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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-Methy l-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-methy l-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 Khodiary, 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

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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-Carbethoxythiazole (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 1 H 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 carbethoxythiazole for mild steel surface with the aria 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 carbethoxythiazole at the concentrations 0.001, 0.05, 0.10, 0.15, 0.2.0, 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:

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

where, W1/W2 point to weight of MS in presence/ absence 2-Amino-4-Methyl-5-Carbethoxythiazole (AMC).

Computational details: A geometrical optimization for 2-amino-4-methyl-5-carbethoxythiazole 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 = -EHOMO), Electron affinity (A = -ELUMO) and the inhibition efficiency (%) was calculated based on Al-Amiery (Obayes *et al*., 2017), methodology (Eq. 2-4):

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

$$Ie_{add}\% = I_{add}\%\times Ie_{AMC}\% \quad (3)$$

$$Ie_{theory}\% = I_{AMC}\%\times Ie_{add}\% \quad (4)$$

Where:

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

Ie_{add} and $Ie_{theory}\%$ = 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-Carbethoxy thiazole (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-carbethoxythiazole has been elucidate. In infrared spectrum of 2-amino-4-methyl-5 carbethoxythiazole has a carbonyl absorption band for ester group that appeared for 2-amino-4-methyl-5 carbethoxythiazole also the amino group at 3344.2. The nuclear magnetic resonance spectrum shoed singlet at δ 6.47 ppm due to the proton of N-H. 2-amino-4-methyl-5 carbethoxythiazole was synthesized from ethyl 2-chloro-3 oxobutanoate and thiourea as in Fig. 1. The mechanism of 2-amino-4-methyl-5-carbethoxythiazole 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

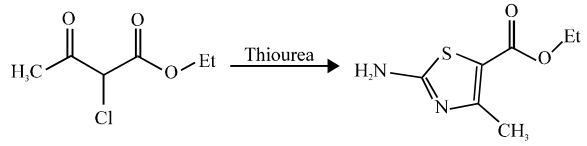

Fig. 1: 2-Amino-4-methyl-5-carbethoxythiazole synthesis

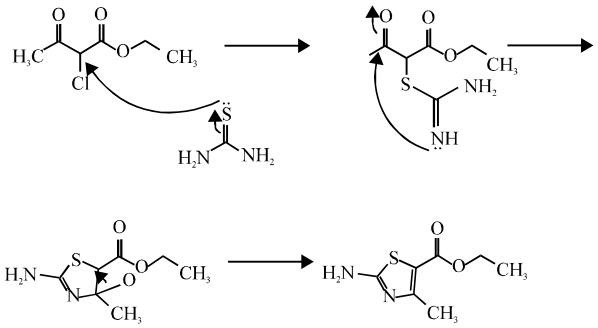

Fig. 2: Mechanism for the formation of 2-amino-4-methyl 5-carbethoxythiazole

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 figurate 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 thetemperature 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 deferent 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 it ability to

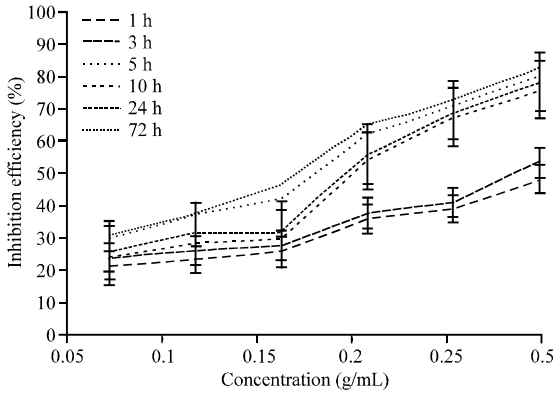

Fig. 3: Function of time at concentrations of 2-amino-4 methyl-5-carbethoxythiazole

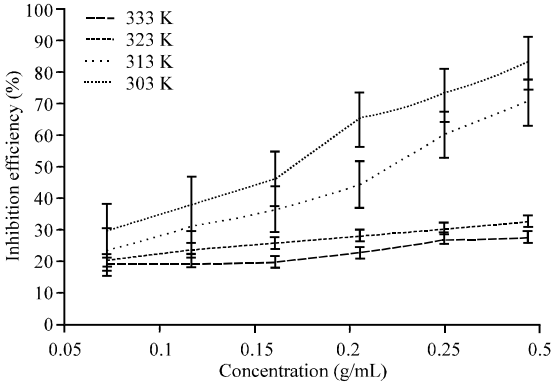

Fig. 4: AMC concentrations at various temperature degrees

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.

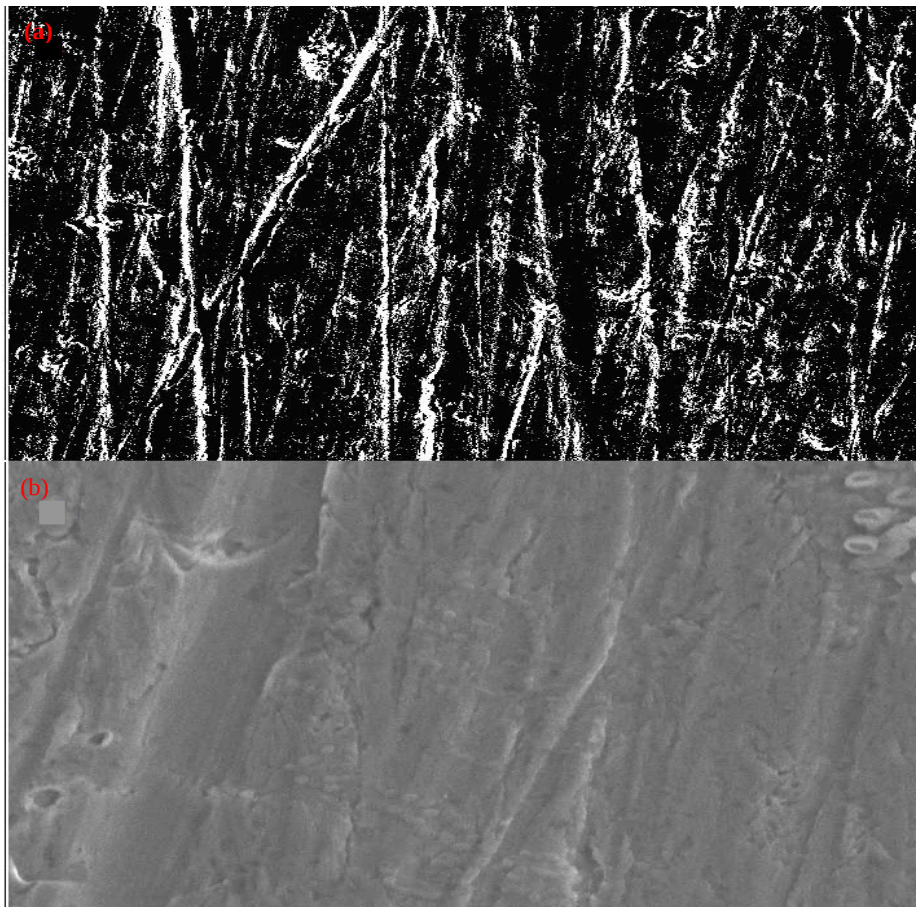

Fig. 5: SEM images of surface of mild steel in presence: a) Absence and b) AMC

Computational studies: To figuration 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 style was establishing to be effective in providing glance about reactivity in addition to selectivity in term of comprehensive parameters (electro-negativity, v, hardness, g, softness, S and local softness (sd¬rÞ) (Ebenso *et al*., 2010; Ashassi-Sorkhabi *et al*., 2005). The purpose of the AMC was for utilized 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 organic molecule which offer electrons to vacant metal orbitals and also accept the metal electrons (Khaled *et al*., 2009). Quantum calculations were employed to investigated the interactions metal and

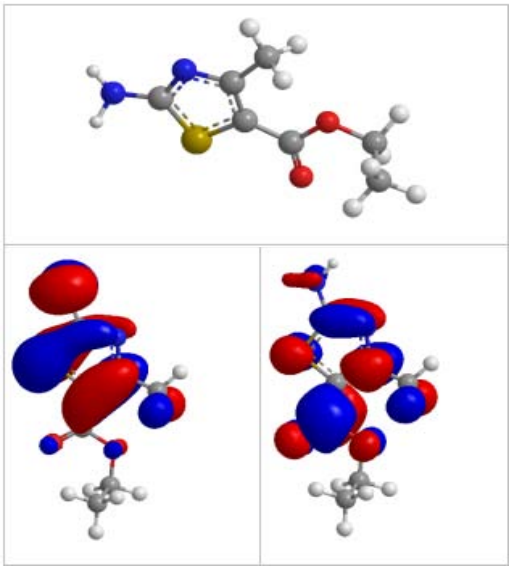

Fig. 6: a) Optimized geometrical structure; b) HOMO and c) LUMO of AMC

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

	Inhibition efficiency (%)	
Compound	Theoretical (Ie_{theor})	Experimental
AMC	83.96	82.5

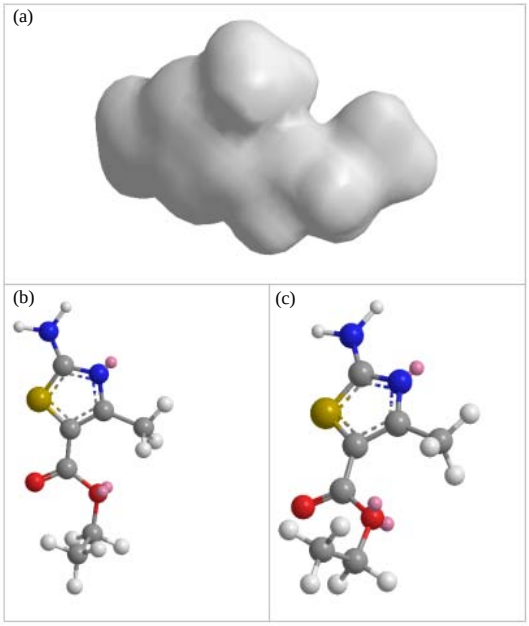

Fig. 7: a) Charge distribution; b) Fukui (f-) function; c) Fukui (f+) function

inhibitor (Bahrami *et al*., 2010). Highest occupied, lowest unoccupied molecular orbitals (HOMO and LUMO) andFukui 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 EHOMO, EHOMO 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 EHOMO 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 Lluch, 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 mils steel surface. A relation of inhibition efficiency of AMC with EHOMO, ELUMO 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 EHOMO and lowest value of ELUMO improve the inhibition efficiency. The rising of EHOMO signalize a higher orientation for the giving electrons to vacant orbital of molecule. EHOMO 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. ELUMO refer to the capability of the AMC molecules to take electrons, so, a lowest ELUMO 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	x	-	S
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. Highvalues 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 ere 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 has 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-Carbethoxythiazole (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 carbethoxythiazole was elucidate according to spectroscopical techniques. Inhibition efficiency of the 2 amino-4-methyl-5-carbethoxythiazole in HCl solution with 1 M for mild steel was studied. 2-Amino-4-methyl-5 carbethoxythiazole, 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.

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