Use of Tetra-N-Propyl Ammonium Iodide Along with Calcium Oxide for the Inhibition of Corrosion of Aluminium in 1N $N_a$oh

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***Abstract* - The stability of metals is determined by the events at the interface between these metals and their environment. The internal strength of a metal (particularly a metal under stress) is influence in the long run by happening at its surface.Moisture in contact with the terrestrial atmosphere become an ionically conducting medium, an electrolyte. When aluminium is kept in alkaline medium and connected to an air electrode it can produce high energy density and very high power[3]. In the present work experiments were carried out with a view to examining the ability of tetra-n-propyl ammonium bromide alone as well as the ability of the quaternary salt in conjunction with calcium oxide to inhibit the corrosion of commercial aluminium in alkaline media. It was found that the quaternary ammonium salt inhibits corrosion with an increase of its concentration. A maximum percentage inhibition of 43.87 was observed. However the addition of calcium oxide of concentration 8.9 x 10^{-4-} M increased the maximum inhibition efficiency to 52.62. The polarisation studies revealed that the corrosion of aluminium in the absence and in the presence of the inhibitor appeared to be under anodic control.**

Keywords - Local-Cell-Action, Relative Potential, Current Density

I.INTRODUCTION

The atmosphere is essentially moist air containing dissolved carbon dioxide, marine atmospheres .

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consists of moist air often containing in suspension sodium chloride. Moisture in contact
With the terrestrial atmosphere becomes an ionicallyconducting medium, an electrolyte.Metals become unstable when allowed to come into contact with the moist atmosphere. This instability of metals results from charge-transfer reactions at their interfaces. Therefore the rate of corrosive destruction of the surface of a metal is greatly reduced by removal of moisture from the atmosphere. Keeping a metal in vacuum is equivalent to removal of the electrolyte in contact with the metal and therefore to the prevention of charge-transfer reactions leading to the spontaneous instability (or corrosion) of metals.

Metallic corrosion arises from the electrodic charge-transfer at the interface between a metal and its electrolyte. Consider a bar of Zinc with microscopic inclusion of copper, say with copper impurities. Suppose the zinc bar is immersed in water. Even if the aqueous electrolyte has no Cu^{++} ions but it is ionically conducting the following electronation reactions are possible hydrogen evolution $2H_3O^+ + 2e^-$ ======= $H_2 + 2H_2O$ or oxygen reduction $O_2 + 4H^+ + 4e^-$ ====== $2H_2O$. As long as these electronation reactions take place, zinc dissolution will continue. The bar of zinc is undergoing corrosion; it becomes unstable and eventually destroys itself as a consequence of the electro-chemical reaction occurring at the interface of the metal and ionically conduction aqueous solutions.

A corroding metal consists of an electron source area at which a de-electronation reaction (i.e. metal dissolution) occurs, an electronic conductor to carry the electrons to the electron-sink area where an electronation reaction occurs, and an inonic conductor to keep the ion current flowing and to function as a medium for the electrodic reaction. This model of corrosion is often termed the local-cell theory of corrosion.

II. EXPERIMENTAL

Specimens of commercially pure aluminium samples were used for the studies. It has been referred to as ‘aluminium’ throughout this project record. These specimens were polished with emery papers of different grades, 1/0 to 4/0, degreased with trichloroethylene, pickled in 6% NaOH solution at 60^0C for 1 min, washed with distilled water, dipped in concentrated nitric acid for 20 s and again washed with distilled water. The aluminium coupons, treated in this way, were used after drying with filter papers. All the chemicals used were of AnalaR grade or chemically pure products and were used without further purification. All the solutions were prepared in deionised, doubly distilled water.
The aluminium specimens which were prepared for the study as described above and having the dimensions of 20 x 10 x 1.5 mm were weighed and immersed in 80 ml of aerated, unstirred 1N NaOH solution without and with the inhibitor for a stipulated period of time. The aluminium samples were then cleaned by brushing under running tap water to remove the corrosion products, dried and reweighed to determine the weight loss. The experiments were carried out in triplicate to ensure reproducibility. The mean values of weight loss were calculated and the percentage inhibition efficiency was computed using the following equation.

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$$\text{Percentage inhibition} = \frac{Wo-W}{} \text{ x } 100 \qquad Wo$$

Where W_o and W_i are the weight losses in uninhibited and inhibited corroding solutions respectively.

RESULT AND DISCUSSION

Hydrogen evolution measurements were made with the aluminium specimens immersed in 1 N sodium hydroxide solution without and with the inhibitor as shown in the diagram. The liberated hydrogen gas displaced equal volume of air. The volume of displaced air was measured at the atmospheric pressure for different intervals of time.

The aluminium specimens were immersed in the test solutions without and with the inhibitor and the potentials were measured, under open-circuit condition, as a function of time against a saturated calomel electrode using a high impedance multimeter. The measurements were made until a steady state value was attained.

The galvanostatic polarization studies were performed in a conventional three electrode cell, containing a platinum electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the aluminium specimen as the working electrode. The aluminium electrode and the aluminium specimen as the working electrode. The aluminium electrode was immersed in the test solutions for 30 minutes. The polarization measurements were then started so that a steady state open circuit potential was reached. Constant current densities, increasing in steps, were impressed on the working electrode from a current regulator made in the Central electrochemical Research Institute, CECRI, Kariakudi. The steady potential was measured at each current density. The measurements were carried out in unstirred test solutions. Corrosion currents, $I_{corr,}$ were evaluated by the extrapolation of the cathodic Tafel plots to the corrosion potential, $E_{corr.}$ Each experiment was duplicated and the mean value was calculated. When aluminium dissolves anodically both Al^{3+} and $Al^+$are formed initially.The univalent ion reduces H_2O to form the trivalent ion in accord with the following equation[6].

$$Al \longrightarrow Al^+ + e^-$$
$$Al^+ + 2H2O \longrightarrow Al^{3+} + H_2 + 2OH^-$$

When aluminium is anodized H_2 is evolved at the anode as well as at the cathode. Hydrogen evolution at the anode can be explained by increased local action corrosion during anodic dissolution.

The corrosion behaviour of aluminium is sensitive to small amounts of impurities in the metal and all of which except Mg tend to be cathodic to aluminium. In general highly pure aluminium metal is much more corrosion resistant than the commercially pure aluminium which in turn, is more resistant than aluminium alloys.

Aluminium corrodes more rapidly both in acids and in alkalies compared with distilled water. The rates of corrosion of aluminium in acids depends on the nature of the anion. 37

Rate of corrosion of aluminium, in the alkaline solution, greatly increases with pH, unlike the situation for iron and steel which remain corrosion resistant. The difference in corrosion rate arises due to the reason that Al^{3+} readily complexed by OH^- forming AlO_2 in accord with the following equation[6].

The reaction proceeds rapidly at room temperature.The reaction, at the cathodic site, is given below,

$$H + H \longrightarrow H_2\,(g)$$
$$H_2O + e \longrightarrow OH + H$$
$$H + H \longrightarrow H_2\,(g)$$

Due to the above vigorous reaction Al^{3+} with OH^- the concentration of Al^{3+} is so
reduced that the potential Al --- Al^{3+} electrode is decreased much below that of H^+ - H_2 (g) electrode i.e. a highly negative potential for Al – Al^{3+} electrode.

Since aluminium electrode surface has highly negative potential in NaOH solution we intended to reduce its corrosion in the solution by incorporating the positively charged quarternary ammonium salt in the NaOH solution.

Table 1: Effect of tetra-n-propylammonium bromide on the rate of corrosion of aluminium in 1. 0 N NaOH at 30±1° C in 1. 0 N NaOH at 30±1° C

[Tetra n-propylammonium bromide] x 10^4, M	Rate of corrosion x 10^4, g $cm^{-2}h^{-1}$	Percentage inhibition
--	2.94	--
4.76	2.70	8.16
9.53	2.57	12.58
14.3	2.40	1.36
19.0	2.21	24.2
23.8	2.01	31.63
28.6	1.89	35.71
33.3	1.76	40.13
38.1	1.70	42.17
42.9	1.65	43.87

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 10^4, M	Rate of corrosion x 10^4, g $cm^{-2}h^{-1}$	Percentage inhibition g $cm^{-2}h^{-1}$
1.78	1.45	4.60
3.56	1.41	7.23
5.34	1.36	10.52
7.13	1.25	17.76
8.9	1.18	17.76

Table 3: Effect of tetra-n-prophylammonium bromide in conjuction with calcium oxide on the rate of corrosion of aluminium in 1. 0N NaOH at 30±1° C

[Tetra-n-prophylammonium bromide] x 10^4, M	Rate of corrosion x 10^4, g $cm^{-2}h^{-1}$	Percentage inhibition g $cm^{-2}h^{-1}$
--	1.94	--
4.76	1.67	13.91
9.53	1.47	24.22
14.3	1.38	29.89
19.0	1.36	2.89
23.8	1.27	34.53
28.6	1.20	38.14
33.3	1.09	43.81
38.1	0.959	50.56
42.9	0.919	52.62

[CaO] x 10^4, M = 8.9

Table 4: Corrosion parameters for Aluminium in 1.0N NaOH solution without and with Tetra n-propylammonium bromide

[Tetra-n-propyl ammonium bromide] x 10^4, M	OCP V	$E_{corr.}$ V	I_{corr} $mAcm^{-2}$
--	1.54	1.52	19.95
4.76	1.55	1.54	17.78
9.53	1.54	1.56	15.48
14.3	1.57	1.53	14.45
19.0	1.56	1.55	13.80
23.8	1.55	1.54	12.88

Table 5: Corrosion parameters for Aluminium in 1. 0 N NaOH solution without and with Tetra n-propylammonium bromide in conjunction with Calcium oxide.

[Tetra-n-propyl ammonium bromide] x 10^4, M	OCP V	$E_{corr.}$ V	I_{corr} mAcm-2
--	1.52	1.55	25.90
4.76	1.54	1.57	23.99
9.53	1.55	1.58	20.89
14.13	1.56	1.59	19.95
19.0	1.54	1.59	17.31
23.8	1.53	1.54	15.84
28.6	1.55	1.55	15.48
33.3	1.56	1.54	14.12
38.1	1.52	1.53	12.58
42.9	1.50	1.54	12.02

CONCLUSIONS

The effect of the addition of tetra-n-propyl ammonium bromide as well as the addition of tetra-n-propylammonium bromide in conjuction calcium oxide on the corrosion of aluminium in 1.0 N NaOH solution was studied by weight loss, gasometry and polarization techniques. It was found that the quaternary ammonium salt inhibits corrosion with an increase of its concentration. A maximum percentage inhibition of 43.87 was observed. However the addition of calcium oxide of concentration 8.9 x 10^{-4-} M increased the maximum inhibition efficiency to 52.62. The open circuit potential of aluminium in 1.0 N in the presence of the inhibitors of varying concentration did not show any significant shift in its values. The polarisation studies revealed that the corrosion of aluminium in theabsence and in the presence of the inhibitor appeared to be under anodic control. The inhibitor was found to be of mixed type.

REFERENCES

[1] O.M. Bockris and K. N. Reddy, Modern electrochemistry, Plenum Press, New York, (1970) 1279 – 1309.
[2] S.N. Banerjee, An Introduction to Science of Corrosion and its inhibition, Oxanion Press, New Delhi, (1985) p^{-3}.
[3] N. Subramanyan, V. Kapali and S. Venkatakrishna Iyer, Corrosion Sci., 11 (1971) 115
[4] J. Cooper, Aluminium – air battery development towards an electric car, Energy and Technology Review, Lawrence Livermore National Laboratory, 1983.
[5] N. P. Fitzpatric, F.N. Smith and P.W. Jaffery, the aluminium – air battery
[6] SAE Meeting, Detroit, Michigan, February , March 4, 1983.
[7] E. Raijola and A. Davidson, J. Am. Chem.Soc., 78 (1956), 556.
[8] L. I. Antropov, Proc. 1^{St} Int. Congr. Metal Corros., London, 1961, Butterworth, London, (1961) p-148.
[9] SAE Meeting, Detroit, Michigan, February , March 4, 1983.
[10] E. Raijola and A. Davidson, J. Am. Chem.Soc., 78 (1956), 556.
[11] L. I. Antropov, Proc. 1^{St} Int. Congr. Metal Corros., London, 1961, Butterworth, London, (1961) p-148.
[12] SAE Meeting, Detroit, Michigan, February , March 4, 1983.
[13] E. Raijola and A. Davidson, J. Am. Chem.Soc., 78 (1956), 556.
[14] L. I. Antropov, Proc. 1^{St} Int. Congr. Metal Corros., London, 1961, Butterworth, London, (1961) p-148.