Int. J. Electrochem. Sci., 10 **(2015)** 1292 - 1304

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

2-((5-Mercapto-1,3,4-thiadiazol-2-ylimino)methyl-6-methoxy) phenol Schiff base as a New and Effective Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution

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Received: 27 October 2014 / *Accepted:* 7 December 2014 / *Published:* 16 December 2014

Corrosion inhibition of 2-((5-Mercapto-1,3,4-thiadiazol-2-ylimino)methyl- 6-methoxy) phenol Schiff base (MTMMP) as a new and effective corrosion inhibitor for mild steel in 1M HCl was investigated by means of weight loss (WL), potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The results show that the MTMMP Schiff base has excellent inhibition efficiency for mild steel in 1M HCl. The inhibition efficiency increases with the increase inhibitor concentration, and decreases with increasing temperature in the studied temperature range. The studied inhibitor acts as a mixed type corrosion inhibitor. The adsorption of MTMMP Schiff base on the mild steel surface conforms to Langmuir adsorption isotherm. The quantum chemical calculations were carried out to explain a relationship between the adsorption behavior and the structure of MTMMP molecule.

Keywords: 2-((5-Mercapto-1,3,4-thiadiazol-2-ylimino)methyl- 6-methoxy) phenol (MTMMP); Corrosion Inhibition; Mild Steel; Electrochemical Impedance Spectroscopy; Weight Loss; potentiodynamic polarization

1. INTRODUCTION

Iron and its alloys which are widely used in industry, agriculture and other fields could corrode in acid solutions particularly with the use of sulfuric acid and hydrochloric acid [1-3]. Metal corrosion that troubles national economic development around the world, and produces huge economic losses has caused extensive concerns of many domestic and international scholars. How to prevent the corrosion of iron and its alloys has become an important topic. Use of inhibitor is one of the most effective strategies to improve the corrosion resistance of metal, compared with other corrosion protection technologies [4-5].The past decades, considerable efforts have been made to find novel, environment friendly, economical and efficient corrosion inhibitors. Most inhibitors are chemical compounds that bear heteroatoms with high electron density such as nitrogen, oxygen, sulphur, phosphor, or contain rich electronic chemical bonds like π bond [6-8]. These compounds contain more active sites that can easily adsorb on the metal surface than those containing none heteroatoms or multiple bonds [9].

Recently, Schiff base compounds have caused widespread concern due to providing much greater inhibition efficiency compared with corresponding aldehydes and amines [10-12]. The presence of –C=N– double bond in Schiff base compounds can improve their adsorption ability and corrosion inhibition efficiency [13,14]. 2-Amino-5-mercapto -1,3,4-thiadiazoles (2A5MT) as one of heterocyclic thiadiazole derivatives is environment friendly compound and widely used in antibacterial activities. 2A5MT that is valuable intermediates for the synthesis of pharmaceuticals, photography chemicals, corrosion inhibitors and pesticides can be easily prepared in very high yields from carbon disulphide and thiosemicarbazides [15,16]. 2A5MT has been extensively investigated as corrosion inhibitor for copper, bronze, iron and its alloys [17-19]. In this study, MTMMP was synthesized from 2A5MT and 3-Methoxysalicylaldehyde (MSA) to further improve corrosion inhibition effect of 2A5MT. 3-Methoxysalicylaldehyde which can be easily obtained from the extracts and essential oil of many plants has been used as important synthetic intermediates for pharmaceuticals. The synthesized molecular structure has additional –C=N- π bond as well as a phenol hydroxy group containing several active centers of adsorption. In a word, the compound is expected to show corrosion inhibition efficiency and better adsorption ability on mild steel surface. The inhibition effect of MTMMP is investigated by using WL, potentiodynamic polarization and EIS techniques in 1M HCl solution.

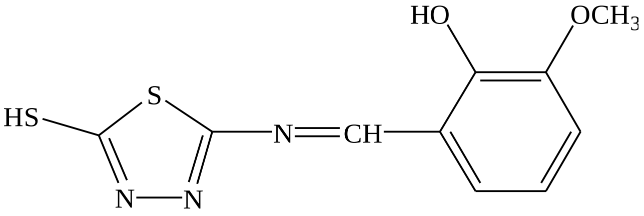

Figure 1. Molecular structure of 2-((5-Mercapto-1,3,4-thiadiazol-2-ylimino)methyl-6-methoxy) phenol

2. EXPERIMENTAL

2.1 Material and solution

2-((5-Mercapto-1,3,4-thiadiazol-2-ylimino)methyl-6-methoxy) phenol (MTMMP) was generally synthesized by a condensation reaction between 2A5MAT and the MSA in ethanol and recrystallized from ethanol according to the modified references [20,21]. The target molecule is shown in Figure. 1. 2A5MT and all the other chemicals were purchased from ENERGY CHEMICAL and used without further purification. The test solution which was prepared in distilled water was 1M HCl solution with and without different concentrations of MTMMP (from 0.02mM to 1.0mM). When each experiment was tested, a freshly prepared solution was used once. All the test solutions were opened to air and the temperature was controlled thermostatically by using constant temperature water-bath.

2.2 Weight loss measurements

The Q235 mild steel of weight loss experiment that was purchased from Yangzhou Xiang Wei machinery CO, LTD has the dimensions of 5.0cm×2.5cm×0.2cm. The chemical composition (wt) of specimens consisted of C(0.17%), Si(0.46%), Mn(0.0047%), S(0.17%), P(0.0047%) and Fe(remainder). The specimens were mechanically polished with 200, 400, 600, 1000, 1200 different grade emery paper to light, successively rinsed with distilled water, ethanol and acetone, then dried and kept in a vacuum desiccator. Immersion test was carried out in 1M HCl solution in the absence and presence of different concentrations of MTMMP for 24h at 298 K, 308 K and 318 K by using constant temperature water-bath. After rinsing with distilled water, the specimens were dried and weighted accurately. The weight loss corrosion rate v (g m^{-2} h^{-1}) was calculated by using the following equation (1):

$$v = \frac{W_0 - W}{s \times \mathrm{t}} \qquad (1)$$

Wherein W_0 and W are the average weight of specimen before and after immersion respectively; t is immersion time; s is the immersed surface area of specimens. So, inhibition efficiency of MTMMP can be calculated from the following equation (2) [22].

$$\eta = \frac{v_0 - v_{inh}}{v_0} \times 100 \qquad （2）$$

Wherein v_0 and v_{inh} are the weight loss corrosion rates in 1M HCl solution in the absence and presence of different concentrations of MTMMP respectively; η is inhibition efficiency.

2.3 Electrochemical measurements

The working electrode of electrochemical measurement was a cylindrical disc with a 1cm diameter cut from a Q235 mild steel specimen. The chemical composition of working electrode is the same as the weight loss of steel specimens. The working electrode was coated with epoxy resin except its working surface with surface area of 0.785 cm^2. The surface of working electrode were mechanically polished with 200, 400, 600, 1000, 1200 different grade emery paper to light, successively rinsed with distilled water, ethanol and acetone, then dried and kept in a vacuum desiccator.

Electrochemical measurement were carried out in a three neck flat bottom flask with a three electrode system, consisting of mild steel working electrode (WE), a platinum counter electrode(CE) with a $2cm^2$ surface area, and a saturated calomel electrode (SCE) as a reference electrode. The potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) were performed by using a CHI660C Electrochemical workstation and PASSTAT2273 Electrochemical testing system under computer control at 298 K, respectively. Firstly, the working electrode was immersed in test solution for 0.5 h to establish steady state. After open circuit potential (E_{ocp}) was steady, the polarization curves and EIS test were performed respectively. The polarization curves were obtained potentiodynamically at the rate of 0.05 mV. The potential ranges were from−1.0V to 0.50V (vs E_{ocp}). The EIS test was operated in the frequency range of 0.01Hz to 100 kHz at open circuit potential. The alternating current amplitude was 0.5mV.

2.4 Quantum chemical calculations

In this study, the complete geometry of molecule was optimized at 6-31G(d,p) basis set of the DFT B3LYP with Gaussian 03 W program[23]. Then, quantum chemical parameters were obtained for the optimized structure. The following quantum chemical parameters were taken into account, such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy band gap ($\triangle E=E_{LUMO}-E_{HOMO}$), the dipole moment ($\mu$), and Nature bond orbital (NBO) charges.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

Table 1. Corrosion parameters for mild steel in 1M HCl with and without various concentrations of MTMMP obtained from weight loss measurements at different temperatures

Temperature (K)	C (10^{-6} mol/L)	Corrosion rate (mg/cm^2 h)	Inhibition efficiency (η)	Surface coverage (θ)
298	Blank	5.49	-	-
	20	2.72	50.5	0.505
	40	2.22	59.6	0.596
	200	0.97	82.3	0.823
	400	0.52	90.5	0.905
	1000	0.21	96.1	0.961
308	Blank	9.82	-	-
	20	5.04	48.7	0.487
	40	4.20	57.2	0.572
	200	1.88	80.9	0.809
	400	1.06	89.2	0.892
	1000	0.41	95.8	0.958
318	Blank	16.20	-	-
	20	8.94	44.8	0.448
	40	7.40	54.3	0.543
	200	3.58	77.9	0.779
	400	2.19	86.5	0.865
	1000	1.04	93.6	0.936

Weight loss data of mild steel in 1M HCl solution with and without various concentrations of MTMMP at temperatures ranging from 298 to 318 K were obtained and are listed in Table 1. It can be clearly seen from Table 1 that corrosion rate decreases and the corrosion inhibition efficiency increases with increasing inhibitor concentration. However, the corrosion inhibition efficiency is clearly showed to decrease with increasing temperature from 298 to 318 K. It may be explained that corrosion inhibitor is difficult to adsorb on the mild steel surface due to molecular thermal motion speeding up with increasing temperature.

3.2 Tafel polarization measurements

Figure. 2 shows the Tafel curves of mild steel in 1M HCl solution with and without various concentrations of MTMMP. Polarization parameters of mild steel corrosion are calculated from Tafel curves by using extrapolation methods.

It can be clearly seen from Figure. 2 that both catholic and anodic current densities have decreased with the addition of MTMMP to the aggressive solution [25]. The decrease in i_{corr} with the increase concentration of MTMMP shows the good corrosion efficiency for mild steel in 1M HCl solution. The cathodic current-potential curves bring out parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled mainly and that the mechanism of corrosion process is not modified after the addition of the MTMMP Schiff base [24]. However, a different behavior in the anodic part of current-potential curves was observed in comparison with cathodic part. There is a region in the high concentration of MTMMP Schiff base that the corrosion current rises suddenly. The behavior may be due to a significant dissolution of iron, leading to desorption of corrosion inhibitor film from the mild steel surface. Addition of studied corrosion inhibitor affected both cathodic and anodic reaction. However, the E_{corr} (vs, SCE) value didn't absolutely shift to more anodic or more cathodic potentials in contrast with corrosion potential obtained in blank solution. Therefore, MTMMP Schiff base can be classified as a mixed type inhibitors [25,26].

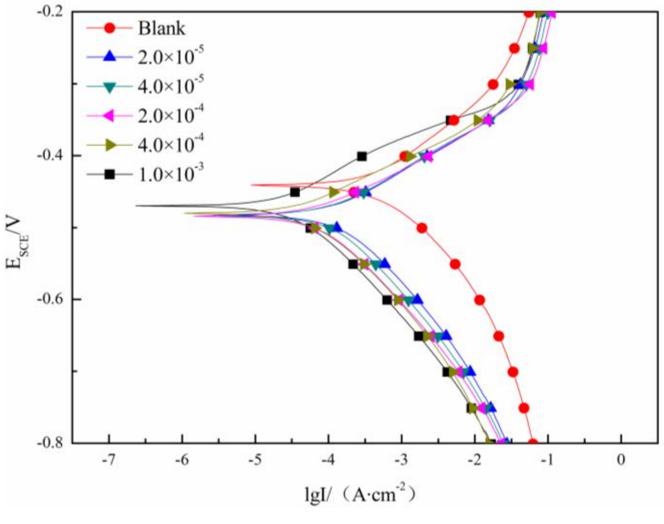

Figure 2. Tafel curves of mild steel in 1M HCl solution with and without various concentrations of MTMMP

The corresponding Tafel polarization curves parameters, including corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a), and inhibition efficiency (*IE%*), are given in Table 2. The *IE%* was calculated according to the following equation (3) [27].

$$IE\% = \left(\frac{i^{0}_{corr} - i_{corr}}{i^{0}_{corr}} \right) \times 100 \qquad (3)$$

Wherein i^{0}_{corr} and i_{corr} are current densities in the absence and presence of various concentrations of MTMMP, respectively. The results show that the corrosion inhibition efficiency increases with increasing concentration of MTMP Schiff base. The results obtained from the Tafel polarization measurements are in good agreement with those obtained from the weight loss method.

Table 2. Polarization curves parameters for mild steel in 1M HCl in the presence various concentrations of MTMMP

C(10^{-6} mol/L)	E_{corr}(V)	I_{corr}(mA)	β_c(mV)	β_a(mV)	*IE*(%)
Blank	-0.4415	0.4692	113.7	79.3	
20	-0.4842	0.2271	110.4	58.7	51.60
40	-0.4842	0.1862	110.2	57.9	60.32
200	-0.4843	0.0702	105.5	57.4	85.04
400	-0.4803	0.0457	105.3	48.7	90.26
1000	-0.4711	0.0226	103.9	42.3	95.18

3.3 Electrochemical impedance spectroscopy (EIS)

In order to discuss corrosion behavior of MTMMP in more detail, ESI experiments of MTMMP Schiff base were operated. Figure. 3 shows the Nyquist diagram for mild steel in 1M HCl solution with and without various concentration of MTMMP Schiff base. Here, the symbols represent the original experimental data and the solid lines are the fitted curves based on the electrical equivalent circuit show in Figure. 4 [28]. It can be clearly seen from Figure. 3 that the Nyquist plots were considered as a single capacitive reactance semicircle. The shape of Nyquist plots in the presence of MTMMP Schiff base is the same as the blank solution. The result suggests that addition of MTMMP Schiff base does not modified corrosion reaction on the mild steel surface, and corrosion of mild steel is a typical acid corrosion [29]. Furthermore, the radius of semicircle increases with increasing concentration of MTMP Schiff base. The obtained result indicates that the corrosion of mild steel is obviously inhibited in the presence of the inhibitor.

The corresponding impedance quantitative parameters are given in Table 3. Where *CPE* is constant phase element, R_s is solution resistance, R_{ct} is charge-transfer resistance. *CPE* was substituted for a double layer capacitance (C_{dl}) to give a more accurate fit to the experimental results [30]. The inhibition efficiency of EIS is calculated according to the following equation (4) [29].

$$\eta_{ct}\% = \left(\frac{R_{ct} - R^{0}_{ct}}{R_{ct}} \right) \times 100 \qquad (4)$$

Wherein R_{ct} and R^0_{ct} are the charge-transfer resistance values with and without inhibitor for mild steel in 1M HCl, respectively. The results clearly indicate that addition of MTMMP Schiff base inhibits obviously the corrosion of mild steel.

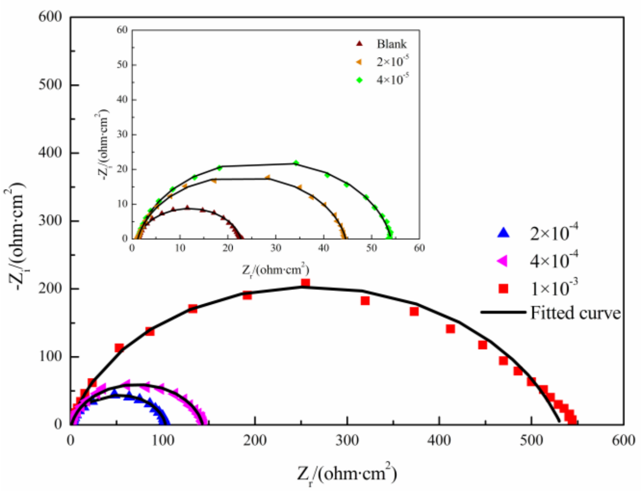

Figure 3. EIS obtained in 1M HCl solution with and without various concentrations of MTMMP

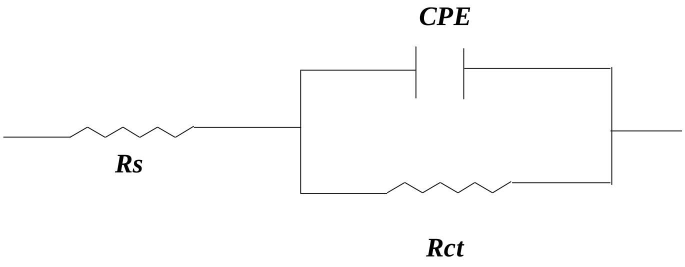

Figure 4. Electrical equivalent circuit model of the studied system

It is clear that, the impedance response for mild steel in HCl solution changes effectively, the CPE values decreased and polarization resistance increased with increasing concentration of MTMMP Schiff base. The decrease in the CPE values that can be caused by a decrease in local dielectric constant and/or an increase in the double layer thickness was ascribed to the gradual replacement of water molecules and other ions originally adsorbed on the surface by adsorption of inhibitor molecules on the mild steel surface. Larger MTMMP molecules adsorb on the mild steel to form the double layer thickness, which also reduces the capacitance [31]. An increase of polarization resistance which reduces corrosion rate of mild steel is resulted from the adsorption of inhibitor molecules on metal/solution interface.

Therefore, these results sufficiently demonstrate that MTMMP Schiff base performs favourable inhibition efficiency for mild steel in good agreement with those obtained from weight loss and Tafel polarization curves measurements.

Table 3. EIS parameters of carbon steel in 1M HCl with different concentration of MTMMP

$C(10^{-6}$ mol/L)	$R_S(\Omega\cdot cm^2)$	$CPE(F,10^{-6})$	$R_{ct}(\Omega\cdot cm^2)$	$\eta_{ct}(\%)$
Blank	1.19	25.3	21.5	
20	1.20	15.5	43.4	50.5
40	1.24	12.6	52.8	59.3
200	1.23	9.0	101.8	78.9
400	1.22	7.9	148.0	85.5
1000	1.19	7.7	523.1	95.9

3.4 Adsorption isotherm

It is generally known that the inhibition efficiency of Schiff base molecules as an efficient corrosion inhibitor primarily depends on their adsorption ability on the mild steel surface. The adsorption process is regarded as a replacement of water molecules by organic molecules according to the following process (5) [32,33].

$$Org_{(s)} + xH_2O_{(ads)} \longleftrightarrow Org_{(ads)} + xH_2O_{(s)} \qquad (5)$$

Wherein $Org_{(s)}$ and $Org_{(ads)}$ are the organic molecules in the aqueous solution and adsorbed on the mild steel surface, respectively, and x represents the number of water molecules replaced by the organic molecules [34]. Therefore, it is necessary to understand the mode of adsorption and the adsorption isotherm which can bring out important information about the relationship between inhibitor and mild steel surface. Surface coverage (θ) is often carried out to explain inhibitor adsorption behavior, its values can be calculated from weight loss data [$\theta=\eta/100$] and are given in Table 1. Various adsorption isotherms including Langmuir, Temkin, Frumkin and Flory-Huggins were attempted to fit the θ values, and the best fit only conforms to Langmuir adsorption isotherm. The Langmuir adsorption isotherm can be expressed according to the following equation (6) [35].

$$\frac{\theta}{1-\theta} = K_a C \qquad (6)$$

Wherein K_a is the equilibrium constant on adsorption-desorption process, θ is the surface coverage, and C is the inhibitor concentration. Figure. 5 shows langmuir adsorption isotherms of MTMMP on the mild steel surface at different temperatures. It can be seen that the linear correlation coefficient (R^2) is almost equal to 1 (R^2_{298K}=0.9993, R^2_{308K}=0.9982, R^2_{318K}=0.9998), The results indicate that the adsorption of MTMMP on mild steel surface obeys the langmuir adsorption isotherm at different temperatures [36].

The free Gibbs energy of adsorption at different temperature was evaluated from the following equation (7) [37].

$$K_a = \frac{1}{55.5} e^{-\left(\Delta G^0 / RT\right)} \qquad (7)$$

Wherein T is the absolute temperature, R is the universal gas constant and the value of 55.5 is the molar concentration of H_2O in solution. The values of equilibrium constant (K_a) were 2.419×10^5 M^{-1}, 2.236×10^5 M^{-1} and 1.44×10^5 M^{-1} at 298 K, 308 K and 318 K, respectively. The values of ΔG^0

calculated from equation (7) are around to -35.0kJ/mol, -35.9 kJ/mol, and -35.9 kJ/mol at 298 K, 308 K and 318 K, respectively.

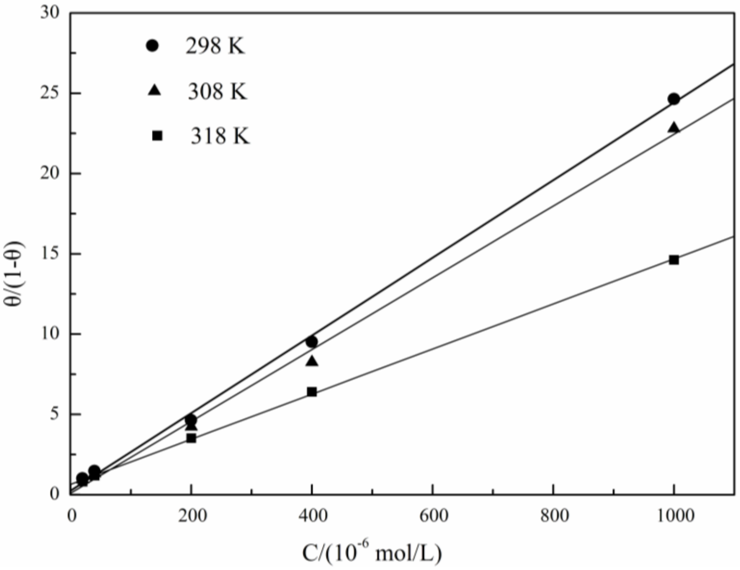

Figure 5. Langmuir adsorption isotherms of MTMMP on the mild steel surface at different temperatures

Generally, the values of $\varDelta G^0$ can reflect the adsorption of inhibitor on the mild steel surface whether or not it is spontaneous process. When the values of $\varDelta G^0$ is equal to -20 kJ/mol or less negative, the adsorption of inhibitor on the mild steel surface is associated with physical adsorption, which is an electrostatic interaction between the charged inhibitor molecules and the charged metal surface. On the other hand, when the values of $\varDelta G^0$ is equal to -40 kJ/mol or more negative, the adsorption of inhibitor on the mild steel surface is assigned to chemical adsorption, which involves charge sharing of transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond [38-40]. Because of the values of the calculated free Gibbs energy of adsorption between -20 kJ/mol and -40 kJ/mol, it can be suggested that the adsorption of MTMMP Schiff base on the mild steel surface is mixed combination of physical adsorption and chemical adsorption with predominantly chemical adsorption.

3.5 Quantum chemical calculations

In order to probe further the interaction of the adsorbate and surface, the Gaussian 03 W software package was carried out to calculate quantum chemical parameters of MTMMP molecule. The complete geometry of molecular structure was optimized and the energies were evaluated at B3LYP/6-31G(d,p) level. Nature bond orbital (NBO) charges of MTMMP molecule as well as HOMO and LUMO were calculated and shown in Figure. 6.

Generally, the absorption ability of inhibitor on the mild steel surface has been related to its spatial molecular structure, as well as with their electronic structure of the molecule [41]. The use of Nature bond orbital (NBO) analyses to predict adsorption centers of inhibitors has been widely reported, which more accurately reflects the charge distribution of molecules compared with Mulliken charge analyses [42]. There is a general consensus that electrophiles always attack molecules at sites of negative charges, which means that the more negatively charged on heteroatom is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction. According to Figure. 6, it can be clearly seen that all the nitrogen atoms embody a considerable excess of negative chares -0.302, -0.303 and -0.586 and negative charges around most carbon atoms of the aromatic ring and 1,3,4-thiadiazole moiety. Similar observation can be given for charge distribution of oxygen atoms (-0.657 and -0.523). Therefore, these N and O atoms should be the active sites for the adsorption of MTMMP on the mild steel surface. This suggests that N and O atoms of MTMMP molecule could be easily transfer electron to the mild steel surface and form coordinate bond with Iron atom. So, an ordered hydrophobic monolayer is formed on the mild steel surface, which acts as a barrier to prevent mild steel corrosion.

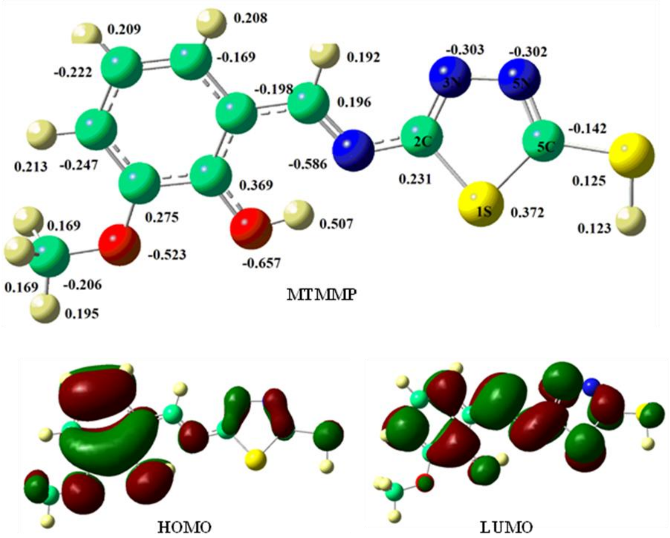

Figure 6. NBO distribution of MTMMP molecule and frontier molecular orbitals of MTMMP

In addition, frontier orbital theory was useful in exploring the interaction of the adsorption centers of the inhibitor molecule and surface metal atoms [43]. In general, the value of E_{HOMO} is often associated with the electron donating ability of a molecule, whereas E_{LUMO} reflects its ability to accept electrons. According to Figure. 6, it can be clearly seen that the frontier orbital were distributed around the complete molecular structure. The corresponding calculated quantum chemical data was given, including the energy of MOMO (E_{HOMO}=-0.228 ev), energy of LUMO (E_{LUMO}=-0.099 ev), the energy band gap (ΔE=0.129 ev), and dipole moment (μ=3.693 Debye). These results show that MTMMP Schiff base has a relatively higher energy of HOMO and lower energy of LUMO, which can be in favor of bonding with metal surface [44]. As a result of high values of HOMO, MTMMP Schiff base has a tendency to donate electrons to those acceptor molecules with empty molecular orbital. The ground-state electronic configuration of Fe atom is $1S^22s^22p^63s^23p^64s^23d^6$. The incompletely occupied 3P orbital of Fe could bond with HOMO of MTMMP Schiff base, while the filled 3S orbital of it could interact with LUMO of MTMMP.

Furthermore, another important factor is worth noting that the influence of the dipole moment on corrosion inhibition was caused considerable concerns in a lot of literatures [45,46]. The dipole moment that is one of important electronic parameters arises from non-uniform distribution of charges on the various atoms in a molecule. The adsorption of MTMMP Schiff base can be regarded as a quasi-substitution process between the MTMMP molecules and water molecules on the mild steel surface [47]. The dipole moment of MTMMP molecule (3.691 Debye (12.31×10^{-30}Cm)) is higher than that of H_2O molecule (μ= 6.23×10^{-30}Cm), which is probably in favor of the adsorption between organic molecule and mild steel surface via physical interaction [48].

4. CONCLUSIONS

The MTMMP Schiff base was investigated as a new and effective corrosion inhibitor for mild steel in 1 M hydrochloric acid solution by a series of techniques. The following conclusions can be made from the experimental results:

1. The MTMMP Schiff base for mild steel in 1 M HCl solution is a significant inhibitor and acts as the mixed type inhibitor.
2. The inhibition efficiency of MTMMP Schiff base increases with increasing inhibition concentration and decreases with the increase of temperature in the studied temperature range.
3. The adsorption behavior of MTMMP on the mild steel surface conforms to the Langmuir adsorption isotherm and the values of the free Gibbs energy of adsorption suggest a mixed combination of physical adsorption and chemical adsorption with predominantly chemical adsorption.
4. The quantum chemical calculations indicate that N and O atoms of MTMMP molecule donate electrons to the incompletely occupied 3P orbital of Fe, and act as most probable nucleophilic centers to bond with metal iron surface.

ACKNOWLEDGEMENTS
This article is supported by the Natural Science Foundation of China (NSFC21276027), the Scientific Research Award Foundation for Shandong Provincial Outstanding Young and Middle-aged Scientists (2008BS04030), Science and Technology Development Program of Binzhou (2013ZC0201), the Scientific Research Fund Project of Binzhou University (BZXYG1206, BZXYG1315).

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