



## Study on Environmental Friendly Corrosion Inhibitor in Seawater

XIN WANG<sup>1,\*</sup>, ZHENFA LIU<sup>2,3</sup>, YUHUA GAO<sup>2,3</sup> and ZHAN LIU<sup>1</sup>

<sup>1</sup>College of Chemical Engineering, Hebei University of Technology, Tianjin, P.R. China

<sup>2</sup>Institute of Energy Resources, Hebei Academy of Sciences, Shijiazhuang, Hebei Province, P.R. China

<sup>3</sup>Hebei Engineering Research Center for Water Saving in Industry, Shijiazhuang, Hebei Province, P.R. China

\*Corresponding author: E-mail: hbsjzwx06@163.com

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An environmental friendly corrosion inhibitor was prepared from polyaspartic acid, zinc sulphate, hexadecyldimethyl (2-sulphite) ethyl ammonium and hydroxyphosphonoacetic acid. The corrosion inhibition performance of the environmentally friendly corrosion inhibitor on A3 carbon steel in seawater was studied by rotary hanging-piece corrosion tests and steady polarization. The corrosion testing pieces were characterized by scanning electron microscope. The result showed that the corrosion inhibition rate could reach 95 % when the concentration of the corrosion inhibitor was 100 mg L<sup>-1</sup> at temperatures 40, 50 or 60 °C in seawater and the efficiency of biodegradability was 86.57 % in 28 days.

**Key Words:** Corrosion inhibition, Steady polarization, Carbon steel, Seawater.

### INTRODUCTION

Natural seawater contains not only most of the elements present on the earth but also a great amount of organic molecules and marine living beings<sup>1,2</sup>. The use of corrosion inhibitors was one of the most practical methods for protection against corrosion in seawater<sup>3</sup>. Corrosion inhibitors has many advantages such as convenience and low price<sup>4,5</sup>. Gong Ping *et al.*<sup>6</sup>, developed a composite which is composed of OTCA, phosphate, calcium gluconate, zinc sulphate and studied its corrosion inhibition performance in seawater. Zhu Linqun *et al.*<sup>7</sup>, composited sodium gluconate with other three kinds of corrosion inhibitors and studied the corrosion inhibition performance of the composite in seawater. Polyaspartic acid was biodegradable and was used as corrosion inhibitor and scale inhibitor in recirculating cooling water<sup>8,9</sup>. When polyaspartic acid was used in seawater, the corrosion inhibition performance was not satisfactory.

In this paper, an environmentally friendly corrosion inhibitor was prepared. The corrosion inhibition performance and biodegradation of the inhibitor were studied. The surface of the hanging-pieces were characterized by means of SEM.

### EXPERIMENTAL

**Preparation of environmentally friendly corrosion inhibitor:** the environmentally friendly corrosion inhibitor was prepared by mixing polyaspartic acid (PASP), zinc sulphate, hexadecyldimethyl (2-sulphite) ethyl ammonium and

hydroxyphosphonoacetic acid (HPAA) in beaker according to mass ratio.

**Measurement of the rate of corrosion inhibition:** The corrosion inhibition performance of modified polyaspartic acid was estimated by rotary hanging-piece corrosion tests and steady polarization. The test water was seawater of Huanghua area.

**Rotary hanging-piece corrosion tests:** The main steps are as follows: A 1600 mL seawater with environmentally friendly corrosion inhibitor was prepared in a beaker. The beaker was put in a constant temperature bath. The test piece was hung in seawater and rotated at stated velocity. The test piece was taken out from the solution after 72 h, then dipped in the hydrochloric acid pickling for 3-5 min, washed with water, dipped in pure ethanol for 3 min, blot up with filter paper and dried in dryer for 4 h. The rate of corrosion of the test piece was calculated by formula (1).

$$X = \frac{87600 \times (W_0 - W)}{A \times D \times T} \quad (1)$$

where W was the mass of the corrosive test piece, g; W<sub>0</sub> was the initial mass of the test piece, g; A was surface area of the test piece, cm<sup>2</sup>; D was the density of test piece, g cm<sup>-3</sup>; T was test time of test piece, h.

The corrosion inhibition efficiency of the corrosion inhibitor was calculated by formula (2).

$$\eta = \frac{(X_0 - X_1)}{X_0} \times 100 \% \quad (2)$$

where  $X_0$  was the rate of corrosion of the test piece without the corrosion inhibitor,  $\text{mm a}^{-1}$ ;  $X_1$  was the rate of corrosion of the test piece with the corrosion inhibitor,  $\text{mm a}^{-1}$ .

**Electrochemical experiments:** The electrochemical measurements were performed in a typical three-compartment glass cell consisting of the A3 carbon steel specimen as a working electrode, platinum mesh as a counter electrode and a saturated calomel electrode as the reference electrode. Measurements were carried out on A3 carbon steel electrode molded in polyester leaving an exposed area of  $1.5 \text{ cm}^2$ . The electrode surface was polished with abrasive paper from 1200-800 grade and washed with alcohol cotton, then dried naturally. The electrodes were placed in the test solution for 0.5 h prior to each experiment. Potentiostatic polarization measurements were carried out using CHI660B electrochemical workstation. The polarization curves were obtained from the corrosion potential ( $E_{\text{corr}}$ ) up to  $\pm 300 \text{ m}$  at a potential scan rate of  $1.0 \text{ mV/s}$ . The corrosion inhibition efficiency was calculated by formula (3)

$$\eta = \frac{(i_0 - i_{\text{corr}})}{i_0} \times 100 \% \quad (3)$$

where  $i_{\text{corr}}$  and  $i_0$  represented the corrosion current of the blank seawater and the seawater with the corrosion inhibitor.

**Surface characterization:** The surface of the test piece was examined by China KYKY-2800B scanning electron microscope (SEM). The optical photograph of the test piece was taken by SONY DSC-W310.

**Estimation of biodegradability:** The biodegradability of the environmentally friendly corrosion inhibitor was estimated by shaking-bottle incubating test. The main method was as follows: a 500 mL solution of  $100 \text{ mg L}^{-1}$  corrosion inhibitor with 1 mL inoculum was prepared in a conical flask. The conical flask was placed on a shaking-bottle incubating device at room temperature and the chemical oxygen demand (COD) was detected at the 7<sup>th</sup>, 14<sup>th</sup>, 21<sup>st</sup> and 28<sup>th</sup> day, respectively. The inoculum was prepared by adding 100 g nutritious soil into 1000 mL deionized water and filtering. The rate of biodegradability of the corrosion inhibitor was calculated by formula (4):

Rate of biodegradation

$$= \left( 1 - \frac{(C_t - C_{b_t})}{(C_0 - C_{b_0})} \right) \times 100 \% \quad (4)$$

where  $C_0$  was the initial numerical value of COD in the inoculated seawater with corrosion inhibitor;  $C_t$  was the time numerical value of COD in the inoculated seawater with corrosion inhibitor;  $C_{b_0}$  was the initial numerical value of COD in the blank seawater;  $C_{b_t}$  was the time numerical value of COD in the blank seawater.

## RESULTS AND DISCUSSION

### Performance of corrosion inhibition

**Effect of environmentally friendly corrosion inhibitor on inhibition efficiency:** The optimum proportion of zinc sulphate, polyaspartic acid (PASP), hexadecyldimethyl (2-sulphite) ethyl ammonium and hydroxyphosphonoacetic acid (HPAA) was 3:6:1:0.5 by means of orthogonal test.

Fig. 1 was the effect of dosage of environmentally friendly corrosion inhibitor on corrosion inhibition performance on A3 carbon steel in seawater. It was observed that the corrosion inhibition rate of corrosion inhibitor increased with the increase of concentration from 50-100  $\text{mg L}^{-1}$  and the corrosion inhibition rate was very low when the concentration of corrosion inhibitor was less than  $100 \text{ mg L}^{-1}$ . When the concentration of corrosion inhibitor was  $100 \text{ mg L}^{-1}$ , the corrosion inhibition rate was 98.02 %. And the corrosion inhibition rate reached 99.09 % when the concentration was  $200 \text{ mg L}^{-1}$ .

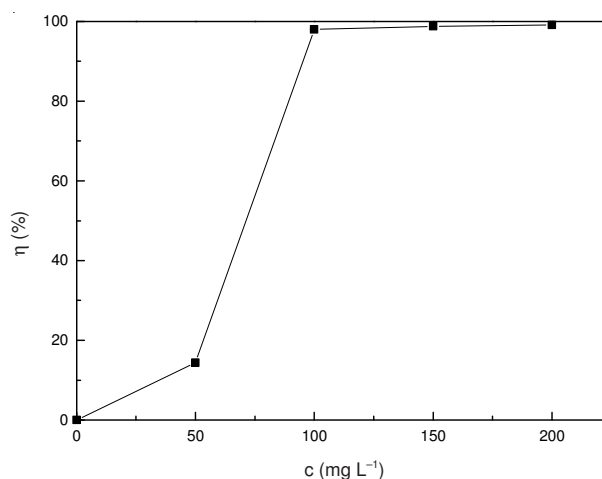


Fig. 1. Effect of dosage of corrosion inhibitor on corrosion inhibition efficiency at  $40 \text{ }^\circ\text{C}$

Fig. 2 was the potentiodynamic polarization curves of A3 carbon steel in the seawater at different concentration of corrosion inhibitor. Table-1 was the electrochemical parameters of A3 carbon steel in the seawater at different concentration of corrosion inhibitor at  $40 \text{ }^\circ\text{C}$ . As shown in Fig. 2 and Table-1, the decrease in current density with the inhibitor concentration was associated with a shift of corrosion potential  $E_{\text{corr}}$  to moved anodic values, indicating that environmentally friendly corrosion inhibitor acted as anodic type inhibitor.

Concentration ( $\text{mg L}^{-1}$ )	$I_{\text{corr}}$ (A)	$\eta$ (%)
0	$2.854 \times 10^{-5}$	–
50	$2.383 \times 10^{-5}$	16.51
100	$1.104 \times 10^{-6}$	96.13
150	$7.849 \times 10^{-7}$	97.25
200	$3.539 \times 10^{-7}$	98.76

**Effect of temperature on inhibition efficiency:** Corrosion inhibition performance of environmentally friendly corrosion inhibitor in seawater measured by rotary hanging-piece corrosion tests at 40, 50 and  $60 \text{ }^\circ\text{C}$  (Table-2). It showed that corrosion inhibition rate didn't decrease obviously with the increase in temperature from 40 to  $60 \text{ }^\circ\text{C}$  and the concentration of the corrosion inhibitor was the same. This meant that the environmentally friendly corrosion inhibitor has stable and reliable corrosion inhibition performance on A3 carbon steel in seawater.

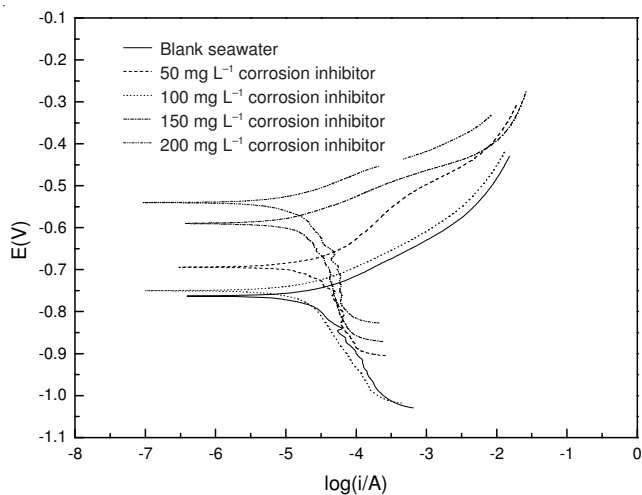


Fig. 2. Potentiodynamic polarization curves of A3 carbon steel in the seawater at different concentration of corrosion inhibitor at 40 °C

**TABEL-2**  
**EFFECT OF CONCENTRATION OF CORROSION INHIBITOR AND TEMPERATURE ON CORROSION INHIBITION PERFORMANCE**

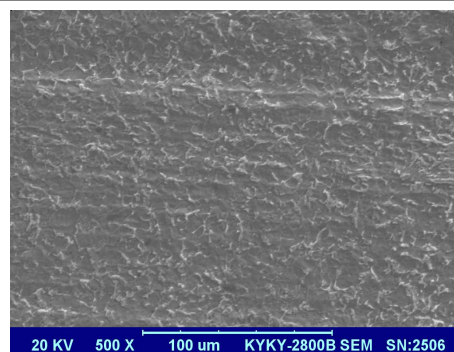
Temperature (°C)	Concentration (mg L <sup>-1</sup> )	Corrosion rate (mm a <sup>-1</sup> )	η (%)
40	50	0.6059	16.57
	100	0.0144	98.02
	150	0.0099	98.63
	200	0.0066	99.09
	Blank seawater	0.7262	—
50	50	0.6571	21.17
	100	0.0403	95.16
	150	0.0303	96.37
	200	0.0148	98.22
	Blank seawater	0.8336	—
60	50	0.8211	10.15
	100	0.0645	92.98
	150	0.0184	97.99
	200	0.0177	98.06
	Blank seawater	0.9139	—

**Characterization of test pieces:** The surface of the test pieces were examined by SEM under the condition of acceleration voltage 20 KV and amplified factor 500. The results were showed in Fig. 3. As shown in Fig. 3, clear pits were visible due to pitting type of the corrosion specimens in blank seawater in SEM images. No such pits was visible on the corrosion specimens when added 150 mg L<sup>-1</sup> environmentally friendly corrosion inhibitor in seawater.

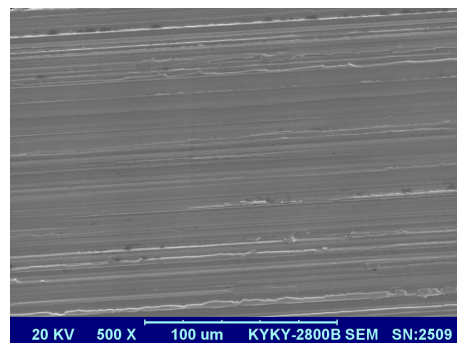
The optical photograph of the test pieces were taken by SONY DSC-W310. The results were showed in Fig. 4.

As shown in Fig. 3, there was no corrosion on A3 carbon steel piece and the surface was very smooth and clear when added 150 mg L<sup>-1</sup> environmentally friendly corrosion inhibitor in seawater, as shown in the photos.

This was because the adsorption of the environmentally friendly corrosion inhibitor adsorbed on metal surface was not merely a physical or a chemical adsorption but a comprehensive adsorption. Polyaspartic acid can form chelates with Fe<sup>2+</sup> ion to protect the surface of test pieces. The Zn<sup>2+</sup> can form precipitation in the surface of the test pieces and it can also accelerate the protective film. To sum up, the environmentally



(a)



(b)

Fig. 3. SEM images of test pieces at 40 °C. (a) Blank seawater, (b) with 150 mg L<sup>-1</sup> corrosion inhibition in seawater



(a)



(b)

Fig. 4. Photograph of test pieces at 40 °C. (a) Blank seawater, (b) with 150 mg L<sup>-1</sup> corrosion inhibition in seawater

friendly corrosion inhibitor could protect the surface of test pieces very well in seawater.

**Biodegradation performance:** The results of biodegradation of environmentally friendly corrosion inhibitor were showed in Fig. 5. Fig. 5 showed that the environmentally friendly corrosion inhibitor has better biodegradation performance and the highest biodegradation rate can reach 86.57 %.

**Conclusion**

In summary, the environmentally friendly corrosion inhibitor was prepared using zinc sulphate, polyaspartic acid, hexadecylldimethyl (2-sulphite) ethyl ammonium and hydroxyphosphonoacetic acid. By means of the orthogonal test, the optimum proportion was 3:6:1:0.5. Its corrosion

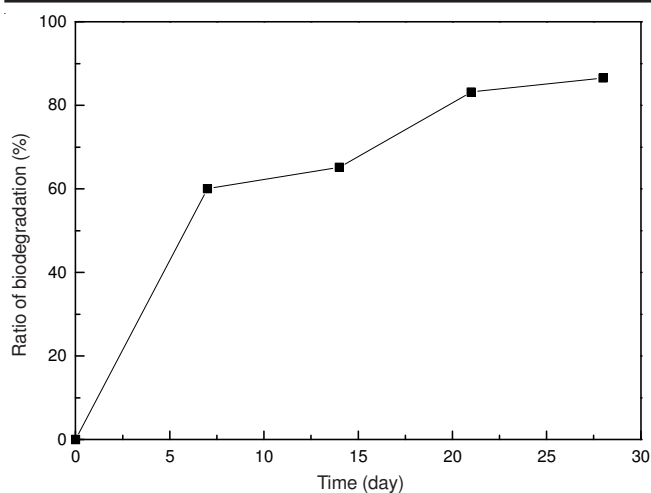


Fig. 5. Biodegradation of environmentally friendly corrosion inhibitor

inhibition performance on A3 carbon steel in seawater was good obviously. The corrosion inhibition rate could reach above 95 % at temperatures 40, 50 and 60 °C when the concentration of polyaspartic acid composition was 100 mg L<sup>-1</sup>. And the efficiency of biodegradability was 86.57 % in 28 days.

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