Study on Corrosion of Zinc Metal in Acid Environment

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Abstract. The experiment was carried out in the acidic conditions to test three kinds of organic compounds, the cetyltrimethyl ammonium bromide (CTAB), nicotinic acid and bromohexadecyl pyridine on the corrosion inhibition performance of metal Zinc by means of the experiment and testing methods of the static rotary coupon test, electrochemical polarization and SEM (Scanning Electron Microscope). The purpose is to study a kind of compound organic corrosion inhibitor which has the best inhibition effects on the metal Zinc. The static coupon experiment showed that the weight loss ratio of metal Zinc specimens was relatively small in CTAB and bromohexadecyl pyridine composition and the weight loss ratio of metal Zinc specimens was relatively large in the nicotinic acid composition. The electrochemical polarization test result showed that CTAB, nicotinic acid and bromohexadecyl pyridine can induce the shifting of the corrosion potential of metal Zinc (E_0) in the acidic environment. SEM showed that CTAB and bromohexadecyl pyridine composition formed a uniform and compact film on the metal Zinc surface. The conclusion can be drawn that CTAB, nicotinic acid and bromohexadecyl pyridine can be combined with one another in the acidic conditions. Among them, the CTAB and bromohexadecyl pyridine composition has a good inhibition effect on the corrosion of metal Zinc in that it forms a uniform and compact film on the surface of metal Zinc.

Introduction

Zinc is commonly used in numerous industries and fields. It is often used as a sacrificial metal in coatings to protect other metals, particularly ferrous metals. The galvanized metals used in water-circulating systems often produce white rust, so the method of prevention of removal of corrosion is important[1-3]. Investigation into the corrosion tendencies of zinc can lead to important applications in production and economics. The use of inhibitors is one of the most practical methods by which to protect zinc from corrosion, particularly in acidic mediums[4-13]. Organic inhibitors with electron-donating groups such as nitrogen, sulphur and oxygen often play an important role in zinc corrosion prevention[14-19].

The present work investigates the effects three organic compounds on the corrosion inhibition of zinc in 0.5M hydrochloric acid: cetyltrimethyl ammonium bromide (CTAB), nicotinic acid and bromohexadecyl pyridine. CTAB is a cationic surface active agent; nicotinic acid and bromohexadecyl pyridine are heterocyclic compounds. The effect of single inhibitor concentration on the anticorrosion efficient was investigated, as well as the anticorrosion efficiencies of CTAB, nicotinic acid and bromohexadecyl pyridin.

ExperImental Methods

Materials. CTAB(Tianjin Guangfu Fine Chemical Research insitute, AR); nicotinic acid(Tianjin kemi'ou Chemical Reagent Co., Ltd. AR); bromohexadecyl pyridine(Tianjin Guangfu Fine Chemical Research insitute, AR); hydrochloric acid(Tianjin Guangfu Fine Chemical Research insitute, AR).

Inhibitors Prepared. The following inhibitors were prepared for experimental analysis:

1) 4.0 g of CTAB were dissolved at 70 °C. A volume of 100ml was set aside for experimental use.

2) 1.5 g of bromohexadecyl pyridine were disoolved at 50 °C. A volume of 250 ml was set aside for experimental use.

3) 4.0 g of acid were dissolved at 40 °C. A volume of 250 ml was set aside for later use.

Inhibitor solutions were then prepared according to the following mixtures:

Compound 1: CTAB 200 mg.L^{-1} nicotinic acid 100 mg.L^{-1} and bromohexadecyl pyridine 60 mg.L^{-1}.

Compound 2: CTAB 20 mg.L^{-1} and bromohexadecyl pyridine 60 mg.L^{-1}.

Instruments. Potentiostat/galvanostat CS2305, JSM-6510; scanning electron microscopy(SEM), BT224S Electronic Balance.

Experimental Procedure

Weightloss Test of Zinc. The corrosion of zinc after exposure to inhibition solutions was evaluated according to the static hanging piece test, reference HG/T2387-2007. The corrosion inhibition test was conducted at 25 °C for 96 hours in a testing solution of 0.5M hydrochloric acid. The experimental solution was comprised of 0.5M HCl and inhibitor solution. The corrosion rate was calculated according to the following formula:

$$K = \frac{W_1 - W_2}{S \cdot T} .$$ (1)

Where K is the corrosion rate, g.m^{-2}.h^{-1}; W_1 is the weight of the zinc plate before the test, g; W_2 is the weight of the zinc plate after the test, g; S is the initial area of the plate, m^2; and T is the time elapsed during the experiment, h.
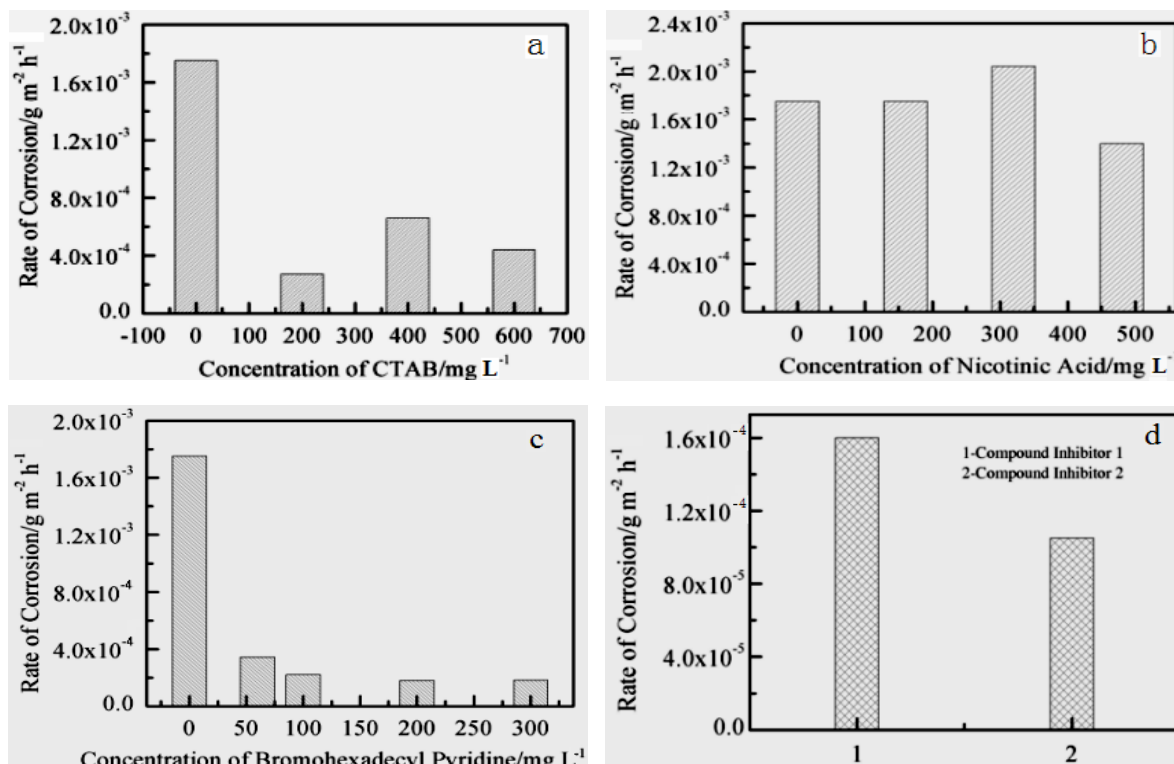
Electrochemical Test of Zinc. Zinc electrodes were sealed in epoxy resin, except for an exposed cross-section at the working surface with an area of 1cm^2. The counter electrode for the electrochemical test was made of platinum, while a saturated calomel electrode (SCE) was used as the reference electrode. The electrochemical studies were conducted on the potentiostat/galvanostat CS2305. Linear polarization measurement were conducted with a potential perturbation of ±100 mV around the open circuit potential (OCP). The electrolyte was prepared by adding various concentrations of different inhibitors to 0.5M hydrochloric acid solution.

SEM Test. The zinc plates were observed on SEM JSM6510 after testing. The operation parameters were set to 20 kV acceleration voltage.

Results And Discussion

Corrosion Test Results. Figure 1(a) displays the corrosion rates of zinc after exposure to various concentrations of CTAB inhibitor solutions. Results indicate that the introduction of CTAB (in the experimental range 0 mg.L^{-1}~600 mg.L^{-1}) can protect zinc immersed in 0.5M HCl from corrosion. The corrosion rate of zinc in 0.5M HCl solution is 17.5x10^{-4} g.m^{-2}. h^{-1}, while the corrosion rate of zinc in 0.5M HCl in the presence of CTAB is reduced to below 6.6x10^{-4} g.m^{-2}.h^{-1}. Increases in CTAB concentration does not significantly alter the rate of zinc corrosion in HCl. Figure1(b) displays the corrosion rate of zinc in various concentrations of nicotinic acid inhibitor solutions. Results indicate that the nicotinic acid (in the experimental range 160 mg.L^{-1}~480 mg.L^{-1}) does not significantly alter the corrosion rate of zinc in HCl. When the concentration of nicotinic acid was 300 mg.L^{-1}, the corrosion rate (20.4 x10^{-4} g.m^{-2}.h^{-1}) is higher than that observed in 0.5m HCl (17.5x10^{-4} g.m^{-2}.h^{-1}). When the concentration of nicotinic acid is 480 mg.L^{-1} the corrosion rate is 14.01 g.m^{-2}.h^{-1}, which does not meet industrial requirements. Figure 1(c) displays the corrosion rate of zinc in various concentrations of bromohexadecyl pyridine inhibitor solution. Results indicate that the introduction of bromohexadecyl pyridine to 0.5M HCl solution can protect zinc from corrosion. The corrosion rate of zinc in 0.5M HCl solution decreases with increasing bromohexadecyl pyridine concentrations.

When the bromohexadecyl pyridine concentration is 100 mg.L^{-1}, the corrosion rate of zinc is 2.17x10^{-4} g.m^{-2}.h^{-1}. Figure 1(d) depicts the anti-corrosion efficiency of inhibitor mixtures in relation to zinc corrosion. Results indicate that compound 1, consisting of CTAB, nicotinic acid and bromohexadecyl pyridine, is more effective than any single inhibitor. The corrosion rate of zinc in HCl in the presence of compound 1 is 3.2x10^{-4} g.m^{-2}.h^{-1}. Additionally, a mixture of CTAB and bromohexadecyl pyridine without nicotinic acid is more effective than compound 1 and any single inhibitor.

Fig. 1. Corrosion rate of zinc in varying concentrations of inhibitor solutions (a) CTAB; (b) nicotinic acid; (c) bromohexadecyl pyridine; (d)compound

Electrochemical Test Results. Table 1 displays the E_0 of zinc in the presence of various inhibitor solutions, obtained from Tafel fitting results. As shown in Table 1, the change of E_0 in the presence of CTAB and bromohexadecyl pyridine solutions is irregular with variations in inhibitor concentrations, while the change of E_0 in nicotic acid solution is regular. The addition of CTAB nicotinic acid and bromohexadecyl pyridine all induce a positive shift in E_0 values. As shown in Table 2, the I_0 of zinc indicates better anti-corrosion performance correlated to smaller values in different inhibitor solutions results indicate that the tendency of I_0 changes in the presence of CTAB is similar to changes in the presence of HCl alone.

**Table 1** E_0 of zinc in various inhibitor solutions

CTAB	E_0[V]	Nicotinic acid	E_0 [V]	Bromohexad ecyl pyridine	E_0 [V]
0	-1.0384	0	-1.0384	0	-1.0384
200	-1.0027	160	-0.9960	60	-0.9695
400	-1.0112	320	-0.9931	100	-0.9829
600	-1.0224	480	-0.9760	200	-0.9822
800	-1.0111			300	-0.9791
Compound 1		-1.0008	Compound 2		-0.9897

Table 2 I_0 of zinc in various inhibitor solutions

CTAB	$I_0[A.cm^{-2}]$	Nicotinic acid	$I_0[A.cm^{-2}]$	Bromohexad ecyl pyridine	$I_0[A.cm^{-2}]$
0	6.8×10^{-4}	0	6.8×10^{-4}	0	6.8×10^{-4}
200	5.7×10^{-4}	160	6.9×10^{-4}	60	1.2×10^{-4}
400	2.4×10^{-3}	320	4.3×10^{-4}	100	1.7×10^{-4}
600	6.4×10^{-4}	480	5.3×10^{-4}	200	1.2×10^{-4}
800	2.8×10^{-3}			300	1.0×10^{-4}
Compound 1			4.0×10^{-4}	Compound 2	3.9×10^{-5}

The change in I_0 in the presence of nicotinic acid concentration is not significant, while the I_0 of zinc in inhibitor solutions is smaller than in the presence 0.5m HCl alone.

Figure 2 shows the polarization curves of zinc in various inhibitor solutions. Results indicate that the introduction of CTAB, nicotinic acid and bromohexadecyl pyridine causes significant alteration in the cathode curve. Inhibitor compouns 1 and 2 cause obvious changes in anode and cathode reactions. The changes in open potential and cathode reaction may be caused by the film formed by the compound solution of CTAB, nicotinic acid, and bromohexadecyl pyridine.
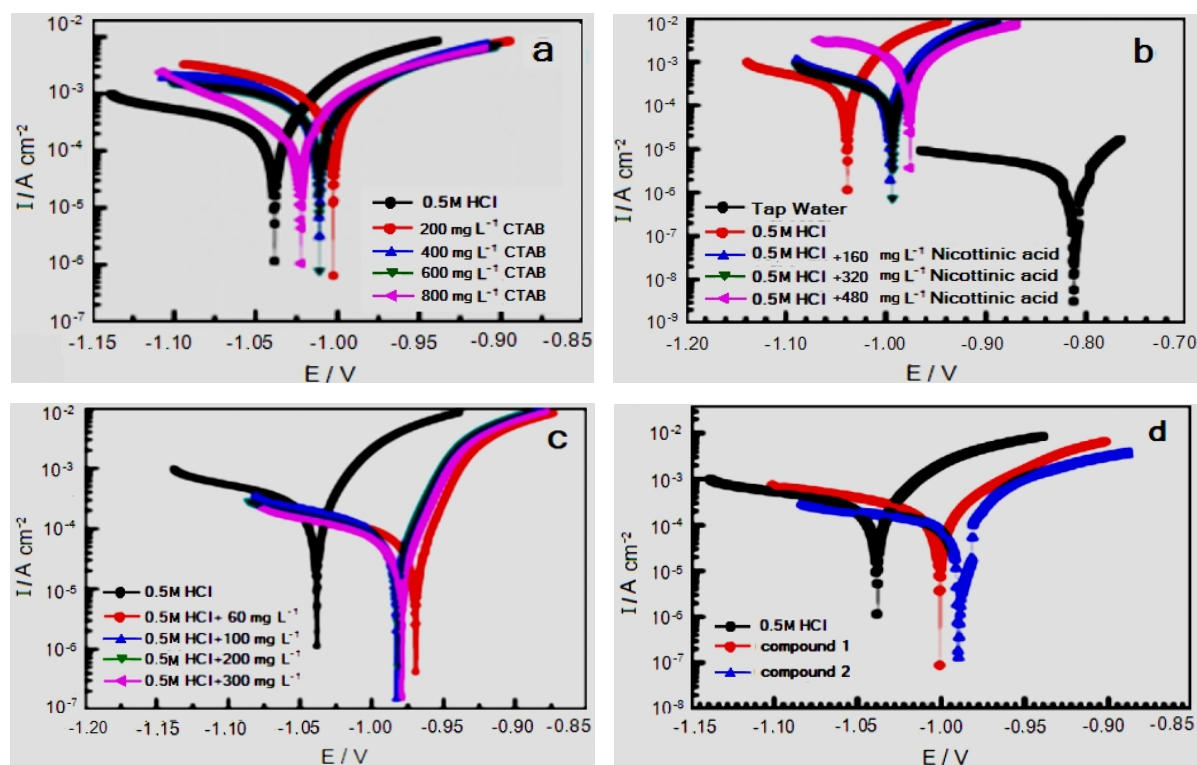

Fig. 2. Polarization curves of zinc in (a) CTAB solution; (b) nicotinic acid; (c) bromohexadecyl pyridine and (d) inhibitor compounds

In summary, the corrosion and electrochemical test results indicated that compound 2 demonstrates better anti-corrosion performance than any other tested compound or single inhibitor solution.

Results of SEM test. Figure 3 depicts SEM photos of zinc after exposure to different inhibitor solutions in HCl for 96 hours at 25 °C. Figure 3(a) demonstrates microcosmic scratches on the surface of the zinc. Figure 3(b) shows that when zinc is immersed in 0.5M HCl, a large number of corrosion pits formed on the surface of the zinc. The presence of CTAB in Figure 3(c), nicotinic acid in Figure
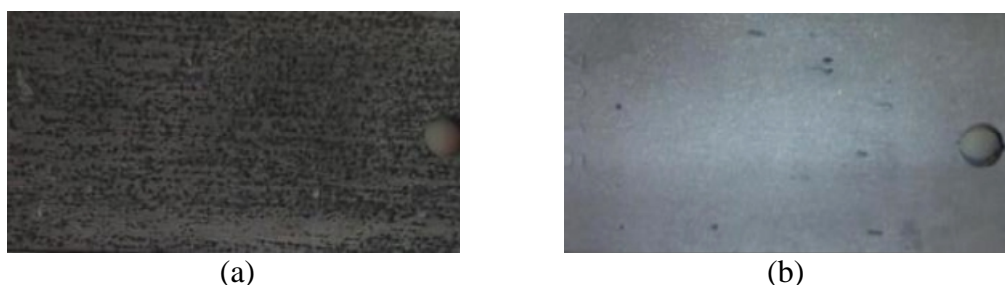
3(d) and bromohexadecyl pyridine in Figure 3(e) can form a uniform and compact film that prevents zinc from corrosion in the presence of HCl. And zinc in inhibitor compounds in Figure 3 (f).
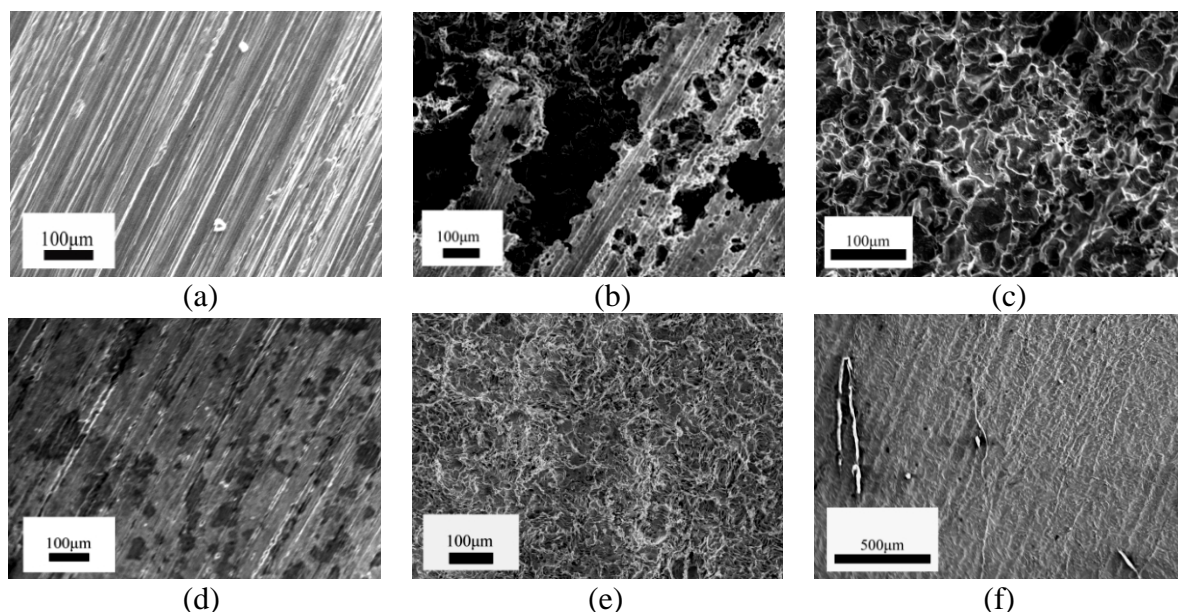
Fig. 3. SEM photos of (a) pure zinc; (b) zinc in 0.5M HCl; (c) zinc in CTAB solution;
(d) zinc in nicotinic acid solution; (e) zinc in bromohexadecyl pyridine solution;
and (f) zinc in inhibitor compounds

Figure 4(a) (b) depicts photos of zinc plate immersed in 0.5M HCl alone and 0.5M HCl in the presence of compound 2 inhibitor solutions for 96 hours at 25 ℃. The results indicate the formation of a macroscopic film on the zinc plate.

Fig. 4. Photos of zinc in (a) 0.5m HCl; (b) inhibitor compound solutions

Conclusion

1. Weight loss results indicate that CTAB and bromohexadecyl pyridine can protect zinc from corrosion in the presence of HCl. The weight loss does not alter markedly with increasing concentrations of either inhibitor. The introduction of nicotinic acid displayed no effect on zinc corrosion.

2. Polarization and SEM results indicate that CTAB and bromohexadecyl pyridine form a compact and uniform membrane on the surface of zinc.

3. The weight loss tendency of zinc in the presence of various inhibitors result in similar I_0 values, which indicates the anti-corrosion performance of inhibitor solutions in reference to zinc.

Acknowledgements

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