

# The Effects of Benzoic Acid in Chloride Solutions on the Corrosion of Iron and Aluminum

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In this work, the corrosion behavior of iron and aluminum was investigated in 0.1 M NaCl solutions with an initial pH value of 8 and containing various concentrations (0, 30, 150, 300 ppm) of benzoic acid. For this purpose, the anodic and cathodic semilogarithmic current-potential curves, weight loss and pH of the solution were determined over time. The changes in the concentrations of benzoic acid in the solutions with time were determined by a UV spectrophotometer. According to the results obtained in this investigation, benzoic acid in 0.1 M NaCl acts on iron and aluminum as an inhibitor. This effect gets stronger with increasing concentrations of benzoic acid in 0.1 M NaCl solution.

## Introduction

Iron and aluminum are engineering materials in widespread use. Therefore, it is very important to protect these metals from corrosion. Corrosion of metals depends on the kind of metal, the environmental conditions (temperature, pH, pressure, concentration, etc.) and the kind of the ions present in the environment. It is impossible to prevent the corrosion of the metals especially in the environments containing active ions like chloride ions. In this situation, the chloride ions selectively adsorbed on the surface of the metal hinder the formation of a preventive oxide layer on the surface. Consequently, this accelerates the dissolution of the metal<sup>1-4</sup>. In corrosion prevention studies, inhibitor applications are of vital importance. In recent years some organic compounds have been used as corrosion inhibitors to prevent the corrosion of iron and aluminum<sup>4-12</sup>. In particular, the studies concentrated on aromatic compounds have shown that the inhibitory effectiveness of organic molecules depends on the molecular structure and the polar groups on the molecule<sup>4-12</sup>.

It is often reported in the literature that in the studies conducted on organic molecules, sodium benzoate is very effective in protecting aluminum and aluminum alloys from hole corrosion<sup>13,14</sup>. It is claimed that the benzoate ion in natural and basic environments is an effective inhibitor for iron and iron alloys<sup>5</sup>. This effect has been explained as adsorption of benzoate ions on the iron surface<sup>5</sup>. Davies and Slaiman showed the relationship among corrosion inhibition factors in benzoate solutions, concentration of benzoate ions, pH of the solution and dissolved oxygen concentration<sup>15</sup>. This result was also described by Turgoose<sup>16</sup>.

In this study, the corrosion behavior of iron and aluminum under the influence of various concentrations of benzoic acid was investigated in 0.1 M NaCl solution. For this purpose, corrosion rates of iron and

aluminum were determined utilizing electrochemical and nonelectrochemical methods. Additionally, the change in the benzoic acid concentration with time was also obtained.

## Experimental

Solutions of 0.1 M NaCl with various concentrations (30, 150, 300 ppm) of benzoic acid were used as electrolyte. Initial pH values of the solutions were adjusted to 8 using NaOH. The metallic materials used in the experiments were iron (99.5%) and aluminum (99%).

In order to determine the corrosion rates of the metals, electrochemical and nonelectrochemical methods were used.

Before determining the corrosion rates by the nonelectrochemical method, iron and aluminum plates with dimensions of 5 x 2 x 0.1 cm were prepared. Then the surfaces of these plates were chemically cleaned. The masses of these plates were measured in an oven, bringing them to a constant weight. These metal plates were plunged in to 0.1 M NaCl solutions containing benzoic acid at various concentrations. Mass losses of the metal plates were determined at the end of certain time periods and consequently the corrosion rates of the iron and aluminum were determined.

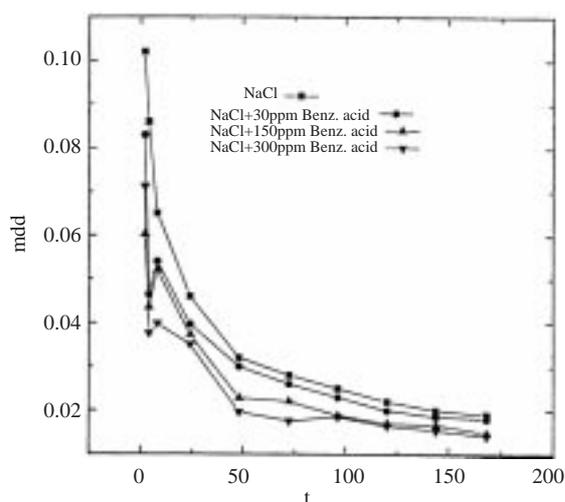
In the electrochemical method, current potential values were determined potentiokinetically by means of a potentiostat (TACUSSEL, PRT). Iron and aluminum were used as the working electrode while the opposite electrode was platinum (1 cm<sup>2</sup>) and the reference electrode was a saturated calomel electrode (SCE). After measuring the equilibrium potential of the working electrode against the reference electrode on the potentiostat, current potential values ranging between -1.6 V and + 1.6 V were obtained. The current values determined were converted to current densities and log<sub>10</sub> ( $\mu\text{A}\cdot\text{cm}^{-2}$ ) was graphed against the potential. Utilizing current potential curves,  $i_{\text{corr}}$  values were also obtained. Utilizing corrosion current densities with benzoic acid ( $i_{\text{corr}(\text{ben})}$ ) and without benzoic acid ( $i_{\text{corr}(\text{o})}$ ), effectiveness values in percentage terms were determined using the equation below.

$$E\% = (i_{\text{corr}(\text{o})} - i_{\text{corr}(\text{ben})}) / i_{\text{corr}(\text{o})}$$

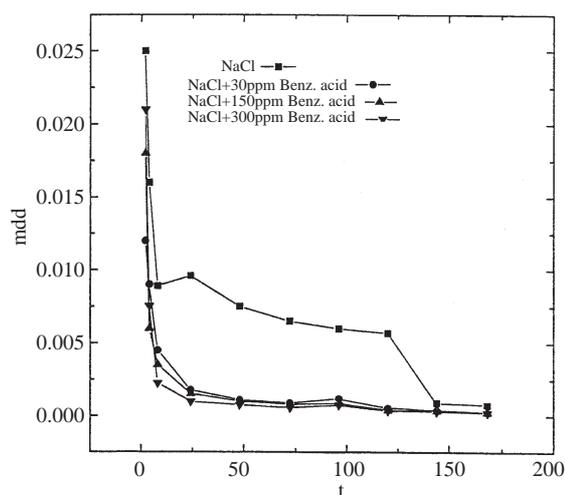
While determining the corrosion rates, the changes in the pH values of the solutions were measured using a pH-meter (Orion 720A), and the amounts of the benzoic acid were determined spectrophotometrically by means of a UV spectrophotometer (Shimadzu 8201/86601 PC). The solution used for UV measurement was taken out from the bulk solution in which there was no coagulant. Therefore the solution was centrifuged by a centrifuge rotating speed of 20,000 per minute. The concentrations of benzoic acid obtained were calculated by  $C\% = (C/C_0) \times 100$ , where  $C$  is the concentration of the benzoic acid at time  $t$ , and  $C_0$  is the initial concentration of the benzoic acid ( $t=0$ ).

## Results

The corrosion rates (mdd) of iron and aluminum in the solutions of 0.1 M NaCl with and without benzoic acid and with an initial pH of 8 were shown in Figures 1 and 2.



**Figure 1.** Corrosion rate (mdd) of iron in the solutions of 0.1 M NaCl with and without benzoic acid versus time (hour).



**Figure 2.** Corrosion rate (mdd) of aluminum in the solutions of 0.1 M NaCl with and without benzoic acid versus time (hour).

As shown in Figure 1, the corrosion rate of the iron in the chloride solutions containing 30, 150 and 300 ppm benzoic acid decreases with increasing concentration over time compared to 0.1 M NaCl. This decrease in the corrosion rate of the iron was particularly observed in benzoic acid solutions with 150 and 300 ppm (Figure 1).

Changes in the corrosion rate of the aluminum with time in the chloride solutions with and without benzoic acid are shown in Figure 2. The corrosion rate of the aluminum 0.1 M NaCl increases between the 2nd and 120th hours, and after the 120th hour it changes in the same way as corrosion rate of the aluminum in the solutions containing benzoic acid (Figure 2). Addition of benzoic acid causes a decrease in the corrosion rate of the aluminum compared to 0.1 M NaCl when time elapses, this decrease changes between 0.0025 and 0.0010 mdd in all concentrations (Figure 2).

The potentiokinetic polarization curves obtained in chloride solutions with benzoic acid at 30, 150 and 300 ppm or without benzoic acid and with an initial pH value of 8 when an iron electrode was used are shown in Figure 3. In all concentrations of benzoic acid (0, 30, 150, 300 ppm), when the iron electrode was polarized in anodic direction starting from  $-1.6$  V, current densities decrease until equilibrium potential and after equilibrium potential current densities increase until  $+1.6$  V (Figure 3). This increase in the current densities in anodic direction decreases with increasing concentrations of benzoic acid (Figure 3).

The potentiokinetic polarization curves of aluminum in chloride solutions with and without benzoic acid are shown in Figure 4. As observed with the iron electrode, in all solutions when the aluminum electrode was polarized in anodic direction starting from  $-1.6$  V, current densities decrease until equilibrium potential, and after equilibrium potential current densities increase until  $+1.6$  V (Figure 4). These increases in the current densities were small in the solutions containing benzoic acid (Figure 4). The  $i_{corr}$ ,  $E_{corr}$  and  $E\%$  values for chloride solutions with and without benzoic acid when the electrodes were iron and aluminum are shown in Tables 1 and 2. It is clear in these tables that the corrosion current densities of the iron ( $i_{corr}$ ) peaks in 0.1 M NaCl and 30 ppm benzoic acid solutions, whereas the current densities of the aluminum were maximum for 0.1M NaCl, and  $i_{corr}$  diminishes with the addition of benzoic acid  $E_{corr}$  changes in the same range, whereas  $E\%$  increases depending on the concentrations of benzoic acid (Figures 1,2).

**Table 1.**  $i_{corr}$ ,  $E_{corr}$  and E % Values of the iron for chloride solutions with and without benzoic acid.

C (Concentration)	$i_{corr}(\mu A.cm^{-2})$	$E_{corr}(mV, SCE)$	E %
0.1 M NaCl	104	-530	–
0.1 M NaCl + 30 ppm Benzoic acid.	100	-500	4.5
0.1 M NaCl + 150 ppm Benzoic acid.	56	-525	50
0.1 M NaCl + 300 ppm Benzoic acid.	63	-500	43

**Table 2.**  $i_{corr}$ ,  $E_{corr}$  and E % values of the aluminum for chloride solutions with and without benzoic acid.

C (Concentration)	$i_{corr}, (\mu A.cm^{-2})$	$E_{corr}(mV, SCE)$	E %
0.1 M NaCl	100	-223	—
0.1 M NaCl + 30 ppm Benzoic acid.	11. 22	-220	88. 8
0.1 M NaCl + 150 ppm Benzoic acid.	11. 80	-219	88. 2
0.1 M NaCl + 300 ppm Benzoic acid.	9. 60	-215	90. 4

For the time periods when the corrosion rates were determined, concentration changes in benzoic acid (C%) in chloride solutions containing benzoic acid (30, 150 and 300 ppm) with iron and aluminum plates are given in Tables 3 and 4. The concentration of benzoic acid decreases with time for both metals (Fe, Al).

**Table 3.** Concentration changes in benzoic acid (C%) in chloride solutions with iron plate.

Time t,(hour)	0.1 M NaCl + 30 ppm Benzoic acid (C%)	0.1 M NaCl + 150 ppm Benzoic acid (C%)	0.1 M NaCl + 300 ppm Benzoic acid (C%)
0	100	100	100
4	91. 95	92. 97	90. 46
8	78. 15	84. 49	89. 16
24	80. 12	88. 49	86. 73
48	69. 42	81. 49	88. 73
72	63. 45	84. 49	86. 73
96	65. 12	79. 80	82. 82
120	60. 42	80. 80	81. 21
144	59. 08	78. 80	80. 10
168	62. 11	78. 00	79. 05

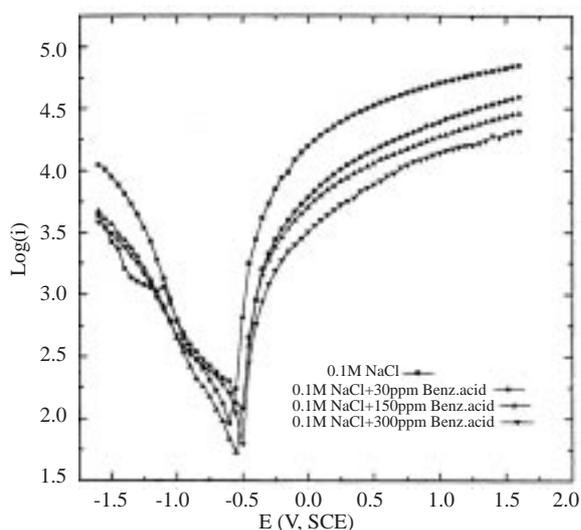
In all solutions (0, 30, 150, 300 ppm benzoic acid) with iron and aluminum plates, pH values shift from the initial value of 8 to basic values of 8.8 – 9.0.

## Discussion and Conclusions

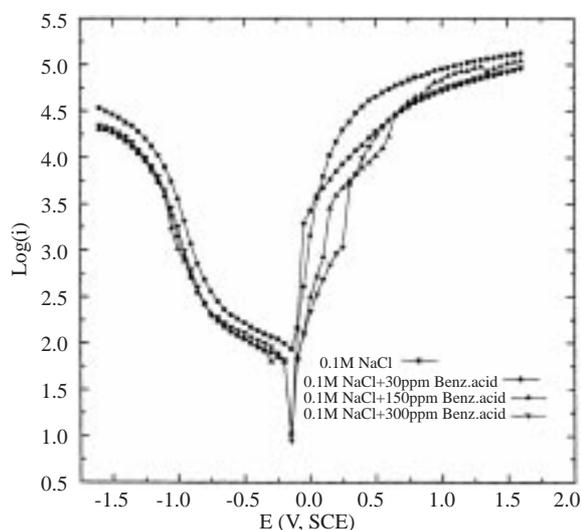
According to the experimental results obtained using electrochemical and nonelectrochemical methods, benzoic acid decreases the corrosion rates of iron and aluminum in 0.1 M NaCl with benzoic acid (Figures 1-4, Tables 1,2).

**Table 4.** Concentration changes in benzoic acid (C%) in chloride solutions with aluminum plate.

Time t, (hour)	0.1 M NaCl + 30 ppm Benzoic acid (C%)	0.1 M NaCl + 150 ppm Benzoic acid (C%)	0.1 M NaCl + 300 ppm Benzoic acid (C%)
0	100	100	100
4	81. 49	84. 49	89. 16
8	70. 12	79. 12	86. 73
24	69. 73	81. 49	87. 26
48	69. 73	82. 12	85. 13
72	65. 42	78. 80	86. 73
96	60. 15	78. 12	81. 26
120	65. 42	77. 10	82. 35
144	58. 18	77. 20	81. 15
168	60. 08	75. 80	78. 10

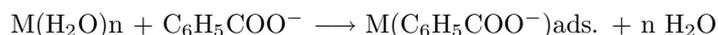


**Figure 3.** Potentiokinetic polarization curves when an iron electrode was used, obtained for 0.1M NaCl solutions with and without benzoic acid.



**Figure 4.** Potentiokinetic polarization curves when an aluminum electrode was used, obtained for 0.1M NaCl solutions with and without benzoic acid.

The adsorption of benzoic acid molecules on the metal surface, which separate as benzoate ions ( $C_6H_5COO^-$ ) in the solution, can be considered as shown below:



According to this equation,  $n H_2O$  molecules on the metal surface replace one benzoate ion. Adsorption of benzoate ions on iron and aluminum increases the adsorption ability of the molecules due to the increase in the electron density  $\pi$  at the adsorption center. Therefore, the molecules become strongly fastened on the metal surface and dissolution of the metal is prevented (Figures 1,2). This situation is also backed up by the literature<sup>5,14</sup>. In the pH value interval of 8-9, organic anion activity ( $C_6H_5COO^-$ ) increases, causing adsorption on the metal oxide or hydroxide surface<sup>9-13</sup>. Furthermore, adsorption of benzoate ions on the metal surface prevents probable corrosion reactions, and current densities at definite potentials decrease

compared to 0.1 M NaCl (Figures 3, 4). This decrease is supported by corrosion rate results determined according to mass loss (Figures 1, 2).

In this study, the behavior of iron and aluminum in the same conditions was investigated. According to the results, benzoic acid is more effective in decreasing the corrosion rate of aluminum than that of iron (Figures 1-4). This may result from the fact that chloride ions selectively adsorbed on the iron form complex ions with iron and accelerate the corrosion rate of the iron<sup>1-4</sup>. However, aluminum metal is covered by a preventive oxide layer in the solutions with pH values between 4 and 9. This oxide layer does not decompose enough due to the effect of Cl<sup>-</sup><sup>4-17</sup>. It is also seen from E% values that benzoic acid molecules are particularly effective on aluminum metal (Tables 1,2). This result is in good agreement with the literature<sup>5,13,14</sup>. Since benzoic acid molecules are adsorbed on the active adsorption regions of the metals, adsorption diminishes with increasing concentration (Tables 3,4).

In conclusion, the corrosion rates of both iron and aluminum decrease with increasing concentrations of benzoic acid in 0.1 M NaCl solutions. This effect varies, depending on the concentrations of benzoic acid. It is also seen that benzoic acid is more effective in decreasing the corrosion rate of aluminum than that of iron.

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