2',3-Dicarboxylato-4-Hydroxyazobenzene as Corrosion Inhibitor for Aluminium in Sodium Hydroxide

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Abstract

A study involving both weight loss and electrochemical techniques has been undertaken to understand the effect of 2',3-dicarboxylato-4-hydroxyazobenzene on the corrosion of Al in NaOH solution. The inhibitive effect increases with the increase in the concentration of the inhibitor. The maximum inhibition efficiency for the dye was found to be 55.72. The addition of calcium oxide of concentration, 1.0×10^3 M, increase the above maximum inhibition efficiency to 76.52. The inhibitor appears to operate through its adsorption over the metal surface and through its ability to slow down the discharge of H^+ as H_2 gas at the cathodic sites on the metal surface. There is no definite shift in the open circuit potential, OCP, due to increasing addition of dye without and with a particular concentration of calcium oxide. The polarisation studies revealed that the corrosion of aluminium in the presence and the absence of inhibitor was under the anodic control. The corrosion inhibition was found to be of mixed type.

Introduction

Earlier research [1,2] on the development of electrolytes and cathodes for aluminium batteries is extended to examine the corrosion behaviour of aluminium in aqueous alkaline media. The accelerating and inhibiting effects of different additives in alkaline aluminium battery electrolytes has been examined by Zaromb and co-works[3,4] and summarised in subsequent paper[5]. Krishnan and Subramanyan[6] studied the effect of calcium combined organic acids on corrosion behaviour of aluminium in alkaline solutions. In the present investigation the effect of the combination of an azo dye and calcium oxide on the corrosion of aluminium in sodium hydroxide has been studied with a view to understand the efficiency of this combination to control the wasteful corrosion of aluminium in 1.0 N sodium hydroxide.

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Experimental

The commercially pure aluminium specimens were used in our studies. These specimens were mechanically polished with pumice powder and degreased with trichloroethylene. All the chemicals used in the present investigation were of AnalaR grade. The solutions were prepared in deionised water.

Preparation of 2',3- dicarboxylato-4-hydroxyazobenzene

The azo dye, 2',3-dicarboxylato-4-hydroxyazobenzene, was prepared[7] by diazotizing anthranilic acid (9.75 g) in 2.5 ml of conc.HCl and 7.5 ml of water with aqueous solution of sodium nitrite (1.8 g) at 0 – 5 °C by usual method and coupling the diazotised solution with an alkaline solution of salicylic acid (3.69 g). The dye was filtered, washed with water and dried.

Weight loss studies

The corrosion studies were carried out with aluminium

specimens of size, 20 X 10 X 1.5 mm³. The aluminium specimens were weighed and dipped in 100 ml of 1.0 N NaOH solution with and without the inhibitor for a specified length of time. It was removed from the solution and then washed by brushing under running tap water to remove the corrosion products, dried with filter papers and reweighed to find out the weight loss. The experiments were repeated until reproducible data were obtained.

OCP measurement

The steady value of open circuit potential of aluminium electrode, immersed in the test solutions, were measured without passing current after it is kept in the solution for about 45 minutes, using saturated calomel electrode as a reference electrode.

Polarization studies

The cell was constructed with three electrodes in a beaker with a platinum electrode as the counter electrode, a saturated calomel electrode as the reference electrode and the aluminium electrode as the working electrodeThe ganvanostatic polarization experiment were carried out using flag-shaped aluminium electrode with 1 cm² working area. The aluminium electrode was dipped in 100 ml of 1.0 N NaOH solution with and without the inhibitor. The measurements were made with the aerated unstirred test solutions. The power supply was a galvanostat fabricated in CECRI, Karaikudi. The values of potential were recorded by means of a high impedance multimeter. After measuring the steady open circuit potential value the aluminium electrode was polarized, cathodically by passing known values of current in the increasing steps of 10 mA min $^{-1}$ and the steady values of potential was measured at each current density.

After cathodic polarization was over the working electrode was brought back to the open circuit condition and then polarized anodically as explained above. The corrosion current, $I_{corr.}$ and corrosion potential, $E_{corr.}$ were evaluated by the extrapolation of the cathodic and anodic Tafel plots. The measurements were repeated until reproducible data were obtained.

Results and discussions

The dissolution of a metal like Al, in alkalis, leading to the evolution of hydrogen, is due to the formation of aluminate, $[AlO_2^-]$. The formation of such complex ion reduces the concentrations of $Al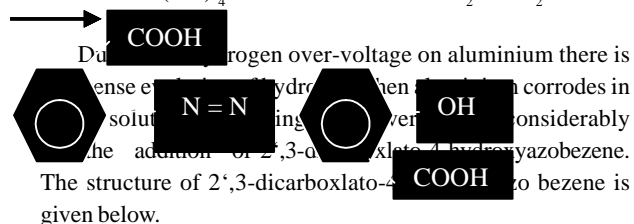^{3+}$ ions to such an extent that the potential of Al^{3+} - Al electrode is decreased well below the potential of the H^+ - ½ H_2 electrode (-0.83 V at pH = 14) and therefore dissolution of the metal can proceed readily [8]. The concentration of H^+ ions in alkaline solutions being rather small, the cathodic process is probably as shown below.

$$H_2O + e^- \longrightarrow OH^- + H \qquad and$$
$$H + H \qquad\qquad H_2$$
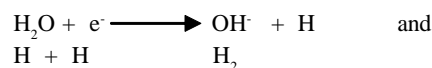
In alkaline solutions the OH⁻ ions, which are specially adsorbed on the aluminium surface, introduce partial negative charge at the point of interactions and these changes develop into large negative charge of the metal surface [9]. Thus the dissolution of aluminium in the alkaline medium occurs at a very high negative potential.

$$Al \qquad\qquad\qquad Al^{3+} + 3e^-$$

The Al^{3+} is readily complexed by OH⁻ resulting in the formation of AlO_2^-.

$$Al^{3+} + 4OH^- \qquad\qquad Al(OH)_4^-$$
$$Al(OH)_4^- \qquad\qquad AlO_2^- + 2H_2O$$

Due to high hydrogen over-voltage on aluminium there is intense evolution of hydrogen when the Al than corrodes in NaOH solution.The anodic dissolution is reduced considerably by the addition of 2´,3-dicarboxylato-4-hydroxyazobezene. The structure of 2´,3-dicarboxlato-4-hydroxyazo bezene is given below.

The rate of corrosion of aluminium by NaOH (1.0 N) , in the absence and in the presence of various concentrations of 2´,3- dicarboxylato–4-hydroxyazobenzene of various concentrations (Table 1), various concentrations of calcium oxide and (Table 2) various concentrations of 2´,3-dicarboxylato–4-hydroxyazobenzene in conjunction with a particular concentration of calcium oxide (Table 3) decreased with the increasing concentration of the inhibitor.

Table 1.   Effect of 2',3-dicarboxylato-4-hydroxyazobenzene on the rate of corrosion of aluminium in 1.0 N NaOH at 30± 1°C

[Dye] X 10³, M	Percentage inhibition	
	From mass loss studies	From polarization studies
Blank	--	--
0.5	27.83	24.14
1.0	32.33	27.56
1.5	33.89	30.82
2.0	34.97	33.93
2.5	35.54	38.34
3.0	36.93	39.74
3.5	38.73	42.45
4.0	39.36	45.05
4.5	46.04	48.71
5.0	55.72	52.21

Table 2.   Effect of calcium oxide on the rate of corrosion of aluminium in 1.0 N NaOH at 30± 1°C

[Calcium Oxide] X 10⁴, M	Rate of corrosion X 10⁴, g cm⁻² h⁻¹	Percentage inhibition
2.0	1.45	4.60
4.0	1.41	7.23
6.0	1.36	10.52
8.0	1.25	17.76
10.0	1.18	22.36

Use of increasing concentrations of 2',3- dicarboxylato–4- hydroxyazobenzene with calcium oxide of a particular concentration (Table 3) had the inhibitive influence almost equal to the sum of the individual inhibitive influences of 2',3-dicarboxylato–4-hydroxyazobenzene and calcium oxide, used separately.

Table 3. Effect of 2',3 –dicarboxylato– 4-hydroxyazobenzene in conjunction with calcium oxide on the rate of corrosion aluminium in 1.0 N NaOH at 30± 1°C

[Dye] X 10³, M	Percentage Inhibition	
	From mass loss studies	From polarization studies
Blank	-	-
0.5	34.96	35.40
1.0	39.03	41.43
1.5	43.15	48.62
2.0	48.04	52.17
2.5	54.21	58.31
3.0	60.41	65.32
3.5	63.77	68.38
4.0	65.84	69.80
4.5	67.67	71.15
5.0	70.20	72.45
5.5	73.65	73.69
6.0	74.25	74.88
6.5	74.69	75.45
7.0	74.80	76.01
7.5	75.56	77.09
8.0	75.76	78.12
8.5	75.86	78.62
9.0	76.62	79.10
9.5	76.52	79.21

Addition of the inhibitor caused small shift in values of the steady OCP values. Since the shifts in the OCP values are small an attempt was made to confirm the nature of inhibition from the analysis of complete polarization curves.

The corrosion parameters such as OCP, $I_{corr.}$, and $E_{corr.}$ were determined from galvanostatic polarization studies (Table 4 & 5). The $I_{corr.}$ was found to decrease with the increase in concentration of the inhibitor. It was observed the anodic

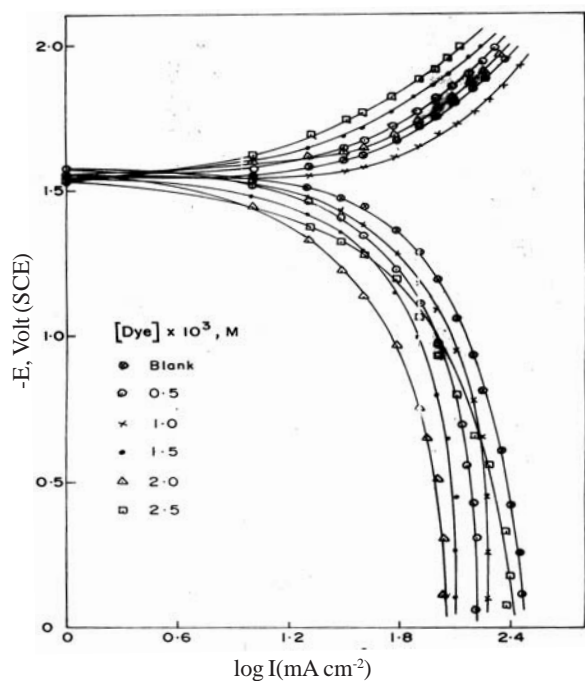Fig.1. Anodic and cathodic polarization of aluminium in 1 N NaOH without and with 2', 3 – dicorboxylato-4-hydroxyazobenze
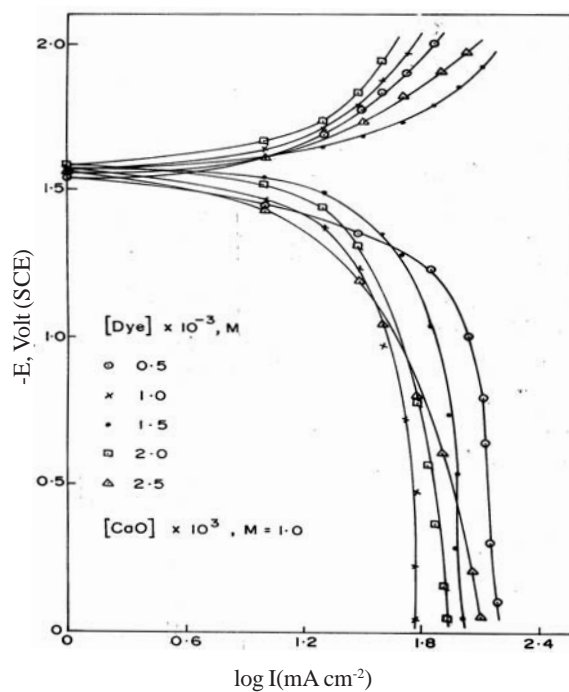

Fig.3. Anodic and cathodic polarization of aluminium in 1 N NaOH without and with 2'3-dicorboxlato-4-hydroxyazobenzene in conjunction with CaO
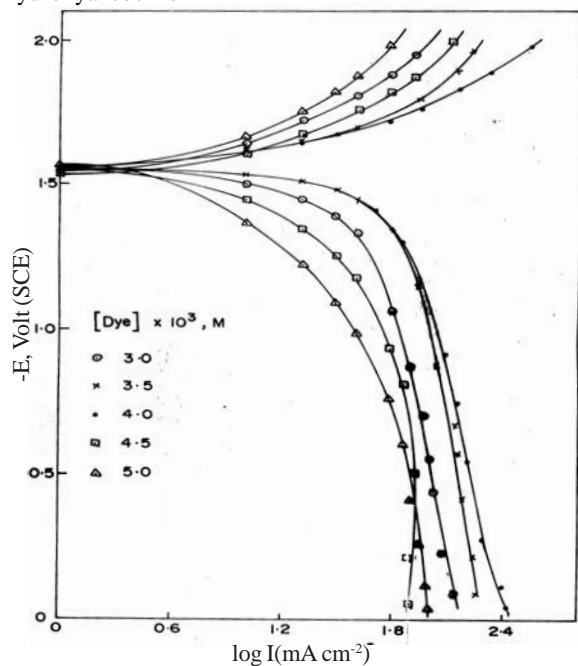

Fig.2. Anodic and cathodic polarization of aluminium in 1 N NaOH without and with 2'3-dicorboxlato-4-hydroxyazobenzene
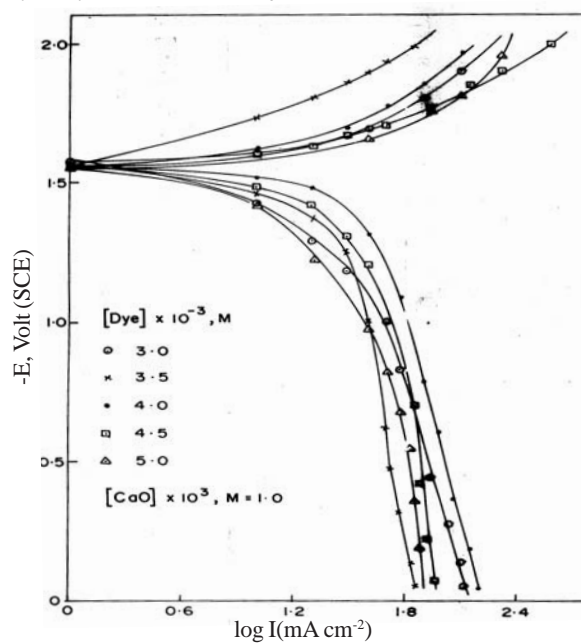

Fig.4. Anodic and cathodic polarization of aluminium in 1 N NaOH without and with 2'3-dicorboxylato-4-hydroxyazobenzene in conjunction with CaO

polarization was greater than cathodic polarization in all solutions. It is thus clear that the corrosion is predominantly under anodic control, in the presence and in the absence of the inhibitor. Since the slopes of both anodic and cathodic polarization curves are changed by the addition of inhibitor of various concentrations, the inhibition is of mixed type.

Table 4. Corrosion parameters for aluminium in 1.0 N NaOH solution without and with 2',3 –dicarboxylato –4-hydroxyazobenzene

[Dye] x 10^3 , M	OCP, Volt	$E_{corr.}$, Volt	$I_{corr.}$, mA cm^{-2}
Blank	1.54	1.56	36.31
0.5	1.56	1.53	27.54
1.0	1.57	1.54	26.30
1.5	1.57	1.55	25.12
2.0	1.57	1.58	23.99
2.5	1.55	1.57	22.99
3.0	1.56	1.54	21.88
3.5	1.57	1.55	20.89
4.0	1.55	1.56	19.96
4.5	1.57	1.53	18.62
5.0	1.58	1.54	17.38

Within a certain range of inhibitor and temperature, where monolayer adsorption is readily maintained over the aluminium surface, the Langmuir adsorption isotherm may be used.

$$\frac{\theta}{(1-\theta)} \, AC \exp \, (-Q/RT)$$

where A is a constant dependent on characteristics of the system of adsorption, C the concentration of inhibitor, Q the heat of the adsorption, B the occupied area and (1-θ) the vacant sites not occupied by the inhibitor. The degree of coverage è is given by

$$\theta = 1 - \frac{i_{inh}}{i_{uninh}}$$

Table 5. Corrosion parameters for aluminium in 1.0 N NaOH solution without and with 2',3 –dicarboxylato –4-hydroxyazobenzene in conjunction with calcium oxide

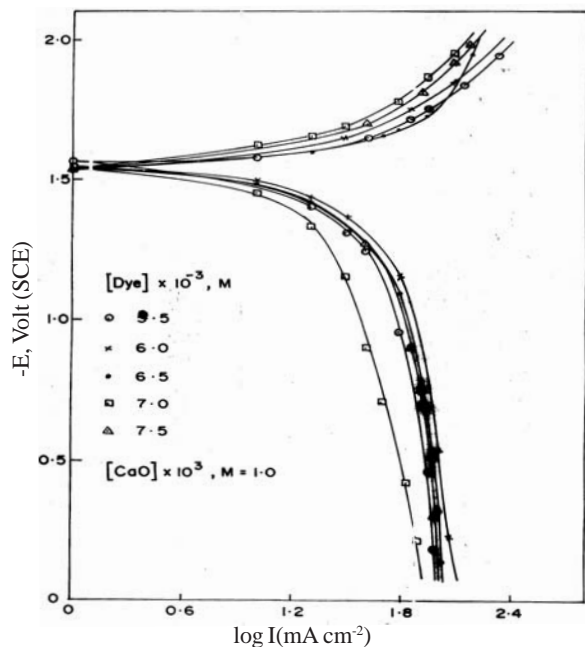| [Dye] X 10^3 , M	OCP, Volt	$E_{corr.}$, Volt	$I_{corr.}$, mA cm^{-2}
Blank	1.54	1.56	36.31
0.5	1.54	1.53	23.45
1.0	1.58	1.55	21.27
1.5	1.57	1.54	18.67
2.0	1.58	1.56	17.86
2.5	1.57	1.55	15.14
3.0	1.56	1.54	12.59
3.5	1.56	1.53	11.48
4.0	1.55	1.56	10.96
4.5	1.56	1.57	10.47
5.0	1.54	1.56	10.00
5.5	1.53	1.55	9.55
6.0	1.54	1.52	9.12
6.5	1.53	1.56	8.91
7.0	1.55	1.57	8.71
7.5	1.54	1.55	8.83
8.0	1.53	1.56	7.94
8.5	1.56	1.54	7.76
9.0	1.58	1.57	7.58
9.5	1.56	1.58	7.59

Fig.5. Anodic and cathodic polarization of aluminium in 1 N NaOH without and with 2'3-dicorboxylato-4-hydroxyazobenzene in conjunction with CaO
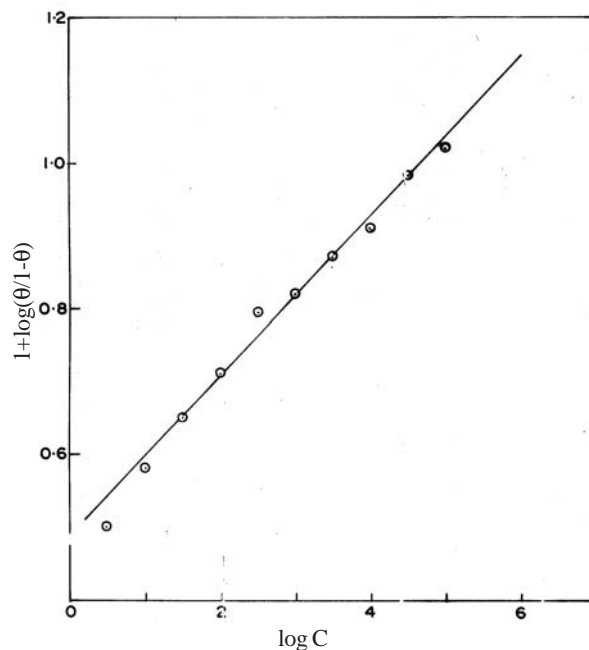

Fig.7. Langmuir plot for the inhibition of corrosion of aluminium by 2', 3-dicorboxylato-4-hydroxyazobenzene in aqueous alkaline medium (1 N NaOH)
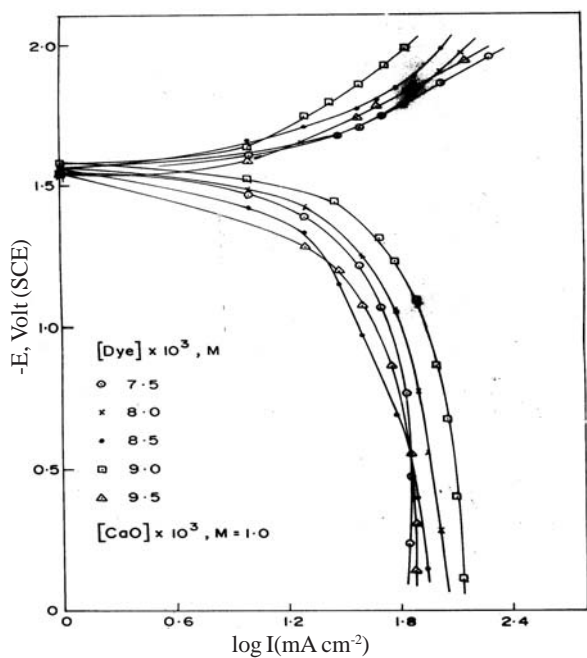

Fig.6. Anodic and cathodic polarization of aluminium in 1 N NaOH without and with 2'3-dicorboxylato-4-hydroxyazobenzene in conjunction with CaO
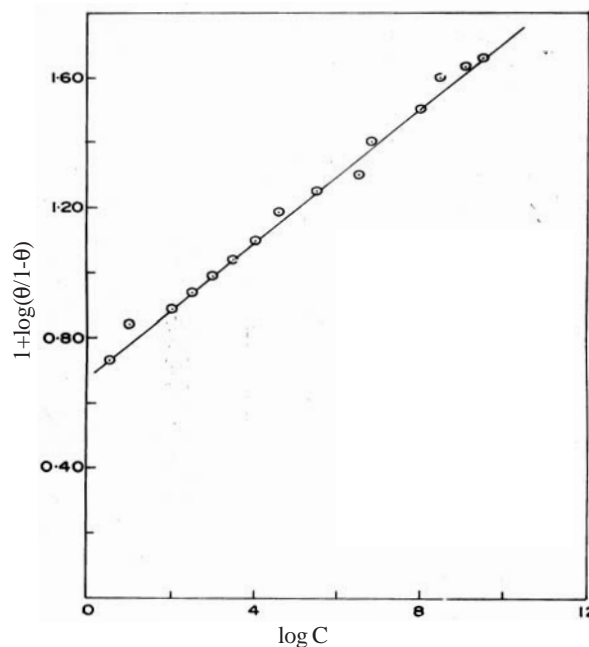

Fig.8. Langmuir plot for the inhibition of corrosion of aluminium by 2', 3-dicorboxylato-4-hydroxyazobenzene in aqueous alkaline medium (1 N NaOH) in conjunction with CaO

Where i_{inh} and i_{uninh} are the corrosion rates in solutions with and without inhibitor, respectively.

The above equation can be represented in the following form,

$$\log \frac{\theta}{1 - \theta} = \log A \ + \ \log \ C \ - \frac{Q}{RT}$$

Thus the plot of $\log \dfrac{\theta}{1 - \theta}$ against log C should be linear at constant temperature. This expectation is realized from the plots in fig. (5 & 6) and within a certain range of approximation the curves are linear.

Conclusion

The inhibitive efficiency increased with the increasing concentration of the inhibitor in the test solutions with and without calcium oxide. It was found from polarisation studies that the inhibitor inhibits both anodic and cathodic reactions indicating thereby a mixed type inhibition. The percent inhibition efficiency calculated from corrosion current was found to be of the same order of effectiveness as that obtained from weight-loss studies. The linearity of the plot of log è / 1-è versus log C, where è is the surface coverage obtained from corrosion current for the inhibitor concentration, C, reveals that the inhibition is due to the chemisorption of the inhibitor on aluminium surface.

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