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The effect of organic based inhibitor on inhibiting the mild steel corrosion in Citric acid medium

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ABSTRACT

Formazan of benzaldehyde (FB) has been prepared as a corrosion inhibitor to control the rate of corrosion. This compound has been investigated as corrosion inhibitor at room temperature for preventing mild steel corrosion in Citric acid mediums by weight loss method and by adsorption isotherm. The result showed that the corrosion inhibition efficiency of these compounds was found to vary with different acid concentration. Also, it was found that the corrosion inhibition behavior of FB is greater in 1M Citric acid and 2M Citric acid. But when it has been compared the results revealed that the inhibitor efficiency is better in 1M Citric acid than 2M Citric acid. So FB can be used has a good inhibitor for preventing mild steel material. The surface analysis study also confirms that the corrosion of the mild steel and its inhibition efficiency by the inhibitor FB.

Introduction

Mild steel is widely used in many applications; the intensified the research in corrosion resistance in various aggressive environments [1-3]. It is very often that several problems arise from some industries; several researchers devoted their attention to develop more effective and non-toxic inhibitors to reduce both acid attack and protection aspects [4-9]. Amongst the various methods available, the use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media [10-15]. The use of organic compounds based corrosion inhibitors against metal dissolution is often associated with chemical and/ or physical adsorption, involving a variation in the charge of adsorbed substance and a transfer of charge from one phase to other. Special attention was paid to the effect of electron donating on the atom, electron withdrawing or groups responsible for adsorption mainly depends on steric factors, aromaticity, the structural properties of the organic compounds studied such as the presence of π-electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the surface of mild steel [16-18] .Therefore, in this investigation, the corrosion inhibition of mild steel in 1M Citric acid and 2M Citric acid solution is studied in the absence and presence of Formazan of benzaldehyde (FB) at two hour at room temperature.

Experimental

Specimen Preparation

According to ASTM method as reported already [19], cold rolled mild steel strips were cut into pieces of 5 cm × 1 cm having the following composition (in percentage) % C=0.017; Si=0.007; Mn=0.196; S=0.014; P=0.009; Ni=0.013; Mo=0.015; Cr=0.043 and Fe=99.686 was used. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with various grades of SiC abrasive papers (from grits 120 to 1200) and degreased using Acetone.

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Preparation of Solutions:

All the solutions were prepared using NICE brand AR grade chemicals in double distilled water and bubbling purified by nitrogen gas for 30 minutes to carry out de-aeration of the electrolytes. 1M and 2M Citric acid solution was prepared by double distilled water. The corrosion inhibitor solution of 0.1% Formazan benzaldehyde was prepared by dissolving 0.1 gms of Formazan benzaldehyde in 100ml of test solution. Various milli molar (mM) concentration solutions of FB were also prepared.

Weight loss measurement:

Mild steel specimens were immersed in 1M and 2M Citric acid for 2 h at room temperature (28 ± 2 ºC) for each inhibitor concentration. Then the specimens were removed, rinsed in double distilled water, acetone and the loss in weight of the specimen were determined. From this the inhibiton efficiency (IE %) was calculated using the formula,

$$IE\,\% = \frac{W_o - W_i}{W_o} \times 100 \quad (1)$$

Where, W_O and W_i (in g) are the values of the weight loss observed of mild steel in the absence and presence of inhibitor respectively.

Scanning Electron Microscope (SEM analysis):

The mild steel specimens were immersed in the blank (1M Citric acid and 2M Citric acid) containing the inhibitor Formazan of benzaldehyde (FB) for 2 h after which they were taken out, washed with distilled water and then the specimens was observed under Scanning Electron Microscope (SEM-HITACHI S3000H, Japan).

FT-IR Studies:

The corrosion products formed on the steel surface during weight loss measurement was removed by scrapping and was used for recording FT-IR spectra. This study reveals the possibility of the adsorption of the inhibitor on the metal surface. The Fourier transform infrared (FT-IR) spectra of the scraped films were recorded using a (Perkin Elmer-1400) FT-IR spectrophotometer.

Result and Discussion

Weight loss method

The comparison graph of corrosion behaviour and inhibitor efficiency of mild steel in 1M and 2M Citric acid with Formazan of benzaldehyde (FB) was given in Figure1 (a) and (b), which was studied by weight loss method at 2 h at room temperatures. From the graph, it was observed that the weight loss of mild steel in the acid decreases with increasing concentration of additives. The values were tabulated in Table 1. From Table 1, it was clear that the corrosion rate was decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor. In addition, the maximum corrosion inhibition efficiency of FB was 43.88 % at 1M Citric acid and 37.81 % at 2M Citric acid respectively at 36.85 mM concentration of the inhibitor solution at two hour at room temperature.

It was also concluded that the inhibitor was best inhibitor in mild steel corrosion in 1M and 2M Citric acid. But when comparing with both the concentration the inhibitor efficiency was best in 1M Citric acid than 2M. Figure 1(a) revealed the comparison of corrosion rate (CR) with concentration of FB (in %) in 1M and 2M Citric acid solution at two hour at room temperature. Comparison of inhibition efficiency (IE) with concentration of (FB) (in %) in 1M Citric acid and 2M Citric acid solution at two hour at room temperature is shown in Figure 1(b).

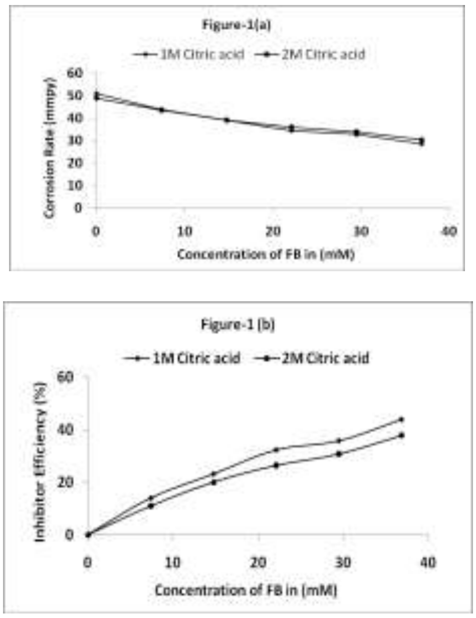

Figure 1- Comparison of corrosion rate and inhibition efficiency with concentration of FB on the corrosion of mild steel in Citric acid media (1M and 2M Citric acid)

Adsorption Isotherm:

Basic information on the interaction between the inhibitor and the mild steel surface can be proved by the adsorption isotherm and in general, inhibitors can function either by physical (electrostatic) adsorption or chemisorption with the metal. To obtain more information about the interaction between the inhibitor molecules and the metal surface, different adsorption isotherms were tested. The fractional surface coverage θ at different concentrations of inhibitors 1M and 2M Citric acid solutions were determined from the weight loss measurements data [20] using the formula,

$$(\theta) = \frac{Wo - Wi}{Wo} \qquad (2)$$

where, Wo and Wi are the values of weight loss of uninhibited and inhibited specimens, respectively.

$$Kc = \frac{\theta}{1-\theta} \quad \text{-------------} \qquad (3)$$

where, c is the concentration of the inhibitor, θ is the fractional surface coverage. The Langmuir isotherm, Eq. (5.2), which is based on the assumption that all adsorption sites are equivalent and that molecular binding, occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied inhibitors. The adsorption equilibrium constant *K* is related to the free energy of adsorption ΔG_{ads} as,

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \text{--------} \quad (5.3)$$

where, $C_{solvent}$ represents the molar concentration of the solvent, which in the case of water is 55.5 mol dm^{-3}, R is the gas constant and T is the thermodynamic temperature in K. The Langmuir isotherm, Eq. (5.4), can be rearranged to obtain the following expression,

$$\frac{c}{\theta} = \frac{1}{K} + c \quad \text{-----------------------} \qquad (5.4)$$

so that a linear-relationship can be obtained on plotting c/θ as a function of c, with a slope of unity. The thermodynamic parameters K and ΔG_{ads} for the adsorption of the studied inhibitors on mild steel is obtained by Langmuir's adsorption isotherm are plotted in Figure 2 and the obtained values are given in Table 2. It was found that the linear correlation coefficients clearly prove that the adsorption of the FB from 1M and 2M Citric acid solutions on the mild steel corrosion obeys the Langmuir adsorption isotherm. The negative values of ΔG^0_{ads} for the addition of inhibitors indicate that the process of adsorption of studied inhibitors is spontaneous in nature [21]. The free energy of adsorption of (ΔG_{ads}), in 1M Citric acid was found to be -6.786 $kJmol^{-1}$while for 2M Citric acid it was found to be -5.227 $kJmol^{-1}$ respectively. It is well known that the values of ΔG_{ads} in the order of −20 kJ mol^{-1} or lower indicate a physisorption while those about −40 kJ mol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [22].

The calculated adsorption values for all the studied inhibitor show that the adsorption is of physical in nature, and there is no chemisorption between the inhibitor molecule and the metal surface. This indicates that the adsorption of FB at 2 h takes place through electrostatic interaction between the inhibitor molecule and the metal surface. Hence it indicates that the interaction between the inhibitor molecule and metal surface is physisorption.

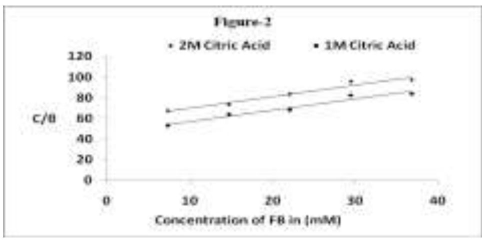

Figure 2- Langmuir isotherm for adsorption of FB on mild steel surface studied at two different acid concentrations (1M and 2M Citric acid)

SEM Analysis:

The polished mild steel specimens were immersed in the acid solution (1M Citric acid and 2M Citric acid) and the acids containing inhibitor FB for the period of 2 h, and then the specimens were taken out, dried and observed under Scanning Electron Microscope (SEM). The micrograph are shown in the Figure 3 & 4 shows polished specimen which was kept in the blank solution of 1M and 2M Citric acid, which is associated with polishing scratches. Figure 5 & 6 shows specimen which was kept in the 36.85 mM concentration of inhibitor solution with 1M and 2M Citric acid depends upon the concentration of the inhibitor solution suggesting that the presence of adsorbed layer of the inhibitor on mild steel surface which impedes corrosion rate of metal appreciably.

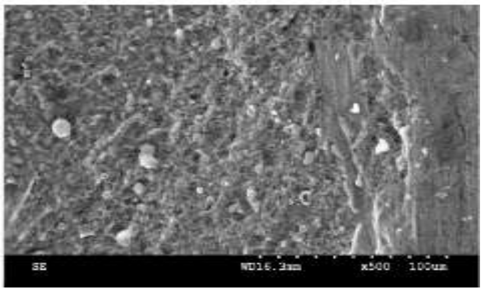

Figure 3 SEM images obtained for the mild steel surfaces immersed for 2 h in 1M Citric acid (blank acid solution)

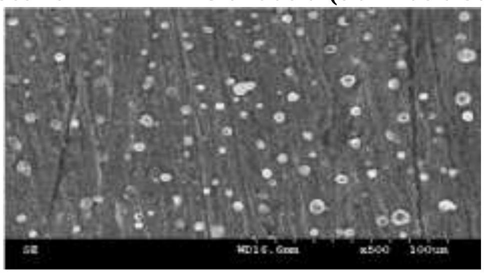

Figure 4 SEM images obtained for the mild steel surfaces immersed for 2 h in 2M Citric acid (blank acid solution)

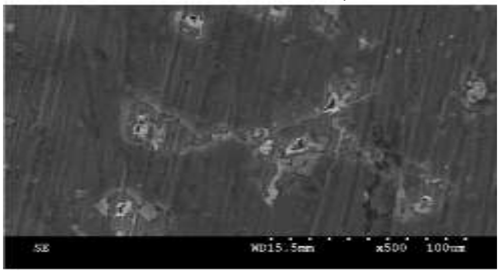

Figure 5 SEM images obtained for the mild steel surfaces immersed for 2 h in 1M Citric acid with 36.85mM inhibitor solution

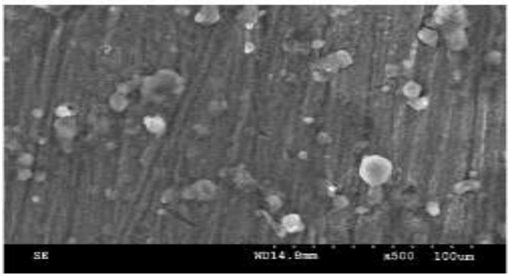

Figure 6 SEM images obtained for the mild steel surfaces immersed for 2 h in 2M Citric acid with 36.85 mM inhibitor solution

FT-IR Studies:

The FT-IR analyses of metal surface (scraped corrosion product) can be useful for predicting whether organic inhibitors are adsorbed or not adsorbed on the metal surface [23]. Therefore, FT-IR spectra were used to support the fact that corrosion inhibition of mild steel in acid medium is due to the adsorption of inhibitor molecules on the mild steel surface as well as providing new bonding information on the steel surface after immersion in H_2SO_4 solution containing inhibitor. Figure 7.1(a) shows the FT-IR spectrum of the Formazan of benzaldehyde. In this spectrum the peak appeared at 3204cm^{-1} corresponds to amide N-H stretching, 1571 cm^{-1} corresponds to C=0 group overlapping with –NH deformation bending, 1412 cm^{-1} corresponds to C-C stretching and 1012 cm^{-1} corresponds C-H in-plane bending. Figure 7.1 (b) is similar to Figure 7.1 (a) which indicates that the scarped corrosion product contains Formazan of benzaldehyde. Moreover, there is no additional peak observed in the spectrum. Therefore from these spectra it is reveled that the inhibition is due to the physical adsorption occurred on the surface of the metal. This is already confirmed from the Langmuir adsorption isotherm studies.

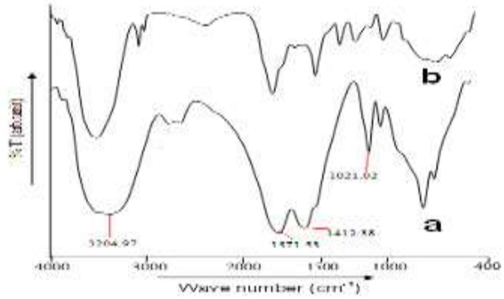

Figure 7.1 IR spectrum of the corrosion product showing adsorption in the presence of aqueous extract of Formazan of benzaldehyde

Conclusions:

The present study leads to the following conclusion in controlling the corrosion of mild steel by Formazan of benzaldehyde in 1M and 2M Citric acid.

1. Formazan of benzaldehyde was found to be effective inhibitor in the acidic medium giving inhibition efficiency upto 43.88 % in 1M Citric acid and 37.81 % in 2M Citric acid respectively.
2. The inhibition efficiency increased with increase in concentration of inhibitors from 7.37 mM to 36.85 mM.
3. From the comparative studies of weight loss method, it was concluded that the inhibitor efficiency is better in 1M Citric acid than 2M.
4. The adsorption of the compound investigated follows the Langmuir isotherm and the adsorption is physical in nature.
5. The FT-IR results also reveal the adsorption of inhibitor molecule on the metal surface and blocking the active sites.

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Table 1:Corrosion parameters in absence and presence of Formazan of benzaldehyde (FB) with 1M and 2M Citric acid

Inhibitor	Conc. of inhibitor (mM)	Corrosion Rate (mm/y)		Inhibitor Efficiency (%)	
		1M Citric acid	2M Citric acid	1M Citric acid	2M Citric acid
Formazan of benzaldehyde (FB)	Blank	51.0442	48.9267	---	---
	7.37	43.9114	43.5770	13.97	10.93
	14.74	39.2305	39.1190	23.14	20.04
	22.11	34.5496	35.9984	32.31	26.42
	29.48	32.7664	33.8809	35.80	30.75
	36.85	28.6427	30.4259	43.88	37.81

Table 2: Thermodynamic parameters for the adsorption of FB in Citric acid (1M and 2M Citric acid) on the corrosion of mild steel

Name of the Acid	Concentration in (mM)	Surface coverage (θ)	ΔG_{ads} KJ / mol^{-1}	K x (10^{-2} M^{-1})
1M Citric acid	36.85	0.4388	-6.786	1.80
2M Citric acid	36.85	0.3781	-5.277	1.80