EFFECT OF MOLYBDATE ION ON THE CORROSION BEHAVIOUR OF ALUMINIUM IN NaOH SOLUTIONS

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The corrosion rate and potential of aluminium were measured in 0.01-0.2 M NaOH solution containing 10^{-3} - I M Na_2MoO_4 at 30°C. It was found that above 0.05 M Na_2MoO_4 , the corrosion rate and potential increase with molybdate concentration. Anodic polarisation curves measured in alkali solutions containing (0.001-1 M) Na_2MoO_4 revealed that MoO_4^{-2} ions participate only in the electrolytic transport of current, but they are not involved in the anodic reaction. Cathodic polarisation curves were also measured in the different solutions. The results confirmed the acceleration of the cathodic reaction. This is attributed to the adsorption of Na^+ ions on the metal surface.

It has been suggested by Brasher [1] that all anions are corrosive when present in large dilutions and become inhibitive at high concentrations. In testing this theory, the corrosion characteristics of aluminium in NaOH solution containing sodium phosphate and sodium chromate were previously studied [2,3].

In the this investigation we studied the corrosion behaviour of aluminium in alkaline molybdate solutions.

EXPERIMENTAL

Polarisation measurements on the aluminium electrode were carried out in a cell constructed from the arsenic-free hard boro-silicate glass (Hysil), which permitted the vigorous purification of the solutions under investigation through pre-electrolysis [4]. For this purpose a platnium electrode (2 cm^2) was used.

The electrodes of 1 cm^2 area, were prepared from extra pure aluminium rods 3 mm in diameter (Shering Kahlbaun Company). Each run was carried out with a new electrode. All solutions were prepared from A.R materials. Before each run, the cell was cleaned with a mixture of nitric and sulphuric acids (A.R) and throughly washed with conductance water; the potential of the aluminium electrode was followed as a function of time over a period of 3 h. In all solutions studied the potential became constant within ca 2 h.

Determination of the corrosion rate was carried out using the weight-loss technique using aluminium pieces measuring 5 x 10 cm^2 and 0.8 mm thick, cut out from AnalaR Aluminium sheet. The test pieces were first degreased with acetone, washed with conductivity water, dried in alchol and ether, weighed; the specimen was suspended in the test solution in a wide 200 ml jar. After 2 hrs, the specimen was removed, rinsed with conductivity water, dried and weighed. All corrosion tests were carried out in aerated, unstirred solutions. Results were duplicated and the mean was computed.

All measurements were carried out at 30° C in an air thermostat controlled to ± 0.5°C.

RESULTS AND DISCUSSION

Corrosion Potential and Corrosion Rate

The potential of the Aluminium electrode was measured in 0.01 - 0.2 M NaOH solutions, containing 0.001-1 M Na_2MoO_4. The steady state potentials obtained were plotted vs the logarithm of the molar molybdate concentration for the different NaOH solutions (Fig. 1).

The first part, designated by (a), represents a region of almost constant potential. The second part (b), shows considerable increase of potential with molybdate concentration.

The corrosion rate, V_{corr} (mg/hour) has also been determined in the different solutions, and the results are shown in Fig. 2. These are similar in nature to Fig. 1

Part a covers the concentration range 0.01-0.2 M MoO_4^{-2}. At such concentrations, molybdate

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ions hardly affect the corrosion rates. However, in very dilute alkali solutions (0.01-0.02 M NaOH) addition of small amounts of molybdate leads to the decrease of the corrosion rate down to a minimum value at 0.005 M MoO_4^{-2}

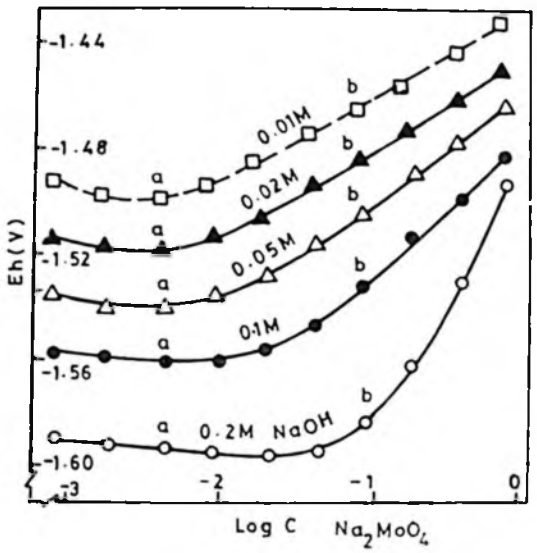


Fig. 1 Effect of concentration of Na_2MoO_4 dissolved in different concentrations of NaOH , on the potential of aluminium.

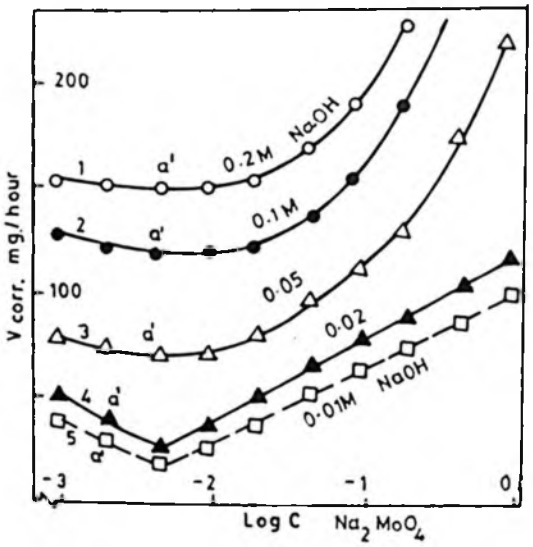


Fig. 2 Effect of molybdate concentration on the corrosion rate of aluminium in different concentrations of NaOH solutions

Part b covers the concentrations range 0.02-1 M MoO_4^{-2} . In this range, increase of molybdate concentration brings about marked increase in the corrosion rate in all NaOH solution studied. It is to be observed that hydrogen was observed to evolve, while there was no indication for the reduction of molybdate ion.

Bracher's equation requires that, the potential of the corroding metal decreases linearly with the logarithm of the corrosion activating anion concentration. In the present investigation, increase of the corrosion rate is accompained with increase of the corrosion potential. This shows that the addition of Na_2MoO_4 accelerates the cathodic reaction. Similar behaviour was observed in case of Na_2Po_4 [2].

Galvanostatic Corrosion Current

Suppose one aluminium electrode is immersed in the pure alkali solution (reference electrode) and the other immersed in the same alkali solution containing sodium molybdate (test electrode). The difference in corrosion potential brought about by the molybdate leads to the passage of the so called galvanostatic corrosion current. This current as well as the potential during the passage of current were followed as a function of time, and the steady state values are plotted versus log C of MoO_4 for the different NaOH solutions. A typical graph is given in Fig 3.

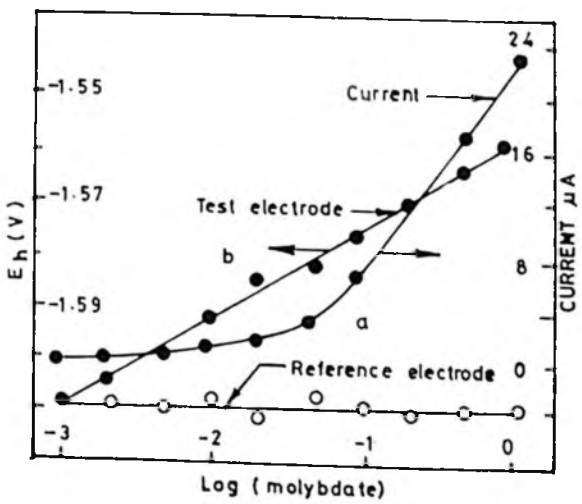


Fig.3a Corrosion current of aluminium in 0.2 M NaOH at different concentrations of molybdate

3b Potential of aluminium (polarised) in 0.2 M NaOH at different concentrations of molybdate

It is found that the potential of the reference electrode remains practically constant but that of the test electrode increases linearly with log [MoO_4^{-2}], in agreement with the behaviour observed from the measurements of corrosion potential under open-circuit conditions. As a result of increase of the potential with molybdate, galvanostatic corrosion current flows from the reference electrode (at which anodic reaction occurs) to the test electrode (at which a cathodic reaction proceeds). We have, therefore, assigned negative signs to the values of galvanostatic corrosion currents. As evident from Fig.3, minute corrosion currents are observed at low molybdate concentrations. The galvanostatic current begins to increase significantly with increase of MoO_4^{-2} concentration after a critical value; this is dependent on the alkali concentration. The results of these experiments show again that the presence of Na_2MoO_4 accelerates the cathodic reaction.

Anodic Polarisation

In order to throw light on the anomalous corrosion behaviour in the molybdate solution, anodic polarisation measurements were carried out in 0.2, 0.1, 0.05 and 0.01 M NaOH solution containing different Na_2MoO_4 concentrations. Polarisation was conducted within the current density range 10^{-6} - 10^{-8} A/cm^2. A typical result is given in Fig 4.

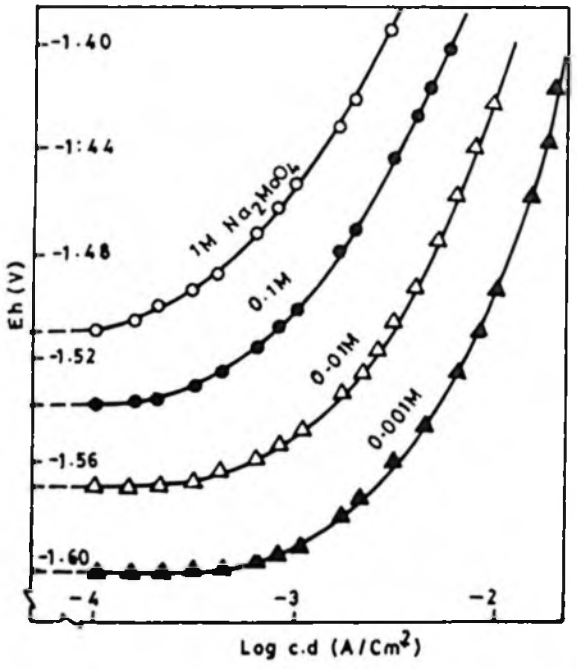


Fig.4 Anodic polarisation curves for aluminium in different concentrations of Na_2MoO_4, dissolved in 0.1 M NaOH

Generally the polarisation curves exhibit a region of stationary potential which extends to a certain current density dependent on the molybdate concentration. The electrode is subjected to low overpotential and then at higher current densities the potential rises rapidly. The rapid increase is likely to be due to lack of supply of OH^- to the anode leading to incomplete dissolution of metal oxide as aluminate AlO_2^-. The metal oxide accumulates on the metal surface, with the result that the metal is passivated.

The important phenomenon exhibited by polarisation measurements is that passivation occurs at a decreasing current density as the concentration of molybdate is increased. Such a behaviour may reveal that MoO_4^{-2} ions participate only in the electrolytic transport of the current, but they are not involved in the anodic reaction. Passivation current decreases with molybdate concentration owing to the decrease of the supply of OH^- ions to the anode. This is because the fraction of the current carried by OH^- ions (viz. their transport number) decreases as more molybdate ions are added. According to this argument, the passivation current at a given molybdate concentration should increase as the alkali concentration is increased. This is found to be true as evident from Fig.5, which shows the passivation currents in 0.5, 0.2, 0.1, 0.05 & 0.01 M NaOH in presence of I M molybdate. Moreover, some experiments were carried in stirred solutions, whereby the passivation currents increase markedly.

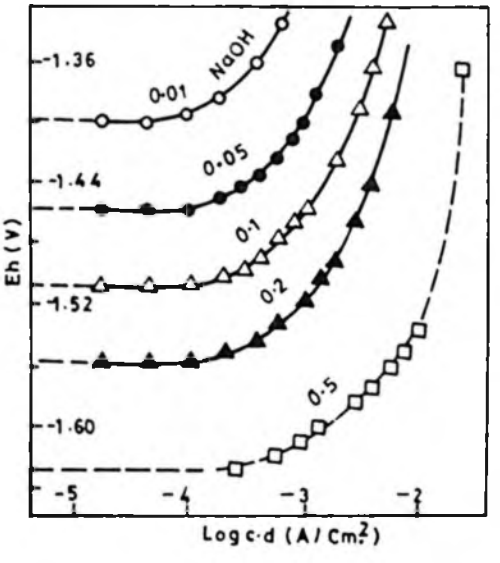


Fig. 5 Anodic polarisation curves for aluminimum in 1 M Na_2MoO_4 containing different concentrations of NaOH

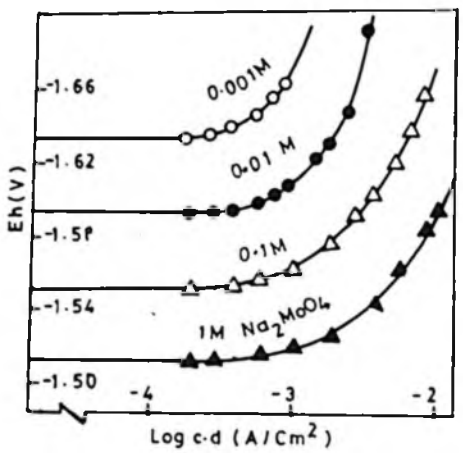


Fig. 6 Cathodic polarisation curves for aluminium in different concentration of Na_2MoO_4, dissolved in 0.2 M NaOH

Cathodic Polarisation

Cathodic polarisation measurements were carried out in 0.01-0.2 M NaOH at different concentrations of $Na_2MoO_4^{-2}$ Hydrogen was always observed to evolve at the cathode. Fig.6 shows the results in case of 0.2 M NaOH. It is clear that the polarisation curve is markedly shifted to less negative potentials as the salt concentration is increased. This confirms the activation of the cathodic reaction.

The activation of the cathodic reaction, and consequently the promotion of corrosion rate on adding the salt might be attributed to the adsorption of Na^+ ion on the electrode surface [5].

This is because the adsorption of a Na^+ ion leads to the increase of the negative charge density on the area around the ion, and consequently, an active cathodic area is formed.

Behaviour in Low Alkali Concentration

At low alkali concentration (0.01 M), addition of very small amounts of Na_2MoO_4 leads to the decrease of the corrosion rate to a certain minimum (Fig. 2).

This is of course important from the economic point of view. More interesting however, is the theoretical meaning of the phenomenon. From the observation that the corrosion potential is also decreased on adding the molybdate salt (Fig. 1), it is concluded that the cathodic reaction is retarded. This most probably indicated that the activity of the reacting entities, viz, the water molecules in the double layer, decrease as the activity of the Na^+ ions in solution is increased. It seems that Na^+ ions are preferentially attracted to the double layer while the originally oriented water molecules are displaced. On further increase of sodium molybdate concentration Na^+ ions become absorbed and usual increase of V_{corr} with Na_2MoO_4 concentration is observed.

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