

Study on Corrosion Inhibition and Adsorption of Polyaspartic Acid Corrosion Inhibitor to Seawater Copper

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Abstract: The inhibitory performance and adsorption behavior of green inhibitor polyaspartic acid (PASP) on copper in 3% NaCl solution was studied by electrochemical impedance and polarization curve method. The results showed that when PASP was used at an optimal concentration of 15 mg/L, the corrosion inhibition rate could reach 77.2%. The adsorption of PASP significantly reduced the erosion of Cl⁻, which belongs to the anode type corrosion inhibitor. The adsorption behavior of PASP obeys the Langmuir adsorption isotherm. The formula is a spontaneous and exothermic process that belongs to chemical adsorption.

1. Introduction

As the coastal areas are facing a crisis of severe shortage of fresh water resources, it is imperative to vigorously develop and use sea water resources [1-3]. As an industrial cooling water, seawater not only helps alleviate the problems of the shortage of fresh water that is inconsistent with industrial development, but also has the advantages of low water intake temperature, good cooling effect, and simple operation and management. Since the seawater circulation cooling technology has a small amount of water and a low water price, it is economically more reasonable. In the circulating water cooling system material, the application of steel is more common, but relative to copper, the steel is more susceptible to corrosion in seawater [4]. Copper has become an important industrial material due to its high positive potential, excellent heat conduction and mechanical processing properties, and excellent corrosion resistance and other characteristics. It has begun to replace carbon steel in electronic equipment in more fields. However, copper is also susceptible to different forms of corrosion through different corrosive factors, such as the corrosion promoting effects of chlorides, sulfates, nitrates, etc., particularly in chloride-ion containing media [5, 6].

For corrosion of metals, the use of corrosion inhibitor is a cost-effective method. Copper corrosion inhibitors are required for pickling. Most of the acid and corrosion inhibitors contain nitrogen and sulfur. Oxygen-containing organic compounds can form a corrosion-inhibiting film on the surface of copper to reduce corrosion. With the increasing awareness of environmental protection for humans, environmentally-friendly corrosion inhibitors become the development direction of copper corrosion inhibitors as corrosion inhibitors in industrial cooling water treatment chemicals. In the 1970s, the application of corrosion inhibitors of Cr series and P series was relatively popular, but in recent years it has been limited by the environment [7].

At present, the development of environmentally friendly corrosion inhibitors that are non-toxic and conducive to environmental protection has been developed industrially. Polyaspartic acid (abbreviated as PASP) is a biopolymer developed in recent years and has excellent scale inhibition and dispersion properties and good biodegradability. In neutral systems, the study of polyaspartic acid as a metal corrosion inhibitor has become a hot topic at home and abroad. Especially in the acidic environment, polyaspartic acid is a green product [8, 9]. It is a polymer made from the shrinkage of amino and carboxyl groups of aspartic acid monomers, and can be completely biodegraded into substances harmless to the environment. It is non-toxic. Non-pollution, is a kind of environment-friendly polymer research found that polyaspartic acid has various functions such as corrosion inhibition, scale inhibition, chelation, moisturizing, and dispersion, and the economic and

social benefits are very considerable.

In this paper, the corrosion inhibition and adsorption behavior of polyaspartic acid (PASP) for copper in seawater was studied by electrochemical method.

2. Corrosion Mechanism of Copper in Seawater

2.1 Electrochemical Characteristics of Corrosion in Seawater and Simulated Seawater

Seawater is a typical electrolyte, so the basic laws of electrochemical corrosion are applicable to seawater corrosion [10]. However, starting from the characteristics of seawater, the electrochemical process of seawater corrosion has the following features:

1) Halogen ions such as chlorine ions in seawater can hinder and destroy the passivation of metals, and the anodic process of seawater corrosion is easier to perform. The destructive effects of chloride ions including: osmotic destruction of oxide films and destructive destruction of colloidal protective films; easier adsorption than certain deactivators; adsorption on metal surfaces or on thin passive films, forming strong electric field which makes the metal ions easy to elute; the complex with metal to chlorine accelerates the dissolution of the metal. All these effects can reduce the anodic polarization retardation and cause the seawater to be highly corrosive to metals.

2) The cathode depolarizer for seawater corrosion is oxygen, and the cathode process is the controlling link of the corrosion reaction. At the pH value of seawater, the corrosion of most metals in seawater depends on oxygen depolarization.

3) The resistive block of seawater corrosion is small, and the contact of dissimilar metals can cause significant galvanic corrosion.

4) In seawater, local corrosion such as pitting corrosion and crevice corrosion is prone to occur due to the local destruction of passivation.

2.2 Corrosion mechanism of copper

The content of oxygen and Cl^- in the chloride medium is the main factor affecting the corrosion. Cl^- can increase the corrosion activity, damage the passivation film on the metal surface, and easily generate pitting corrosion.

When the mass concentration of Cl^- is less than 1 mol/L, the reactions shown in Figure 1 occur when the copper is corroded:

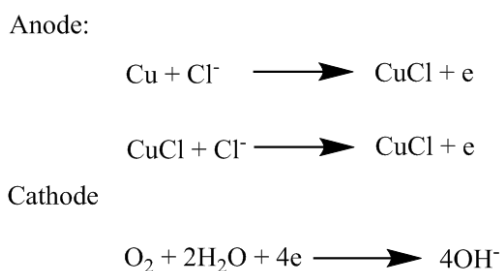


Fig.1 Electrode reaction when copper is corroded

The use of corrosion inhibitors is one of the important means to control the corrosion of copper and copper alloys.

3. Experimental Materials and Methods

3.1 Electrochemical test system

The experimental material is pure copper (>99.9%). The pure copper is cut into electrodes (10 mm×5 mm×1 mm) and the epoxy resin is solid-sealed on its non-working surface, get a working surface area of 0.5 cm². Before test, the electrode is polished by metallographic sandpaper, then washed by ionized water, anhydrous ethanol, and deionized water and dried with cold air. When using electrochemical calorimetry, use a saturated calomel electrode as the reference electrode and a Pt electrode as the counter electrode. The etching solution used is a 3% NaCl solution (analytically

pure) made of deionized water. Corrosion inhibitor PASP is homemade with a molecular weight of 5000. The experimental temperature is controlled by the constant temperature water bath.

3.2 Test method

The electrode was soaked in the solution for 1 h and tested for AC impedance and polarization curves. The frequency range of the AC impedance was 100 kHz-0.05 Hz. The equivalent circuit was analyzed and processed by EQUIVCRT software.

4. Results and Discussion

4.1 Polarization curve

The pure copper electrode was immersed in 3% NaCl simulated sea solutions with different PASP concentrations for 30 minutes to perform polarization curve test. Figure 2 shows the polarization curve obtained by the test. As can be seen from Figure 2, the self-corrosion potentials of the different citric acid solutions are positively shifted compared to the citric acid stock solutions. After adding different corrosion inhibitors, it can be seen from the figure that both the anode and the anode reactions been somewhat inhibited. It shows that the addition of corrosion inhibitors(PASP) well inhibits the corrosion of pure copper electrodes.

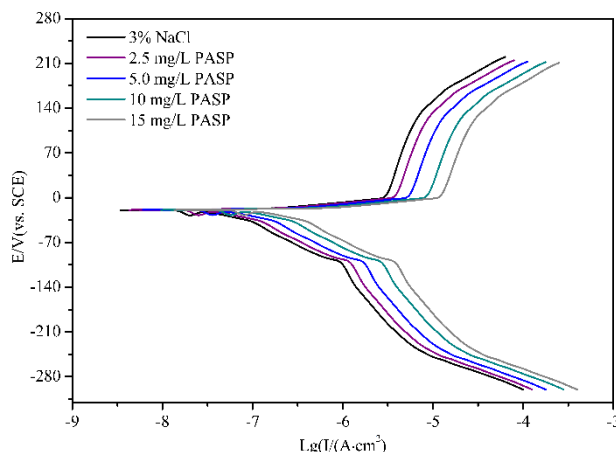


Fig.2 Polanization curves for copper in sea water in the different concentrations of PASP

The corrosion inhibition efficiency is calculated according to the following formula:

$$\eta = \frac{J_0 - J_{corr}}{J_0} \times 100\%$$

In the formula, J_0 represents the self-corrosion current density of the pure copper electrode in the citric acid stock solution; J_{corr} represents the self-corrosion current density of the pure copper electrode after adding different corrosion inhibitors.

The corresponding electrochemical parameters are shown in Table 1. As can be seen from Table 1, under the same conditions, add more PASP would get a better effect.

Table 1 Elaetrochemical parameters of copper electrodes with different concentrations of PASP at 25°C

C_{PASP} (mg/L)	I_{corr} ($\mu A/cm^2$)	$E_{corr}/mV(vs\ SCE)$	β_a (mv)	β_c (mv)	$\eta(\%)$
0	3.266	-56.8	110.6	137.3	-
2.5	1.652	-54.2	188.5	125.6	49.4
5	0.986	-51.3	436.5	201.4	69.8
10	0.865	-48.2	556.7	235.4	73.5
15	0.745	-44.7	671.5	243.7	77.2

β_a :anodic Tafel slop; β_c :cathodic Tafel slope; η : inhibition efficiency; E_{corr} : corrosion potential

With the addition of PASP, the corrosion current density of the electrode gradually decreases. When the PASP concentration is 15 mg/L, the corrosion current density is the smallest in the 3% NaCl simulated sea water corrosion solution. The amount of PASP added is 15 mg/L is the best, and the corrosion inhibition rate can reach 77.2%. The tendency of Tafel slope in the anode area is greater than the Tafel rate in the cathode area, which can be judged by the corrosion potential. So the PASP is an anode typ corrosion inhibitor under this condition.

4.2 Impedance spectrum

The impedance spectrums of copper electrode when treated with different concentrations of PASP were tested using the simulated analog circuit shown in Figure 3.

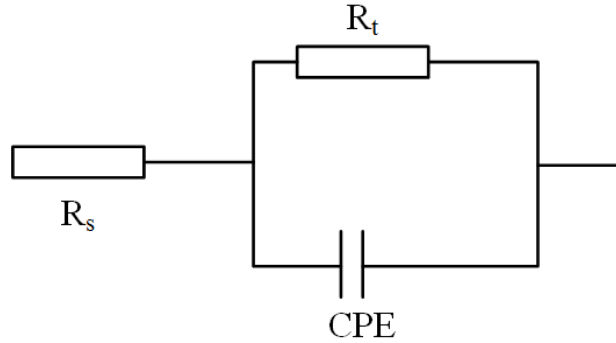


Fig.3 Power power short-run balance

R_s is the solution resistance, R_t is the interface transfer resistance, and CPE is the double-layer constant phase angle element.

The CPE element can be expressed by the following equation:

$$Z_{CPE} = \frac{1}{Y_0^{-1}(j\omega)^{-n}}$$

In the formula, Z_{CPE} is the impedance of CPE, Y_0 is the admittance of CPE, ω is the angular frequency of perturbation signal, and n is the dispersion index of CPE (depending on the roughness of the electrode surface and current distribution). When n is 0, 0.5, respectively, At 1 o'clock, CPE stands for pure resistance, warburg impedance, and pure capacitance.

At room temperature (25°C), different mass concentrations of polyaspartic acid were added to the medium and the complex impedance planogram was obtained, as shown in Figure 4.

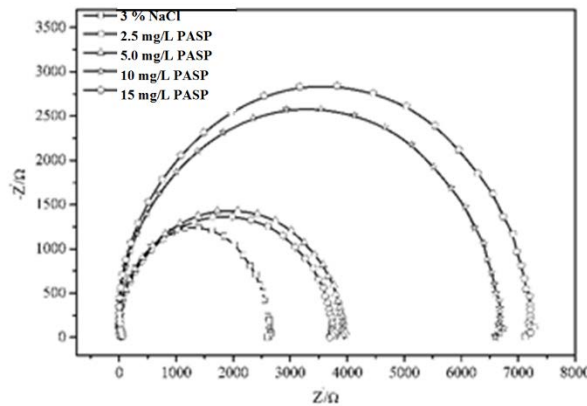


Fig.4 Nyquist plots for the copper in the different of PASP at 25 °C

It can be seen from Figure 4 that the impedance spectrum shows different degrees of major semi-circle characteristics. As the concentration of PASP increases, the semicircle increases and the R_t value of the electrode increases. Therefore, the corrosion rate decreases and the corrosion inhibition efficiency increases.

Considering the analog circuit shown in Figure 4, fit the curve data in the graph and calculate the R_t and η values at 20 °C. Then get another corrosion inhibition efficiency as shown in Table 2. Among them:

$$\eta = \frac{R_t - R_0}{R_t} \times 100\%$$

Where η is the corrosion inhibition efficiency; R_{t0} is the charge transfer resistance of the blank solution; R_t is the charge transfer resistance after the addition of the corrosion inhibitor.

Table 2 According to Nyquist workout resistance and the inhibitor efficiency

C_{PASP} (mg/L)	R_t (Ω)	η (%)
0	2603.4	-
2.5	3696.9	27.6
5	3881.7	32.9
10	6598.9	60.5
15	7126.9	63.5

As can be seen from Table 2, different concentrations of polyaspartic acid are added to the medium, and the resistance R_t is transmitted as the concentration increases. As the value increases, the corrosion inhibition rate η increases. The conclusions obtained have slightly difference with those obtained by the steady state polarization test but have similar trend.

4.3 Adsorption Mechanism of PASP on Copper Electrodes

Assuming there is no other process on the metal surface, only the adsorption and desorption process of the corrosion inhibitor, the adsorption coverage rate of the corrosion inhibitor on the metal surface when the adsorption and desorption processes reach equilibrium, and the concentration C of the corrosion inhibitor in the solution. There is a balance relationship. This equilibrium relationship can be expressed by the adsorption isotherm. According to the experimental results, several isothermal equations of Frumkin, Temkin, Langmuir, and Freundlich were used to fit. The results show that the experimental results agree well with the Freundlich isothermal equation.

For example, the experimentally measured corrosion inhibition rate η is used instead of the surface adsorption coverage θ . According to the data shown in Table 2, we can get free energy of the adsorption during this process.

The corrosion potential data in Table 2 shows that with the addition of PASP, the corrosion potential E_{corr} does not change significantly, and it can be inferred that the corrosion mechanism is a “covering effect” and the corrosion rate is turbid, indicating its coverage. Assuming PASP is on the copper surface and adsorption conforms to Langmuir adsorption isotherm

$$\frac{C}{\theta} = C + \frac{1}{B}$$

Where B is the Langmuir constant and c is the inhibitor concentration:

Figure 5 is obtained by plotting $\frac{C}{\theta}$ versus c , and the slope and intercept are obtained by fitting the line. Then we get the following relationship:

$$\frac{C}{\theta} = 6.12C + 1.14$$

The fitting $R = 0.95$ indicates that the adsorption of PASP on the copper surface is in good agreement with Langmuir isotherm adsorption. Substituting the fitting data into equation (3) yields $B = 100 \text{ L} \cdot \text{mol}^{-1}$ (The standard of B should be $\text{L} \cdot \text{mol}^{-1}$, and the amount of aspartic acid per monomer in polyaspartic acid is $114 \text{ g} \cdot \text{mol}^{-1}$, so $1/B = 1.14/114$, that is, $B = 100 \text{ L} \cdot \text{mol}^{-1}$). The relation between B and the adsorption Gibbs free energy ΔG_0 is: $B = \frac{e^{-\Delta G_m / 2.3RT}}{C^*}$

Where $C^* = 55.5$ is the solubility of water in solution in mol/L. Then calculated by equation, ΔG_0

= - 49.13 kJ/mol.

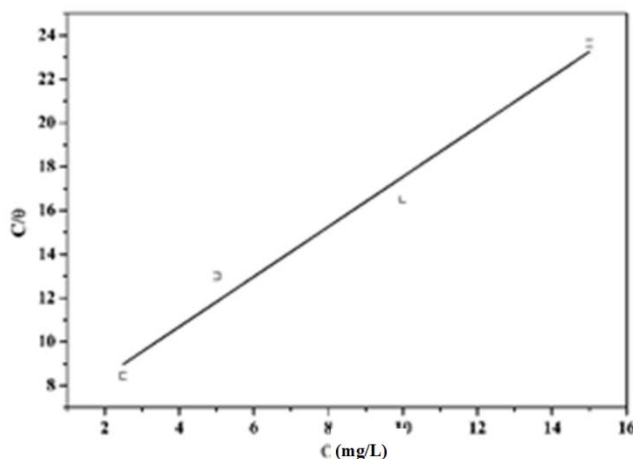


Fig.5 Langmuir isotherm model of PASP on copper

According to Brdika's research results, the standard adsorption free energy of chemisorption and physisorption is limited to about 100 kJ/mol, which greater than this value is chemical adsorption, and less than this value is physical adsorption. This article yielded -49.13 kJ/mol, indicating PASP. The inhibition effect on the copper surface may be due to chemical adsorption.

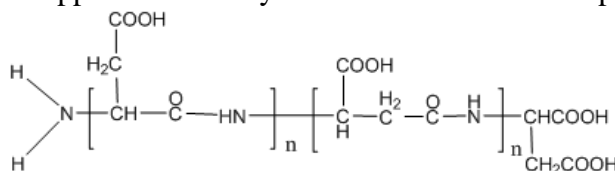


Fig.6 Molecular structure of PASP

From the perspective of the molecular structure of PASP in Figure 6, it is a water-soluble macromolecular polypeptide chain, with polar groups such as carboxyl, carbonyl, amino and nitrogen hydrogen bonds. Oxygen and nitrogen atoms in the carbonyl group contain lone pair electrons. Oxygen atoms also contain π bonds, which can both chemically adsorb with copper atoms, align polar groups on the metal surface, and increase the anodic reaction resistance; non-polar groups have a large steric hindrance, hindering the cathode oxygen. Copper surface diffusion inhibits the reduction of the cathode. Therefore, it is a physical combine with chemical adsorption process.

5. Conclusions

The following conclusions were obtained from electrochemical experiments:

(1) In simulated sea water systems, PASP has a corrosion-inhibiting effect on carbon steel, which is a corrosion inhibitor that mainly suppresses the anode. With the increase of the concentration of PASP, the corrosion inhibition efficiency increases; when the concentration reaches 15 mg / L, corrosion inhibition efficiency can reaches 77.2%.

(2) In the experimental temperature range, the adsorption of PASP on the copper surface follows the Langmuir adsorption isotherm; at 25°C, $B=100$, $\Delta G_0 = - 49.13$ kJ/mol.

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