



Acetylacetonate Complexes as New Corrosion Inhibitors in Phosphoric Acid Media: Inhibition and Synergism Study

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ABSTRACT

he corrosion inhibition performance of acetylacetonate complexes of zinc(II), manganese(II), cobalt(II) and copper(II) on the mild steel substrate in $1M H_3PO_4$ was studied using DC polarization. It was seen that the mentioned complexes decreased corrosion rate of mild steel in phosphoric acid media due to the adsorption on metal surface. The potential of mild steel shifted toward more active potentials. The cathodic Tafel slopes increased showing that acetylacetonate complexes are cathodic inhibitors. Presence of chloride ions in the electrolyte enhanced inhibition performance of acetylacetonate complexes due to synergism. Chloride ions provided by HCl had a better performance compared to NaCl. Prog. Color Colorants Coat. 2(2009), 115-122. © Institute for Color Science and Technology.

1. Introduction

Acid pickling process is a common method to remove undesired rust and scale from metal surface. Sulphuric acid, hydrochloric acid, nitric acid and phosphoric acid are used in the acid pickling process [1, 2]. Among inorganic acids, phosphoric acid is used frequently in many industries. It should be noted that phosphoric acid is an aggressive acid solution for the acid pickling, acid cleaning and acid descaling which results in rapid corrosion of the substrate [2].

Using inhibitors is an effective method to reduce corrosion damage of metals [3-6]. One of the mechanisms of inhibition is the adsorption of inhibitors on the metal surface preventing cathodic and anodic reactions [7]. In recent years metal acetylacetonate complexes have become a viable ion-containing precursor for the preparation of supported metal catalysts [8-12]. Applications of acetylacetonate complexes are

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based on good adsorption properties on metallic supports [11-15]. As a result, acetylacetonate complexes can be used as inhibitors due to good adsorption properties on metals.

Synergistic effects describe the increase in the effectiveness of a corrosion inhibitor in the presence of another substance in corrosive media. This phenomenon has been frequently used in practice due to the increasing inhibition efficiency. Some researchers found that positively charged compounds are better corrosion inhibitors of mild steel in hydrochloric acid compared to sulfuric acid [2,4,6]. The possible reason is that there is a synergistic effect between chloride ions of hydrochloric acid and positively charged inhibitors [2]. As a result, in this study chloride ion was added in phosphoric acid media to increase inhibition efficiency of inhibitors. For synergistic evaluation HCl and NaCl as two different sources of chloride ions were studied. HCl and NaCl can be dissociated completely in aqueous solutions and provide chloride ions in electrolyte.

For corrosion inhibition studies different methods including weight loss measurements [16,17], electrochemical AC [18,19] and DC [20,21] methods have been used. These methods almost have a same result. In this study DC polarization was used as a powerful technique to evaluate inhibition performance of inhibitors and calculate corrosion rate of bare metal in different media accurately.

2. Experimental

Phosphoric acid solution was prepared from laboratory grade phosphoric acid detained from Mojalali Company. Four acetylacetonate complexes, hydrochloric acid and sodium chloride salt were prepared from Merck and used without further purification. Inhibition of acetylacetonate complexes was studied in the concentration of 10⁻²M and at temperature of 298K in 1M phosphoric acid as a corrosive media. The synergism was studied in chloride ion concentration of 10⁻¹M. Mild steel sheets (ST37 with 6mm thickness) were obtained from Mobarake Steel Company. Samples were polished with magnetic polisher to remove mill scale of surface and degreased by acetone twice. An area of 1 cm² of samples was exposed to electrolytes whilst other area of plates were sealed with the beeswax-colophony mixture. Each test was carried out twice to ensure repeatability and average data were reported in this article. Each sample was immersed in 75cm³ of prepared electrolytes. DC polarization was carried out using Autolab PG STAT12 with scan rate of 1 mV/s. The reference electrode and counter electrode were silver-silver chloride and platinum, respectively.

3. Results and discussion

3.1. Inhibition study

The DC polarization curves of mild steel in 1M phosphoric acid without and with acetylacetonate complexes in concentration of 0.01M at 298K are presented in Figure 1. This figure shows that acetylacetonate complexes shift corrosion potential toward more negative potentials. The cathodic current versus potential gives rise to Tafel lines indicating that the hydrogen evolution reaction is activation controlled. The calculated parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and inhibition efficiency (E%) are shown in Table 1. Inhibition efficiency is calculated by Eq. 1.

$$(E\%) = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} *100$$
(1)

Where I_{corr} and $I_{corr(inh)}$ are corrosion current densities without and with inhibitors, respectively determined by extrapolation of cathodic and anodic Tafel lines. Table 1 shows that adding of acetylacetonate complexes in 1M H₃PO₄ reduces corrosion rate of mild steel and it could be referred to adsorption of acetylacetonate complexes on the metal surface. Adsorption of acetylacetonate complexes can block anodic areas of mild steel surface resulting in reduction of electrochemical reaction rate. According to Table 1 cathodic Tafel slope increases indicating that acetylacetonate complexes can reduce rate of the cathodic reaction. In acidic media, hydrogen reduction is dominant cathodic reaction.

The decrease of cathodic reaction rate can be referred to the formation of a corrosion protective film on metal surface by inhibitors. Acetylacetonate complexes shifted potential toward more active potentials and increased cathodic Tafel slope showing that acetylacetonate complexes are cathodic inhibitors. On the other hand, inhibitors did not change anodic Tafel slope significantly confirming that inhibitors are cathodic inhibitors.

3.2. Synergism study

To study the synergism effect between inhibitors and

chloride ions on the corrosion of mild steel, NaCl and HCl were added to $1M H_3PO_4$ to provide chloride ions. Figure 2 shows the polarization curves of mild steel in $1M H_3PO_4$ containing chloride ions provided by NaCl and HCl without inhibitor. Table 2 presents electrochemical parameters of mild steel in solution of 1M phosphoric acid containing 0.1M chloride ions.

According to Table 2, adding chloride ions increases corrosion rate of mild steel in phosphoric acid. It can be noted that chloride-containing acidic solutions make an aggressive environment for mild steel and accelerate corrosion rate of mild steel [22].

Figure 3 shows the polarization curves of mild steel in 1M phosphoric acid solution containing both 10^{-2} M acetylacetonate complexes and 10^{-1} M chloride ions. Table 3 presented the calculated corrosion parameters such as E_{corr} , I_{corr} , β_c , inhibition efficiency and synergism index (S) in the presence of chloride ions and inhibitor. Synergism index (S) can be calculated by Eq. 2.

$$S = \frac{v_1 \cdot v_2}{v_{1,2} \cdot v_0}$$
(2)

Where v_1 and v_2 are corrosion rates of solution containing compound 1 and 2, respectively . $v_{1,2}$ is the measured corrosion rate of solution containing mixture of compounds 1 and 2. v_0 is the corrosion rate measured in the inhibitor free solution. In Eq. 2, while for S>1 inhibitors have synergism effect on each other, if S<1 inhibitors have antagonism effect on each other and in the case of S=1 inhibitors have no effect on each other.

According to Table 3, inhibition efficiency increased by adding of chloride ions to solution. Table 3 shows that S>1, indicating that chloride ions have synergistic effect with acetylacetonate complexes in phosphoric acid media. Acetylacetonate complexes are partially positive in acidic media due to protonation. Hence, tendency of acetylacetonate complexes for negatively charged surfaces increases in acidic media. It is well known that chloride ions can bring excess negative charge in the vicinity of interface, and then, positively charged ions adsorb onto the negative surface better than neutral surface [2,4,6]. By considering this fact, chloride ions can be used to make a synergistic effect with acetylacetonate complexes in phosphoric acid media.

According to Table 3 synergism index in the solutions containing HCl is more than solutions containing NaCl and it shows that presence of hydrochloric acid is more effective than sodium chloride salt. It could be explained that Na^+ ions provided by sodium chloride salt are interfering ions in solution and they could neutralize the negative charge of surface and prevent adsorption of inhibitor molecule on metal surface.

	Concentration (M)	E _{corr} (mV/Ag-AgCl)	B _c (mV/dec)	B _a (mV/dec)	I _{corr} (μA/cm ²)	E (%)
Blank	-	-478	345	307	392	-
$Co(acac)_2$	10 ⁻²	-503	553	310	250	36.22
$Zn(acac)_2$	10 ⁻²	-492	469	295	321	18.11
Cu(acac) ₂	10 ⁻²	-612	895	289	196	50.00
$Mn(acac)_2$	10 ⁻²	-557	711	299	222	43.36

Table 1: Electrochemical parameters of mild steel in 1M H₃PO₄ containing different acetylacetonate complexes at 298K.

 Table 2: Electrochemical parameters of mild steel in solution of 1M phosphoric acid containing 0.1M chloride ions at 298K.

	E _{corr} (mV/Ag-AgCl)	I _{corr} (μA/cm ²)
Blank	-478	392
$H_3PO_4 + HCl$	-465	532
H ₃ PO ₄ +NaCl	-478	475

	E _{corr} (mV/Ag-AgC)	B _c (mV/dec)	I _{corr} (μA/cm ²)	E (%)	S
Co(acac) ₂ +NaCl	-497	613	207	56.42	1.46
Co(acac) ₂ +HCl	-489	537	181	65.97	1.87
Zn(acac) ₂ +NaCl	-487	517	210	55.78	1.85
Zn(acac) ₂ +HCl	-481	611	180	66.16	2.42
Cu(acac) ₂ +NaCl	-510	811	161	66.10	1.47
Cu(acac) ₂ +HCl	-503	805	132	75.18	2.01
Mn(acac) ₂ +NaCl	-507	731	201	57.68	1.33
Mn(acac) ₂ +HCl	-496	708	173	67.48	1.74

Table 3: Electrochemical parameters of mild steel in 1 M phosphoric acid containing 10⁻² M acetylacetonate complexes and 10⁻¹ M chloride ion at 298 K.



Figure 1: DC polarization curves of mild steel in 1 M phosphoric acid without and with acetylacetonate complexes in concentration of 10⁻² M at 298 K.







Figure 3: DC polarization curves of mild steel in 1 M phosphoric acid containing 10⁻² M acetylacetonate complexes and 10⁻¹ M chloride ion at 298 K (a: Zn(acac)₂, b: Co(acac)₂, c: Mn(acac)₂ and d: Cu(acac)₂).



4. Conclusions

Four acetylacetonate complexes $(Cu(acac)_2, Mn(acac)_2, Co(acac)_2 and (Zn(acac)_2) as new corrosion inhibitors were studied in 1 M phosphoric acid. The following results can be inferred:$

- It was seen that acetylacetonate complexes reduced corrosion rate of mild steel due to the adsorption on metal surface. Adsorption of inhibitors on mild steel surface blocked anodic areas and reduced cathodic reaction (hydrogen reduction).
- Potential of mild steel shifted toward more negative potentials and cathodic Tafel slope increased. Potential changes and cathodic Tafel slope show that acetylacetonate complexes are cathodic inhibitors.

- Cathodic Tafel slope increased by addition of acetylacetonate complexes confirming that inhibitors decreased reduction rate of hydrogen ions on mild steel surface.
- Inhibition performance of acetylacetonate complexes enhanced by addition of chloride ions in solution. Chloride ions adsorb on mild steel surface and make a negatively charged surface. As a result, chloride ions help adsorption of positively charged inhibitor ions on metal surface.
- In same proportion of chloride ions, HCl had a better inhibition performance in comparison with NaCl. This could be due to the neutralization of surface by Na⁺ ions.

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