

Study of the Influence of Amorphous Tricalcium Phosphate on Corrosion Inhibition of Mild Steel in Hydrochloric Acidic Medium 1M

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ABSTRACT

In this study, the inhibition effect of amorphous tricalcium phosphate (TCPam) on mild steel corrosion in 1.0M HCl solution was studied. For this aim, electrochemical techniques such as potentiodynamic polarization curves, weight loss (WL) and electrochemical impedance spectroscopy (EIS) were used. It was shown that, the amorphous tricalcium phosphate (TCPam) acts as a good inhibitor for mild steel corrosion in 1 M HCl solution. Its inhibition efficiency increased with concentration and reaches 87 % at 5×10^{-6} M, and decreased with temperature and immersion time. Polarization measurements indicated that TCPam acts as mixed type inhibitor. In addition, Mechanism of physical adsorption is proposed from the apparent activation energy (E_a).

Keywords : Amorphous Tricalcium Phosphate ;TCPam; Corrosion and Inhibition; Acidic medium, EIS

1 INTRODUCTION

IRON and its alloys find utility in a wide spread spectrum of many industrial units because of its low-cost and excellent mechanical properties. For this reason, the corrosion behavior of these materials has attracted the attention of several investigations. The mild steel has many industrial applications because of its easy availability, uncomplicated fabrication of it into water pipe lines [1- 2], cooling water systems [3], boilers etc. However, they are susceptible to different forms of corrosion induced by chloride and so on. Steel is the most corrosion vulnerable metal. Thus, much attention is given for its protection from the hostile environments. Acid solutions are widely used in industry. The most important areas of application are acid pickling, industrial acid cleaning, acid descaling, and oil-well acidizing[4-9]. HCl solution is one of the most widely used agents for these goals. However, iron and its alloys could be corroded during these applications which result in a waste of resources. Corrosion prevention systems favor the use of chemicals with low or no environmental impacts. The reduction in the corrosion rate of metals has numerous advantages such as saving of resources, economic benefits during the industrial applications, increasing the lifetime of equipment and decreasing the dissolution of toxic metals from the components into the environment. Therefore, inhibitors are commonly used to minimize metal dissolution and acid consumption. Various types of organic compounds are widely used as corrosion inhibitors for protection materials against corrosion deterioration [10]. A perusal of the literature on acid corrosion inhibitors reveals that most organic substance employed as corrosion inhibitors act by adsorption on the metal surface. Most of the efficient inhibitors used in industry are

organic compounds which mainly contain oxygen, sulphur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on metal surface [11-19]. In recent years, the mineral inhibitors have attracted more attention for their excellent corrosion inhibition performance. These products dissociate in solution and it is their dissociation products that ensure the phenomena of inhibition.

The aim of this study is to investigate the inhibition effect of amorphous tricalcium phosphate (TCPam) on the mild steel corrosion in 1.0 M HCl solution using weight loss and electrochemical measurements.

2 EXPERIMENTAL DETAILS

2.1 Materials

The steel used in this study is a mild steel (MS) with a chemical composition (in wt%) of 0.21 % C, 0.38 % Si, 0.05% Mn, 0.05 % S, 0.09 % P, 0.01 % Al and the remainder iron (Fe). For weight loss tests, the rectangular coupons with the size of 3,7 cm × 1 cm × 0.2 cm were used. A columned mild steel specimen, embedded in Teflon holder using epoxy resin with an exposed area of 1 cm², was used as the working electrode for electrochemical measurements. The coupons and electrodes were abraded with emery paper (up to 1200 grit), cleaned with acetone and washed with distilled water, and finally dried at hot air before being immersed in the acid solution. The aggressive solution (1 M HCl), used as blank, was prepared by dilution of analytical grade 37%. The concentrations of inhibitor were ranged from 10^{-6} to 10^{-4} M. The inhibitor used was an amorphous tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) n

H₂O), denoted (TCPam), which its structure is shown in Figure 1.

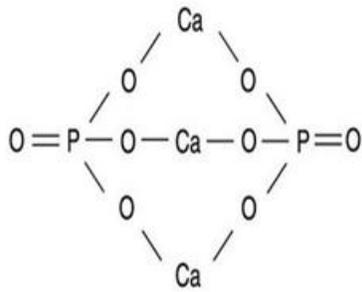


Fig 1. Chemical structure of amorphous tricalcium phosphate

2.2 Electrochemical measurements

A saturated calomel electrode (SCE) was used as a reference electrode and all potentials were given with it. The counter electrode was a platinum plate of large surface area. The electrodes were carefully positioned in the cell for reproducible geometry. In addition, the working electrode was immersed in the test solution during half an hour until a steady state open circuit potential (E_{ocp}) was obtained. The steady-state polarization curves were recorded potentiodynamically using a VoltaLab PGZ 100 and controlled by a personal computer. The cathodic polarization curve was recorded by polarization from E_{ocp} to negative direction under potentiodynamic conditions corresponding to 1 mV s^{-1} (sweep rate) and under air atmosphere. After this scan, the anodic polarization curve was recorded by polarization from E_{ocp} to positive direction under the same conditions as said before. To evaluate corrosion kinetic parameters, a fitting by Stern-Geary equation was used. To do so, the overall current density values, i , were considered as the sum of two contributions, anodic and cathodic current i_a and i_c , respectively. For the potential domain not too far from the open circuit potential, it may be considered that both processes followed the Tafel law [20]. Thus, it can be derived from equation (1):

$$i = i_a + i_c = i_{corr} \left\{ \exp[b_a \times (E - E_{corr})] - \exp[b_c \times (E - E_{corr})] \right\} \quad (1)$$

where i_{corr} is the corrosion current density (A cm^{-2}), b_a and b_c are the Tafel constants of anodic and cathodic reactions (V^{-1}), respectively. These constants are linked to the Tafel slopes β (V/dec) in usual logarithmic scale given by equation (2):

$$\beta = \frac{\ln 10}{b} = \frac{2.303}{b} \quad (2)$$

The corrosion parameters were then evaluated by means of nonlinear least square method by applying equation (2) using Origin software. However, for this calculation, the potential range applied was limited to $\pm 0.100\text{V}$ around E_{corr} , else a significant systematic divergence was sometimes observed for both anodic and cathodic branches. The corrosion inhibition

efficiency is evaluated from the corrosion current densities values using the relationship (3):

$$\eta_{PP} = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad (3)$$

where i_{corr}^0 and i_{corr} are the corrosion current densities values without and with inhibitor, respectively.

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyzer (VoltaLab PGZ 100), with a small amplitude a.c. signal (10 mV rms), over a frequency domain from 100 kHz to 100 mHz with five points per decade. The EIS diagrams were done in the Nyquist representation. The results were then analyzed in terms of an equivalent electrical circuit using Bouckamp program [21]. The inhibiting efficiency derived from EIS, η_{EIS} is also added in Table 3 and calculated using the following equation (4):

$$\eta_{EIS} = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (4)$$

where R_{ct}^0 and R_{ct} are the charge transfer resistance values in the absence and in the presence of inhibitor, respectively.

2.3. Weight loss measurements

Weight loss measurements were carried out in glass beakers containing 100 mL solution without and with different concentrations of inhibitor in 1 M HCl solutions. The temperature of the solutions was controlled by a thermostat water bath. After 2 h of immersion in the acid solutions in air without bubbling, the samples were taken out and were cleaned carefully according to ASTM G-81 [22] and reweighed for determining corrosion rate applying the following equation 5:

$$\omega_{corr} = \frac{m_i - m_f}{S.t} \quad (5)$$

where m_i , m_f , S and t denote initial weight, final weight, surface of specimen and immersion time, respectively. The inhibition efficiency $\eta_{wl} \%$ derived from this method was estimated by the following relation 4:

$$\eta_{wl} \% = \frac{\omega_0 - \omega}{\omega_0} \quad (6)$$

where ω_0 and ω are the corrosion rate of steel without and with each inhibitor, respectively.

3. RESULTS AND DISCUSSIONS

3.1 Potentiodynamic Polarization Curves

Figure 1 illustrates the potentiodynamic polarization

curves of mild steel in 1 M HCl solution without and with various concentrations of TCPam at 298 K. Electrochemical parameters extracted from this curves are given in Table 1. It can be noted that the TCPam bring down the current densities (i_{corr}) value at all concentrations suggesting that this compound is effective corrosion inhibitor. Moreover, it can be also seen that the inhibitor doesn't have an effect on the E_{corr} . These results indicate that this compound act as a mixed-type inhibitor. In addition, it is noted that the cathodic Tafel slopes change with the inhibitor concentration indicating a change in evolution hydrogen. So, the inhibition efficiency increases with increase in inhibitor concentration reaching a maximum of 87 % at 5×10^{-6} M.

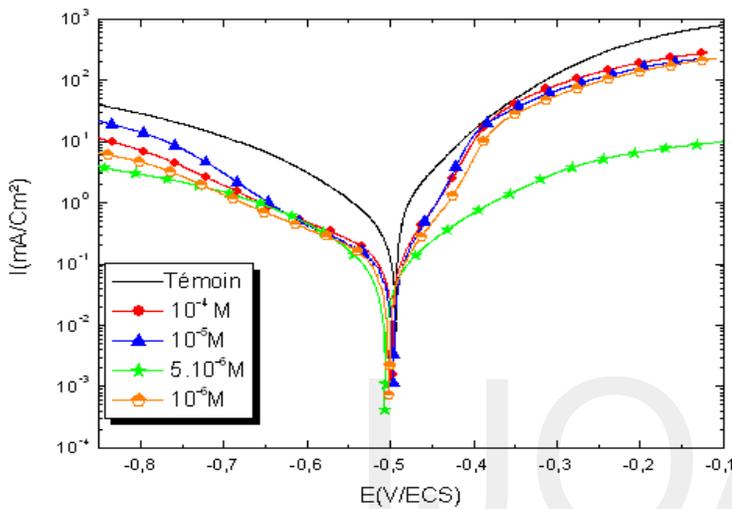


Fig 2: Potentiodynamic polarization curves of mild steel in 1M HCl contain ing different concentration of TCPam.

TABLE 1

ELECTROCHEMICAL PARAMETERS OBTAINED FOR MILD STEEL IN 1M HCLAT THE PRESENCE OF DIFFERENT CONCENTRATIONS OF TCPAM

C (M)	E_{corr} (mV/SCE)	i_{corr} (μ A cm ⁻²)	β_c (mV dec ⁻¹)	β_a (mV dec ⁻¹)	η_{pp} %
00	-495	470	200	4	-
10^{-4}	-489	96	155	3.7	80
10^{-5}	-491	72	136	3.1	85
5×10^{-6}	-498	60	93	3.8	87
10^{-6}	-496	85	157	3.3	82

3.2. Electrochemical Impedance Spectroscopy (EIS) measurements

Electrochemical impedance spectroscopy (EIS) is an effective method for corrosion studies of metallic materials. The effect of TCPam concentration on the impedance spectra of mild steel in 1.0 M HCl solutions at 298 K is recorded in Fig 3 (Nyquist plots). The impedance diagrams show only one capacitive loop represented by slightly depressed semicircle which indicates that the corrosion of mild steel in 1.0 M HCl solution is mainly controlled by charge transfer process and

formation of a protective layer on the mild steel surface. Therefore, a constant phase element CPE is used to replace a capacitive element to acquire a more accurate fit of experimental data. Fig. 4 displays the equivalent circuit, which consists of a solution resistance R_s , the constant phase element CPE and the charge transfer resistance R_{ct} . The impedance of CPE is described as the mathematical expression given below [23].

$$Z_{CPE} = \frac{1}{Y_0} \times \frac{1}{(j\omega)^n} \tag{7}$$

Where Y_0 is the magnitude of the CPE, j is the imaginary unit, ω is the angular frequency and n is the phase shift.

The fitted impedance parameters derived from Nyquist diagrams and inhibition efficiency are listed in Table 2. Data in Table 3 shows that additional TCPam inhibits the corrosion of mild steel in 1.0 M HCl solution. By increasing the inhibitor concentration R_{ct} values and inhibition efficiency increase. The increase in the charge transfer resistance values with increasing inhibitor concentration suggests the formation of a protective layer on the mild steel electrode surface. This protective layer behaves as a hindrance for mass and charge transfer [24.]

The kinetic parameters derived from the Nyquist plots and percentage inhibition efficiency are given in Table 2. It is clear to see that the impedance spectra are significantly changed with addition of different TCPam concentration, it was also observed that the TCPam does not alter the style of impedance plots, thus indicating the addition of TCPam does not change the mechanism for the dissolution of mild steel in 1.0 M HCl solution[25,26] The diameter of the capacitive loop increases with the increase of TCPam concentration proposing that the formed inhibitive film was strengthened by the addition of TCPam [27].

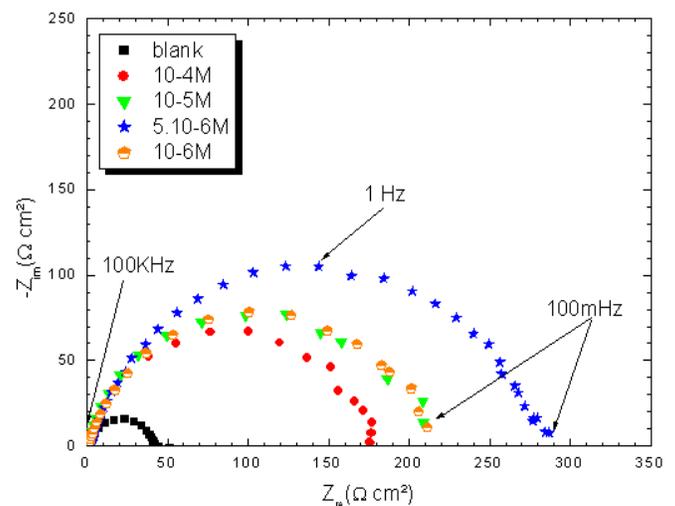


Fig 3. Nyquist diagrams plots for mild steel in 1 M HCl containing different concentrations of TCPam at the corrosion potential (T=308 K)

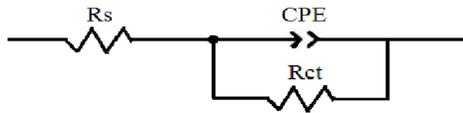


Fig 4. The electrochemical equivalent circuit used to fit the impedance measurements

TABLE 3

CORROSION PARAMETERS OBTAINED FROM IMPEDANCE MEASUREMENTS FOR MILD STEEL IN 1 M HCL IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF TCPAM.

C (M)	R_{ct} ($\Omega \text{ cm}^2$)	C_{ct} ($\mu\text{F cm}^{-2}$)	$\eta_{EIS}\%$
00	40	295	-
10^{-4}	184	173	78
10^{-5}	216	123	82
5×10^{-6}	290	66	86
10^{-6}	232	95	83

3.3 Immersion Time

Figure 5 shows the impedance spectra at different immersion time in 1.0 M HCl containing 5.10^{-6} M of TCPam. It is marked that these diagrams exhibit one capacitive loop. It is also note that the increasing of immersion time affects the diameter loops. It is clear from the figure 5 that the increase in the immersion time affects on the inhibition efficiency. These results indicate that this compound physic-sorbed at the metallic surface.

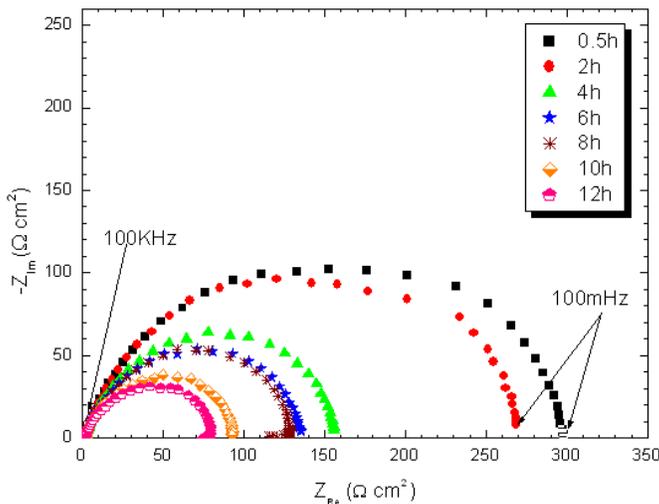


Fig 5: Nyquist diagrams plots for mild steel in 1 M HCl containing different concentrations of TCPam at the corrosion potential (T=298 K)

3.4. Effect of temperature

Temperature, as is well known, can modify the interaction between the mild steel electrode surface and the acidic media without and with inhibitors. Influence of temperature on the inhibition efficiency of TCPam was investigated by weight loss measurements. The results are given in table 3. From Copyright © 2014 SciResPub.

these results, we can deduce that the corrosion rate increases in the blank with the rise of temperature, but in the presence of 5.10^{-6} M of TCPam, the dissolution of mild steel is widely retarded. The values of inhibition efficiency obtained from the weight loss measurements at various temperatures show that the inhibition efficiency decreases with increasing temperature suggesting that the adsorption mechanism of TCPam on metallic surface is physical adsorption. The decrease in inhibition efficiency shows that the film formed on the metal surface is less protective at higher temperatures, since desorption rate of the inhibitor is greater at higher temperatures. However, the corrosion process and protectiveness of an inhibitor are significantly dependent on the temperature. In addition, the activation energy (E_a) for mild steel corrosion in the absence and the presence of 5.10^{-6} M of TCPam was calculated using Arrhenius theory:

$$\omega_{\text{corr}} = K_{\text{ads}} \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

where ω_{corr} is the corrosion rate, T the absolute temperature, R is the universal gas constant and K_{ads} is the Arrhenius pre-exponential factor.

Plots of the logarithm of corrosion rate vs. $1/T$ are given in Fig. 6. The plots obtained are straight lines and the slope of each straight line gives its activation energy E_a . The calculated values of the apparent activation corrosion energy in the absence and presence of 5×10^{-6} M of TCPam are 144,8 and 197,4 kJ. mol^{-1} , respectively. The great value of the activation energy of the process, in presence of inhibitors when compared to that in its absence, is can attributed to the physic sorption of inhibitor on steel surface.

TABLE 3

VARIOUS CORROSION PARAMETERS FOR MILD STEEL IN 1 M HCL IN THE ABSENCE AND PRESENCE OF 5×10^{-6} M OF TCPAM AT DIFFERENT TEMPERATURE.

Inhibitor	Température (K)	ω ($\text{mg cm}^{-2} \text{ h}^{-1}$)	η_{wt} (%)
Blank	298	$3,14.10^{-2}$	-
	308	0.14	-
	318	1.55	-
	328	5.37	-
5×10^{-6} M of TCPam	298	$3,79.10^{-3}$	88
	308	$3,23.10^{-2}$	77
	318	0.587	62
	328	2.67	50

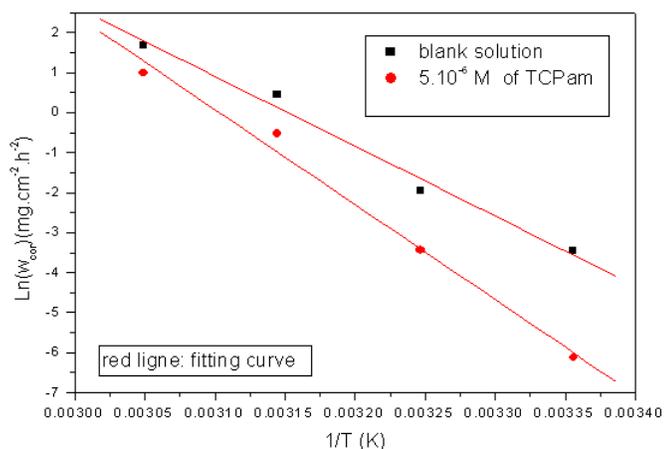


Fig 6: Arrhenius plots calculated from weight loss values for mild steel in 1 M HCl in the absence and presence 5×10^{-6} M of TCPam at different temperature.

4. CONCLUSION

The corrosion inhibition of mild steel in 1 M HCl solution using TCPam was studied using common electrochemical techniques and weight loss measurements. According to experimental findings, it could be concluded that:

1. TCPam is a good corrosion inhibitor for mild steel in 1 M HCl solution and its inhibition efficiency depends on its concentration.
2. TCPam acts by reducing the rates of cathodic and anodic reactions.
3. The high inhibition efficiency of the inhibitor was explained by the physic adsorption of the compound molecules on the mild steel.
4. AC impedance confirms the results obtained by the potentiodynamic polarization curves.
5. The effect of temperature and immersion time on the performance of TCPam on mild steel corrosion indicated that it acts by physic sorption.

ACKNOWLEDGMENT

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