

## **EFFECT OF ANION GROUPS ON CORROSION INHIBITION BEHAVIOURS OF VIETNAM ORANGE PEEL ESSENTIAL OIL FOR MILD STEEL IN THE ACIDIC MEDIA**

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### **ABSTRACT**

This paper deals with the effect of anion groups ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) on inhibition behaviours of Vietnam orange peel essential oil (OPE) for corrosion process of mild steel in acidic media. The electrochemical techniques (potentiodynamic, electrochemical impedance spectroscopy (EIS)), weight loss and scanning electron microscopy (SEM) analyses are used in this study. The results show that anion groups do not affect the inhibition mechanism of OPE. The OPE behaves as mixed inhibitor for mild steel corrosion in both 1N HCl and  $\text{H}_2\text{SO}_4$  acid. The inhibition efficiency of OPE in 1N HCl is greater than that in 1N  $\text{H}_2\text{SO}_4$  which implies that the adsorption of the inhibitor is influenced by the nature of anions in acidic solutions. Moreover, the OPE inhibits both general and pitting corrosion for mild steel in the acidic media.

*Keywords:* corrosion inhibition, OPE, mild steel, anion groups, electrochemical techniques.

### **1. INTRODUCTION**

Acids are used to remove the undesirable scales and rust in several industrial processes, including pickling and descaling operations [1]. The corrosion inhibitors are one of the most effective and economical methods to protect metal from corrosion in acid media [1, 2]. The organic compounds have been used to control the corrosion, especially those containing nitrogen, oxygen, sulfur, phosphorus, and multiple bonds or aromatic rings in their structures [3]. Those are toxic in nature and pollute the environment. Hence the use of natural products is eco-friendly, low cost, readily available and non-toxic corrosion inhibiting additives. Some investigators studied that the plant extracts are readily available and renewable source for a wide range of corrosion inhibitors [4, 5]. These inhibitors are biodegradable and rich source of organic compounds which have high corrosion inhibition efficiency. Generally, it is assumed that the first stage in the action mechanism of the inhibitor in the aggressive acid media is based on its adsorption on the metal surface. The process of adsorption of inhibitors is influenced by the nature and surface of the metal, the chemical structure of the organic inhibitor, the distribution of charge in the molecule, the type of aggressive electrolyte and the type of interact ion between organic molecules and the metallic surface [6, 7].

It has been reported that the Vietnam orange peel essential oil (OPE) serves as a good corrosion inhibitor for mild steel in acid media and the optimal concentration of the inhibitor is 3 g/L OPE in both acids [8, 9]. However, effect of anion groups of acid ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) on inhibition behaviours of OPE for the steel in acid solutions are not yet compared and discussed. The aim of this work is to study on the effect of anion groups ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) on inhibition behaviours of OPE for corrosion process of mild steel in acidic media. The potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS), weight loss and scanning electron microscopy (SEM) analyses are used in this study.

## 2. EXPERIMENTAL AND METHODS

### 2.1. Materials and solutions

**Materials.** The test samples were made of carbon steel (cylinders form, diameter of 8 mm) with compositions of 0.174 % C; 0.368 % Mn; 0.017 % P; 0.041 % S; 0.223 % Si; 0.214 % Cu; 0.014 % Nb; 0.106 % Cr; 0.015 % Mo; 0.087 % Ni; 0.012 % Co and the remainder iron. The working electrode for electrochemical measurements had area of  $0.5 \text{ cm}^2$  and the rest of the surface was covered by epoxy. Samples in the form of cylinders 2.5 cm long and  $0.5 \text{ cm}^2$  cross-sectional area were used for weight-loss measurements. Before each test, specimens were mechanically ground down to 1000 grit SiC abrasive paper, then degreased with soap and rinsed in distilled water, after that were dried by blotting paper with alcohol.

**Solutions.** The electrolytes were 1N HCl and 1N  $\text{H}_2\text{SO}_4$  acid prepared respectively with analytical grade 36 % HCl ( $d = 1.18 \text{ g/mL}$ ), 98 %  $\text{H}_2\text{SO}_4$  ( $d = 1.84 \text{ g/mL}$ ) and distilled water. The Vietnam orange peel essential oil (OPE) was produced by Hanoi Essential Company. Investigations on corrosion inhibition and comparison effect of acid anion were carried out in 1N HCl and 1N  $\text{H}_2\text{SO}_4$  acids with the addition of 3 g/L OPE at room temperature.

### 2.2. Methods

**Polarization curves** were measured by potentiodynamic technique. The working electrode potentials were scanned from -0.3 V to +0.3 V versus open circuit potential with scanning rate of 5 mV/s. Determination of the corrosion current was based on Tafel extrapolation method.

**Electrochemical impedances** were measured by perturbing the free corrosion potential of the specimen with a 10 mV AC signal of decreasing frequency from 10 kHz to 5 mHz.

All the electrochemical tests with conventional three-electrode cell were carried out by Autolab PGSTAT 302N (Netherlands). A platinum mesh and a silver/silver chloride reference electrode (Ag/AgCl) were the counter-electrode and the reference-electrode respectively. Before each electrochemical experiment, the electrode was allowed to corrode freely up to 30 min to get the steady state.

**Weight-loss method** was used to determine corrosion rate and inhibition efficiency of OPE after 1 hour and 24 hours immersion time in both 1N HCl and 1N  $\text{H}_2\text{SO}_4$  acids. The corrosion rate (W) of each specimen was calculated as follows:

$$W = \frac{m_1 - m_2}{S \cdot t} \quad (\text{mg/cm}^2 \cdot \text{h}) \quad (1)$$

where, S is the test sample area ( $\text{cm}^2$ );  $m_1$ ,  $m_2$  are the weight of test sample before and after testing (mg); t is the testing time (h).

The average corrosion rate was calculated from the three parallel specimens for each test. The weighing instrument is the TE214S balance (Germany) with 0.0001g accuracy.

**Surface morphology** of samples before and after 1 hour exposed in the testing solutions at room temperature were observed by scanning electron microscope (SEM) with JEOL 6490, Jed 2300 (Japan).

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Effect of anion groups on inhibition behaviors of OPE for mild steel corrosion in acid media

Beside hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) is often used as industrial acid cleaners and pickling acids. Therefore, anion group SO<sub>4</sub><sup>2-</sup> was selected to compare with anion Cl<sup>-</sup> in this study. The experiment was conducted with the same acid concentration (1N) of HCl and H<sub>2</sub>SO<sub>4</sub>.

Effect of anion groups on polarization curves of mild steel in acid solutions was illustrated in Figure 1. The corrosion potential E<sub>c</sub> in both 1N HCl and H<sub>2</sub>SO<sub>4</sub> acid were approximately the same. Adding OPE contributes to the shift of both cathode and anode branches of the curves towards to the smaller current density than that in the blank solutions, meanwhile E<sub>c</sub> was more slightly positive (lower 20 mV). This implies that both the hydrogen evolution and anodic iron dissolution reactions of iron electrode corrosion were inhibited. This may be ascribed to adsorption of OPE over the corroding surface [10] and OPE behaved as a mixed inhibitor for mild steel in both 1N HCl and H<sub>2</sub>SO<sub>4</sub> media. The results showed that anion groups did not influence on inhibition mechanism of OPE for corrosion process of steel in acid media.

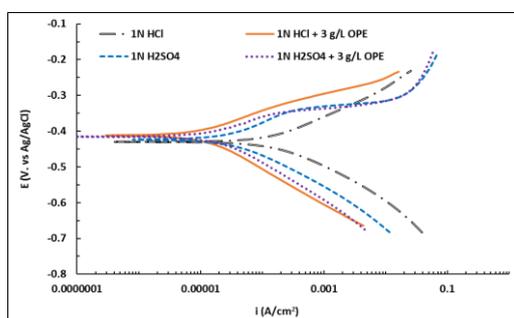


Figure 1. Effect of anion group on polarization curves of mild steel in the solutions with and without 3 g/L OPE.

Table 1. Effect of anion group on potentiodynamic polarization parameters for mild steel in the solutions with and without 3 g/L OPE.

Solution	C <sub>OPE</sub> (g/L)	E <sub>c</sub> (mV vs Ag/AgCl)	i <sub>c</sub> (mA/cm <sup>2</sup> )	R <sub>p</sub> (Ω.cm <sup>2</sup> )
1N HCl	0	-429.24	125.12	66.71
	3	-411.71	9.86	852.53
1N H <sub>2</sub> SO <sub>4</sub>	0	-423.6	69.59	135.75
	3	-415.25	36.67	246.56

The values of corrosion potential (E<sub>c</sub>), corrosion current densities (i<sub>c</sub>), polarization resistances (R<sub>p</sub>) obtained by the Tafel extrapolation method from polarization curves are listed in Table 1. The results in the table indicate that corrosion current density decreases markedly in the presence of OPE compared to the blank solution in both acids.

Nyquist plots of mild steel in studied solutions are illustrated in Figure 2, large capacitive loops at high to medium frequency and inductive loops at low frequency were observed. A “depressed” semicircle with single capacitive loop, attributed to charge transfer of the corrosion process. The depressed capacitive loop corresponds to surface heterogeneity which may be the result of surface roughness, dislocation, distribution of active sites, or adsorption of the inhibitor molecules [4]. The diameters of the loops increased with the following order:

$$1\text{N HCl} < 1\text{N H}_2\text{SO}_4 < 1\text{N H}_2\text{SO}_4 + 3 \text{ g/L OPE} < 1\text{N HCl} + 3 \text{ g/L OPE}.$$

The presence of this low frequency inductive loop may be attributed to the relaxation process obtained by adsorption of species  $\text{H}_2\text{O}$ ,  $(\text{Cl}^-)_{\text{ads}}$ ,  $(\text{SO}_4^{2-})_{\text{ads}}$  and  $(\text{H}^+)_{\text{ads}}$  and/or OPE moleculars on the electrode surface. The second parallel combination of L and  $R_L$  was introduced to account for the inductive loop observed in the Nyquist diagrams [12, 13].

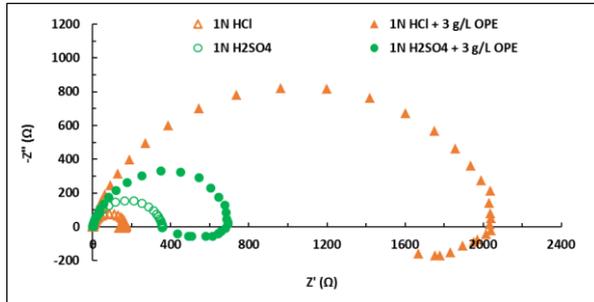


Figure 2. Effect of anion group on Nyquist plots of mild steel in the solutions with and without 3 g/L OPE.

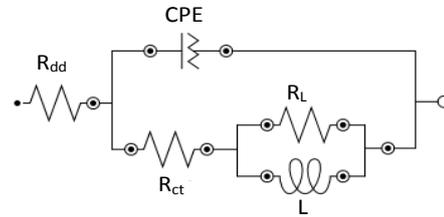


Figure 3. Equivalent circuit model used to fit the EIS experiment data of mild steel in the solutions with and without 3 g/L OPE [11, 12].

$R_{dd}$  is solution resistance;  $R_{ct}$  is charge transfer resistance; CPE is the constant phase element;  $R_L$  and L are inductive parameters.

The impedance data were analyzed by fitting to the equivalent circuit in Figure 3 [11,12]. CPE is a constant phase element that is often used instead of a double layer capacitance in the case of the non-ideal capacitance response from the interface. The impedance function of CPE is as follows [4,11],

$$Z_{\text{CPE}} = [Y_0 \cdot (j\omega)^n]^{-1} \quad (2)$$

where,  $Y_0$  is the magnitude of the CPE,  $\omega$  is the angular frequency, n is the CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface. For ideal capacitance,  $n = 1$ , for the non-ideal capacitance,  $n < 1$ .

$C_{dl}$  values listed in Table 2 were derived from the CPE parameters by using the following equation:

$$C_{dl} = \left( \frac{Y_0}{R_{ct}^{1-n}} \right)^{\frac{1}{n}} \quad (3)$$

Table 2. EIS parameters for mild steel in 1N HCl and 1N  $\text{H}_2\text{SO}_4$  solution in the absence and presence of OPE fitted by the equivalent circuit in Figure 3.

Solution	$C_{\text{OPE}}$ (g/L)	$R_{dd}$ ( $\Omega \cdot \text{cm}^2$ )	$R_{ct}$ ( $\Omega \cdot \text{cm}^2$ )	$Y^0$ ( $\mu\text{F}$ )	N	$C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ )
1N HCl	0	0.7	80	56.10	0.911	75.53
	3	0.6	980	19.20	0.865	23.05
1N $\text{H}_2\text{SO}_4$	0	0.9	183	79.2	0.869	92.84
	3	1.1	367	39.4	0.882	49.05

The electrochemical parameters  $R_{dd}$ ,  $R_{ct}$ ,  $Y_0$  and n obtained from the fitting of the recorded data using the equivalent circuit are listed in Table 2.

It can be seen that charge transfer resistance  $R_{ct}$  in the acids with the presence of OPE is significantly higher than those without OPE, especially in the case of HCl acid. The increase in

$R_{ct}$  values is attributed to the formation of the protective film of the inhibitor on metal/solution interface. This indicates that OPE makes decrease the corrosion process of mild steel in both HCl and  $H_2SO_4$  acids.

The values of  $C_{dl}$  decreased with the presence of OPE in both acids. According to the Helmholtz model, the change in the value of  $C_{dl}$  might be attributed to a gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface result in a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer [11]. Whereas the value of  $C_{dl}$  in the HCl acid with OPE is smaller than that in the  $H_2SO_4$  acid with OPE, which is due to the thickness of protective layer in the former is higher than the one in the later. This suggests that the OPE adsorbs at the steel-solution interface in both solutions and the adsorption of OPE in HCl acid can be higher than  $H_2SO_4$  acid.

The data in Table 1 and Table 2 show the similarity between the two methods. The presence of OPE makes decreasing corrosion current density of mild steel  $i_c$  and increasing charge transfer resistance  $R_{ct}$  of steel in acids, however, the degree of change depends on anion groups of acid.

### 2.3. Effect of anion groups on inhibition efficiency of OPE for mild steel in acid media

Besides electrochemical techniques, weight-loss method was used to clarify the effect of anion groups on corrosion inhibition of OPE. The corrosion rate of steel and inhibition efficiency of OPE in both acids after 1 hour and 24 hours immersion are presented in Table 3.

Table 3. Effect of anion groups on corrosion rate of mild steel and inhibition efficiency of OPE.

Solution	Time $C_{OPE}$ (g/L)	1 hour		24 hours	
		$W_{corr}$ ( $mg/cm^2.h$ )	$H_W$ (%)	$W_{corr}$ ( $mg/cm^2.h$ )	$H_W$ (%)
1N HCl	0	0.3098	-	0.4817	-
	3	0.0570	81.6	0.0249	94.8
1N $H_2SO_4$	0	0.2313	-	0.3130	-
	3	0.0616	73.4	0.0234	92.5

The corrosion rate of mild steel in  $H_2SO_4$  acid is smaller than in HCl acid after both 1 hour and 24 hours. This is due to the corrosion of steel in HCl acid not only occur on steel surface, but also in holes which exist by pitting corrosion in the solution with the presence of chloride ion ( $Cl^-$ ). On the contrary, when the presence of OPE in the acid solutions, the corrosion rate of steel in  $H_2SO_4$  acid and HCl acid are approximately after both 1 hour and 24 hours immersion.

The inhibition efficiency of OPE for the steel corrosion in 1 N HCl acid is greater than that in 1N  $H_2SO_4$  acid after both 1 hour and 24 hours which implies that the adsorption of inhibitor could be influenced by the nature of anions in acidic solutions. This can be explained by the following reasons: (i) The  $Cl^-$  ions have stronger [14] and faster [1] tendency to adsorb than do  $SO_4^{2-}$  ions and the electrostatic influence on the inhibitor adsorption may be the reason for an increased protective effect in halide containing solution; (ii) Adsorption of organic molecules is not always a direct combination of the organic molecule with the metal surface. In some cases the adsorption occurs through already adsorbed chloride ions in case of HCl or sulfate ions in case of  $H_2SO_4$  that interfere with the adsorbed organic molecules. The lesser interference of  $SO_4^{2-}$

ions with the adsorbed protonated cations may lead to lower adsorption and inhibition of corrosion [14, 15]; (iii) Moreover, it is thought that the halide ions are able to improve adsorption of the organic cations by forming the intermediate bridges between the positively charged metal surface and the positive end of the inhibitor [16]. Therefore, the adsorption of OPE on steel surface in 1N HCl solution is stronger than that in 1 N H<sub>2</sub>SO<sub>4</sub> solution, which leads to higher inhibition performance in HCl than that in H<sub>2</sub>SO<sub>4</sub>.

#### 2.4. Effect of anion groups on surface morphologies of mild steel in acid media with OPE

The SEM images of the mild steel surfaces before testing and after 1 hour exposed in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> with and without 3 g/L OPE are illustrated in Figure 4.

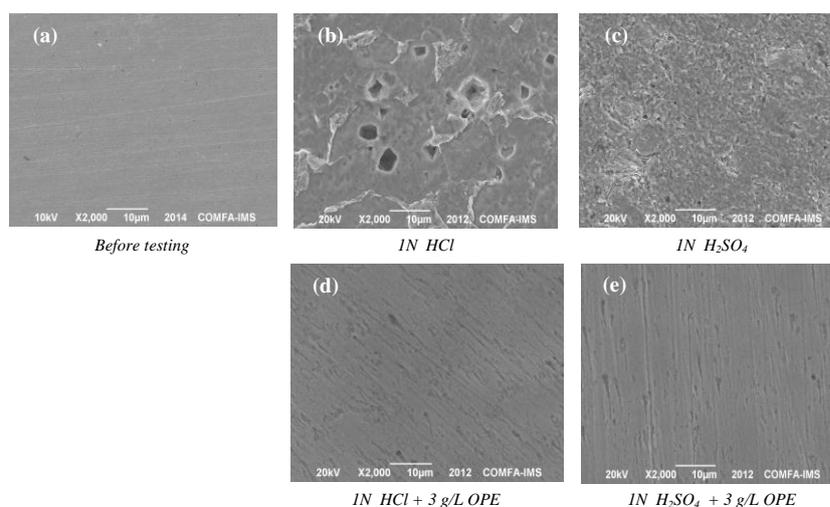


Figure 4. Effect of anion groups on surface morphology of mild steel: before testing (a); after testing in 1N HCl (b); in 1N H<sub>2</sub>SO<sub>4</sub> (c); in 1N HCl + 3g/L OPE (d) and in 1N H<sub>2</sub>SO<sub>4</sub> + 3g/L OPE (e).

The SEM images show that the mild steel surface before testing is quite smooth (Fig. 4a), but the specimen in 1N HCl solution is rough and appeared like full of larger pits and cavities (Fig. 4b), while the metal surface immersed in 1N H<sub>2</sub>SO<sub>4</sub> is general corrosion (Fig. 4c) after 1 hour immersion. According to some authors, the pitting corrosion on metal surface is due to the exposure of the surface to aqueous solutions containing aggressive anions such as ion Cl<sup>-</sup> [17]. When the presence of OPE in acids, the steel surfaces in the both acids are in better condition having a smooth surface. This is evident that OPE is a good inhibitor in both 1N HCl and H<sub>2</sub>SO<sub>4</sub> acids. This suggests that OPE inhibits well not only general corrosion, but also pitting corrosion for mild steel in acid media.

#### 4. CONCLUSIONS

The anion groups do not affect the inhibition mechanism of OPE. The OPE behaves as a mixed-type inhibitor for mild steel corrosion in both 1N HCl and 1 N H<sub>2</sub>SO<sub>4</sub> acids.

The inhibition efficiency of OPE in 1N HCl is greater than that in 1N H<sub>2</sub>SO<sub>4</sub> which implies that the adsorption of the inhibitor is influenced by the nature of anions in acidic solutions. Moreover, the OPE inhibits both general and pitting corrosion for mild steel in the acidic media.

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