Effect of Arginine in Conjunction with Calcium Oxide on the Corrosion of Aluminium in 1.0 N Sodium Hydroxide

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Abstract

Arginine acts as a good inhibitor. Its inhibition efficiency reaches 50.09 at its maximum concentration of 34.5×10^{-4} M. However a combination of calcium oxide and arginine has the maximum inhibition efficiency of 60.65%. The shift in the steady OCP values for aluminium electrode dipped in 1.0 N NaOH, caused by the increasing addition of the inhibitor, was not considerable. Polarisation studies revealed that the corrosion process was found to be under anodic control in the absence or in the presence of inhibitor. The inhibition was found to be of mixed type. The inhibiting effect of these additives is attributed to their adsorption on the electrode surface. The adsorption of arginine obeys Langmuir adsorption isotherm.

Keyword: Arginine

Introduction

Caustic soda solutions are frequently employed for cleaning aluminium surfaces. As the action of caustic alkali on aluminium is very rapid and severe the cleaning solutions need to be   inhibited. Desai etal[1,2] and Subramanyan etal[3] have studied the use of various organic compounds in inhibiting the corrosion of 2S and 3S aluminium in sodium hydroxide. Various organics have also been reported as corrosion inhibitors for 3S aluminium alloy (an aluminium alloy containing 1.3% Mn) in potassium hydroxide solutions[4]. In the present paper the effect of arginine and calcium oxide individually and the effect of a mixture of these substances on the corrosion of 2S aluminium in sodium hydroxide solution has been studied.

Experimental

The pure aluminium specimens, used for the study, were polished with emery papers of different grades. The aluminium specimens were cleaned by boiling with the dilute NaOH solution (2 N) for about 2-3 minutes, washed thoroughly with distilled water and finally with conductivity water and dried with filter papers. All the chemicals used were of AnalarR grade. All solutions were prepared in double distilled water.

Weight loss studies

The self corrosion studies were made with the aluminium specimens of size, $2.0 \times 1.0 \times 0.15$ cm^3. The metal coupons was weighed and immersed in 100 ml of 1 N NaOH solution without and with the inhibitor for a stipulated period of time. It was removed from solution. The aluminium sample was cleaned, by brushing under running tap water to remove the corrosion products, dried and found out the weight loss. The experiments were carried out in triplicate to ensure reproducibility. The mean value of weight loss was calculated.

From the weight loss values, the percentage efficiency (P.I) was calculated using the following equation.

$$P.1 = \frac{W_o - W_i}{W_o} \times 100$$

where W_o and W_i are the weight losses in the absence and in the presence of inhibitor, respectively.

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OCP measurements

The potentials of aluminium coupons, immersed in the test solutions, were measured under open circuit condition, as a function of time against a saturated calomel electrode used as the reference electrode. The measurements were made until a steady state potential value was attained.

Polarization studies

The galvanostatic polarization studies were carried out in a beaker containing three electrodes-aluminium electrode as the working electrode, a saturated calomel electrode as the reference electrode and platinum electrode as the auxillary electrode.

Polarization experiments were carried out using flag shaped aluminium electrode with $1 \, cm^2$ working area. The aluminium electrode was dipped in 1 N NaOH solution without and with inhibitor. The distance between the calomel electrode and the Luggin capillary was kept constant throughout the experiment to minimize the ohmic IR drop. The measurements were made in aerated unstirred test solution throughout the studies. The power supply was a galvanostat. The potential values were recorded by means of high impedance multimeter. After measuring the steady OCP, the specimen was first cathodically polarized by passing known value of current increasing in the range of 10 mA min^{-1} and steady potential was measured at each current density. After cathodic polarization was over, the aluminium electrode was brought back to OCP and then polarized anodically to derive the corresponding polarization curve. The corrosion current and corrosion potential values were evaluated. The measurements were repeated until reproducible data were obtained.

Results and discussions

A close examination of the potential – pH diagram of the Al-H_2O system indicates clearly that high negative potentials are attained by aluminium in the alkaline pH range. In alkaline media[5-9] aluminum readily dissolves and generates a useful voltage at a reasonable current.

When Al is introduced into an alkaline solution of high concentration, the OH$^-$ ions are first adsorbed on its surface. Owing to the acidic nature of the oxide it is chemically attacked through following reactions.

$$Al_2O_3 \; + \; 2OH^- \longrightarrow \; 2AlO_2^- + H_2O$$
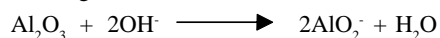
The metal is also dissolved as shown below.

$$Al + 4OH^- \qquad H_2AlO_3^- + H_2O + 3e^-$$

These wasteful corrosion reactions have to be stopped. This can be achieved to a considerable extent by the use of inhibitor.

The percentage efficiency of inhibition of corrosion of aluminium in 1.0 N NaOH solution by varying amounts of arginine (Table 1) and varying concentrations of arginine along with a particular concentration of calcium oxide (Table 2) were determined at 303 K by weight loss method. The values are found to gradually increase with increase in concentration of the inhibitor. The maximum percentage inhibition efficiency was 50.09, when arginine alone was used as the inhibitor. Moreover the inhibitor efficiency of various concentrations of arginine in conjunction with calcium oxide of particular concentration, that is 1.0 X 10^{-3} M, showed no significant increase. The increase, in this case, was only 60.65.

Table 1. Effect of arginine on the rate of corrosion of aluminium in 1.O N NaOH at 30 $\pm$ 1°C

[Arginine] X 10^4, M	Percentage Inhibition	
	From Weight loss studies	From polarization studies
Blank	-	-
5.7	10.02	8.80
8.6	14.04	14.89
11.5	18.18	16.82
14.4	22.68	20.57
17.2	24.59	24.14
20.1	28.98	27.75
22.9	30.57	29.21
25.9	34.04	30.82
28.7	39.17	35.43
31.6	44.16	39.74
34.5	50.09	45.04

The structure of arginine is
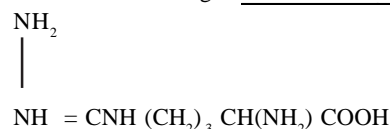
$$NH_2$$
$$|$$

$$NH \; = CNH \, (CH_2)_3 \; CH(NH_2) \; COOH$$

Table 2. Effect of arginine in conjunction with calcium oxide on the rate of corrosion of aluminium in 1.O N NaOH at 30±1°C114

[Arginine] X 10^4, M	Percentage Inhibition	
	From Weight loss studies	From polarization studies
Blank	-	-
5.7	14.21	16.35
8.6	19.23	20.42
11.5	26.45	26.26
14.4	29.01	30.54
17.2	34.42	33.75
20.1	38.18	36.90
22.9	41.02	38.94
25.9	46.44	44.73
28.7	50.72	49.92
31.6	55.67	55.86
34.5	60.65	57.34

[CaO] X 10^3 , M = 1.0

The effect of different concentrations of arginine on the open circuit potential of Al in 1.0 N NaOH was examined using the following cell. The additives caused no significant differences in the OCP values of the tested aluminium, immersed in 1.0 N NaOH solutions.

Al / NaOH (1.0 N) , arginine // SCE

The corrosion parameters such as OCP, $I_{corr.}$, and $E_{corr.}$, were determined from galvanostatic polarization studies (Table 3 and 4). The $I_{corr.}$, was found to decrease with the increase in concentration of the inhibitor. It was observed that anodic polarization was greater than cathodic polarization in all solutions (Fig. 1, 2, 3 &4). It is thus clear that the corrosion is predominantly under anodic control in the presence and in the absence of the inhibitor. The inhibition is of mixed type because both anodic and cathodic polarization are increased with increasing concentration of inhibitor.

Also, the surface coverage, q can be determined from polarization data [10] according to the following equation

$$\theta = 1 - \frac{i_{inhibited}}{i_{uninhibited}}$$

Table 3. Corrosion parameters for aluminium in 1.O N NaOH solution without and with arginine

[Arginine] X 10^4,M	OCP, V	$E_{corr.,}$ V	$I_{corr.,}$ mA cm^{-2}
Blank	1.54	1.61	22.91
5.7	1.56	1.59	20.89
8.6	1.56	1.58	19.50
11.5	1.54	1.60	19.05
14.4	1.59	1.55	18.20
17.2	1.58	1.55	17.34
20.1	1.56	1.56	16.60
22.9	1.58	1.65	16.22
25.9	1.55	1.60	15.85
28.7	1.57	1.62	14.79
31.6	1.52	1.57	13.80
34.5	1.48	1.54	12.59

Table 4. Corrosion parameters for aluminium in 1.O N NaOH without and with arginine in conjunction with calcium oxide

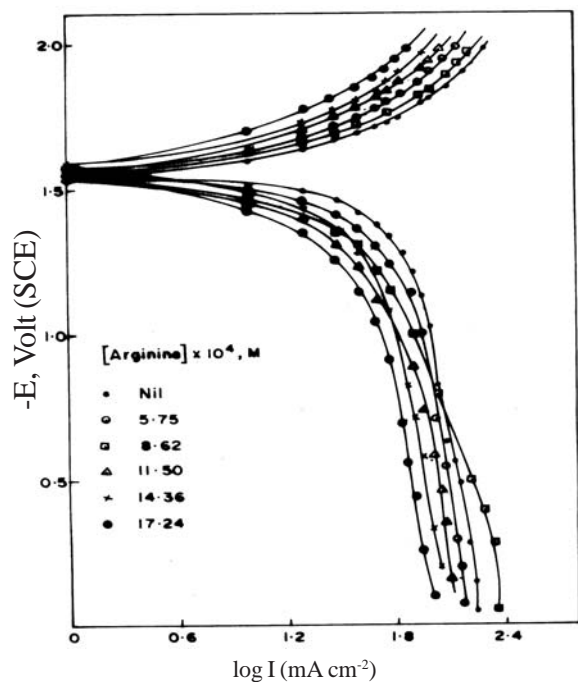| [Arginine] X 10^4,M	OCP, V	$E_{corr.,}$ V	$I_{corr.,}$ mA cm^{-2}
Blank	1.54	1.56	22.91
5.7	1.55	1.58	19.16
8.6	1.54	1.55	18.23
11.5	1.58	1.56	16.90
14.4	1.52	1.58	15.91
17.2	1.56	1.65	15.18
20.1	1.54	1.62	14.45
22.9	1.56	1.60	13.99
25.9	1.58	1.53	12.66
28.7	1.54	1.55	11.47
31.6	1.52	1.56	10.11
34.5	1.49	1.54	9.70

[CaO] X 10^3, M = 1.0

Fig.1. Anodic and cathodic polarisation of aluminium in 1.0 N NaOH without and with arginine
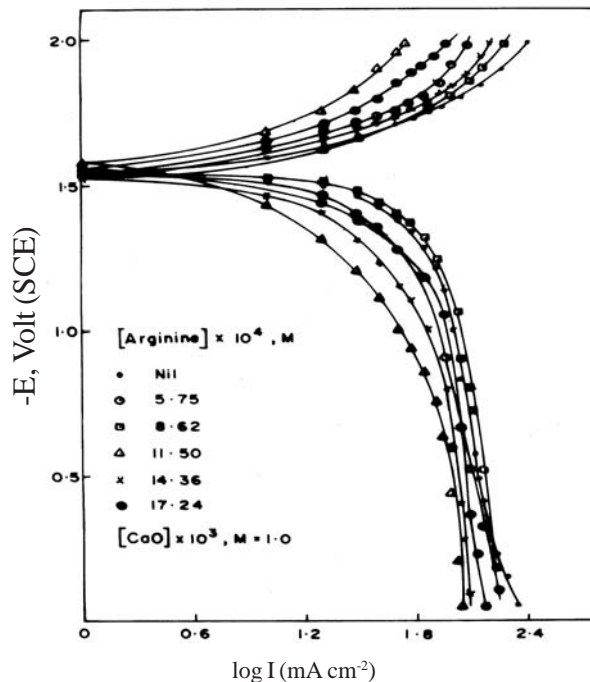

Fig.3. Anodic and cathodic polarisation of aluminium in 1.0 N NaOH without and with arginine in conjunction with calcium oxide
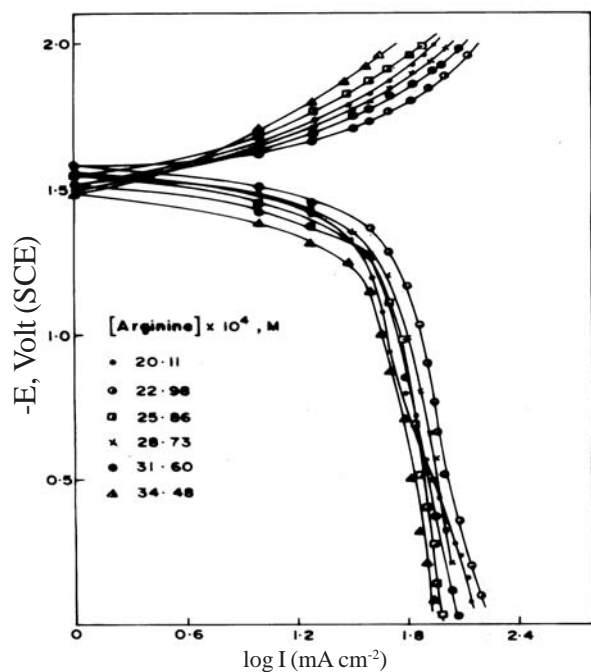

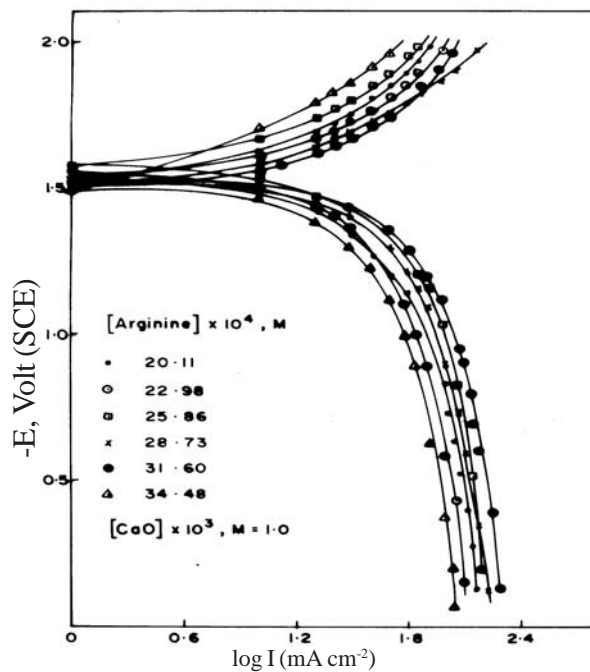Fig.2. Anodic and cathodic polarisation of aluminium in 1.0 N NaOH without and with arginine

Fig.3. Anodic and cathodic polarisation of aluminium in 1.0 N NaOH without and with arginine in conjunction with calcium oxide

where, $i_{uninhibited}$ and $i_{inhibited}$ are the current densities measured at constant potential in the absence and presence of inhibitor, respectively. The values of q as a function of inhibitor concentration are shown in Fig. 5 & 6.
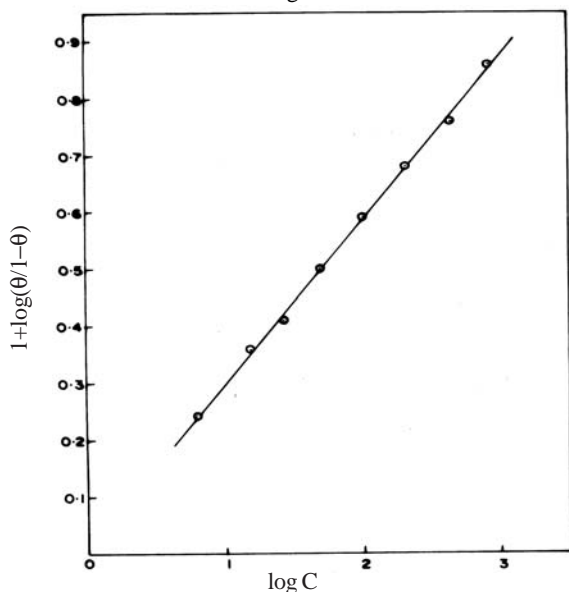

Fig.5. Langmuir plot for the inhibition of corrosion of aluminium by arginine in aqueous alkaline medium (1N NaOH)
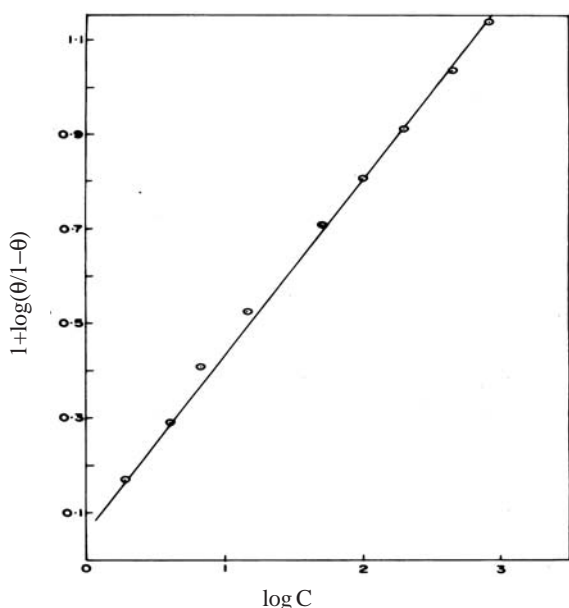

Fig.6. Langmuir plot for the inhibition of corrosion of aluminium by arginine in aqueous alkaline medium (1 N NaOH) in conjunction with calcium oxide

It is clear from Fig. 5 & 6 that log (q/1-q) varies linearly with the logarithm of inhibitor concentration, fitting a Langmuir adsorption isotherm.

$$q/1-q = A.C. \exp (-\ddot{A}G_{ads}/RT)$$

where, C is the additive concentration, A is a constant depending on intermolecular interactions in adsorption layer and on the heterogeneity of the surface and $\ddot{A}G_{ads}$ is adsorption energy.

Conclusion

The inhibitor shows maximum inhibition at the maximum concentration taken. Both the anodic and cathodic polarization curves are shifted in the presence of inhibitor, to low current density region revealing mixed type of inhibition, though the corrosion process in the presence as well as in the absence of inhibitor is anodically controlled.

Acknowledgement

References

1. M.N. Desai, R.R. Shah and M.H. Gandhi, *4th European Symp. on Corrosion Inhibitors,* Ferrara(Italy) (1978) 338.

2. M.N. Desai and S.M. Desai, *2nd Symp. on Corrosion Inhibitors,* Ferrara(Italy) (1966) 207.

3. N. Subramanyan and M. Krishnan, *Corros. Sci.*, 17 (1977) 893.

4. J.D. Talati and N.H. Joshi, *Workstoffe and Corrosion*, 29 (1978) 461.

5. S.Zaromb, *J. Electrochem. Soc.*, 109 (1962) 1125.

6. V. Kapali and N. Subramanian, *Indian Patent,* 104 (1966) 523.

7. N.Subramanian, M.G.Potdar and A.R.Yamuna, *Ind. Engg. Chem.Process Design and Development* 8 (1969)31

8. N.Subramanian and A.R.Yamuna, *Br.Corros.J.,* 4 (1969) 32.

9. V. Kapali, S. Venkatakrishna Iyer and N. Subramanian, *Br.Corros.J.,*4 (1969)305.

10. I.A. Ammar and S. Darwish, *Corros. Sci.,*7 (1967) 579.