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CORROSION BEHAVIOUR OF LEAD IN SOLUTIONS OF MIXED ANIONS

By

A.A. Misbah, Z.A. El-Hady and O.R. Khalifa
Chemistry Department, University College for Women,
Ain Shams University, Heliopolis, Cairo. Egypt.

ABSTRACT

In this work we studied the corrosion behaviour of lead in neutral solutions containing $Cr_2O_7^{--}$ as a passivating anion, and Cl^-, Br^- or NO_3^- as corrosive anions. The results indicated that the passivating anion does not simply counteract the promoting action of the corrosive anion. The corrosion rate of lead increases on adding small amounts of $K_2Cr_2O_7$, up to 0.002 M, to the halide solutions. At higher concentration the inhibiting action of the dicrhomate predomenates. The same behaviour was observed in nitrate solutions.

INTRODUCTION

From studies on the corrosion of iron and steel,. Brasher, D.M. (1962) advanced a theory in which the rigid classification of anions into corrosion promoeters and inhibitors is disclained. According to this theory, all anions when present in large dilution are corrosive but act as inhibitors in relatively concentrated solutions. When an anion behaves as corrosion promoter, the potential of the corroding metal decreases linearly with the logarithm of the anion concentration. At a certain salt concentration depending on the nature of the anion, the potential changes to more positive values inhibiting corrosion process.

In order to test Brasher's theory, extensive studies on the corrosion behaviour of lead, Awad, S.A. and Elhady, Z.A. (1969), tin, Awad, S.A. and Kassab A., (1969), zinc, Awad, S.A. and Kamel, Kh.M. (1970), and aluminium, Awad, S.A., Kamel, Kh.M. and Kassab, A., (1974) in phosphate solutions have been carried out. Also, Leo Corallaro and Antonio Indelli (1950) demonstrated that chromate in neutral solutions acts as anodic and cathodic inhibitor with soft steel, but in acid medium as a cathodic stimulator. In this paper, the effect of adding Cl^-, Br^- and nitrate ions to dichromate solutions on the corrosion behaviour of lead has been studied.

EXPERIMENTAL

The electrodes used for measuring the anion potentials were prepared from Analar lead rods 5mm in diameter (Johnson and Mattey). Before experiment, the electrode was abraded with 00 grade emery paper, degreased with acetone, washed thourghly with water and then rinsed in the test solution. Each experiment was carried out with a newly polished electrode and with a fresh portion of the solution.

Determination of the corrosion rate was carried out using the weight loss technique. Experiments were performed on pieces of lead measuring 5x10 cm and 1mm thick, cut from analar lead sheet. The test pieces were first degreased with acetone, washed with conductivity water, dried in alcohol and ether and then weighed. All corrosion tests were carried out in aerated, unstirred solutions. Results were duplicated and the mean values were computed. All solutions were prepared from A.R. materials.

RESULTS AND DISCUSSION

Anodic polarisation experiments were carried out first in pure potassium dichromate solutions, 0.01M, 0.1M and 0.5M $K_2Cr_2O_7$, and the results are shown in Fig.(1). The curves exhibited two dissolution potentials for lead, the first dissolution potential lies at about-0.02V, and this is assigned to the participation of the bichromate ion in the anodic reaction. The potential then jumps to about

+1.2V, at which the bichromate ions are involved in the reaction.

The cathodic polarisation curves measured also in 0.01, 0.1 and 0.5M $K_2Cr_2O_7$, and the results are shown in Fig.(2). The curves almost coincide with each other, and exhibit two reduction potentials. The first reduction potential is -0.05V, which corresponds to the reduction of $HCrO_4^-$ ions. The potential then jumps to about -0.7V, at which dichromate ions are reduced.

1- Effect of Dichromate on the corrosion of lead in Nitrate solutions:

The corrosion rates and potentials of lead in 0.05 and 0.1M KNO_3 were measured as a function of K_2Cr_2O7 concentration with the range $5x10^{-3}$ to $5x10^{-1}$, and the results are given in Figs. (3 and 4). The curves show that at constant NO_3^- concentration, the corrosion potential remains almost constant up to 0.002 M $K_2Cr_2O_7$, above which it shows an increase with concentration. It is also clear that at constant dichromate concentration the potential decreases as the nitrate concentration increases. This indicates that the aggressive anion (NO_3^-) counteracts the effect of the inhibiting anion $(Cr_2O_7)^{--}$.

The corrosion rate was then measured in the different solutions, and the results are shown in Fig. (3). It is clear that V_{corr} is almost independent of the dichromate concentration. From this behaviour, together with the increase of corrosion potential with dichromate concentration, it is concluded that the dichromate ion inhibits the anodic reaction and promotes the cathodic reaction.

To support the above conclusion, lead was anodically polarised in 0.1M KNO_3 in presence of different concentrations of dichromate, and the curves are shown in Fig. (5). The curves show that with increasing the dichromate concentration the dissolution becomes less active, and the current decreases. This behaviour denotes the inhibition of the anodic reaction with $Cr_2O_7^{--}$ ions.

The cathodic polarisation curves for 0.1M KNO_3 containing different amounts of $K_2Cr_2O_7$ are shown in Fig. (6). It is clear that the reduction potential is shifted to less negative values as the dichromate concentration is increased. Moreover, the tendency towards the onset of a limiting current diminishes as the $Cr_2O_7^{--}$ concentration is increased. These phenomenon indicates that the cathodic reaction is accelerated with dichromate ions.

2- Effect of $K_2Cr_2O_7$ on the corrosion of lead in chloride solutions:

For investigating the effect of additions of $K_2Cr_2O_7$ on the corrosion of lead in chloride solutions, we meaured the corrosion rates, V_{corr}, in pure 0.05 and 0.1M KCl solutions. Then the corrosion rates in these solutions were followed as a function of $K_2Cr_2O_7$ concentration within the range 0.001 to 0.5M. The results are shown in Fig. (7), in which the values of V_{corr} for the dichromate free chloride solutions are represented by dotted horizontal lines. It is evident that the corrosion rate remains constant up to $5x10^{-2}$. Above this concentration V_{corr} markedly increases with the increase of dichromate concentration. The corrosion potentials of lead were also found to increase with the increase dichromate concentration in 0.05 and 0.1M KCl solutions Fig. (8). From the kinetic view point as well as from Evans polarisation curves, the results of corrosion potentials and rates reveal that dichromate ion accelerates corrosion through promoting the cathodic reaction.

Polarisation measurements were also carried out to get information about the action of the dichromate ions. From the anodic polarisation curves Fig. (9), it is obvious that the dissolution potential is shifted to less negative values as the dichromate ion in increased. Another feautre of these results is that the anode is subjected to more over potential with increase of dichromate concentration. This phenomenon indicates that $Cr_2O_7^{--}$ ions exerts an inhibitive action on the dissolution of the metal.

The effect of dichromate on the cathodic reaction is investigated by measuring the cathodic polarisation curves in 0.1M KCl solutions containing different dichromate concentrations. As evident from Fig. (10), the curves shift to less negative potential and the limiting current increases with the increase of bichromate concentration. These features reveal that the cathodic reaction is highly accelerated on increasing $K_2Cr_2O_7$ concentration.

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في هذا البحث تم دراسة سلوك التآكل لفلز الرصاص في محاليل متعادلة تحتوى على أيون البيكرومات كأنيون معطل للتآكل مع أيون الكلوريد أو البروميد أو النترات كأيونات مساعدة على التآكل . ولقد أوضحت النتائج أن الأنيون المعطل للتآكل لايعارض ببساطة الأنيون المساعد على التآكل فمعدل التآكل زاد باضافة كميات قليلة من البيكرومات الى محاليل الهاليدات (Cl^- ، Br^-) حتى تركيز ٠٠٢ر٠ جزىء . أما عند تركيزات أعلى من ذلك فان السلوك المعوق لأيون البيكرومات يسود . وقد تشابها في حالة محاليل النترات لمحاليل الكلوريد والبروميد .

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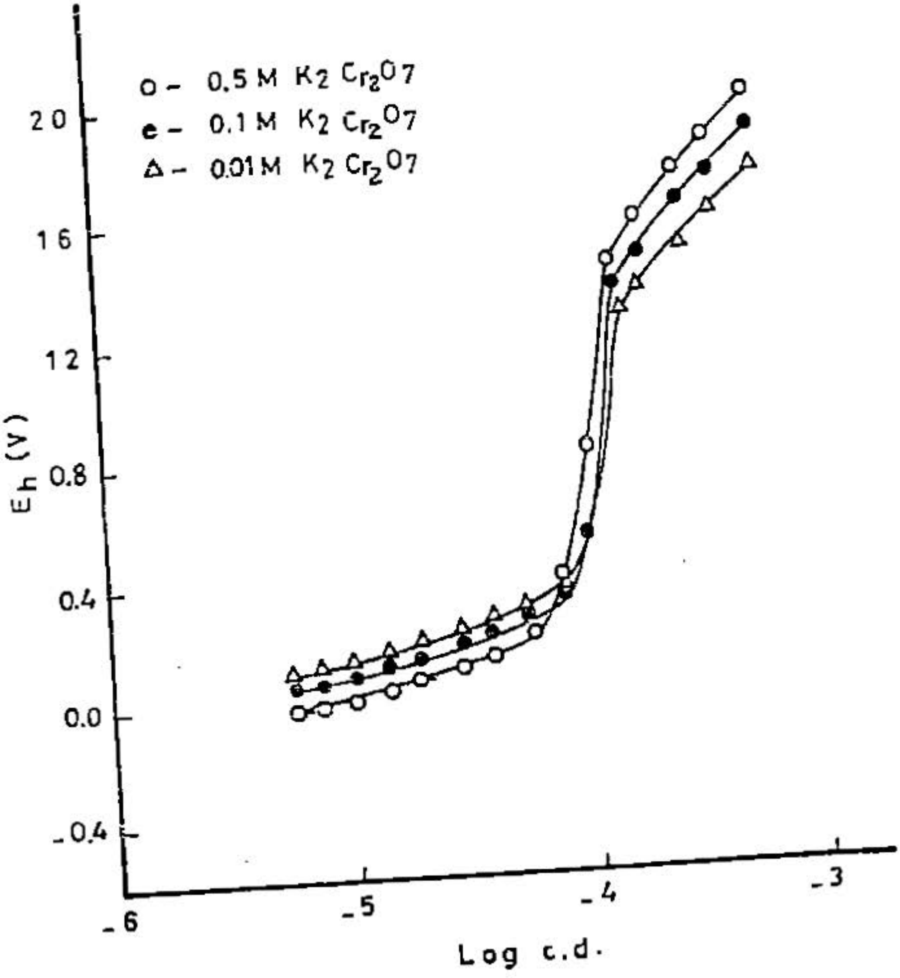

Fig. 1. Anodic polarisation curves for lead in $K_2Cr_2O_7$.

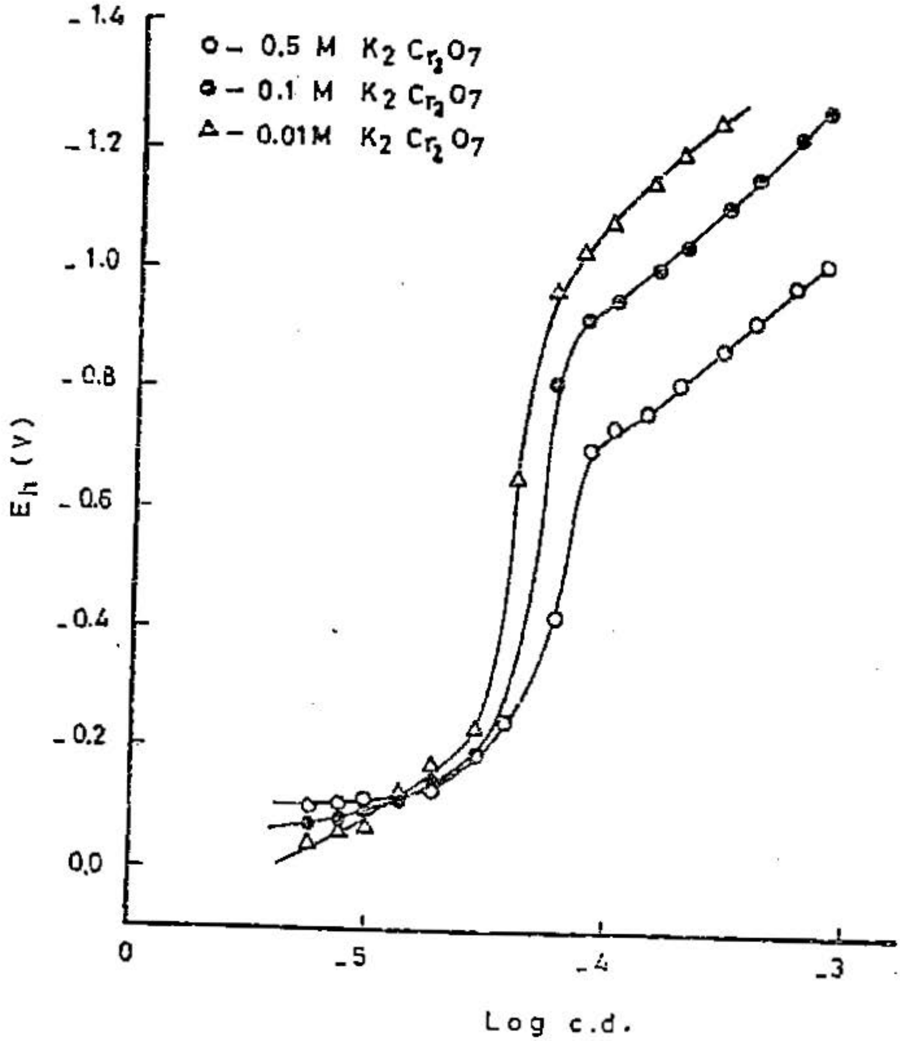

Fig. 2. Cathodic polarisation curves for lead in $K_2Cr_2O_7$.

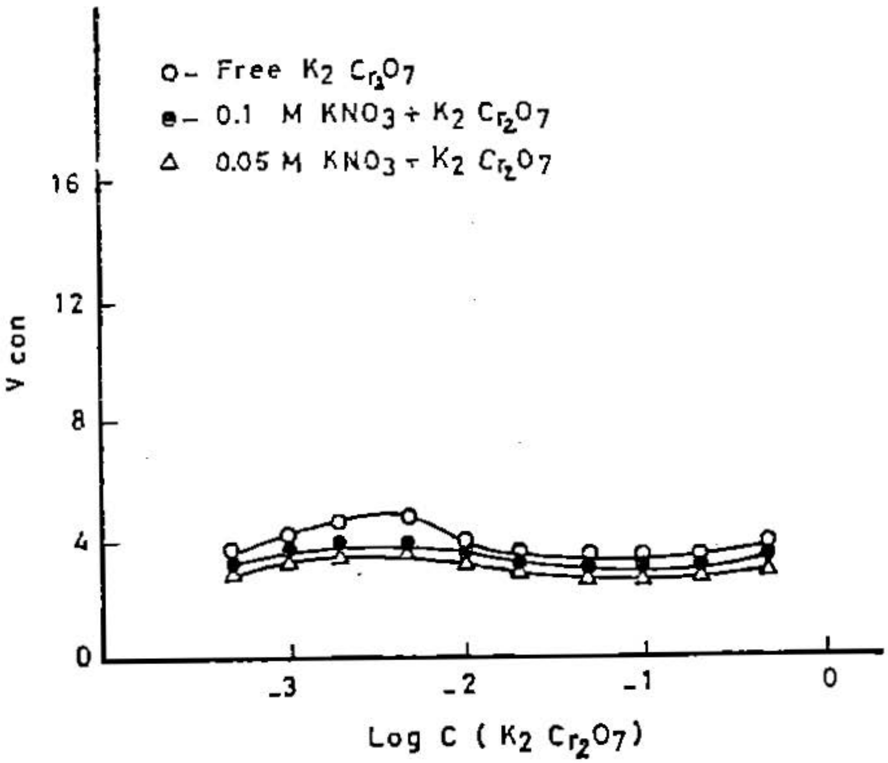

Fig. 3. Effect of KNO_3 concentration on the rate of corrosion of lead in different concentration of $K_2Cr_2O_7$.

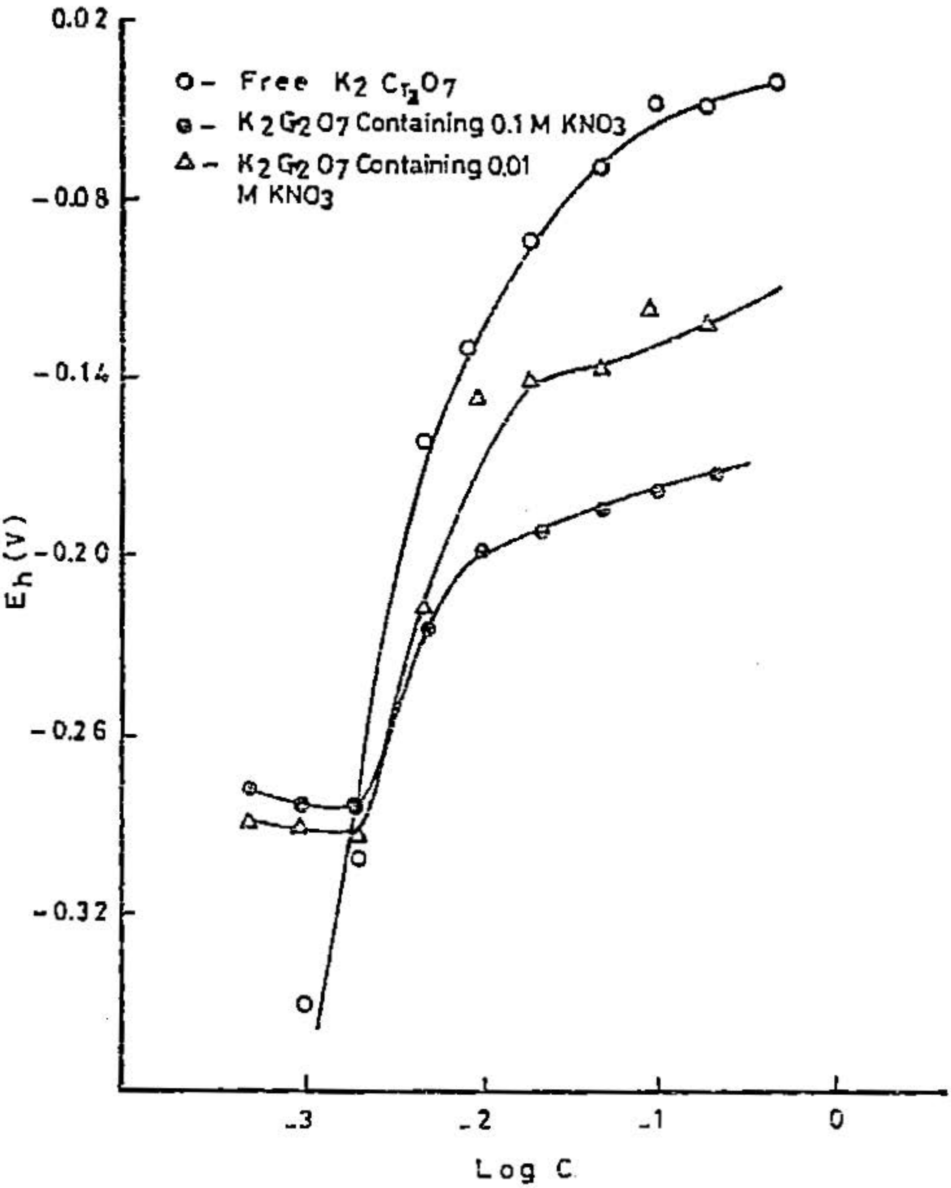

Fig. 4. Effect of KNO_3 concentration of the potential of lead in different concentration of $K_2Cr_2O_7$.

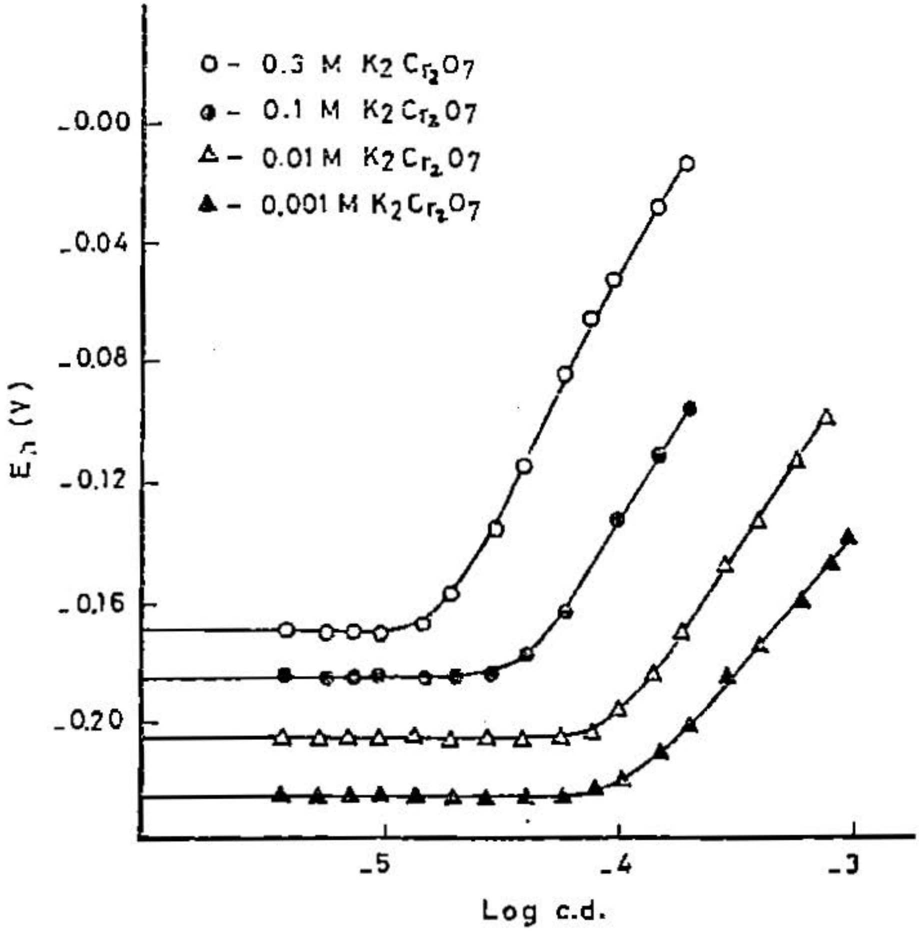

Fig. 5. Anodic polarisation curves for lead in different concentration of $K_2Cr_2O_7$ containing 0.1M KNO_3.

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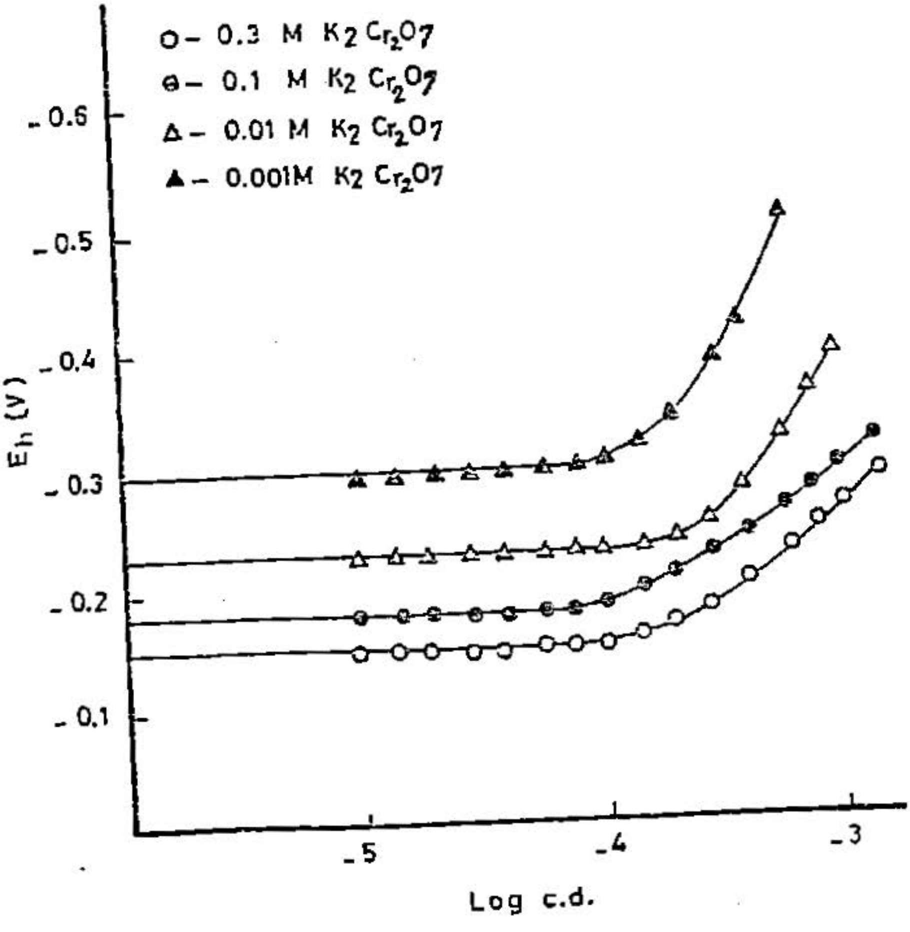

Fig. 6. Cathodic polarisation curves for lead in different concentration of $K_2G_2O_7$ containing 0.1M KNO_3.

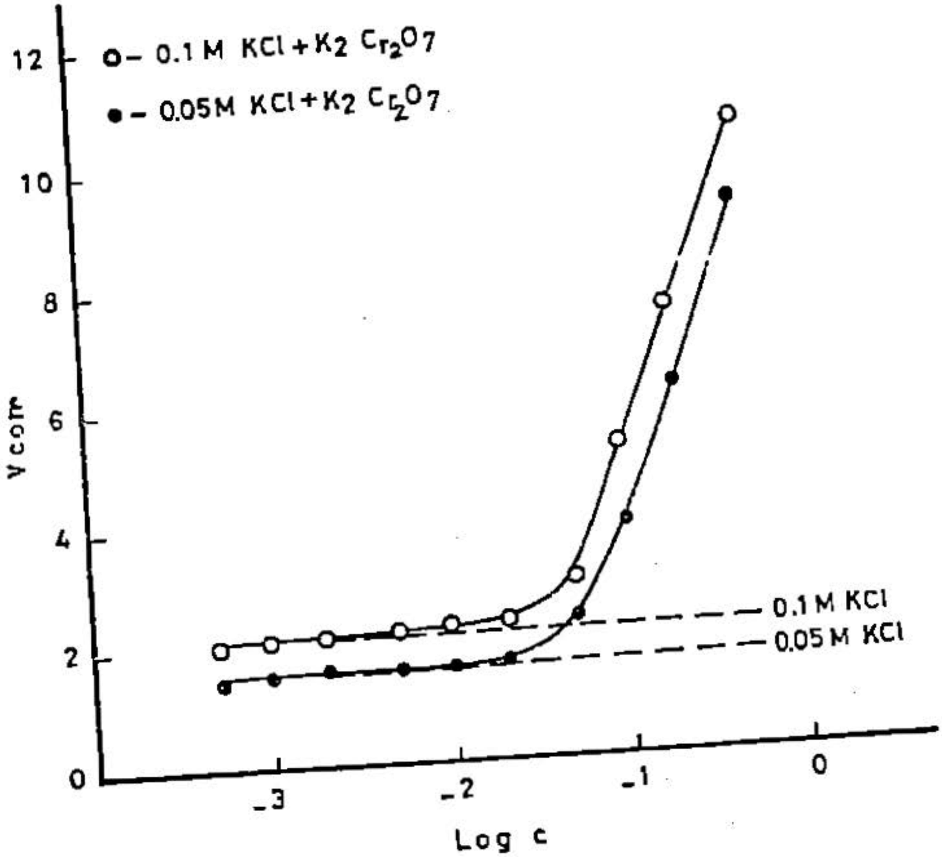

Fig. 7. Effect of $K_2Cr_2O_7$ concentration on the corrosion rate of lead in 0.1M and 0.05M KCl.

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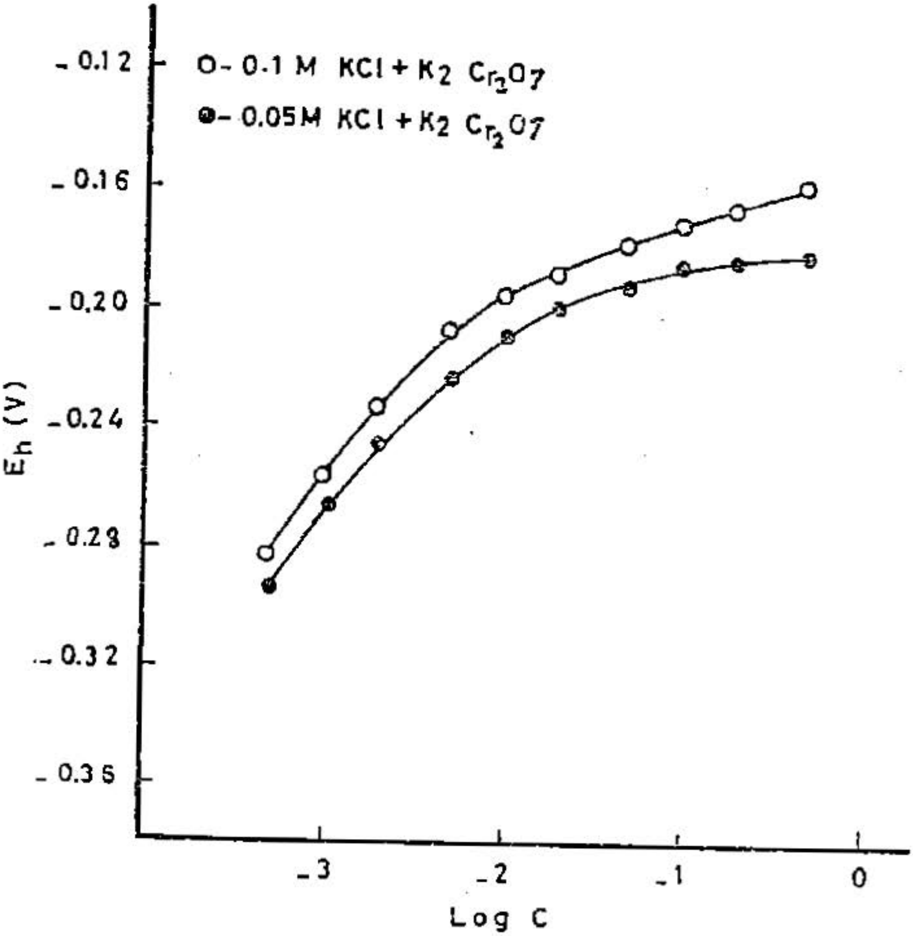

Fig. 8. Effect of $K_2Cr_2O_7$ concentration on the potential of lead in 0.1M and 0.05M KCl.

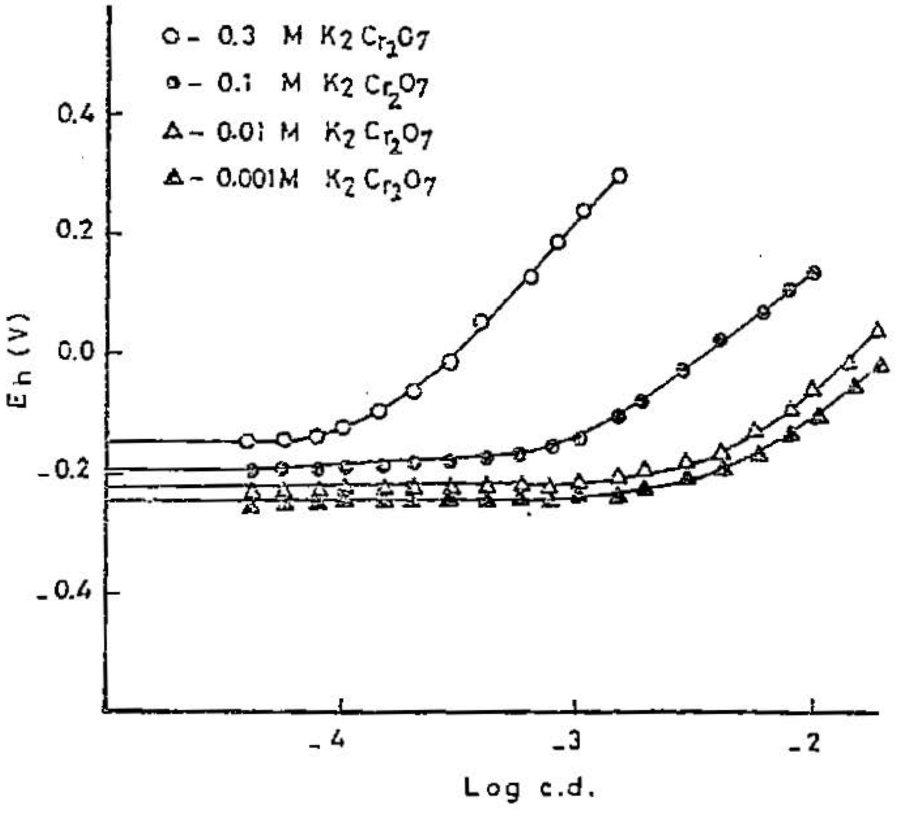

Fig. 9. Anodic polarisation curves for lead in different solutions of $K_2Cr_2O_7$ containing 0.1M KCl.

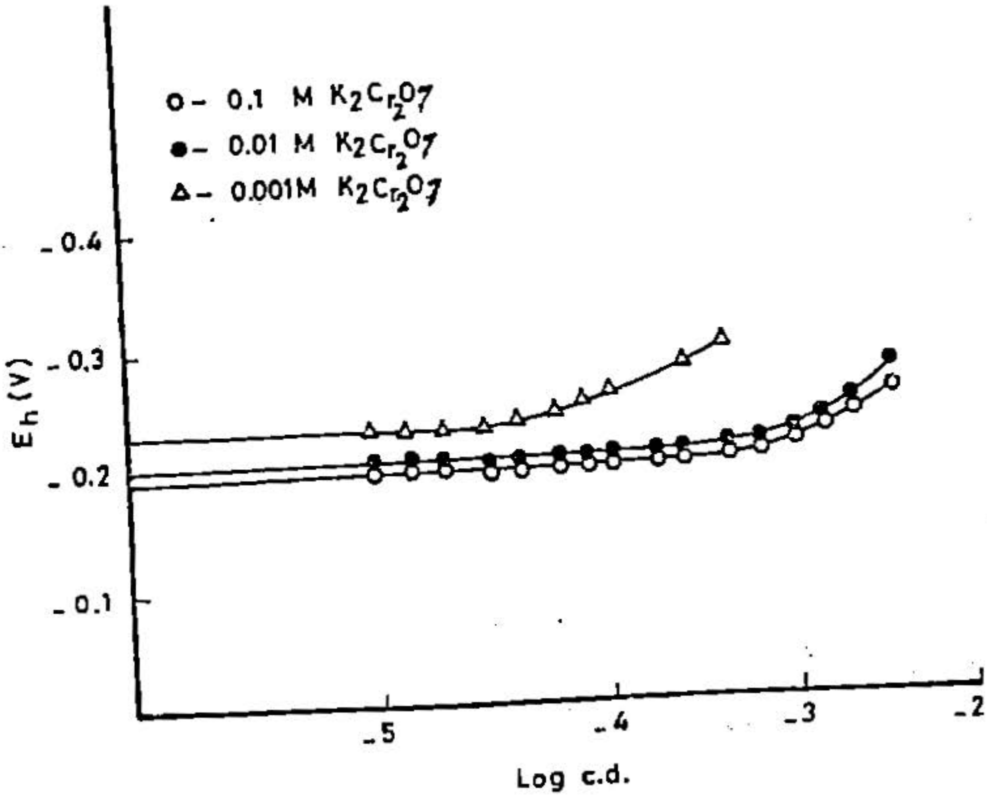

Fig. 10. Cathodic polarisation curves for lead in different solutions of $K_2Cr_2O_7$ containing 0.1M KCl.

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