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Study on a Novel Composite Eco-Friendly Corrosion and Scale Inhibitor for Steel Surface in Simulated Cooling Water

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ABSTRACT

The use of organophosphorus inhibitor is diminishing because of its toxic effects on aquatic and other life. In this study, a composite eco-friendly phosphate-free corrosion and scale inhibitor HS has been developed using hydrolyzed polymaleic anhydride (HPMA), sodium gluconate, Zn^{2+} synergist and sulfamic acid. And the formula ratio of each component is 9:5:4:2. The performance of the corrosion and scale inhibitor was evaluated by weight loss experiment and the static scale inhibition test, respectively. The results indicated that HS had positive corrosion and scale inhibition effect at a dosage of 40 $mg \cdot L^{-1}$ or higher. Potentiodynamic polarization curves indicated that HS inhibits the corrosion of steel based on controlling the anodic reaction. And the surface morphology of the carbon steel was studied by scanning electronic microscope (SEM). The inhibition effects were due to the formation of protective films.

Keywords: Corrosion and Scale Inhibitor; Steel; Cooling System

1. Introduction

Circulating cooling water system is a commonly used instrument in industry. Two of the main operating problems of the cooling water system are corrosion and scale because of the electrochemical oxidation reduction reaction and the metal salt sediments on the metal surface [1]. Therefore, numerous inhibitors have been used in cooling water system to solve these problems [2-10].

Organophosphorus compound was a type of corrosion inhibitor of choice because of its long-term successful commercial usage and their excellent effectiveness at a wide range of conditions extensively used since 1980s [11]. However, industrial requirements for chemical compounds refer not only to their efficacy but to safety as well. The requisites for these compounds should focus on the non-mutagenic, non-carcinogenic products with characteristics more environmentally acceptable than systems currently in use [12]. So the use of organophosphorus inhibitors is diminishing because of its toxic effects on aquatic and other life [13]. Therefore, the current trend toward the inhibitors is to use more environmentally friendly phosphate-free inhibitors such as hydrolyzed polymaleic anhydride (HPMA) and Zn^{2+} synergist [14].

Some investigations have been reported that the effect of sodium gluconate as an effective non-toxic corrosion and scale inhibitor for ordinary mild steel in simulated cooling water [15]. Gluconate and gluconic acid as well as sodium, calcium and zinc salts of gluconic acid are reported as successful inhibitors against corrosion of tin, iron and mild steel in near neutral media and in simulated cooling water [16].

In this paper, a multi-component phosphate-free corrosion and scale inhibitor has been prepared by sodium gluconate, hydrolyzed polymaleic anhydride (HPMA), Zn^{2+} synergist and sulfamic acid. The performance of the phosphate-free corrosion and scale inhibitor was evaluated by rotary hanging sheet corrosion test and static scale inhibition test. The mechanism of corrosion and scale inhibition was preliminarily investigated by corrosion electrochemistry test [17].

2. Experimental

2.1. Main Materials

Sodium gluconate was purchased from Wujiang City Xiaolong Fine Chemical Co. Ltd., Hydrolyzed polmaleic anhydride (HPMA) was supplied by Daqing Fine Chemical Company of China. Zn^{2+} synergist and sulfamic acid were produced by Nanjing Fine Chemical Company. All chemicals were of analytical reagent grade.

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Double distilled water and analytical reagent-grade $CaCl_2$, $NaHCO_3$ were used for preparing the simulated cooling water. And the characteristics of the simulated cooling water were given in **Table 1**.

2.2. Determination of Static Corrosion Inhibition Efficiency

The static corrosion inhibition efficiency was tested by weight loss experiment, which was conducted in the simulated cooling water at 45˚C ± 1˚C using a thermostat. Dried and accurately weighed the polished carbon steel sheets. Then put the carbon steel sheets into a beaker with the 1 L the simulated cooling water with and without HS. Distilled water was supplied for evaporating every 4 hours. After a period of 72 h, the carbon steel sheets were taken out, washed by ethanol, dried, and accurately weighed. The corrosion inhibition efficiency was calculated by the Formula (1).

$$\text{n}(\%) = \frac{M0 - M1}{M1} \times 100 \qquad (1)$$

In the formula, n presents the corrosion inhibition efficiency, *M*0 and *M*1 are the values of the weight loss of carbon steel after 72 hours being immersed in the simulated cooling water without and with HS.

2.3. The Static Scale Inhibition Test

HS was infused into the 1 L solution containing 120 $mg \cdot L^{-1}$ Ca^{2+}, 240 $mg \cdot L^{-1}$ HCO_3^-. And the mixture was incubated for 10h at 80˚C. After a period of 72 h, the filter liquor was titrated by Ethylene Diamine Tetraacetic Acid (EDTA). The static scale inhibition efficiency was calculated by the Formula (2).

$$R(\%) = \frac{V0 - V1}{V0 - V2} \times 100 \qquad (2)$$

In the formula, *V*0 is the amount of consumed EDTA of the sample without the addition of HS before incubation, *V*1 is the amount of consumed EDTA of the sample with the addition of HS after incubation, and *V*2 is the amount of consumed EDTA of the sample without the addition of HS after incubation.

Table 1. The simulated cooling water characterization data.

Parameter	pH	Conductivity	Total hardness	Total alkalinity	Calcium	Chloride
Value	7.66	692	295	15	144.26	273.05
Units	-	$\mu S \cdot cm^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	Ca^{2+} $mg \cdot L^{-1}$	Cl^- $mg \cdot L^{-1}$

2.4. Electrochemical Experiments

The electrochemical measurements were carried out in a cell with three-electrode mode; platinum sheet and saturated calomel electrode (SCE) were used as counter and reference electrodes.

The 1 cm^2 steel sample was abraded, washed, finally immersed in the simulated cooling water. Polarization curves measurements were performed using SC350 Electrochemical System. When polarization curve test was carried out, the potential scan rate was adjusted to 0.01 $v \cdot s^{-1}$. Polarization curves could be achieved after data process.

2.5. Surface Analyses

Corrosion crystal morphology on the surface of carbon steel was observed by scanning electronic microscope (SEM). In this experiment, the carbon steel was immersed in water sample with and without HS at the dosage of 40 $mg \cdot L^{-1}$, respectively. Afterwards the test coupon was washed with 98% (w/w) anhydrous alcohol and dried. Accelerating voltage of the SEM was 25 kV, and amplification factor was 200.

3. Results and Discussion

3.1. Confirming the Optimal Dosage of HS

The data in **Table 2** indicated that the corrosion inhibition efficiency of HS increased as the dosage increased. And the corrosion inhibition efficiency reached more than 94%, when the dosage higher than 40 $mg \cdot L^{-1}$.

Table 2. Influence of the dosage of HS on corrosion inhibition efficiency.

Dosage of HS ($mg \cdot L^{-1}$)	No. of the steel sheets	Weight loss of carbon steel (g)	Average weight loss of carbon steel (g)	Corrosion inhibition efficiency (%)
0	1085	0.2018	0.1966	0.00
0	1083	0.1914		
20	1792	0.0387	0.0373	81.02
20	1797	0.0359		
40	1081	0.0110	0.0112	94.30
40	1795	0.0114		
60	1794	0.0103	0.0101	94.86
60	1798	0.0099		

3.2. Static Scale Inhibition Performance Analysis

Figure 1 showed the scale inhibition performance of HS. When the dosage of HS changed from 0 to 50 $mg \cdot L^{-1}$, the scale inhibition efficiency of HS increased only from 0% to 98.97%. The results showed that HS had excellent scale inhibition ability at the higher dosage, and the static scale inhibition efficiency of HS increased with the increase of the dosage of HS.

3.3. Corrosion Electrochemistry Results Analysis

The corrosion inhibition property of the HS was measured using electrochemical method, and the results were given in **Table 3**. And the inhibition efficiency of HS for the carbon steel corrosion was calculated by Formula (3):

$$\eta = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100\% \quad (3)$$

where I_{corr} and I'_{corr} are the corrosion current density values with and without HS, respectively.

The data in **Table 3** showed that the self-corrosion current of carbon steel changed from 221 $\mu A \cdot cm^{-2}$ in the absence of HS into 12 $\mu A \cdot cm^{-2}$ at the dosage of 60 mg/L HS in the simulated cooling water. These results illustrated that HS had the properties of corrosion inhibition, the achieved efficiency reaching a maximum value of around 94%, at the dosage of 60 mg/L.

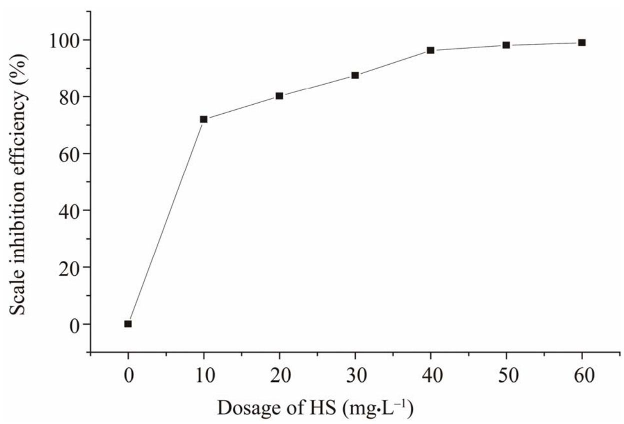


Figure 1. Influence of the dosage of HS on scale inhibition efficiency.

Table 3. Electrochemical parameter with different concentrations of HS in the simulated cooling water.

Concentration of corrosion inhibitor ($mg \cdot L^{-1}$)	E_{corr} (*v*sSCE) (mV)	I_{corr} ($\mu A \cdot cm^{-2}$)	Corrosion rate η (%)
0	–472	221	0
20	–451	42	81.00
40	–433	14	93.67
60	–426	12	94.55

The polarization curves of carbon steel with the addition of HS in the simulated cooling water were given in **Figure 2**.

In **Figure 2**, the corrosion potential was shift to the positive after the inhibitor was added. The increasing in anodic current density indicated that the dissolution of the anode materials. **Figure 2** showed the anode I_{corr} was reduced from 201 $\mu A \cdot cm^{-2}$ to 21 $\mu A \cdot cm^{-2}$ after adding the inhibitor. It indicated that the anode corrosion process was inhibited. And the anodic inhibition effect was more significantly than the cathode with the inhibitor. **Table 2** and **Table 3** showed consistent results in the aspect of corrosion inhibition efficiency.

3.4. Surface Analyses

Figure 3 showed that the morphology of the corrosion products formed without HS was granular, irregular, and contains a number of voids. In comparison, the surface of the carbon steel with 40 $mg \cdot L^{-1}$ of HS was flat and smooth. The scratch and few corrosion products on the surface of the carbon steel formed because of polishing hang-parcel. But there were little corrosion marks. Results illustrated that a complete coherent protective film formed on carbon steel surface after adding HS. It protected the carbon steel from corrosion by the simulated cooling water.

4. Conclusion

A composite eco-friendly phosphate-free corrosion and scale inhibitor HS has been developed using hydrolyzed polymaleic anhydride (HPMA), sodium gluconate, Zn^{2+} synergist and sulfamic acid. And the formula ratio of each component is 9:5:4:2. The experimental results showed that HS was a kind of good corrosion and scale

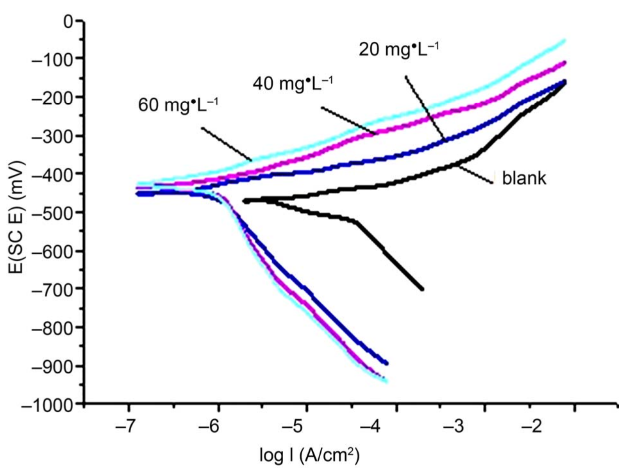
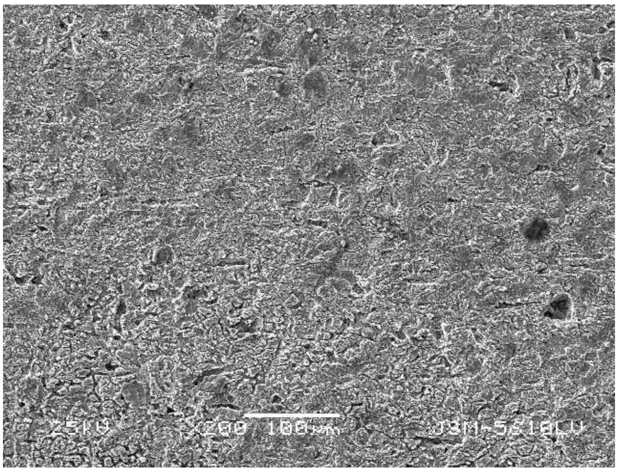
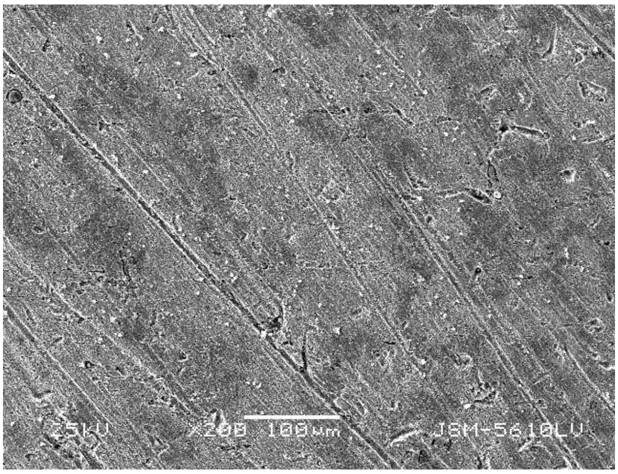


Figure 2. The polarization curve of blank and adding phosphate-free scale corrosion inhibitor treated samples in the simulated cooling water.



(a)



(a)

Figure 3. (a) and (b) were corrosion crystal on the carton steel surface without and with HS, respectively.

inhibitor whose corrosion inhibition rate and scale inhibition rate surpassed 94% and 98%, respectively. Polarization curve test showed that HS was a kind of corrosion and scale inhibitor by mainly controlling anodic reaction. The surface morphology of the carbon steel was observed by SEM showed that a protective film was formed on the surface of the carbon steel with HS.

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