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 ompound namely " Methyl Carbazodithoate " has been studied at temperature 30 ℃ by weight loss technique. Adsorption isotherms were tested for their relevance to describe the adsorption behavior 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, Inhibitor efficiency.

Introduction

Organic corrosion inhibitors are an attractive field of research, due to their usefulness in various industries. Organic molecules can form a barrier through adsorption on the metal surface to reduce the corrosion of metal in acidic solution[1]. Acid solutions are generally used for the removal of rust and scale in several industrial processes. Sulphuric acid is often used as a pickling acid for steel and its alloys [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 [4]: 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. Inhibitors are generally used in these processes to control metal dissolution. Acid

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inhibitors are essentially used in metal finishing industries, acidizing of oil wells, cleaning of boilers and heat exchangers [5].

Corrosion of metals is a serious environmental problem that has been given adequate attention in the oil and gas industries because, during industrial processes such as acid cleaning and etching, metal surfaces are often made to come in contact with acidic medium, indicating that the use of inhibitors is necessary [6]. Although there are numerous options for controlling the corrosion of metals, the use of inhibitors is one of the best methods for protecting metals against corrosion.

Steel is the most important engineering and construction material in the world. It is used in every aspect of our lives (automotive manufactures, construction products, steel toecaps, protective footwear, refrigerators, washing machines, cargo ships and so on) [7] .

Oxidation occurs at anodic site and reduction occurs at cathodic site. In acidic medium, hydrogen evolution reaction predominates. Corrosion inhibitors reduce or prevent these reactions; they are adsorbed onto the metal surface and act by a forming barrier to oxygen and moisture, and some of the inhibitors facilitate the formation of a passive film on the metal surface. Several works have studied the influence of organic compounds containing nitrogen on the corrosion of steel in acidic media [8-11]. Most organic inhibitors act by adsorption on the metal surfaces [4].

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 " 60, 100, 120, 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

C	Si	Mn	P	S	Cr	Ni	Cu	Al
0.32%	0.75%	0.014%	0.004%	0.014%	0.002%	0.001%	0.001%	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 distilled 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 both inhibitor solution temperature 30 °C.

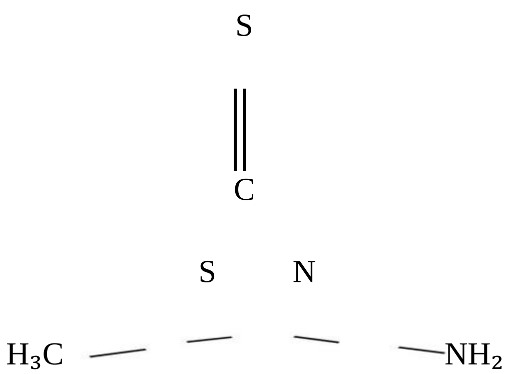

Figure 2: Formula Structure of Used Organic Inhibitor [13]

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:

$$Wt= (W_\circ - Wi / A) \qquad (1)$$

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

$$IE\% = (W_\circ - Wi / W_\circ) \times 100 \qquad (3)$$

where is $W_\circ$ is the original weight (mg) and Wi the weight after immersion in the test electrolyte, t the immersion time (min), and R'_{ORR} and R_{CORR} are the corrosion rates with and without an inhibitor, respectively.

Results and Discussion

The Inhibitor Efficiency (IE %) was found as shown in table 2.

Table 2: Area of Specimens and Inhibitor Concentration of the Research

S. No.	S. Area cm²	Expos. Time min	Inhibitor Concentration (I)
1	7.58	99	Blank
2	7.94	99	$7.50x10^{-4}$
3	8.40	99	$1.00x10^{-3}$
4	7.90	99	$1.25x10^{-3}$
5	7.64	99	$1.75x10^{-3}$
6	7.67	99	$2.00x10^{-3}$
7	8.32	99	$2.50x10^{-3}$
8	8.12	99	$3.00x10^{-3}$
9	8.11	99	$3.50x10^{-3}$
10	8.12	99	$4.00x10^{-3}$

Table 3: Weight Loss and Corrosion Rate Calculations

S.NO	Weight Loss mg	CR mg cm^{-2} min^{-1}	Inhib.Efficiency IE %
1	80.40	0.11785	0
2	54.20	0.07585	32.59
3	54.30	0.07183	32.46
4	56.96	0.08011	29.15
5	42.20	0.06137	47.51
6	29.60	0.04288	63.18
7	19.60	0.02618	75.62
8	17.80	0.02436	77.86
9	16.80	0.02302	79.10
10	15.70	0.02148	80.47

According to the data in previous table it's clear that the corrosion rate decreases gradually with increasing the inhibitor concentration at a temperature 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 increase progressively with increase in concentration of the added inhibitor as shown on table (3). Maximum inhibition efficiency of the compound at was 80.47 % which achieved at concentration 4.00x10^{-3} M, According to results a "*Methyl Carbazodithioate*" inhibitor given acceptable level of inhibition efficiency against low carbons steel corrosion in acid solution, at both used of inhibitor temperatures.

Table 4: ***Logarithm Inhibitor Concentration***

S. No.	Inhibitor Concentra. (I) M	log (I) M	Inhib. Coverage Area (θ)
1	Blank	0.000	0
2	7.50x10^{-4}	- 3.125	0.3259
3	1.00x10^{-3}	- 3.000	0.3246
4	1.25x10^{-3}	- 2.903	0.2915
	1.75x10^{-3}	- 2.757	0.4751

5			
6	2.00×10^{-3}	- 2.699	0.6318
7	2.50×10^{-3}	- 2.602	0.7562
8	3.00×10^{-3}	- 2.523	0.7786
9	3.50×10^{-3}	- 2.456	0.7910
10	4.00×10^{-3}	- 2.398	0.8047

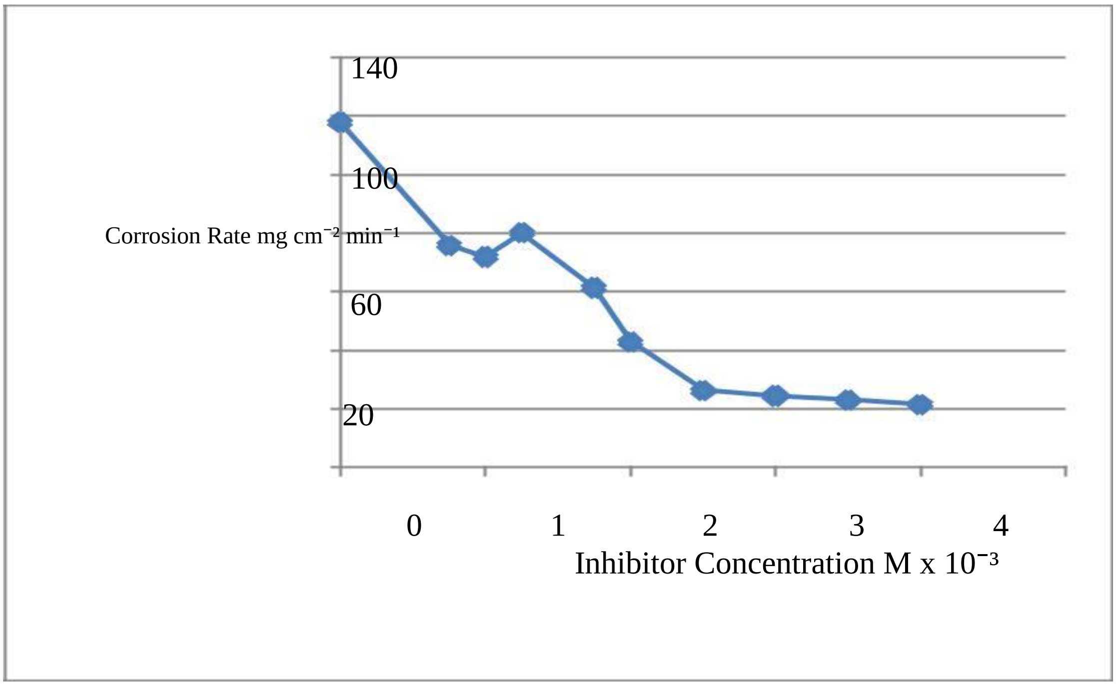

Figure 3: Corrosion Rate Related to Inhibitor Concentration

As shown on Fig.3, the increasing in inhibitor concentration causes decreasing in corrosion rate in the both temperatures, 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 ability degree and of inhibition depends on the concentration of the sulphur containing inhibitor. compound.

Fig. (3) shows the variation of weight loss as a function of the inhibition of low carbon steels corrosion 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 ability degree and of inhibition depends on the concentration of the sulphur containing inhibitor. compound. Effect of inhibitor concentration gives the best corrosion inhibition when the concentration of inhibitor is exceeding to 2.00 x 10^{-3} M.

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 [12].

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 [13].

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.

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