# Synthesis of Bimannich Base with Thiazole and Its Corrosion Inhibition Effect on H2S and CO2 at High Temperature

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# Synthesis of Bimannich Base with Thiazole and Its Corrosion Inhibition Effect on $H_2S$ and $CO_2$ at High Temperature

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**Abstract** A bimannich base TZBM containing a thiazole structure was obtained by the mannich base synthesis method. TZBM can maintain a stable structure at 260°C, and has a good corrosion inhibition effect on carbon steel in a gas-liquid environment containing $Cl^-$+$H_2S$+$CO_2$ at 180°C. Through the weight loss test of steel under different concentrations of TZBM, the degree of surface coverage of the adsorbed inhibitor is determined, and it was found that the results obey the Langmuir adsorption isotherm. And the negative Gibbs free energy indicates that the adsorption is spontaneous.

**Keywords** Thiazole，Bimannich base，Corrosion inhibitor，High temperature resistant

## 1.Introduction

In the process of sour gas and liquid passing through the pipeline, it often causes serious corrosion to the metal material of the channel. For example, the pipeline of sour natural gas wells and natural gas transportation to the purification plant usually needs to add corrosion inhibitors to inhibit the corrosion of metal pipelines[1-3]. Ensure safe production and extend the service life of metal pipes. At present, corrosion inhibitors for gathering and transportation have been studied more maturely because of their mild application conditions[4-7]. As for the corrosion inhibitors used in downholes, because of the complex downhole conditions and the deeper and deeper development wells, the downhole temperature continues to increase, making it difficult for the existing corrosion inhibitors to cope with more severe conditions.

At present, the most commonly used type of corrosion inhibitor for $H_2S$ and $CO_2$ corrosion is imidazoline corrosion inhibitor, which is widely used in oil and gas fields, especially in pipelines, and has good corrosion inhibition effects. The synthesis of imidazoline corrosion inhibitors is mainly completed by the two-step dehydration of polyvinyl polyamines and long-chain acids. The first step of dehydration requires 140-160°C, and the second step of dehydration requires 200-230°C[8-14]. The reaction conditions are strict. Organic compounds containing hetero-atoms such as N, O and S have been reported effificient corrosion inhibitors for metals and alloys [15–20]. The Mannich base, which is usually used as an acidizing corrosion inhibitor, requires only one step for the reaction, with a reaction temperature of 60-80°C and mild conditions[21-26], but it is rarely used for $H_2S$ and $CO_2$ corrosion research. Studies have shown that the synthetic bis-Mannich base has a greater corrosion inhibition performance than the Mannich base.

In this paper, a kind of bis-Mannich bases with thiazole which was synthesized in the laboratory was found that it has a good corrosion inhibitory effect on steel in the corrosive liquid containing $Cl^-$+$H_2S$+$CO_2$, which provides a new idea for the selection of $H_2S$ and $CO_2$ corrosion protection agents.

# 2. Experimental

## 2.1 Materials

2-Acetylthiazole(AR), Benzaldehyde(AR), Tetraethylenepentamine(AR), Hydrochloric Acid (AR), Absolute Ethanol (AR)，Petroleum Ether (AR), NaCl (AR), Carbon dioxide (99.999%), Nitrogen (99.999%), Hydrogen sulfide (99.99%).

## 2.2 Synthesis

A one-pot method was used to synthesize bis-Mannich base TZBM. Using ethanol as the solvent, first add benzaldehyde to the three-necked flask, then slowly add tetraethylenepentamine, and then add 2-acetylthiazole, the molar ratio of the three is 2:2:1, slowly add concentrated hydrochloric acid to adjust the pH to 4~5, then heati it to 80°C, condense and reflux, after 6 hours reaction, a reddish brown liquid is obtained, and crude TZBM can be obtained after distillation under reduced pressure. Finally, recrystallize it with absolute ethanol 2 to 3 times to obtain a purer product. Reaction equation illustrated in Scheme 1.

## 2.3 Thermogravimetric analysis

The thermogravimetric analysis experiment of TZBM was carried out using the thermal analyzer (DSC823) of METTLER TOLED. The experimental atmosphere is nitrogen. The starting temperature is 40°C, and the heating rate is 10°C/min.

## 2.4 Gravimetric measurements

The specimens for weight loss measurements were 30 mm by 15 mm by 3 mm.They were polished with emery paper(from 400 to 1000 grade).

Atmospheric pressure experiment: The oxygen in 5.0L of 5.0% NACl solution is expeled by nitrogen for 8 hours. $CO_2$ is bubbled into 2.5L deoxygenated 5.0% NACl solution for 8 hours, At the same time $H_2S$ is bubbled into 2.5L deoxygenated 5.0% NACl solution for 8 hours, and then the two solutions are mixed 1:1 as the corrosion solution. Two specimens are hung into a glass container, use nitrogen to drive oxygen. After 72 h of immersion in the corrosion solution with and without addition of TZBM at different concentrations in 80°C oil bath, the specimen was withdrawn, rinsed with distilled water, washed with the membrane-removing acid solution, alcohol and petroleum ether, dried and weighed using an analytical balance accurate to 0.01 mg.

High-temperature and high-pressure test: 650mL 5.0% NACl solution and a calculated amount of corrosion inhibitor are added into the autoclave, and two specimens are hung into the autoclave（Ensure that the liquid immerse the specimens）.

Nitrogen is blow in to drive out oxygen for 6 hours and then seal the autoclave again.After that 2.0MPa $CO_2$ and 1.0MPa $H_2S$ are inserted in the autoclave, then nitrogen is inserted to control the total pressure to 10MPa. After 72 h of immersion in the corrosion solution with and without addition of TZBM at different concentrations in 180°C, the specimen was withdrawn, rinsed with distilled water, washed with the remove-membrane acid solution, alcohol and petroleum ether, dried and weighed using an analytical balance accurate to 0.01 mg.

### 2.5 Corrosion morphology observation

The surface of the specimen after the high temperature and high pressure test without being rinsed is observed by an electron microscope. It can help analyzing the influence of TZBM on the corrosion of the specimen in gas-liquid environment containing $Cl^-$+$H_2S$+$CO_2$.

# 3. Results and discussion

### 3.1 Structure Characterization

Figure 1 shows the TZBM infrared characterization spectrum. It can be seen from the figure that 3542cm$^{-1}$ is a single peak, which is the characteristic peak of the stretching vibration of the secondary amine N-H bond, 2862cm$^{-1}$ is the stretching vibration peak of the methylene CH bond, and 1646cm$^{-1}$ is the carbonyl group connected to the heterocyclic ring. The C=N double bond in the thiazole at 1461cm$^{-1}$ stretching vibration peaks, fingerprint regions 745cm$^{-1}$ and 675cm$^{-1}$ are characteristic peaks of CH deformation vibrations monosubstituted by benzene ring. At the same time, there is no obvious sharp double peak at 3500~3400cm$^{-1}$, indicating that there is no primary amine functional group, and no strong peak at 1720cm$^{-1}$, indicating that there is no C=O double bond of aldehyde. It can be proved that the reaction is complete and the target product is successfully synthesized.

### 3.2 Thermogravimetric analysis

It can be seen from Fig.2 that the initial weight of the test TZBM sample is 9.8234 mg. As the temperature gradually increases, the weight of TZBM firstly stabilizes and then drops sharply and finally stabilizes again. In the temperature range of 260-400℃, the weight of TZBM dropped sharply, losing 53% of its weight. The rate of weight loss first increased and then decreased, reaching a maximum value of about 0.8mg/min near 360℃. This can indicate that the chemical structure of TZBM is stable at 260°C, and the structure becomes unstable after 260°C, and the chemical bond will break. In summary, for the current natural gas gathering pipelines and downhole application environments, the chemical structure of TZBM has high temperature resistance.

### 3.3 Weight loss measurements

Table 1 collects the values of inhibitor effificiency and corrosion rate obtained from weight loss measurements for different concentrations of the inhibitor in the prepared corrosion solution at 80±0.1C. From the calculated weight loss values, the percentage inhibitor effificiency η was calculated using the equation:

$$\eta = (R_0 - R)/R_0 \times 100\% \qquad \text{Eq.1}$$

Where R and $R_0$ are rates of corrosion (mm/a) with and without inhibitor, respectively.

Fig.3 shows that corrosion rates decreases with increase in TZBM concentration. From 50-200ppm TZBM concentration, the corrosion rates reduce slowly. It means that when the corrosion inhibitor is small, it cannot be completely covered on the surface of the specimen. When the concentration of the corrosion inhibitor exceeds 300ppm, the corrosion rate is significantly reduced. At 400ppm, the corrosion rate is only 0.0479mm/a, indicating that when the corrosion inhibitor covering the surface of the specimen relatively completely, it can effectively block the corrosive medium and protect the steel.

### 3.4. Adsorption isotherm

To understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the metal surface must be known.

The basic ideas of the single molecule adsorption model proposed by Langmuir are: ①The adsorption on the surface is a dynamic equilibrium process of adsorption and desorption; ②The surface of the adsorbent still has residual valence and can be adsorbed. The adsorption capacity is the same; ③The adsorption is single-molecule adsorption, and the maximum surface coverage θ is 1; ④The adsorbed medium have no influence on each other. According to the hypothesis, the Langmuir isotherm equation can be expressed as Eq.2[27-29].

$$\theta = \mathrm{K}\alpha/(1+\mathrm{K}\alpha) \qquad \text{Eq.2}$$

Where θ is the degree of surface coverage, K is the thermodynamic equilibrium constant of adsorption, ɑ is the activity of corrosion inhibitor.

If simple molecule adsorptive behavior is assumed for TZBM, inhibition effificiency η can takes place surface coverage θ. And in low concentration. The activity of corrosion inhibitor ɑ can be taken place by the concentration C. Therefor Eq.2 can transform to Eq.3.

$$C/\eta = C + 1/K \qquad \text{Eq.3}$$

Consider the influence of other factors, we correct the above formula by multiply a correction factor f to the right side of formula, and form Eq.4.

$$C/\eta = \mathrm{f}C + \mathrm{f}/K \qquad \text{Eq.4}$$

According to Table.4, the surface coverage dgree was tested graphically to allow fitting of a suitable adsorption isotherm. The plot of C/η versus C (Fig.4) yielded a straight line with nearly unit slope.clearly proving that the adsorption of the TZBM from the prepared corrosion solution on the steel obeys the Langmuir adsorption isotherm[30-31].

The value of equilibrium adsorption constant K obtained from the Langmuir plot is about $0.65\times10^{3}$l/mol. From Van't Hoff equation (Eq.5), the value of ΔG can be calculated to be -19.02KJ/mol, which indicated that TZBM was strongly adsorbed on the steel surface, and this adsorption process is spontaneous.

$$\Delta G = -RT\ln K \qquad \text{Eq.5}$$

From this analysis, TZBM blocks corrosive media through single molecules adsorbed on the surface of the stee. The principle of adsorption is that the N and O atoms in the molecule contain a lone pair of electrons, which can enter the hybrid orbital of the iron atom in the steel to form a coordination bond. Because of the special structure of TZBM, this coordination bond just establishes a stable six-membered ring structure, and each molecule can form two adsorption points, as shown in Fig.5, so that TZBM can be more firmly adsorbed on the surface of steel, which improves the high temperature resistance of adsorption.

### 3.5 High-temperature and high-pressure test

Since temperature has a great influence on the corrosion rate, in order to ensure the corrosion inhibition effect of TZBM, the concentration of TZBM was increased to 1500ppm in the high-temperature and high-pressure test. Table 2 shows the results of high temperature and high pressure test for corrosion inhibition performance of TZBM. Fig.6 is the photo of the appearance of after-cleaning specimens with and without inhibitor, respectively. The high-temperature and high-pressure test certificates that TZBM has good corrosion inhibition performance at high temperature.

### 3.6 Corrosion morphology observation

Fig.7 shows the micro corrosion morphology of the specimens after the high-temperature and high-pressure test without being rinsed. It can be observed that there were large quantities of overlapping loose structures on the surface of the specimen which from the test without inhibitor TZBM. The overlapping loose structures should be the corrosion products of steel. Differently, some crystalline objects can be observed on a flat surface of the specimen which from the test with 1500ppm inhibitor TZBM. Those crystalline objects should be NaCl precipitating from the corrosion solution.

By corrosion morphology observation, the result of adsorption behavior research is confirmed. TZBM can indeed adsorb stably on the surface of steel to block corrosive medium at high temperature.

## 4. Conclusions

(1) The bis-Mannich base TZBM containing thiazole structure has a stable structure at the temperature below 260℃.

(2) TZBM inhibits the corrosion of steel in a gas-liquid environment containing $Cl^-$+$H_2S$+$CO_2$ .

(3) Weight loss experiments show increased inhibitor effificiency with increasing inhibitor concentration.

(4) The inhibition is due to adsorption of the inhibitor molecules on the steel surface and blocking corrosive medium. Adsorption of the inhibitor fits a Langmuir isotherm model.

(5) A sufficient amount of TZBM can form a stable protective layer on the surface of the steel in the corrosive solution at 180°C, so that the corrosion rate of the steel is lower than 0.076mm/a. This shows that TZBM is an excellent high temperature corrosion inhibitor.

## Ethics approval and consent to participate

Not applicable.

## Consent for publication

Informed consent for publication was obtained from all participants.

## Availability of data and materials

All data generated or analysed during this study are included in this published article.

## Competing interests

All authors have no competing interest to declare.

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## Author contributions

Zhuoke Li contributed to the conception of the study. Jun Cao and Ting Mao performed the experiment. Dan Ni contributed to analysis and manuscript preparation

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## References

[1] S Papavinasam, A Doiron, R W Revie. *Corrosion*, 2009, 65(10):663.

[2] Liangshan Q . *PETROLEUM PLANNING & ENGINEERING*, 2000.

[3] Radkevych O I , Chumalo H V . *Materials ence*, 2003, 39(4):596.

[4] Hu Tao, Wang Qian, Tao Gang, Zhou Yun. *Corrosion & Protection in Petrochemical Industry*, 2008.

[5] Li, Chong. *Dissertations & Theses - Gradworks*, 2009, 27(11):2765.

[6] Shuai Z , Wei L . *Surface Technology*, 2015.
[7] D. Martínez, Gonzalez R , Montemayor K , et al. *Wear*, 2009, 267(1-4):255.
[8] Akindeju M K , Obanijesu E O , Edwards R B M , et al. *Structural Chemistry & Crystallography Communication*, 2017, 3(1).
[9] Lucio-Garcia M A , Gonzalez-Rodriguez J G , Martinez-Villafa E A , et al. *Journal of Applied Electrochemistry*, 2010, 40(2):393.
[10] Junlong L , Xing X , Lifei Z . *Natural Gas and Oil*, 2016.
[11] Yang J , Jovancicevic V . *CORROSION INHIBITORS FOR OILFIELD APPLICATIONS*: WO 2009.
[12] Xia L , Yugui Z . *Journal of Chinese Society for Corrosion & Protection*, 2009.
[13] Wahyuningrum D , Achmad S , Syah Y M , et al. *Itb Journal of ence*, 2008, 40(1):6432.
[14] Heydari M , Javidi M . *Corrosion ence*, 2012, 61(8):148.
[15] A. Popova, M. Christov, Corros. Sci. 2006, 48:3208.
[16] S. Li, S. Chen, S. Lei, H. Ma, R. Yu, D. Liu, *Corros. Sci*, 1999, 41:1273.
[17] H. Ashassi-Sorkhabi, E. Asghari, *Electrochim. Acta,* 2008,54:162.
[18] H. Shokary, M. Yuasa, I. Sekine, R.M. Issa, H.Y. El-Baradie, G.K. Gomma, *Corros. Sci,* 1998, 40:2173.
[19] X. Li, S. Deng, H. Fu, G. Mu, *Corros. Sci,* 2009,51:620.
[20] Ahamad I , Prasad R , Quraishi M A . *Corrosion ence*, 2010, 52(3):933.
[21] Luoping F , Fei Y , Bo Z , et al. *Russian Journal of Applied Chemistry*, 2018, 91(3):499.
[22] Quraishi M A , Ahamad I , Singh A K , et al. *Materials Chemistry and Physics*, 2008, 112(3):1035.
[23] Umoren S A , Banera M J , Alonso-Garcia T , et al. *Cellulose*, 2013, 20(5):2529.
[24] Tai Z X , Fei Y Y , Min Q C . Materials Protection, 2007.
[25] Michael, Arend, Bernhard. *Angewandte Chemie International Edition*, 1998.
[26] El-masry, Afaf H, Fahmy. *Molecules*, 2000.
[27] Liu Y . *Colloids & Surfaces A Physicochemical & Engineering Aspects*, 2006, 274(1-3):34
[28] Jacek, Jagiełło, et al. J*ournal of Colloid and Interface Science*, 1991.

[29] E. Cano, J.L. Polo, A. La Iglesia, J.M. Bastidas, *Adsorption*, 2004, 10:219.

[30] Larabi L , Benali O , Mekelleche S , et al. *Applied Surface ence*, 2006, 253(3):1371.

[31] S. Bilgic, N. Caliskan, Appl. *Surf. Sci*. 1999, 152:107.

# Figures

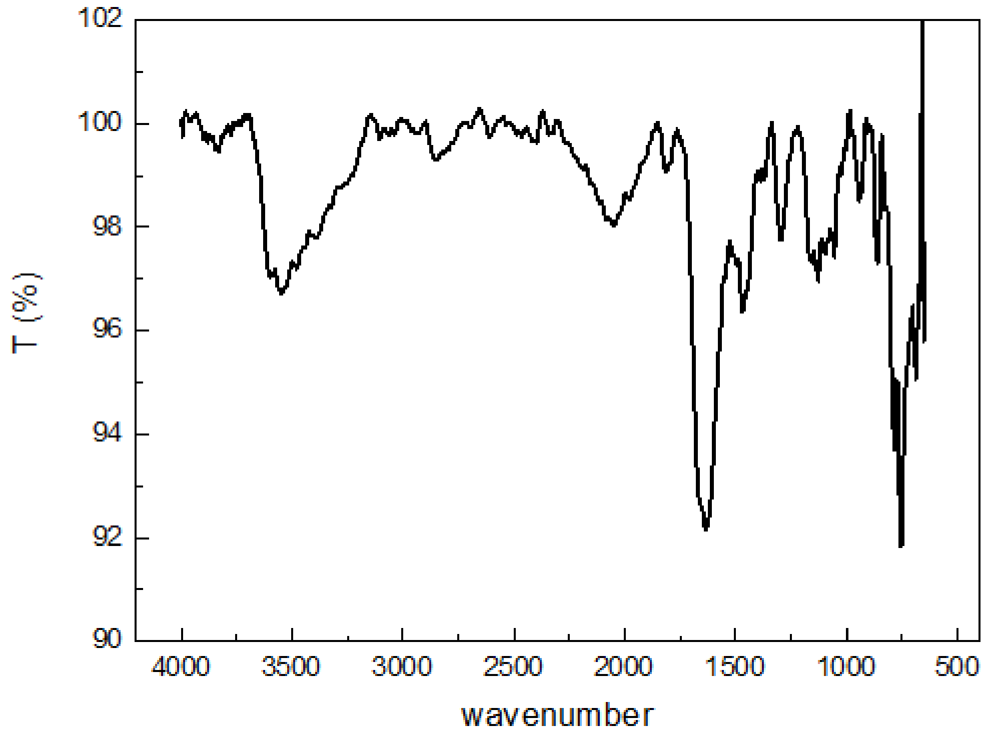


**Figure 1**

TZBM infrared characterization spectrum.

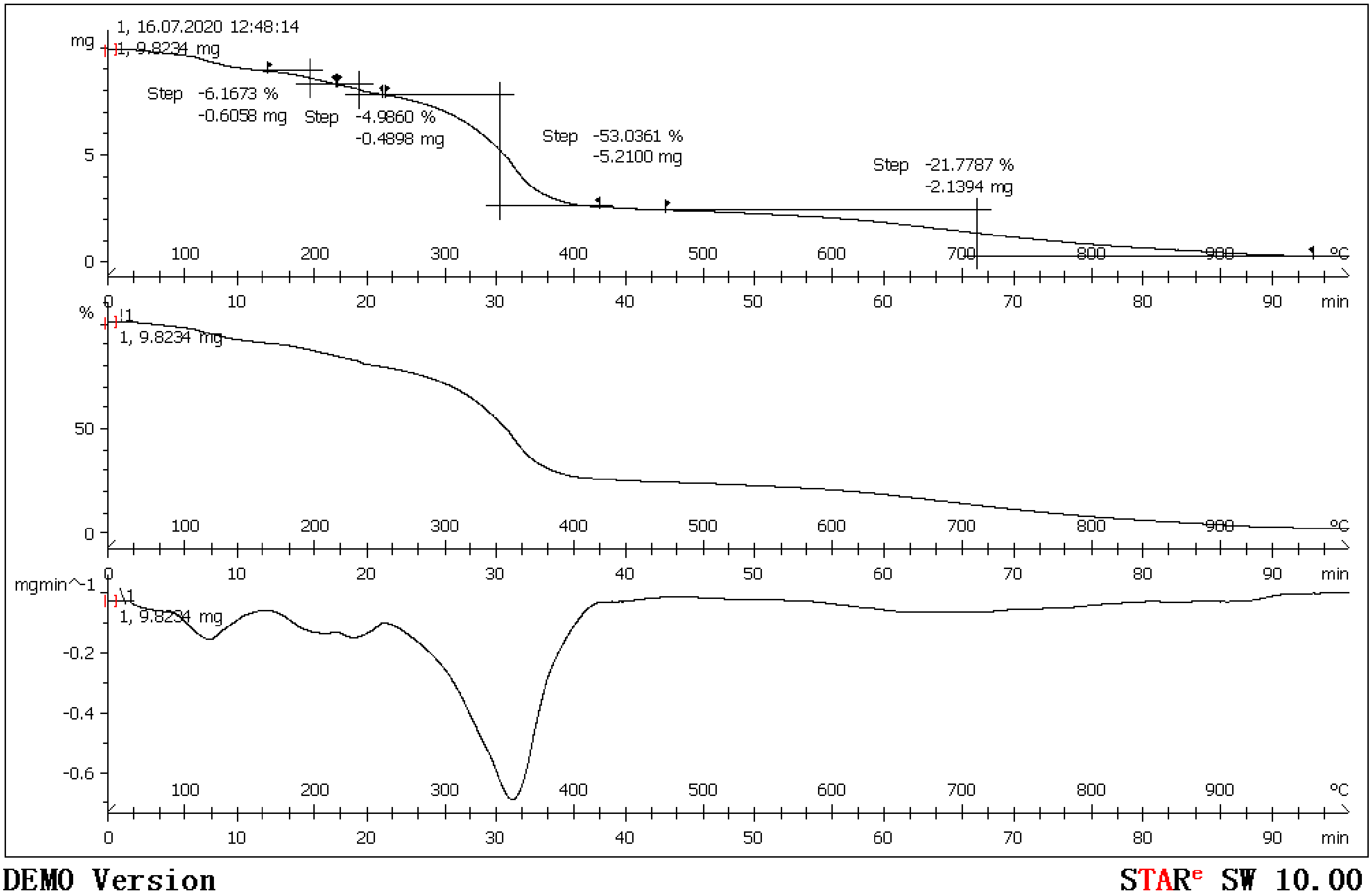


**Figure 2**

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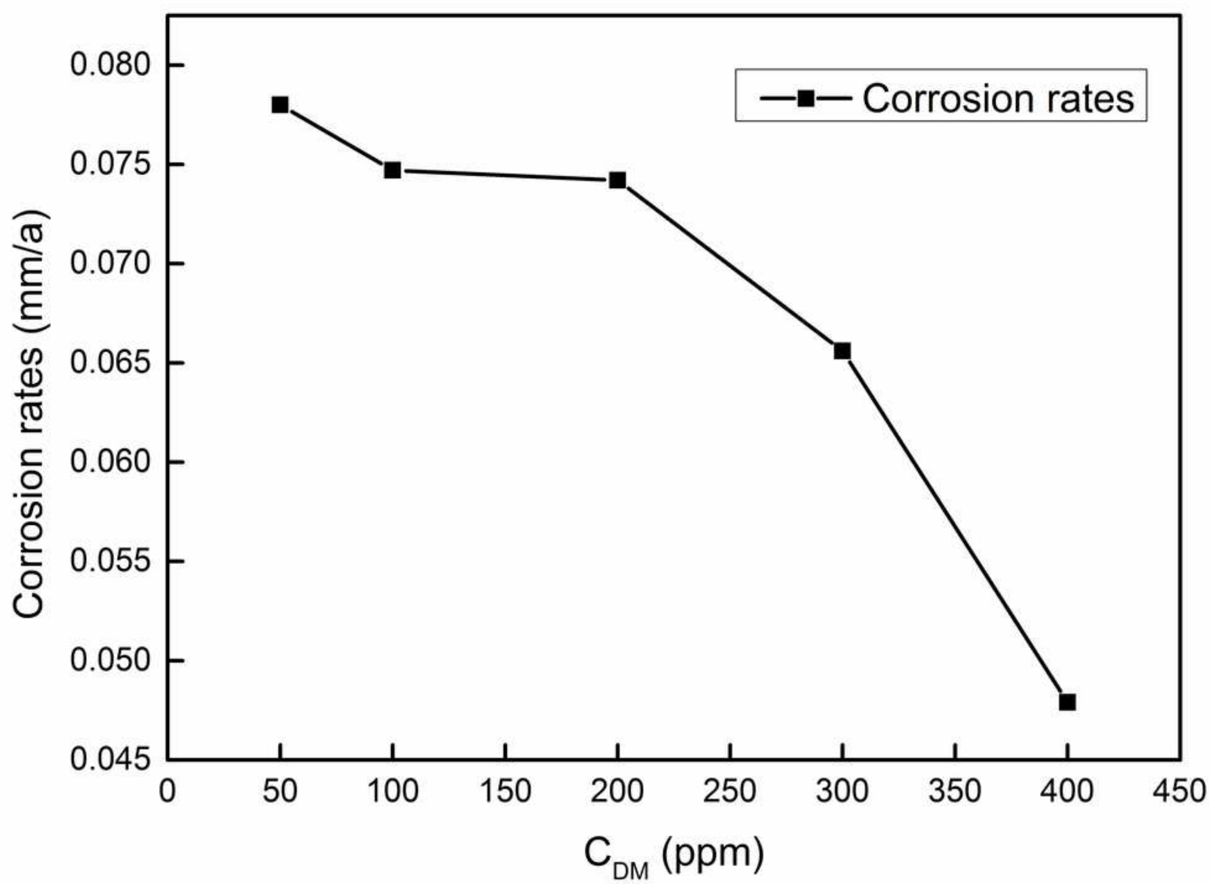


**Figure 3**

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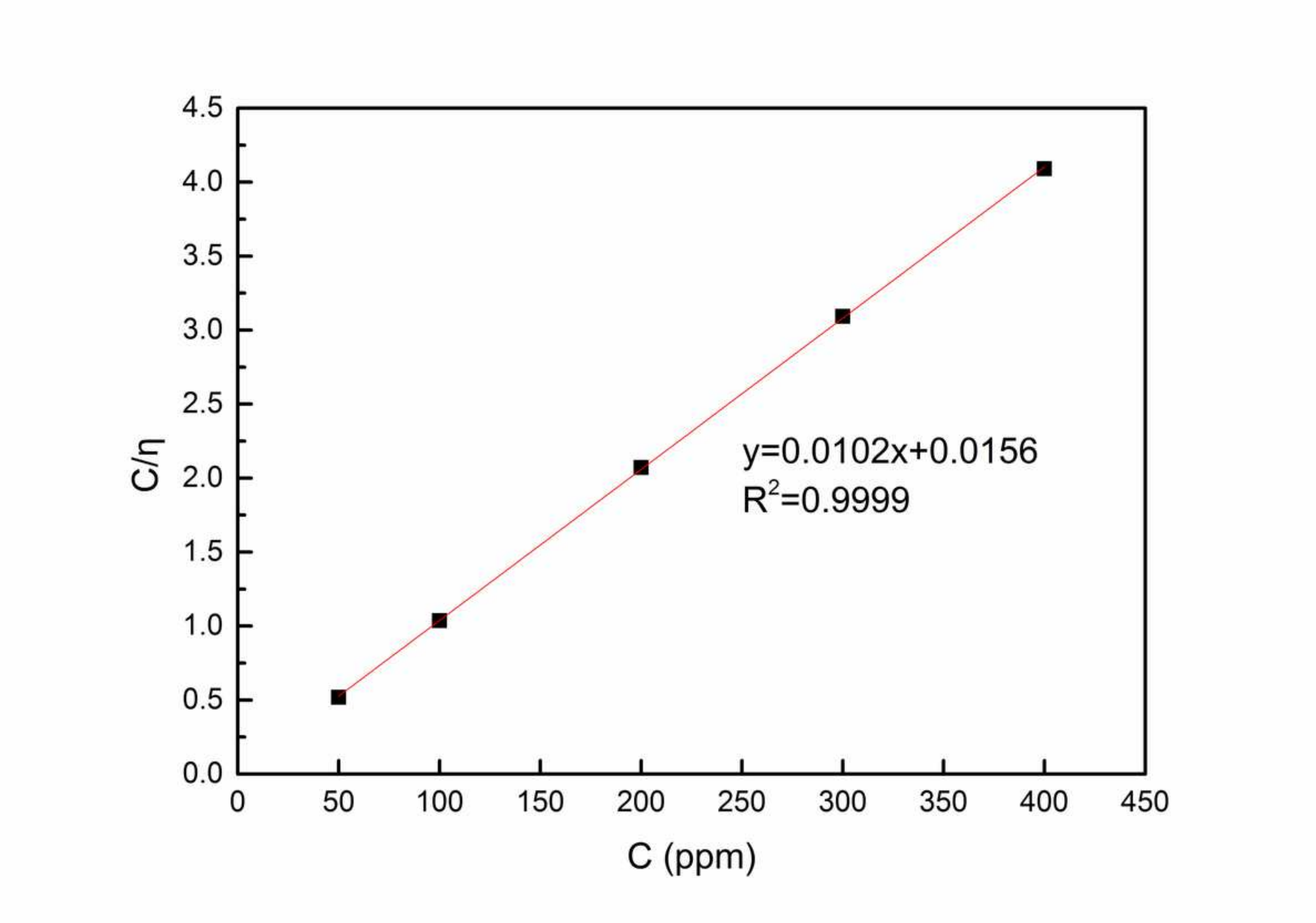


**Figure 4**

The surface coverage dgree was tested graphically to allow fitting of a suitable adsorption isotherm.

**Figure 5**

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**Figure 6**

The photo of the appearance of after-cleaning specimens with and without inhibitor, respectively.

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**Figure 7**

The micro corrosion morphology of the specimens after the high- temperature and high-pressure test without being rinsed.

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