Synthesis and comparative study of novel triazole derived as corrosion inhibitor of mild steel in HCl medium complemented with DFT calculations

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Abstract

Here, 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone (MPTE) was successfully synthesized and fully characterized, that acting as the new corrosion inhibitor for mild steel in corrosive environment (hydrochloric acid) was investigated by weight loss measurements at temperatures ranging from 303 to 343 K. The nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) spectroscopy techniques were used to characterize the molecular structure of the tested inhibitor. The inhibition efficiency increases with MPTE concentration increasing and decreases with temperature increasing. The percentage inhibition reached 95.10% at the concentration of 0.5 mM and 303 K. The surface morphology of the tested mild steel specimen was tested by scanning electron microscopy (SEM) and the results showed MPTE to have inhibited corrosion on the surface of mild steel in corrosive environment. Using the Langmuir adsorption isotherm, the thermodynamic parameters for the adsorption of new synthesized inhibitor on the surface of metal were studied. Quantum chemical calculations using density functional theory (DFT) were used to investigate the relationships between inhibitive efficiencies and chemical structure of the studied inhibitor. DFT results agree with experimental approach. 1-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone (MPTE) was found to be a potential corrosion inhibitor since it contained not only nitrogen and oxygen atoms, but also benzene and triazole rings that are joined together with a carbon–nitrogen single bond and α,β -unsaturated carbonyl in conjugation with triazole rings.

Keywords: mild steel, weight loss, corrosion, HCl.

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1. Introduction

Industrial process includes cleaning, chemical decaling and pickling through utilizing of corrosive solutions in order to treat various alloys and equipment [1–3]. The primary processing stage for mild steel was pickling by using of acids in order to remove the oxide compounds which were formed through annealing process [4–10]. Actually, using the natural or synthetic organic inhibitors through pickling process of alloys such as mild steel appears to become further significant due to the presence of unfavorable and comprehensive acid attack [11, 12], that was regard as the major industrial technique for protecting alloys from dissolution [13, 14]. In general the comparison techniques of mild steel protection from corrosion, the efficient and promising one was to using inhibitors due to various advantages such as low cost, simple technology and no particular apparatus required, *etc.* In previous studies, a significant number of corrosion inhibitors were published. The efficient inhibitors are organic molecules that have such as, nitrogen, phosphorus, sulfur and oxygen atoms in addition to double and/or triple bonds and aromatic rings in the structure of these molecules [15–21]. Few articles concerning the using of 1,2,3-triazol derivatives as corrosion. To improve a novel efficient inhibitors [22–48], the target of the current investigation is to study the corrosion inhibition of mild steel in corrosive environment by 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone (MPTE). MPTE have been synthesized, and the chemical structure was elucidates by spectroscopically techniques and elemental analysis. The corrosion inhibition of mild steel in hydrochloric acid environment by MPTE was investigated weight loss methods and scanning electron microscope (SEM) technique. The impacts of concentrations, temperature and immersion time on inhibition effectiveness, have been studied amply. Moreover, the adsorption isotherms on the surface of mild steel were also investigated.

2. Experimental section

2.1. Materials and methods

Mild steel coupons (25 mm×20 mm×0.6 mm and 80 mm×10 mm×0.6 mm) were supplied from Metal Samples Company (USA, Pa, Saint) and were used as base substrates for the weight loss techniques and have following composition: C 0.210%, C 0.066%, Si 0.380%, P 0.090, S 0.05, Mn 0.050, Al 0.010, and remaining iron (wt.%). Before each test, the ASTM standard steps G1-03 were used to washed and cleaned the MS (mild steel) coupons [49]. The analytical-grade 37% hydrochloric acid was diluted with double-distilled water to produce the experimental solution.

2.2. Inhibitor

The tested inhibitor 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone (MPTE) was synthesized according to the following method: added equimolar quantities with stirring at room temperature of pentane-2,4-dione and phenylazide to solution of sodium methoxide.

Continue the stirring until formation of a precipitate, filtered, added water and extracted. Recrystallized from ethanol. Yield 43%, mp 99–101°C. The ^1H NMR spectrum was recorded using a Bruker instrument at 400 MHz. Perkin Elmer was used to record the IR spectrum. The spectral data for MPTE: ^1H NMR (400 MHz, DMSO-d_6) δ : 2.21 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 7.34–7.57 (d, 4H, aromatic-H) and 7.63 (dd, 1H, aromatic-H). ^{13}C NMR (DMSO-d_6) δ : 9.7, 28.1, 124.6, 124.9, 127.8, 128.3, 128.9, 135.1, 141.3, 191.3.

2.3. Gravimetric measurements

The weight loss measurements were done utilizing mild steel coupons with the composition provided above in 1 M hydrochloric acid solution in the absence and presence of MPTE as a corrosion inhibitor. First of all the mild steel coupons were cleaned utilizing SiC papers. Ethanol was used as a sonicated solution for 15 min. Distilled water and acetone were used for washing. The coupons were immersed for 6 h at 303 K in the absence and presence of MPTE. After the specified exposure duration, the coupons were washed and dried. The weight losses were calculated through the variation of coupon's weight before exposure and after it. Corrosion rate (C_R), inhibition efficiency ($IE\%$), and surface coverage (θ) were calculated according to the equations 1–3.

$$C_R = \frac{W}{at} \quad (1)$$

Where W is the coupon weight loss in (mg), a is the area in (cm^2) and t is the exposure time in (h).

$$IE\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \quad (2)$$

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \quad (3)$$

where C_R represents the corrosion rate in the absence of MPTE and $C_{R(i)}$ represents the corrosion rate in the presence of MPTE.

2.4. Scanning electron microscope (SEM) technique

The coupon surface was characterized by scanning electron microscopy (SEM) in order to investigate the changes in the coupon's morphology in the absence and presence of MPTE as a corrosion inhibitor at concentration of 0.5 mM for 5 hours as exposure time at 308 K. The coupons were taken out and rinsed with water then ethyl alcohol and the surface was analyzed after drying.

2.5. DFT investigations

Quantum chemical calculations for MPTE molecules as corrosion inhibitor have been done by density function theory (DFT) with GAUSSIAN 03W software [50], apply B3LYP

functional through a 6-31G basis set. The B3LYP, a version of DFT, apply Beche's three-parameter functional along with the Lee–Yang–Paar correlation functional. The obtained frontier molecular orbital energies such E_{HOMO} and E_{LUMO} help calculate further important factors including ΔE , η , σ , χ , and ΔN using the equations (4–8)

$$\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}} \quad (4)$$

$$\eta = -\frac{1}{2}(E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (5)$$

$$\sigma = \frac{1}{\eta} \quad (6)$$

$$\chi = -\frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \quad (7)$$

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})} \quad (8)$$

where χ_{Fe} is the electronegativity of iron and η_{inh} is the hardness of iron.

Recently, value $\chi_{\text{Fe}} = 7 \text{ eV}$ is not acceptable due to negation the interaction of electron–electron. To avoid this oddity, the work function (ϕ) of the coupon surface has been utilized in place of χ_{Fe} as in equation 9.

$$\Delta N = \frac{\phi - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})} \quad (9)$$

The coupon surface was characterized by scanning electron microscope (SEM) in order to investigate the changes in coupons morphology in absence and presence of MPTE as corrosion inhibitor at the concentration of 0.5 mM for 5 hours as exposure time at 308 K. The coupons were taken out and rinsed with water then ethyl alcohol and the surface was analyzed after drying.

3. Results and Discussion

3.1. Chemistry

The sequence of the reaction for the synthesis of a novel corrosion inhibitor start with from phenylazide is outlined in Scheme 1. The novel inhibitor (MPTE) was synthesized by reaction of pentane-2,4-dione and phenylazide in sodium methoxide. The ^1H NMR spectrum exhibited a singlet at δ 2.21 ppm and 2.35 ppm due to the three protons of each methyl groups. ^{13}C NMR in DMSO- d_6 (ppm): The spectrum exhibited bands at 9.7 and 28.1 ppm from carbons of each of the methyl groups. The bands at 124.6, 124.9, 127.8, 128.3, 128.9 and 135.1 ppm were from carbons of the aromatic ring. The bands at 141.3 and 191.3 ppm were from the carbon of azomethine and carbon of carbonyl groups respectively, and this band confirmed the formation of the C=N and confirm a hetero cyclic triazole ring.

Scheme 1. The synthesis of the MPTE molecule.

3.2. Weight loss techniques

The gravimetric technique is the most simple observation technique with high accuracy in the estimation of corrosion inhibition ability of natural and synthetic organic inhibitors. The weight loss measurement results for mild steel coupons in the investigated corrosive environment with and without of MPTE molecules are postulated in Figures 1 and 2.

3.3. Concentration effect

Variation in corrosion rates and inhibition efficiencies depend on different corrosion inhibitor (MPTE) concentrations for periods 1.0, 5.0, 10.0, 24.0, 48.0 and 72.0 hours as immersion times in a hydrochloric acid environment at 303 K are demonstrated in Figure 1 and Figure 2. With an increase in the concentration of MPTE as corrosion inhibitor the C_R will decreased, on the other hand the increasing of MPTE as corrosion inhibitor concentration will increase the inhibition efficiency. The experimental results demonstrated that the MPTE molecules were adsorbed on the coupon surface. These inhibitive molecules formed a film which covers the coupon surface as protective layer in low concentration of MPTE and high concentration. From Figure 1 and Figure 2, it can be shown that the variation in corrosion rates and inhibition efficiencies with the times of immersion were significant during the initial five hours. At the first five hours, of immersion, the C_R of MPTE become the lowest value of 0.12 mg/cm²/h and the efficiencies become an excellent value of 95.10%. In general, the MPTE molecules were adsorbed on the coupon surface were considered as elimination reaction which involve the displacement reaction of water molecules from the coupon surface and displace these water molecules by MPTE molecules. The molecules of MPTE were chemically adsorbed on the coupon surface because of the interaction of oxygen and nitrogen unshared pairs of electrons with the coupon surface. The inhibition efficiencies were observed to decrease after ten hours of immersion time and the was imputed to the desorption of MPTE molecules from coupon surface. The inhibition efficiency of MPTE molecules depend on the adsorption capability on the coupon surface. The experimental results signalized that the existence of MPTE molecules could efficiently impedance the corrosion of coupon surface in 1 M hydrochloric acid solution as corrosive environment. The excellent inhibition performance is attributed to the presence of MPTE molecules on the coupon surface, due to presence three nitrogen atoms and one oxygen atom as heteroatoms in MPTE molecule with plane molecular structure and aromatic ring, MPTE molecules have many active centers on the coupon surface.

Figure 1. Corrosion rate *versus* the immersion time for coupon surface in absence and in presence of MPTE in 1 M hydrochloric acid solution at 303 K.

Figure 2. Inhibition efficiency *versus* the immersion time for coupon surface in absence and in presence of MPTE in 1 M hydrochloric acid solution at 303 K.

3.4. Temperature impact

To realize the influence of temperature on the MPTE as synthesized corrosion inhibition, the weight lost of MS coupon have been investigated in corrosive solution at various temperatures (303, 313, 323 and 333 K) in absence and presence of different MPTE

concentration. The effects of temperature were tested based on these factors: C_R and IE . From Figure 3, it is, obvious that the C_R increased with increasing temperature, and this increase was linear, on the other hand the inhibition performance was decreased with the temperature increase. The decrease in the IE of MPTE at 323 K and above was due to the instability of the inhibitor molecules when subjected to higher temperature. In addition, the viscosity of the solution was decreased regarding to the increasing temperature, which refer to increasing diffusion, that permit reactants transport increase and products on the coupon surface. It is clear that the effect of temperature on the C_R in the absence of MPTE molecules were three time that in the presence of MPTE, which was due to the inhibitor isolates the coupon from the media. Rising temperature is actually expected to speed up reaction based on thermodynamic parameters.

Figure 3. Effect of temperature on C_R at various MPTE concentrations for 5 h as an immersion time.

The inhibition efficiency were affected by rising the solution temperature as shows in Figure 4. It illustrated an excellent characteristics for dropping inhibition efficiency regarding to increasing temperature because of the physical adsorption and chemical adsorption. Figures 3 and 4 illustrate that a the higher C_R and lower inhibition efficiency come in parallel with longer immersion time, so MPTE molecules as corrosion inhibitor were unstable to impedance the corrosion at long immersion time.

Figure 5. IE% vs. different temperatures at various concentrations in 1 M HCl solution.

3.5. Adsorption isotherms

The surface coverage (θ) values which obtained weight loss technique for MPTE were utilized to know the adsorption isotherms. The adsorption isotherm assist to realized the interactions of the tested inhibitor molecules (MPTE) with coupon surface. MPTE molecules were adsorbed on the coupon surface through chemically or physically. To recognize the adsorption phenomenon, various adsorption isotherms such as Langmuir isotherm, Temkin isotherm and Freundlich isotherm were used to the methodological results. It was spotted that the Langmuir isotherm is the best one. The intercept and the slope values for the Langmuir adsorption are 0.079 and 0.9173. The plot between C/θ and C illustrate in Figure 5, and represent in equations 10 and 11.

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (10)$$

where C is MPTE the concentration and θ is the surface area were as and K_{ads} is the linear straight fitted plot between C/θ and C (adsorption equilibrium constant).

$$\Delta G_{\text{ads}} = -RT \ln(55.5 K_{\text{ads}}) \quad (11)$$

where as ΔG_{ads} is the free energy of adsorption, where the value 55.5, R and T are concentration of water in Molar, gas constant and T absolute temperature respectively.

Figure 5. Langmuir adsorption isotherms for coupon in presence of various MPTE concentration.

It was published that if ΔG_{ads} value around -40 kJ/mol suggest chemisorption adsorption, where as if around -20 kJ/mol or less negative suggest physisorption adsorption [51, 52]. The ΔG_{ads} value for MPTE, *i.e.*, 39.94 kJ/mol, proposed chemisorption adsorption

3.6. Surface characterization

Figure 6. The SEM micrographs of (a) corroded MS surface in the presence of MPTE, (b) in the presence of MPTE at 0.5 mM.

Figure 6 illustrates the SEM image of coupon surface immersed in corrosive acid environment in absence and presence of 0.5 mM MPTE as inhibitor for 5 h. From Figure 6a, the investigated coupon surface it is obvious that coupon surface seriously corroded due to the action of corrosive solution, the mild steel surface is not shiny and not satin, in addition to holes which were formed by acid. Figure 6b, the corrosion rate of coupon surface is significantly reduced. It can be proposed that the MPTE molecules have the ability to form a protective film, which protects the mild steel surface.

3.7. Density function theory

Theoretical calculations are quite important in acquire much data about inhibition phenomenon. The inhibition efficiency of inhibitor molecules are related with the some theoretical parameters such as HOMO (high occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), ΔE (energy gap), σ (softness), (η) hardness, χ (electronegativity), and ΔN (fraction of electrons transferred) in addition to Mulliken charges. Theoretical factors could observe through the optimum structure of the investigated corrosion inhibitor molecules [53, 54]. Theoretical factors are also significant in prediction of the interaction between coupon surface and inhibitor molecules. In the current investigation the quantum chemical parameters were calculated for neutral molecule and the results were illustrated in Table 1. The optimum structure of the MPTE molecule is demonstrated in Figure 7.

Table 1. Calculated quantum chemical parameters for the most stable conformation of MPTE.

Quantum chemical parameters	Values
E_{HOMO}	−8.019 eV
E_{LUMO}	−2.451 eV
$E_{\text{HOMO}} - E_{\text{LUMO}}$	−5.568 eV
Dipole moment (μ)	−4.55 Debye
$I = -E_{\text{HOMO}}$	8.019 eV
$A = -E_{\text{LUMO}}$	2.451 eV
η	2.784
σ	0.359
χ	5.235
ΔN	0.276

The reactivity of MPTE molecules could be understood through the HOMO and LUMO and were also illustrated in Figure 7. Generally, the HOMO shows the electron donating ability of the inhibitor molecules, so HOMO with the high value indicates that the inhibitor molecules have affinity to offer electrons to Fe empty d-orbitals on the coupon surface. On

the other hand, the LUMO value infers the ability to accept electron from Fe (coupon surface). In general, the E_{LUMO} with low value implies that the inhibitor molecules can accept electrons from the coupon surface (Fe-metal) through back-donation. The energy gap with low value imply excellent inhibition efficiency [55, 59]. The calculated parameters are presented in Table1.

Figure 7. Electronic properties of MPTE (a) optimization (b) HOMO orbital (c) LUMO orbital.

ΔN was evaluated and demonstrates that the IE resulting from electron donation is conformable with Lukovits's investigation [60]. If $\Delta N < 3.6$, the IE increases through rising ability of donating electron to the iron surface. The ΔN value is not quite the number of electrons departing the giver molecule and sharing the acceptor molecule. Moreover, the significant utilized parameter to characterize the polarity is the dipole moment. Dipole moment is the polarity measurement of the polar covalent bonds. Dipole moment can be defined as the charges and the distance of the bonded atoms. The dipole moment considers the polarity of molecules. The theoretical investigation demonstrates that the dipole moment is in good agreement with IE . IE increase with increasing dipole moment.

Hardness value and softness value of the studied corrosion inhibitor, demonstrated in Table 1 are significant factors to evaluate the stability of inhibitor molecules and reactivity. It is obvious that the hardness refers the impedance towards the deformation/polarization of the molecules. Hard molecules have high large energy gap but soft molecules have low energy gap. Soft molecule is more reactive due to readily released electrons. So, inhibitor molecule with big value of softness is declared to be good corrosion inhibitor.

Mulliken charges are significant to calculate the adsorption centers of inhibitor. High negative charged value indicates the ability to be adsorbed on the coupon surface. The highest negatively charge is located on the oxygen atom followed, nitrogen and carbon atoms, that indicate that these atoms have the ability coordinate with the inhibitor, especially the oxygen (O15) which have higher negative Mulliken charges. The Mulliken charges are given in Table 2.

Table 2. Mullikan charges of MPTE.

Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
C(1)	0.453	C(6)	−0.019	C(11)	−0.082	H(16)	0.054	H(21)	0.025
C(2)	−0.183	C(7)	0.026	C(12)	−0.023	H(17)	0.062	H(22)	0.022
N(3)	0.697	C(8)	0.163	C(13)	−0.182	H(18)	0.062	H(23)	0.137
N(4)	−0.212	C(9)	−0.090	C(14)	−0.297	H(19)	0.023	H(24)	0.159
N(5)	−0.283	C(10)	−0.025	O(15)	−0.623	H(20)	0.024	H(25)	0.062

4. Conclusions

The synthesized 1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone (MPTE) showed excellent inhibition efficiency of 95% at 0.5 mM. MPTE having a nitrogen and oxygen hetero atom in addition to phenyl ring and carbonyl group. MPTE demonstrated that an increase in the concentration increases the inhibition efficiency and forming a protective layer on the coupon surface. The quantum chemical (using DFT method) parameters and methodological results were observed to be in an excellent agreement.

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