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Anodic Dissolution of lead in Acid Solution

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Galvanostatic polarisation measurements were carried out in order to elucidate the anodic dissolution of lead in solutions of HCl, H_2SO_4 and HNO_3. The polarisation curves exhibited similar shapes and characteristics indicating that the nature of the anion has a great influence on the anodic reaction. It was therefore concluded that the anion is directly involved in the anodic dissolution which proceeds in two steps: the first is the formation of a charged complex and the second is the dissociation of the complex and the regeneration of the anion. This is for the acids which did not form insoluble salts. Also, the anodic polarisation of lead was measured in acid-salt mixtures in which the anion concentration was kept constant (1 molar). The polarisation curves more or less coincide with each other.

INTRODUCTION

The behaviour of lead in acid solutions depends on the solubility of the corrosion products formed. It is noted that the stimulating effect of a certain anion on the anodic dissolution reactions is manifested only when a certain critical potential has been reached. At this potential, the strength of covalent bond between the surface atoms of the metal and the adsorbed ions equals the covalent bond strength in the corresponding individual compound. Evidently, the different anions must have different values of the critical potentials. Consequently, it could be expected that if at a given potential several components of the solution are adsorbed, then all the surface complexes can not pass into solution, but only those with the required chemical bond strength. This probably explains the passivating effect of iodide and chloride ions on the spontaneous dissolution of iron in sulphuric acid.[1, 2]

The knowledge of the minimum concentration of a certain passsivator that can withstand the corroding action of a particular agressive anion is of importance from the theoretical as well as the practical points of view, in continuation of the work carried out in this laboratory[4]. The present study was undertaken to investigate the dissolution of lead in different acid solutions and the effect of adding their salts.

EXPERIMENTAL

The electrodes were prepared from AnalaR lead rods 4 mm in diameter (Johnson and matthey). Before experiment, the electrode was abraded with 00 grade emery paper, degreased with acetone, washed thoroughly with water and then rinsed

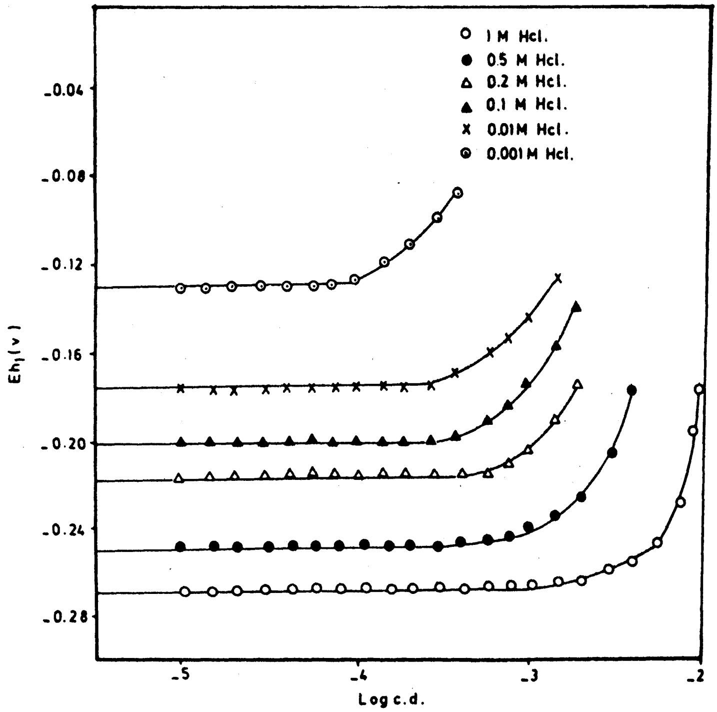

Fig. 1. Anodic polarisation curves for lead in different concentrations of HCl.

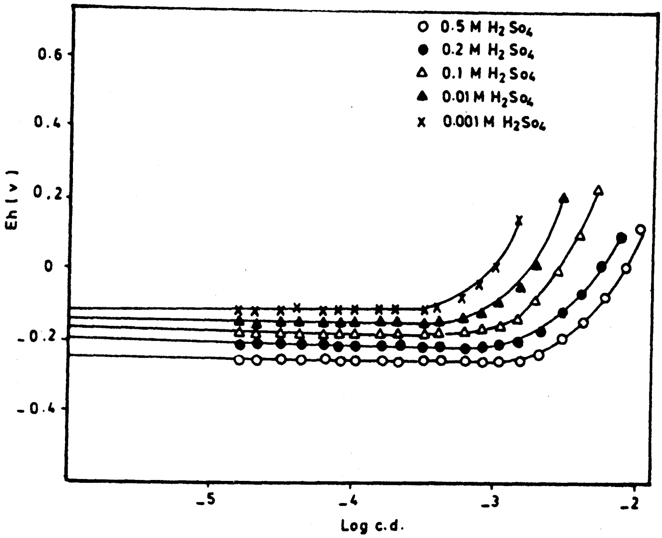

Fig. 2. Anodic polarisation of lead in different of concentrations of H_2SO_4.

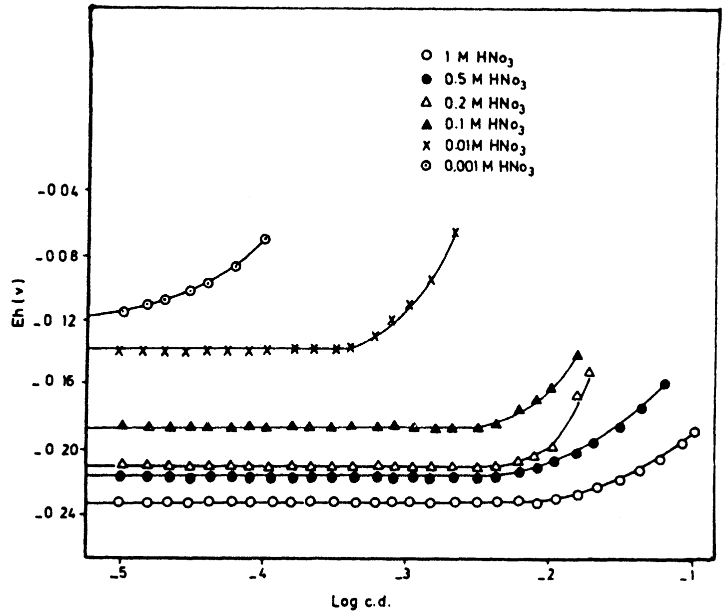

Fig. 3. Anodic polarisation curves for lead in different concentration of HNO3.

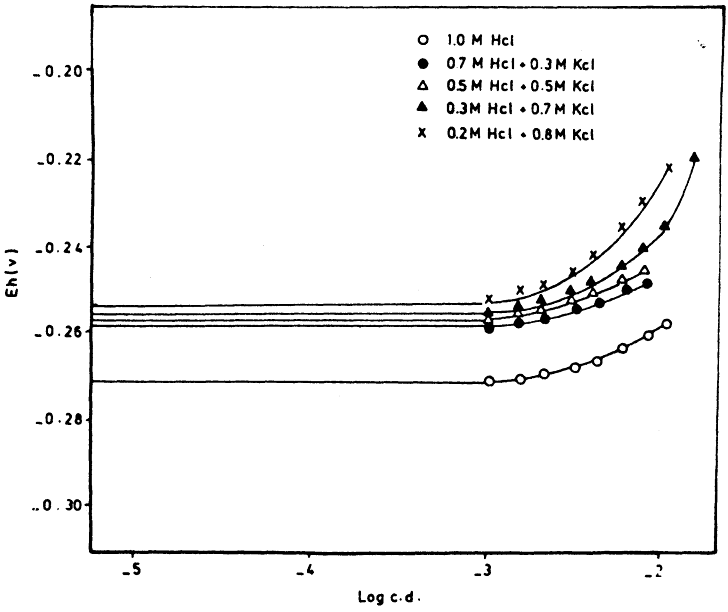

Fig. 4. Anodic polarisation curves for lead in different concentration of HCl + KCl.

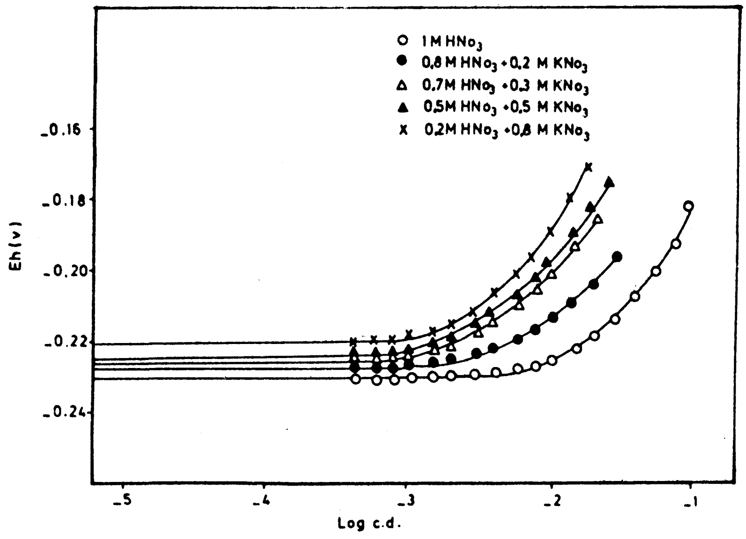

Fig. 5. Anodic polarisation curves for lead in different concentration of HNO3 + KNO3.

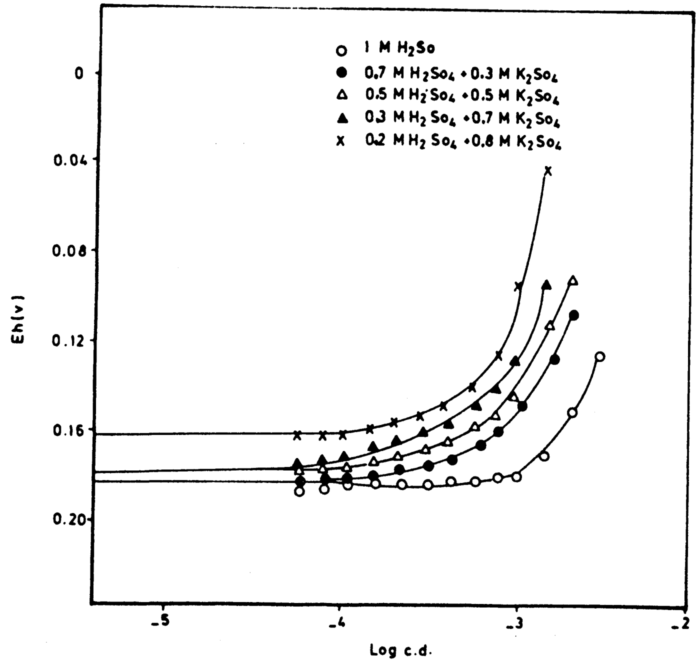

Fig. 6. Anodic polarisation curves for lead in different concentration of H2SO4 + K2SO4.

with test solution. Each experiment was carried out with a newly polished electrode and with a fresh portion of the solution.

The electrolytic cell used for anodic polarisation measurements was constructed of an arsenic-free glass, technically known as *Hysil.* The cell was composed of three compartments connected together by means of water-sealed taps, ungreased taps were always used[5, 6]. The impurities which are likely to occur in the aqueous solution used are removed by pre-electrolysis; before each run, the cell was cleaned with a mixture of nitric and sulphuric acids (A.R.) and thoroughly washed with conductivity water. All the experimental measurements were carried out in an air thermostat, the temperature of which was kept constant within ± 0.5°.

RESULTS AND DISCUSSION

The lead electrode was anodically polarised at 30°C in solutions of different acids HCl, HNO_3 and H_2SO_4 within wide range of current density. The polarisation curves obtained are shown in Figs. 1–3. As a general feature, the polarisation curves exhibit a region of stationary potential in which the potential remains constant and independent of the current density. The stationary potential remains up to a certain limiting current density, which depends on the nature and concentration of the acid, and then rapidly increases. One may think of passivation, due to complete surface coverage of the metal with an insoluble salt, as a reason for the limiting current density. However the dependence of the limiting current on the acid concentration ruled out this explanation.

The phenomenon of limiting currents can be understood in the light of the well accepted idea that the metal dissolves under the catalytic effect of the anion. The metal dissolves almost reversibly at constant potential (observed experimentally) and goes into solution perhaps in the form of positively charged complex, *e.g.*, $(PbNO_3)^+$ which dissociates giving Pb^{++} and the anion is regenerated. In order to interpret this behaviour, we must take into consideration that dissociation of the lead complex ion proceeds at a rate which depends on the characteristics of the anion. It is assumed that the rate of dissociation of the lead complex is appreciably small, with the result that at high currents, the rate of anodic formation of these ions exceeds the rate of their dissociation. It follows that the concentration of the acid anions decreases near the electrode surface provided that they diffuse slowly from the bulk of solution. Consequently, the activity of adsorbed anions decreases, and the potential has to rise in order to activate the adsorption process.

Effect of acidity

The explanation given above for the onset of a limiting current is based on the slow diffusion of the anions to the anode. This explanation is confirmed by carrying out series of measurements in acid-salt mixtures in which the anion concentration was kept constant (1 M), while the H^+ ion concentration was changed from 0.001 M–1 M. The results are depicted in Figs. 4–6. It is obvious that the polarisation curves more or less coincide with each other, indicating that the limiting current is determined by the anion concentration.

In Figs. 1–3, it is observed that the dissolution potential decreases with the increase of acid concentration. This behaviour is expected on the assumption that the metal dissolves under the catalytic effect of the anion.

From a previous study[4], on anodic polarisation of lead in chromic acid solutions, it was shown that the dissolution potential values are compared with those in HCl, HNO_3 and H_2SO_4 solutions. Moreover, the change of dissolution potential in chromic acid, with acid concentration, followed an opposite trend. Passivation of lead in chromic acid was attributed to the formation of a surface oxide film.

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