CORROSION BEHAVIOUR OF LEAD IN SOLUTIONS
OF MIXED ANIONS

By

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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 dichromate
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 disclaimed. 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 ½mm 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

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+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 5×10^{-3} to 5×10^{-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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الملخـــص العربـــى

ســلوك تآكل فلز الرصاص فى محاليـــل تحتــوى علــى

أنيونـــات مختلفـــة

فى هذا البحث تم دراسة سلوك التآكل لفلز الرصاص فى محاليـــــل متعادلة تحتوى على أيون البيكرومات كأنيون معطل للتآكل مع أيون الكلوريـــد أو البروميد أو النترات كأيونات مساعدة على التآكل . ولقد أوضحت النتائــح أن الأنيون المعطل للتآكل لايعارض ببساطة الأنيون المساعد على التآكل فمعــــدل التآكل زاد باضافة كميات قليلة من البيكرومات الى محاليل الهاليـــــدات (Cl^- ، Br^-) حتى تركيز ٢٠٠٢,٠ جزئى . أما عند تركيزات أعلــــى من ذلك فان الــلوك المعوق لأنيون البيكرومات يــود . وقد تشابها فى حالــة محاليل النترات لمحاليل الكلوريد والبروميد .

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6- Indelli, A., Ann. Chim. (Rome) 40, 189, (1950).

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

Fig. 2. Cathodic polarisation curves for lead in
$K_2Cr_2O_7$.
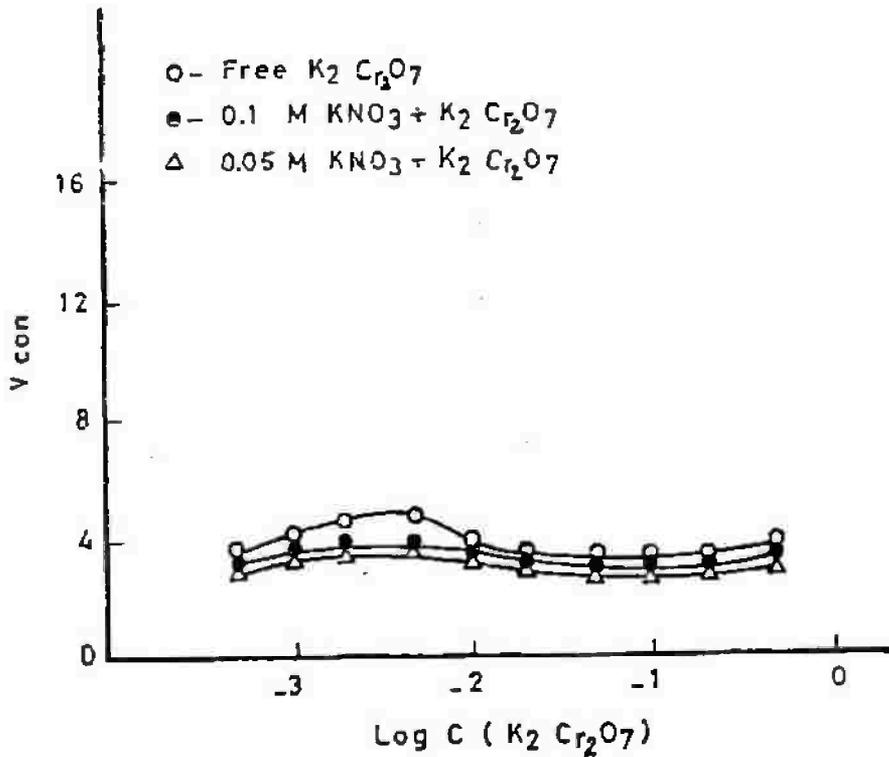
Fig. 3. Effect of KNO_3 concentration on the rate of corrosion of lead in different concentration of $K_2Cr_2O_7$.
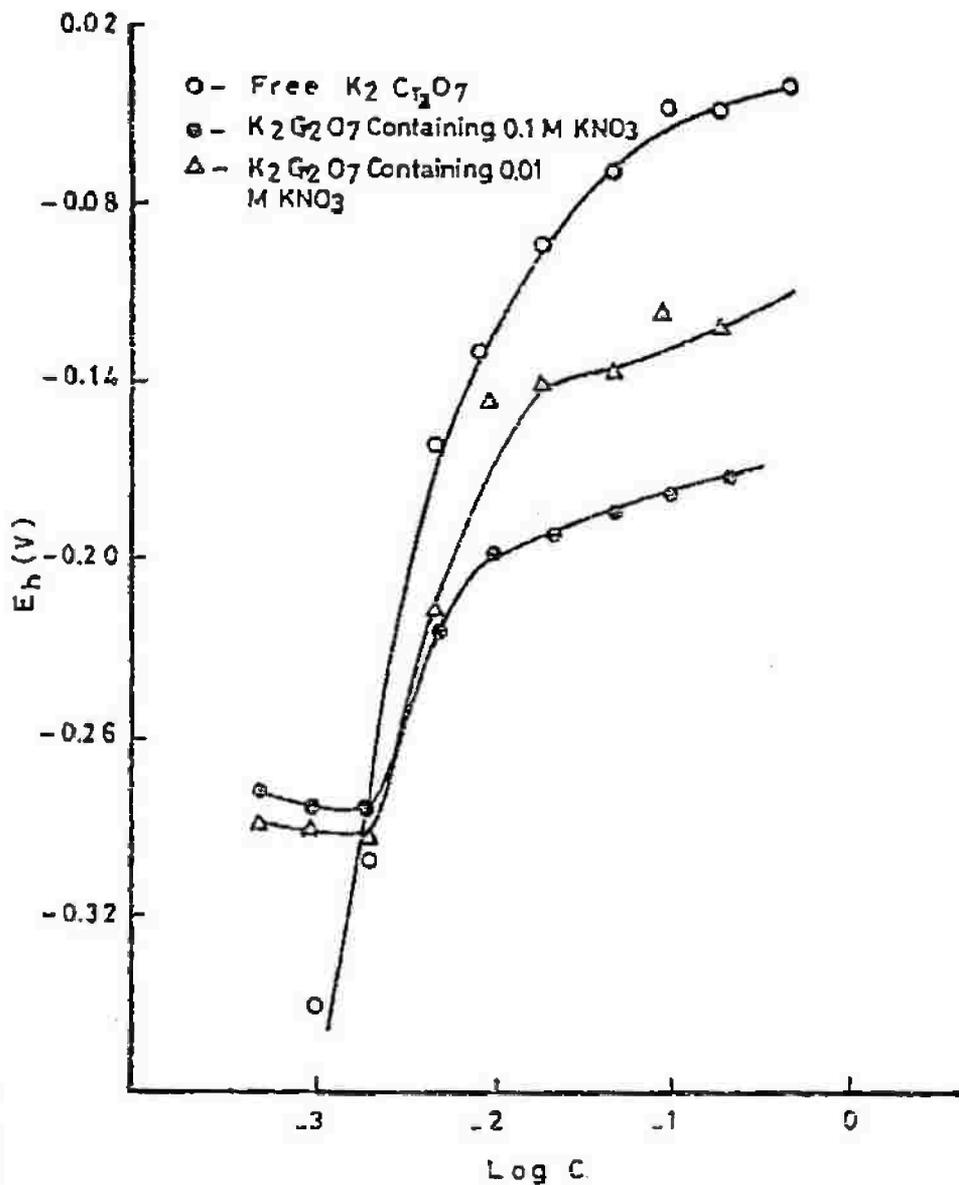
Fig. 4. Effect of KNO_3 concentration of the potential of lead in different concentration of $K_2Cr_2O_7$.
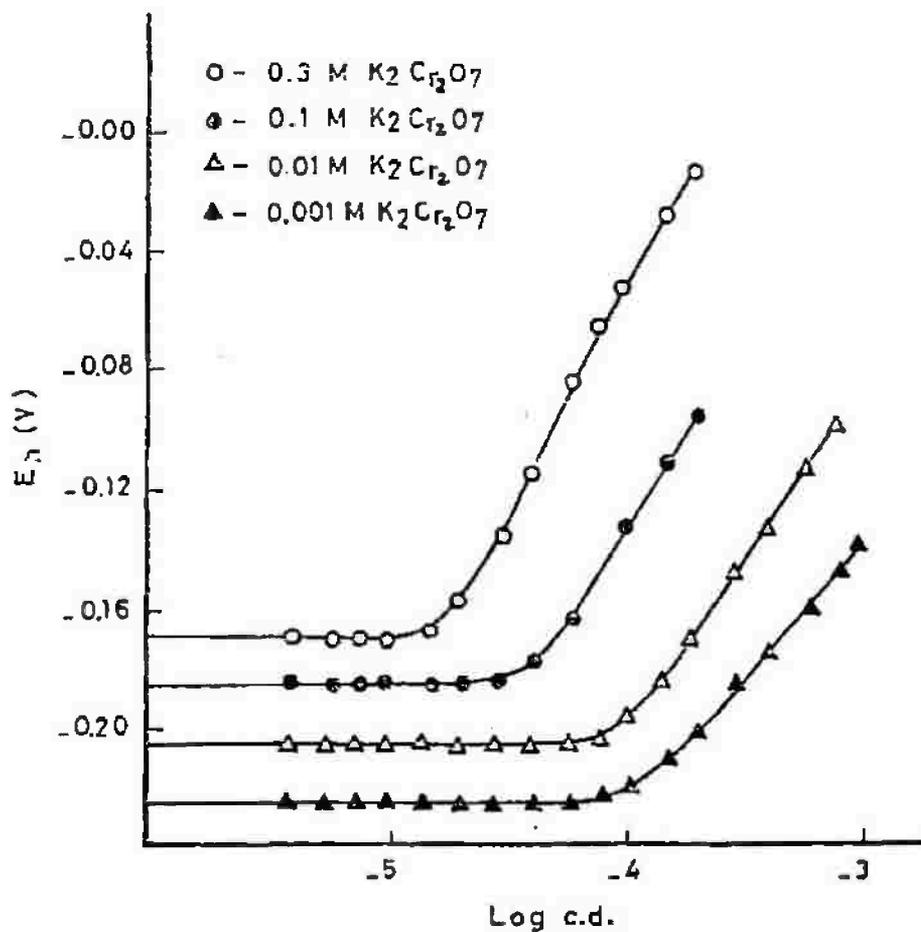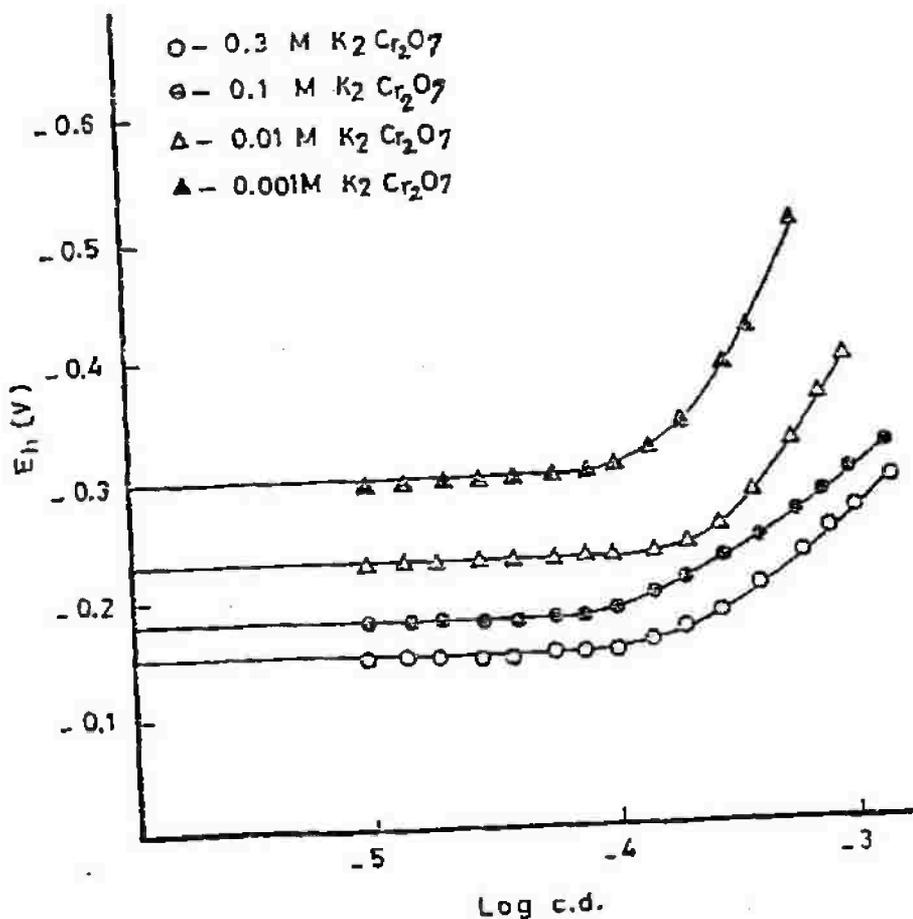
Fig. 5. Anodic polarisation curves for lead in
different concentration of $K_2Cr_2O_7$ containing
0.1M KNO_3.

Fig. 6. Cathodic polarisation curves for lead in
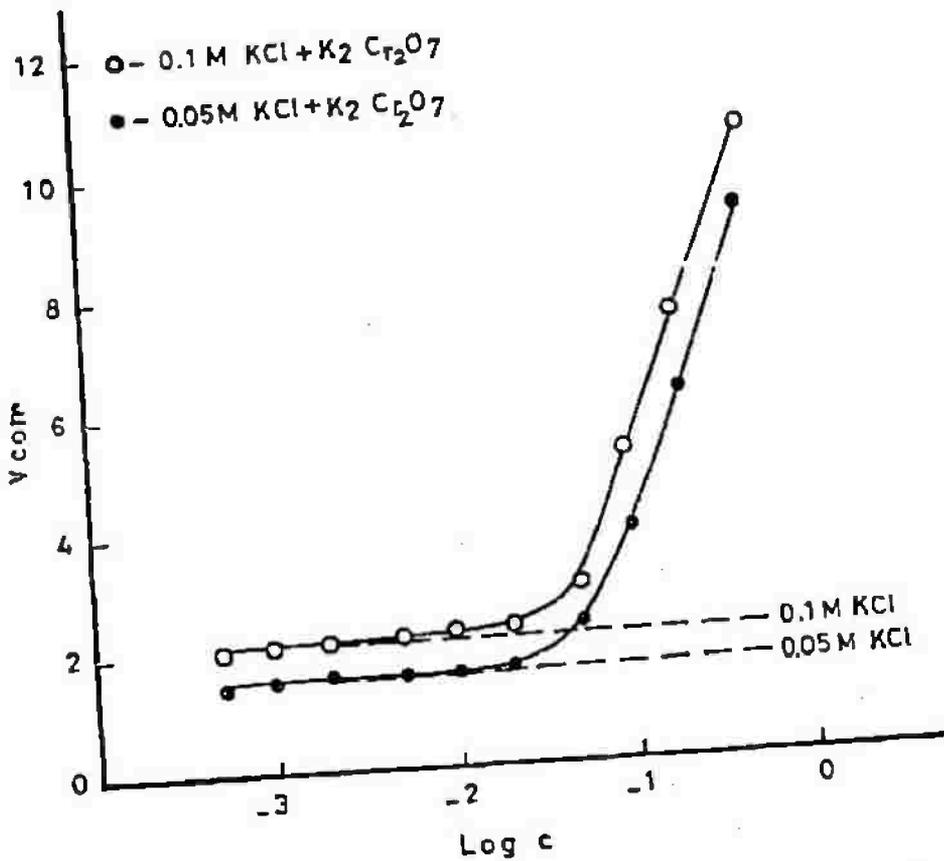different concentration of $K_2Cr_2O_7$ containing
0.1M KNO_3.

Fig. 7. Effect of $R_2Q_2O_7$ concentration on the corrosion rate of lead in 0.1M and 0.05M KCl.
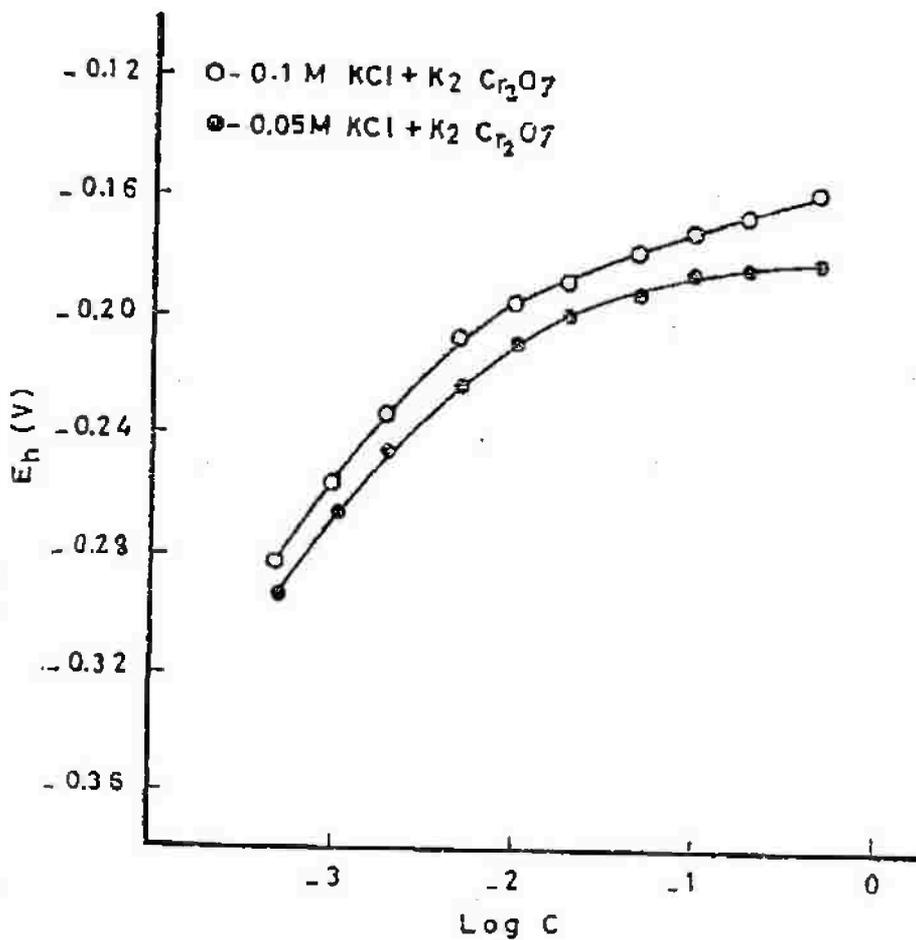
Fig. 8. Effect of $K_2Cr_2O_7$ concentration on the potential of lead in 0.1M and 0.05M KCl.
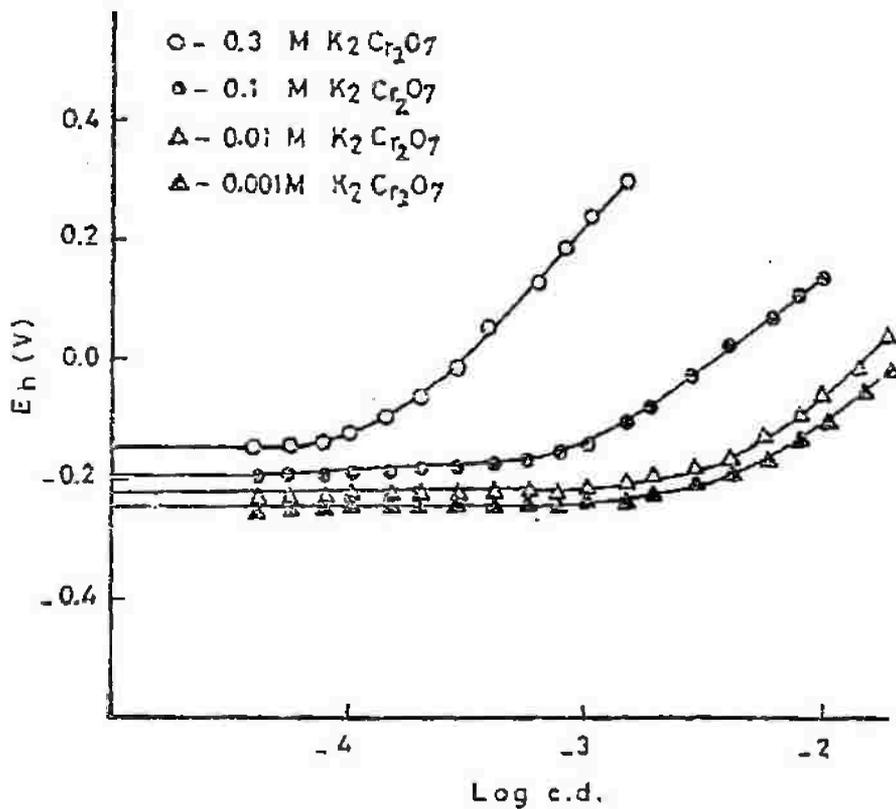
Fig. 9. Anodic polarisation curves for lead in
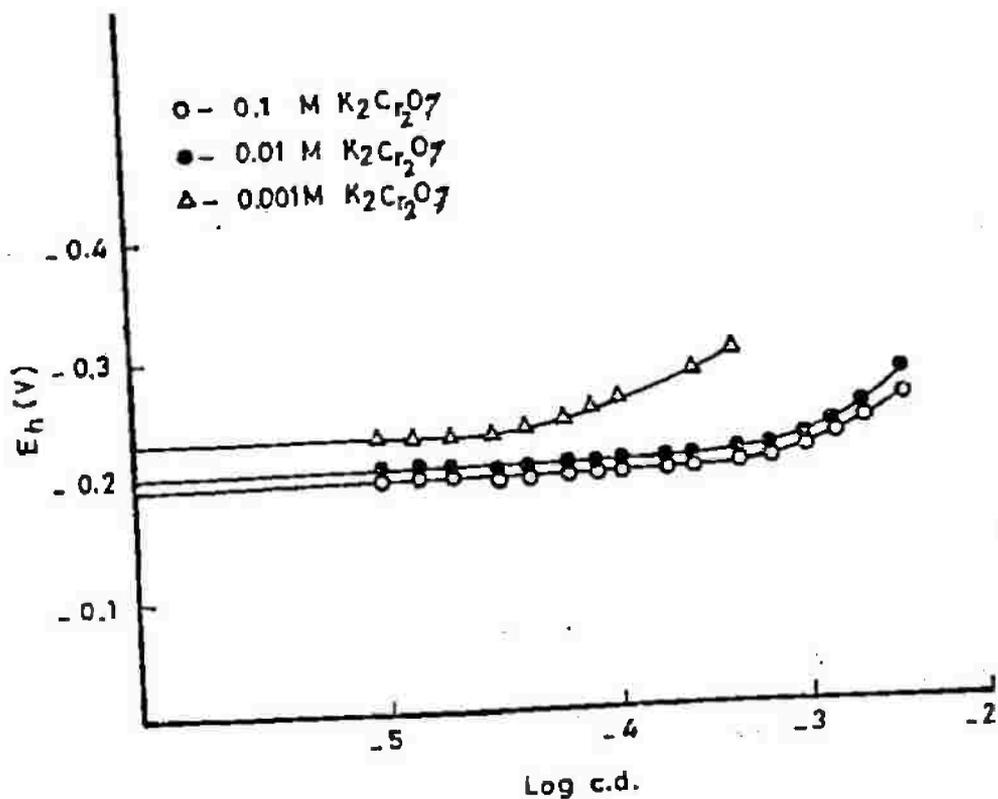different solutions of $K_2Cr_2O_7$ containing
0.1M KCl.

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

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الملخـــص العربـــــى

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سلوك تآكل فلز الرصــاص فى محاليـــل تحتـــوى علـــى

أنيونـــــات مختلفـــــــة

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فى هذا البحث تم دراسة سلوك التآكل لفلز الرصاص فى محاليـــــل
متعادلة تحتوى على أيون البيكرومات كأنيون مثبط للتآكل مع أيون الكلوريــــد
أو البروميد أو النترات كأيونات مساعدة على التآكل . ولقد أوضحت النتائـــج
أن الأنيون المثبط للتآكل لايعارض ببساطة الأنيون المساعد على التآكل نعــــدل
التآكل زاد بإضافة كميات قليلة من البيكرومات الى محاليل الهاليـــــدات
(Cl⁻ ، Br⁻) حتى تركيز ٠٠٠٢. جزء . أما عند تركيزات أعلـــى
من ذلك فإن السلوك المعوق لأنيون البيكرومات يسود . وقد تشابها فى حالة
محاليل النترات لمحاليل الكلوريد والبروميد .