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Short Communication

Study on the Pyrazole Corrosion Inhibition and Synergistic Effect for Copper in Alkaline Solution

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The corrosion inhibition behavior of pyrazole and the synergistic effect with benzotriazole (BTA) or 2-mercaptobenzothiazole (MBT) on the corrosion of copper in 0.05 M $NaHCO_3$ solution were studied using cyclic voltammetry techniques (CV) and rotating disc electrode (RDE). The results showed that the adsorption of Pz on the surface of copper obeyed Frumkin adsorption isotherm, and the anodic dissolution of copper is determined by the electrochemical step. There was a synergetic effect between pyrazole and BTA, but it was unconspicuous between pyrazole and MBT.

Keywords: pyrazole, corrosion inhibition, synergistic effect, copper

1. INTRODUCTION

Significant progress has been made in the study of copper corrosion inhibitors [1-5], especially on the inhibition mechanism of benzotriazole (BTA) and 2-mercaptobenzothiazole (MBT) [3,5]. It is usually believed that the adsorption of organic compounds on the surface of copper through nitrogen or sulfur atom prevents the dissolution of copper. Gad Allah *et al* [6] studied the corrosion inhibition of copper and copper alloys in hydrochloric acid by amino pyrazole derivates using electrochemical impedance spectroscopy and polarization curve method. They found that the inhibitors adsorbed on the surface of copper without changing the mechanism of copper dissolution [6]. The research of Geler and Azambuja [7] indicated that pyrazole-Cu(II) complex was formed on the surface of copper in hydrochloric acid solution. However, a large amount of research had been done in acid solutions, but little in alkaline solution.

This work studies the inhibition behavior of pyrazole (Pz) and its synergistic effect with BTA or MBT on the corrosion of copper in 0.05 M $NaHCO_3$ solution using cyclic voltammetry techniques (CV) and rotating disc electrode (RDE).

2. EXPERIMENTAL

2.1 Materials and solutions

The rectangular samples（5×2.5×0.2cm）of copper were used for weight loss measurements. For galvanostatic polarization measurements, cylindrical copper electrodes (Φ 5.1mm×1mm) were mechanically polished using different grades of emery papers to 1200 grit, rinsed with redistilled water, degreased ultrasonically in acetone before use and dried at room temperature.

Industrial reagent-grade Pz, BTA and MBT were used as received. Analytical reagent $NaHCO_3$ was used to make alkaline solution.

2.2 Electrochemical measurements

A conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference was used. The copper RDE working electrode was embedded in epoxy resin with a 0.2042cm^2 exposing surface to the solution.

Electrochemical experiments were carried out using a CHI660B electrochemical workstation. Cyclic voltammetry sweep started at -0.7V and the scan rate was 1mVs^{-1}.

2.3 Weight loss measurement

Traditional weight loss tests were carried out in 0.05 M $NaHCO_3$ solution using a cylindrical copper rod at 50 ℃ for 72 hours.

3. RESULTS AND DISCUSSION

3.1 Electrochemical measurements

Fig. 1 shows the cyclic voltammetry curves of copper in 0.05M $NaHCO_3$ solution containing different concentrations of Pz. It is apparent from these plots that the critical passivation current density (i_{pp}) decreased with the increase of the concentration of Pz in the solution, which suggests that a film has formed on the surface of copper to inhibit the dissolution of the substrate. When the concentration of Pz reaches a certain value, the decrease of the i_{pp} becomes not appreciable. No distinct change is observed for both anodic and cathodic peak potentials in the presence of various

concentrations of Pz, while the peak current for both anodic and cathodic decreases when the concentration of the Pz has been increased.

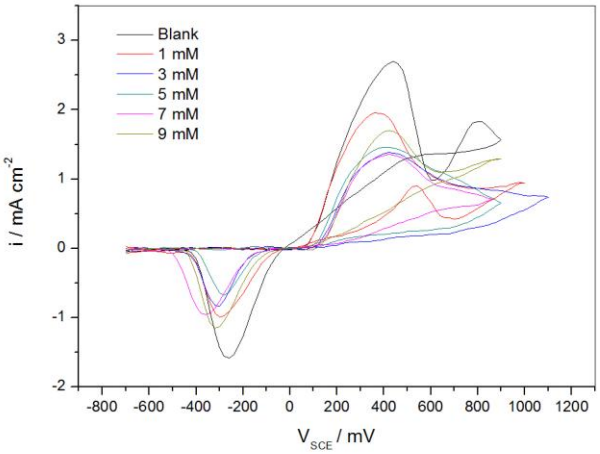

Figure 1. Cyclic voltammetry curves for copper in 0.05 M $NaHCO_3$ solution with different concentrations of pyrazole (30 ℃, 1000 rpm).

The corrosion inhibition of copper by adsorptive inhibitors has been considered as "coverage effect" [8]. The degree of surface coverage (θ) is obtained from $\theta = (i_0 - i_{pp})/i_0$, in which i_o is the critical passivation current density of the blank without Pz; i_{pp} is the critical passivation current density of so called solution with different concentration of Pz. The $\theta \sim c$ curve between the degree of surface coverage and the concentration of Pz in 0.05 M $NaHCO_3$ solution is presented in the inset of Fig. 2. As it can be seen from the inset fig, the curve of θ changed with c and showed S pattern, suggests that the existence of saturated adsorption of Pz on the surface of copper in $NaHCO_3$ solution [8].

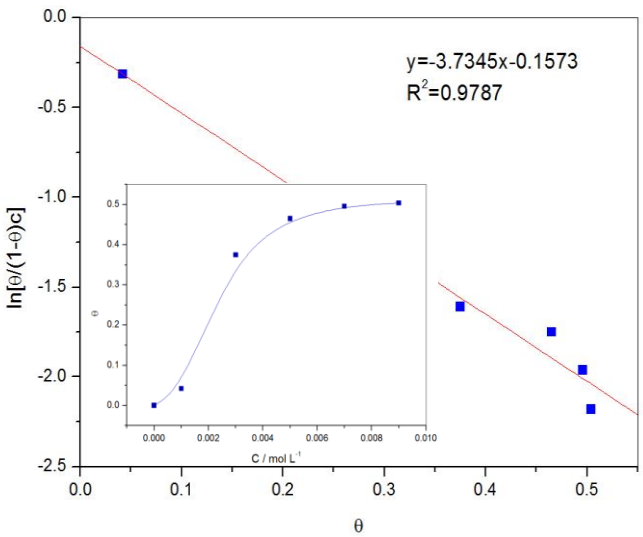

Figure 2. The plot of $\theta \sim c$ curve and relationship between ln[θ/(1-θ)c] and θ of pyrazole in 0.05M $NaHCO_3$.

Several adsorption isotherms, such as Langmuir, Temkim and Frumkin isotherms, have been tested for the description of adsorption behavior of the inhibitor. The plot of ln[θ/(1-θ)c] vs. θ give straight line as shown in Fig. 2 with the slope of -3.734, and the value of correlation coefficient is 0.978. The results indicate that obeys the Frumkin adsorption isotherm of Pz on the surface of copper in the $NaHCO_3$ solution in accordance with equation (1):

$$\ln \frac{\theta}{(1-\theta)c} = -2a\theta + \ln K \quad (1)$$

Where a is the interaction parameter of the adsorbate, K is the equilibrium constant of the adsorption process, c is the concentration of Pz in the solution. The free energy of adsorption processs ΔG^0_{ads} can be calculated from the equation (2) [9]:

$$K = \frac{1}{55.5}\exp(\frac{-\Delta G^0_{ads}}{RT}) \quad (2)$$

The value of ΔG^0_{ads} from the Frumkin adsorption isotherm in 0.05M $NaHCO_3$ solution was calculated to be -9.72 kJ mol^{-1}. It illustrates that the adsorption of Pz on the surface of copper is a spontaneous process [9].

3.2 Influence of electrode rotation rate

Cyclic voltammentry curves in 0.05 M $NaHCO_3$ solution with 0.005 mM Pz at different electrode rotation rates are shown in Fig. 3. It can be seen that the anodic dissolution current density and the peak potential do not change with the rotation rate, which indicates that the anodic dissolution process of copper is controlled by the electrochemical reaction [10].

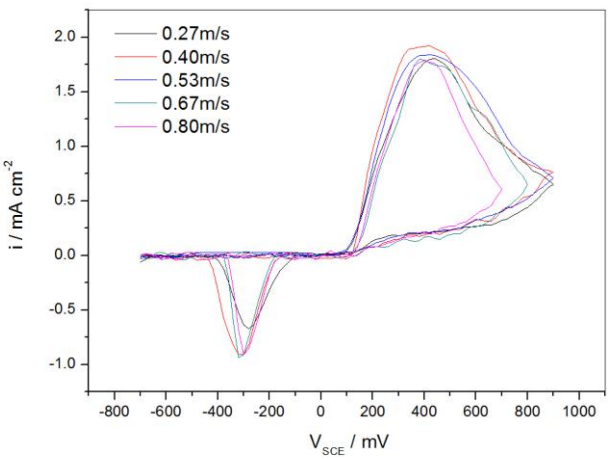

Figure 3. Cyclic voltammetry curves for copper in 0.05M $NaHCO_3$ solution containing 0.005M Pz with different electrode rotation (ω).

The ionization of pyrazole in solution is shown in equation (3):

$$H{\cdot}Pz \rightarrow Pz^{-} + H^{+} \qquad (3)$$

Pz^{-} reacts with dissolved Cu(II) from anode to form Pz_2-Cu(II) layer (4):

$$Cu^{2+} + 2Pz^{-} = Pz_2\text{-Cu (II)} \qquad (4)$$

Since the ionization of Pz is an irreversible reaction in alkaline solution, the controlling process of the reaction on the surface of copper electrode is the following reaction (5):

$$Cu^{+} \rightarrow Cu^{2+} + e \qquad (5)$$

Therefore, the anodic dissolution process of copper in $NaHCO_3$ solution is controlled by the electrochemical reaction.

3.3 Weight loss measurements

The weight loss of copper in 0.05M $NaHCO_3$ solution containing different concentrations of Pz was determined after 72hours. The values of percentage inhibition efficiency (*E*, %) and corrosion rate (C_R) obtained from weight loss method at 30℃ are summarized in Table 1.

Table 1. Corrosion parameters for copper in aqueous solution of 0.05 M $NaHCO_3$ in absence and presence of different concentration of Pz from weight loss measurements at 30℃.

Inhibitor concentration (mM)	Weight loss (mg cm-2)	CR (mm year-1)	E (%)
0	0.194	0.00583	--
0.5	0.145	0.00435	25
3	0.122	0.00366	37
5	0.062	0.00186	68
10	0.029	0.00087	85

It is obvious that the inhibition efficiency increases with increasing concentration of Pz, which is in accordance with the result from electrochenmical measurements.

3.4 The inhibition of Pz with BTA or MBT

Cyclic voltammentry curves for copper in 0.05 M $NaHCO_3$ solution with different concentrations of Pz with 0.03mM BTA and/or 0.03mM MBT are shown in Fig. 4 and Fig. 5 respectively.

The inhibition reaches the highest value when the concentration of Pz is 9mM with 0.03mM BTA in Fig. 4. Compared to the passivation potential in the presence of pyrazole or BTA individually,

the parameter in the mixture is 680mV or 540mV higher respectively. The passivation current density in the mixture is lower than that in the presence of BTA only, which indicates that the exist of the synergistic effect between Pz and BTA.

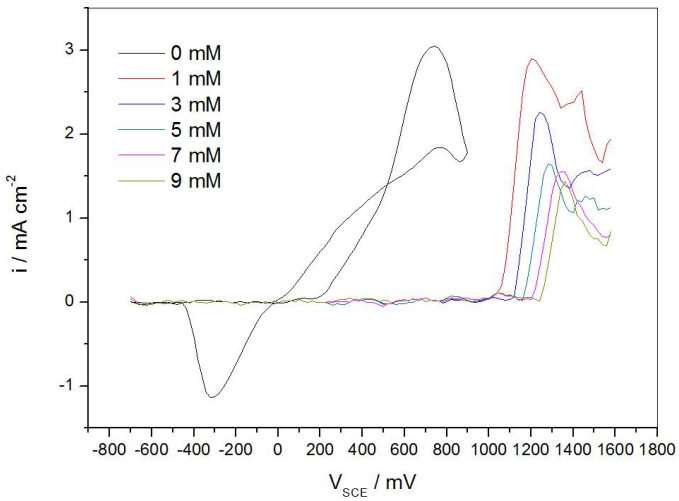

Figure 4. Cyclic voltammetry curves for copper in 0.05M $NaHCO_3$ solution with different concentrations of Pz and BTA (30℃, C_{BTA}=0.03mmol/L)

The inspection of Fig. 5 shows that the passivation current density and passivation potential have little change in different proportion of Pz and MBT, but the passivation potentials are 500 mV higher than in the absence of Pz and MBT. With decreasing the proportion of Pz, the first anodic peak disappears, and the value of cathodic peak shifts towards the negative direction. It is probably due to the composition change of the complex compound generated on the surface of electrode [11].

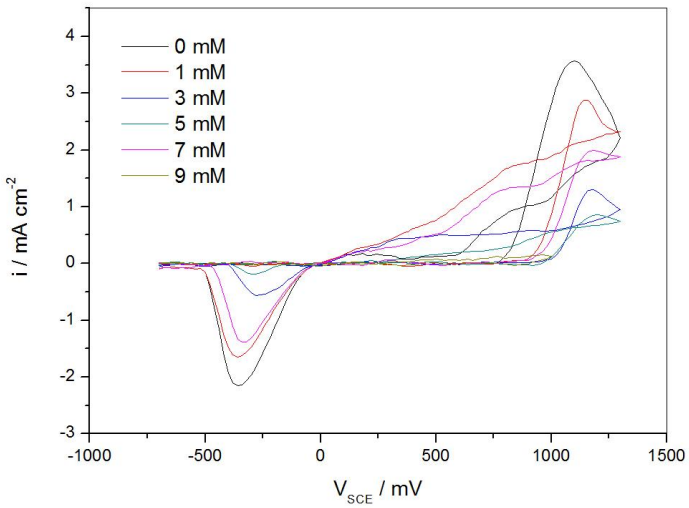

Figure 5. Cyclic voltammetry curves for copper in 0.05M $NaHCO_3$ solution with different concentrations of Pz and MBT (30℃, C_{MBT}=0.03mmol/L)

4. CONCLUSIONS

1. Pz is an effective inhibitor for the dissolution of copper in alkaline solution; the adsorption of Pz on the surface of copper obeys the Frumkin adsorption isotherm.
2. The anodic dissolution process of copper is controlled by the electrochemical reaction in alkaline solution in the presence of Pz.
3. A synergistic effect exists between Pz and BTA, but it is not remarkable between Pz and MBT.

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