Corrosion Inhibition Performance of Mixed Fatty Imidazoline Guanidinium Salts

Guanning He[1], Song Lv[1], Qunpo Jia[1], and Bin Yuan[1,*]

[1] College of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou, 510006, China

* Corresponding author:gdyb1960@126.com

Abstract： With novel mixed aliphatic imidazoline guanidinium as corrosion inhibitor, static weight-loss method and electrochemical polarization curve method were utilized to investigate the corrosion inhibition performance of the compound inhibitor on Q235 steel in 5% HCl solution, and scanning electron microscopy (SEM) was used to observe the corrosion morphology of the metal surface. The experiment results of static weight-loss method showed that the corrosion inhibition rate of carbon steel was 98.39% under the experimental conditions of concentration of 10 mg/L, corrosion time of 18 h, and temperature of 60°C; the results of electrochemical experiments indicated that the corrosion inhibitor was of a kind of adsorption membrane inhibitor dominantly inhibiting anode inhibition.

1. Introduction

It is well known that the corrosion of steel will not only cause serious economic losses but also bring potential security risks. Corrosion may lead to leakages of oil tanks, the casing, oil tubes, pipelines, etc., especially when corrosion occurring in acidic media, the risk of corrosion is particularly obvious. The use of corrosion inhibitors is considered to be the most effective method for protecting carbon steels [1-2], because some inorganic corrosion inhibitors (such as chromates, etc.) will bring about higher risks of environmental pollution, DNA damage and cancer; usually organic corrosion inhibitors are preferred in practice. Most organic corrosion inhibitors contain heteroatoms such as oxygen, nitrogen, and sulfur that can be adsorbed on the surface of the metal, which enables to increase the redox potential, thereby slowing down the corrosion rate. Imidazoline corrosion inhibitors are commonly used in many industrial fields owing to their good thermal stability and good biodegradability [3].

In this paper, with a novel mixed aliphatic imidazoline guanidinium as corrosion inhibition (its structural formula shown in Figure 1), static weight-loss method and electrochemical method were utilized to evaluate the performance of corrosion inhibition. Meanwhile, the effects of corrosion inhibitor concentration and corrosion time on the corrosion inhibition rate of Q235 steel were studied. Scanning electron microscopy was used to observe the morphology of the corroded surface [4-6], demonstrating that the corrosion inhibitor was of adsorption membrane type.
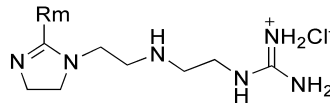
Fig.1 Structural formula of novel mixed aliphatic imidazoline guanidinium

2. Experimental section

2.1 Materials and instruments

Mixed aliphatic imidazoline guanidinium was self-produced. Multi Autolab/M204 electrochemical workstation and SU8220 field emission scanning electron microscope (SEM) were employed.。

2.2 Static weight-loss method

After being rubbed and degreased, the Q235 steel disc was placed in a desiccator and dried to a constant weight. The steel disc was immersed in 5% HCl solution containing the corrosion inhibitor, removed after 6 hours, and washed with distilled water. Afterwards, the steel sheet was derusted and dried to a constant weight. At the same time, blank control was set. The corrosion inhibition rate η of the steel disc was calculated by equation (1).

$$\eta = \left[(m_1 - m_{2)}/m_1\right] \times 100\% \tag{1}$$

where m_1 and m_2 are the weight loss of the carbon steels corroded in HCl solution without and with inhibitor, respectively, g.

2.3 Electrochemical method

The electrode polarization curve and the alternating-current (AC) impedance were measured with Multi Autolab/M204 electrochemical workstation. The working area of the electrode was 1.0 cm^2, with Q235 steel as the electrode material. The scanning range for polarization curve measurement was -300mV ~ -700mV, with the scan rate of 5mV/s. The corrosion inhibition rate was calculated from the corrosion current according to equation (2). When the AC impedance test was performed, the scanning frequency was 10^{-2}Hz ~ 10^5Hz, with a test amplitude of 10mV. The corrosion inhibition rate was calculated by equation (3).

$$\eta = \left[(I_0 - I_1)/I_0\right] \times 100\% \tag{2}$$

where I_0 and I_1 are the corrosion current density applied to the steel corroded without and with inhibitor, respectively, mA/cm^2.

$$\eta = \left[(R_0 - R_1)/R_0\right] \times 100\% \tag{3}$$

where R_0 and R_1 are the charge transfer resistance of the steel corroded without and with inhibitor, respectively, mA/cm^2.

2.4 SEM morphology method

The Q235 carbon steel was suspended in 5% HCl solution at 60°C, with the inhibitor concentration of 10mg/L and the corrosion time of 18 h. Afterwards, the Q235 carbon steel was taken out and sliced to 10 × 10 × 2 mm small test piece, of which the surface morphology was observed through SU8220 field emission SEM.

3. Results and discussions

3.1 Corrosion inhibition performance measurement by static weight-loss method.

3.1.1 Effect of corrosion inhibitor concentration on corrosion inhibition rate

The Q235 steel sheet was suspended in 5% HCl solution for 6 h at 60°C, and the effect of corrosion inhibitor concentration on the steel sheet is shown in Fig. 2.
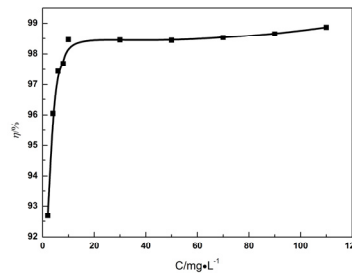
Fig.2 Impact of inhibitor concentration to corrosion
inhibition rate

As can be seen from Fig. 2, with the increase of the inhibitor concentration, the corrosion inhibition rate is increased, and when the concentration of the corrosion inhibitor is 10 mg/L, the corrosion inhibition rate reaches the highest value and trends to flat as the concentration of the inhibitor continue to grow. Therefore, the optimal concentration of corrosion inhibitor is 10mg/L, at the moment the inhibition rate can reach 98.46%.

3.1.2 Effect of corrosion medium temperature on corrosion inhibition rate
The Q235 steel sheet was immersed in 5% HCl solution for 6 h, at the concentration of the inhibitor of 10mg/L, and the corrosion effect of corrosion inhibitor at different temperatures on the steel sheet is displayed in Fig. 3.
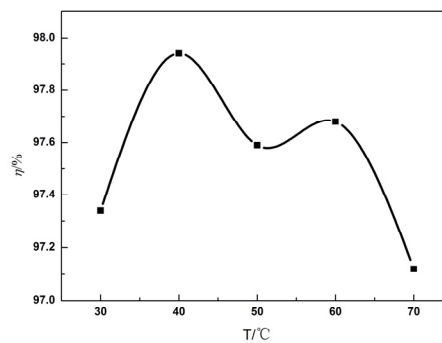

Fig.3 Impact of temperature to corrosion
inhibition rate

Shown as Fig. 3, with the increase of the corrosive medium temperature, the corrosion inhibition rate increases first and then slightly decreases. It is probably because the metal surface absorbing the inhibitor is an endothermic process, resulting in that the corrosion rate of the corrosion inhibitor on the surface of the steel sheet is accelerated as the temperature climbs, within a certain temperature range. However, when the temperature raises to a certain extent, due to too severe molecular thermal motion, the stability of the membrane is reduced, followed by a reduction of corrosion inhibition rate. When the corrosion temperature is 70°C, the corrosion inhibition rate can still reach 97.12%, indicating that the corrosion inhibitor has a high temperature resistance. The optimal temperature for the corrosion inhibitor is 40°C.

3.1.3 Effect of corrosion time on corrosion inhibition rate
The Q235 steel sheet was immersed in 5% HCl solution at 40°C, at the concentration of the inhibitor of 10mg/L, and the corrosion effect of different corrosion time on the steel sheet is presented in Fig. 4.

As we can see in Fig.4, with the increase of corrosion time, the corrosion inhibition rate first grows and then declines. The reason is likely that with the prolongation of the corrosion time, the compactness of the organic film is reduced resulting in corrosive pitting, which brings about a slight decrease in the corrosion inhibition rate. When the corrosion time is 18h, the optimal corrosion inhibition effect is achieved, at this moment the corrosion inhibition rate is 98.39%. When the

corrosion time lasts 24h, the corrosion inhibition rate can still reach 96.97%, proving a good long-term effect of the corrosion inhibitor.
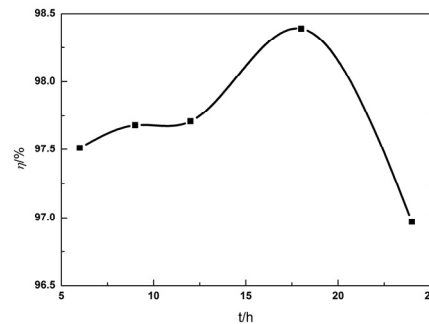

Fig.4 Impact of corrosion time to corrosion inhibition rate

3.2 Corrosion inhibition performance measurement by electrochemical method

3.2.1 Polarization curve measurement results

The Q235 steel sheet as the corrosive material was immersed in 5% HCl solution at 40°C, and the polarization curves corresponding to the inhibitors at different concentrations are shown in Fig. 5. The corrosion electrochemical parameters calculated based on the Tafel slope of the polarization curve are shown in Table 1. In the table, E_{corr} is the corrosion potential, I_{corr} is the corrosion current densit, r_c is the corrosion rate, and η is the corrosion inhibition rate.

Table 1 Corrosion electrochemical parameters calculated based on Tafel slope of the polarization curve

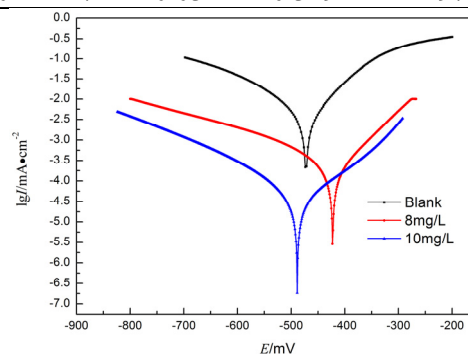| C	E_{corr}	I_{corr}	r_c	η
mg/L	mV	mA/cm^{-2}	g•cm^{-2}•h^{-1}	%
0	-472	1.181	12.287	/
8	-443	0.097	1.001	91.79
10	-474	0.034	0.349	97.15

Fig.5 Influence of corrosion inhibitor concentration on polarization curve in 5%HCl

As can be seen in Fig. 5 and Table 1, compared with the blank experiment, cathode and anode polarization curves are both significantly reduced after adding the corrosion inhibitor, indicating that the compact organic film produced by the corrosion inhibitor on the metal surface prevents the corrosive medium and metal contact. At the inhibitor concentration of 10 mg/L, the corrosion inhibition rate is 97.15%, which is also basically coincided to the corrosion inhibition rate measured by static weight-loss method.

3.2.2 AC impedance measurement results

The Q235 steel sheet as the corrosive material was immersed in 5% HCl solution at 40°C, and the Nyquist curves corresponding to the inhibitors at different concentrations are shown in Fig. 6. Data fitting analysis on the AC impedance spectra was performed, and the calculated EIS parameters are
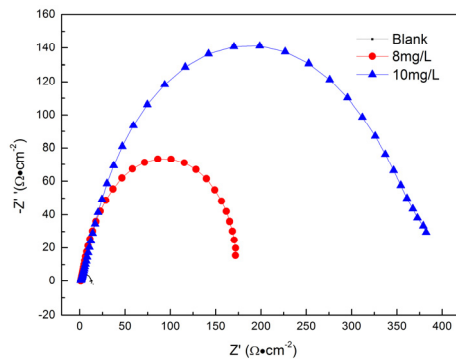
presented in Table 2.

Fig.6 Nyquist plot under different concentration for inhibitor

Table 2 Impedance fitting parameters and corrosion Inhibition efficiency of Q235 steel in 5% HCl solution

C /mg•L^{-1}	R_{ct} /Ω•cm^{-2}	η /%
0	5.412	/
8	180	96.99
10	400	98.64

Fig. 6 and Table 2 show that in addition with the corrosion inhibitor, the radius of the capacitive arc and the charge transfer resistance R_{ct} in the solution system are increased significantly compared with the blank system, indicating that the compact organic film generated by the corrosion inhibitor on the metal surface enhances the resistance to corrosion, playing a role in inhibiting corrosion. At the corrosion inhibitor concentration of 10 mg/L, the corrosion inhibition rate is 98.64%, which is basically consistent with the corrosion inhibition rate measured by static weight loss method.

3.3 SEM morphology of Corrosion surface
The Q235 carbon steel was suspended in a 5% HCl solution at 40°C, at the corrosion inhibitor concentration of 10 mg/L and the corrosion time of 18 h. The electron micrographs (magnification of 8000) of the surface morphology of Q235 carbon steel are shown in Fig. 7.

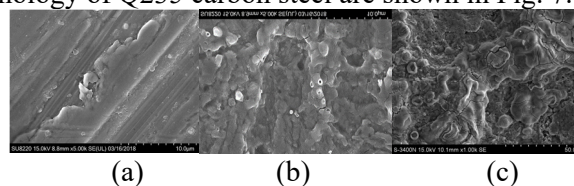(a)   (b)   (c)
Fig. 7 SEM for the steel in 5% HCl without
and with inhibitor

It can be seen from the results of SEM that: (a) there are obvious scratches on the specimen surface of the original Q235 carbon steel , (b) the surface of the blank tested specimen is seriously corroded and a lot of rugged corrosion pits is existed, (c) compared to the specimens of (a) and (b), a compact adsorptive film is observed in (c), and the increased corrosion time brings about irregular cracks. Hence, the corrosion inhibitor can effectively inhibit metal corrosion and generate a compact protective film on the metal surface.

4. Conclusions
1.   The results of the static weight-loss corrosion inhibition experiment showed that, the corrosion inhibition rate reached 98.39% when the corrosion time was 18h and the inhibitor concentration was 10mg/L in 5% HCl solution at 40°C.

2.   The results of electrochemical polarization curves indicated that: the synthesized corrosion inhibitor was a mixed inhibitor dominately inhibiting the anode reaction. The corrosion inhibition rate measured by the AC impedance method was basically consistent with the results by polarization curve method and the weight loss method.

3.   SEM observations results showed that: in 5% HCl solution, a compact organic film was adsorbed on the surface of the steel sheet that has been corroded by corrosion inhibitor for 18 h, and the corrosion degree was significantly reduced compared to the blank group without corrosion inhibitor, demonstrating that the synthesized imidazoline guanidinium had a good corrosion inhibition effect on Q235 steel in acidic medium.

References

[1]Zhang. K, Yang. W, Xu. B, et al. J. Taiwan. Inst Chem. E, **57**, 167 (2015) .

[2]Umoren. S. A, Obot. I. B, Gasem. Z. M. Ionics, **21,**1171(2015).

[3]Yoo. S. H, Kim. Y. W, Chung. K, et al. Corros. Sci, **59,** 42(2012).

[4]Azzouzi. M. E, Aouniti. A, Tighadouin. S, et al. J. Mol. Liq, **221,**633(2016).

[5]Govindasamy. R, Ayappan. S. J. Chil. Chem. Soc, **60,** 2786(2015).

[6]Sonia. B, Tahar. D, Saïfi. I, et al. Measurement, **99**, 53(2017).