

A Dialkyldithiophosphate Derivative as Mild Steel Corrosion Inhibitor in Sulfuric Acid Solution

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In the present work, N,N-Diethylammonium O,O'-di(4-chlorophenyl)dithiophosphate (Cl-EPP) acting as a mild steel corrosion inhibitor was synthesized. Potentiodynamic polarization measurements, weight loss measurements and scanning electron microscopy were used to evaluate the corrosion inhibition of Cl-EPP for mild steel in sulfuric acid. The results of electrochemical measurements indicate that the Cl-EPP is a mixed type inhibitor. Meanwhile, the inhibition efficiency increase with the increasing of concentration of inhibitor concentration, decrease with the increasing of temperature, sulfuric acid concentration and storage time. In addition, the adsorption of Cl-EPP on mild steel surface is chemical adsorption, and obeys Langmuir isotherm.

Keywords: Corrosion inhibitor; Mild steel; Sulfuric acid; O,O'-dialkyldithiophosphate.

1. INTRODUCTION

Mild steel is widely used in a broad spectrum of industries and machinery. However, it is easily attacked and solubilized in acidic solutions which are widely used to remove rust and mill scale in many industrial processes [1-3]. Sulfuric acid is one of the most frequently used. In the presence of inhibitors, a lower iron dissolution rate was observed, and which is one of the most practical methods to prevent mild steel dissolution in acidic solutions [4-5].

Most of well-known acid inhibitors are organic compounds with electronegative atoms (N, P, S and O atoms), the unsaturated bonds and the plane conjugated systems including all kinds of aromatic cycles [6-7]. In fact, the O,O'-Dialkyldithiophosphate and their derivatives, in their structure, which contain N, P, S and O electronegative atoms [8-9], it could be acted as a kind of the potential corrosion

inhibitors. As a result, in order to develop effective inhibitor, the aim of this study is to evaluate the corrosion inhibition of N,N-Diethylammonium O,O'-di (4-chlorophenyl)dithiophosphate (Cl-EPP) for mild steel in sulfuric acid (H_2SO_4) solution. Firstly, the compound of Cl-EPP was synthesized. Meanwhile, Cl-EPP acting as corrosion inhibitor for mild steel in H_2SO_4 solution was studied using potentiodynamic polarization measurements, weight loss measurements and scanning electron microscopy. In addition, the effects of inhibitor concentration, H_2SO_4 concentration, temperatures and storage time on inhibition action were fully investigated.

2. MATERIALS AND METHODS

2.1 Materials

In this work, the test samples and working electrode were prepared by mild steel which has the following components (in wt.%): C (0.15%), Si (0.28%), Mn (0.41%), P (<0.014%), S (<0.011%) and Fe for balance. Sulfuric acid (A.R., 98%, H_2SO_4), phosphorus pentasulphide (A.R., P_2S_5), diethylamine (A.R., NHEt_2), 4-chlorophenol (A.R.), toluene (A.R.) and acetone (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the above reagents were commercially available and used without further purification. H_2SO_4 solutions for testing were prepared by sulfuric acid (98%) and distilled water. During the electrochemical and weight loss measurements, the temperature of test solutions were controlled by a water thermostat, and all experiments were open to the air and carried out under static conditions. Meanwhile, CHI 660D electrochemical workstation (China) was used for electrochemical measurements.

2.2 Synthesis of inhibitor

The corrosion inhibitor of N,N-Diethylammonium O,O'-di(4-chlorophenyl) dithiophosphate (Cl-EPP) was synthesized according to the method described in our previous works [8,9], and the synthetic procedures showing in figure 1, which prepared by the reaction of phosphorus pentasulphide, 4-chlorophenol with diethylamine in toluene as the solvent.

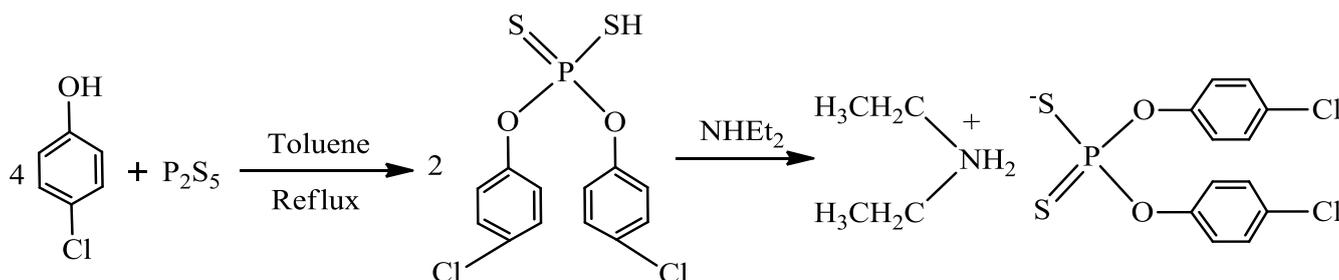


Figure 1. The synthetic procedures for the investigated inhibitor (Cl-EPP)

2.3 Electrochemical measurements

Electrochemical measurements was done by conventional three-electrode system consisting of mild steel working electrode with an exposed area of 0.785 cm², a graphite electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. The potential sweep rate for potentiodynamic polarization (Tafel) curves was 0.166 mV s⁻¹. Corrosion current density (i_{corr}) was determined from the intercept of extrapolated cathodic and anodic Tafel lines at the corrosion potential (E_{corr}). According to electrochemical measurements, the inhibition efficiency (IE_{Tafel}) was calculated from the following equation [10-11]:

$$IE_{\text{Tafel}} (\%) = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \times 100 \quad (1)$$

where i_{corr} and $i_{\text{corr(inh)}}$ are the corrosion current density values of mild steel in H₂SO₄ solution without and with Cl-EPP, respectively.

2.4 Weight loss measurements

Before weight loss measurements, all of the standard mild steel samples (40 mm×15 mm×5 mm) were mechanically abraded with emery paper up to 1000 grit, then rinsed with distilled water, degreased in acetone and dried at room temperature. The finely polished and dried mild steel samples were weighed on a digital balance with 1 mg sensitivity and immersed in H₂SO₄ solution with and without Cl-EPP at various temperatures for testing. After corrosion testing, the samples were rinsed with distilled water, cleaned with acetone, dried and reweighed. The weight loss was calculated as the difference in weight of the sample before and after immersion in test solutions.

Using weight loss measurements to evaluate the corrosion inhibition, at least three closer results were considered, and their average values have been reported. The corrosion rate (v , g m⁻² h⁻¹) and inhibition efficiency ($IE_{\text{Weight loss}}$) were calculated from equation 2 and equation 3 [12-13], respectively.

$$v = \frac{m_1 - m_2}{St} = \frac{\Delta m}{St} \quad (2)$$

$$IE_{\text{Weight loss}} (\%) = \frac{v_0 - v}{v_0} \times 100 \quad (3)$$

where m_1 and m_2 are the mass of the sample before and after corrosion, Δm is the weight loss of the sample before and after corrosion, S is the total surface area of the sample, t is the immersion time, v_0 and v are corrosion rate of the mild steel sample in H₂SO₄ solution without and with different concentration of Cl-EPP.

2.5 Scanning electron microscopy

The surface morphologies of mild steel samples before and after immersion in 0.5 M H₂SO₄ at 298 K in the absence and presence of 80 mg L⁻¹ Cl-EPP for 2 h were examined by scanning electron microscopy (SEM, Tescan Vega III).

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization measurements

3.1.1 Effect of Cl-EPP concentration

At 298 K, the potentiodynamic polarization curves for mild steel in 0.5 M H₂SO₄ in the absence and presence of different concentrations of Cl-EPP are shown in figure 2. Meanwhile, the corrosion potential E_{corr} (mV, vs. SCE), corrosion current density i_{corr} ($\mu\text{A cm}^{-2}$), cathodic Tafel slopes b_c (mV dec⁻¹), anodic Tafel slopes b_a (mV dec⁻¹) and inhibition efficiency (IE_{Tafel}) are given in table 1. The inhibition efficiency was calculated by equation 1.

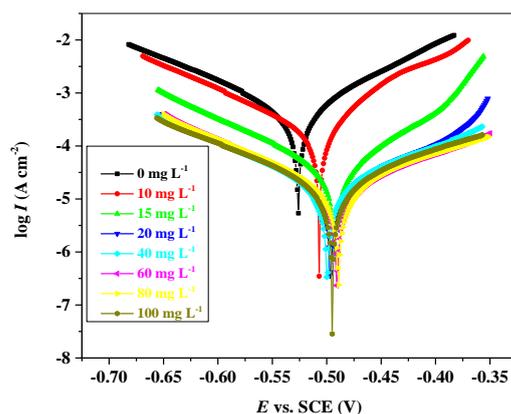


Figure 2. The potentiodynamic polarization curves for mild steel corrosion in 0.5 M H₂SO₄ in the absence and presence of different concentrations of Cl-EPP at 298 K

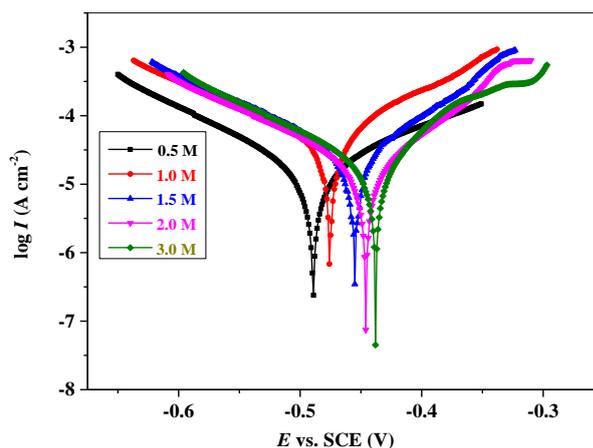
It could be observed from figure 2 and table 1, that the anodic and cathodic reactions affected by the addition of Cl-EPP. Both the anodic and cathodic curves shift to lower current densities, it indicate that the addition of Cl-EPP can reduce the mild steel anodic dissolution and also retard the hydrogen ions (H⁺) reduction. Clearly, the corrosion current density decreases considerably in the presence of Cl-EPP comparing with that in the absence of Cl-EPP, and decreases with the Cl-EPP concentration increasing. Correspondingly, the inhibition efficiency increases with the Cl-EPP concentration, due to the increase in the blocked fraction of the mild steel electrode surface by adsorption. The inhibition effect enhances with the increase in Cl-EPP concentration, resulting from the adsorption of Cl-EPP on the mild steel electrode surface. One possible mechanism is the adsorption of Cl-EPP on mild steel surface through the electron pair of heteroatoms (S and O atoms), the π electron of benzene rings in the molecular structure of Cl-EPP, which blocks the mild steel surface and reduces the corrosive attraction of mild steel in H₂SO₄ media. When the concentration of Cl-EPP increase to 80 mg L⁻¹, the inhibition efficiency reaches up to 96.55%, which present that the Cl-EPP is a good inhibitor for mild steel in H₂SO₄ solution.

Table 1. The polarization parameters and corresponding inhibition efficiency for mild steel in 0.5 M H₂SO₄ in the absence and presence of different concentrations of Cl-EPP at 298K

<i>C</i> (mg L ⁻¹)	<i>E</i> _{corr} (mV)	<i>i</i> _{corr} (μA cm ⁻²)	<i>b</i> _c (mV dec ⁻¹)	<i>b</i> _a (mV dec ⁻¹)	<i>IE</i> _{Tafel} (%)
0	-525	579.43	109.21	95.92	-
10	-513	230.34	118.06	118.64	60.25
15	-502	64.89	109.51	121.97	88.80
20	-500	50.45	113.39	129.57	91.29
40	-499	39.73	114.73	138.01	93.14
60	-496	35.63	116.18	143.29	93.85
80	-492	19.96	113.81	151.15	96.55
100	-490	19.58	110.07	153.37	96.62

In addition, it is clear from Table 1 that there is a small shift towards anodic region in the values of corrosion potential (*E*_{corr}). In literature [14], it has been reported that if the displacement in *E*_{corr} (i) is >85 mV with respect to *E*_{corr}, the inhibitor can be seen as a cathodic or anodic type inhibitor and (ii) if displacement in *E*_{corr} is <85, the inhibitor can be seen as a mixed type inhibitor. In our study the maximum displacement in *E*_{corr} value was 35 mV towards anodic region, which indicates that this corrosion inhibitor is a mixed type inhibitor.

3.1.2 Effect of H₂SO₄ concentration

**Figure 3.** The potentiodynamic polarization curves for mild steel corrosion in different concentration H₂SO₄ with 80 mg L⁻¹ Cl-EPP at 298 K

The potentiodynamic polarization curves for mild steel in different concentration H₂SO₄ solution with 80 mg L⁻¹ Cl-EPP at 298 K are shown in figure 3. Meanwhile, according to equation 1, the effect of H₂SO₄ concentration on the inhibition efficiency is listed in table 2. It can be found that the increase of H₂SO₄ concentration resulted in decrease of inhibition efficiency gradually, and the

minimum inhibition efficiency in 3.0 M H₂SO₄ is 83.41%. The hydrogen ions (H⁺) concentration increases with H₂SO₄ concentration increasing, which leads to the corrosion current density increase with H₂SO₄ concentration. Based on equation 1, it clearly shows that the decrease of the inhibition efficiency is due to the increase of H⁺ concentration resulting from corrosion current density increasing. A similar result has been reported in previous work [15].

3.1.3 Effect of temperature

Temperature is an important factor that influences the corrosion of mild steel in H₂SO₄ solution and modifies the adsorption of inhibitor on mild steel surface. In order to study the effect of temperature on the inhibition characteristics, experiments were conducted at 298 K to 343 K. The potentiodynamic polarization curves for mild steel corrosion in 0.5 M H₂SO₄ with 80 mg L⁻¹ Cl-EPP at different temperature are shown in figure 4. Meanwhile, based on equation 1, the effect of temperature on the inhibition efficiency also listed in table 2. Clearly, inhibition efficiencies decrease with the experimental temperature, which can be attributed to that the higher temperatures might cause desorption of inhibitor molecule from mild steel surface. Increase as the temperature from 298 K to 333 K, the inhibition efficiency has dropped from 96.65% to 86.88%. Meanwhile, the inhibition efficiency decreases sharply when the temperature is higher than 333 K.

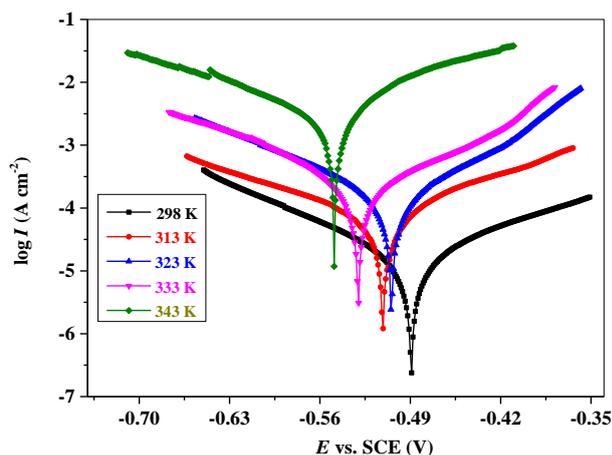


Figure 4. The potentiodynamic polarization curves for mild steel corrosion in 0.5 M H₂SO₄ with 80 mg L⁻¹ Cl-EPP at different temperature

3.1.4 Effect of storage time

The storage time was defined as the time interval from the time of addition Cl-EPP in H₂SO₄ solution to the time of using the test solution for electrochemical measurements, which described in literature [15]. The potentiodynamic polarization curves for mild steel corrosion in 0.5 M H₂SO₄ with 80 mg L⁻¹ Cl-EPP at 298 K for different storage time are shown in figure 4, and the effect of

temperature on inhibition efficiency listed in table 2. As can be seen from table 2, the inhibition efficiency slightly decreases with storage time increasing, but addition of Cl-EPP in 0.5 M H₂SO₄ at 144 hours later, the inhibition efficiency is 91.29%, which show that Cl-EPP still exhibit the excellent corrosion inhibition for mild steel in 0.5 M H₂SO₄ for a long time.

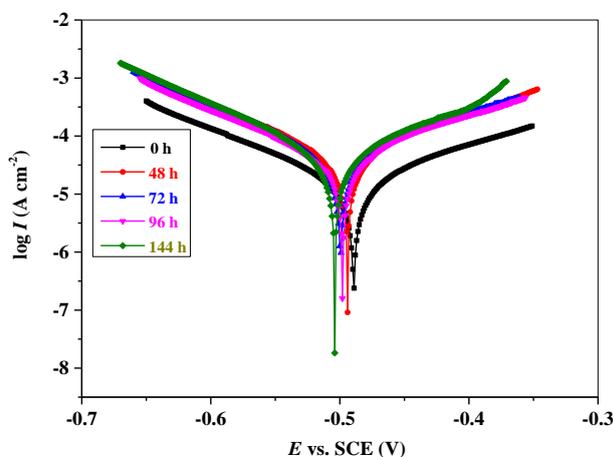


Figure 5. The potentiodynamic polarization curves for mild steel corrosion in 0.5 M H₂SO₄ with 80 mg L⁻¹ Cl-EPP at 298 K for different storage time

Table 2. The effects of H₂SO₄ concentration, temperatures and storage time on inhibition efficiency from potentiodynamic polarization measurements

$C_{\text{H}_2\text{SO}_4}$ (M)	IE_{Tafel} (%)	Temperature (K)	IE_{Tafel} (%)	Storage time (h)	IE_{Tafel} (%)
0.5	96.65	298	96.65	0	96.65
1.0	95.30	313	94.58	48	94.17
1.5	94.05	323	91.48	72	93.18
2.0	92.65	333	86.88	96	91.48
3.0	83.41	343	32.32	144	91.29

3.2 Weight loss measurements

3.2.1 Effect of Cl-EPP concentration

Based on equation 2 and equation 3, the corrosion rate (v) and inhibition efficiency ($IE_{\text{Weight loss}}$) from weight loss measurements are shown in figure 4. The mild steel corrosion in 0.5 M H₂SO₄ with different concentrations of Cl-EPP at 298 K, it can be found that the corrosion rate and inhibition efficiency have an obvious change as Cl-EPP concentration increase from 0 mg L⁻¹ to 100 mg L⁻¹. The inhibition efficiency is approximately proportional to Cl-EPP concentration, whereas the corrosion rate was reversely related to Cl-EPP concentration.

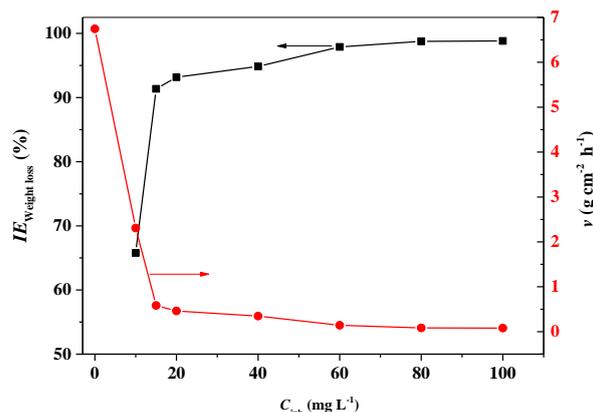


Figure 6. The corrosion rate and inhibition efficiency for mild steel in 0.5 M H₂SO₄ in the absence and presence of different concentrations of Cl-EPP at 298 K from weight loss measurements

When the concentration of Cl-EPP are 80 mg L⁻¹ and 100 mg L⁻¹, the inhibition efficiency are 98.77% and 98.83% respectively, which confirms that the Cl-EPP can act as a effective corrosion inhibitor for mild steel in 0.5 M H₂SO₄. It is a good agreement with potentiodynamic polarization measurements, both of which gave a same trend of mild steel corrosion in H₂SO₄ solution with Cl-EPP at 298 K.

3.2.2 Adsorption isotherm

The adsorption of inhibitor molecules on study metal surface is one of the most important topics in corrosion researches, which can give important information about the interaction of the inhibitor and metal surface. Its importance comes from not only due to its ability to provide structural information of the double layer but also due to the thermodynamic information can provide. In general, two main types of interaction can be used to describe the adsorption behavior of the inhibitor, which are physisorption and chemisorption [16-17]¹. These processes depend on the chemical structure of the inhibitor molecule, the temperature during the experiments, the electrochemical potential, the charge, and nature of the metal. The adsorption of organic inhibitor molecules from the aqueous solution can be considered as a quasi-substitution process between the organic compounds in the aqueous phase and water molecules associated with the metallic surface [15, 18].

In this study, in order to identify the nature (physisorption) and the strength (chemisorption) of adsorption, a series of experimental adsorption isotherms including Langmuir, Temkin, Frumkin and Flory–Huggins adsorption isotherms [15, 19] are employed to fit the experimental data from weight loss measurements. It can be found that the best fit was determined with the use of Langmuir adsorption isotherm, which shows as the following equation [12, 19]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{4}$$

where C_{inh} is the concentration of Cl-EPP (mol L⁻¹), K_{ads} is the adsorption equilibrium constant (mol L⁻¹)⁻¹, and θ is the surface coverage. The surface coverage (θ) for different concentrations of Cl-

EPP in 0.5 M H₂SO₄ is obtained according to the following equation (Eq. 5) by weight loss measurements [12, 19, 20]:

$$\theta = \frac{v_0 - v}{v_0} \tag{5}$$

where v_0 and v are corrosion rate (g cm⁻² h⁻¹) of the test samples in 0.5 M H₂SO₄ solution without and with Cl-EPP, respectively.

Additionally, the adsorption equilibrium constant (K_{ads} , (mol L⁻¹)⁻¹) is obtained according to equation 6.

$$K_{ads} = M_{Cl-EPP} \times K \times 10^3 \tag{6}$$

where M_{Cl-EPP} is the molar mass of Cl-EPP (g mol⁻¹), K is the adsorption equilibrium constant ((mg L⁻¹)⁻¹).

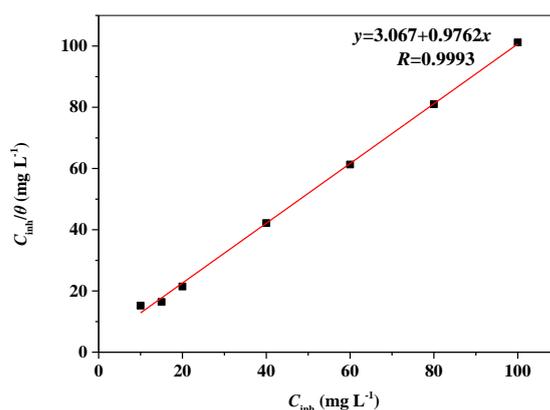


Figure 7. Langmuir adsorption isotherm of Cl-EPP on mild steel in 0.5 M H₂SO₄ at 298 K from weight loss measurements

The plots of C_{inh}/θ versus C_{inh} yield the straight lines as shown in figure 7. The strong correlation ($R > 0.9993$) suggests that the adsorption of Cl-EPP on mild steel surface in H₂SO₄ solution obeys the Langmuir adsorption isotherm. The K_{ads} value can be determined from the intercepts of the straight lines ($1/K$), $K_{ads} = M_{Cl-EPP} \times K \times 10^3 = 424/3.067 \times 10^3 = 1.3825 \times 10^5$ (mol L⁻¹)⁻¹. Meanwhile, the K_{ads} is also related to the standard free energy of adsorption (ΔG_{ads}^0), using the following expression (Eq. 7) [21-22]:

$$\Delta G_{ads}^0 = -RT \ln (55.5 K_{ads}) \tag{7}$$

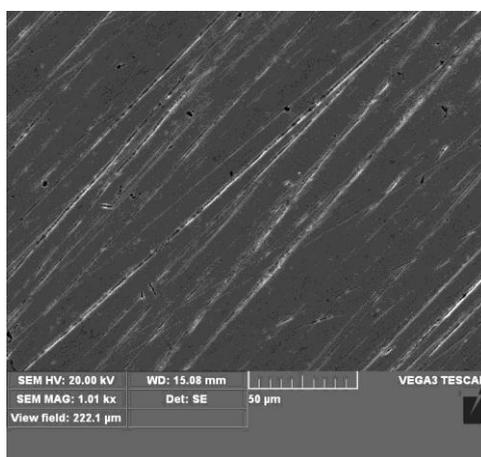
where R is gas constant (8.314 J K⁻¹ mol⁻¹), T is absolute temperature (K) and 55.5 is the molar concentration of water in the solution expressed in molarity units (mol L⁻¹).

Based on equation 7 and figure 7, the calculated value of ΔG_{ads}^0 for Cl-EPP on mild steel in H₂SO₄ solution is -39.28 kJ mol⁻¹. The large values of ΔG_{ads}^0 and its negative sign are usually characteristic of a strong interaction and a high efficient adsorption. In general, the values of ΔG_{ads}^0 around -20 kJ mol⁻¹ or less negative are associated with an electrostatic interaction between charged inhibitor molecules and charged metal surface (physisorption) and those of -40 kJ mol⁻¹ or more negative involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type bond (chemisorption) [16,17]. The value of ΔG_{ads}^0 is very closer to -

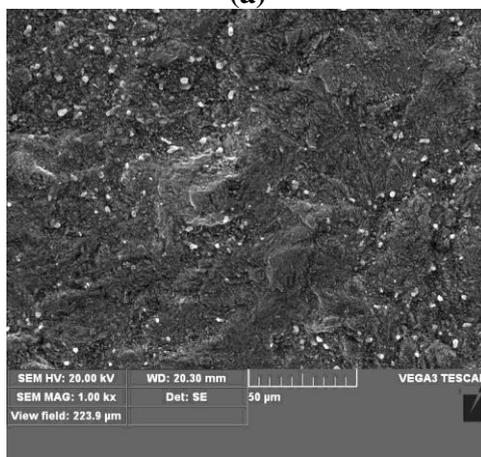
40 kJ mol⁻¹, which shows that the adsorption of Cl-EPP on mild steel surface in H₂SO₄ solution is chemical adsorption.

3.3 Scanning electron microscopy

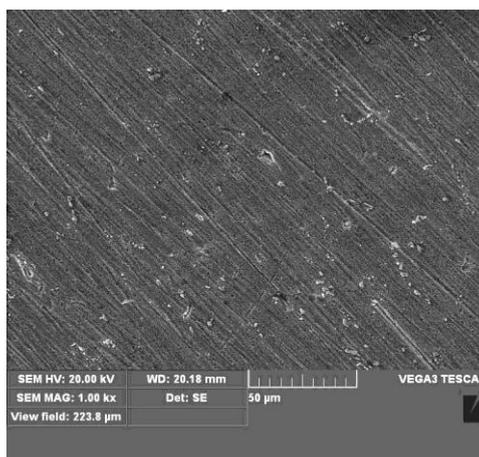
Figure 8 shows the scanning electron microscopy (SEM) images of mild steel before and after immersed in 0.5 M H₂SO₄ without and with 80 mg L⁻¹ Cl-EPP at 298 K for 2 h, which is recorded in order to see the changes occurred during corrosion process in the absence and presence of the inhibitor of Cl-EPP. Figure 8 (a) shows the surface morphology of the sample before immersion in 0.5 M H₂SO₄, which appears more uniform and some abrading scratches. However, as can be seen from figure 8 (b), the sample treated with uninhibited solution (0.5 M H₂SO₄ without Cl-EPP) is deeply corroded, the corrosion products appear too uneven, and the surface becomes rough, which reveal that the mild steel surface is highly corroded and damaged in blank solution. In contrast, it can be seen from figure 8 (c), in the presence of 80 mg L⁻¹ Cl-EPP, the corrosion degree is suppressed and much less damaged, which further confirms the inhibition action and adsorption of Cl-EPP on mild steel surface.



(a)



(b)



(c)

Figure 8. SEM micrographs of mild steel before (a) and immersed in 0.5 M H₂SO₄ without (b) and with 80 mg L⁻¹ Cl-EPP (c) at 298 K for 2 h

Consequently, SEM examinations of the mild steel surface support the experimental results from weight loss and potentiodynamic polarization measurements.

4. CONCLUSIONS

(1) N,N-Diethylammonium O,O'-di(4-chlorophenyl)dithiophosphate (Cl-EPP) show good inhibition properties for the corrosion of mild steel in H₂SO₄ solution, and the inhibition efficiency increases with increasing concentration of Cl-EPP, decreases with an increasing of temperature, H₂SO₄ concentration and storage time.

(2) Polarization measurements show that the synthesized inhibitor of Cl-EPP is a mixed type inhibitor, the corrosion current density significantly decreases and corrosion potential slightly changes with the addition of Cl-EPP in H₂SO₄ solution.

(3) The inhibition efficiencies obtained by potentiodynamic polarization measurements, weight loss measurements and scanning electron microscopy are in good agreement.

(4) The adsorption of Cl-EPP on mild steel surface is chemical adsorption, and obeys Langmuir adsorption isotherm model.

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