

THE CORROSION BEHAVIOUR OF ALUMINIUM IN SODIUM HYDROXIDE SOLUTIONS CONTAINING TUNGSTATE IONS.

by

Kh.M.Kamel, A.Kassab and E.Abdel Hamid.
Chemistry department, University college
for girls, Heliopolis, Cairo (Egypt).

INTRODUCTION

Brasher⁽¹⁾ suggested that some anions are corrosive when present in large dilutions and become inhibitive at high concentrations. In testing this theory the corrosion behaviour of aluminium in sodium hydroxide solutions containing sodium phosphate and sodium chromate were previously studied.^(2,3)

In this work we studied the corrosion behaviour of Aluminium in alkaline tungstate solutions.

EXPERIMENTAL

The polarisation measurements on the aluminium electrode were carried out in a cell described in an earlier publication⁽⁴⁾ This cell is constructed from the arsenic-free hard borosilicate glass, Hysil, and thus it permits the vigorous purification of the solutions under investigation through pre-electrolysis.

For this purpose we used a platinum electrode (2 cm² platinum sheet welded to a platinum wire sealed to glass).

The electrode were prepared from extra-pure aluminium rods 3 mm in diameter (Shering Kahlbaum company).

The electrode area was 1 cm^2 . 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 thoroughly washed with a conductance water.

Determination of the corrosion rate was carried out using the weight-loss technique. Experiments were performed on pieces of aluminium measuring $5 \times 10 \text{ mm}$ and 0.8 mm thick, cut from analar aluminium sheet.

The test pieces were first degreased with acetone, washed with conductivity water, dried in alcohol and ether, and then weighed.

Corrosion tests were carried out in a wide 200 ml Jar, in which the specimen was suspended for 2 hours in the test solution. The specimen was then removed, rinsed with conductivity water and finally dried and weighed.

All corrosion tests were carried out in aerated, unstirred solutions. Results were duplicated and the mean was computed.

For measuring the corrosion potential, the potential of the aluminium electrode was followed as a function of time over a period of 3 hours. In all solutions studied the potential became constant within ≈ 2 hours. All measurements were carried out at 30°C in an air thermostat controlled to $\pm 0.5^\circ \text{C}$.

RESULTS AND DISCUSSION

-Corrosion potential and corrosion rate:

The potential of aluminium electrode was measured in 0.01-0.2 M NaOH solutions containing 0.001-1 M Na_2WO_4 . The steady state potentials obtained after 4 hours immersion were plotted against the logarithm of the molar tungstate concentration for the different NaOH solutions.

As evident from Fig(1): the first part designated by (a) represents a region of almost constant potential. The range of tungstate concentration within which the potential remains constant increases with the alkali concentration. The second part designated by (b) shows considerable increase of potential with tungstate concentration.

The corrosion rate, V_{corr} mg/hour, has also been determined in the different solutions. An example of the results is shown in Fig(2). In this figure the corrosion rates in the corresponding free sodium hydroxide solutions are represented by dotted lines, these are taken as reference values to those obtained in presence of the different tungstate concentration. The plots can be roughly divided into two parts a, b which correspond respectively to the parts a and b of the potential log C relationships.

Part a covers the concentration range 0.001-0.05 M Na_2WO_4 . At such concentrations tungstate ions hardly affect the corrosion rates. However, in very dilute alkali solutions (0.01-0.02 M NaOH) addition of small amounts of tungstate leads to the decrease of the corrosion rate down to a minimum value at 0.005 M WO_4^{2-} .

Part b covers the concentration range 0.02 - 1 M Tungstate. In this range, increase of tungstate concentration bring about marked increase in the corrosion rate in all NaOH solutions studied. It is to be observed that hydrogen evolved, while there was no indication for the reduction of tungstate ion.

The above results are interesting so far as Bracher's equation is concerned. This equation requires that, for a corrosion activating anion the potential of the corroding metal decreases linearly with the logarithm of the anion concentration. In the present investigation, increase of the corrosion rate is accompanied with increase of the corrosion potential. This shows that the addition of Na_2WO_4 accelerates the cathodic reaction. Similar behaviour was observed in case of $\text{Na}_3\text{PO}_4^{(2)}$

Galvanostatic corrosion current:

In this technique we measured the current passing in a cell composed of two aluminium electrodes, one immersed in the pure alkali solution and referred to "Reference electrode", and the other immersed in the same alkali solution containing sodium tungstate "Test electrode". The difference in corrosion potential brought about by the tungstate leads to the passage of the so called galvanostatic corrosion current. The galvanostatic corrosion currents as well as the potentials during the passage of those currents were followed as a function of time, and the steady state values are plotted versus $\log C$ of WO_4^{2-}

for the different NaOH solutions. As example, Figs 3a and 3b show the results obtained in case of 0.2 M NaOH.

It is obvious that the potential of the reference electrode remains practically constant. For the test electrode, on the other hand, the potential increases linearly with $\log C$ of Na_2WO_4 , 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 tungstate, galvanostatic corrosion current flows from the reference electrode (negative pole), which undergoes anodic reaction, to the test electrode at which a cathodic reaction proceeds. We have, therefore, assigned negative signs to the value of galvanostatic corrosion currents.

As evident from Fig 3a minute corrosion currents are observed at low tungstate concentrations. Then at a certain tungstate concentration dependent on the alkali concentration, the galvanostatic current begins to increase significantly with further increase of WO_4^{2-} concentration. The results of these experiments show again that the presence of sodium tungstate accelerates the cathodic reaction.

-Anodic polarisation:

In order to throw light on the anomalous corrosion behaviour in the tungstate solutions, anodic polarisation measurements were carried out in 0.2, 0.1 and 0.05 NaOH

solutions, containing different Na_2WO_4 concentrations. An example of the results is given in (Fig 4). Polarisation was conducted within the current density range $10^{-6} - 10^{-2}$ A/cm².

Generally, the polarisation curves exhibit a region of stationary potential which extends up to a certain current density dependent on the tungstate concentration. The electrode is subjected to low overpotential and then at higher current densities the potential rises rapidly. The rapid increase is likely due to the lack of supply of OH^- ions at the anode leading to incomplete dissolution of metal oxide as Aluminium 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 tungstate is increased. Such a behaviour may reveal that WO_4^{2-} ions participate only in the electrolytic transport of the current, but they are not evolved in the anodic reaction. Passivation current decreases with tungstate 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 tungstate ions are added. According to this argument, the passivation current, at a given tungstate concentration, should increase as the alkali concentration increased.

This is actually true as evident from (Fig 5) which shows

the passivation currents in 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 M NaOH solutions in presence of 1 M tungstate. Moreover, some experiments were carried out in stirred solutions, whereby the passivation currents increased markedly.

-Cathodic Polarisation:

Cathodic polarisation measurements were carried out in 0.05 - 0.2 M NaOH solutions at different concentrations of Na_2WO_4 . 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 activations 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 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 concentrations (0.1 M), addition of very small amounts of Na_2WO_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 tungstate salt (Fig I), it is concluded that the cathodic reaction is retarded. This most probably indicated that the activity of 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 tungstate concentration Na^+ ions became adsorbed, and the usual increase of V_{corr} with Na_2WO_4 concentration is observed.

SUMMARY

The corrosion rate and potential of aluminium were measured in 0.01-0.2 M NaOH solutions containing 10^{-3} - 1 M Na_2WO_4 at 30° c. It was found that above 0.05 M Na_2WO_4 , the corrosion rate and potential increase with tungstate concentration. The galvanostatic corrosion current increased also with the salt concentration. The results of these measurements indicated the activation of the cathodic reactions.

Anodic polarisation curves were measured in alkali solutions containing (0.001 - 1 M) Na_2WO_4 . The results revealed that WO_4^{2-} ions participate only in the electrolytic transport of current but they are not involved in the anodic reaction. The results confirmed the acceleration of the cathodic reaction. This is attributed to the adsorption of Na^+ ions on the metal surface.

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EFFECT OF CONCENTRATION OF Na_2WO_4 DISSOLVED IN DIFFERENT CONCENTRATIONS OF NaOH , ON THE POTENTIAL OF ALUMINIUM.

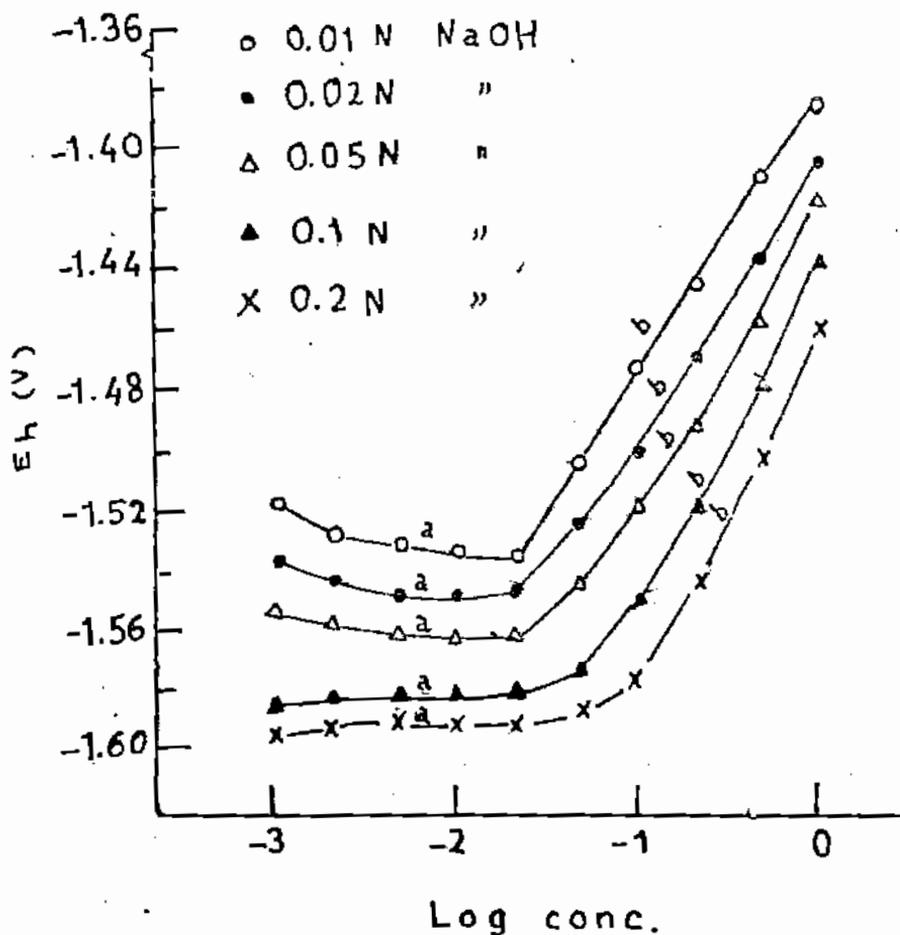
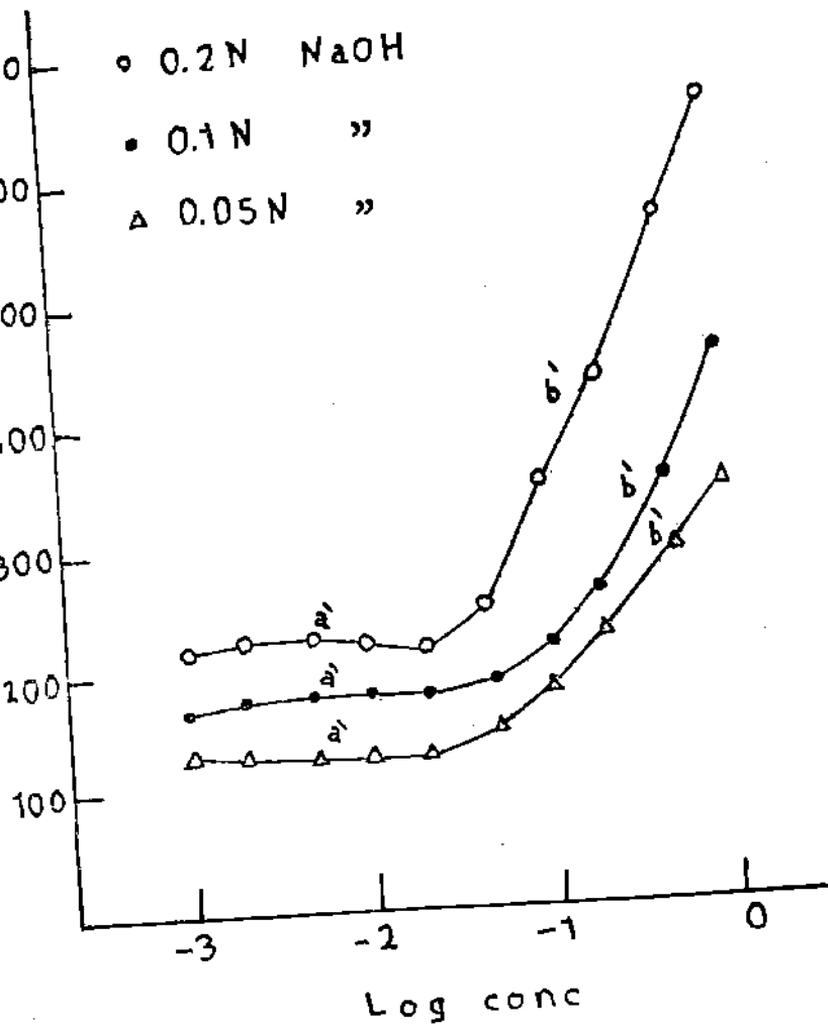
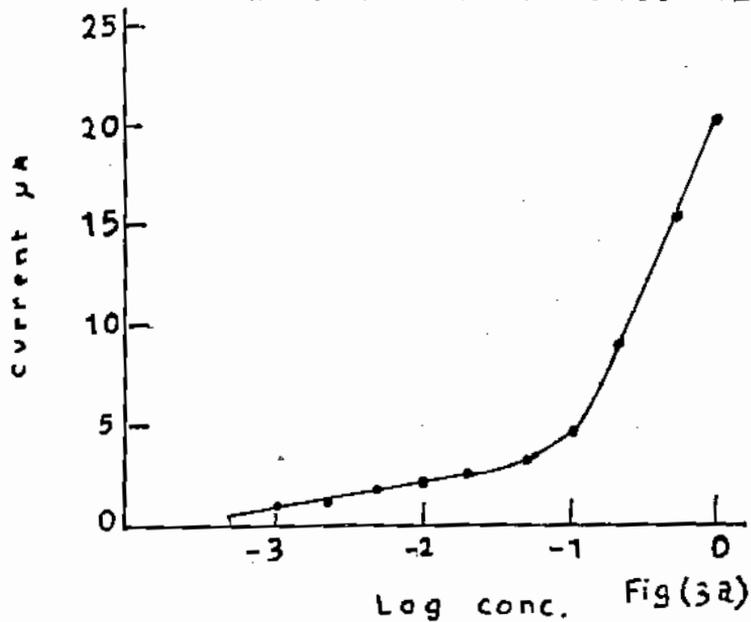


Fig (1)

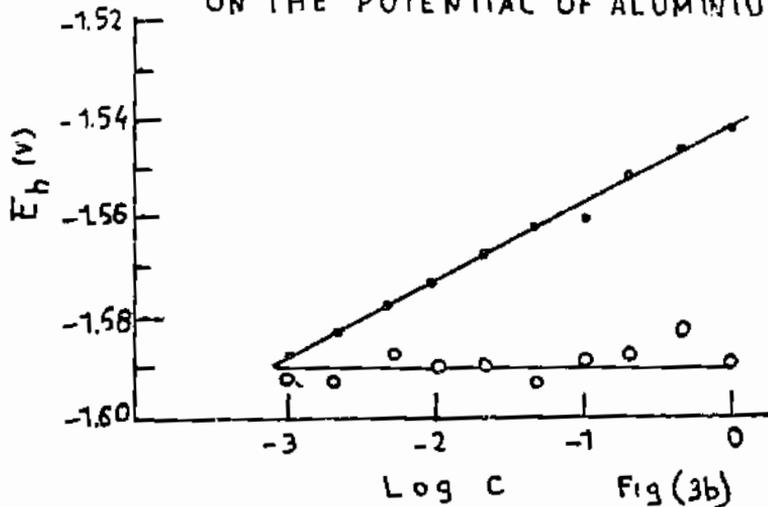
EFFECT OF TUNGSTATE CONCENTRATION ON THE CORROSION RATE OF ALUMINIUM IN 0.2M, 0.1M AND 0.05N NaOH.



CORROSION CURRENT OF ALUMINIUM
IN 0.2N NaOH AT DIFFERENT
CONCENTRATION OF TUNGSTATE



EFFECT OF CONCENTRATION OF
TUNGSTATE DISSOLVED IN 0.2N NaOH
ON THE POTENTIAL OF ALUMINIUM



ANODIC POLARISATION CURVES FOR ALUMINIUM IN DIFFERENT CONCENTRATIONS OF Na_2WO_4 , DISSOLVED IN 0.1N NaOH .

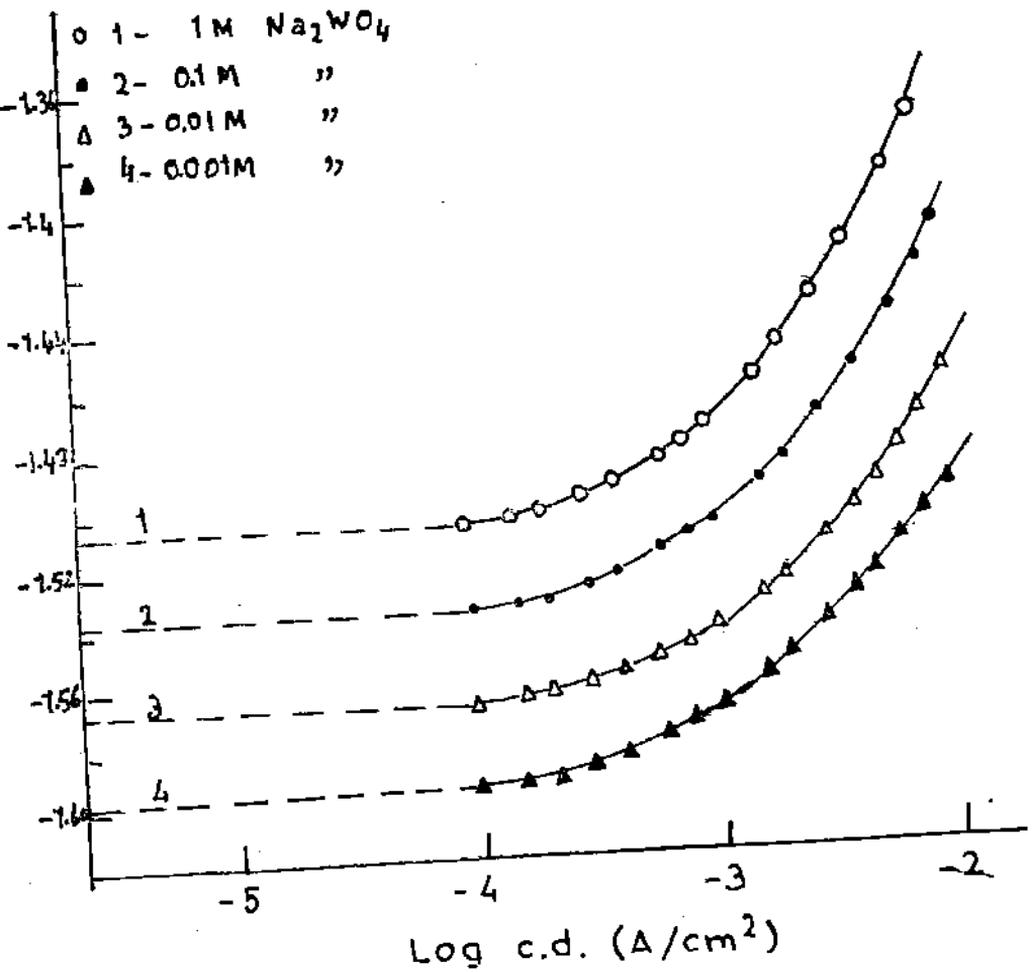


Fig (4)

ANODIC POLARISATION CURVES FOR ALUMINIUM IN DIFFERENT CONCENTRATIONS OF NaOH, DISSOLVED IN 1M TUNGSTATE.

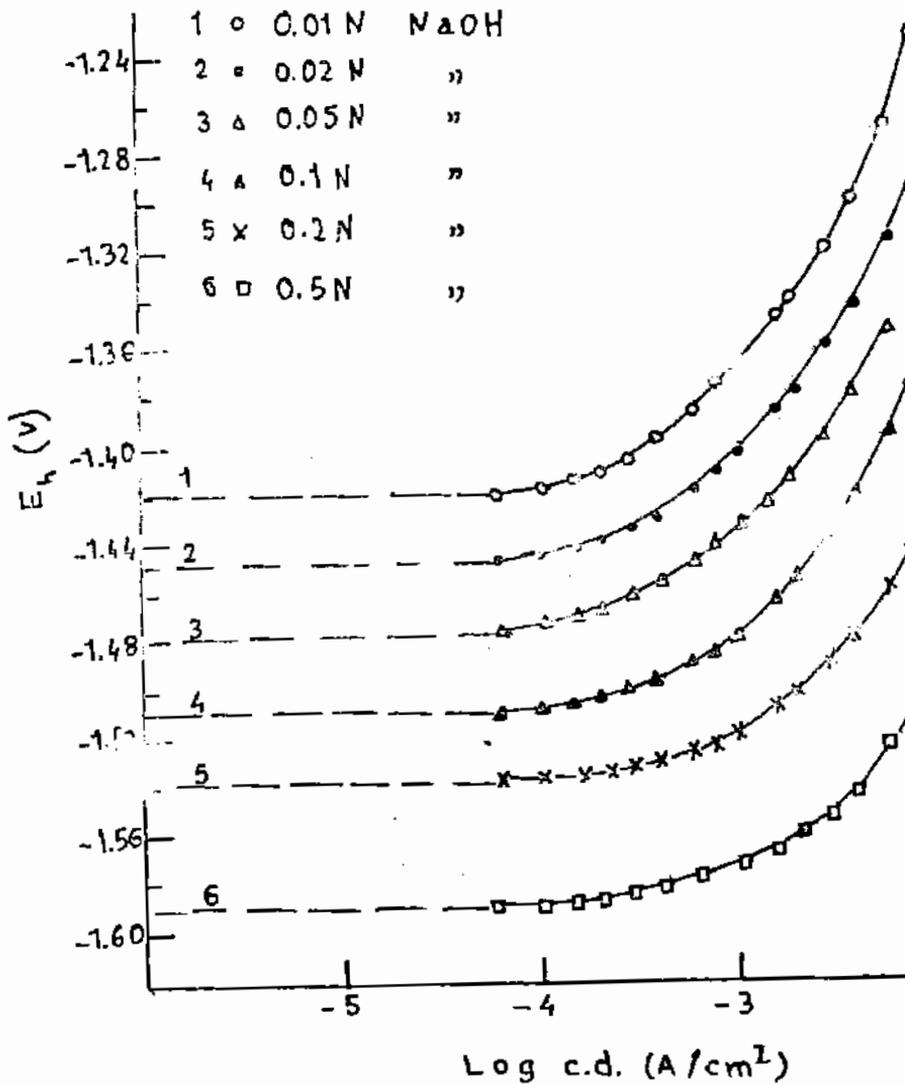


Fig (5)

CATHODIC POLARISATION CURVES FOR ALUMINIUM IN DIFFERENT CONCENTRATIONS OF Na_2WO_4 , DISSOLVED IN 0.2 N NaOH.

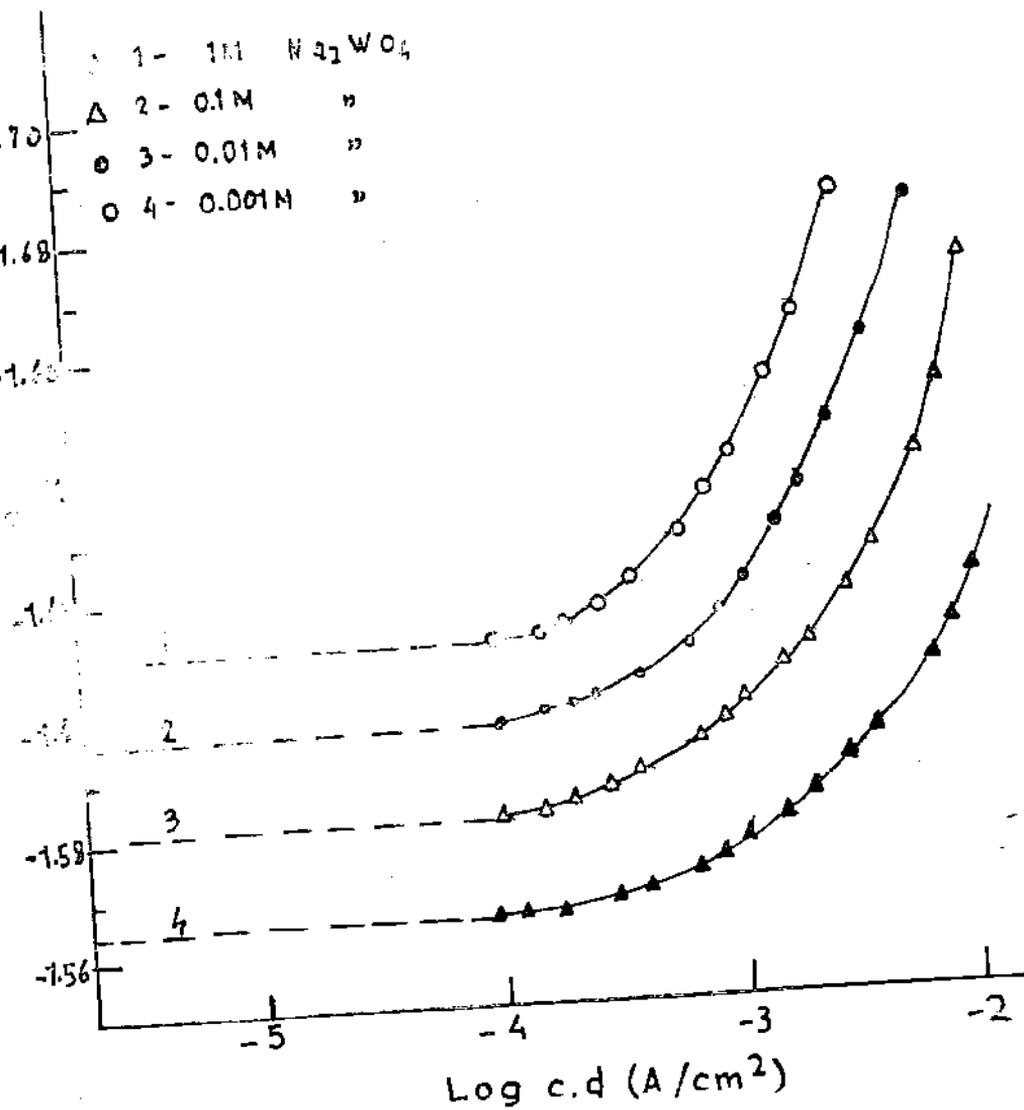


Fig (6)