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Investigation on Two Compounds of O,O'-dithiophosphate Derivatives as Corrosion Inhibitors for Q235 Steel in Hydrochloric Acid Solution

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Abstract: In this work, the O,O'-dithiophosphate derivatives of S-4-methylbenzyl-O,O'-di(phenyl) dithiophosphate (Inhi-Ph) and S-4-methyl benzyl-O,O'-di(4-bromophenyl) dithiophosphate (Inhi-BrPh) were synthesized and characterized by elemental analysis, FT-IR, ^{1}H, ^{13}C and ^{31}P NMR. Meanwhile, the corrosion inhibition of Q235 steel in HCl solution by synthesized inhibitors was evaluated by weight loss and electrochemical measurements. Measurement results indicate that the two inhibitors of Inhi-Ph and Inhi-BrPh are mixed-type inhibitor, the inhibition efficiency increase with inhibitor concentration increasing, decrease with HCl concentration and temperature increasing. The adsorption of Inhi-Ph and Inhi-BrPh on Q235 steel surface obeys Langmuir isotherm, which belongs to chemical adsorption.

Keywords: Dithiophosphate; Inhibitor; Electrochemical; Weight loss; Langmuir

1 Introduction

It is well known that the use of inhibitor is one of the most practical and simple methods to protect metals containing alloys against corrosion, especially under the acidic environment for cleaning, chemical decaling and pickling in various fields [1-3]. In past decade, a number of organic compounds have been reported as corrosion inhibitor in acid media. As everyone knows that most of the effective corrosion inhibitors are organic compounds, in their molecular structure, which often contain the electronegative atoms including N, S, P and O atoms, unsaturated bonds and the plane conjugated systems [4-6]. The corrosion inhibition of the reported organic inhibitors is mainly because of physical, chemical or the mixed adsorption involving both physisorption and chemisorption resulting from the interaction of polar centers of the inhibitor's molecule with active sites on metal surface. As a fact, the O,O'-diaryldithiophosphates can act as the potential effective inhibitors for metals protecting resulting from their molecular structure containing P, S and O atoms. The dialkyldithiophosphates and their derivatives are versatile compounds, which usually can be used as the anti-oxidants, insecticides, flotation reagents and additives to lubricating oils [7-8]. Based on our previous works [9-11], the ammonium salts of O,O'-dialkyldithiophosphoric acid as the ionic compounds acting as the corrosion inhibitors were studied and reported in recent years. However, there are few reports about the covalence compounds of S-4-methylbenzyl-O,O'- di(phenyl)dithiophosphate (Inhi-Ph) and S-4-methylbenzyl-O,O'-di(4-bromophenyl)dithiophos-phate (Inhi-BrPh) as the new excellent corrosion inhibitors.

Therefore, the aim of the present work is to develop the new potential effective corrosion inhibitor and evaluate the performance of corrosion inhibition. After the covalence compounds of Inhi-Ph and Inhi-BrPh synthesized and characterized by elemental analysis, FT-IR, ^{1}H, ^{13}C and ^{31}P

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NMR. The corrosion inhibition of Q235 steel in HCl solution by Inhi-Ph and Inhi-BrPh were evaluated by weight loss and electrochemical measurements.

2 Materials and methods

2.1 Materials

In this study, all the chemical reagents and solvents involving toluene, acetone, hydrochloric acid (37%, HCl), phosphorus pentasulphide (P_2S_5), 4-bromophenyl (4-BrPhOH), phenol (PhOH), dichloromethane (CH_2Cl_2), 4-methylbenzyl chloride (4-MePhCH$_2$Cl), diethylamine (NHEt$_2$) and sodium sulfate (Na_2SO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd, which were commercially available and analytically pure.

The target synthesized inhibitors were characterized by elemental analysis (Carlo Erba 1106 instrument, Italy), FT-IR (Nicolet- 6700 FT-IR spectrometer, USA), NMR (^{1}H, ^{13}C and ^{31}P, Bruker-500 NMR spectrometer, Germany). Meanwhile, the electrochemical measurements using to evaluate the performance of corrosion inhibition were employed by CHI 660D electrochemical workstation (China). The working electrode and test specimens in present work were prepared by Q235 steel. Electrochemical measurements were conducted by conventional three-electrode system consisting of Q235 steel working electrode with an exposed area in 0.785 cm^2, a counter graphite electrode and a saturated calomel reference electrode (SCE). All of specimens with sizes of 5 mm×20 mm×50 mm were used by weight loss measurement.

In addition, the different concentrations of HCl solutions as testing solution were prepared by HCl (37%) and deionized water. During the whole testing process, temperature of solution was controlled by the water thermostat (DF-101S, China), and all the experiments were carried out under static conditions and open to the air.

2.2 Synthesis

In order to prepare the target inhibitors of S-4-methylbenzyl-O,O'-di(phenyl) dithiophosphate (Inhi-Ph) and S-4-methylbenzyl-O,O'-di(4-bromophenyl) dithiophosphate (Inhi-BrPh), the starting compounds of O,O'-dithiophosphoric acid ammonium salt ((RO)$_2$PS$_2$NH$_2$Et$_2$) were synthesized by reaction of P_2S_5, ROH (R=4-BrPh and Ph) with NHEt$_2$ in toluene based on reported methods [9,10,11]. After (RO)$_2$PS$_2$NH$_2$Et$_2$ prepared, the inhibitors of Inhi-Ph and Inhi-BrPh were synthesized in the following same procedure. Firstly, (4-BrPhO)$_2$PS$_2$NH$_2$Et$_2$ and (PhO)$_2$PS$_2$NH$_2$Et$_2$ (10 mmoL) were dissolved in CH_2Cl_2 (60 mL) at room temperature, respectively, with that the 4-methylbenzyl chloride (10.2 mmoL) was added in the solution over a period of 30 min, and the mixture was stirred about 12 h. Afterwards, the solvent was removed under vacuum, and the residue was then taken up in 100 mL of H_2O/CH_2Cl_2 solution (1:1 v/v). The organic phase was separated and washed with 6×100 mL of H_2O, and dried over Na_2SO_4. The organic phase was purified by column chromatography (1:l CH_2Cl_2/hexane) to obtain Inhi-Ph and Inhi-BrPh. After that, the target synthesized compounds were characterized by different technologies including elemental analysis, FT-IR, ^{1}H, ^{13}C and ^{31}P NMR.

2.3 Weight loss measurement

In present work, the weight loss measurement was used to study the corrosion inhibition of Q235 steel in HCl solution by Inhi-Ph and Inhi-BrPh. Before measurement, all of specimens were mechanically abraded with emery paper up to 1200 grit, rinsed with distilled water, degreased in acetone, and then dried at room temperature. The finely polished and dried Q235 steel samples were weighed on a digital balance with 1 mg sensitivity and immersed in HCl solution in the absence and presence of synthesized inhibitors at various temperatures for 12 h. After immersing, the tests 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. Based on this method, at least three closer results were considered, and their average values have been reported. The corrosion rate (v, g m^{-2} h^{-1}) and the corresponding inhibition efficiency (η_W (%)) were obtained by Equation 1 and 2 [10,12], respectively.

$$v = \frac{m_1 - m_2}{St} = \frac{\Delta m}{St} \tag{1}$$

$$\eta_W(\%) = \frac{v_0 - v}{v_0} \times 100\% \tag{2}$$

where m_1 and m_2 are the mass of the test specimens before and after testing, Δm is average weight loss, S is the total surface area of the test specimen, t is the immersion time, v_0 and v are corrosion rate of the test specimens corrosion in HCl solution without and with different concentrations of Inhi-Ph and Inhi-BrPh.

2.4 Electrochemical measurements

Electrochemical measurements including potentiodynamic polarization (Tafel) measurement and electrochemical impedance spectroscopy (EIS) were conducted by conventional three- electrode system, and all potential in this study were referred to the saturated calomel electrode (SCE). Before electrochemical measurements, the working electrode was immersed in test solution at open circuit potential (OCP) for 30 min to be sufficient to attain a stable state.

The potential sweep rate for Tafel curves was 0.5 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}). The corresponding inhibition efficiency (η_P(%)) based on Tafel curves were calculated according to Equation 3 [9, 13]:

$$\eta_{\mathrm{P}}\ (\%) = \frac{I_{\mathrm{corr}} - I_{\mathrm{corr(inh)}}}{I_{\mathrm{corr}}} \times 100\% \quad (3)$$

In Equation 3, I_{corr} and $I_{corr(inh)}$ are the corrosion current density of working electrode in HCl solution without and with different concentrations of Inhi-Ph and Inhi-BrPh. EIS was performed in frequency range from 100 kHz to 10 mHz using a sinusoidal AC perturbation with amplitude of 10 mV. EIS parameters were fitted by using Z-View software. The charge transfer resistance (R_{ct}) was obtained from the diameter of the semicircle of the Nyquist plot. The corresponding inhibition efficiency (η_E(%)) was calculated using the following Equation [11,14]:

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

where R_{ct}^{0} and R_{ct} are the values of charge transfer resistance of working electrode in HCl solution without and with different concentrations of Inhi-Ph and Inhi-BrPh.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and discussion

3.1 Characterization

In order to confirm the molecular structure of target synthesized corrosion inhibitors, the different technologies including elemental analysis, FT-IR, ^{1}H, ^{13}C and ^{31}P NMR were employed to analyze the chemical structural of Inhi-Ph and Inhi-BrPh. The characterization results were presented in Table 1 (elemental analysis), Table 2 and Figure 1 (FT-IR), Table 3 (^{1}H, ^{13}C and ^{31}P NMR), respectively.

Table 1: Elemental analysis of Inhi-Ph and Inhi-BrPh.

Inhibitor	Molecular formula	Anal. Calcd			Anal. Found		
		C(%)	H(%)	S(%)	C(%)	H(%)	S(%)
Inhi-Ph	$C_{20}H_{19}O_2PS_2$	62.16	4.96	16.59	62.15	4.98	16.56
Inhi-BrPh	$C_{20}H_{17}O_2PS_2Br_2$	44.14	3.15	29.36	44.15	3.14	29.35

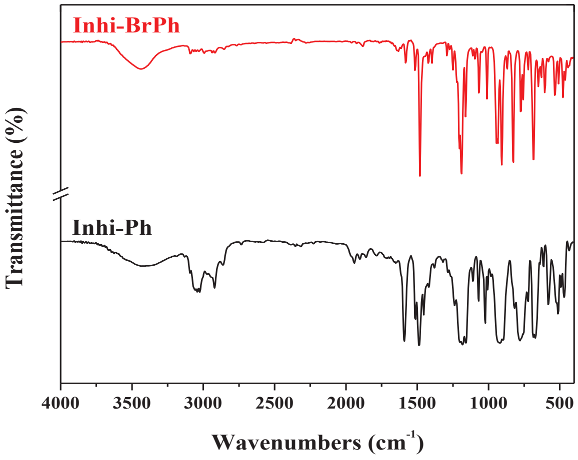

Figure 1: Infrared spectra of Inhi-Ph and Inhi-BrPh.

From Table 1, according to the results of elemental analysis, the calculated and observed elemental analysis data for the synthesized inhibitors are in good agreement and fit well the structure of Inhi-Ph and Inhi-BrPh showing in Figure 2. Meanwhile, the FT-IR, ^{1}H, ^{13}C and ^{31}P NMR results were further confirmed that the target chemical structures are also in good agreement the Inhi-Ph and Inhi-BrPh structure showing in Figure 2.

3.2 Weight loss measurement

The effect of inhibitors concentration on the corresponding inhibition efficiency (η_W(%)) for Q235 steel in 1.0 M HCl at 30°C from weight loss measurement was exhibited in Figure 3. From this figure, it can be found that the inhibition efficiencies increase with concentration of Inhi-Ph and Inhi-BrPh increasing, when the concentration of inhibitor increase to 60 mg L^{-1}, the inhibition efficiency change slightly with inhibitor concentration further increase. This is due to the surface coverage of the inhibitors on Q235 steel surface increase with inhibitors concentration increasing. The results also show that the inhibition efficiency for Inhi-

Table 2: Infrared spectra data of Inhi-Ph and Inhi-BrPh (cm^{-1}).

Inhibitor	v (=C-H)	v (C=C)	v ((P)-O-C)	v (P-O-(C))	v (S-C)	v_{asym} (PS_2)	v_{sym} (PS_2)
Inhi-Ph	3024.8(w)	1513.5(s) 1590.4(s)	1159.0(s) 1182.2(s) 1237.6(m)	919.1(s) 1023.5(s) 1069.9(m)	898.7(s)	672.3(s) 723.0(m) 780.3(s)	469.4(m) 512.2(s) 580.7(m)
Inhi-BrPh	3039.5(w)	1480.9(s) 1514.8(w) 1581(w)	1160.8(m) 1189.6(s) 1203.6(s)	907.4(s) 934.8(s) 1010.5(m) 1066.6(m)	827.2(s)	684.7(s) 757.4(m) 773.4(m)	477.7(m) 534.3(m) 605.1(m)

w=weak, s=strong, m=medium.

Table 3: ^{1}H, ^{13}C and ^{31}P NMR spectra data of Inhi-Ph and Inhi-BrPh.

Inhibitor	^{1}H NMR	^{13}CNMR	^{31}PNMR
Inhi-Ph	2.41 (s, 3H, CH_3), 4.30 (dd, J =15.22, 3.96 Hz, 2H, SCH_2), 7.17 -7.44 (m, 14H, 3Ph-H)	21.25 (SCH_2), 38.91 (CH_3), 121.68, 121.71, 125.77, 129.66, 133.12, 137.71, 150.66 (Ph-C, MeC_6H_4)	89.38 (t, J=15.22 Hz)
Inhi-BrPh	2.38 (s, 3H, CH_3), 4.23 (d, J =17.46Hz, 2H, SCH_2), 7.08-7.21 (m, 8H, BrC_6H_4), 7.46-7.48 (m, 4H, MeC_6H_4)	21.22 (SCH_2), 39.26 (CH_3), 119.02, 123.401,123.44, 129.00, 129.81, 132.65, 133.12, 137.86, 149.26, 149.34 (C_6H_4)	90.81 (t, J=17.46 Hz)

s=singlet, d=doublet, t=triplet, q=quartet.

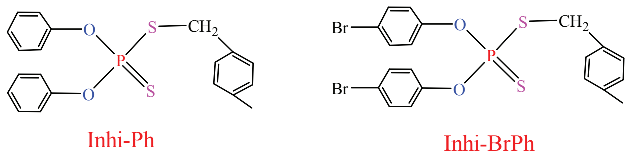

Figure 2: Chemical structures of Inhi-Ph and Inhi-BrPh.

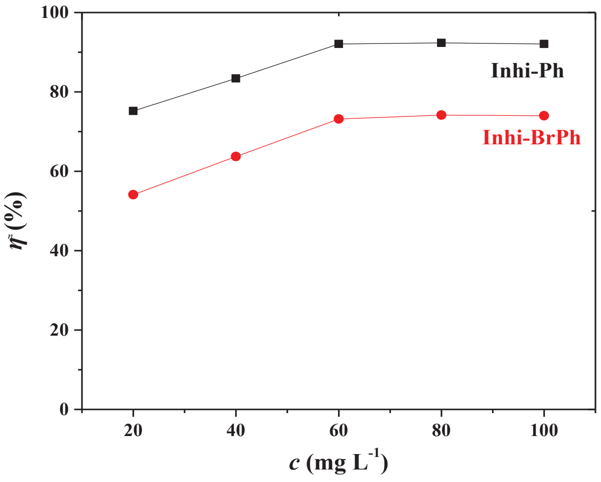

Figure 3: The effect of inhibitors concentration on inhibition efficiency for Q235 steel in 1.0 M HCl at 30°C from weight loss measurement.

Ph higher than the inhibition efficiency for Inhi-BrPh. The difference in corrosion inhibition is due to the bromine atom as electron drawing group lead to the decrease in the electron density of benzene rings. The decrease in the electron density of benzene rings will weaken the adsorption between benzene rings and Q235 steel surface, and leading to the decrease of the corrosion inhibition performance. With the concentration of Inhi-Ph and Inhi-BrPh increase to 100 mg L^{-1}, the inhibition efficiencies are 92.05% and 73.98%, which further demonstrate that the inhibitor of Inhi-Ph can act as an effective corrosion inhibitor for Q235 steel in 1.0 M HCl. The inhibition behavior of Q235 steel by Inhi-Ph and Inhi-BrPh in HCl solution can be attributed to the adsorption of components on Q235 steel surface, which retards the dissolution of Q235 steel by blocking its active corrosion sites.

3.3 Potentiodynamic polarization measurement

At 30 °C, all polarization curves of Q235 steel in 1.0 M HCl with different concentrations of Inhi-Ph and Inhi-BrPh obtained from potentiodynamic polarization measurement were shown in Figure 4 (a) and (b), respectively. Based on this measurement, the electrochemical parameters for Q235 steel corrosion in 1.0 M HCl with different concentrations of Inhi-Ph and Inhi-BrPh including corrosion potential E_{corr} (mV, vs SCE), corrosion current density I_{corr} ($\mu A\ cm^{-2}$), cathodic and anodic Tafel slopes b_c and b_a (mV dec^{-1}) and the corresponding inhibition efficiency (η_P(%)) were listed in Table 4.

According to Figure 4 (a), (b) and Table 4, it can be found that both the anodic and cathodic curves shift to lower current densities after addition of inhibitor in 1.0 M HCl, which indicate both Inhi-Ph and Inhi-BrPh can reduce the Q235 steel anodic dissolution and retard the hydrogen ion reduction. The inhibition effect enhances with the increase of Inhi-Ph and Inhi-BrPh concentration, resulting from the adsorption of inhibitors on the Q235 steel electrode surface. The possible mechanism is the adsorption of the inhibitors on Q235 steel surface through the electron pair of heteroatoms (S and O), and the π electron of benzene rings in the molecular structure of Inhi-Ph and Inhi-BrPh, which can block the Q235 steel surface and reduces the corrosive attraction of Q235 steel in HCl media.

Apparently, according to Table 4, the corrosion current density is much smaller in the presence of Inhi-Ph and Inhi-BrPh comparing with that in the absence of Inhi-Ph and Inhi-BrPh for Q235 steel in 1.0 M HCl, and which decreases with inhibitors concentration increasing. The inhibition efficiency increase with inhibitors concentration increasing is due to the increase of the blocked fraction of the Q235 steel electrode surface by adsorption. With Inhi-Ph and Inhi-BrPh concentration increase to 60 mg L^{-1}, the inhibition efficiencies are 94.63% and 75.86%, this result also reveal that the Inhi-Ph can act as good corrosion inhibitor for Q235 steel in 1.0 M HCl, and the performance of corrosion inhibition for Q235 steel in 1.0 M HCl by Inhi-BrPh lower than it by Inhi-Ph.

In addition, based on potentiodynamic polarization measurement, the corrosion inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the HCl blank solution [15-16]. According to the polarization curves showing in Figure 4 and the polarization parameters listing in Table 4, it can be found that the corrosion potentials shift slightly in the negative direction. All corrosion potential of Q235 steel in 1.0 M HCl with Inhi-Ph and Inhi-BrPh at 30°C K shift less than 85 mV, which indicate that the Inhi-Ph and Inhi-BrPh are mixed-type inhibitor.

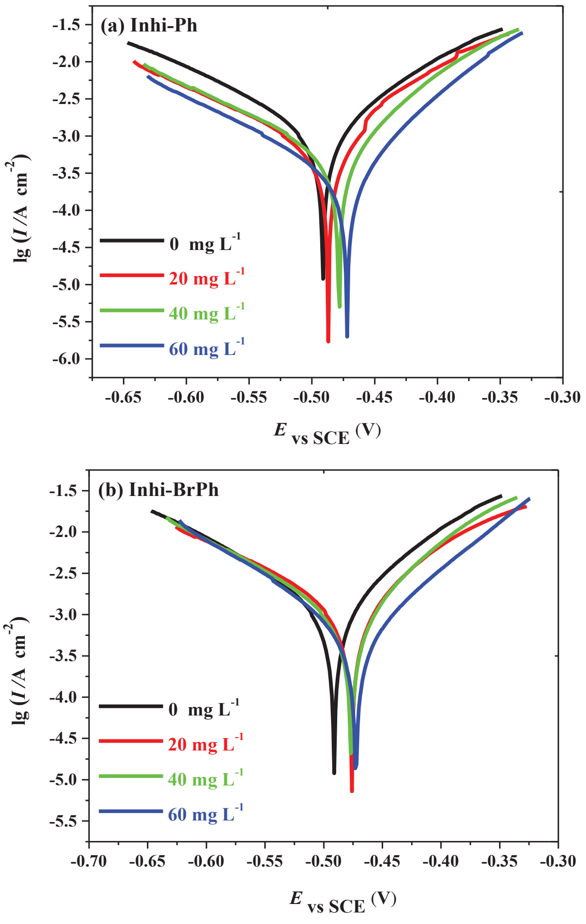

Figure 4: Polarization curves of Q235 steel in 1.0 M HCl solution with different concentrations of Inhi-Ph(a) and Inhi-BrPh (b) at 30°C.

3.4 Electrochemical impedance spectroscopy

Figure 5 (a) and (b) show the Nyquist diagrams of Q235 steel in 1.0 M HCl with various concentrations of Inhi-Ph and Inhi-BrPh at 30°C from electrochemical impedance spectroscopy (EIS) based on the equivalent circuit mode showing in Figure 6. The double layer capacitance (*C*dl), charge transfer resistance (*R*ct) and the corresponding inhibition efficiency (η_E(%)) obtained from EIS were listed in Table 5. From Figure 5 (a) and (b), it can be found that all the Nyquist plots show a single capacitive loop, in both uninhibited (HCl blank solution) and inhibited (HCl with Inhi-Ph and Inhi-BrPh) solutions, which is attributed to the charge transfer of corrosion process. The impedance spectra show that the single semicircle and the diameter of semicircle increase with the concentration of the inhibitors. According to Table 5, it reveals that the charge transfer resistance increase and the double layer capacitance decease with the concentration of inhibitors increasing. The decrease of double layer capacitance may be due to the decrease of the local dielectric constant or the increase of the thickness of the electrical double layer, indicating that the inhibitors adsorbed on the Q235 steel surface. The increase of charge transfer resistance can be attributed to the formation of protective film on the

Table 4: The polarization parameters and the corresponding inhibition efficiency of Q235 steel in 1.0 M HCl with different concentrations of Inhi-Ph and Inhi-BrPh at 30°C.

Inhibitor	C (mg L^{-1})	E_{corr} (mV)	I_{corr} (μA cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	η_P (%)
Blank solution	0	-494	1714.65	151.56	153.37	-
Inhi-Ph	20	-460	371.05	163.13	144.09	78.36
	40	-456	234.74	124.07	115.87	86.31
	60	-449	92.08	83.89	103.84	94.63
Inhi-BrPh	20	-477	770.05	139.66	121.65	55.09
	40	-482	577.67	103.09	98.43	66.31
	60	-473	438.03	82.19	83.69	74.45

Q235 steel/solution interface. The inhibition efficiencies recorded by EIS are 81.79% and 73.71% for Q235 steel in 1.0 M HCl with 60 mg L^{-1} Inhi-Ph and Inhi-BrPh. This results obtained from EIS are in good agreement with the results obtained from weight loss and potentiodynamic polarization measurement.

3.5 Adsorption isotherm

The adsorption isotherm can be used to analyze the interaction of the Inhi-Ph and Inhi-BrPh on Q235 steel surface. Usually, both the physisorption and chemisorption as two main types of interaction are used to describe the adsorption of inhibitor molecules on metal surface.

In order to confirm the reasonable adsorption isotherm for Inhi-Ph and Inhi-BrPh on Q235 steel surface in HCl solution, various isotherms including Frumkin, Flory–Huggins, Temkin and Langmuir adsorption isotherms are employed based on the data of weight loss measurement according to Figure 3. Fitting results reveal that the adsorption of Inhi-Ph and Inhi-BrPh on Q235 steel surface obey Langmuir adsorption isotherm (Equation 5)[10,11]:

$$\frac{C}{\theta} = \frac{1}{K_{\mathrm{ads}}} + C \qquad (5)$$

where C is the concentration of Inhi-Ph and Inhi-BrPh, K_{ads} is the adsorption equilibrium constant and θ is the surface coverage. The surface coverage (θ) for different concentrations of Inhi-Ph and Inhi-BrPh in 1.0 M HCl is obtained based on the following equation by weight loss measurement:

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

where v_0 and v are corrosion rate of the Q235 steel in HCl solution without and with different concentrations of Inhi-Ph and Inhi-BrPh.

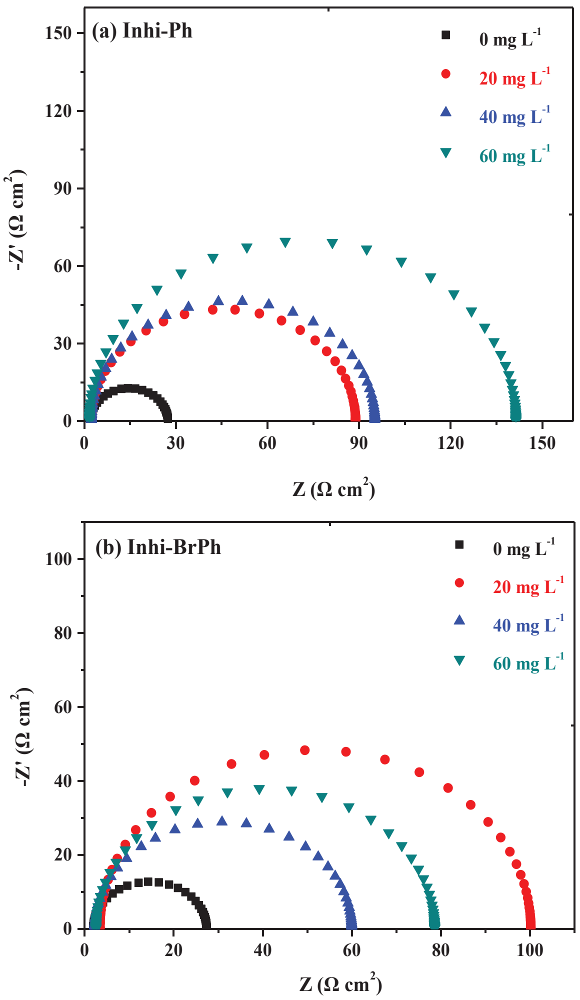

Figure 5: Nyquist diagrams of Q235 steel in 1.0 M HCl solution with different concentrations of Inhi-Ph (a) and Inhi-BrPh (b) at 30°C.

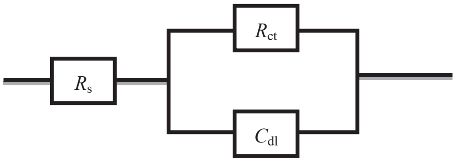

Figure 6: Equivalent circuit mode.

Table 5: The electrochemical parameters of impedance and the corresponding inhibition efficiency of Q235 steel in 1.0 M HCl with various concentration of Inhi-Ph and Inhi-BrPh at 30°C.

Inhibitor	C (mg L^{-1})	R_p (Ω cm^{-2})	C_{dl} (μF cm^{-2})	η_E (%)
Blank solution	0	25.44	78.36	—
Inhi-Ph	20	86.53	20.43	70.60
	40	92.89	19.48	72.61
	60	139.7	10.14	81.79
Inhi-BrPh	20	57.75	60.02	55.95
	40	76.02	38.59	66.54
	60	96.77	25.37	73.71

The plots of C/θ versus C yield the straight lines shown in Figure 7. While the strong correlation (R^2>0.9959) suggest that the adsorption of Inhi-Ph and Inhi-BrPh on Q235 steel surface in 1.0 M HCl obey Langmuir adsorption isotherm. The standard free energy of adsorption (ΔG^0_{ads}) can be determined from the intercepts of the straight lines according to the following expression:

$$K_{\mathrm{ads}}=\frac{1}{55.5}\exp\left(-\frac{\Delta G^0_{\mathrm{ads}}}{RT}\right) \tag{7}$$

where R=8.314 J K^{-1} mol^{-1} is the gas constant, 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, the obtained values of K_{ads} and ΔG^0_{ads} for Inhi-Ph and Inhi-BrPh were listed in Table 6, as can be seen that the calculated values of ΔG^0_{ads} of Inhi-Ph and Inhi-BrPh all lower than -40.00 kJ mol^{-1}, which are -42.51 and -42.93 kJ mol^{-1}, and it also indicates that the adsorption processes of Inhi-Ph and Inhi-BrPh on Q235 steel surface in 1.0 M HCl belongs to chemical adsorption [10,17-18].

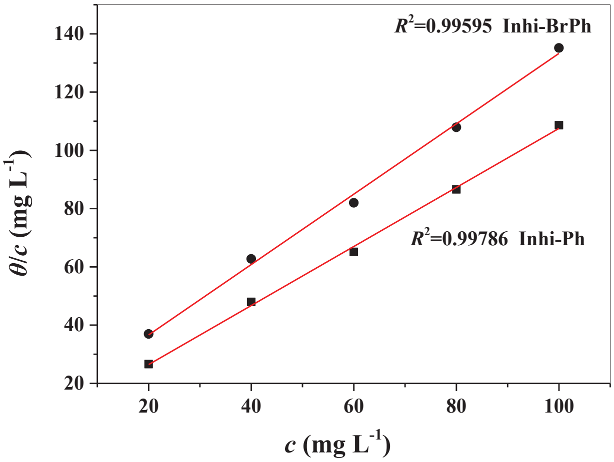

Figure 7: Langmuir adsorption isotherm for Inhi-Ph and Inhi-BrPh on Q235 steel in 1.0 M HCl at 30°C.

Table 6: The adsorption parameters for Inhi-Ph and Inhi-BrPh on Q235 steel in 1.0 M HCl at 30°C.

Inhibitor	ΔG^0_{ads} (kJ mol^{-1})	M	R^2	K_{ads} (L mol^{-1})
Inhi-Ph	-42.51	386	0.9992	3.807×10^5
Inhi-BrPh	-42.93	544	0.9985	4.503×10^5

3.6 Effect of temperature, HCl concentration and storage time

According to potentiodynamic polarization measurement, the effects of temperature (T, °C), HCl concentration (c_{HCl}, M) and storage time (t, h) on the corresponding inhibition efficiency (η_p(%)) were presented in Figure 8 (a), (b) and (c). From Figure 8 (a), as can be seen in 1.0 M HCl with 60 mg L^{-1} Inhi-Ph and Inhi-BrPh, the inhibition efficiency decrease with temperature increasing, with temperature increase from 25°C to 45°C that the inhibition efficiency of Inhi-Ph and Inhi-BrPh drop from 96.17%, 76.04% (25°C) to 91.08%, 60.54% (45°C), respectively. The decrease of inhibition efficiency is due to the increasing of inhibitor molecules desorption from Q235 steel surface in 1.0 M HCl.

Meanwhile, from Figure 8 (b), it is obvious that the inhibition efficiency decrease with HCl concentration increasing, the minimum inhibition efficiency for Inhi-Ph and Inhi-BrPh (60 mg L^{-1}) on Q235 steel in 5.0 M HCl at 30°C are 70.01% and 56.33%. The decrease of the inhibition efficiency from 98.86%, 93.67% (0.1 M HCl) to 70.01%, 56.33% (5.0 M HCl) are contributed to the increase of hydrogen ion concentration. The similar results were reported by Lu and Su [19-20].

Additional, according to the effect of storage time on inhibition efficiency from Figure 8 (c), it is quite clear that the inhibition efficiency slightly fluctuate with storage time changing. At 30°C, in 1.0 M HCl with 60 mg L^{-1} Inhi-Ph and Inhi-BrPh at 168 hours later, the inhibition efficiency still up to 94.90% and 76.91%, respectively. The results show that Inhi-Ph and Inhi-BrPh can act as the long-acting corrosion inhibitor, and which further reveal that Inhi-Ph can exhibit the excellent corrosion inhibition for Q235 steel in HCl solution. Compare the ionic compounds of N,N-diethylammonium O,O'-di(p-methoxyphenyl) dithiophosphate in our previous work [11] with the covalence compounds of Inhi-Ph and Inhi-BrPh in this work, it is clearly that the covalence compounds of Inhi-Ph and Inhi-BrPh can stable present in HCl solution.

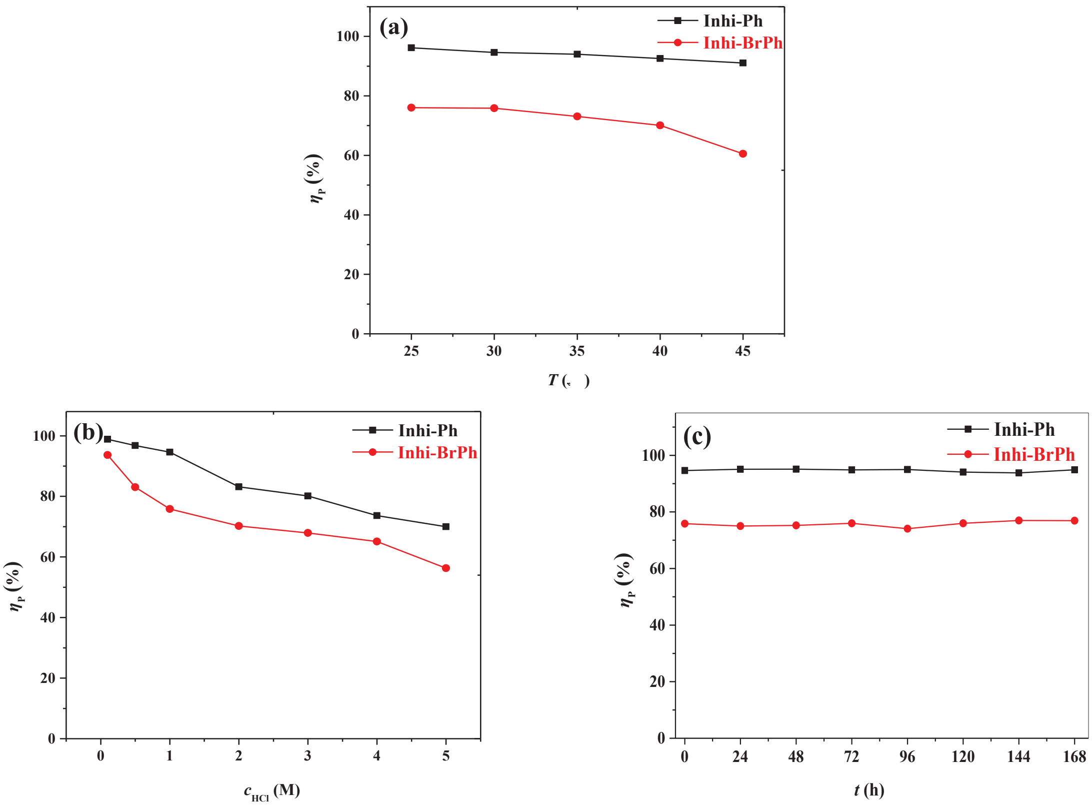

Figure 8: The effect of temperature (a), HCl concentration (b), and storage time (c) on inhibition efficiency from potentiodynamic polarization measurement.

4 Conclusions

In conclusion, the new corrosion inhibitors of S-4-methylbenzyl-O,O'-di(phenyl) dithiophos- phate (Inhi-Ph) and S-4-methylbenzyl-O,O'-di(4-bromophenyl) dithiophosphate (Inhi-BrPh) were synthesized and confirmed by elemental analysis, FT-IR, ^{1}H, ^{13}C and ^{31}P NMR in this work. The evaluation of corrosion inhibition performance show that the corrosion inhibitors of Inhi-Ph and Inhi-BrPh for Q235 steel in HCl solution both are mixed-type inhibitor, the inhibition efficiency increase with Inhi-Ph and Inhi-BrPh concentration increasing, decrease with HCl concentration and temperature increasing. In addition, the adsorption of Inhi-Ph and Inhi-BrPh on Q235 steel surface obeys Langmuir isotherm, which belongs to chemical adsorption.

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