Effect of 2-[substituted-hydrazine]carbothioamide as corrosion inhibitors for mild steel in sulphuric acid solution

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Abstract :

Prepared thiosemicarbazide derivatives (SB1, SB2, SB3, SB4 and SB5) were investigated as corrosion inhibitors for mild steel in 1M H_2SO_4 solution by weight loss measurements, the inhibition efficiency increased by increasing the inhibitor concentration, and the inhibition efficiency orders are SB1 > SB5 > SB3 > SB2 > SB4 with the highest inhibiting efficiency of 95.39% for 10^{-3}M. The values of ΔG^o_{ads} showed physisorption effect for (SB1, SB2, SB4 and SB5) and chemisorption effect for SB3. Semiempirical molecular orbital calculations for (SB1, SB2, SB3, SB4 and SB5) gave useful information to explain the interaction between the surface of metal and the organic molecules.

الخلاصة:

تم تحضير مشتقات الثايوسيمي كاربازايد والتي تم الرمز لها بالرموز (SB5,SB4,SB3,SB2,SB1) وتم تحقيق عملها كمثبطات لتآكل الحديد الصلب الموضوع في محلول حامض الكبريتيك بتركيز1مولاري بواسطة قياسات الخسارة بالوزن ,كفاءة التثبيط تزداد بزيادة تركيز المثبط المستعمل ,وترتيب كفاءة التثبيط لهذه المركبات هو كالآتي(SB1 > SB5>SB3>SB2>SB4) مع اعلى قيمة لكفاءة التثبيط هي 95,39% للتركيز 10^{-3}مولاري.

قيم الطاقة الحرة للامتزاز(ΔG^o_{ads}) تبين تأثيرين للامتزاز الاول تأثير فيزيائي للمركباتSB1, SB2 ,SB4, SB5 والثاني تأثير كيميائي للمركبSB3.الحسابات الشبه تجريبية للأوربتالات الجزيئية للمركبات SB5,SB4,SB3,SB2,SB1 اعطت معلومات مفيدة لتوضيح التآثر بين سطح المعدن والجزيئات العضوية .

1. Introduction

Due to prominent industrial applications of mild steel, several inhibitors have either been synthesized or chosen from organic compounds having heteroatom in their molecular structures [1], as practical methods for protection against corrosion especially in acidic media [2,3]. In addition, various protective methods have been adopted; one of the frequently used is the use of organic compounds containing nitrogen, oxygen and sulphur atoms [4-8].Organic molecules of this type can adsorb on the metal surface and form coordination between their N-electron pair and / or π electron cloud and the metal surface, thereby reducing the corrosion in acidic solutions [9–11].

Some Schiff bases inhibitors have been previously reported as effective corrosion inhibitors for various metals in acid media, such as Schiff bases containing thiophene substituents [12,13] and furoin thiosemicarbazone [14].

In the present work, some Schiff bases of corrosion inhibitors, namely 2-[substituted-hydrazine]carbothioamides were prepared. The aim of this work is to investigate the efficiency of these organic compounds as corrosion inhibitor for mild steel in solution of 1M sulfuric acid.

2. Experimental

2.1. Materials

The sheet of mild steel used has the composition percentages (0.002% P, 0.288% Mn, 0.03% C, 0.0154% S, 0.0199% Cr,0.002% Mo ,0.065% Cu , 0.0005% V, and the remainder iron). The mild steel sheet was mechanically press-cut into disc shape with diameter (2.5 cm). These disc shapes were polished with emery papers ranging from 110 to 410 grades to get very smooth surface. However, surface treatments of the mild steel involve degreasing in absolute ethanol and drying in acetone. The treated specimens were then stored in a moisture-free desiccator before their use in corrosion studies.

The Schiff base inhibitors, namely: (E)-2-benzylidine hydrazine carbothioamides (SB1), (E)-2-(4-(dimethylamino) benzylidine) hydrazine carbothioamide (SB2), (E)-2-(4-nitro benzylidine) hydrazinecarbothioamide (SB3) , (E)-2-(3-nitro benzylidine) hydrazinecarbothioamide(SB4) and (Z)-2-(1-phenyl ethylidene)hydrazine carbothioamides (SB5), were synthesized as follow[15,16]: A mixture of thiosemicarbazide (1g,0.01mol), abs. ethanol (20ml) and appropriate aromatic carbonyl compounds (aldehyde or ketone) (0.01mol) with few drops of glacial acetic acid were refluxed for (4-5) hours. After cooling to room temperature the precipitate was filtered and dried. The product was recrystallized from ethanol. The molecular formula of suggested inhibitors is shown in Figure 1. Inhibitor concentrations of $1x10^{-3}$ to $1x10^{-5}$ M were prepared in 1M H_2SO_4 solution at 30^oC. Solutions of 1M H_2SO_4 were prepared by dilution of analytical grade 98% H_2SO_4 with bidistilled water.

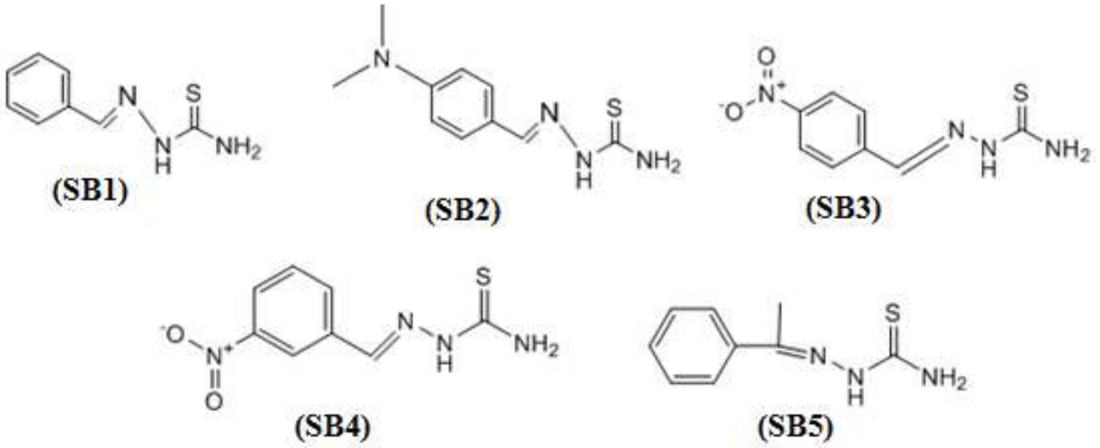

Figure 1.The molecular formula of suggested inhibitors

2.2. Weight loss method

Mild steel specimens were initially weighed in an electronic balance. After that the specimens were suspended and completely immersed in 250 ml beaker containing 1M sulphuric acid in the presence and absence of inhibitors. The specimens were removed after 8 hours exposure period at 30ºC, washed with water to remove any corrosion products and finally washed with acetone. Then they were dried and reweighed. Mass loss measurements were performed as per ASTM method described previously [17,18]. The tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss is reported.

Weight loss allowed calculation of the mean corrosion rate in (mg cm^{-2} h^{-1}). The corrosion rate of mild steel was determined using the relation[19]:

$$W = \frac{\Delta m}{St} \qquad (1)$$

Where Δm is the mass loss, S the area and t is the immersion period.

The percentage inhibition efficiency (E (%)) was calculated using the relationship[20]:

$$E\% = \left(\frac{W_{corr} - W_{corr(inh)}}{W_{corr}}\right) x\ 100 \qquad (2)$$

Where W_{corr} and $W_{corr(inh)}$ are the corrosion rates of mild steel in the absence and presence of inhibitor, respectively.

2.3. Theoretical calculations

The correlation between theoretically calculated properties and experimentally determined inhibition efficiencies has been studied successfully for uniform corrosion [21-24]. The purpose of this work is to provide information about the electron configuration of several organic inhibitors by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency.

All the calculations were performed using the semi-empirical calculations with PM3 method [25]. For this purpose the Hyperchem Program [26] with complete geometry optimization was used. This computational method has been proven to yield satisfactory results [23,24]. The easiest way to compare the inhibition efficiency of (SB1, SB2, SB3, SB4 and SB5) is to analyze the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The optimized molecular structures are shown in Figure 2 and the calculated energies E_{HOMO}, E_{LUMO}, energy gap ($\Delta E=E_{LUMO}-E_{HOMO}$) and other indices are given in Table 2.

3. Results and discussion

The FT-IR spectra of 2-[substituted-hydrazine] carbothioamides (SB1, SB2, SB3, SB4 and SB5) showed disappearing of ν(C=O) peak of component products that indicated formation of the suggested inhibitors.

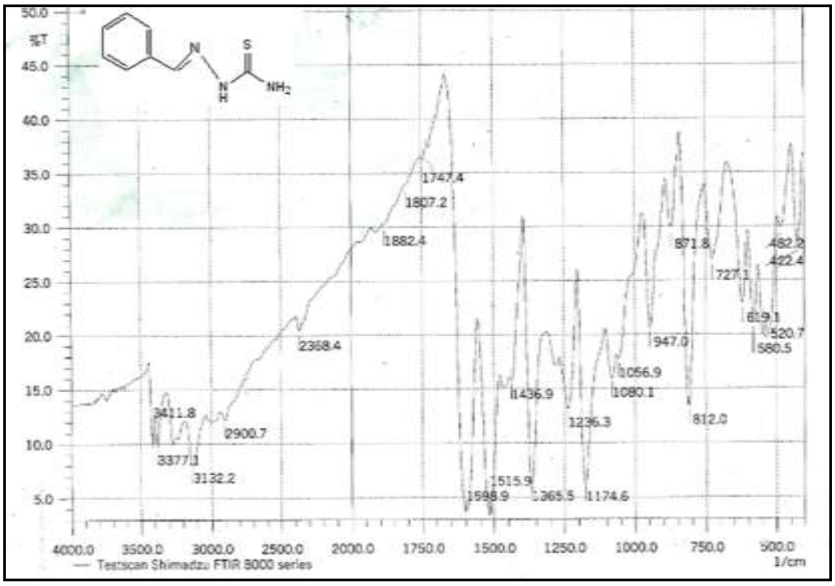

Figure (2): FTIR spectrum for compound [1]

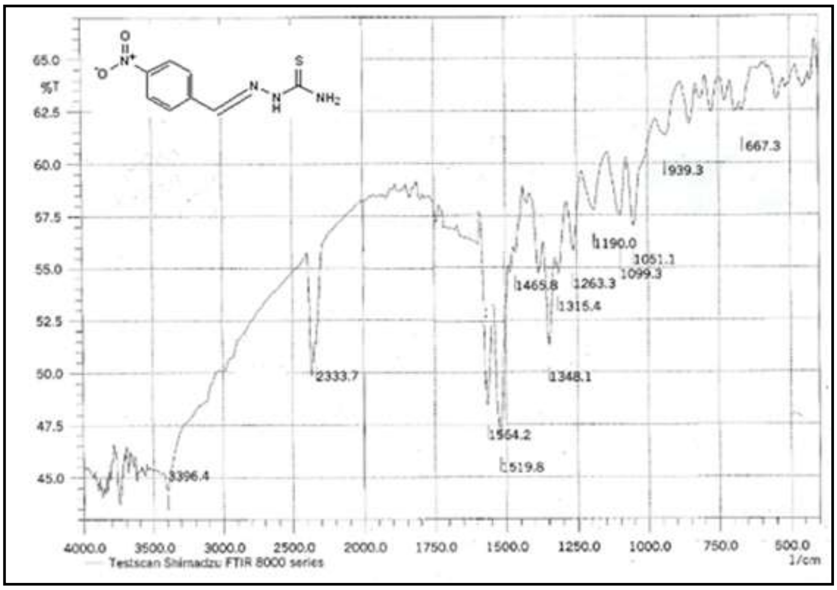

Figure (3): FTIR spectrum for compound [2]

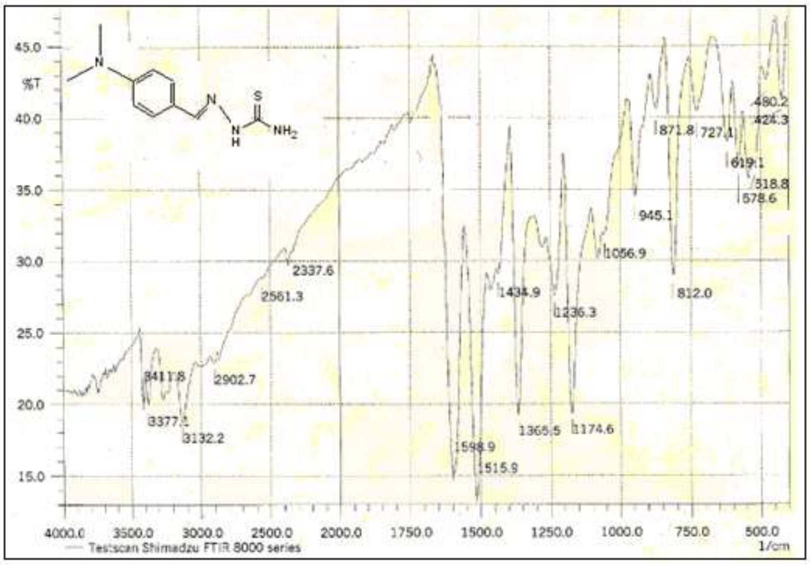

Figure (4): FTIR spectrum for compound [3]

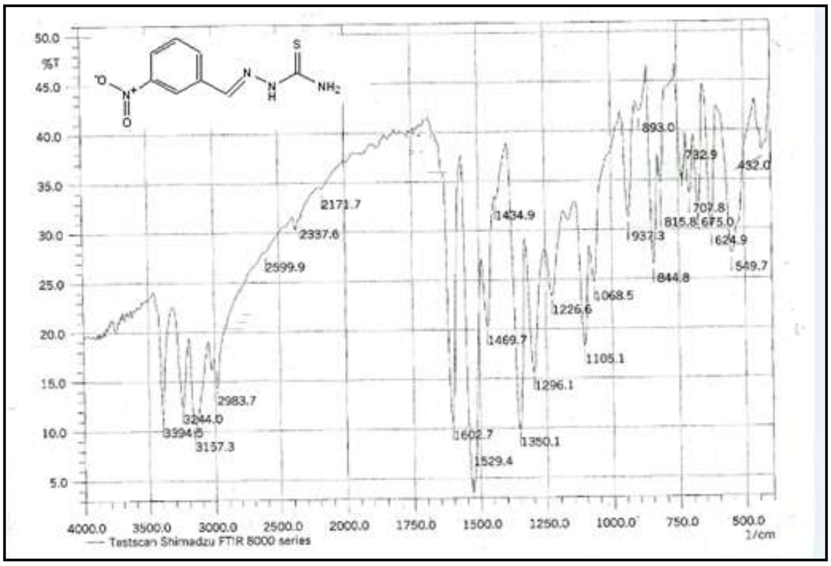

Figure (5): FTIR spectrum for compound [4]

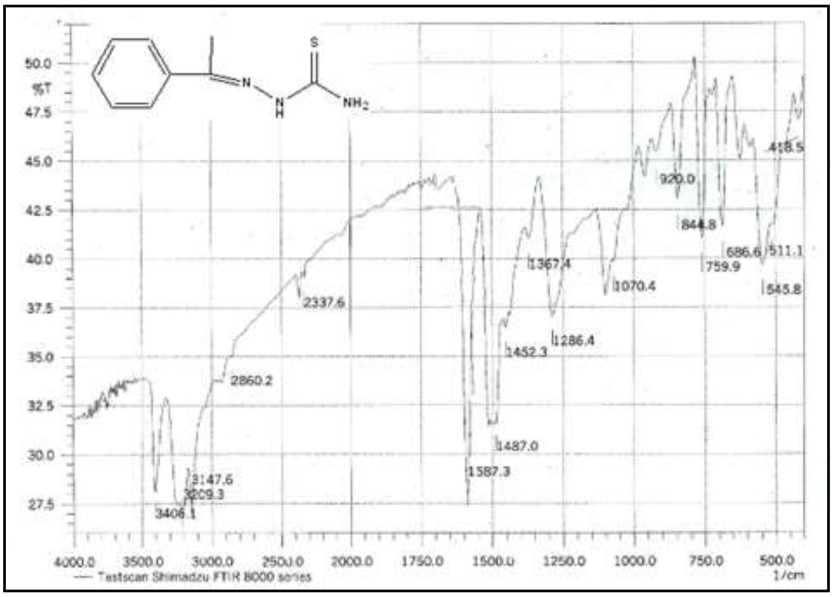

Figure (6): FTIR spectrum for compound [5]

The results of corrosion rate and inhibition efficiency from weight loss measurements at different concentrations of (SB1, SB2, SB3, SB4 and SB5) after 8 h immersion at 30^{o}C are depicted in Figure 7 and summarized in Table 1. These values indicates that the mild steel corrosion is reduced by the presence of suggested inhibitors in 1M H_2SO_4 at all concentrations used in this study, since there is a general decrease in the original weight of mild steel specimens after 8 hours. That's could be explain by adsorption of organic compounds on the mild steel surface which makes impediment towards corrosion environment.

Table 1. Corrosion rate, inhibition efficiency, surface coverage (θ) and standard free energy of adsorption in the presence and absence of different concentrations of 2-[substituted-hydrazine] carbothioamides for the corrosion of mild steel in 1M H_2SO_4 from weight loss measurements.

Inhibitor concentration (M)	1M H_2SO_4				
	ΔM(g)	Corrosion rate (mg cm^{-2} h^{-1})	E%	θ	ΔG^o_{ads} (KJ/mol)
Uninhibited	0.113	2.8775	-	-	
SB1					
0.001	0.0052	0.1324	95.39	0.9539	-33.26 (R^2=0.970)
0.0001	0.0788	2.0066	30.26	0.3026	
0.00005	0.0839	2.1365	25.75	0.2575	
0.00001	0.0893	2.274	20.97	0.2097	
SB2					
0.001	0.0376	0.9574	66.72	0.6672	-35.56 (R^2=0.998)
0.0001	0.0621	1.5813	45.04	45.04	
0.00005	0.0632	1.6093	44.07	0.4407	
0.00001	0.0653	1.6628	42.21	0.4221	
SB3					
0.001	0.0344	0.8759	69.55	0.6955	-41.35 (R^2=0.999)
0.0001	0.0373	0.9498	66.99	0.6699	
0.00005	0.0383	0.9753	66.1	0.661	
0.00001	0.0396	1.0084	64.95	0.6495	
SB4					
0.001	0.0474	1.207	58.05	0.5805	-34.54 (R^2=0.999)
0.0001	0.061	1.5533	46.01	0.4601	
0.00005	0.0721	1.8131	36.99	0.3699	
0.00001	0.0995	2.5337	11.94	0.1194	
SB5					
0.001	0.017	0.4329	84.95	0.8495	-31.51 (R^2=0.996)
0.0001	0.0737	1.8767	34.78	0.3478	
0.00005	0.0941	2.3962	16.72	0.1672	
0.00001	0.1071	2.7273	5.22	0.0522	

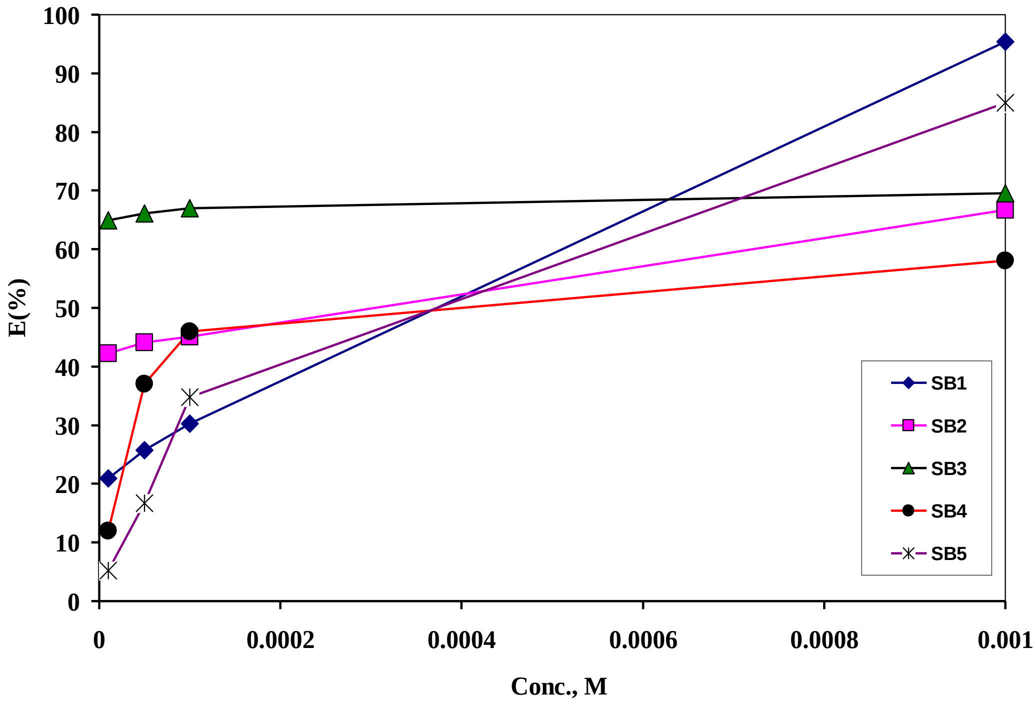

Figure 7. Effect of inhibitor concentration on the efficiencies of mild steel obtained at 30°C in 1M H_2SO_4 containing different concentrations of suggested inhibitors.

The increase in efficiency of inhibition with concentration indicates that more inhibitor molecules are adsorbed on the metal surface at higher concentration, leading to greater surface coverage.

The inspection of results of E (%) in Table 1 indicates that the protection efficiency E (%) increases with increasing the concentration of suggested inhibitors with the maximum inhibition efficiencies were achieved at 10^{-3} M. Thus, the comparative study reveals that order of maximum inhibition efficiency as follow: SB1> SB5> SB3> SB2> SB4. That order could be explain by the effect of molecular structure of organic inhibitors on inhibition efficiency, as well as adsorption process.

Basic information can be provided from the adsorption isotherms to explain the interaction between the organic compounds and metal surfaces. So that, the degree of surface coverage values (θ) at different inhibitor concentrations in 1M H_2SO_4 was achieved from weight loss measurements (θ = E (%)/100) at 30°C and tested with Langmuir isotherm relationship [27].

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (3)$$

Where K_{ads} is the equilibrium constant of the adsorption process.

According to the Langmuir isotherm, K_{ads} values can be calculated from the intercepts of the straight line of plotting C/θ versus C. K_{ads} is related to the standard free energy of adsorption, ΔG^o_{ads}, with the following equation: (The value 55.5 is the molar concentration of water in the solution in M)

$$K_{ads} = \frac{1}{55.5}\exp(-\Delta G^o_{ads}/RT) \qquad (4)$$

From Table 1, the values of standard free energy of adsorption are negative to indicate that the processes of adsorption of all suggested inhibitors (SB1, SB2, SB3, SB4 and SB5) were spontaneous on the mild steel surface after 8 h immersion at 30°C and that's given sense for remarkable interaction between suggested inhibitors and metal surface.

Here, adsorbed molecule moves closer to the surface of metal making electrons start to overlap with that of the surface atoms which causes physisorption for suggested inhibitors (SB1, SB2, SB4 and SB5) [28-31].

It is generally accepted that the adsorption of an organic inhibitor on a metal surface in acidic media usually involves formation of a metal–inhibitor complex by combining an inhibitor with freshly generated Fe^{2+} ions on the steel surface [32]:

$$Fe + 2H^{+} \rightarrow Fe^{+2} + H_2 \qquad (5)$$

$$Fe^{+2} + Inh_{(ads)} \rightarrow [Fe\text{-}Inh]^{+2}_{(ads)} \quad \text{(metal–inhibitor complex)} \qquad (6)$$

Therefore, formation of a metal–inhibitor complex could work as protective layer for anodic cell to reduce formation of Fe^{+2} sites. Thus it could be suggested that at low concentrations of suggested inhibitors probability of formation a compact metal–inhibitor complex is low.

The adsorption mechanism for given inhibitors depends on adsorption behavior of organic molecules containing both N and S atoms. The presence of more than one functional group has been reported to often lead to changes in the electron density of a molecule, which could influence its adsorption behavior [33]. The suggested inhibitor could adsorb with the corroding steel surface via the compact metal–inhibitor complex on anodic sites and reduces Fe electro-dissolution. According to the value of ΔG^{o}_{ads} (see Table 1) for suggested inhibitors (SB3), it is shown to preferentially chemisorb on the surface of mild steel in acidic media through both N and S atoms [34].

Such behavior may also be considered [31] that a molecule may first physically adsorb, and then slowly reacts with the metal surface to form a chemisorbed layer. In another words, inhibition corrosion properties are usually obtained by organic molecule that offers electrons to unoccupied orbitals of the metal to form a co-ordinate type of bond (chemisorption).

To study the relationship between molecular structure and inhibitive effect of the suggested inhibitors, we used molecular orbitals of semi-empirical calculations with PM3 method. All the theoretical quantum calculations were performed suggested inhibitors (SB1, SB2, SB3, SB4, SB5) using more energetically stable conformations in gas phase at 25°C (Figure 8).

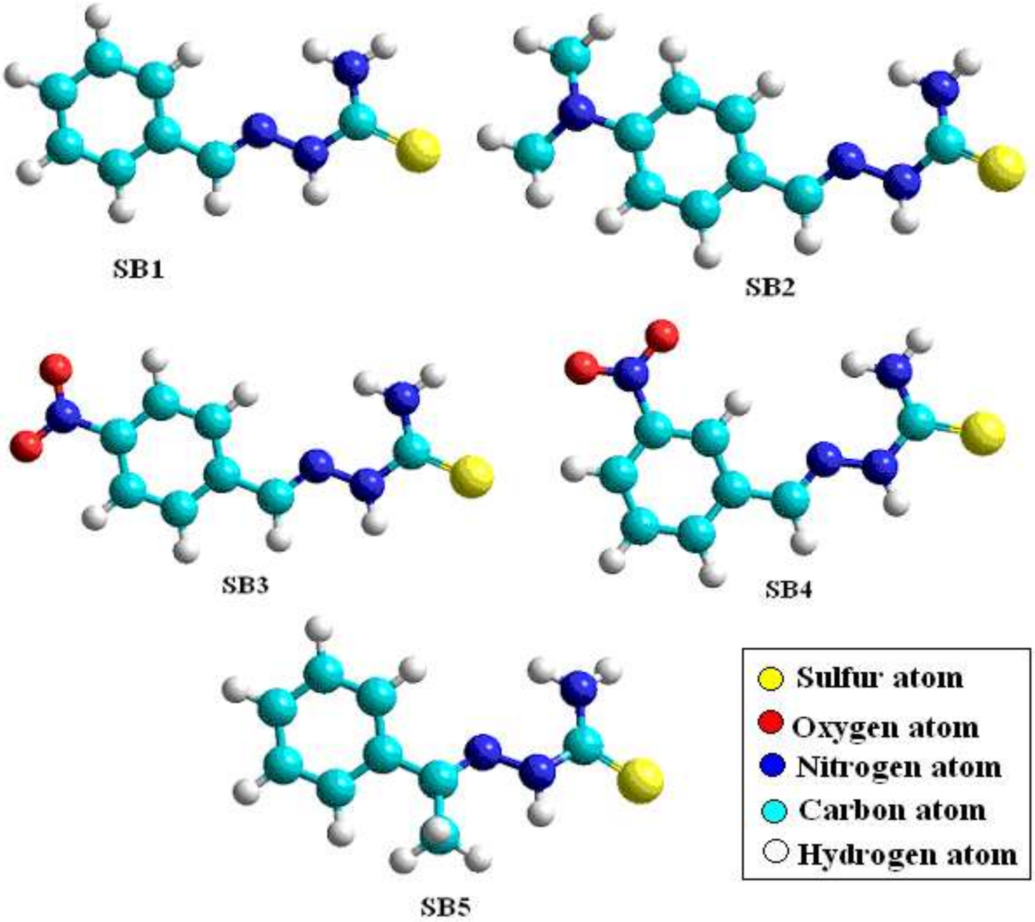

Figure 8. More energetically stable conformations of suggested inhibitors(SB1,SB2,SB3,SB4,SB5) with PM3 method.

The calculated quantum chemical parameters of suggested inhibitor forms are reported in Table 2.

Table 2.Calculated quantum chemical parameters of suggested inhibitor forms by using PM3 method.

inhibitor	HOMO(eV)	LUMO (eV)	$\Delta E(E_{HOMO}-E_{LUMO})$ (eV)	μ (Debye)	planarity
SB1	-8.6986	-1.0319	-7.6667	6.13	planar
SB2	-8.5374	-0.9339	-7.6035	7.40	Semi-planar
SB3	-9.0797	-1.8667	-7.2130	0.39	planar
SB4	-8.9428	-1.6019	-7.3409	5.54	planar
SB5	-8.7146	-0.9378	-7.7768	5.89	Semi-planar

A typical electron density distribution of HOMO and LUMO for suggested inhibitors (SB1, SB2, SB3, SB4 and SB5) is shown in Figure 4. Depending on the presence of N and S atoms in suggested inhibitors, the repartition density of the HOMO and LUMO is preferentially localized on N (C=N) and S atoms for all molecules. Table 2 shows also different dipole moments for suggested inhibitors (SB1, SB2, SB3, SB4 and SB5). The values of dipole moment can explain due to non-uniform distributions of positive and negative charges on the various atoms, which could be related to improvement the dipole–dipole interaction of organic molecules and mild steel surface. Electrostatic potential maps for suggested inhibitors (SB1, SB2, SB3, SB4 and SB5) are depicted in Figure 10. Non uniform distribution of electronic density (see Figure 9) and concentration of negative charges on N (C=N) and S atoms for all molecules, which are reflected the different values of calculated dipole moment (see Table 2). From all above, we obtained different experimental and theoretical results due to different molecular structures, which effected on inhibitive effect of the suggested inhibitors. There are steric and electronic effects to understand the role of molecular structure on inhibitive effect. Inhibitive effect of the suggested inhibitors depends on N (C=N) and

S atoms for all molecules. Semi-planarity of SB2 and SB5 (see Table 2) is improve the E% (see Table 1) to make N and S atoms more closed to the surface of metal and that improved the physisorption at high concentrations. But the planar molecules still prefer for improving the inhibitive effect [35] (SB1, SB3 and SB4 are planar, see Table 2). According to values of E% (see Table 1) the donor and acceptor groups on benzene ring for suggested inhibitors (SB2, SB3 and SB4) did not show interesting effect on the values of E% comparing with SB1.

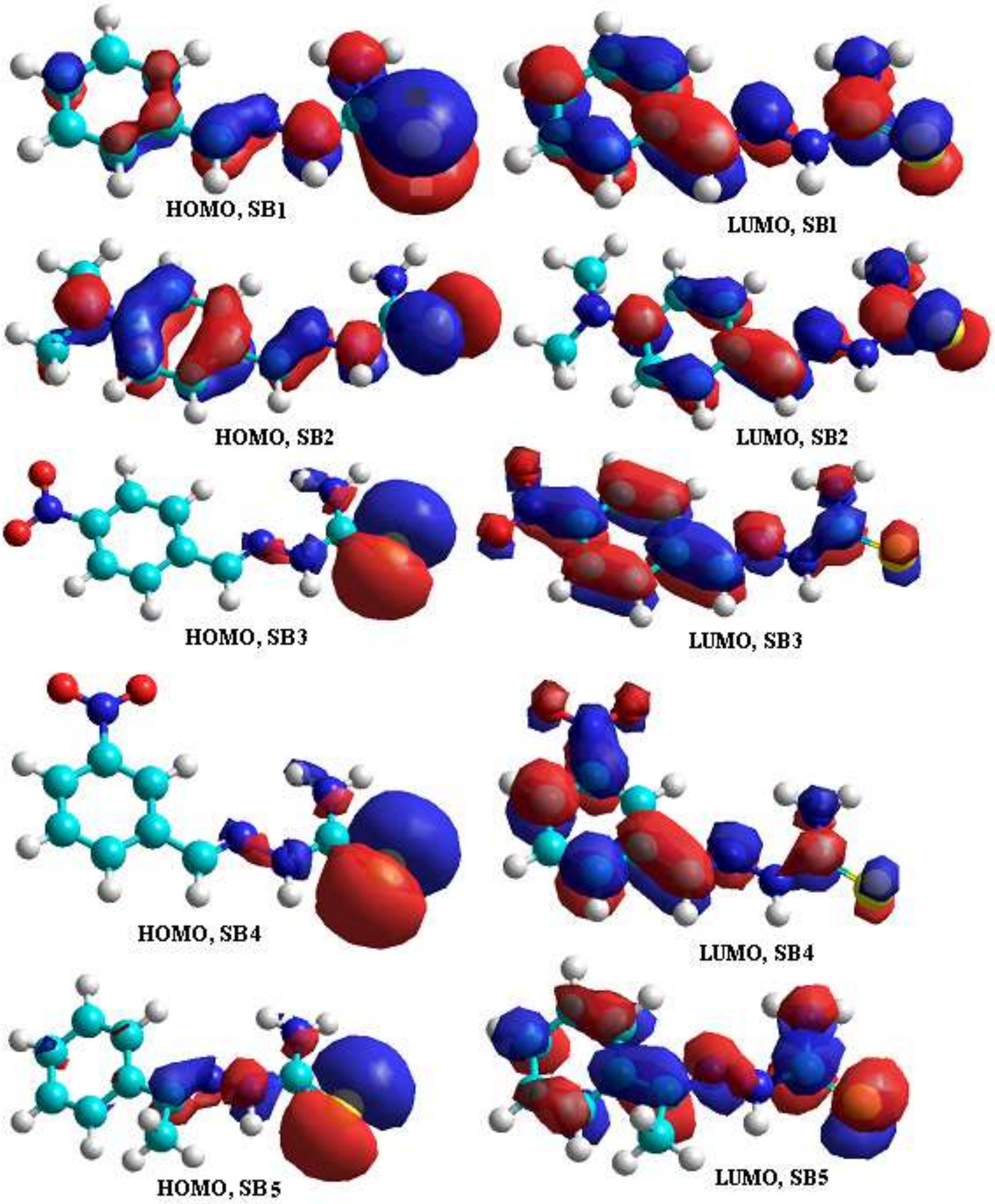

Figure 9. The frontier molecular orbital density distributions (HOMO and LUMO) by using PM3 method.

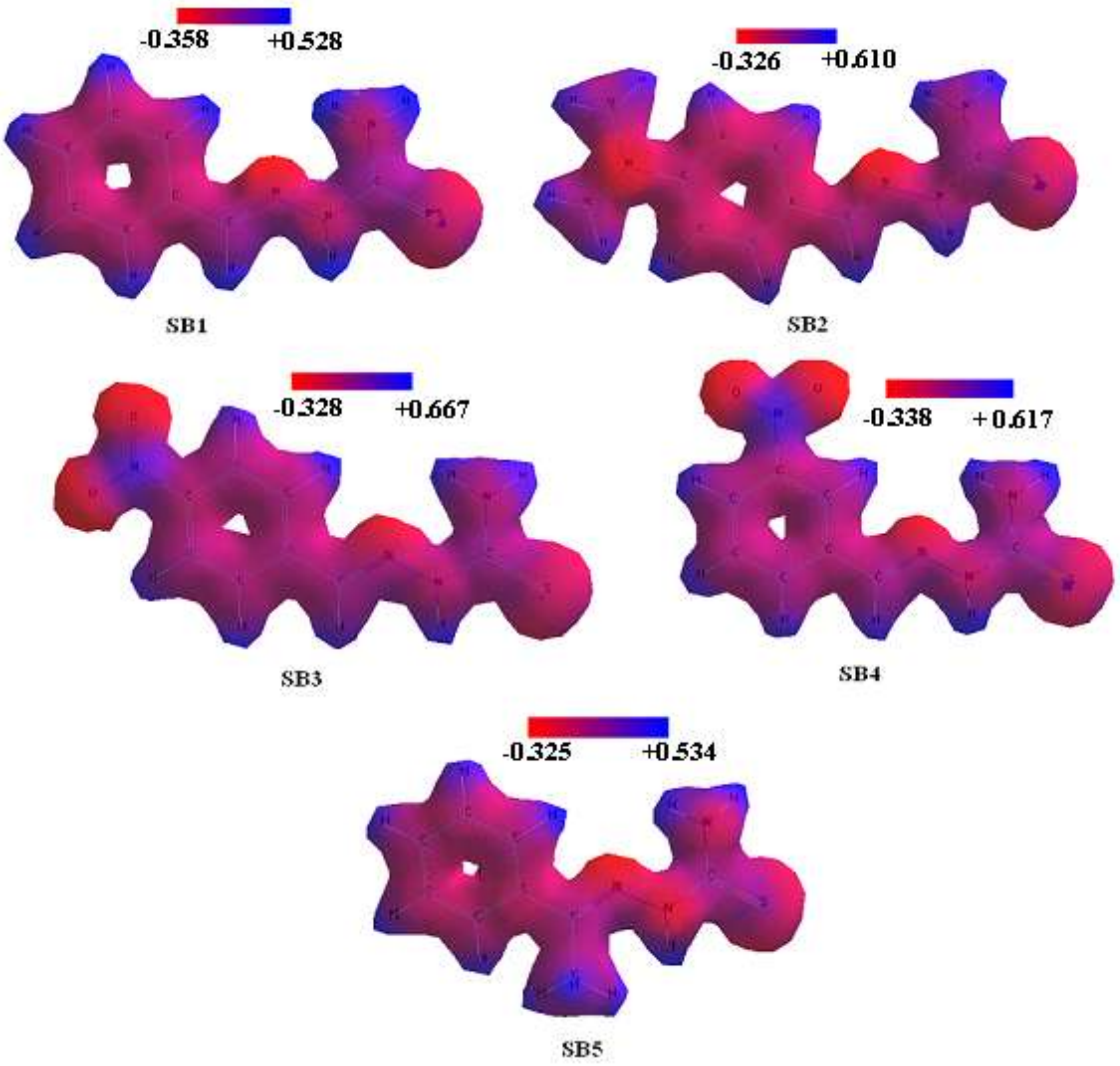

Figure 10. Electrostatic potential maps for suggested inhibitors (SB1, SB2, SB3, SB4 and SB5) by using PM3 method.

Finally, we demonstrate the orders below:
SB1> SB5> SB3> SB2> SB4 (related to E%(at 0.001M), see Table 1)
SB3> SB2> SB4> SB1> SB5 (related to ΔG^{o}_{ads}, see Table 1)
SB3> SB4> SB2> SB1> SB5 (related to ΔE (energy gap), see Table 2)

From the orders above the more interesting suggested inhibitor is SB3, which showed chemisorption with ΔG^{o}_{ads}= -41 kJ/mol, it's confirmed from the closed values of E% (≈70-65 for different concentrations, see Table 1) comparing with the others (physisorption). In spite of low concentration (10^{-5}M) of SB3 but still E% is very high comparing with the E% of (SB1, SB2, SB4 and SB5). We think that the nitro group plays important role in the molecular structure of SB3. it is contributed through its position with high planarity for the molecule to distribute the electronic density on the surface of organic molecule regularly. We believe that the regular distribution of the electronic density on the surface of organic molecule will improve the interaction between the organic molecule and metal surface.

4. Conclusion.

The prepared 2-[substituted-hydrazine]carbothioamides (SB1, SB2, SB3, SB4 and SB5) used as corrosion inhibitors on the mild steel surface in 1M H_2SO_4 solution at 30^{o}C. The results of inhibitive efficiency (E%) showed interesting inhibitive effects of suggested inhibitors. The values free energy of adsorption revealed physisorption effect for (SB1, SB2, SB4 and SB5) and chemisorption effect for SB3. Molecular modeling for (SB1, SB2, SB3, SB4 and SB5) by using semiempirical molecular orbital calculations gave useful information to explain the interaction between the surface of metal and the organic molecules.

Acknowledgments

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