

Short Communication

Study on corrosion inhibition of Q235 steel in HCl solution by 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate

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The corrosion inhibition of Q235 steel in HCl solution by 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (HMTADE-2HClO₄) has been studied using potentiodynamic polarization, weight loss measurement and microstructure analysis. Measurements results suggest that HMTADE-2HClO₄ is an effective mixed-type inhibitor, the inhibition efficiency increase with HMTADE-2HClO₄ concentration increasing, decrease with temperature and HCl concentration increasing, and slightly fluctuate with storage time changing. The experimental results are further suggest that the adsorption of HMTADE-2HClO₄ on Q235 steel surface obeys Langmuir isotherm, which is a mixed adsorption involving both physisorption and chemisorption.

Keywords: Macrocyclic; Corrosion; Inhibitor; Polarization; Adsorption.

1. INTRODUCTION

Corrosion is an afflicting problem associated with every use of metals, especially in acidic environment. It is well known that the use of inhibitors for the control of metals corrosion is a simple and accepted method [1-2]. Large numbers of the excellent corrosion inhibitors are organic compounds containing electronegative atoms such as N, P, S and O atoms, the unsaturated bonds including C=C bonds, C≡C bonds and C=N bonds, and the plane conjugated systems involving all kinds of aromatic cycles [3-4]. The corrosion inhibition of reported organic inhibitors is mainly because of physical or

chemical adsorption resulting from the interaction of polar centers of the inhibitor's molecule with active sites on metal surface [5-7]. In the past decades, a considerable amount of interest has been generated to evaluate the potential of macrocyclic compounds as inhibitors for metals in acid medium, such as the macrocyclic compounds of porphyrins [8], phthalocyanines [8], 1,4,8,11-tetraazacyclotetradecane[9], 2,3:9,10-dibenzo-7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraazacyclotetradeca-1,7-diene[10], 7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraazacyclotetradeca-1,7-diene [10], 7,8:15,16-dibenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane[10], 2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane [10], 1,3,4-thiadiazole moiety including (2,3,8,9-dibenzo-4,7-dioxa-13-thia-11,12-diazabicyclo [8.2.1] trideca-10,12-diene [11], 2,3,11,12-dibenzo-4,7,10-trioxa-16-thia-14,15-diazabicyclo[11.2.1]hexadeca-13,15-diene [11], 2,3,14,15-dibenzo-4,7,10,13-tetraoxa-19-thia-17,18-diazabicyclo[14.2.1]nonadeca-16,18-diene[11], 2,3,17,18-dibenzo-4,7,10,13,16-pentaoxa-22-thia-20,21-diazabicyclo[17.2.1]docosa-19,21-diene [11], 2,3,20,21-dibenzo-4, 7,10,13,16,19-hexaoxa-25-thia-23,24-diazabicyclo [20.2.1] pentacoza-2,24-diene [11]. Based on these literatures [8-11], it is obvious that the macrocyclic compounds contain polar atom(s) in their structure which can constitute a potential class of corrosion inhibitors. In an attempt to explore more macrocyclic compounds as effective corrosion inhibitors, the present work would be synthesized the macrocyclic compound of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (HMTADE-2HClO₄), and evaluated the corrosion inhibition of Q235 steel in HCl solution by HMTADE-2HClO₄.

2. MATERIALS AND METHODS

2.1 Materials

The used reagents of acetone (CH₃COCH₃), ethylenediamine (H₂NCH₂CH₂NH₂), perchloric acid (72%, HClO₄) and hydrochloric acid (37%, HCl) were purchased from Kelong Chemical Reagent Co. Ltd. (Sichuan, China), which are analytically pure. The samples and working electrode for corrosion inhibition performance evaluating were prepared by Q235 steel. The rectangular samples with dimension 50 mm×20 mm×5 mm were used in weight loss measurement. Before testing, all of the samples were mechanically abraded with emery paper up to 1200 grit, rinsed with distilled water, degreased in acetone. Potentiodynamic polarization measurement was conducted by three-electrode system consisting of Q235 steel working electrode with an exposed area in 0.5024 cm², a graphite electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. Moreover, the testing solutions of aggressive medium were prepared by HCl (37%) and deionized water. During the whole evaluating experiment process, the temperature of different solutions was controlled by DF-101S water thermostat (China).

2.2 Synthesis

The macrocyclic compound of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (HMTADE-2HClO₄) was synthesized by reaction of acetone, perchloric acid

and ethylenediamine in the laboratory based on following procedures as described in literature [12]. Firstly, 0.66 mol (4.0 g) ethylenediamine and 100 mL acetone are mixed and added in a 500 mL beaker. Then, the mixed solution is stirred while 0.66 mol (9.284 g) HClO_4 (72%, wt.) is added slowly from a dropping funnel over a 45 min period. After dripping, the solution is stirred rapidly and allowed to cool to room temperature. And then the fine white crystalline compound is removed by filtration, washed thoroughly with acetone, and dried in a vacuum drying oven. And the synthetic process is shown in figure 1. After inhibitor prepared, which would be characterized by elemental analysis (Carlo Erba 1106 instrument, Italy), and the result was listed in table 1. The melting point of HMTADE- 2HClO_4 is 162-163°C. The calculated and observed elemental analysis data for the synthesized corrosion inhibitor ($\text{C}_{16}\text{H}_{34}\text{Cl}_2\text{N}_4\text{O}_8$) are in good agreement and fit well the structure of HMTADE- 2HClO_4 showing in figure 1.

Table 1. Elemental analysis of HMTADE- 2HClO_4

Molecular formula	Molecular weight	Anal. Found			Anal. Calcd		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
$\text{C}_{16}\text{H}_{34}\text{Cl}_2\text{N}_4\text{O}_8$	480	40.09	7.11	11.69	40.00	7.08	11.67

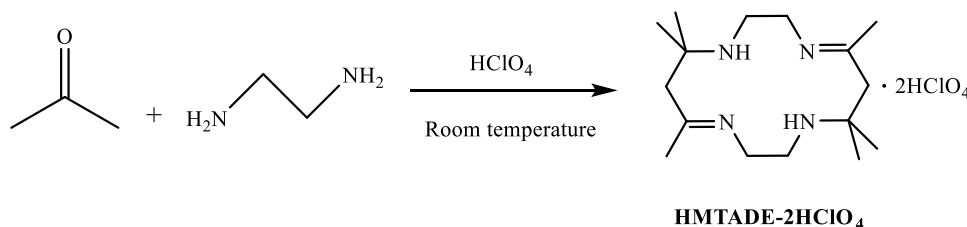


Figure 1. The synthetic reaction and chemical structure of HMTADE- 2HClO_4

2.3 Weight loss measurement

According to weight loss measurement, the corrosion rate (v) and corresponding inhibition efficiency (IE_W (%)) were obtained based on equation 1 and 2 [3, 13-14]. In the two equations, m_1 and m_2 are the mass of the Q235 steel samples before and after corrosion testing, Δm is average weight loss, S is the total surface area of the Q235 steel sample, t is the immersion time, v and v_0 are corrosion rate of Q235 steel samples corrosion in HCl solution with and without HMTADE- 2HClO_4 .

$$v = \frac{m_1 - m_2}{St} = \frac{\Delta m}{St} \quad (1)$$

$$IE_W (\%) = \frac{v_0 - v}{v_0} \times 100\% \quad (2)$$

2.4 Potentiodynamic polarization measurement

The corrosion inhibition evaluating by potentiodynamic polarization measurement was carried out by CHI 660D electrochemical workstation. This measurement was conducted by three-electrode

system, and all potential in this study were referred to the saturated calomel electrode (SCE). The potential sweep rate was 0.5 mV s^{-1} . Corrosion current density (i) was determined from the intercept of extrapolated cathodic and anodic Tafel lines at the corrosion potential (E). The corresponding inhibition efficiency ($IE_{\text{Tafel}}(\%)$) based on Tafel curves were calculated as equation 3 [15-16]. In this equation, i and i_0 are the corrosion current density for Q235 steel in HCl solution with and without HMTADE-2HClO₄.

$$IE_{\text{Tafel}}(\%) = \frac{i_0 - i}{i_0} \times 100\% \quad (3)$$

2.5 Microstructure analysis

Microstructure analysis was carried out using a Nikon Model Epiphot 200 optical microscope equipped with 3CCD Sony Color Video Camera. Before each electrochemical evaluating experiment, the Q235 steel electrode was polished with emery paper up to 1200 grit, and the photomicrographs were taken at points of interest.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurement

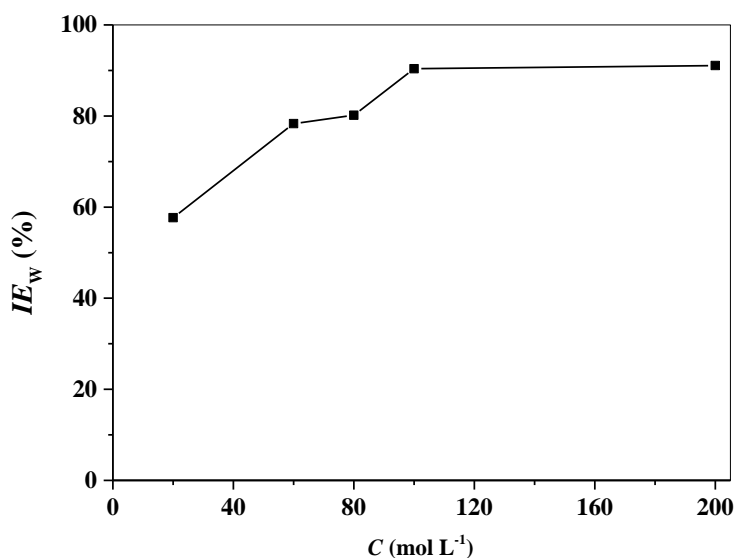


Figure 2. The relationships between HMTADE-2HClO₄ concentration and the inhibition efficiency for Q235 steel in 1.0 M HCl at 30 °C by weight loss measurement

According to weight loss measurement, the relationships between inhibitor concentration and corresponding inhibition efficiency ($IE_w(\%)$) for Q235 steel in 1.0 M HCl at 30 °C is exhibited in figure 2. From this figure, it can be found that the inhibition efficiency obvious increase with concentration of HMTADE-2HClO₄ increase from 20 mg L⁻¹ to 100 mg L⁻¹, and which changes slightly as the inhibitor concentration more than 100 mg L⁻¹. This is due to the surface coverage of the

HMTADE-2HClO₄ on Q235 steel surface increase with HMTADE-2HClO₄ concentration increasing. At the concentration of HMTADE-2HClO₄ in 100 mg L⁻¹ and 200 mg L⁻¹, the inhibition efficiency are 90.39% and 91.08%, which further demonstrate that the HMTADE-2HClO₄ can act as an effective corrosion inhibitor for Q235 steel in 1.0 M HCl. The corrosion inhibition action of Q235 steel in HCl solution by HMTADE-2HClO₄ is also thought to result from the strong adsorption of the macrocyclic compound on Q235 steel surface, which can be attributed to the presence of nitrogen as donor atoms in inhibitor molecular structure. The donor atoms function as adsorption centers on Q235 steel surface to form a protective layer for retarding the dissolution of Q235 steel by blocking its active corrosion sites. It concludes that the strong interaction with HMTADE-2HClO₄ and Q235 steel surface to form a protective layer is attributed to the chelation and coordination of nitrogen atoms with Q235 steel surface atoms.

3.2 Potentiodynamic polarization measurement

The polarization curves for Q235 steel in 1.0 M HCl with various concentrations of HMTADE-2HClO₄ at 30 °C obtained by potentiodynamic polarization measurement are presented in figure 3. Based on this method, the electrochemical parameters for Q235 steel corrosion, involving the current density i ($\mu\text{A cm}^{-2}$), potential E (V, vs SCE), cathodic and anodic Tafel slopes b_c and b_a (mV dec⁻¹), and corresponding inhibition efficiency ($IE_{\text{Tafel}}(\%)$) are listed in table 2.

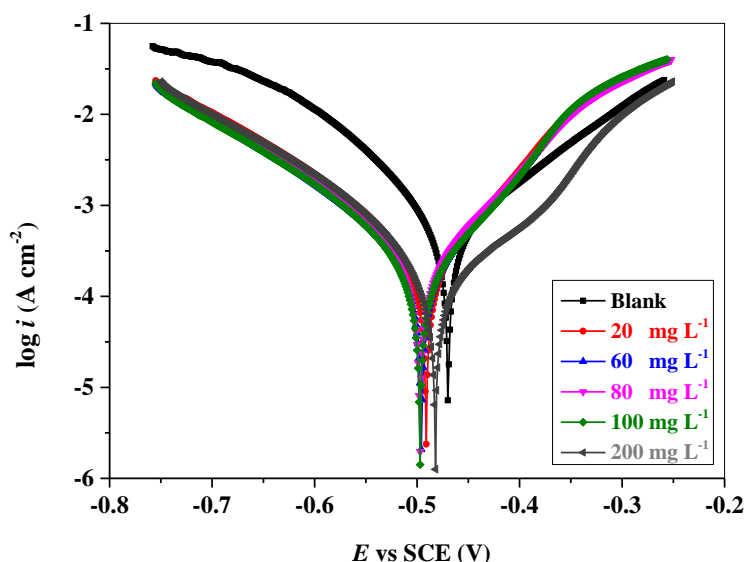


Figure 3. The polarization curves for Q235 steel in 1.0 M HCl with various concentrations of HMTADE-2HClO₄ at 30°C

According to table 2 and figure 3, it can be found that both the anodic and cathodic curves shift to lower current densities after addition of HMTADE-2HClO₄ in 1.0 M HCl, which indicate that HMTADE-2HClO₄ can reduce the Q235 steel anodic dissolution and retard the H⁺ reduction. From table 2, it is obvious that the corrosion current density is much smaller in the presence of HMTADE-

2HClO₄ comparing with that in the absence of HMTADE-2HClO₄ for Q235 steel in 1.0 M HCl, and decreases with HMTADE-2HClO₄ concentration increasing. Anodic Tafel slopes increase with concentration of HMTADE-2HClO₄ increase from 20 mg L⁻¹ to 200 mg L⁻¹, and cathodic Tafel slopes showing a slightly fluctuate with HMTADE-2HClO₄ concentration changing. Moreover, the inhibition efficiency increase with HMTADE-2HClO₄ concentration increasing, the increasing is due to the increase of the blocked fraction of the Q235 steel surface by adsorption. At the concentration of HMTADE-2HClO₄ in 100 mg L⁻¹ and 200 mg L⁻¹, the inhibition efficiencies are 92.69% and 92.86%. The inhibition effect enhances with the increase of HMTADE-2HClO₄ concentration, resulting from the adsorption of HMTADE-2HClO₄ molecules on the Q235 steel surface. It is postulated that the adsorption of HMTADE-2HClO₄ on Q235 steel surface is due to the chelation and coordination of nitrogen atoms with Q235 steel surface atoms. The donor atoms of nitrogen atoms as function as adsorption centers on Q235 steel surface to form a protective layer for retarding the dissolution of Q235 steel by blocking its active corrosion sites. Furthermore, the effective corrosion inhibition maybe contribute to the cooperative formation mechanism of adsorption and block effect resulting from the macrocyclic molecular structure containing multiple methyl can block the H⁺ tack the Q235 steel surface and reduces the corrosive attraction of steel in HCl solution.

Table 2. The polarization parameters and corresponding inhibition efficiency for Q235 steel in 1.0 M HCl with various concentrations of HMTADE-2HClO₄ at 30 °C

<i>C</i> (mg L ⁻¹)	<i>E</i> (V)	<i>b_c</i> (mV dec ⁻¹)	<i>b_a</i> (mV dec ⁻¹)	<i>i</i> (μA cm ⁻²)	<i>IE</i> _{Tafel} (%)
0	-0.470	114.76	83.03	1257.8	-
20	-0.491	118.36	74.34	453.4	63.95
60	-0.496	119.09	91.84	224.4	82.16
80	-0.497	122.38	93.42	196.6	84.37
100	-0.497	117.63	95.47	91.90	92.69
200	-0.482	112.57	107.9	89.74	92.86

In addition, according to the change of corrosion potential for Q235 steel in 1.0 M HCl with various concentrations of HMTADE-2HClO₄ at 30 °C by potentiodynamic polarization measurement, which suggest that HMTADE-2HClO₄ is an effective mixed-type inhibitor [17-18]. This present result is similar to the result reported by Khaled[9] and Ajmal [10], that the type of reported macrocyclic compounds also belong to mixed-type inhibitor.

3.3 Adsorption isotherm

The adsorption isotherm can be used to study the interaction of the HMTADE-2HClO₄ 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 HMTADE-2HClO₄ on Q235 steel surface in HCl solution, different isotherms involving Langmuir, Temkin, Frumkin and Flory–Huggins adsorption isotherms [2, 3] are employed based on the data of weight loss measurement, and the Langmuir adsorption isotherm show

in equation 4, [3, 19-20]. From equation 4, C is the HMTADE-2HClO₄ concentration, K_{ads} is the adsorption equilibrium constant and θ is the surface coverage. The surface coverage (θ) for various concentrations of HMTADE-2HClO₄ in 1.0 M HCl are obtained according to equation 5, in this equation, v and v_0 are corrosion rate of the Q235 steel in HCl solution with and without HMTADE-2HClO₄, respectively.

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (4)$$

$$\theta = \frac{v_0 - v}{v_0} \quad (5)$$

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{\text{ads}}^0}{RT}\right) \quad (6)$$

In order to obtain the standard free energy (ΔG_{ads}^0) of HMTADE-2HClO₄ adsorption on Q235 steel surface. The plots of C/θ versus C yield the straight line is shown in figure 4. The strong correlation ($R^2 > 0.996$) reveals that the adsorption of HMTADE-2HClO₄ on aQ235 steel surface in 1.0 M HCl obeys Langmuir adsorption isotherm. A similar result was reported by Bentiss [11], and the adsorption of all the reported macrocyclic compounds was found to follow the Langmuir adsorption isotherm.

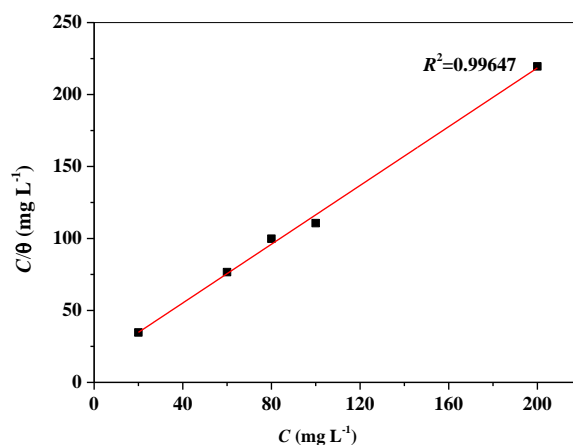


Figure 4. Langmuir adsorption isotherm for HMTADE-2HClO₄ on Q235 steel in 1.0 M HCl at 30 °C

Meanwhile, the standard free energy of adsorption can be determined from the intercepts of the straight lines according to equation 6, in this equation, R is the gas constant (8.314 J K⁻¹ mol⁻¹), T is absolute temperature and 55.5 is the molar concentration of water in the solution expressed in molarity units (mol L⁻¹).

Based on equation 6, the values of standard free energy (ΔG_{ads}^0) for HMTADE-2HClO₄ adsorption on Q235 steel is obtained, -36.38 kJ mol⁻¹, which slightly higher than -40.00 kJ mol⁻¹. It indicates that the adsorption of HMTADE-2HClO₄ molecules on Q235 steel surface is not merely physisorption or chemisorption, which is a complex comprehensive kind of interaction involving both physisorption and chemisorption (mixed adsorption) [21-23].

3.4 Effect of temperature, HCl concentration and storage time

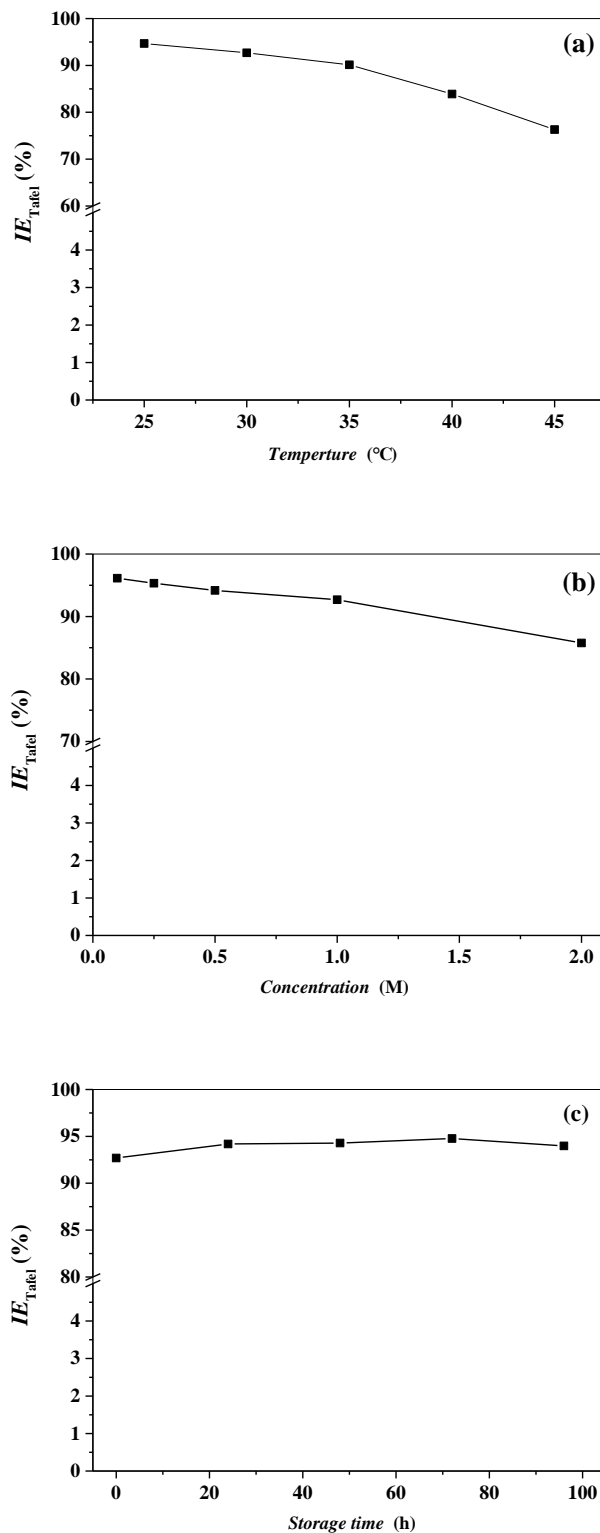


Figure 5. The effect of temperature (a), HCl concentration (b) and storage time (c) on corresponding inhibition efficiency for Q235 steel in 1.0 M HCl at 30 °C by potentiodynamic polarization measurement

To investigate and evaluate the corrosion inhibition of Q235 steel in HCl solution by HMTADE-2HClO₄, based on equation 2, the potentiodynamic polarization measurement is employed to study the relationships between temperature, HCl concentration, storage time and corresponding inhibition efficiency ($IE_{Tafel}(\%)$) for Q235 steel in 1.0 M HCl at 30 °C, the results are presented in figure 5 (a), (b) and (c), respectively.

From figure 5 (a), it can be found that the inhibition efficiency decrease with temperature of testing solution increasing, with temperature increase from 25 °C to 45 °C that the inhibition efficiency drop from 94.67% at 25 °C to 76.31% at 45 °C. The decrease of inhibition efficiency is due to the desorption of HMTADE-2HClO₄ molecules from the Q235 steel surface occurs at a faster rate at high temperature. This result show the fact that the inhibitor film formed on Q235 steel surface is less protective in nature at high temperature.

According to figure 5 (b), it is obvious that the inhibition efficiency decrease with HCl concentration increasing, and the minimum inhibition efficiency of HMTADE-2HClO₄ for Q235 steel in 2.0 M HCl at 30 °C is 85.76%. The decrease of the inhibition efficiency from 96.13% (0.1 M HCl with 100 mg L⁻¹ HMTADE-2HClO₄) to 85.76% (2.0 M HCl with 100 mg L⁻¹ HMTADE-2HClO₄) is contributed to the increase of H⁺ concentration. The similar result was reported by Zou [24].

Additional, based on the effect of storage time on inhibition efficiency from figure 5 (c), the inhibition efficiency slightly fluctuate with storage time changing. At 30 °C, in 1.0 M HCl with 100 mg L⁻¹ HMTADE-2HClO₄ at 96 hours later, the inhibition efficiency still up to 93.98%. The same tendency of storage time effect on inhibition efficiency was reported by Wei [25]. Result shows that the macrocyclic compound of HMTADE-2HClO₄ can stable present in HCl solution, and further confirm that HMTADE-2HClO₄ can act as an excellent long-acting corrosion inhibitor for Q235 steel in HCl solution.

3.5 Microstructure analysis

In order to further confirm the corrosion inhibition of Q235 steel in HCl solution by HMTADE-2HClO₄, the microstructure analysis was carried out by optical microscope to observe the microstructure of Q235 steel electrode surface before and after corrosion in 1.0 HCl with different concentration of HMTADE-2HClO₄, and the micrographs are presented in figure 6 (a)-(f).

Figure 6 (a) shows the surface morphology of the Q235 steel electrode before immersion and corrosion in HCl solution, which mostly seems smooth with only some nicks from the electrode surface polishing by emery paper. However, as can be seen from figure 6 (b), after the electrode corrosion in 1.0 M HCl as blank solution, which is strongly corroded by the aggressive solution. The surface of the electrode is too bumpy and rough, and there some gullies present on surface. This micrograph reveals that the Q235 steel electrode surface is highly corroded and damaged in 1.0 M HCl without HMTADE-2HClO₄. In addition, in 1.0 M HCl with 20 mg L⁻¹ HMTADE-2HClO₄, after electrochemical evaluating experiment, the surface morphology of the electrode is shown in figure 6 (c). According to this figure, it also can be found that the surface of the electrode is bumpy and rough, and there are only some unsharp gullies on surface. Figure 6 (c) shows that the low concentration of

HMTADE-2HClO₄ in HCl solution cannot effectively prevent the corrosion of Q235 steel in HCl solution. In contrast, in HCl solution with the higher concentration of HMTADE-2HClO₄ (100 mg L⁻¹), the electrode surface is too smooth and much less damaged (showing in figure 6 (d)), which further confirms the inhibition action and adsorption of HMTADE-2HClO₄ on Q235 steel surface. Moreover, the microstructure analysis results are in good agreement with the results achieved from potentiodynamic polarization measurement and weight loss measurement.

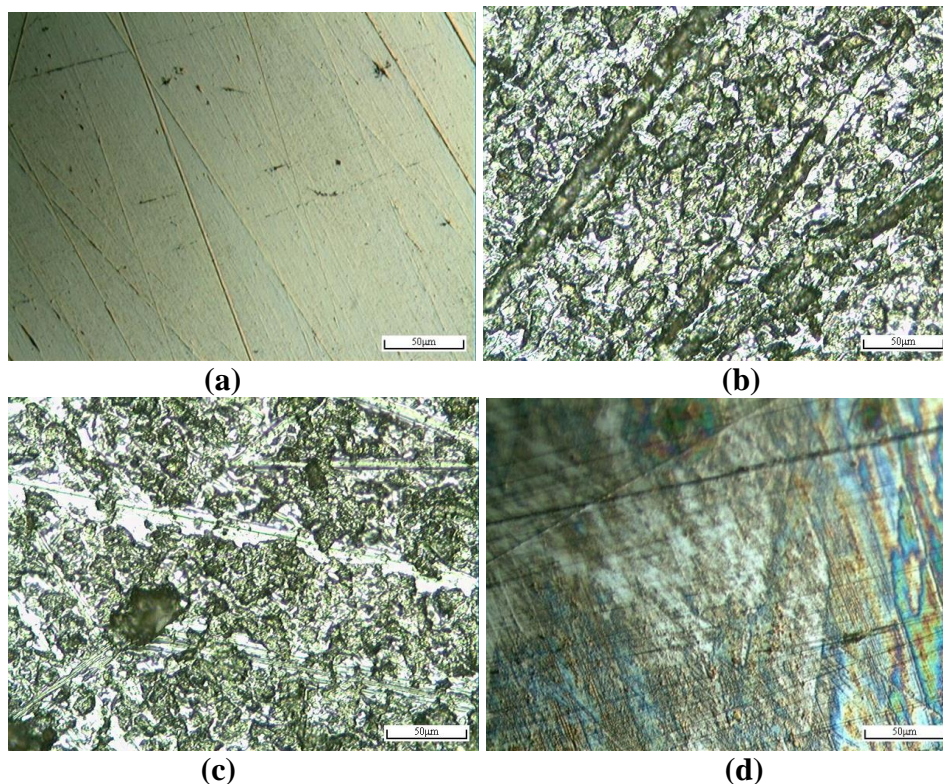


Figure 6. Optical micrographs of Q235 steel electrode before and after corrosion in 1.0 HCl with various concentration of HMTADE-2HClO₄: Before corrosion (a), After corrosion in 1.0 HCl (blank solution) (b), in 1.0 HCl with 20 mg L⁻¹ HMTADE-2HClO₄ (c) and 1.0 HCl with 100 mg L⁻¹ HMTADE-2HClO₄ (d)

4. CONCLUSIONS

In conclusion, the corrosion inhibition of synthesized effective inhibitor of the 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (HMTADE-2HClO₄) was evaluated by potentiodynamic polarization measurement, weight loss measurement and microstructure analysis. The present study show that HMTADE-2HClO₄ is an effective mixed-type inhibitor, and the adsorption of HMTADE-2HClO₄ on Q235 steel surface in HCl solution obeys Langmuir isotherm, which is a mixed adsorption involving both physisorption and chemisorption.

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