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Corrosion inhibition of Q235 steel in HCl medium by 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane

Wan Gou[1], *Chuan Lai*[1], *Zhen Xiang*[2,*], *Li Yang*[1], *Ping Zhang*[1], *Wenke Xie*[1],
Luo Chen[1], *Guangbing Luo, Xiaolong Li*[1], *Zongxin Chen*[1]

[1] School of Chemistry and Chemical Engineering, Eastern Sichuan Sub-center of National Engineering Research Center for Municipal Wastewater Treatment and Reuse, Sichuan University of Arts and Science, Dazhou 635000, PR China
[2] College of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Zigong 643000, PR China
[*]E-mail: tougaolc@163.com

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The corrosion inhibition of Q235 steel in HCl solution by 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane (HMETD) as a fully saturated macrocyclic has been studied using potentiodynamic polarization, weight loss measurement and microstructure analysis. Results indicate that the saturated macrocyclic inhibitor of HMETD is an effective mixed-type inhibitor, the inhibition efficiency slightly fluctuate with storage time changing, increase with HMETD concentration increasing, decrease with HCl concentration and temperature increasing. The adsorption of HMETD on Q235 steel surface obeys Langmuir isotherm, which is a mixed adsorption containing physisorption and chemisorption.

Keywords: Inhibitor; Acid; Corrosion; Adsorption; Steel; Macrocyclic.

1. INTRODUCTION

Acid solutions including different concentration of hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) medium are generally used for cleaning, pickling and chemical decaling in several industrial processes [1-3]. Especially the different concentrations of HCl are usually widely used in the pickling processes of various metals involving different steels, alloys, copper, etc. It is well known that the corrosion and dissolution are prominent problems for metals using acid medium for pickling, and everyone knows that use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent metal corrosion and dissolution [4-6]. During the past decade, a large number of organic compounds have been presented as effective inhibitors and used in several industrial processes to control metals dissolution and corrosion [7-9]. As a fact, the organic compounds containing nitrogen and sulphur atoms often can be act as effective corrosion inhibitors in acid media. For example, the amines and heterocyclic compounds with nitrogen toms as effective corrosion inhibitors for steel in aggressive acidic media have been reported by several workers [10-14]. But the fully saturated macrocyclic of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (HMETD, see Figure 1) as inhibitor containing multiple nitrogen atoms have not been reported. In our previous work, we have found that the unsaturated macrocyclic compound of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (HMTADE-2$HClO_4$) can act as an effective inhibitor for Q235 steel in HCl solution. The aim of present work is to extend the investigation by studying the inhibitive properties of the fully saturated macrocyclic compound of HMETD on the corrosion of Q235 steel in HCl medium using potentiodynamic polarization, weight loss measurement and microstructure analysis.

2. MATERIALS AND METHODS

2.1 Materials

Reagent: All the used reagents of acetone (CH_3COCH_3), ethylenediamine ($H_2NCH_2CH_2NH_2$), perchloric acid (72%, $HClO_4$), methanol (CH_3OH), sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH), hydrochloric acid (37%, HCl) and sulfuric acid (98%, H_2SO_4) were purchased from Kelong Chemical Reagent Co. Ltd. (Sichuan, China)， which are analytically pure.

Electrode and samples: The working electrode and test samples used in this work were prepared by Q235 steel. The rectangular specimens with dimension 50 mm×20 mm×5 mm were used in weight loss measurement. Before weight loss measurement, all the test specimens were pre-treated prior to the experiment by grinding with emery paper (grade 240, 600, 800, 1000 and 1200) then cleaned with double distilled water, degreased with acetone and dried. Potentiodynamic polarization measurement were conducted by three-electrode system consisting of Q235 steel working electrode with an exposed area in 0.5024 cm^2, a graphite counter electrode and a saturated calomel reference electrode (SCE).

Test solution: The different concentrations HCl and H_2SO_4 solution as aggressive medium were prepared by HCl (37%), H_2SO_4 (98%) and deionized water. During the whole testing process, the temperature of aggressive solution was controlled by DF-101S water thermostat (China).

2.2 Synthesis

In order to prepare the inhibitor of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (HMETD), the precursor compound of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (HMTADE-2$HClO_4$) was synthesized by the reaction of acetone, ethylenediamine and perchloric acid ($HClO_4$) reported by Douglas [15]. After precursor compound prepared, 50.4 g (0.105 mol) HMTADE-2$HClO_4$ was dissolved in 200 mL methanol (CH_3OH) in a beaker (1000 mL) at room temperature. After dissolving, 11.9 g (0.315 mol) $NaBH_4$ and 8.4 g (0.21

mol) NaOH were added in alternate small portions over a 1.5 hour period under the stirring condition. This step should be conducted in a well-ventilated fume hood and in a cold-water bath to moderate the temperature. After $NaBH_4$ and NaOH were completely added, the solution is stirred for 2 hour at room temperature and then heated to reflux for 30 minutes. Finally, after it is cooled, 1000 mL NaOH (2.5%) solution is added and stirred until precipitation of the inhibitor and then filtered. The white product is washed with cold water and fully dried in a vacuum. The synthesis process was shown in figure 1.

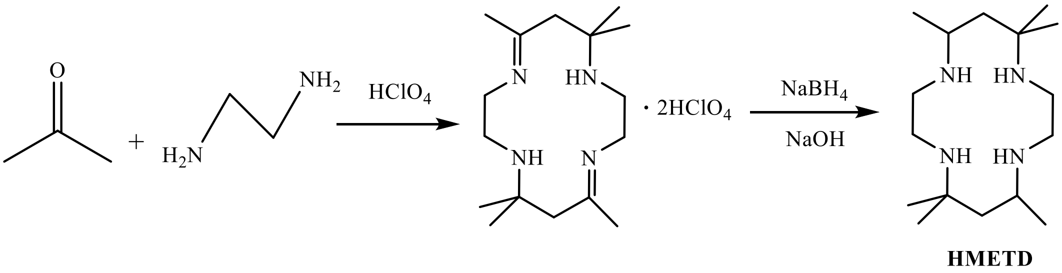


Figure 1. The synthetic reaction and chemical structures of HMETD

2.3 Experimental

Potentiodynamic polarization measurement: This measurement was done according to the method described in our previous works [16-17], and conducted by three-electrode system. The potential sweep rate was 0.5 mV s^{-1}. The corrosion current density (i) was determined from the intercept of extrapolated cathodic and anodic Tafel lines at the corrosion potential (E). Moreover, the corresponding inhibition efficiency (IE_P (%)) based on Tafel curves were calculated as equation 1 (i and i_0 are the corrosion current density of Q235 steel in HCl solution with and without HMETD).

$$IE_P(\%) = \frac{i_0 - i}{i_0} \times 100\% \qquad (1)$$

Weight loss measurement: The measurement was done also according to the method described previously [16-17], the corrosion rate (v) and corresponding inhibition efficiency (IE_W (%)) would be obtained based on equation 2 and 3, respectively. Where 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 in HCl and H_2SO_4 solution with and without HMETD.

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

$$IE_W(\%) = \frac{v_0 - v}{v_0} \times 100\% \qquad (3)$$

Microstructure analysis: Before potentiodynamic polarization measurement, the Q235 steel working electrode was polished with emery paper up to 1200 grit. The microstructure analysis was carried out using a Nikon Model Epiphot 200 optical microscope equipped with 3CCD Sony Color Video Camera. And the photomicrographs are taken at points of interest.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization measurement

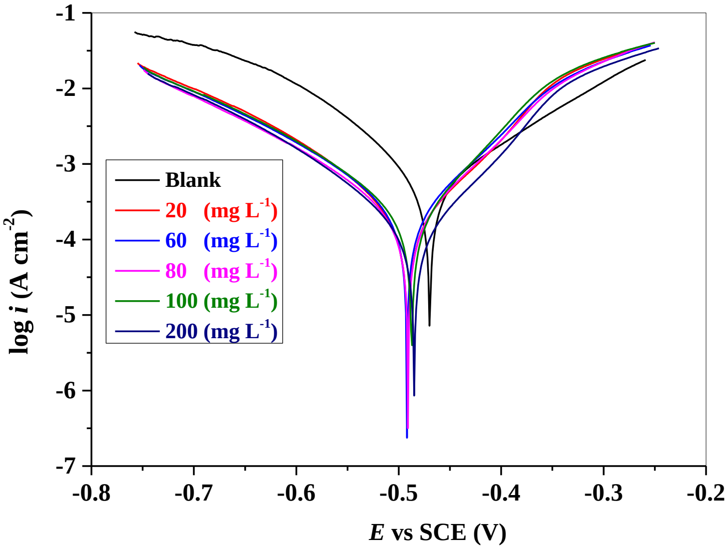


Figure 2. The polarization curves for Q235 steel in 1.0 M HCl with various concentrations of HMETD at 30 °C

Table 1. The polarization parameters and corresponding inhibition efficiency for Q235 steel in 1.0 M HCl with various concentrations of HMETD at 30 °C

C (mg L^{-1})	E (V)	b_c (mV dec^{-1})	b_a (mV dec^{-1})	i (μA cm^{-2})	IE_P (%)
0	-0.47	114.76	83.03	1257.8	-
20	-0.491	110.56	67.53	363.7	71.08
60	-0.492	119.82	74.58	201.9	83.95
80	-0.491	118.88	73.51	143.1	88.62
100	-0.487	116.09	68.02	82.7	93.43
200	-0.485	107.17	64.88	78.1	93.79

The polarization curves for Q235 steel in 1.0 M HCl with various concentrations of HMETD at 30 °C obtained by potentiodynamic polarization measurement are presented in figure 2. Based on this method, the electrochemical parameters of Q235 steel corrosion in different testing solution, including current density i (µA cm^{-2}), potential E (V, vs SCE), cathodic and anodic Tafel slopes bc and ba (mV dec^{-1}), and corresponding inhibition efficiency (IE_P (%)) are listed in table 1.

According to figure 2 and table 1, it can be found that both the anodic and cathodic curves shift to lower current densities after addition of HMETD in 1.0 M HCl, which indicates that HMETD can reduce the Q235 steel anodic dissolution and retard the H$^+$ reduction. From table 1, it is obvious that the corrosion current density is much smaller in the presence of HMETD comparing with that in the absence of HMETD for Q235 steel in 1.0 M HCl, and decreases with HMETD concentration increasing. Anodic Tafel slopes increase with concentration of HMETD increase from 20 mg L^{-1} to 200 mg L^{-1}, and cathodic Tafel slopes showing a slightly fluctuate with HMETD concentration changing. Meanwhile, the corresponding inhibition efficiency increase with HMETD concentration increasing, the increasing is due to the increase of the blocked fraction of the Q235 steel surface by adsorption. At the concentration of HMETD in 20 mg L^{-1}, 100 mg L^{-1} and 200 mg L^{-1}, the inhibition efficiencies are 71.08%, 93.43% and 93.79%. The inhibition effect enhances with the increase of HMETD concentration, resulting from the adsorption of HMETD molecules on the Q235 steel surface. It is postulated that the adsorption of HMETD 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. In addition, based on this measurement, the present result suggests that HMETD is mixed-type inhibitor, which is similar to the results reported by Khaled [18] and Ajmal [19] using the macrocyclic compounds of 1,4,8,11-tetraazacyclotetradeca-1,7-diene derivatives and 1,4,8,11-tetraazacyclotetradecane as corrosion inhibitors, that the type of reported macrocyclic compounds also belong to mixed-type inhibitor [18,19].

3.2 Weight loss measurement

3.2.1 Effect of inhibitor concentration

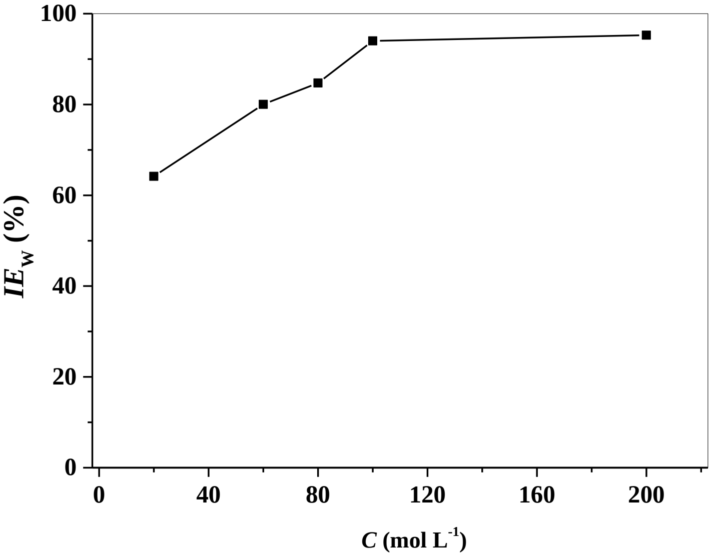


Figure 3. The relationship between HMETD concentration and corresponding inhibition efficiency for Q235 steel in 1.0 M HCl at 30 °C from weight loss measurement

According to weight loss measurement, the relationships between inhibitor concentration and corresponding inhibition efficiency (IE_W(%)) of Q235 steel in 1.0 M HCl at 30 °C is exhibited in figure 3. From this figure, it can be found that the inhibition efficiency obvious increase with concentration of HMETD 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 HMETD on Q235 steel surface increase with HMETD concentration increasing. At the concentration of HMETD in 20 mg L^{-1}, 100 mg L^{-1} and 200 mg L^{-1}, the inhibition efficiencies are 64.17%, 94.01% and 95.26%, which further demonstrate that the HMETD can act as an effective corrosion inhibitor for Q235 steel in 1.0 M HCl with the higher concentration. The corrosion inhibition action of Q235 steel in HCl solution by HMETD is also thought to result from the strong adsorption of the macrocyclic compound on Q235 steel surface by the multiple nitrogen atoms as donor atoms in inhibitor molecular structure. The variation tendency of inhibition efficiency for HMETD concentration increasing is similar to the result reported by Quraishi [20] using the macrocyclic compounds of 2,3,9,10-tetrapheny1-6,13-dithia-1,4,5,7,8,11,12,14-octaaza-cyclotetradeca-1,3,6,8,10,13-hexaene (PTAT), 3,4,9,10-tetraphenyl-7,12-dithia-1,2,5,6,8,11-hexaazacyclobidecane-2,4,7,8,10,12-hexaene (PTAB), 3,4,9,10-tetrapheny1-7,12-dioxo-l,2,5,6,8,l1-hexaazacyclobidecane hexaene (POAB) as corrosion inhibitors for mild steel in different concentrations of HCl solution. Compared the results reported by Quraishi [20] and result in this work, it can be found that the inhibition efficiency of PTAT, PTAB and POAB for mild steel in 1.0 M HCl at 40 °C are 81.40%, 79.20% and 78.10%, respectively, which further confirm that HMETD can act as effective inhibitor.

3.2.2 Effect of temperature

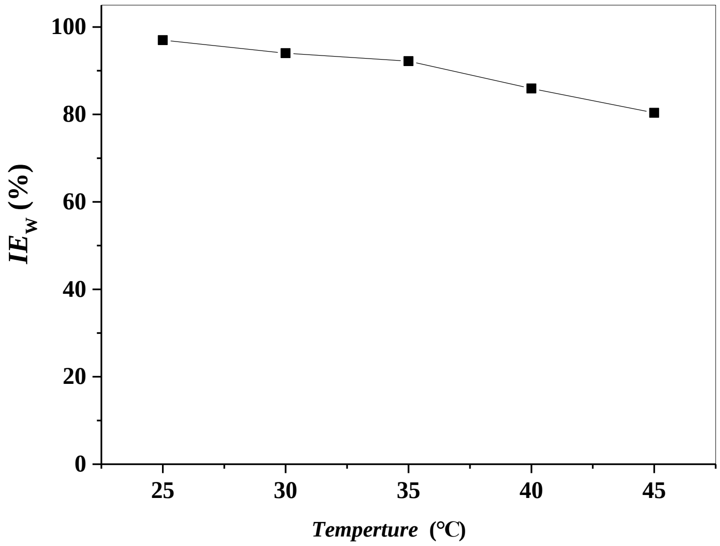


Figure 4. The relationship between temperature and corresponding inhibition efficiency for Q235 steel in 1.0 M HCl with 100 mg L^{-1} HMETD from weight loss measurement

To study the effect of temperature on the inhibition efficiency (IE_W(%)), the weight loss measurement was carried out in 1.0 M HCl with 100 mg L^{-1} HMETD at different temperatures, and the result is shown in figure 4. According to this figure, it can be found that the inhibition efficiency decrease with temperature of testing solution increasing, with temperature increase from 25 °C to 45 °C, the inhibition efficiency drop from 96.97% at 25 °C to 80.36% at 45 °C. The decrease of inhibition efficiency is due to the aggravation of inhibitor molecules desorption from Q235 steel surface [21]. This result show the fact that the inhibitor film formed on Q235 steel surface is less protective in nature at high temperature. The tendency of inhibition efficiency is similar to the tendency of 7,8:15,16-dibenzo-2,5,10,13-tetraoxo-l,6,9,14-tetraazacyclo-hexadecane (BOAH), 7,14-dimethyl-5,12,dioxo-l,4,8,ll-tetraazacyclotetradeca-l,7-diene (MOAT), 2,3:9,10-dibenzo-7,14-dime-thyl-5,12-dioxo-1,4,8,11-tetraaza-cyclotetradeca-1,7,-diene (BMOAT) and 3,4:7,8:11,12:15,16-tetra-benzo-2,5,10,13-tetraoxo-l,6,9,14-tetraazacyclohexadecane (TBOAD) as corrosion inhibitors for mild steel in 1.0 M HCl at different temperatures reported by Quraishi [20].

3.2.3 Effect of HCl concentration

Meanwhile, the relationship between HCl concentration and the corresponding inhibition efficiency (IE_W(%)) for Q235 steel corrosion in HCl solution at 30 °C is shown in figure 5. From this figure by weight loss measurement, it also can be found that the inhibition efficiency decrease with HCl concentration increasing, and the minimum inhibition efficiency of HMETD for Q235 steel in 4.0 M HCl at 30 °C is 60.77%. The decrease of the inhibition efficiency from 98.36% (0.1 M HCl with 100 mg L^{-1} HMETD) to 60.77% (4.0 M HCl with 100 mg L^{-1} HMETD) is contributed to the increase of H^+ concentration. The same tendency of HCl concentration effect on inhibition efficiency was reported by Zou [22].

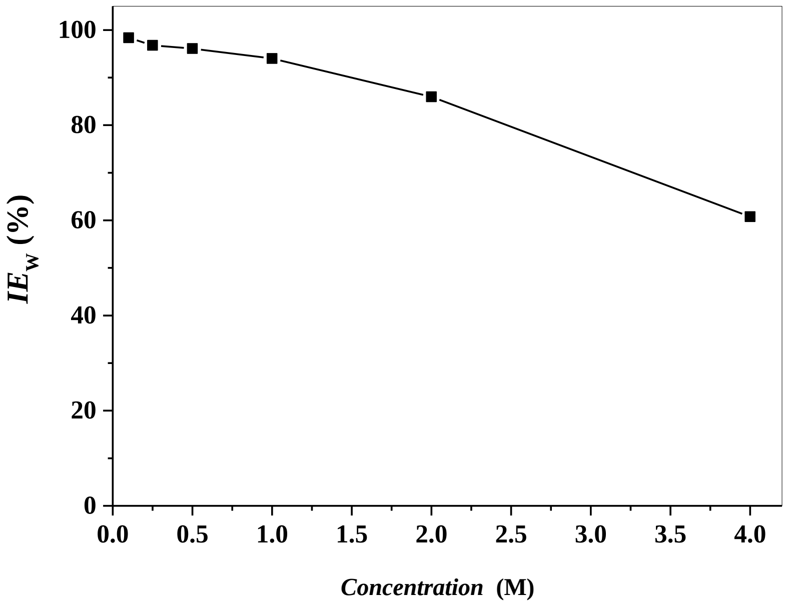


Figure 5. The relationship between HCl concentration and corresponding inhibition efficiency for Q235 steel corrosion in HCl with 100 mg L^{-1} HMETD at 30 °C from weight loss measurement

3.2.4 Effect of storage time

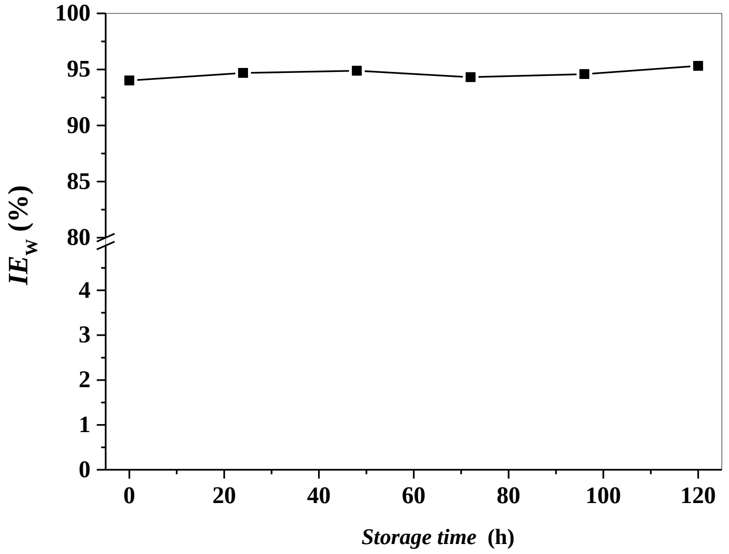


Figure 6. The relationship between storage time and corresponding inhibition efficiency for Q235 steel in 1.0 M HCl with 100 mg L^{-1} HMETD at 30 °C from weight loss measurement

In addition, according to the effect of storage time on inhibition efficiency from figure 6 obtained by weight loss measurement, the inhibition efficiency (IE_W(%)) slightly fluctuate with storage time changing. At 30 °C, in 1.0 M HCl with 100 mg L^{-1} HMETD at 120 hours later, the inhibition efficiency still up to 95.32%. The results show that HMETD can exhibit the excellent corrosion inhibition for Q235 steel in HCl solution for a long time, which is a long-acting corrosion inhibitor. And the result further suggests that the fully saturated macrocyclic compound of HMETD can stable present in HCl solution.

3.2.5 Effect of acid types

Moreover, both HCl and H_2SO_4 medium were used as the aggressive solution to evaluate the corrosion inhibition of Q235 steel by HMETD. Based on weight loss measurement, the inhibition efficiencies of Q235 steel corrosion in various concentrations of HCl (1.0 M, 2.0 M) and H_2SO_4 (0.5 M, 1.0 M) with 100 mg L^{-1} HMETD at 30 °C are presented in figure 7. It can be found that the corrosion inhibition performance of Q235 steel in HCl by HMETD is superior to the performance of Q235 steel in H_2SO_4 with the same H^+ concentration. A similar result was reported by Ajmal [19].

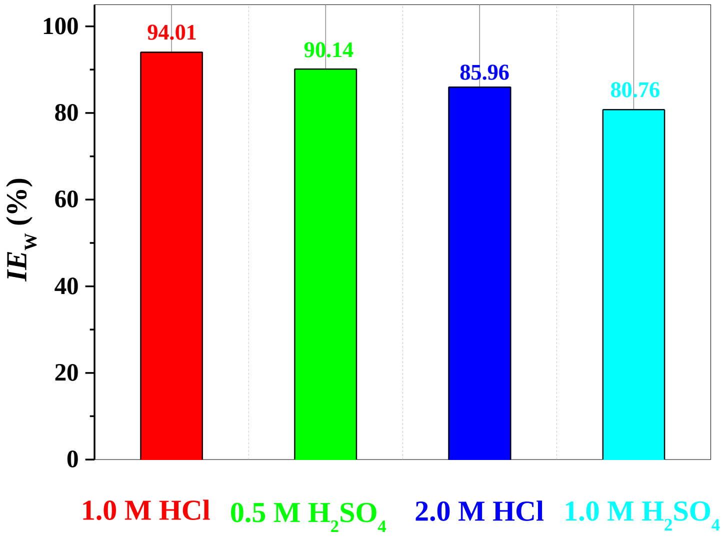


Figure 7. The relationship between acid types and corresponding inhibition efficiency for Q235 steel in HCl and H_2SO_4 with 100 mg L^{-1} HMETD at 30 °C from weight loss measurement

3.3 Adsorption isotherm

In order to confirm the reasonable adsorption isotherm for HMETD in HCl solution on Q235 steel surface, different isotherms involving Langmuir, Temkin, Frumkin and Flory–Huggins adsorption isotherms were employed based on the data of weight loss measurement from figure 3. The Langmuir adsorption isotherm is described in equation 4 (C is the HMETD concentration, K_{ads} is the adsorption equilibrium constant and θ is the surface coverage). The surface coverage (θ) for various concentrations of HMETD in 1.0 M HCl are obtained according to equation 5 (v and v_0 are corrosion rate of the Q235 steel in HCl solution with and without HMETD, respectively).

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

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

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

In order to obtain the standard free energy (ΔG^0_{ads}) of HMETD adsorption on Q235 steel surface. The plots of C/θ versus C yield the straight line is shown in figure 8. The strong correlation (R^2=0.9967) reveals that the adsorption of HMETD on Q235 steel surface in 1.0 M HCl obeys Langmuir adsorption isotherm. Meanwhile, the standard free energy of adsorption can be determined from the intercepts of the straight lines according to equation 6 (R 8.314 J K^{-1} mol^{-1} is the gas constant, 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^0_{ads}) for HMETD adsorption on Q235 steel is obtained, -35.30 kJ mol^{-1}, which higher than -40.00 kJ mol^{-1}. It indicates that the adsorption of HMETD 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) [23-25].

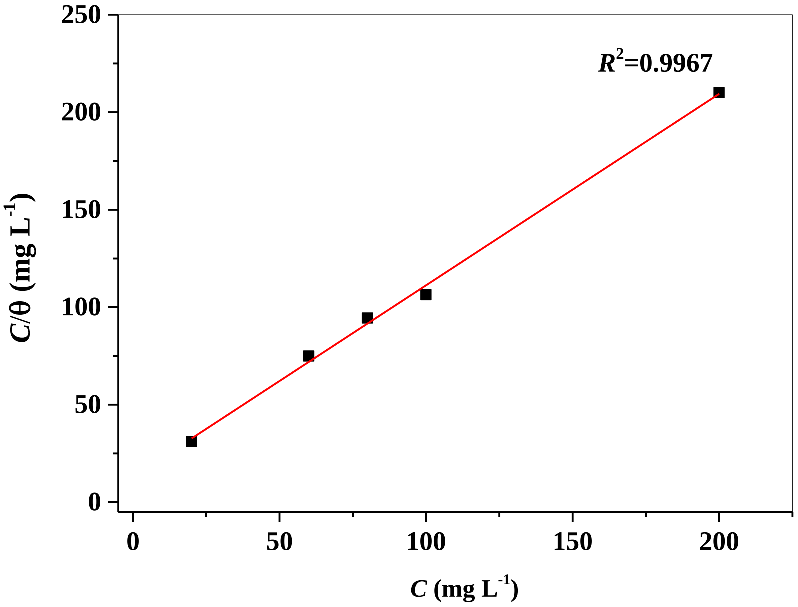
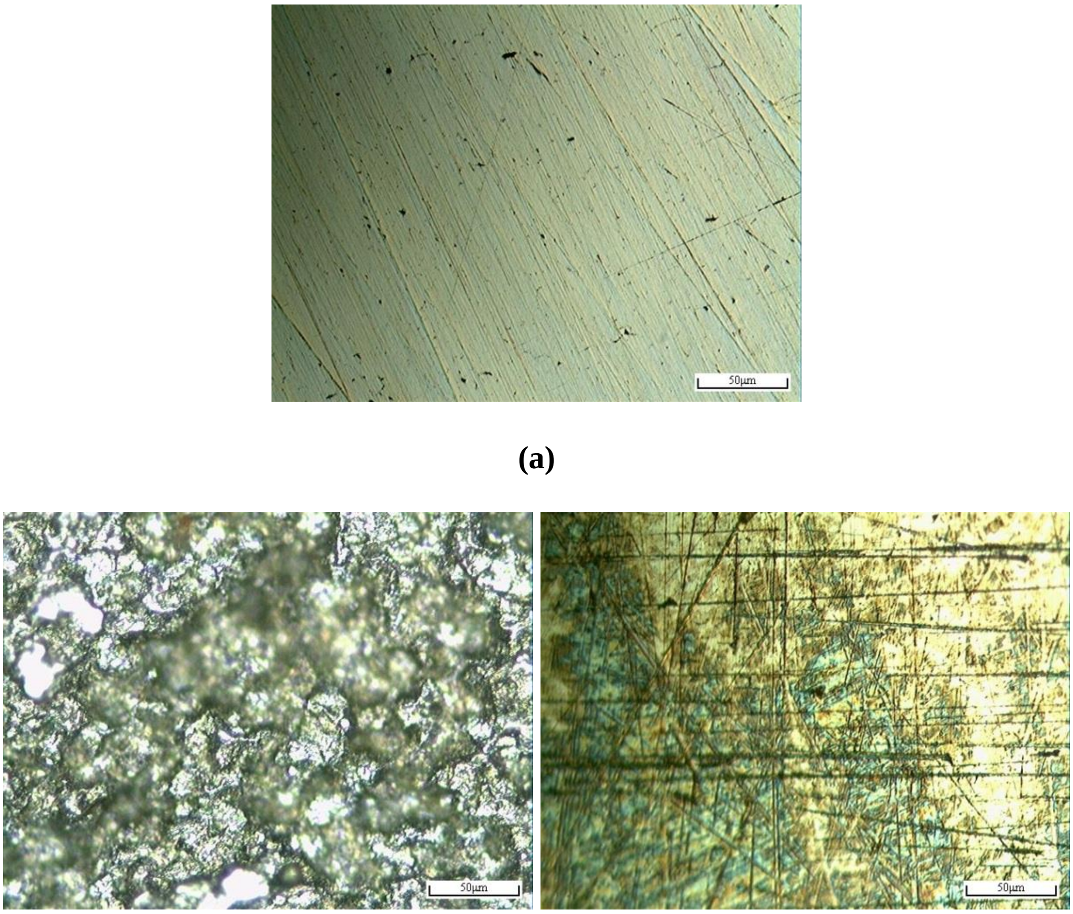


Figure 8. Langmuir adsorption isotherm for HMETD on Q235 steel in 1.0 M HCl at 30 °C

3.4 Microstructure analysis

In order to further confirm the corrosion inhibition of Q235 steel in HCl solution by HMETD, 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 without and with 100 mg L^{-1} HMETD, and the micrographs are presented in figure 9 (a)-(c). Figure 9 (a) shows the surface morphology of the electrode before immersion and corrosion in 1.0 HCl without and with 100 mg L^{-1} HMETD, which mostly seems smooth with only some nicks from the electrode polishing by emery paper. However, as can be seen from figure 9 (b), after the electrode corrosion in 1.0 M HCl without HMETD, which is strongly corroded by the aggressive media. It can be found that the surface of the electrode is too bumpy and rough. This result reveals that the Q235 steel electrode surface is highly corroded and damaged in 1.0 M HCl without HMETD. In addition, after accomplished the electrochemical evaluating experiment for the electrode testing in 1.0 M HCl with 100 mg L^{-1} HMETD, the electrode surface is too smooth and much less damaged (see figure 9 (c)), which further confirms the inhibition action and adsorption of HMETD on Q235 steel surface. Moreover, the microstructure analysis results are in good agreement with that achieved from the other evaluating results including potentiodynamic polarization and weight loss measurement results in this work.



(a)

(b) **(c)**

Figure 9. Optical micrographs of Q235 steel electrode before (a) and after (b, c) electrochemical testing in 1.0 HCl without (a, b) and with 100 mg L^{-1} HMETD (c) at 30 °C

4. CONCLUSIONS

In conclusion, the fully saturated macrocyclic of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane (HMETD) as corrosion inhibitor was evaluated by potentiodynamic polarization measurement, weight loss measurement and microstructure analysis. This work present that HMETD is an effective mixed-type corrosion inhibitor, the inhibition efficiency slightly fluctuate with storage time changing, increase with HMETD concentration increasing, decrease with HCl concentration and temperature increasing. And the adsorption of HMETD on Q235 steel surface in HCl solution obeys Langmuir isotherm, which is a mixed adsorption containing physisorption and chemisorption.

ACKNOWLEDGMENTS
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