showed singlet at δ 6.47 ppm due to the proton of N-H. 2-amino-4-methyl-5-carboxythiazole was synthesized from ethyl 2-chloro-3-oxobutanoate and thiourea as in Fig. 1. The mechanism of 2-amino-4-methyl-5-carboxythiazole can be shown according to Fig. 2.

Results of weight loss technique: Employing of the inhibitor in industries become the highest economic manner because of the protection of metal or alloy surface from effects of acidic or basic solutions (Al-Amiery *et al.*, 2014a, b). Natural and/or synthetic corrosion inhibitors have been required for alloys in oil and/or gas industries due to barrier formation that required for protection for the

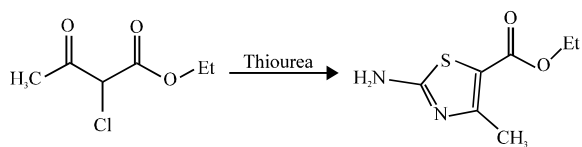


Fig. 1: 2-Amino-4-methyl-5-carbethoxythiazole synthesis

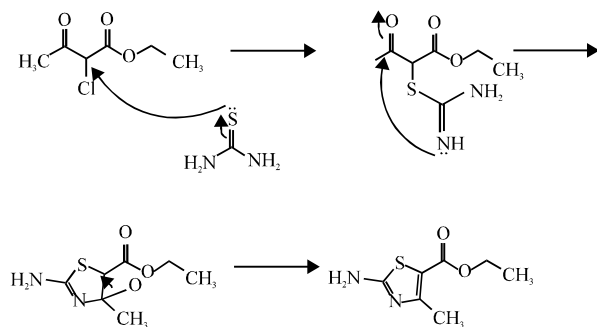


Fig. 2: Mechanism for the formation of 2-amino-4-methyl 5-carbethoxythiazole

surface of alloys and metals. The using of corrosion inhibitors that have nitrogen, oxygen and/or sulfur atoms in their structures were very important due to capability of these atoms to bonded in coordination bonds with the atoms at the surface of alloys and metals in order to form stable complexes (Mohamad *et al.*, 2014; Al-Amiery *et al.*, 2014a, b; Kadhum *et al.*, 2013).

Concentration effect: To figure the inhibition efficiency of the synthesized inhibitor 2-amino-4-methyl-5 carbethoxythiazole weight loss procedure (Musa *et al.*, 2012; Junaedi *et al.*, 2012) was employed for that purpose with inhibition molecules at the concentrations (0.05, 0.1, 0.15, 0.2, 0.25 and 0.5 g/L) for time period (1, 3, 5, 10, 24 and 72 h) and 25°C in solution of hydrochloric acid for the mild steel surface. The results of using 2-amino-4-methyl 5-carbethoxythiazole as inhibitor were showed in Fig. 3 and point to the performance of 2-amino-4-methyl-5 carbethoxythiazole to reduce the corrosion at acidic solution of mild steel surface with highest inhibition qualification 82.5% regarding to higher concentration of 2-amino-4-methyl-5-carbethoxythiazole.

Temperature effect: To figuration the impact of the temperature degrees on the inhibition efficiency of 2-Amino-4-Methyl-5-Carbethoxythiazole (AMC) as corrosion inhibitor, the methodologies were carried out without or with AMC for different temperature degrees 303-333 K with increasing 10°. AMC with the concentration of 0.5 g/L has excellent inhibition efficiency at the lowest temperature degree 303 K and its ability to

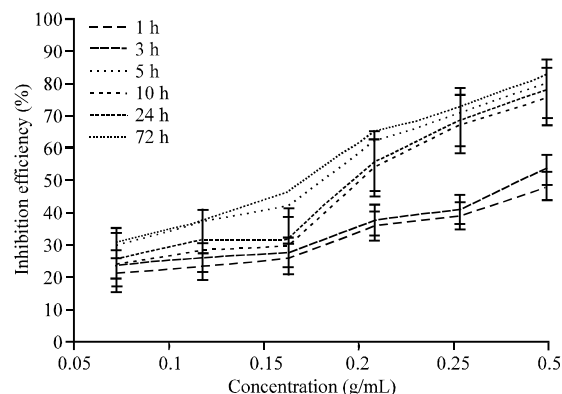


Fig. 3: Function of time at concentrations of 2-amino-4 methyl-5-carbethoxythiazole

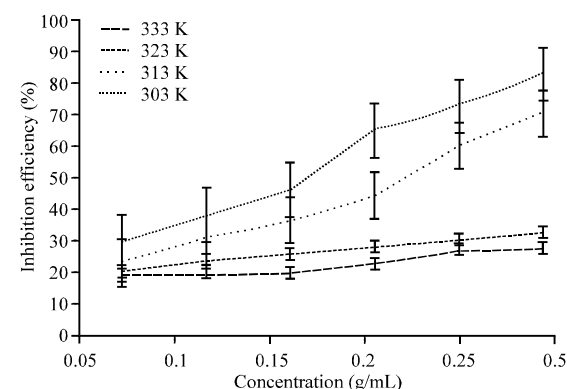


Fig. 4: AMC concentrations at various temperature degrees

reduce the corrosion was decreasing regarding to increasing of temperature degrees. Figure 4 demonstrated temperature degree's effect of AMC on inhibition efficiency. The negative charge of adsorption heat of AMC on mild steel was point to an exothermic process which explains the reducing ability of AMC as corrosion inhibitor with increasing temperature.

Scanning electron microscopy: The analyzing of the surface of mild steel was performed through SEM in 1.0 M HCl in absence and presence of AMC at the concentration 0.5 g/L for 5 h. and fixed temperature degree 303 K. In corrosive solution the mild steel surface was observed damaged because of the high rate dissolution of iron. On the other hand AMC will form a barrier that could be appeared on the surface of the mild steel in presence of AMC. From Fig. 5, it can be shown that AMC adsorbed by the surface of mild steel and formed a protective film against corrosive media.

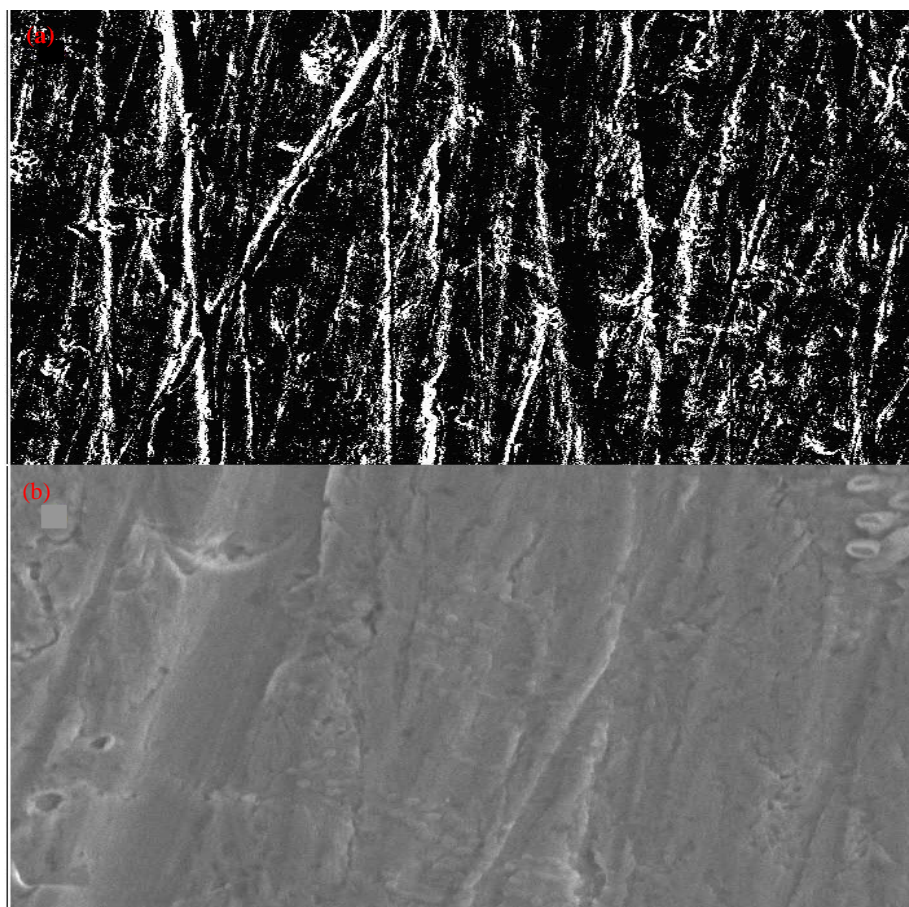


Fig. 5: SEM images of surface of mild steel in presence: a) Absence and b) AMC

Computational studies: To figure out the significant electronic impacts of AMC DFT was used. The optimized geometrical structure with HOMO and LUMO were displayed in Fig. 6 and electronic energies are posted in Table 1.

From Eq. 2-4 we can calculate the theoretical value of inhibition efficiency for the tested inhibitor AMC as in Table 2.

Such study was establishing to be effective in providing a glance about reactivity in addition to selectivity in terms of comprehensive parameters (electro-negativity, χ , hardness, η , softness, S and local softness ($sd-rP$)) (Ebenso *et al.*, 2010; Ashassi-Sorkhabi *et al.*, 2005). The purpose of the AMC was for utilizing it as an inhibitor regarding to the number of oxygen, nitrogen and sulfur atoms in the molecule as active centers and planarity with the resonance structure of AMC. Superior inhibitor is ordinarily an organic molecule which offers electrons to vacant metal orbitals and also accepts the metal electrons (Khaled *et al.*, 2009). Quantum calculations were employed to investigate the interactions between metal and

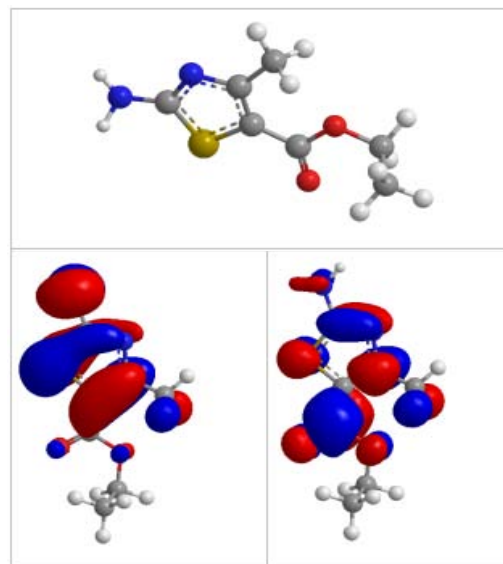


Fig. 6: a) Optimized geometrical structure; b) HOMO and c) LUMO of AMC

Table 1: Calculated HOMO and LUMO energies, energy gaps, ionization potential and electron affinity (eV) for AMC

E_{HOMO}	E_{LUMO}	μ	Energy gap	Ionization potential (I)	Electron affinity (A)
-9.118	-1.981	2.928	7.137	9.118	1.981

Table 2: Theoretical inhibition efficiency for AMC

Compound	Inhibition efficiency (%)	
	Theoretical (IE_{theo})	Experimental
AMC	83.96	82.5

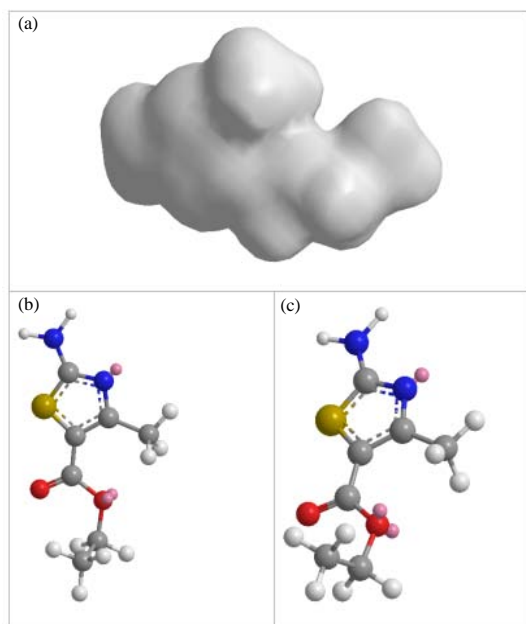


Fig. 7: a) Charge distribution; b) Fukui (f-) function; c) Fukui (f+) function

inhibitor (Bahrami *et al.*, 2010). Highest occupied, lowest unoccupied molecular orbitals (HOMO and LUMO) and Fukui functions in addition to total electron density of AMC are posted in Fig. 7. Blue and red iso-surfaces characterize the electron density variation, the blue one demonstrate electron gathering on the other hand the red one demonstrate the electron loss. The parameters E_{HOMO} , E_{LUMO} and dipole moment are posted in Table 1. The HOMO regions for AMC represent the active centers and also has the sites at which electrophiles attack with the utmost capability to interact with the atoms at surface of the metal and for our inhibitor AMC that has carbonyl amines and sulfur may link to the metal through these groups. While, the LUMO orbital has the ability to accept metal electrons employing antibonding orbitals to form feedback bonds are saturated around the thiazole ring (Cruz *et al.*, 2005). Moreover, the E_{HOMO} with high value indicates the tendency of a molecule to

donate electrons to an appropriate acceptor molecule with low energy or an empty electron orbital whereas LUMO energy of the characterizes the susceptibility of AMC toward nucleophilic attacks (Costa and Lluh, 1984). The energy gap ΔE with low values reveal to electron removing from the last occupied orbital will be minimized, regarding to enhanced the ability of AMC to inhibit the corrosion (Khalil, 2003). The observed high value of energy gap was in accordance with the nature (non-specific) of interaction of AMC with mild steel surface. A relation of inhibition efficiency of AMC with E_{HOMO} , E_{LUMO} and from the methodological results it can be conclude that increasing AMC concentration led to enhancement of inhibition efficiency. Also from DFT calculations the highest value of E_{HOMO} and lowest value of E_{LUMO} improve the inhibition efficiency. The rising of E_{HOMO} signalize a higher orientation for the giving electrons to vacant orbital of molecule. E_{HOMO} that has high value has the ability to adopted by the metal surface of the inhibitor. Thus, improving the transfer process via adsorbed layer may improve the capability of inhibitor to reduce the corrosion. This result could be demonstrating as follows. E_{LUMO} refer to the capability of the AMC molecules to take electrons, so, a lowest E_{LUMO} value refer to that these molecules may take electrons (Al-Amiery, 2012). The tendency of a process of corrosion inhibition may be portend regarding to the dipole moment (μ). Dipole moment defined as the measurement of bond polarity and is concerning to the electrons distribution of a molecule of AMC. In literatures there is conflicting on the employment of μ as a corrosion inhibition reaction indicator, dipole moment may agree that the adsorption of polar molecules have with high value of dipole moments were have excellent inhibition efficiencies. Our investigation indicates that AMC as an inhibitor with dipole moment equal to 2.928 and maximum inhibition efficiency (82.5%). Researchers showed that the inhibition efficiency raise with raising of dipole moment that depend on class and nature of molecules. Also, insufficiency of agreement in the literatures of the correlation of μ with $IE\%$ as in several issues there are no considerable relationship between the values of μ with $IE\%$ (Xia *et al.*, 2008; Musa *et al.*, 2010). The charge distribution (Fig. 7a) that around molecule of AMC, give hint and expectation about orientations of adsorption (Cruz *et al.*, 2005). The local reactivity of AMC has defined regarding to Fukui Indices (FI) to consider the reactive region in terms of nucleophilic (f+) and electrophilic (f-) behavior. Figure 7b demonstrate that functions of f- for AMC match with the locations of HOMO indicate the sites through which the molecules of AMC have the ability to be adsorbed on surface of the

Table 3: Fukui (f-) function and Fukui (f+) function for AMC

Compound	Fukui (f-)	Fukui (f+)
AMC	0.127	0.084

Table 4: Quantum chemical parameters for AMC

Inhibitor	χ	S	σ
AMC	5.5495	3.5685	0.2802

metal, on the other hand, f^+ as in Fig. 7c LUMO locations, demonstrate sites that AMC molecules have the ability to interact with the non-bonding electrons of the metal. High values of f^- are correlating with the carbonyl amine and ester groups of AMC in addition to thiazole ring and also to carbon-carbon atoms bridge (Table 3 and 4).

The high electronegativity refers to high inhibition efficiency and in our investigations it was high value and reach to 5.54 (Geerlings and Proft, 2002). Chemical hardness and softness were the requisite chemical significance called global or universal reactivity descriptors that are theoretically justified through the domain of DFT (Density Functional Theory) (Udhayakala, 2014). These are the significant characteristics to evaluate the stability and reactivity of molecules. It is clear that the hardness mainly indicates the impedance towards the polarization of the electron can of the atom, ion or molecule under small disruption of chemical reaction. Hard molecules have great energy gap and soft molecules have good energy gaps (Obi-Egbedi *et al.*, 2011). In our present study AMC with hardness value 3.5685 eV and usually, the inhibitor with the minimum value of hardness was predictable to have the superior inhibition efficiency (Ebenso *et al.*, 2010). For the easy transfer of electron, adsorption may exist at the side of molecule where S has a maximum value (Hasanov *et al.*, 2007). AMC with the softness value of 0.2802 eV has the maximum inhibition efficiency.

CONCLUSION

2-Amino-4-Methyl-5-Carboethoxythiazole (AMC) as inhibitor for surface of the mild steel that was prepared from ethyl 2-chloro-3-oxobutanoate and thiourea. The chemical structure of this compound 2-amino-4-methyl-5-carboethoxythiazole was elucidated according to spectroscopical techniques. Inhibition efficiency of the 2-amino-4-methyl-5-carboethoxythiazole in HCl solution with 1 M for mild steel was studied. 2-Amino-4-methyl-5-carboethoxythiazole, demonstrated a good performance as inhibitor 82.5% at the maximum concentrations of AMC. Inhibition efficiency of AMC was increased regarding to increasing of ACM concentration on the other hand the inhibition efficiency of AMC decreased when the temperature raised. The SEM images of AMC displayed that the investigated inhibitor forms a protective film for

the surface of mild steel surface. Computational calculations were carried out to find out the relation of AMC electronic structure to inhibition efficiency. The theoretical and methodological inhibition efficiency of AMC was in a perfect agreement, demonstrating the reliability of the methodology used.

REFERENCES

- Al-Amiery, A.A., 2012. Antimicrobial and antioxidant activities of new metal complexes derived from (E)-3 ((5-phenyl-1,3,4-oxadiazol-2-ylimino)methyl) naphthalen-2-ol. *Med. Chem. Res.*, 21: 3204-3213.
- Al-Amiery, A.A., A.A.H. Kadhum, A.H.M. Alobaidy, A.B. Mohamad and P.S. Hoon, 2014a. Novel corrosion inhibitor for mild steel in HCl. *Mater.*, 7: 662-672.
- Al-Amiery, A.A., Y.K. Al-Majedy, A.A.H. Kadhum and A.B. Mohamad, 2014b. New coumarin derivative as an eco-friendly inhibitor of corrosion of mild steel in acid medium. *Mol.*, 20: 366-383.
- Al-Azawi, K.F., S.B. Al-Baghdadi, A.Z. Mohamed, A.A. Al-Amiery and T.K. Abed *et al.*, 2016. Synthesis, inhibition effects and quantum chemical studies of a novel coumarin derivative on the corrosion of mild steel in a hydrochloric acid solution. *Chem. Central J.*, 10: 1-23.
- Al-Majedy, Y.K., A.A.H. Kadhum, A.A. Al-Amiery and A.B. Mohamad, 2014. Synthesis and characterization of some new 4-Hydroxy-coumarin derivatives. *Mol.*, 19: 11791-11799.
- Ashassi-Sorkhabi, H., B. Shabani and D. Seifzadeh, 2005. Effect of some pyrimidinic Schiff bases on the corrosion of mild steel in HCl solution. *Electrochim. Acta*, 50: 3446-3452.
- Costa, J.M. and J.M. Lluch, 1984. The use of quantum mechanics calculations for the study of corrosion inhibitors. *Corros. Sci.*, 24: 929-933.
- Cruz, J., T. Pandiyan and E. Garcia-Ochoa, 2005. A new inhibitor for mild carbon steel: Electrochemical and DFT studies. *J. Electroanal. Chem.*, 583: 8-16.
- Ebenso, E.E., D.A. Isabirye and N.O. Eddy, 2010. Adsorption and quantum chemical studies on the inhibition potentials of some thiosemicarbazides for the corrosion of mild steel in acidic medium. *Intl. J. Mol. Sci.*, 11: 2473-2498.
- El-Agrody, A.M., M.S. Abd El-Latif, N.A. El-Hady, A.H. Fakery and A.H. Bedair, 2001. Heteroaromatization with 4-hydroxycoumarin part II: Synthesis of some new pyrano[2,3-d]pyrimidines, [1,2,4] triazolo[1,5-c]pyrimidines and pyrimido [1,6-b]-[1,2,4]triazine derivatives. *Molecules*, 6: 519-527.

- El-Saghier, A.M.M. and A. Khodairy, 2000. New synthetic approaches to condensed and spiro coumarins: Coumarin-3-thiocarboxamide as building block for the synthesis of condensed and spiro coumarins. *Phosphorus Sulfur Silicon Relat. Elem.*, 160: 105-119.
- Flasik, R., H. Stankovicova, A. Gaplovsky and J. Donovalova, 2009. Synthesis and study of novel coumarin derivatives potentially utilizable as memory media. *Mol.*, 14: 4838-4848.
- Garazd, M.M., O.V. Muzychka, A.I. Voyk, I.V. Nagorichna and A.S. Ogorodnichuk, 2007. Modified coumarins. 27. Synthesis and antioxidant activity of 3-substituent 5, 7-dihydroxy-4-methylcoumarins. *Chem. Nat. Compd.*, 43: 19-23.
- Geerlings, P. and F.D. Proft, 2002. Chemical reactivity as described by quantum chemical methods. *Intl. J. Mol. Sci.*, 3: 276-309.
- Hasanov, R., M. Sadykoglu and S. Bilgic, 2007. Electrochemical and quantum chemical studies of some Schiff bases on the corrosion of steel in H_2SO_4 solution. *Appl. Surf. Sci.*, 253: 3913-3921.
- Heravi, M.M., S. Sadjadi, H.A. Oskooie, R.H. Shoar and F.F. Bamoharram, 2008. The synthesis of coumarin-3-carboxylic acids and 3-acetyl-coumarin derivatives using heteropolyacids as heterogeneous and recyclable catalysts. *Catal. Commun.*, 9: 470-474.
- Issa, A.Y., K.S. Rida, A.Q. Salam and A.A. Al-Amiery, 2016. Acetamidocoumarin as a based eco-friendly corrosion inhibitor. *Intl. J. Chem. Tech. Res.*, 9: 39-47.
- Junaedi, S., A.A. Al-Amiery, A. Kadhum, A.A.H. Kadhum and A.B. Mohamad, 2013. Inhibition effects of a synthesized novel 4-aminoantipyrine derivative on the corrosion of mild steel in hydrochloric acid solution together with quantum chemical studies. *Intl. J. Mol. Sci.*, 14: 11915-11928.
- Junaedi, S., A.A.H. Kadhum, A.A. Al-Amiery, A.B. Mohamad and M.S. Takriff, 2012. Synthesis and characterization of novel corrosion inhibitor derived from oleic acid: 2-Amino 5-Oleyl-1, 3, 4-Thiadiazol (AOT). *Intl. J. Electrochem. Sci.*, 7: 3543-3554.
- Kadhum, A.A.H., A.B. Mohamad, A.A. Al-Amiery and M.S. Takriff, 2011. Antimicrobial and antioxidant activities of new metal complexes derived from 3-aminocoumarin. *Molecules*, 16: 6969-6984.
- Kadhum, A.A.H., A.B. Mohamad, H.D. Jaffar, S.S. Yan and J.H. Naama *et al.*, 2013. Corrosion of nickel-aluminum-bronze alloy in aerated 0.1 m sodium chloride solutions under hydrodynamic condition. *Intl. J. Electrochem. Sci.*, 8: 4571-4582.
- Kampranis, S.C., N.A. Gormley, R. Tranter, G. Orphanides and A. Maxwell, 1999. Probing the binding of coumarins and cyclothialidines to DNA gyrase. *Biochem.*, 38: 1967-1976.
- Kennedy, R.O. and R.D. Thornes, 1997. Coumarins: Biology, Applications and Mode of Action. Wiley, New York, USA., ISBN: 978-0-471-96997-6, Pages: 360.
- Khaled, K.F., S.A. Fadl-Allah and B. Hammouti, 2009. Some benzotriazole derivatives as corrosion inhibitors for copper in acidic medium: Experimental and quantum chemical molecular dynamics approach. *Mater. Chem. Phys.*, 117: 148-155.
- Khalil, N., 2003. Quantum chemical approach of corrosion inhibition. *Electrochim. Acta*, 48: 2635-2640.
- Kotali, A., I.S. Lafazanis and P.A. Harris, 2008. Synthesis of 6, 7-diacylcoumarins via the transformation of a hydroxy into a carbonyl group. *Syn. Commun.*, 38: 3996-4006.
- Kovalenko, S.M., I.E. Bylov, K.M. Sytnik, V.P. Chernykh and Y.V. Bilokin, 2000. A new pathway to 3-Hetaryl-2-oxo-2H-chromenes: On the proposed mechanisms for the reaction of 3-Carbamoyl-2 iminochromenes with dinucleophiles. *Mol.*, 5: 1146-1165.
- Mao, P.C.M., J.F. Mouscadet, H. Leh, C. Auclair and L.Y. Hsu, 2002. Chemical modification of coumarin dimer and HIV-1 integrase inhibitory activity. *Chem. Pharm. Bull.*, 50: 1634-1637.
- Mashelkar, U.C. and A.A. Audi, 2006. Synthesis of some novel 4-substituted coumarins having potential biological activity (Part III). *Indian J. Chem.*, 45B: 1463-1469.
- Mohamad, A.B., A.A.H. Kadhum, A.A. Al-Amiery, L.C. Ying and A.Y. Musa, 2014. Synergistic of a coumarin derivative with potassium iodide on the corrosion inhibition of aluminum alloy in 1.0M H_2SO_4 . *Met. Mater. Intl.*, 20: 459-467.
- Musa, A.Y., A.A.H. Kadhum, A.B. Mohamad, A.A.B. Rahoma and H. Mesmari, 2010. Electrochemical and quantum chemical calculations on 4, 4-dimethyloxazolidine-2-thione as inhibitor for mild steel corrosion in hydrochloric acid. *J. Mol. Struct.*, 969: 233-237.
- Musa, A.Y., A.B. Mohamad, A.A. Al-Amiery and L.T. Tien, 2012. Galvanic corrosion of aluminum alloy (Al_{2024}) and copper in 1.0 M hydrochloric acid solution. *Korean J. Chem. Eng.*, 29: 818-822.
- Naama, J.H., G.H. Alwan, H.R. Obayes, A.A. Al-Amiery and A.A. Al-Temimi *et al.*, 2013. Curcuminoids as antioxidants and theoretical study of stability of curcumin isomers in gaseous state. *Res. Chem. Intermed.*, 39: 4047-4059.

- Nofal, Z.M., M.I. El-Zahar and S.S. Abd El-Karim 2000. Novel coumarin derivatives with expected biological activity. *Molecules*, 5: 99-113.
- Obayes, H.R., A.A. Al-Amiery, G.H. Alwan, T.A. Abdullah and A.A.H. Kadhum *et al.*, 2017. Sulphonamides as corrosion inhibitor: Experimental and DFT studies. *J. Mol. Struct.*, 1138: 27-34.
- Obayes, H.R., G.H. Alwan, A.H.M. Alobaidy, A.A. Al-Amiery and A.A.H. Kadhum *et al.*, 2014. Quantum chemical assessment of benzimidazole derivatives as corrosion inhibitors. *Chem. Central J.*, 8: 1-21.
- Obi-Egbedi, N.O., I.B. Obot, M.I. El-Khaiary, S.A. Umoren and E.E. Ebenso, 2011. Computational simulation and statistical analysis on the relationship between corrosion inhibition efficiency and molecular structure of some phenanthroline derivatives on mild steel surface. *Intl. J. Electrochem. Sci.*, 6: 5649-5675.
- Rositica, D.N., G.N. Vayssilov, N. Rodios and A. Regio-Bojilova, 2002. Regio- and stereoselective [2+2] photodimerization of 3-substituted 2-alkoxy-2-oxo-2h-1,2-benzoxaphosphorines. *Molecules*, 7: 420-432.
- Rubaye, A., A. Abdulwahid, S.B. Al-Baghdadi, A. Al-Amiery and A. Kadhum *et al.*, 2015. Cheery sticks plant extract as a green corrosion inhibitor complemented with LC-EIS/MS Spectroscopy. *Intl. J. Electrochem. Sci.*, 10: 8200-8209.
- Satyanarayana, V.S.V., P. Sreevani, A. Sivakumar and V. Vijayakumar, 2008. Synthesis and antimicrobial activity of new Schiff bases containing coumarin moiety and their spectral characterization. *Arkivoc*, 17: 221-233.
- Smitha, G. and C.S. Reddy, 2004. ZrCl₄-catalyzed Pechmann reaction: Synthesis of coumarins under solvent-free conditions. *Synth. Commun.*, 34: 3997-4003.
- Udhayakala, P., 2014. Density functional theory calculations on corrosion inhibitory action of five azlactones on mild steel. *J. Chem. Pharm. Res.*, 6: 117-127.
- Wang, H.X. and T.B. Ng, 2001. Examination of lectins, polysaccharopeptide, polysaccharide, alkaloid, coumarin and trypsin inhibitors for inhibitory activity against human immunodeficiency virus reverse transcriptase and glycohydrolases. *Planta Med.*, 67: 669-672.
- Xia, S., M. Qiu, L. Yu, F. Liu and H. Zhao, 2008. Molecular dynamics and density functional theory study on relationship between structure of imidazoline derivatives and inhibition performance. *Corros. Sci.*, 50: 2021-2029.
- Zabradnik, M., 1992. The Production and Application of Fluorescent Brightening Agents. John Wiley and Sons, New York, USA.