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Corrosion Inhibition of Q235 Steel in H_2SO_4 Solution by N,N-Diethylammonium O,O'-di(4-bromophenyl) dithiophosphate

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In sulfuric acid solution, the corrosion inhibition of synthesized compound of N,N-Diethylammonium O,O'-di(4-bromophenyl)dithiophosphate (Br-NOP) was investigated by electrochemical impedance spectroscopy, potentiodynamic polarization measurement, weight loss measurement and scanning electron microscopy. The results indicate that the Br-NOP is a mixed type inhibitor. The inhibition efficiency increases with Br-NOP concentration increasing, decreases with temperature and H_2SO_4 concentration increasing.The adsorption of Br-NOP on Q235 steel surface in H_2SO_4 solution belongs to chemical adsorption, and obeys Langmuir isotherm model. Br-NOP can act as an effective long-acting corrosion inhibitor, and the obtained maximum inhibition efficiency can reach up to 98.53% for Q235 steel in H_2SO_4.

Keywords: Corrosion inhibitor; O,O'-Dialkyldithiophosphate; Q235 steel; Sulfuric acid; Adsorption.

1. INTRODUCTION

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys in contact with aggressive environment [1-3]. Most of the corrosion inhibitors are organic compounds with electronegative atoms including sulphur, nitrogen, phosphorus or oxygen atoms, unsaturated bonds and plane conjugated systems [4-9]. It is well known that the corrosion inhibition of these organic compounds is mainly due to the physical and/or chemical adsorption resulting from the interaction of polar centres of the inhibitor's molecule with active sites on metal surface [10-13].

It is obvious that the O,O'-Dialkyldithiophosphate derivatives contain electronegative atoms (N, P, S and O atoms), unsaturated bonds and plane conjugated systems, it could be acted as a kind of the potential corrosion inhibitors [14-16]. According to our previous works [14-16], O,O'-Dialkyldithiophosphoric acid derivatives acting as corrosion inhibitors had been studied and reported, however, in order to develop more excellent corrosion inhibitors, the purpose of this study is to synthesize a new inhibitor as the effective long-acting corrosion inhibitor. As a result, the compound of N,N-Diethylammonium O,O'-di (4-bromophenyl)dithiophosphate (Br-NOP) acting as the new corrosion inhibitor was synthesized and fully investigated using different methods.

2. MATERIALS AND METHODS

2.1 Materials

Sulfuric acid (98%, H_2SO_4), phosphorus pentasulphide, diaethylamin, 4-bromophenyl, toluene and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. H_2SO_4 solution for corrosion inhibition tests were prepared by 98% H_2SO_4 and distilled water. Meanwhile, the test samples (50 mm×25 mm×2 mm) and working electrode (0.785 cm^2) were prepared by Q235 steel. During electrochemical measurements and weight loss measurement, the temperature was controlled by the water thermostat.

2.2 Synthesis of Br-NOP

The target investigated corrosion inhibitor, N,N-Diethylammonium O,O'-di(4-bromophenyl) dithiophosphate (Br-NOP), was synthesized based on the method described in the literatures [14-16], which synthesized by the reaction of phosphorus pentasulphide, 4-bromophenol with diaethylamin in the toluene as solvent**.**

2.3 Electrochemical measurements

The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (Tafel) measurement were selected as the typical electrochemical measurements for corrosion inhibition evaluating, all of which were done by conventional three-electrode system on CHI 660D electrochemical workstation (China).

EIS measurement was performed in frequency range of 100 kHz to 10 m Hz using a sinusoidal AC perturbation with amplitude of 10 mV. The corresponding parameters were fitted using Zsimpwin software. The inhibition efficiency (IE_{EIS}) derived from EIS was calculated using the following Equation [17-18]:

$$IE_{\text{EIS}}(\%) = \frac{R_{\text{ct}} - R_{\text{ct}}^{0}}{R_{\text{ct}}} \times 100 \qquad (1)$$

where R_{ct}^{0} and R_{ct} are the values of charge transfer resistance for Q235 steel in H_2SO_4 solution without and with different concentrations of Br-NOP, respectively.

According to potentiodynamic polarization (Tafel) measurement, the inhibition efficiency (IE_{Tafel}) was calculated from Equation 2 [17-18]:

$$IE_{\text{Tafel}}\ (\%) = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \times 100 \quad (2)$$

where i_{corr} and $i_{corr(inh)}$ are the corrosion current density values of Q235 steel in H_2SO_4 solution without and with different concentrations of Br-NOP, respectively.

2.4 Weight loss measurement

Weight loss measurement was described in previous works [14-16].The corrosion rate (*v*, mg m^{-2} h^{-1}) and inhibition efficiency (IE_{WLM}) were obtained from Equation 3 and 4 [19-20], respectively.

$$v = \frac{m_1 - m_2}{St} = \frac{\Delta m}{St} \quad (3)$$

$$IE_{\text{WLM}}\ (\%) = \frac{v_0 - v}{v_0} \times 100 \quad (4)$$

where m_1 and m_2 are the mass of the Q235 steel sample before and after immersion in H_2SO_4 solution, *S* is the total surface area of the Q235 steel sample, *t* is the immersion time, v_0 and *v* are corrosion rate of the Q235 steel corrosion in H_2SO_4 solution without and with different concentrations of Br-NOP.

2.5 Scanning electron microscopy

The SEM images of Q235 steel surface before and after corrosion in 0.5 M H_2SO_4 at 300 K in the absence and presence of Br-NOP for 2.0 h were examined by Tescan Vega III scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1 Electrochemical impedance spectroscopy

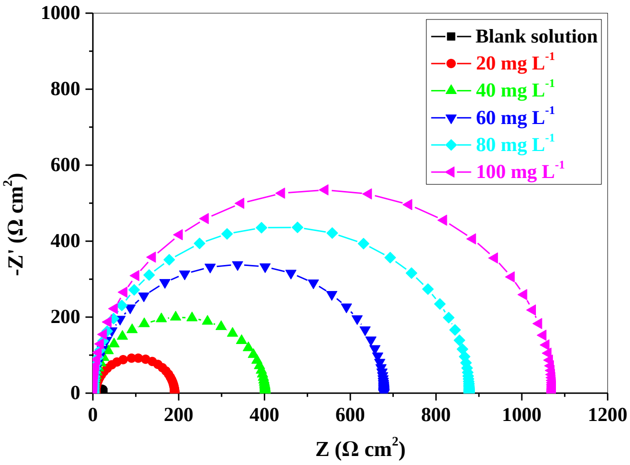


Figure 1. Nyquist plots for Q235 steel in 0.5 M H_2SO_4 without and with different concentrations of Br-NOP at 300 K

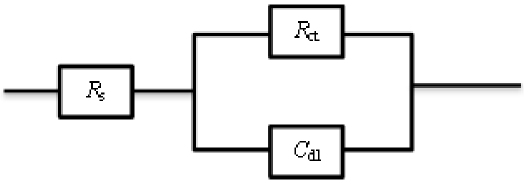


Figure 2. Equivalent circuit mode

Table 1. Electrochemical parameters of impedance and IE_{EIS} for Q235 steel in 0.5 M H_2SO_4 without and with different concentrations of Br-NOP at 300 K

C (mg L^{-1})	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	IE_{EIS} (%)
0	20.14	9.14	-
20	180.23	8.32	88.83
40	414.27	5.95	95.14
60	686.75	4.57	97.07
80	890.32	3.39	97.74
100	1040.91	2.99	98.07

EIS measurement is a well-established and powerful method for study corrosion process [21]. Based on this method, the Nyquist diagrams for Q235 steel in 0.5 M H_2SO_4 without and with different concentrations of Br-NOP at 300 K is shown in Figure 1. The equivalent circuit mode present in Figure 2. In addition, the electrochemical parameters and IE_{EIS} are presented in Table 1.

According to Table 1, it can be found that the IE_{EIS} increases with Br-NOP concentration increasing, and double layer capacitance (C_{dl}) decreases with it increasing. Based on McCafferty [22] attributed, the decrease in C_{dl} values to the gradual replacement of H_2O molecules resulted from the adsorption of Br-NOP molecules on Q235 steel. The diameter of the capacitive loop increase indicates that the inhibition of the corrosion process of Q235 steel in 0.5 M H_2SO_4. The maximum inhibition efficiency recorded by EIS is 98.07% for Q235 steel in 0.5 M H_2SO_4 with 100 mg L^{-1} Br-NOP at 300 K, which confirms that Br-NOP can act as an excellent corrosion inhibitor for Q235 steel in H_2SO_4 solution.

3.2 Potentiodynamic polarization measurement

3.2.1 Effect of Br-NOP concentration

Table 2. Polarization parameters and IE_{Tafel} for Q235 steel in 0.5 M H_2SO_4 without and with different concentrations of Br-NOP at 300 K

C (mg L^{-1})	E_{corr} (mV)	i_{corr} (μA cm^{-2})	b_c (mV dec^{-1})	b_a (mV dec^{-1})	IE_{Tafel} (%)
0	-0.525	587.77	113.21	85.94	-
20	-0.486	42.52	107.79	79.51	92.77
40	-0.485	25.81	90.40	107.87	95.61
60	-0.485	22.57	110.28	125.75	96.16
80	-0.482	20.65	112.89	133.37	96.49
100	-0.481	15.12	92.91	99.61	97.43

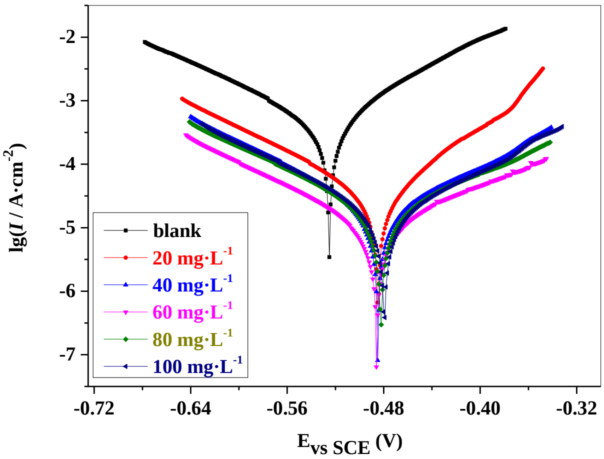


Figure 3. Potentiodynamic polarization curves for Q235 steel in 0.5 M H_2SO_4 without and with different concentrations of Br-NOP at 300 K

At 300 K, the potentiodynamic polarization curves of Q235 steel in 0.5 M H_2SO_4 without and with different concentrations of Br-NOP are shown in Figure 3. Meanwhile, the corresponding inhibition efficiency (IE_{Tafel}) calculated by Equation 2, corrosion current density i_{corr} (μA cm^{-2}), corrosion potential E_{corr} (mV, vs. SCE), anodic Tafel slopes b_a (mV dec^{-1}) and cathodic Tafel slopes b_c (mV dec^{-1}) are given in Table 2.

According to Table 2 and Figure 3, it could be found that the anodic and cathodic reactions affected by the addition of Br-NOP. Both the anodic and cathodic curves shift to lower current densities, which indicates that the corrosion inhibitor of Br-NOP can reduce the Q235 steel anodic dissolution in H_2SO_4 solution. The IE_{Tafel} increases with Br-NOP concentration increasing. A possible inhibition mechanism is the adsorption of Br-NOP molecules on Q235 steel surface through the electronegative atoms including sulphur, nitrogen and oxygen atoms from the Br-NOP, which blocks the Q235 steel corrosion in H_2SO_4 solution. The IE_{Tafel} reaches up to 97.43% when the Br-NOP concentration increase to 100 mg L^{-1}, which present that the Br-NOP is an effective inhibitor for Q235 steel in H_2SO_4 solution. The result obtained from potentiodynamic polarization measurement is in good agreement with it obtained from EIS measurement.

It is clear from Table 2, there is obvious shift towards anodic region in the values of E_{corr}. The maximum displacement in E_{corr} value is 44 mV towards anodic region in this study, According to previous work [23], it indicates that the investigated corrosion inhibitor Br-NOP is a mixed type inhibitor.

3.2.2 Effect of H_2SO_4 concentration

According to potentiodynamic polarization measurement, the impact of H_2SO_4 concentration on inhibition efficiency (IE_{Tafel}) is shown in Figure 4. It can be found that the IE_{Tafel} decreases with H_2SO_4 concentration increasing, and the minimum IE_{Tafel} for Q235 steel in different concentration of

H_2SO_4 solution with 100 mg L^{-1} Br-NOP is 96.12% (3.0 M H_2SO_4). The slightly decrease of the IE_{Tafel} from 97.43% (0.5 M H_2SO_4) to 96.12% (3.0 M H_2SO_4) is contribute to the increase of H^+ concentration.

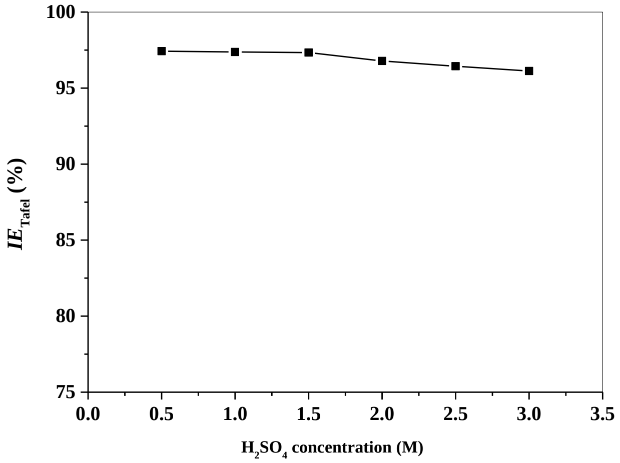


Figure 4. Relationships between IE_{Tafel} and concentration of H_2SO_4 with 100 mg L^{-1} Br-NOP from potentiodynamic polarization measurement at 300 K

3.2.3 Effect of temperature

Temperature influences on acidic corrosion and corrosion inhibition of different metals most often in H_2SO_4 solution had been the object of a large number of studies [24-27]. In this work, experiments temperature were conducted at 300 K to 353 K. Based on potentiodynamic polarization measurement, the influence of temperature on IE_{Tafel} is shown in Figure 5. Clearly, IE_{Tafel} decreases with temperature increasing. Increase as temperature from 300 K to 343 K, IE_{Tafel} has dropped from 97.43% to 86.32%, which sharply decreases for temperature higher than 343 K. When temperature increases to 353 K, IE_{Tafel} dropped to 61.57%.

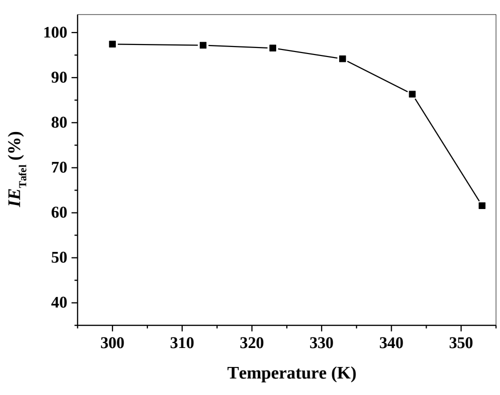


Figure 5. Relationships between temperature and IE_{Tafel} from potentiodynamic polarization measurement in 0.5 M H_2SO_4 with 100 mg L^{-1} Br-NOP

3.2.4 Effect of storage time

The influence of storage time on inhibition efficiency is shown in Figure 6. From this Figure, it can be found that the IE_{Tafel} slightly fluctuates with storage time changing. At 300 K, addition of Br-NOP (100 mg L^{-1}) in 0.5 M H_2SO_4 at 240 hours later, the IE_{Tafel} still up to 97.39%, which shows that Br-NOP still exhibit the excellent corrosion inhibition for Q235 steel in 0.5 M H_2SO_4 for a long time, and further reveals that Br-NOP is a long-acting corrosion inhibitor.

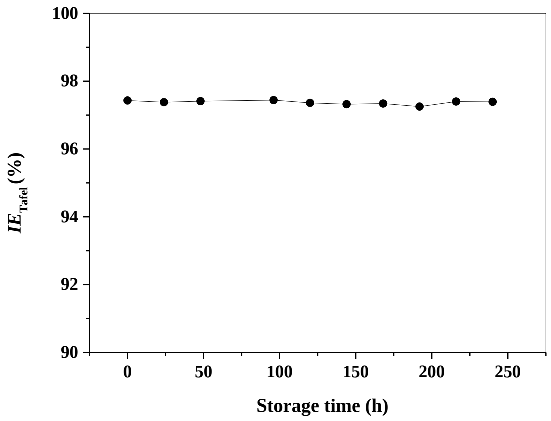


Figure 6. Relationships between storage time and IE_{Tafel} from potentiodynamic polarization measurement in 0.5 M H_2SO_4 with 100 mg L^{-1} Br-NOP

3.3 Weight loss measurement

3.3.1 Effect of Br-NOP concentration

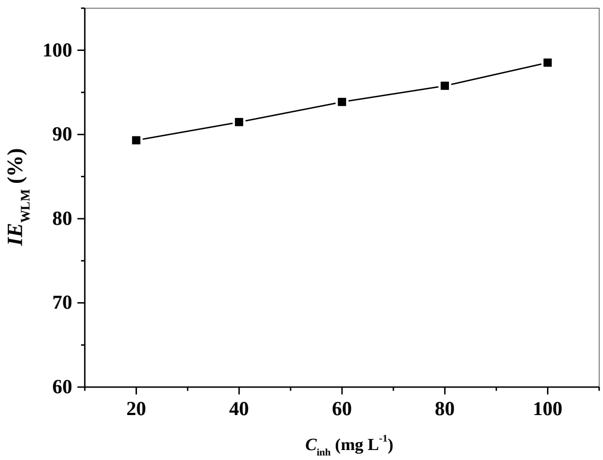


Figure 7. The IE_{WLM} of Q235 steel in 0.5 M H_2SO_4 with different concentrations of Br-NOP at 300 K from weight loss measurement

Based on Equation 3 and 4, the inhibition efficiency (IE_{WLM}) for Q235 steel in 0.5 M H_2SO_4 without and with different concentrations of Br-NOP at 300 K from weight loss measurement is shown in Figure 7. This Figure shows that the IE_{WLM} have an obvious change as Br-NOP concentration increase from blank solution to 100 mg L^{-1}. the IE_{WLM} increase from 97.74% to 98.07% when Br-NOP concentration increase from 80 to 100 mg L^{-1}, which confirms that the Br-NOP can act as an effective corrosion inhibitor. It is a good agreement with EIS and Tafel measurements, and all of which present a same trend of Q235 steel in H_2SO_4 solution with Br-NOP.

3.3.2 Adsorption isotherm

In the present work, in order to identify the adsorption of Br-NOP molecules on Q235 steel surface, different adsorption isotherms including Flory–Huggins, Frumkin, Temkin and Langmuir isotherms [28] are suggested to fit the obtained data according to Figure 7 . It is obvious that the best adsorption isotherm was determined with Langmuir adsorption isotherm, this isotherm represented by Equation 5 [29]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (5)$$

where C_{inh} is the concentration of Br-NOP (mol L^{-1}), K_{ads} is the adsorption equilibrium constant (mol $L^{-1})^{-1}$, θ is the surface coverage, which obtained from Equation 6 according to weight loss measurement [28, 29]:

$$\theta = \frac{v_0 - v}{v_0} \qquad (6)$$

where v_0 and v are corrosion rate (mg cm^{-2} h^{-1}) of Q235 steel in 0.5 M H_2SO_4 without and with different concentrations of Br-NOP, respectively.

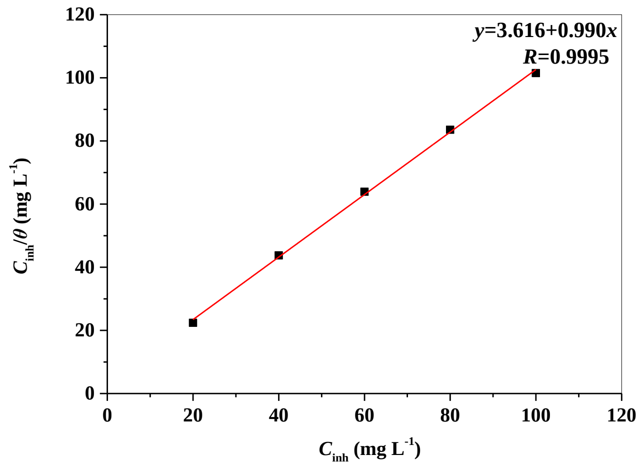


Figure 8. Langmuir adsorption isotherm of Br-NOP for Q235 steel in 0.5 M H_2SO_4 at 300 K from weight loss measurement

The relationships between C_{inh}/θ and C_{inh} are shown in Figure 8. From this fitting result, it can be found the adsorption of Br-NOP in H_2SO_4 solution on Q235 steel surface obeys Langmuir adsorption isotherm (R>0.9995). Meanwhile, the K_{ads} value can be determined from fitting results,

K_{ads}=$M_{Br\text{-}NOP}$×K×10^3=513/3.616×10^3=1.4187×10^5 (mol L^{-1})$^{-1}$. Where $M_{Br\text{-}NOP}$ is the molar mass of Br-NOP (g mol^{-1}), K is the adsorption equilibrium constant ((mg L^{-1})$^{-1}$). Based on K_{ads}, the standard free energy of adsorption (ΔG^0_{ads}) can be calculated by Equation 7 [30-31]:

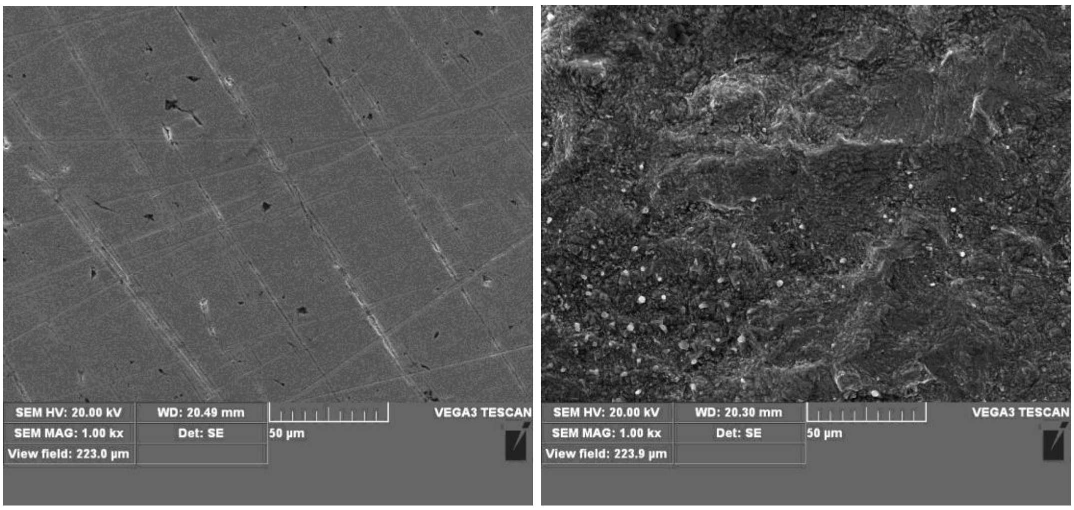
$$\Delta G^0_{ads} = -RT\ln(55.5K_{ads}) \quad (7)$$

where R is 8.314 J K^{-1} mol^{-1}, T is 300 K.

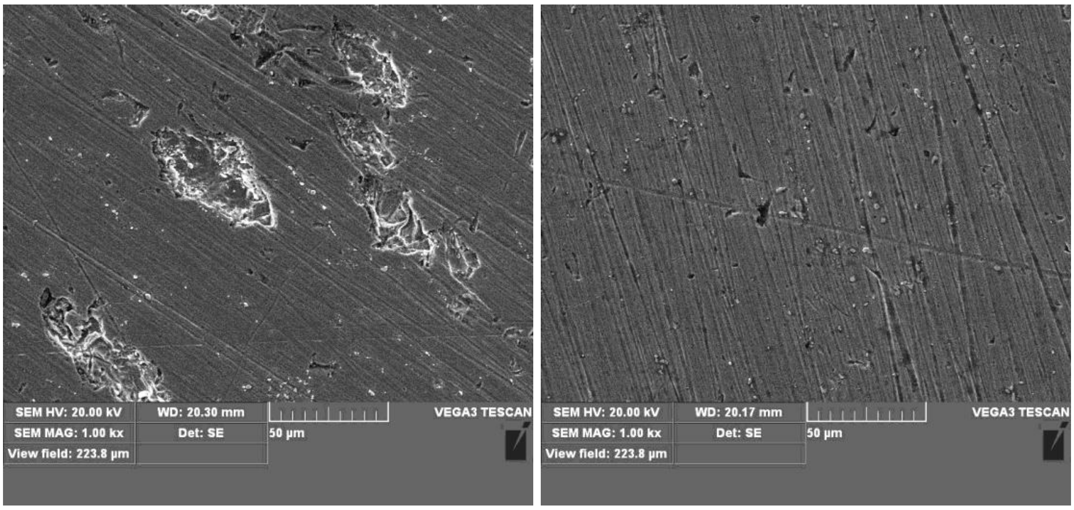
According to Equation 7 and Figure 8, the value of ΔG^0_{ads} for Br-NOP in 0.5 M H_2SO_4 on Q235 steel at 300 K is -39.61 kJ mol^{-1}, the ΔG^0_{ads} is very closer to -40 kJ mol^{-1}, which presents that the adsorption of Br-NOP in H_2SO_4 solution on Q235 steel surface belongs to chemical adsorption [32-35].

3.4 Scanning electron microscopy

Figure 9 shows the SEM images of Q235 steel surface before (a) and after immersion in 0.5 M H_2SO_4 without (b) and with different concentrations of Br-NOP (20 mg L^{-1} (c), 100 mg L^{-1} (d)) at 300 K for 2.0 h. Figure 9 (a) shows the SEM images of the Q235 steel sample before immersion in corrosive medium, it is obvious that the Q235 steel surface appears more uniform and some abrading scratches. However, according to Figure 9 (b), the Q235 steel sample immersion in blank solution (0.5 M H_2SO_4), which is deeply corroded, the surface becomes rough and too uneven, it reveal that the Q235 steel surface is highly corroded and damaged in blank solution. On the contrary, from Figure 9 (c) and (d), with 20 mg L^{-1} (c) and 100 mg L^{-1} (d) Br-NOP, the corrosion degree is suppressed and much less damaged, which further confirms the corrosion inhibition of Br-NOP on Q235 steel surface. Consequently, the SEM morphology of the adsorbed protective film on Q235 steel surface confirms the high performance of inhibitive effect of Br-NOP, which is well-supported by the results from EIS, Tafel and weight loss measurement.



(a) **(b)**



(c) **(d)**

Figure 9. SEM micrographs of Q235 steel before (a) and immersion in 0.5 M H_2SO_4 without (b) and with 20 mg L^{-1} (c), 100 mg L^{-1} (d) Br-NOP at 300 K for 2 h

4. CONCLUSIONS

(1) N,N-Diethylammonium O,O'-di(4-bromophenyl)dithiophosphate (Br-NOP) is an excellent new corrosion inhibitor for Q235 steel in H_2SO_4 solution, and the inhibition efficiency increases with Br-NOP concentration increasing, decreases with temperature and H_2SO_4 concentration increasing.

(2) Br-NOP is a mixed type inhibitor, and the adsorption of Br-NOP on Q235 steel surface belongs to chemical adsorption, and obeys Langmuir adsorption isotherm model.

(3) Corrosion inhibition performance evaluated by EIS, Tafel, SEM, and weight loss measurement are in good agreement.

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