

BRIEF COMMUNICATIONS

CORROSION PROTECTION OF IRON IN CHLORINE MEDIA BY NH_4NO_3 AND Na_2CrO_4 MIXTURES

S. Zor and E. Yakar

In all experiments, solutions were prepared by adding 10^{-1} , 10^{-2} , or 10^{-3} M NH_4NO_3 to a 0.1 M NaCl solution in bidistilled water including different concentrations of Na_2CrO_4 (10^{-1} , 10^{-2} , 10^{-3} , and 10^{-4} M). All experiments were carried out at room temperature.

Platinum wire was used as a counter electrode, a Saturated Calomel Electrode (SCE) was used as a reference electrode, and an Armco iron disc (with an area of 0.785 cm^2) was used as a working electrode. The surfaces of the working electrode were covered with polytetrafluoroethylene (PTFE), with the exception of their parts operating in contact with the solution. Prior to each measurement the surface of the electrode was polished with silicon carbide belts (200 grits to 1200 grits) to obtain shining surface and washed with acetone and bidistilled water. The potentiodynamic polarization curves were obtained by using EG&G PAR Model-263A potentiostat with potential ranging between -0.78 V and -0.28 V at a scanning speed of 25 mV/sec . The chronoamperometric measurements were carried out with fixed potential.

Results and Discussion

Polarization Results. The curves of anodic and cathodic polarization of iron are plotted. The electrochemical parameters I_{cor} (corrosion-current density), E_{cor} (corrosion potential), and R_p (polarization resistance) obtained from these curves are presented in Table 1. The inhibition efficiency (in %) is given by the following formula:

$$E = \frac{(I_{\text{cor}})_0 - I_{\text{cor}}}{(I_{\text{cor}})_0} \times 100,$$

where $(I_{\text{cor}})_0$ is the corrosion-current density in solutions without inhibitors and I_{cor} is the corrosion-current density in the presence of the inhibitor.

The corrosion-current density of iron decreases as a result of the addition of chromate anions to a 0.1 M NaCl solution. Thus, the corrosion rate of iron decreases as the chromate concentration decreases. Moreover, the lower the concentration of anions, the more pronounced the indicated decrease (see Table 1).

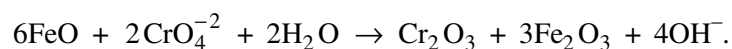
The mechanism of corrosion of iron inhibited by chromates can be written as follows:

Department of Chemistry, Kocaeli University, Kocaeli, Turkey.

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Table 1. Electrochemical Corrosion Parameters for Iron in a 0.1 M NaCl Solution with Inhibitor

Inhibitor	I_{cor} , $\mu\text{A} \cdot \text{cm}^{-2}$	E_{cor} , mV/SCE	R_p	E , %
0.1 M NaCl	32.6	-569.1	272.8	
0.1 M NaCl + 10^{-1} M K_2CrO_4	28.6	-479.8	354.4	12.3
0.1 M NaCl + 10^{-1} M K_2CrO_4 + 10^{-1} M NH_4NO_3	20.4	-465.2	1508.5	37.4
0.1 M NaCl + 10^{-1} M K_2CrO_4 + 10^{-2} M NH_4NO_3	25.8	-486.6	959.7	20.1
0.1 M NaCl + 10^{-1} M K_2CrO_4 + 10^{-3} M NH_4NO_3	28.6	-506.2	914.8	12.3
0.1 M NaCl + 10^{-2} M K_2CrO_4	27.9	-629.3	506.2	14.5
0.1 M NaCl + 10^{-2} M K_2CrO_4 + 10^{-1} M NH_4NO_3	19.2	-512.5	645.0	41.1
0.1 M NaCl + 10^{-2} M K_2CrO_4 + 10^{-2} M NH_4NO_3	22.1	-533.5	548.8	32.2
0.1 M NaCl + 10^{-2} M K_2CrO_4 + 10^{-3} M NH_4NO_3	26.8	-572.3	517	17.8
0.1 M NaCl + 10^{-3} M K_2CrO_4	18.6	-493.8	612.4	43.0
0.1 M NaCl + 10^{-3} M K_2CrO_4 + 10^{-1} M NH_4NO_3	16.4	-488.4	822.3	49.7
0.1 M NaCl + 10^{-3} M K_2CrO_4 + 10^{-2} M NH_4NO_3	16.8	-492.9	730.8	48.6
0.1 M NaCl + 10^{-3} M K_2CrO_4 + 10^{-3} M NH_4NO_3	17.4	-467.3	661.8	46.6
0.1 M NaCl + 10^{-4} M K_2CrO_4	17.9	-454.3	679.6	45.1
0.1 M NaCl + 10^{-4} M K_2CrO_4 + 10^{-1} M NH_4NO_3	16.0	-433.0	984.8	50.1
0.1 M NaCl + 10^{-4} M K_2CrO_4 + 10^{-2} M NH_4NO_3	16.4	-533.1	747.6	49.7
0.1 M NaCl + 10^{-4} M K_2CrO_4 + 10^{-3} M NH_4NO_3	17.1	-512.8	689.2	47.5

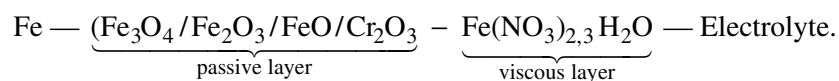


This means that the inhibiting effect of chromate anions at low concentrations can be caused by the reduction of Cr^{+6} to Cr^{+3} (as in Cr_2O_3) in the process of formation of the film [1, 2, 3]. The inhibiting behavior of chromates can be explained by the difference between the polarizability of CrO_4^{-2} anions [$670 \text{ mm}^2 \cdot \text{mole}^{-1}$] and chloride ions [$890 \text{ mm}^2 \cdot \text{mole}^{-1}$] [4]. Hence, the specific adsorption of the CrO_4^{-2} anion is higher than for the aggressive anion (Cl^-), which means that the CrO_4^{-2} anions can displace the adsorbed Cl^- ions and, as a result, improve the protective ability of the passive layer.

The corrosion-current density of iron in all solutions (including chromate-containing) decreases as a result of the addition of various concentrations of NH_4NO_3 (10^{-1} , 10^{-2} , and 10^{-3} M) to chloride solutions containing chromate ions (see Table 1). Thus, the inhibition efficiency of chromate increases with the concentration of NH_4NO_3 . If 10^{-1} M NH_4NO_3 is added to a chloride solution containing 10^{-4} M Na_2CrO_4 , then the corrosion-current density of iron reaches the lowest value, whereas the inhibition efficiency reaches its highest value (see Table 1).

There is a remarkable increase in the inhibition efficiency observed when 10^{-1} M NH_4NO_3 is added to highly concentrated chromate solutions (10^{-1} and 10^{-2} M).

In the previous work, it is shown that nitrate anions are inefficient as inhibitors of corrosion in iron [4]. At the same time, they become efficient in combination with chromate anions (Table 1). The role of nitrate in increasing the inhibiting efficiency of chromate is explained by the formation of a Cr_2O_3 layer as a result of the reduction of chromate anions, as well as by the formation of $\text{Fe}(\text{NO}_3)_{2,3}$ by nitrate anions on the metal surface. Thus, the chromate and nitrate anions may form a synergistic effect schematized as follows [5]:



Stable changes are not observed for corrosion potentials. Generally, the corrosion potential shifts toward more positive values relative to the solutions without inhibitors. As the concentration of chromate decreases, R_p increases. The value of R_p increases with the addition of NH_4NO_3 to chloride solutions containing chromate anions (Table 1). The corrosion current density I_{cor} is inversely proportional to the polarization resistance.

Chronoamperometric Results. The maximum current is observed in a solution containing 0.1 M NaCl and remains stable and equal to -0.015 A. If 10^{-1} , 10^{-2} , 10^{-3} , or 10^{-4} M Na_2CrO_4 is added to the solution, then the flow cathodically decreases for the first 2.5 min and then remains stable at almost the same values. As the concentration of chromate anions decreases, the decrease in the current becomes more pronounced. If NH_4NO_3 is added to a chromate-containing chloride solution, then the current decreases and becomes more negative than in the original chromate-containing solution. The indicated decrease in the current is more pronounced in all chromate solutions containing 10^{-1} M NH_4NO_3 . It is easy to see that NH_4NO_3 is more efficient in solutions with 10^{-1} M Na_2CrO_4 . These results are in good agreement with the potentiostatic data.

As shown above, the molecules adsorbed on the metal surface are efficient in decreasing the current by forming films on the metal surface and limiting the diffusion of ions or molecules from the metal surface to the solution or from the solution to the metal surface.

CONCLUSIONS

The corrosion rate of iron decreases as the concentration of chromate anions decreases. The inhibiting effect of chromate increases with the addition of ammonium nitrate. In chloride solutions, the combined action of chromate and nitrate reveals a synergistic effect.

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