

# Adsorption mechanism of a Phosphorus-Free Inhibitor for Circulation Cooling Systems

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**Abstract.** Adsorption mechanism of a non-phosphorus inhibitor were studied, in the simulate condition of a circulation cooling system. The inhibitor enable control the corrosion of system containing both carbon steel and copper alloy. Morphology analysis and electrochemical studies showed that the inhibitor performed excellently as a corrosion inhibitor and protect metals well. Adsorption isotherm studies showed that the adsorption of inhibitor on sample surface obeyed Langmuir isotherm, and  $\Delta G^{\ominus} < 0$ . Indicated that Multi-Synergy adsorption was the main mechanism for this inhibitor. Therefore, the environment-friendly inhibitor is an efficiency inhibitor and could control both corrosion and scaling for the circulation cooling conditions.

**Keywords:** Phosphorus-free; Corrosion inhibition; Scale inhibition; Mechanism; Circulation cooling system;

## 1. Introduction

The best and economic way is adding inhibitor in water [1]. Phosphorus-free or low-phosphorus inhibitors have become the development trend [2]. And complex inhibitors based on the synergistic effects of organic inhibitors and inorganic inhibitors have become a hotspot [3], these years. Therefore, a complex phosphorus-free inhibitor with synergistic effects was prepared and optimized to solve the main problem of corrosion in circulation cooling system. The properties and mechanism of the complex inhibitor were investigated.

## 2. Experiments

### 2.1. Preparation of Complex Phosphorus-free Inhibitor

The complex phosphorus-free inhibitor was prepared based on the synergistic effects of Gluconate, carboxyl, epoxy-, Zn ion, borate and surfactant. The inhibitor consisted of part A and part B. Part A was prepared by mixing Sodium Gluconate, Poly(acrylic acid) (35%),  $ZnSO_4 \cdot 7H_2O$  and surfactant in 80ml deionized water, in a ratio of 10:5:5:(0~1). Part B was prepared by epoxysuccinic acid (50%), borax and BTA in 20ml ethanol, in a ratio of 10:10:1. And then mix these two parts to prepared final inhibitor.

### 2.2. Surface Morphology

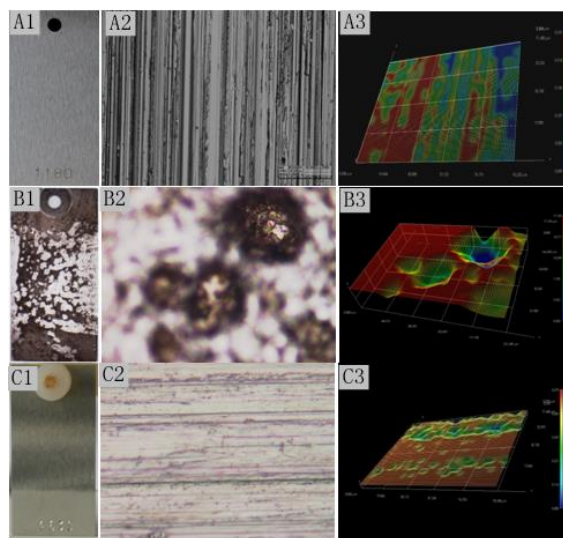
Specimens (50 mm×25mm×2mm) of Carbon steel 20# and copper 70#, bought from Gaoyou Company China, were used in the experiment. The surface morphologies and 3D video were investigated after the standard weight loss experiment. The macro-morphologies of specimens were examined by digital camera. The micro-morphology and 3D images were investigated by 3D Digital Microscope (Hirox HK7700) at the magnification of 3500 times.

### 2.3. Electrochemical Measurement

Samples used in electrochemical tests were abraded with silicon carbide emery paper within a range of 400 to 1500 grit sizes. Electrochemical measurements were taken by VMP3 electrochemical station, with a three-electrode system and SCE electrode reference. The experiments were performed with a scan rate of 1 mV/s.

## 3. Results and Discussions

### 3.1. Morphologies

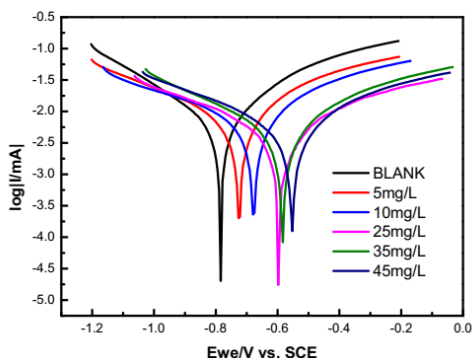


**Fig 1.** Morphologies of carbon steel samples (A before weight loss experiment; B after weight loss experiment without inhibitor; C After weight loss experiments with inhibitor)

As shown in Fig. 1 (A1-A3), the specimens were freshly polished with smooth surface before weight loss experiment, and there were some small scratches with depth about  $0.267\mu\text{m}$ . However, the uninhibited samples surfaces after weight loss experiment were severely damaged and become rough, with depth about  $17.76\mu\text{m}$  (Fig. 1 B1-B3). This could be due to the aggressive attack from corroding solution. The surfaces of specimens with inhibitor were powerfully protected (Fig. 1C1-C3), with depth about  $0.579\mu\text{m}$ , which were lighter than that without inhibitor. Thus it was obvious that corrosive attack was considerably restricted by the inhibitor, indicating a good anti-corrosion ability.

### 3.2. Electrochemical analyses

Carbon steel was more prone to corrosion in the system containing both carbon steel and copper alloys. So, further investigations were carried out on carbon steel specimen. Potentiodynamic polarization curves were presented in Fig. 2. Results showed that all the curves were similar with each other, indicating that the similar inhibition mechanism in the solution. In addition, the corrosion current densities decreased significantly with adding inhibitors. And the polarization curves move to positive potential with the concentration.



**Fig 2.** Potentiodynamic polarization analysis

The electrochemical parameters from Potentiodynamic polarization curves were listed in Tab. 1. Results showed that  $E_{corr}$  shift more than 230 mV towards positive potential. This revealed that the complex inhibitor act as modest cathode inhibitor. Tab. 1 also showed that  $I_{corr}$  decrease obviously and it kept reducing with the concentration, when the inhibitor was added. These indicated that the inhibitor had superior corrosion protection due to its more positive  $E_{corr}$  and significantly lower  $I_{corr}$ . Therefore, the inhibitor could be deemed as effective inhibitors and high concentration could improve their inhibitive performance. The results of the Tafel analysis were in good agreement with those of the weight loss analysis.

**Tab 1.** Potentiodynamic polarization parameters at 298 K

	corrosion potential $E_{corr}(mV \text{ vs SCE})$	corrosion current density $I_{corr}(\mu A)$	cathodic Tafel slope $\beta_c(mV)$	anodic Tafel slope $\beta_a(mV)$
0	-784.213	4.879	286.9	241.6
5	-724.015	4.369	326.0	240.0
10	-678.042	3.973	338.0	237.1
20	-597.231	2.676	312.6	303.2
35	-582.312	2.663	335.1	277.1
45	-553.106	2.653	296.4	249.2

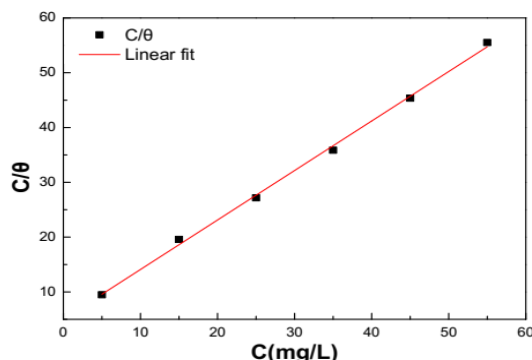
### 3.3. Adsorption Isotherm Studies

Langmuir isotherm and correction Langmuir isotherm modes (Eq. 1 and Eq. 2) were used to analyze adsorption isotherm.

$$\frac{\theta}{1-\theta} = K_{ads} \times C \tag{1}$$

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{2}$$

Where  $\theta$  (defined as  $X_l$ ) is the surface coverage,  $K_{ads}$  is the equilibrium constant of the adsorption process,  $C$  is the inhibitors concentration.



**Fig 3.** Adsorption isotherm studies of this inhibitor

Fig. 3 showed the plots of  $C$  vs.  $C/\theta$  yield straight lines. The intercept was  $1/K$ . Results showed that Langmuir isotherm mode was suitable to fit the results of weight loss measurements, and the linear regression coefficients was approximately  $1$  ( $R^2=0.9991$ ). Indicating inhibitor adsorption at metal surface obeyed the Langmuir isotherm. The  $K_{ads}$  calculated from the linear fitting was  $K_{ads}=0.1975\text{L/mg}$ . In addition,  $\Delta G_{ads}^\theta < 0$  means a spontaneous adsorption process, which can be calculated as Eq. 3.

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-G_{ads}^\theta}{RT}\right) \quad (3)$$

The calculated values of  $\Delta G_{ads}^\theta$  was  $-24.3\text{ kJ/mol}$ , which indicated that the inhibitor was a mix adsorption inhibitor and possess strong adsorption affinity onto the sample surface, which involves both physisorption and chemisorption. And thus the inhibitor exhibit fine inhibition behavior [4]. This result further confirmed the adsorption mechanism.

As analysis above, we can speculate that the studied inhibitor was an adsorption inhibitor. First, the organic inhibitors with heteroatom(s) (N, P, O, or S) had lone pair electrons, and/or delocalized  $\pi$  electrons [5]. Hence, the it can reach the steel surface easily and commence their adsorption, due to its N and O lone pair electron in the organic contents (sodium gluconate, Poly(acrylic acid), epoxysuccinic acid and BTA). Second, the gluconate could connect with anode dissolution products ( $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ ) in the anode zone to form deposition film of insoluble salts or chelate complexes, and could further inhibit the dissolution of the anode. At the same time,  $\text{Zn}^{2+}$  could react with the cathode product  $\text{OH}^-$  and form insoluble hydroxides and deposit on the electrode surface. The above inhibitory factors had a positive synergistic effect and reduce the corrosion rate. Therefore, the sample was protected with complex adsorption of this inhibitor.

## 4. Conclusions

Focus on the corrosion and scaling problems of the cooling system with both carbon steel and copper alloys, a new phosphorus-free inhibitor was published. Electrochemical tests showed that the impedance increased and the corrosion potentials shift towards positive (about 230 mV), in the present of inhibitors. In addition, adsorption isotherm was studied to further understand adsorption mechanism. Results showed that the adsorption of the inhibitor obeyed Langmuir isotherm well, and adsorption free energy ( $\Delta G^\theta$ ) was  $-24.3\text{ kJ/mol}$ . Results indicated that Multi-Synergy adsorption was the main mechanism for the inhibitor, with mixed physisorption and chemisorption.

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