مجلة العلوم البحتة والتطبيقية
Journal of Pure & Applied Sciences
www.Suj.sebhau.edu.ly ISSN 2521-9200
Received 27/10/2018 Revised 28/09/2019 Published online 08/10/2019

The Inhibition of Mild Steel Corrosion by Sulphur Containing Organic Compound

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Abstract The inhibition of mild steel corrosion in "2.0 M sulphuric acid" solution by a Sulphur containing organic compound namely " Methyl Carbazodithoate " has been studied at temperature 30 ℃ by weight loss technique. Adsorption isotherms were tested for their relevance to describe the adsorption behaviour of methyl carbazodithoate. The experimental results show that the test inhibitor has a promising inhibitory action against corrosion of low carbon steel in the medium investigated. The inhibition efficiency was found to increase with a corresponding increase in the concentration of the inhibitor. The adsorption mechanism of methyl carbazodithoate inhibition is also proposed. The lower adsorption of sulphate ions on the carbon steel metal surface permits more space for the adsorption of inhibitor molecules and enhances inhibition of corrosion. Finally, the obtained results in this work indicates that the sulphur-containing inhibitor compound namely; "methyl carbazodithoate" compound is an effective inhibitor for corrosion inhibition of carbon steel in sulphuric acid solution.

Keywords: Corrosion Inhibitors, methyl carbazodithoate, mild steel.

تثبيط تآكل الفولاذ الطري بالكبريت المحتوي على مركب عضوي

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الملخص تمت دراسة تثبيط الفولاذ الطري في محلول "2.0 M حمض الكبريتيك" بواسطة مركب عضوي يحتوي على الكبريت وهو "ميثيل كاربازوديثويت" في درجة حرارة 30 ℃ بواسطة تقنية فقدان الوزن. تم اختبار متساوي درجة الحرارة في الامتزاز لمعرفة مدى ملاءمتها لوصف سلوك امتزاز ميثيل كاربازوديثوات. أظهرت النتائج التجريبية أن مثبط الاختبار له عمل مثبط واعد ضد تآكل الصلب منخفض الكربون في الوسط الذي تم فحصه. تم العثور على كفاءة تثبيط لزيادة مع زيادة مقابلة في تركيز المانع. كما تم اقتراح آلية امتزاز تثبيط ميثيل كاربازوديثويت. انخفاض امتصاص أيونات الكبريتات على سطح المعدن الصلب الكربوني يتيح مساحة أكبر لامتصاص جزيئات المانع ويعزز تثبيط التآكل. أخيراً ، تشير النتائج التي تم الحصول عليها في هذا العمل إلى أن مركب المانع المحتوي على الكبريت هو ؛ مركب "ميثيل كاربازوديثويت" مثبط فعال لتثبيط تآكل الصلب الكربوني في محلول حمض الكبريتيك.

الكلمات المفتاحية: مثبطات التآكل ، ميثيل كاربازوديثويت ، فولاذ خفيف.

Introduction

Corrosion is gradual destruction of a material because of its reaction with environment. It is a major industrial problem that has attracted a lot of investigators in recent years [1,2]. Indeed, corrosion control is an essential issue from application point of view and it has been reported that inhibitors are needed to be used which act as a barrier to reduce the aggressiveness of the environments against the corrosion attack [1,2].

Mild steel is employed widely in most industries due to its low cost and availability in ease for the fabrication of various reaction vessels such as cooling tower tanks, pipelines, etc [3]. Inhibitors are substance which retards substances which retard the cathodic processes and / or the anodic processes, that inhibitors function in one or more ways to control corrosion by adsorption of a thin film onto the surface of a corroding material, by inducing the
formation of a thick corrosion product, or by changing the characteristic of the environment resulting in reduced aggressiveness [4]. Inhibitors are generally used in these processes to control the metal dissolution. Acid inhibitors are essentially used in metal finishing industries, acidizing of oil wells, cleaning of boilers and heat exchangers [5].

Organic compounds have been widely used as corrosion inhibitors for metals in acidic media [6, 7, 8]. The efficient corrosion inhibitors are those compounds which have π-bonds and contains hetero atoms such as sulphur, nitrogen, oxygen and phosphorous which allows the adsorption of compounds on the metal surface [9,10. 11]. The organic inhibitors decrease the corrosion rate by adsorbing on the metal surface and blocking the active sites by displacing water molecules form a compact barrier film on the metal surface. The most of the organic inhibitors are toxic, highly expensive and environment unfriendly. Research activities in recent times are geared towards developing the cheap, non-toxic and environment friendly corrosion inhibitors.

The adsorption processes are described generally using adsorption isotherms which show that the amount of a particular solute is retained by an particular adsorbent in experimental conditions that were well-chosen (pH, temperature, and so on). For a proper understanding of the adsorption process, which allows the design of appropriate experimental strategy, it is necessary to discuss this process, both from the thermodynamic point of view (by using the adsorption isotherms), as well as the kinetic one [12-17]. The selection of the most appropriate model that can best describe the fitting of adsorption data obtained experimentally was made in this study by using linear regression for all cases studied (Lngmir and Temkin and isotherms).

Materials and Methods

The commercial low carbon steel rods were collected from Musirata Steel Factory , they were selected as a test samples for corrosion studies. The analysis data for the low carbon steel rods data were provided by the manufacture, the data are listed in the following table (1). The provided steel rods were cut into cylinder shapes using a diamond wheel cutter. The dimensions of samples were taken as 40 mm length " and 10 mm diameter, after the specimen cut, they are cleaned and polished using emery papers with different grades "180, 220, 320, 400, and 1200 grade ". These activity were done in order to get a smooth specimen surface, free of rust, scale or dust. Following to the polishing procedure, the samples were washed using methanol, acetone and distilled water and then dried. The prepared samples then weighted using electronic balance with accuracy about 0.0001 g. The cleaned specimens were kept in a desiccator in order to protect them against any weather variables, until use them in the experiments.

Table 1: Chemical compositions of Low Carbon Steel Used in this Work

Element	Composition %
S	0.750%
Mn	0.014%
P	0.004%
S	0.014%
Cr	0.002%
Ni	0.001%
Cu	0.001%
Al	0.002%

The organic compound under investigation was prepared by reaction 1:1 carbon disulphide and diamine in presence of potassium hydroxide " KOH ". The obtained potassium carbazodithioate was reacted with idomethane to produce the final product of methyle carbazodithioate which was extracted by eather, filtered and dried from the solvent.

All used chemical are in reagent grade. Freshly distillated deionized water was used in all preparations. Organic compound as an inhibitor in " 2 M sulphuric acid (H_2SO_4) medium was prepared in dimethylformanide " D. M. F". All tested solutions contained " 10 volume percent " of " D. M. F" to maintain complete soluble.

The inhibitor solution used in this work was prepared with different concentrations, a nine different concentration samples in 2.0 M H_2SO_4. The concentration of the first inhibitor sample was carried out as $7.50x10^{-4}$ M and the concentration of the last sample was $4.00x10^{-3}$ M for inhibitor solution temperature 30 ℃.

The corrosion rates for inhibited and a non-inhibited steel samples were measured using a weight loss method. The weight loss measurements were carried out at 30 °C. The loss in weight per area in mg/cm² (Wt) , the corrosion rate (R_{corr}), and the percentage of protection efficiency percent protection IE%, were calculated over different inhibitor concentrations according to the following equation [18]:

$$Wt = (W_{\circ} - Wi/A) \quad (1)$$

$$R_{CORR} = Wt/A \quad (2)$$

$$IE\% = (W_{\circ} - Wi/W_{\circ}) \times 100 \quad (3)$$

where $W_{\circ}$ is the original weight (mg) and Wi the weight after immersion in the test electrolyte, the immersion time (min), and R'_{ORR} and R_{CORR} are the corrosion rates with and without an inhibitor, respectively.

Results and Discussion

Table 2 shows the weight loss and corrosion rate results and table 3 demonstrates the inhibitor efficiency respectively.

Table 2: Weight Loss and Corrosion Rate

Sample No.	Weight Loss mg	Corrosion Rate Mg cm^{-2} min^{-1}
1	80.40	0.1178
2	54.20	0.0758
3	54.30	0.0718
4	56.96	0.0801
5	42.20	0.0613
6	29.60	0.0428
7	17.80	0.0243
8	17.80	0.0243

According to the data in previous table it is clear that the corrosion rate decreases gradually with increasing the inhibitor concentration at a temperature of 30 °C. It seen that the sulphur containing compound inhibit the corrosion of low carbon steels in 2.0 M H_2SO_4 at all concentrations. It was observed that increasing the concentration inhibitor had a significant effect on the corrosion rate of carbon steel shown in table (2). Maximum inhibition efficiency of the compound was 80.47% which achieved at concentration 4.00x10^{-3} M. According to the results a "*Methyl Carbazodithioate*" inhibitor has given an acceptable level of inhibition efficiency against low carbon steel corrosion in acid solution, at a temperature of 30 °C.

Table 3: the effect of concentration of the inhibitor on the efficiency

Sample No.	Inhibitor Concentration M	Inhibitor Efficiency %
1	Blank	00.00
2	7.50×10^{-4}	32.59
3	1.00×10^{-3}	32.46
4	1.25×10^{-3}	29.15
5	1.75×10^{-3}	47.51
6	2.00×10^{-3}	63.18
7	2.50×10^{-3}	75.62
8	3.00×10^{-3}	77.86

Fig. 3 shows, the corrosion rate decreases as the inhibitor concentration increases, this indicates that the presence of "*Methyle carbazodioate*" compound retards the corrosion rate of low carbon steels in 2.0 M H_2SO_4.

The inhibition depends on the concentration of the sulphur containing inhibitor. compound. Fig. (3) showed the Inhibitor Concentration versus the corrosion rate of low carbon steels in "2 M " in absence and presence of different concentration of methyl carbazodithioate inhibitor at 30 °C. As shown in the figure, the increasing in inhibitor concentration causes decreasing in corrosion rate, this indicates that the presence of methyle carbazodioate compound retards the corrosion rate of low carbon steels in " 2 M ". The inhibition depends on the concentration of the sulphur containing inhibitor compound. The inhibitor concentration gives the best corrosion inhibition when the concentration of inhibitor is exceeding to 2.00 x 10^{-3} M.

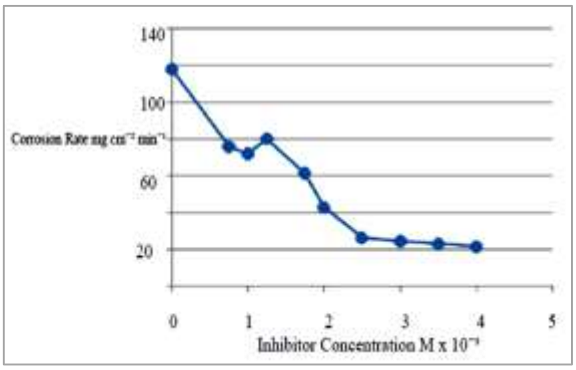

Fig. 3: Corrosion Rate vs. Inhibitor Concentration

In general, adsorption is governed by a number of forces such as covalent bonding, electrostatic attraction, hydrogen bonding and non -polar interactions between the adsorbed species, lateral associative interaction, solvation and desolvation [18].

Inhibition of corrosion of low carbon steels in "2.0 M" at a temperature 30 °C can be explained on the basis of adsorption. The methyl carbazodithoate inhibit the corrosion by controlling both the anodic and cathodic reactions. In sulphuric acid solution this compound exists as protonated species. These protonated species may be absorbed on the cathodic sites of the low carbon steel and decreases the evaluation of hydrogen. The better inhibition efficiency in " 2.0 M " attributed to the difference of adsorption of sulphate ions. The low adsorption of sulphate ions on the metal surface permits more space for the adsorption of inhibitor molecules and enhance the inhibition of corrosion [19].

The relationship between inhibition efficiency and the bulk concentration of the inhibitor at constant temperature, which is known as isotherm, it gives an insight into the adsorption process. Several adsorption isotherms were attempted to fit surface coverage values to classical isotherms of Langmuir, Temkin, Frumkin, Flory-Huggins.

A correlation betweencoverage (θ) defined by (IE %)/100 and the concentration of inhibitor (I) in electrolyte can be represented by the Langmuir adsorption isotherm;

$$\frac{\theta}{1-\theta} = \mathrm{K} \, . \, [I] \qquad (4)$$

where, k is the adsorption constant, it's represents the relationship between surface coverage and the inhibitor concentration. The K values are given in Table (4). Since theefficiency of a given inhibitor is essentially function of the
magnitude of its bindingconstant K, therefore, large K values mean better and stronger interaction, whereassmall K values, mean the interaction between the inhibitor molecules and the metal is weaker. According to the obtained K values, it is concluded that the interaction between the inhibitor molecules and the metal was improved.

Table 4. Inhibitor Surface Coverage, Adsorption Constant and Adsorption Energy Calculation

S. No.	(I) M x 10^{-3}	Surface Cover. (θ)	$\frac{\theta}{1-\theta}$	Adsorp.Const. (K) M^{-1}	Adsorp. Energy (ΔG_{ads}) kJ/mol
1	0.00	0.0000	0.00	000	000
2	0.75	0.3260	0.48	645	- 905
3	1.00	0.3246	0.48	481	- 864
4	1.25	0.2915	0.41	329	- 811
5	1.75	0.4751	0.91	517	- 874
6	2.00	0.6318	1.72	858	- 945
7	2.50	0.7562	3.10	1241	- 997
8	3.00	0.7768	3.48	1160	- 987
9	3.50	0.7910	3.79	1081	- 977
10	4.00	0.8047	4.12	1030	- 971

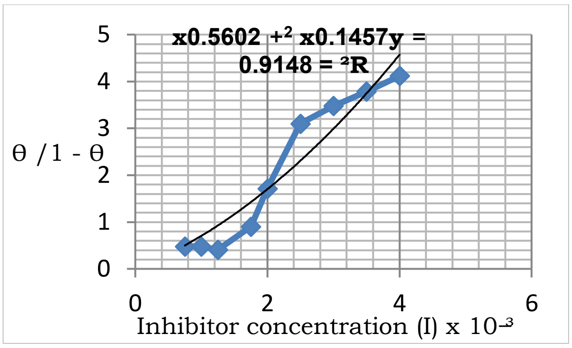

Fig. 4: Langmuir Adsorption Isotherm Methyl Carbozodithoate Inhibitor on Low Carbon Steel in "2 M H_2SO_4"

The value of the correlation " R^2 " isused to determine the best fit isotherm which was obtained for Langmuir. If the value of " R^2" is very close to unity, that is indicated the strong adherence to Langmuir adsorption isotherm. Figure (4) shows a plot of (θ / 1-θ) versus the inhibitor concentration (I) yield a straight line with correlation value " $R^2 = 0.9148$ ". The plot obeys Langmuir adsorption isotherm as the plot has linearity and good correlation coefficient. The" R^2 " value isvery close to unity, indicating strong adherence to Langmuir adsorption isotherm.

The value of adsorption constant " K " at each inhibitor concentration were calculate using equation (4.3). The obtained dataof " K " were relatively high, this another indication that the inhibitor adsorption on the surface of metal obey to Longmair isotherm adsorption model.

In order to calculate the energy of adsorption (ΔG_{ads}), the following equation is used; K $= \frac{1}{55.5} \cdot e^{-\left(\frac{\Delta G_{ads}}{RT}\right)}$ (5)

Where, " R " is the universal constant " 8.314 $\frac{J}{mol.K}$" and" T" is the absolute temperature of " 30 ℃ " and the constant value of " 55.5 " is the concentration of water in solution in" mol/L". The energy adsorption(ΔG_{ads}), values werecalculated using the last formula as listed in table (4).

According to the obtained values of " ΔG_{ads} " , we observed that the all values have a negative sign, thisindicated thatthe spontaneous adsorption of inhibitor on the surface of low carbon steel material (indicates the occurrence of exothermic process). The negative value of " ΔG_{ads} " also suggest the strong interaction ofinhibitor molecules withthe lowcarbon steel surface.

The Temkin model of isotherm adsorption has been chosen secondly to evaluate the adsorption potential of the adsorbent and adsorbed solution. This isotherm contains a factor which explicitly takes into account the interactions of ions of the aqueous solution and the membrane (adsorbent-adsorbate).

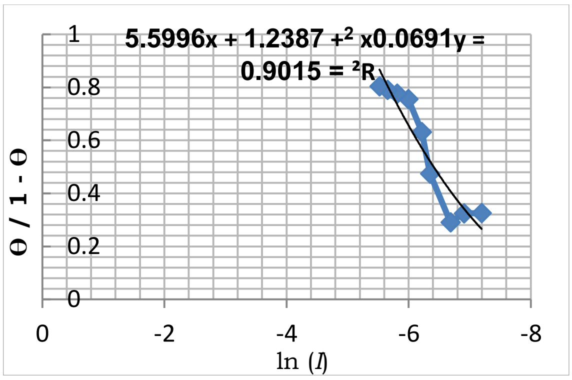

Fig. 5: Tamkin Adsorption Isotherm Methyl Carbozodithoate Inhibitor on Low Carbon Steel in "2 M H_2SO_4"

Figure (5) shows a plot of " (θ / 1-θ) " versus the natural logarithm of inhibitor concentration " ln(I). According to Temkin equation:

$$\frac{\theta}{1-\theta} = 2\,a\,\theta + \ln K\,[I] \qquad (6)$$

According to the equation related to the figure, the value of intercept " a " was found "5.5996 ", this value can be used to calculate the value of adsorption constant " K ", and was found to be " 270 " . The value of " K " was relatively high and this indicated that the there is a good interaction between the inhibitor molecules and the surface of the metal. The inhibitor adsorption on the surface of metal obey to Temkin isotherm adsorption model.

The action of organic inhibitors depends on the type of interactions between the substance and the metallic surface. The interactions can bring about a change either in electrochemical mechanism or in the surface available for the processes [20].

Inhibition of corrosion of low carbon steels in " 2.0 MH_2SO_2 " at a temperature 30 °C can be explained on the basis of adsorption. The methyl carbozodithoate inhibit the corrosion by controlling both the anodic and cathodic reactions. In sulphuric acid solution this compound exists as protonated species. These protonated species may be absorbed on the cathodic sites of the low carbon steel and decreases the evaluation of hydrogen. The better inhibition efficiency in "2.0 MH_2SO_2" attributed to the difference of adsorption of sulphate ions. The low adsorption of sulphat ions on the metal surface permits more space for the adsorption of inhibitor molecules and enhance the inhibition of corrosion [21].

Conclusions

The study of effect of methyl carbazodithoate " an organic sulphur containing compound " on the corrosion of low carbon steels " 0.32 % C " steel in " 2.0 M H_2SO_4 " at a temperature 30 °C, conducted by weight loss method may draw the following conclusions:

1. The methyl carbazodithoate was considered as an efficient inhibitor for corrosion of low carbon steels in " 2.0 M H_2SO_4 " at a temperature 30 °C, the inhibition efficiency increases with increasing of inhibitor concentration to attain a maximum value " 80.47 % " at 4x10⁻³ M methyl carbazodithoate.

2. The obtained values of inhibition efficiencies show the validity of the results.
3. Adsorption methyl carbozodithoate based inhibitor on the low carbon steels in the 2.0 M H_2SO_4 more obeyed to Longmuir adsorption isotherms.
4. According to the binding constant K values, it is concluded that, the interaction between the inhibitor molecules and the metal surface is improved.
5. The negative value of thermodynamic parameter " " suggest the strong interaction of inhibitor molecules with the low carbon steel surface.
6. According to the correlation vales (R^2) obtained by from Lngmir and Temkin isotherms (0.9148) and (0.9015) respectively, the methyl carbozodithoate sulphur containing compound obeyed to the both isotherms, which indicates that the used inhibitor used good adsorption to the surface carbon steel material.

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