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Benzotriazole and its Derivatives as Corrosion Inhibitors for Iron in Sodium Chloride Solutions

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Abstract

Inhibitive effect of benzotriazole (BTA), tolyltriazole (TTA) and benzotriazole carboxylic acid (BTA-COOH) on the corrosion of iron was investigated in the inhibitor concentration range of 10^{-5} to 10^{-3} mol/l in aerated 3 % sodium chloride solutions at 50°C by weight loss measurements using a spinner test assembly and electrochemical techniques. The corrosion test results indicate that the inhibition efficiencies increase with the increasing inhibitor concentration and the effectiveness increases in the order of TTA (inhibition efficiency 18.7%) <BTA (26.5%) <BTA-COOH (34.9%) at the concentration of 10^{-4} mol/l. At the concentration of 10^{-3} mol/l, however, the inhibition efficiency of BTA-COOH remains almost constant because of its solubility limit in the solution while those of TTA and BTA were 57 and 63%, respectively. The potentiostatic polarization curves of iron show that the inhibitors increase both anodic and cathodic polarization and inhibition of the cathodic reaction, mainly oxygen reduction reaction, is more pronounced than that of anodic one. Relationship between the degree of potential change ΔE and the inhibitor concentration C suggests that the inhibition action may be attributed to Langmuir-type adsorption of the organic molecules at cathodic sites on the iron electrode.

1. Introduction

Among the corrosion inhibitors for copper and copper alloys, benzotriazole (BTA) and its derivatives generally rank as the most effective.[1][2] Although these inhibitors have been widely used in various environments for about 30 years, efforts are still being made to improve their effectiveness and to extend their application.[3] This is particularly important for application to multimetal systems as solar energy systems. Hardly any information is available on the corrosion inhibition effect of BTA and its derivatives on other industrial materials, i. e., aluminum, iron and their alloys except for a limited presentation of literature on the iron-BTA system.[4]~[6]

This paper describes the inhibitive action of BTA, tolyltriazole (TTA, a mixture of 4- and 5-methyl-1. H-benzotriazole) and benzotriazole carboxylic acid (BTA

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-COOH, a mixture of 4- and 5-carboxylic-1 . H-benzotriazole) on corrosion behaviors of iron in neutral 3 % NaCl solutions.

2. Experimental

Chemical structures of BTA, TTA and BTA-COOH are shown in Figure 1. BTA and TTA used are commercially available inhibitors of Cobratec-99 and Cobratec-100, respectively, and BTA -COOH is at present being commercially developed. These agents are supplied by Sherwin-Williams Company. Corrosion test speciments were cut from cold rolled iron sheet to the size of 60 x 20 x 1 mm. The iron sheets were supplied by Akashi Alloy Co, Ltd. Its chemical composition is as follows ; Mn 0.13, Si 0.09, Cu 0.06, C 0.02, P 0.006, S 0.015 and the remainder consists of Fe. The surface preparation included mechanical polishing with No 500 SiC paper and degreasing with acetone. Then the samples were rinsed in distilled water, dried, weighed and fixed to the corrosion test spinner which mounts eight pieces of the specimens.(7) Corrosion test were carried out in aerated 3 % NaCl solutions in the presence and the absence of the inhibitors at 50°C using the corrosion test spinner at a rotation speed of 125 r. p. m. The linear velocity at 125 r. p. m. is 0.7265 m/sec. The specimens were exposed to the NaCl solutions of 4 liter at the initial pH of 6.0 for 5 hours. The air was made to bubble through the solutions during the tests. After the corrosion test the specimens were withdrawn from the corrosive medium and were treated with diluted sulfuric acid containing 1 % of thiourea to remove the corrosion product layer formed on the surface during corrosion, and rinsed in distilled water, dried and weighed. During exposure the corrosion potential of iron electrodes were recorded to study the inhibition mechanisms using Hitachi recorder 056 and Nichia model HP V-100 potentiostat. The potentials were measured against a saturated calomel electrode. Anodic and cathodic polarization curves were also measured by polarizing the iron electrode stepwisely by 20 mV each for 10 seconds from the corrosion potential in the solution with and without inhibitors at 50°C.

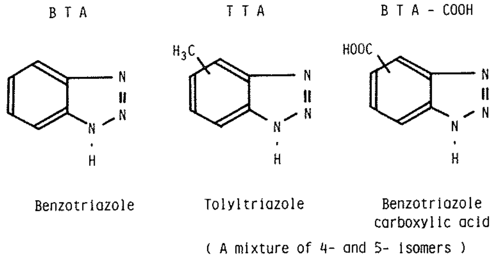

Figure 1. Chemical structures of the three inhibitors used.

3. Results and discussion

Table 1 shows the 5 hour corrosion test results for iron in aerated 3 % NaCl at 50°C in the presence and absence of the inhibitors. The corrosion test was duplicated under the same conditions. Thus 16 pieces of iron specimens were used for each condition. It is noted that in each column in Table 1 the weight loss of iron specimen was tabulated in the increasing order from the top to the bottom. The inhibitor

Table 1 weight loss (in mg/cm^2) of iron in aerated 3 % NaCl for 5 hours at 50℃

nth datum	Blank ★	BTA		TTA		BTA-COOH
		10^{-4}M	10^{-3}M	10^{-4}M	10^{-3}M	10^{-4}M
1	8.7617	7.1306	3.4056	7.6869	3.8385	6.0570
2	9.6231	7.1440	3.4634	7.8388	3.9080	6.3385
3	9.6640	7.1844	3.4758	8.0234	4.0135	6.3417
4	9.7008	7.1860	3.5197	8.2557	4.0338	6.3957
5	9.8927	7.2342	3.5335	8.2804	4.0685	6.4857
6	9.9253	7.3331	3.5861	8.3041	4.0774	6.6225
7	10.0748	7.5337	3.6933	8.3240	4.1625	6.6630
8	10.0857	7.5579	3.7602	8.3612	4.1216	6.6898
9	10.1933	7.5882	4.0569	8.4612	4.5895	6.7156
10	10.2848	7.8276	4.0603	8.5358	4.7217	6.7769
11	10.2877	7.8329	4.0731	8.7094	4.8266	6.8268
12	10.4262	7.9342	4.0942	8.7867	4.8983	6.9717
13	10.6497	8.0541	4.1308	8.8060	4.9041	6.9950
14	10.9110	8.1833	4.1376	8.8208	4.9466	7.1080
15	11.3333	8.2648	4.1628	8.9621	5.0399	7.2350
16	12.7858	8.5035	4.1942	8.9660	5.2386	7.2411

★average 10.2875(±1.956) mg/cm^2

concentration used were in the range of 10^{-5} to 10^{-3} mol/l. At a concentration of 10^{-5} mol/l, however, no significant inhibition action of these inhibitors was observed in the tests. The inhibitive solution of 10^{-3} mol/l BTA-COOH can hardly be obtained because of its lower solubility compared with BTA or TTA. The inhibition efficiency is expressed as $\{(\Delta W_0 - \Delta W_i)/\Delta W_0\}$ X 100, where ΔW_i and ΔW_o are the weight losses in the solution in the presence and the absence of the inhibitor, respectively.

Since the weight loss data are widely scattered, the inhibition efficiency are also scattered. A statistical approach was made. The probability of the inhibition efficiency is calculated as $n/(1+N)$ by the mean rank method,[8] where N is the total number of iron specimens tested ($N=16$) and n is the nth specimen. The inhibition efficiency data are plotted on the normal probability paper as shown in Figure 2. Straight lines are fitted for the three inhibitors at different concentrations. It is concluded that the weight loss in the inhibited solutions obeys a normal distribution. The distribution as indicated by the slopes of the lines shows independence of the inhibitor and of its concentration. The maximum and minimum inhibition efficiencies among the 16 data are 25.3 and 12.8 % for TTA, 30.7 and 17.3 % for BTA, 41.1 and 29.6 % for BTA-COOH at a concentration of 10^{-4} mol/l, and 62.6 and 49.0% for TTA and 66.9 and 59.2 % for BTA at a concentration of 10^{-3} mol/l, respectively. If the inhibition efficiency at $n/(1+N)=0.5$ is used as a representative value for each inhibitor and the two different concentrations, the inhibition efficiency increases in the order of TTA < BTA < BTA-COOH at 10^{-4} mol/l and TTA < BTA at 10^{-3} mol/l. The inhibition efficiency of BTA-COOH at 10^{-3} mol/l was almost the same as that of 10^{-4} mol/l because of its solubility limit.

Figure 3 shows the anodic and cathodic polarization curves of iron electrode in aerated 3 % NaCl in the presence of 10^{-3} mol/l of inhibitor at 50°C. The polarization of iron electrode was accomplished after 10 minutes immersion in the solution by applying successively 20 mV potential steps each for 10 sec. to the electrode in the cathodic direction or anodic direction from its corrosion potential. In the absence of the inhibitor the cathodic current increased sharply with the potential and attained a characteristic diffusion current for oxygen reduction reaction in the potential range from−0.70 to about−0.95 V. The cathodic current was found to decrease considerably in the presence of the inhibitors with decreasing order of BTA>TTA>BTA-COOH. The anodic branch of the curves is seen to depend slightly on the presence of inhibitors. Figure 3 indicates that the inhibitors exerted only minor influences on the anodic iron dissolution reactions, but the inhibitors act as cathodic inhibitor interfering with the occurrence of oxygen reduction reaction on iron surface.

Although iron-benzotriazole compounds may be formed in special environments,[9] BTA and its derivatives do not seem to react with soluble ferrous salts forming a

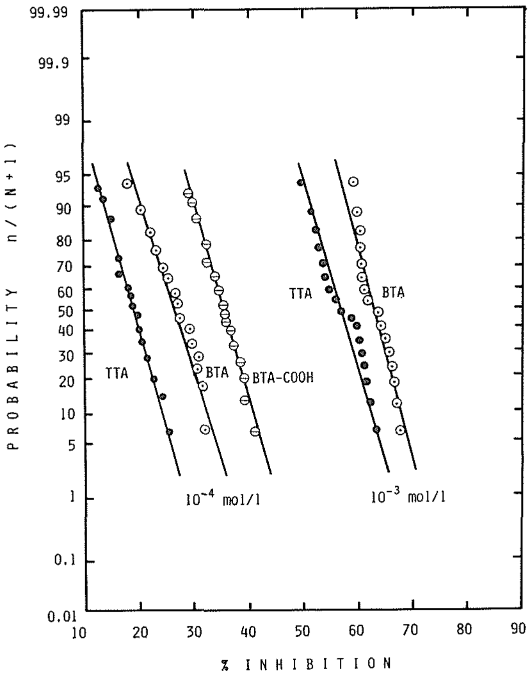

Figure 2. Normal probability plots of inhibition efficiency for BTA, TTA and BTA-COOH at two concentrations of 10^{-4} and 10^{-3} mol/l.

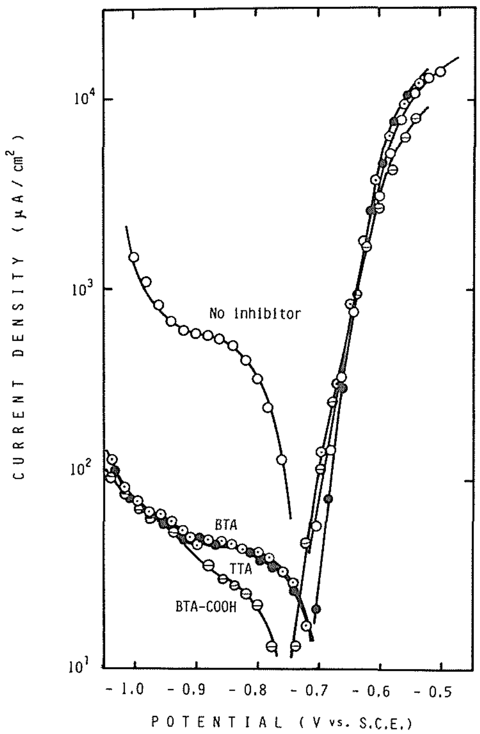

Figure 3. Anodic and cathodic polarization curves of iron in aerated 3 %NaCl in the presence of the inhibitors at concentration of 10^{-3} mol/l at 50°C.

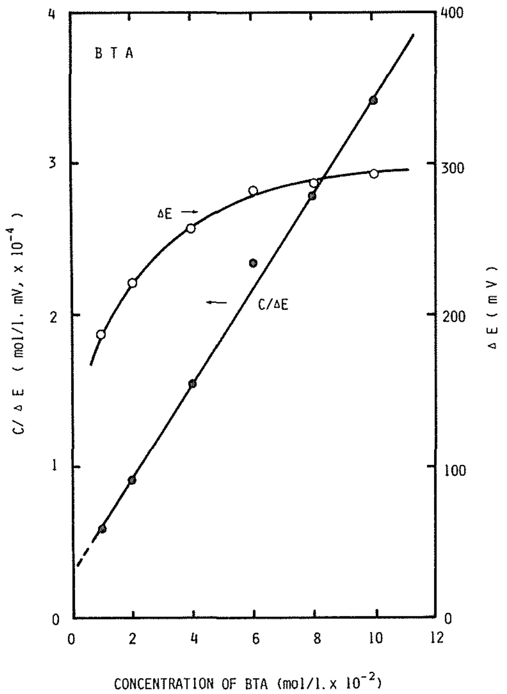

Figure 4. Potential change of iron electrode with the concentration of BTA and Langmuir adsorption plot.

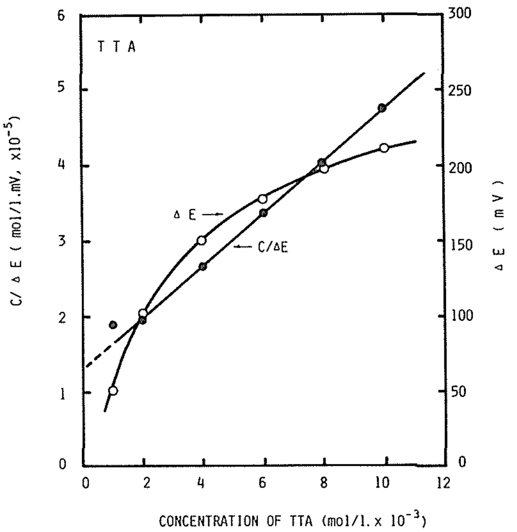

Figure 5. Potential change of iron electrode with the concentration of TTA and Langmuir adsorption plot.

protective film on iron in 3% NaCl solution. No evidence was obtained of insoluble iron complex formation of Fe-BTA, Fe-TTA or Fe-BTA-COOH in the solution.

The Langmuir adsorption isotherm modified by Uhlig and Geary[10] is expressed as follows,

$$C/\Delta E = C/\Delta E_m + 1/a'\Delta E_m$$

where C is the concentration of inhibitor and ΔE is the change of potential. Both a' and ΔE_m are constants depending on inhibitive properties of the inhibitor. It was found that potential change ΔE of iron electrode in the inhibitor solution show a linear relation for C/ΔE vs. C, suggesting that they follow the Langmuir adsorption isotherm, as shown in Figures 4 to 6. The linearity of C/ΔE vs. C is

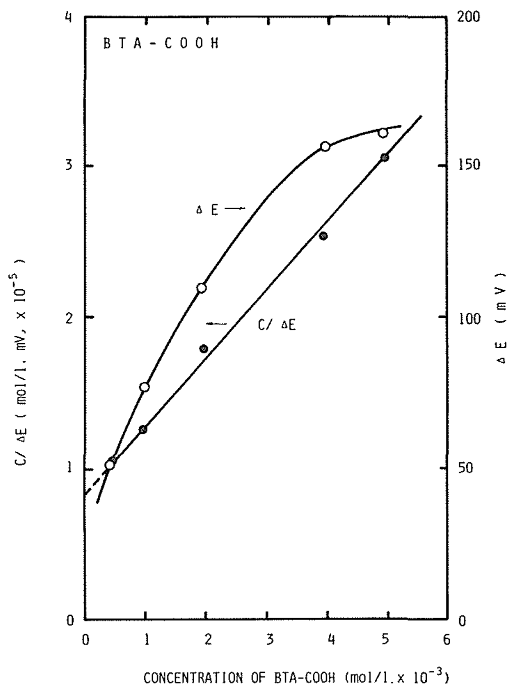

Figure 6. Potential change of iron electrode with the concentration of BTA-COOH and Langmuir adsorption plot.

generally conceded that organic inhibitors function by adsorbing on the metal surface.[11] The values of ΔE_m calculated from the relation for BTA, TTA and BTA-COOH are 104, 289 and 622 and that of a' for BTA, TTA and BTA-COOH are 321, 182 and 189, respectively. In this experiment no direct correlation was found between the order of inhibition efficiencies and that of ΔE_m or a' for the three different inhibitors. Since the potential change measurement was conducted at an early stage of corrosion (within 1 hour), the iron electrode did not reach a steady adsorption state or the surface condition changed during dissolution of iron, where hindrance of the protective action of the inhibitor may occur by corrosion products formed on iron.

4. Conclusion

Benzotriazole and its two derivatives, TTA and BTA-COOH, inhibit iron corrosion in aerated 3 % NaCl solutions and do not accelerate iron corrosion. Inhibition efficiencies were in the range of 19 to 35% at 10^{-4} mol/l for the three inhibitors and of 57 to 63% at 10^{-3} mol/l for BTA and TTA. The inhibition action is due to Langmuir-type adsorption on the iron surface. In order to obtain a higher degree of inhibition efficiency a combination of two or more different inhibitors effective for iron corrosion with these inhibitors are recommended. This is important from a practical point of view in application of the BTA and its derivatives to multimetal system such as iron-copper systems.

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