Corrosion Behaviour of Iron in Phosphate Solutions

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Introduction:

Few studies have been carried out on theelectrochemical behaviour of metals in phosphate solutions. The results obtained for lead[1] and tin[2] showed that the nature of the phosphate film and the concentration ranges within which the electrode exhibits reversible behaviour depend on the electrode material and the solution pH. In case of zinc[3], no thermodynamic behaviour was observed. In addition to given information regarding the charac teristics of metals as phosphate electrodes, these studies help to clarify the mechanism by which phosphate ions inhibit the corrosion of metals. In continuation to our work in this field. We investigate the behaviour of iron.

Experimental:

The potential of the iron electrode was measured as a function of time within a period of four hours in aqueous phosphate solutions of concentration varying between 5×10^{-4} and 1 M. In order to prevent any variation

in potential due to pH changes, the phosphate solutions were adjusted to definite pH values. Various series of solutions covering the pH range 2-11 were used; the composition of these has already been given[1]. The pH values were checked with the hydrogen electrode and when possible, with the quinhydrone electrode.

The electrodes were prepared from Analar iron rods 3 mm in diameter (B.D.H. England). Before use, the electrode was abraded successively to 00 finish, degreased with acetone and then washed thoroughly with water. Each experiment was carried out with a newly polished electrode and with fresh portion of the solution. A saturated calomel electrode was used as a reference electrode and the potentials are corrected to the normal hydrogen scale. The potential ws measured with the aid of a Cambridge potentiometer readible to 0.5 millivolt. The results were reproducible to $\pm$ 5 millivolts.

Determination of the corrosion rate was also carried out using the weight-loss technique. Experiments were performed on iron pieces measuring 5 x 10 cm and 0.8 mm. thick, cut from Analar iron sheet. The test pieces were first degreased with acetone and then etched in a solution containing 15 g/l $Na_3 PO_4$ + 20 g NaOH at 80-85^{o} for 1 min. They were then 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.

The chemicals used in all experiments were of Analar grade. All measurements were carried out at $30^{o}C$ in an air thermostat controlled to $\pm$ 0.5 .

Results and Discussion:

Corrosion of Iron in Acid Phosphate Solutions:

The steady state potentials obtained four hours after immersion in 0.001 - 1 M H_3PO_4 are plotted as a function of the logarithm of the molar acid concentration; and the curve is shown in Fig. 1. As evident from this curve the potential increases with the acid concentration. The increase amounts to 90 mv/unit log C. The potential tends to a more or less constant value at about one molar acid. These results cannot be attributed to the behaviour of the metal as a metal oxide electrode, because the persistence of oxides is not possible in these acid media. We therefore concluded that the observed potentials are corrosion potentials, rather than thermodynamic values.

Comparison of the results obtained in these acid solutions with those observed by Brasher in neutral solutions [4] reveals that corrosion promotion is not necessarily accompanied by a negative slope for the potential - log C relation. Brasher's equation might be understood on the basis that the anions promote the anodic reaction whereas the cathodic reaction is not affected by the anions. Thus, if the concentration of the cathodically reduced entities (H^+ or O_2 molecules) remains constant, equality of the anodic and cathodic reactions rates is brought about through the shift of the corrosion potential to more negative values. In acid solutions, the rate of the cathodic reaction increasees with increase of H^+ ion activity. Thus, if the increase of the cathodio reaction rate is larger than the increase of the anodic reacton rate, the corrosion potential increases. The results of the present investigation indicate that cathodic acceleration predominates.

In order to test whether the increase in the corrosion rate is due only to the increase of H^+ ion activity or the anions contribute in the promotion of corrosion, the corrosion behaviour was studied at constant pH value, ca. pH2. Hence, the corrosion rates were measured in equimolar NaH_2PO_4 -H_3PO_4 mixtures, within the range 0.001-0.2M. The results are shown in Fig. (2). It is clear that $H_2PO_4^-$ ions promote

the corrosion of the metal. This behaviour is important because it indicated that the primary phosphate ion exhibits corrosive action. In this respect the results agree with Brasher's theory[4] . However this ion did not show inhibitive action at higher concentrations as required by Brasher theory[4] for neutral solutions.

Corrosion Inhibition with Phosphate Ions in Neutral and Alkaline Solutions:

Potential-time curves were also constructed for the iron electrode in sodium phosphate solutions of different pH values. The steady state potentials obtained four hours after immersion, are plotted as a founction of the logarithm of the molar concentration. Different relations were obtained depending on the solution pH (cf. Figs. 3 and 4). In none of the solutions studied within the pH range 4.6-13 did the electrode potential show a linear logarithmic decrease with phosphate concentration, indicating that, at least under our experimental condition, iron does not behave as a reversible metal/metal phosphate electrode.

Generally speaking it is clear from these curves that the potential increases with the phosphate concentration till it reaches a maximum value, and then decreases again with further increase of concentration. The maximum concentration C_{max} for the different series are given in the following table.

Series	pH	max	C_{max}
NaH_2PO_4(in acetic acid sodium acetate buffer)	4.6	- 0.408 V	0.005 M
NaH_2PO_4 + Na_2HPO_4	6.5	- 0.394 V	0.01 M
Na_3PO_4	9.4-12.9	- 0.136 V	0.02 M
Na_2HPO_4 + Na_3PO_4	10.96	- 0.094 V	0.05 M
Na_3PO_4 + 0.01N NaOH	11.2 - 13	- 0.083 V	0.02 M

As mentioned above, the increase of potential with phosphate concentration shows that iron does not behave as metal/metal phosphate electrode. The results indicate also that the electrode potential is not governed by an oxide layer. This is because the solutions of a given series are adjusted at a constant pH value, and hence, the potential should have remained constant in the different solutions of each series. The behaviour observed in these solutions is not probably ascribed to the inhibitive effect of phosphate ions on the corrosion of iron. The mechanism of corrosion inhibition and the phenomenon of potential maximum are discussed here below from the stand-point of the rates of the various electrode reactions.

The heterogenity of the surface, in the sense that some sites are anodic and others are relatively

ơthodic, is now a well established fact. At a metal corroding in aerated solutions, the probable reactions expected to proceed are:

i) Anodic dissolution of the metal from the anodic areas

$$M \rightleftharpoons M^{2+} + 2e \quad \ldots\ldots(1)$$

ii) Cathodic deposition of the metal ions at the cathodic areas.

$$M^{2+} + 2e \rightleftharpoons M \quad \ldots\ldots(2)$$

iii) Cathodic reduction of oxygen at the cathodic areas

$$O_2 + 2H_2O + 4e \rightleftharpoons 4\ OH^- \text{(in alkaline solutions)} \quad (3)$$

iv) and finally, the anodic evolution of oxygen at the anodic areas.

$$4\ OH^- \rightleftharpoons 2H_2O + O_2 + 4e \quad \ldots\ldots(4)$$

The rates of these reactions are represented, respectively by:-

$$V_1 = K_1 (x) \exp\left[\frac{2\alpha EF}{RT}\right] \quad \ldots\ldots(5)$$

$$V_2 = K_2(M^{2+})(1-x)\exp\left[\frac{-2(1-\alpha)EF}{RT}\right] \quad \ldots\ldots(6)$$

$$V_3 = K_3(O_2)(1-x) \exp\left[\frac{-4\beta EF}{RT}\right] \quad \ldots\ldots(7)$$

$$V_4 = K_4(OH)(x) \exp\left[\frac{4(1-\beta)EF}{RT}\right] \quad \ldots\ldots(8)$$

Where K_1, K_2, K_3 and K_4 are the rate constants, x is the anodic fraction of the surface and (1-x) the cathodic fraction; α and β are the fractions of the electrode potential, E, which accelerate the metal dissolution and reduction of oxygen, respectively, and $(1-\alpha)$ and $(1-\beta)$ correspond to the reverse reactions.

Under stationary conditions, the metal corrodes at a rate V_{corr} , equal to the net rate of metal dissolution, which is also equal to the net rate of reduction of oxygen;

thus

$$V_{corr} = V_1 - V_2 = V_3 - V_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

The reduction of oxygen is often very slow compared to the metal dissolution. Thus $(V_1 - V_2) \simeq 0$, with the result that $V_1 \simeq V_2$. This means that the potential approaches the reversible value of the metal/metal ion or metal/metal compound when a precipitating anion is present, For noble metals, on the other hand, reduction of oxygen proceeds at a higher rate than metal dissolution Hence, $(V_3 - V_4) \simeq 0$ and accordingly $V_3 \simeq V_4$. The potential approaches, therefore, the reversible value of the oxygen electrode in the given solution. In many other cases, metal dissolution and reduction of oxygen proceed at comparable rates; the electrode thus acquires a potential which is appreciably more positive than that of the metal/metal ion system, and appreciably more negative than that of the oxygen electrode in the given solution. In this case the reverse rections, i.e. the deposition of metal ions and the anodic evolution of oxygen, are neglected, and

$$V_1 \simeq V_3 = V_{corr} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

The potential acquired by the metal in this case satisfies the equality of the anodic and cathodic reaction rates, and is called "corrosion potential".

In view of the above argument we can proceed to explain the experimental results. Thus, in solutions of pH 4.6-13 containing phsophate ions, the anodic areas of the metal surface are covered with a persisting layer of iron oxide or iron phosphate. The shift of potential to less negative values on inoreasing the phosphate concentraton shows that the rate of the anodio reaction, viz., the metal dissolution is being subjected to a decelerating effect, which is possibly the decrease of the ionic conductivity of the iron oxide or iron phosphate layer. In analogy to lead[1], tin[2] and zinc[3], this can be attributed to the adsorption of phosphate ions on the iron oxide or iron phosphate layer, in a highly polymerised form. The interface between the iron phosphate layer and solution acquires a semi-glassy constitution rather than an ionic or crystalline structure, and hence, inhibits the transfer or iron ions to the solution. In order that the equality between the rate of metal dissolution and that of cathodic reduction of oxygen

is restored, the potential rises. This leads to decrease of the rate of the cathodic reaction V_3 , and consequently to diminution of the corrosion rate (of equations 7 and 10).After reaching to a certain maximum, the potential decreases with further increase of concentration. This shift of potential to the active side might be taken as indication to increased corrosion rate, on the basis that some complex compounds might form at high phosphate concentrations.

We therefore measured the corrosion rates in some representative solutions. The results given in fig (5). reveal that the corrosion rates at concentrations higher than C_{max} are generally smaller than the rates at lower concentratons. This means that although the potential decrease the corrosion rate is further diminshed.

The decrease of potential after reaching a maximum value is explained on the basis that further increase of concentration permits adsorption on the cathodic sites of the metal surface. The area available for cathodic reduction of oxygen, (1-x), decreases, and hence, the rate of reduction V_3 , should decrease as equation (7) implies. Accordingly, the potential decreases so that the equilibrium between the anodic and cathodic reaction is again restored. If follows

that v_1 and consequently the corrosion rate is once more diminished (Cf. equation (5) and (10).

Summary:

The potential of the iron electrode in aqueous phosphate solutions was measured at 30° C as a function of pH and electrolyte concentration.

In pure phosphoric acid solutions as well as in phosphoric acid-primary phosphate mixtures having constant pH value, corrosion of iron is promoted as the concentration is increased. This is possibly due to acceleration of the metal dissolution by adsorbed ions on the bare anodic areas.

In solutions of pH 4.6-13, the potential increases with phosphate concentration, and after reaching a maximum value, it decreases again on further increase of concentration. The corrosion rate was always decreasing as the phosphate concentration was increased. A mechanism for corrosion inhibition is proposed, based on the adsorption of phosphate ions, on the surface of a persisting phosphate or oxide layer, in a highly polymerised form. The film/solution interface acquires, therefore, a sani-glassy structure, which hinders the transfer of iron ion to the solution,

[illegible] The decrease of potential after reaching a maximum value was attributed to the adsorption of phosphate ions on the bare cathodic areas of the electrode surface. This leads to the deceleration of the cathodic reduction of oxygen, and results in further inhibition of corrosion.

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السلوك التآكلى للحديد فى محاليل الفوسفات

تم قياس جهد قطب الحديد فى المحاليل المائيه للفوسفات عند درجه ٣٠° مئويه كدالة للرقم الايدروجينى وتركيز الالكتروليت.

وقد وجد انه فى محاليل حمض الفوسفوريك وكذلك فى مخاليط من حمض الفوسفوريك واحادى فوسفات الصوديوم المثبته عند رقم ايدروجينى معين يزداد معدل تآكل الحديد مع زياده التركيز. وقد فسر ذلك على اساس ادمصاص الانيونات على المناطق المصعديه المعراه.

اما فى الفوسفات ذات الرقم الايدروجينى ٤٫٦ ــ ١٣ فقد لوحظ زياده الجهد مع زياده تركيز الفوسفات حتى قيمه معينه ، ثم ينقص الجهد مع زياده التركيز.

اما عن معدل التآكل فقد وجد انه ينقص مع زياده تركيز الفوسفات وقد نسبت زياده الجهد الى تكوين طبقه غير منفذه نتيجه ادمصاص الانيونات على سطح طبقه من اكسيد الحديد او فوسفات الحديد.

وعند التراكيز العاليه فانه يتم ادمصاص الانيونات على المناطق المهبطيه للفلز ، مما يؤدى الى نقص معدل اختزال الاكسجين ، وهذا يؤدى الى نقص الجهد.

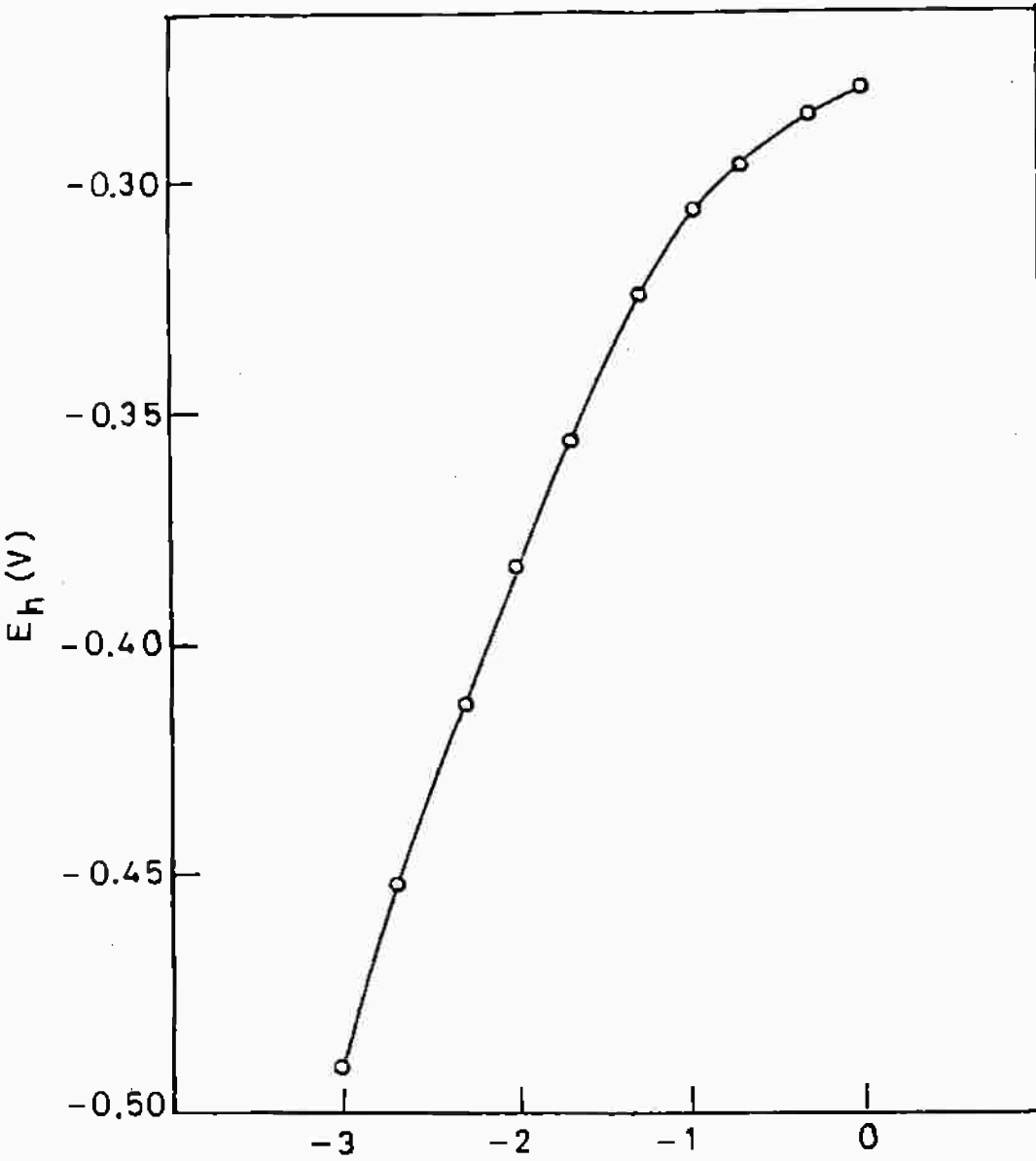

Fig (1)

Effect of Concentration of H_3PO_4 o

the Potential of Iron.

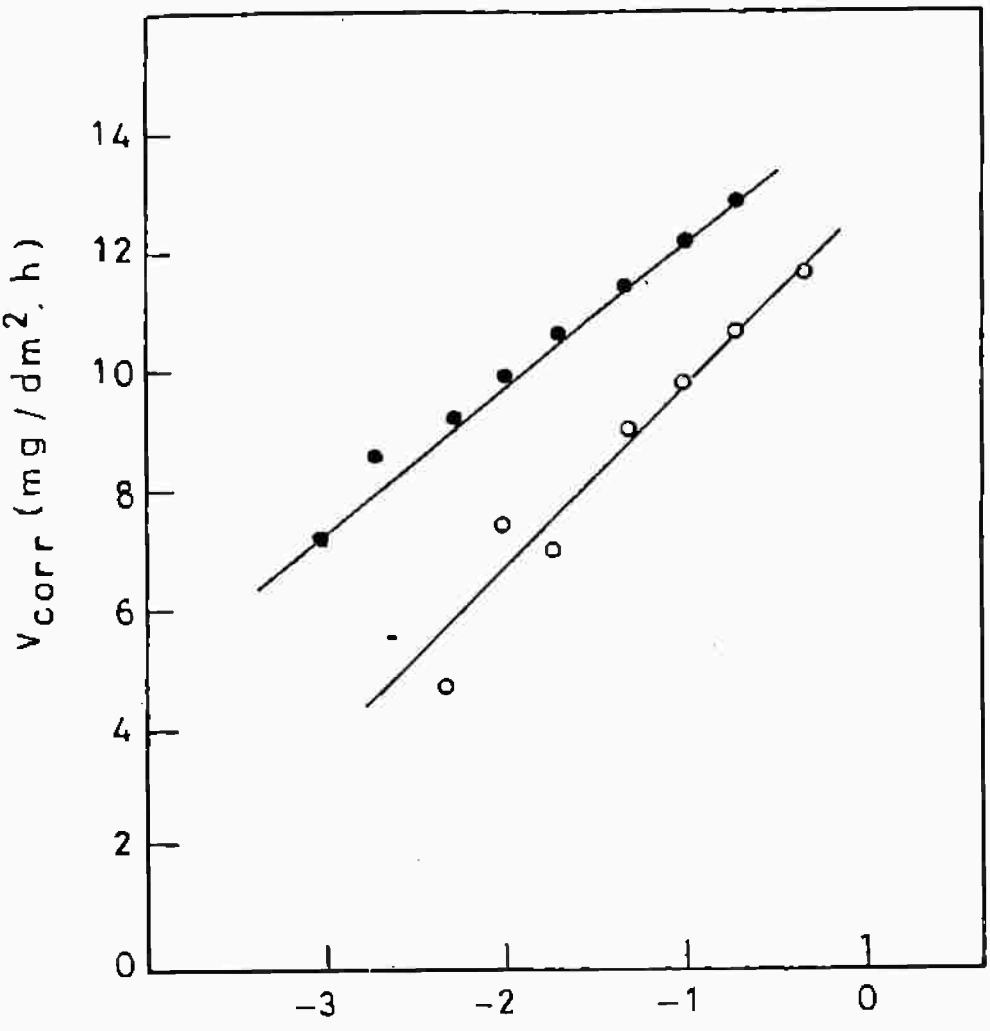

Fig (2)

Rate of Corrosion of Iron in:

- • $NaH_2PO_4 + H_3PO_4$
- o H_3PO_4

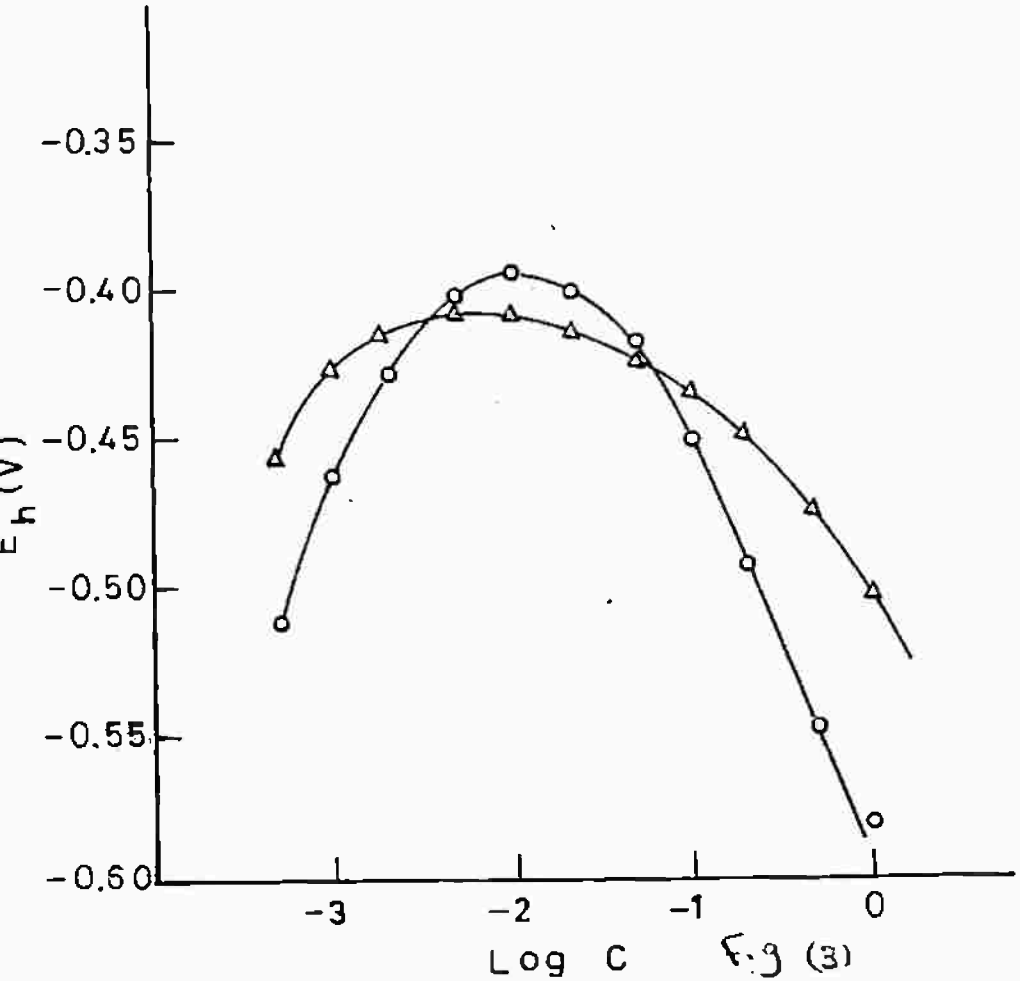

Fig (3)

Effect of Concentration of Simple NaH_2PO_4 and of ($NaH_2PO_4 + Na_2HPO_4$) mixture on the Potential of Iron

o ($NaH_2PO_4 + Na_2HPO_4$)

Δ (NaH_2PO_4) in (Na acetate + acetic acid) Buffer soln.

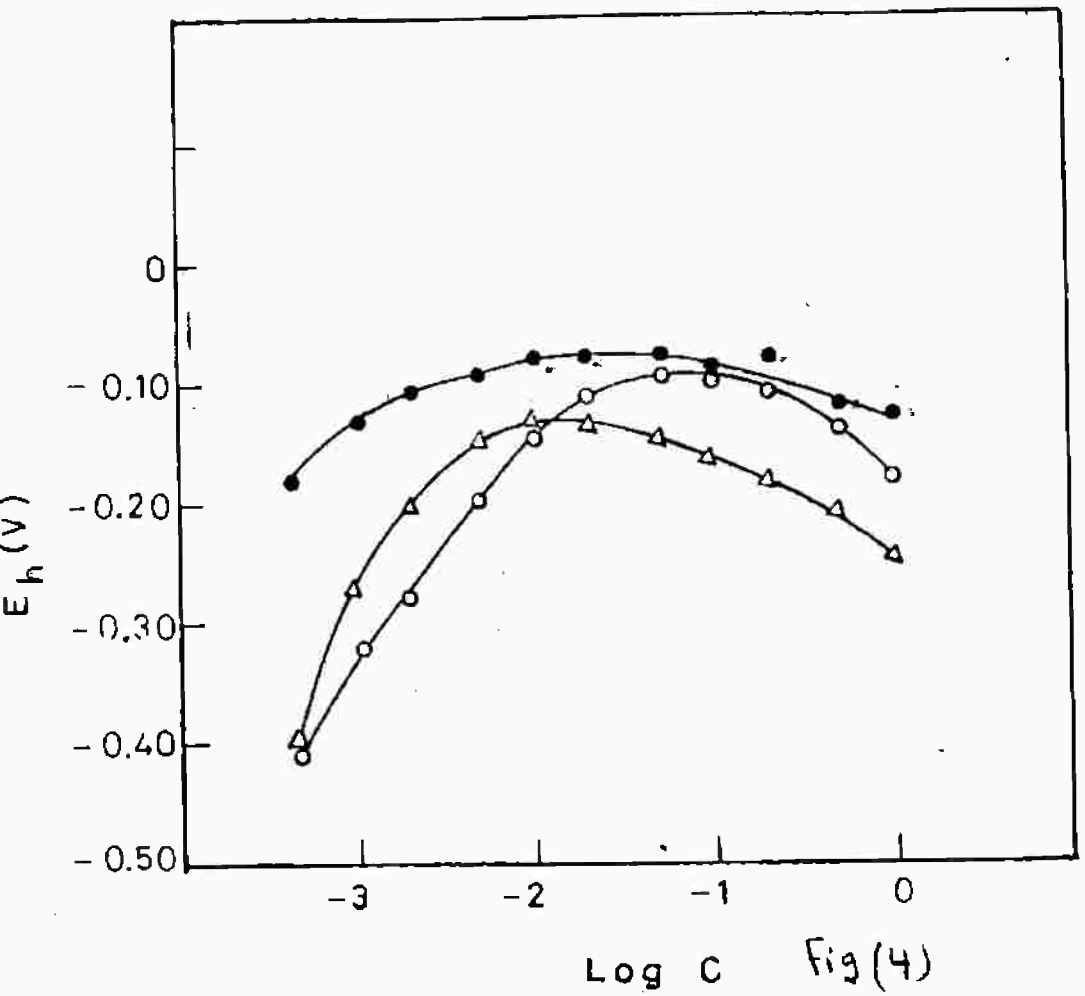

Fig (4)

Effect of Concentration on the potential of Ir

- ● Na_3PO_4 in 0.01 N NaOH
- △ Na_3PO_4
- ○ $Na_2HPO_4 + Na_3PO_4$

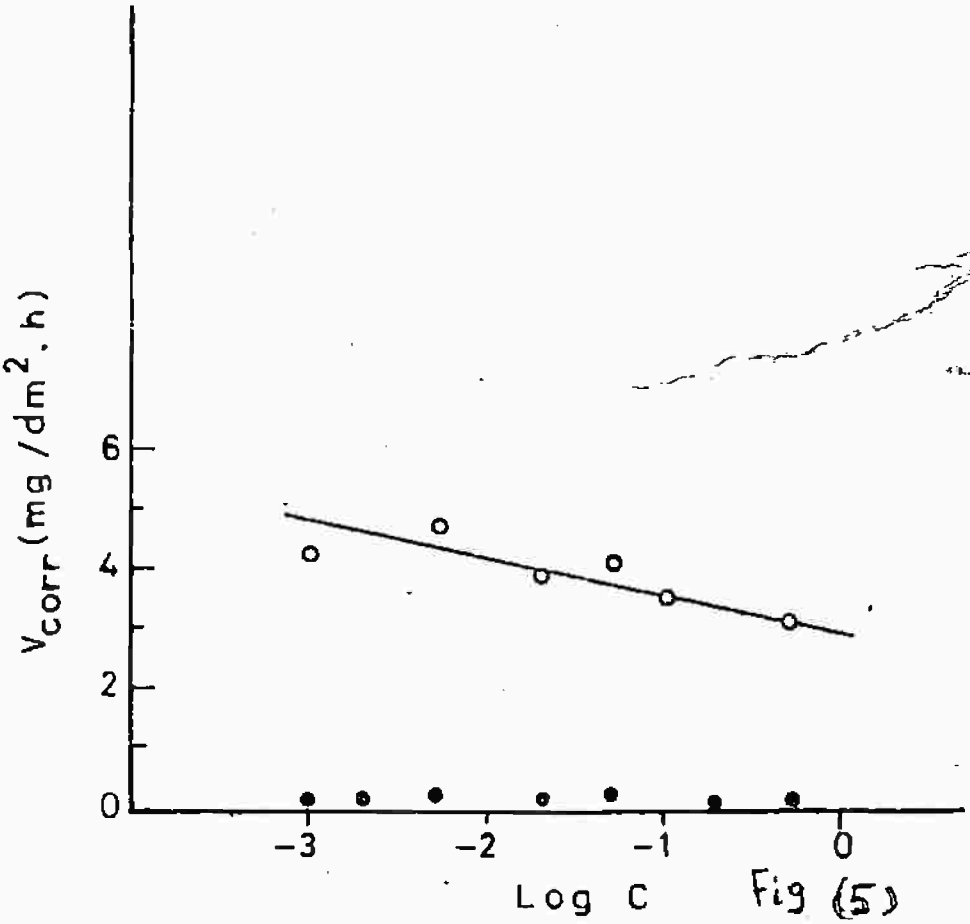

Fig (5)

Corrosion of Iron in:- o NaH_2PO_4 + Na_2H

• Na_3PO_4 Free