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Influence of Some Anions on the Dissolution of 1100 Aluminium in Hydrochloric Acid

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An investigation has been made to find out the influence of sodium acetate, citrate, chromate, nitrate, oxalate, orthophosphate, dihydrogen orthophosphate, phosphate, perchlorate, tartrate, tetraborate, thiosulphate, tungstate and vanadate in the concentration range 10–300 ppm on the dissolution of 1100 aluminium in acidic solution containing chloride ions. It has been observed that chromate, oxalate, thiosulphate, nitrate, acetate, vanadate, tetraborate and perchlorate ions retard dissolution at all the concentrations studied. A slight increase in the corrosion rate has been noticed at lower concentrations in the presence of perchlorate. Citrate, tartrate, orthophosphate, dihydrogen orthophosphate and phosphate ions inhibit corrosion at lower concentration and accelerate at higher ones. It has been noticed that tungstate ions stimulate corrosion at all studied concentrations.

Polarisation studies show that chromate ions inhibit corrosion rate by polarising cathodic reactions and tungstate ions stimulate by its depolarising actions.

INTRODUCTION

Aluminium and its alloys are vulnerable to chloride ions. In acidic solutions the attack of these ions becomes very severe. Aluminium and its alloys, due to the presence of natural oxide film on the surface, withstand the attack up to an induction period and after which they start dissolving. It is reported that the presence of a second (noble) metal in the environment allows the deposition of the metal on the surface of the aluminium and this usually hastens the onset of corrosion. Several investigators have carried out the effect of some ions on corrosion of different metals in various media[1–13]

The effects of anions on the corrosion of aluminium, however, have scarcely been reported especially in acidic chloride media. Therefore, in the present investigation, a study has been made to understand the role of different anions taking these as their sodium salts at low concentrations on the dissolution of 1100 aluminium alloy in chloride solution of pH = 1 interalia with following:

(a) Effect of concentrations of the anions on the corroding surface.

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(b) Influence of the ions on the local anodic and cathodic sites.
(c) Adsorption behaviour of the undertaken ions.

EXPERIMENTAL

Aluminium alloy (1100) manufactured by M/s. Hindalco, Mirzapur, having the composition Si = 0.13%, Fe = 0.52%, Mn = 0.064%, Mg = 0.021%, Cu = 0.01% and remainder aluminium, was used for the present investigation. Hydrochloric acid, BDH, AnalaR grade, was employed for making the electrolyte of pH = 1. The anions employed in the present studies were added as their respective sodium salts.

The preparation of specimens, method of corrosion testing, cleaning of corroded specimens and polarisation studies were same as described earlier[13]. The percentage relative loss was calculated from the equation:

$$\text{RPL} = \frac{W_A}{W_B} \times 100$$

where RPL = the percentage relative loss;
W_A = weight loss in hydrochloric acid (pH = 1) in the presence of anions
W_B = weight loss in hydrochloric acid (pH = 1)

For determination of the adsorption behaviour of the anions the inhibition efficiency (100 − RPL) has been taken into account to assess the surface coverage θ and for the validity of the adsorption behaviour $\log \frac{\theta}{1-\theta}$ vs. $\log C$ were plotted in a graph. All experiments were performed with an electronically controlled air thermostat at a constant temperature of 35° ± 0.2°C.

RESULTS AND DISCUSSION

Table 1 shows the relative percentage loss in the presence of acetate, citrate, chromate, nitrate, oxalate, orthophosphate, dihydrogen orthophosphate, phosphate, perchlorate, tartrate, tetraborate, thiosulphate, tungstate and vanadate ions for 1100 alloy at 35°C. The relative percentage losses have been determined at 10, 50, 100, 200 and 300 ppm concentrations. On the basis of the results shown in Table 1, the anions can be classified into three different groups;

(i) Anions like citrate, tartrate, orthophosphate, dihydrogen orthophosphate and phosphate which have inhibiting effects at their lower concentrations appear as corrosion stimulators at higher concentrations. The dissolution of the alloys in the presence of first two anions is directly proportional to their concentrations whereas latter three ions exhibit maximum corrosion at 200 ppm and beyond this concentration, the corrosion rate decreases gradually.

(ii) Anions like chromate, thiosulphate, nitrate, acetate, oxalate, vanadate, tetraborate and perchlorate for which the corrosion rate is inversely proportional to their concentrations. A slight increase in the corrosion rate in the presence of perchlorate has been noticed at lower concentrations. The former five ions, however, inhibit the corrosion of aluminium at all the concentrations studied.

Chromate and thiosulphate are found to be most efficient in controlling the dissolution.

TABLE 1
PERCENTAGE RELATIVE LOSS (RPL) OF 1100 ALUMINIUM IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF ANIONS AND SLOPES OF THE LANGMUIR ADSORPTION PLOT AT 35° ± 0.2°C.
IMMERSION PERIOD = 24 h

Anions	RPL					Slope of the Langmuir plot
	Concentration of anions in ppm					
	10	50	100	200	300	
Acetate	54.17	48.03	42.42	39.02	37.31	0.206
Citrate	33.42	50.25	66.56	135.21	147.25	—
Chromate	84.73	47.14	25.75	11.45	8.52	1.22
Nitrate	74.23	71.15	69.32	67.18	67.22	0.116
Oxalate	68.44	64.56	44.63	24.38	20.25	0.15 & 1.167*
Orthophosphate	61.86	144.31	185.25	218.37	130.82	—
Dihydrogen orthophosphate	54.95	144.33	196.26	204.57	192.37	—
Phosphate	58.36	158.27	190.94	219.71	180.81	—
Perchlorate	170.43	105.18	103.29	99.48	96.62	—
Tartrate	40.57	43.89	118.20	160.58	175.52	—
Tetraborate	97.12	95.43	93.79	92.47	91.78	0.412
Thiosulphate	45.08	40.72	38.07	37.31	35.61	0.122
Tungstate	393.58	340.82	268.83	195.54	150.37	—
Vanadate	98.05	95.57	93.17	88.29	85.48	0.623

*Value of the slope at higher concentrations of the added anions.

(iii) Tungstate ion which shows the very peculiar behaviour of having the highest stimulating effect at its lowest concentration used (10 ppm); at higher concentrations also tungstate acts as an accelerator, although less aggressive.

Shams El-Din *et al.*[14] have reported that the inhibition by HPO_4^{2-} in the presence of aggressive anions *e.g.* Cl^-, Br^- and I^- are not due to its reduction, but rather to the formation of a compact oxide layer incorporating some phosphate. Therefore, it may be suggested that the retardation in the corrosion at the lower concentration (10 ppm) of the three phosphate ions is probably due to the formation of sparingly soluble salt with aluminium (*e.g.* $AlPO_4$) which get deposited on the metal surface and block the active sites. At higher concentrations a thinner film is formed which is not resistant to the penetration of H^+ or Cl^- toward the base metal. It is clear from the table that tartrate inhibits the attack only upto 50 ppm whereas citrate ion inhibits the corrosion at 100 ppm concentration. It is expected that the sodium salts of these anions give their respective acids in 1% hydrochloric acid. It appears that the presence of two secondary alcoholic groups in tartaric acid make it less inhibitive than the citric acid which has only one such alcoholic group. The stimulation of corrosion at the higher concentrations of these two anions seems to be due to the formation of soluble complex anions. The hydroxyl groups of tartaric and citric acids help to anchor the anions, which, once they reach the surface under the electrical gradient, are likely to be held fast. After certain concentrations these anions (more than 50 ppm and 100 ppm in the presence of tartrate and citrate respectively) are attached with the metal and a soluble complex-anion formation takes place and thereby the corrosion rate is accelerated. Oxalic acid inhibits the corrosion at all the concentrations studied because it has no secondary alcoholic group. However, the inhibition efficiency in the presence of acetate does not depend on the alcoholic or carboxylic group. The inhibitive action of chromate on aluminium may be explained on the basis of the reasoning that any aluminium which enters as Al^{3+} ions, formed by the anodic attack, into the electrolyte immediately interacts with chromate ion and forms a film on the metal surface.

The exact reason for the behaviour of vanadate ion is not yet known because the vanadate in aqueous solution of acid undergoes a series of hydrolysis polymerisation reactions. The reactions are complex and difficult to formulate correctly[15–18]

In the case of tungstate ion a porous and semi-adhesive film is formed which is seen by naked eyes. The thickness of the film increases with concentration of

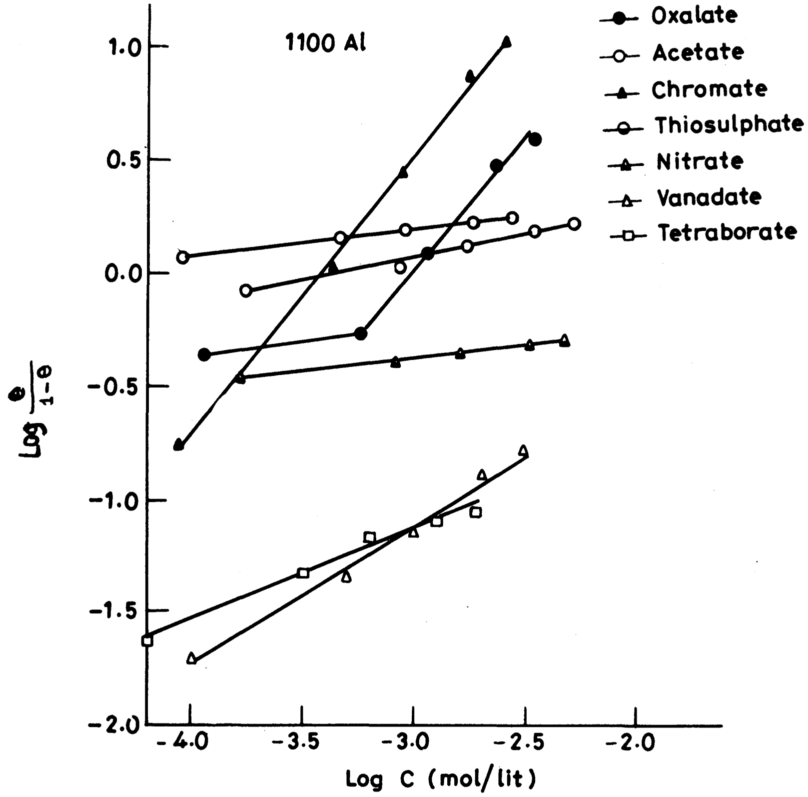

Fig. 1 Langmuir absorption plots for 1100 aluminium in the presence of anions at 35°C.

the ions and, therefore, a decrease in the corrosion rate with the concentration has been observed. The exact composition of the porous film is not known since on acidification tungstate forms polytungstate[19–23]. Aggressiveness of the tungstate ion is probably due to its depolarising effect on the cathodic reaction. This fact was indeed further confirmed by the electrode potential measurements and cathodic polarisation studies.

In order to assess the adsorbability of the anions inhibiting the dissolution of aluminium, the percentage protectivities afforded by the anions at their different concentrations were kept in the Langmuir adsorption isotherm equation. The plot of log $\frac{\theta}{1-\theta}$ vs. log C for inhibiting anions has been shown in Figure 1. It is clear from figure that oxalate, chromate, acetate, thiosulphate, nitrate, tetraborate and vanadate satisfy the adsorption equation. In all the cases straight lines have been

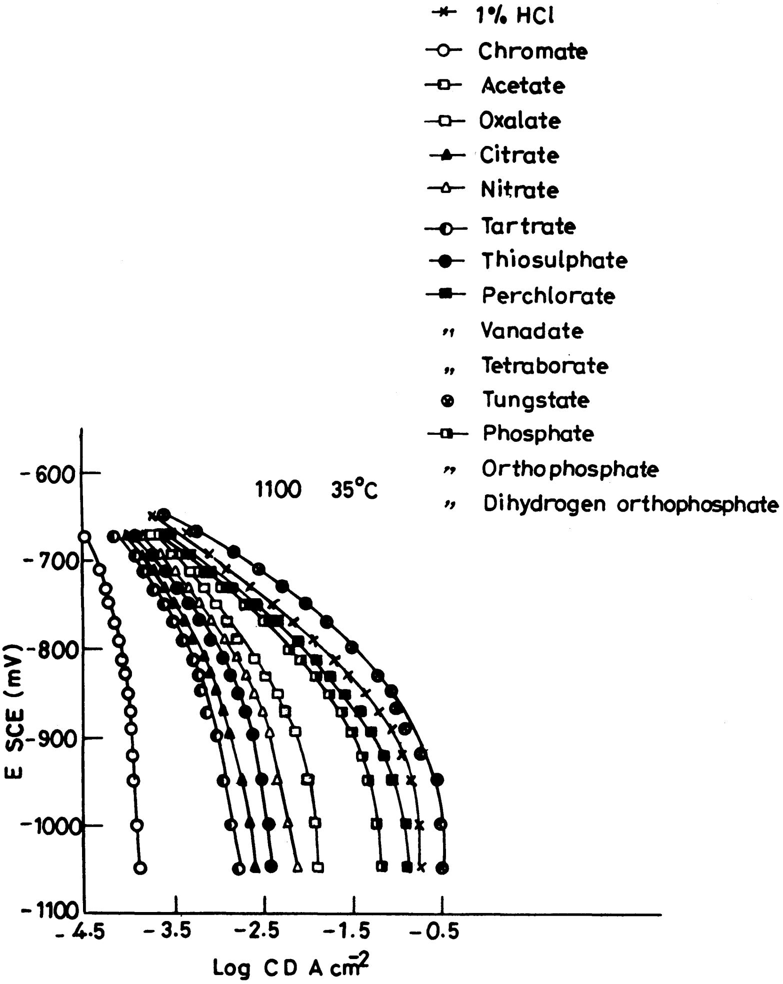

Fig. 2 Cathodic polarisation of 1100 aluminium in presence of anions at 35°C

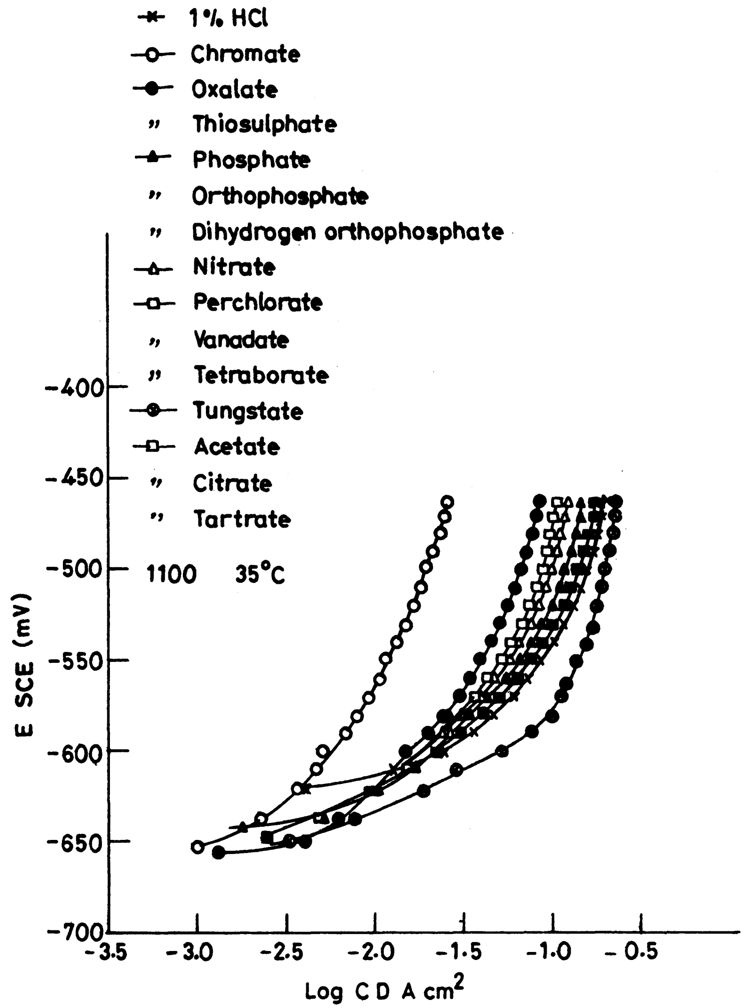

Fig. 3 Anodic polarisation of 1100 aluminium in the presence of anions at 35°C

observed which are in conformity with the equation. This indicates that these anions inhibit the rate of corrosion by getting adsorbed on the reaction sites of the metal surface and thus reducing the area for dissolution. In no case, however, the slopes of the lines are equal to unity[13] (Table 1) as is expected from the Langmuir adsorption isotherm equation. The other anions showing an inhibitive effect for 1100 aluminium dissolution do not satisfy the isotherm equation. The inhibiting tendency due to nitrate ion may also be attributed to their oxidising property and thus assisting in healing the film during the dissolution of the metal.

The polarisation studies have been carried out at the concentration for which corrosion rate is minimum and the cathodic polarisation plot in the presence of ions has been shown in figure 2. It is found that the curve in the presence of 300 ppm of the tungstate is less polarised than the curve in their absence. This confirms the view that the acceleration in the rate of corrosion in the presence of this ion is due to the lowering of the hydrogen over voltage. A little polarisation effect due to perchlorate, tetraborate and vanadate ions has been observed. Acetate, citrate, tartrate, thiosulphate, nitrate and oxalate polarise the cathodic electrode; however, chromate polarises the cathodic reactions to a greater extent indicating its predominant action on the cathodic sites of the internal corrosion cell.

Figure 3 shows that the anodic polarisation curves in the presence of all the anions except chromate and nitrate are little polarised whereas nitrate, a passivating agent polarises the electrode to a greater extent but the polarisation due to this ion is less than the chromate ion. Our observations are in contrast to the findings of Conor *et al.*,[24] who have suggested that phosphate is more strongly adsorbed on aluminium oxide than the chromate. In this study, it is found that the greatest decrease in the current density towards lower region is due to chromate ion which suggests that adsorption of this ion on the metal electrode is maximum.

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