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MECHANISM OF PASSIVITY BREAKDOWN OF PURE IRON AS COMPARED TO OTHER METALS

José R Galvele.

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MECHANISM OF PASSIVITY BREAKDOWN OF PURE IRON AS COMPARED TO OTHER METALS

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ABSTRACT

A model for pit iniciation and pit propagation is proposed. The model was applied to aluminum, chromium, cobalt, iron, nickel, and zinc. The following conclusions were reached:

1. The necessary acidification for pit iniciation can be obtained even for pits as small as 20 Å.

2 The pitting potential (E_p) is a function of NaCl concentration, and a relation of the type:

$$E_p = A - B \log C_{NaCl}$$

should be expected, where A = constant, C_{NaCl} = NaCl concentration, and:

$$B = \frac{R\,T}{F} \ln 10 = 0.059\ V$$

3. For pH > 10 the OH^- ion will inhibit pitting of iron, and a relation of the type:

$$E_p = A' + B' \log C_{OH^-}$$

should be expected (A'; and B' constants).

4. Anions of weak acids, such as those in buffered solutions, will inhibit pitting, and a relation of the type:

$$E_p = A'' + B'' \log C_{L^-}$$

should be found. (A"; and B" constants).

RESUMEN

En el presente trabajo se propone un nuevo modelo de iniciacion y crecimiento del picado El mismo fue aplicado a los siguientes metales: aluminio; cinc, cobalto, cromo, hierro, y niquel; extrayendo las siguientes conclusiones:

1 Contrariamente a lo afirmado por numerosos autores, la acidificacion necesaria para iniciar un pit puede obtenerse aun en pits tan pequeños como 20 Å

2 Tal como se encuentra en la práctica, el potencial de picado resulta ser funcion de la concentracion de cloruros. El modelo aqui propuesto predice que se debe cumplir una relación del tipo:

$$E_p = A - B \log C_{NaCl}$$

donde A y B son constantes. El valor de la segunda constante deberia ser:

$$B = \frac{R\,T}{F} \ln 10 = 0{,}059 \text{ V.}$$

3 En soluciones fuertemente alcalinas, el modelo predice que el ion OH^- inhibe el picado del hierro por cloruros. Según el modelo deberia encontrarse una relación del tipo:

$$E_p = A' + B' \log C_{OH^-}$$

4. El modelo predice tambien que los aniones de acidos débiles actuarán como inhibidores del picado, y que debe esperarse una relacion del tipo:

$$E_p = A'' + B'' \log C_{L^-}$$

It is a generally accepted fact that pitting starts at a certain critical potential, also known as pitting potential. Nevertheless the nature of such a potential still remains uncertain.

In some measurements made with straining metals (1) it was found that the exposure of bare metal to the solution lead to film reformation and repassivation if the potential of the metal was lower than the pitting potential. It was only at potentials equal to or higher than the pitting potential that dissolution of the bare metal began. This was found to be the case with aluminum (2), aluminum alloys (3), stainless steels (4), zirconium (5), zinc (6), and cadmim (7), and it is believed to be a general property of the pitting process.

So it was assumed that one of the main points for pit initiation was some sort of electrochemical reaction taking place on the bare metal at the pitting potential. It seemed that processes like ion adsorption, or film contamination, although important, were not a necessary condition for pit initiation.

Several authors (8-15) have shown that the solution inside a pit, as well as inside a crack or a crevice, has a composition quite different to that of the bulk solution. As early as 1937 Hoar (16) proposed a mechanism of "autocatalytic" pit propagation which considered that the main cause for pitting was the drop of pH inside the pit The origin of such pH drop was the hydrolisis of the metal ions in the aqueous solution, Figure 1.

Assuming that the heterogeneity in the solution composition was a necessary condition for the pit growth, it was tried to evaluate the conditions under which such an heterogeneity would survive.

There are several processes that will oppose to the existence of such an heterogeneity, Figure 2. First of all, there will be diffusion of the metal ions and of the protons from the pit to the bulk of the solution.

Secondly, an important reaction, in those acid solutions, will be hydrogen evolution.

Figure 3 shows the shape of a typical polarization curve of the metal in a pit-like solution. There will be a corrosion potential, or open circuit potential, over which the metal will dissolve quickly, and below which the cathodic reaction of hydrogen evolution will predominate, Figure 4. Since the hydrolisis of the

metal ions is the source of protons for the local acidification, such acidification will not subsist neither at this potential, nor below it In this case the rate of proton production will not be high enough to overcome the rate of proton consumption and dissipation. So it was concluded that there was a minimum potential for pitting survival, and it was the corrosion potential of the metal in the pit-like solution (E_c^*)

This was confirmed for high purity iron in unbuffered, deaerated, sodium chloride solutions, as shown in Figure 5 (17). From the results by Vetter and Strehblow (18), it would seem that the addition of 5×10^{-2} M borate buffer would produce an increase in the pitting potential of nearly 150 mV. We will return to this later on.

There are several other examples where the pitting potential was found to be close to the corrosion potential of the metal in a pit-like solution. Figure 6 shows results for zinc in NaCl; Na_2SO_4; and KI solutions (6) As it is observed, the pitting potentials were all close together, and almost equal to the corrosion potential in the acid solution.

If instead of using electrochemically inactive anions, like chloride, sulfate, or iodide, a reactive anion, like nitrate, was used the situation changed quite a lot Reduction of nitrates in a proton consuming reaction, and it will interfere with the maintainance of an acidified region There will be a higher corrosion potential controlling the acidification The pitting potential in nitrates, Figure 6, was found to be very close to the corrosion potential in nitric acid.

Similar results were found with high purity cadmium, Figure 7. The pitting potentials of cadmium and zinc were close to the equilibrium potentials of the metal dissolution reaction, because of the high overpotential for hydrogen evolution on those metals.

Most clarifying was the study of the effect of alloying elements on the pitting potential of aluminum (3). As shown in Figure 8, alloying with copper increased the pitting potential of the aluminum alloy, while alloying with zinc decreased it, and alloying with magnesium had little or no effect on it By electron microprobe analysis it was found that for aluminum-copper alloys, as well as for aluminum-zinc alloys, there was an enrichment of the alloying element inside the pits In the first case, copper, being a good cathode for hydrogen evolution, increased the corrosion

potential inside the pit In the case of the aluminum-zinc alloy, on the other hand, the corrosion potential was reduced because of the high overpotential of the hydrogen evolution reaction on zinc.

If we look at the literature published on aluminum anodes for cathodic protection, we will find some very interesting results. Reding and Newport (19) made experiments that now would be called galvanostatic pitting potential measurements in sea water. Their results showed that those alloying elements that would have the highest effect on the cathodic reaction of hydrogen evolution, like for example mercury, were those that produced the bigest shift on the pitting potential.

With the idea of local acidification, we can think of some cases where the polarization curve on the metal in the acid solution will have a shape like that in Figure 9. Instead of showing an ever increasing dissolution rate, as for example iron in hydrochloric acid solutions, we could have an active-passive transition like that for iron in sulfuric acid. In such a case, the maintenance of the local acidification will be difficult because of the low current density found in the passive zone. It should be expected then that in increase in the potential over the Flade potential, will lead to pitting inhibition, Figure 10 Curves like these were reported by Leckie and Uhlig (20) for the pitting of stainless steel in mixtures of NaCl plus $NaNO_3$ solutions, and by Vetter and Strehblow (18) for high purity iron in sulfate and perchlorate solutions.

Figure 11 shows the inhibition potentials reported by Vetter and Strehblow for iron in sulfate and perchlorate solutions In the same Figure the Flade potentials for iron were included. The heavier line shows the range of potentials for passivation at the pH values expected inside an iron pit (8, 9). As it is observed, there is a good correlation between the results by Vetter et al and those expected for passivation of the pits.

From their studies on pitting of iron, Vetter and Strehblow (21) developed a pit model. These authors assumed that the causes for pit iniciation should be present in all the stages of pit growth. Therefore they should be present also in the smallest detectable pits. The authors found, for iron, pits as small as 2 microns diammeter, growing with current densities of the order of 1 to 9 A/cm^2 According to their calculations, for iron in a pH 5 buffered solution, the maximum possible change in the smallest pits was: 18 mV potential gradient; 0.9 M change in solution concentration, and an increase of 0.85 units in the pH. These authors concluded that the origin of pitting could not be related to changes in pH,

in potential, or in ionic concentration inside the pit , since they were meaningless in the initial stages of pit growth.

We found that this was not a realistic model, since it was known that the pH inside a pit was usually lower than the pH outside.

Pickering and Frankenthal (22) developed a simpler pit model, and they also analysed the changes in composition to be expected inside a pit. In this model again the pH of the solution inside the pit increased.

Shuch and Swedlow (23) described a one-dimensional analysis of transport in crack-like regions, which could be extended to pitting. But here again we thought that the model was unrealistic, since the pH inside the crack or pit would drop to negative values (up to pH -2 or -3)

A modification of those models was attempted in the present paper Starting from the model by Pickering and Frankenthal, the following modifications were introduced, Figure 12:

1) The metal was assumed to be in presence of a sodium salt of the aggressive anion.

2) The anodic reaction:

$$Me = Me^{n+} + ne \qquad (I)$$

was followed by the equilibrium reaction:

$$Me^{n+} + H_2O \rightleftharpoons Me(OH)^{(n-1)+} + H^{+} \quad ; \quad (^{*}K_1) \qquad (II)$$

and this equilibrium was reached very quickly.

The equilibrium reactions considered in the present model are a simplified description of the processes taking place inside a pit, since polinuclear complexes could be formed. Nevertheless, this reactions will show us the minimum degree of acidification expected inside a pit. On the other hand, calculations were made only for those metals were the formation of polinuclear complexes was known to be small (24).

The third modification was:

3) The salt of the aggressive anion acted as a supporting electrolyte for the ionic species formed in reactions (I) and (II)

The equilibrium reaction considered was:

$$\underset{S_1}{2Me^{n+}} + \underset{S_2}{H_2O} + \underset{S_3}{OH^-} \rightleftharpoons \underset{S_4}{2Me(OH)^{(n-1)+}} + \underset{S_5}{H^+} \qquad \text{(III)}$$

It was written in this way so as to account for the contribution of the OH^- ions at pH values higher than 7.

The mathematical treatment of a system like this is found in Vetter's book on ELECTROCHEMICAL KINETICS (25).

Inside the pits there will be five species of unknown concentrations, and the five equations correlating those concentrations will be:

flow S_{Me} ; $$D_1 \frac{dC_1}{dx} + D_4 \frac{dC_4}{dx} = -\frac{i}{nF}$$

flow S_O ; $$D_2 \frac{dC_2}{dx} + D_3 \frac{dC_3}{dx} + D_4 \frac{dC_4}{dx} = 0$$

flow S_H ; $$2D_2 \frac{dC_2}{dx} + D_3 \frac{dC_3}{dx} + D_4 \frac{dC_4}{dx} + D_5 \frac{dC_5}{dx} = 0$$

$$*K_1 = \frac{C_4 \cdot C_5}{C_1}$$

$$K_w = C_3 \cdot C_5$$

To solve this system of equations, the following boundary conditions were assumed:

$x = 0$

$$C_1 = 0 \text{ mol.liter}^{-1}$$
$$C_2 = 55.5 \text{ mol.liter}^{-1}$$
$$C_3 = 10^{-K_w+pH} \text{ mol.liter}^{-1}$$
$$C_4 = 0 \text{ mol.liter}^{-1}$$
$$C_5 = 1^{-pH} \text{ mol.liter}^{-1}$$

$$D_1 = D_2 = D_4 = 10^{-5}\ cm^2.\ sec^{-1}$$

$$D_3 = 5\ 3 \times 10^{-5}\ cm^2.\ sec^{-1}$$

$$D_5 = 9\ 3 \times 10^{-5}\ cm^2.\ sec^{-1}$$

As a first approximation, the diffusion coefficients of the involved species were taken as equal to $10^{-5}\ cm^2.\ sec^{-1}$, with the only exception of H^+ ions and OH^- ions.

The equilibrium constants used were those given by Sillen and Martell (24).

Calculations were made for Ni; Co; Zn; Fe; Al and Cr.

Figure 13 shows the results obtained for zinc. The ionic concentrations have been ploted as a function of pit depth and current density. In this way, if the current density in the pit is known, the graph will tell us the ionic concentrations at the bottom of the pit, for different pit depths. On the other hand, given a certain pit depth, the graph will tell us the current density required to get a certain change in the ionic concentration. No assumptions were made about the way in which such changes in current density could be obtained. In practice, it will mean that we will have to change the electrode potential the necessary amount so as to get the required current density. In most of the cases of acid solutions, as inside the pits, a logarithmic relation between current density and electrode potential should be expected.

We see in Figure 13 that the concentration of protons inside the pit could change quite a lot. We also see that the pH inside the pit will be lower than the pH of the bulk solution, as occurs in practice.

The next question was, what proton concentration was necessary to start pitting?

In a first approximation the same criterium as applied by Pourbaix in his diagrams was used here (26). Pourbaix divides the passivity areas from the corrosion areas in this way. Knowing the solubility product of the passivating oxide film, the pH value at which such oxide film will be in equilibrium with a solution containing traces of metal ions ($10^{-6}M$) is calculated. Those values were indicated in the present diagrams with a cross (+).

At pH values higher than that of the cross the oxide film will be stable. At pH values lower than that of the cross the oxide film will start to dissolve.

On the right side of Figure 13 results by Davies and Lotlicar (27) were plotted. These authors measured galvanostatically the polarization curves for zinc at different pH values. They found that zinc passivated at pH values equal to 9; 10; and 11 Zinc did not passivate at pH values of 8 and 12. Between pH 8 and pH 9 there was a certain pH value below which zinc does not passivate any more This result is in good agreement with that calculated from the solubility product, and indicated by the cross

According to Figure 13 if we have a current density of 1 A/cm^2 we will reach the necessary acidification in very small pits, of the order of 20 Å. Actually a crack in the oxide film will give a diffusion path big enough to reach such acidification

The same calculations were made for iron, Figure 14 Here again, as for most of the studied metals, it was found that the necessary degree of acidification could be reached at very low X.i values Always in the order of 10^{-6} A/cm It was also found that a very small increase in the current density, or in the size of the pit, would produce a sharp increase in the proton concentration inside the pit.

If instead of using a Log-log representation, the pH changes were ploted as a function of the pit length, for a current density of 1 A/cm^2 the results of the Figure 15 were obtained. As it was measured, for example, for fissures in iron (9), the calculated pH value was almost constant along the pit length, and was in the range of pH 3 to 4.

A similar diagram of ionic concentration was found for Ni, Figure 16 Since Ni and Co have similar *K values, the same diagram applies to Co.

As for Al, Figure 17, the necessary degree of acidification was much higher than for the previous metals, but again the calculations showed that the acidification could be reached with very low X.i values

For Cr it was also found that the necessary degree of acidification was reached at very low X.i values, Figure 18 So far it was considered that the current density inside pit could reach values of the order of 1 A/cm^2 In the already mentioned

cases the diffusion path provided by a crack in the oxide film was long enough to get the necessary degree of acidification. For some metals, as it is probably the case for Cr, it could happen that the necessary current density could not be reached before passivating the metal. In such a case the metal will not be susceptible to pitting. But a given X.i value can be reached even with small current densities, if the diffusion path is long enough. That is the case when there is a crevice on the metal surface. Then the metal could be resistant to pitting, but will be susceptible to crevice corrosion. From an electrochemical point of view, both corrosion processes will be equal.

It was shown by several authors (20, 28) that pitting of iron in NaCl solutions is inhibited by NaOH. This was also found in the present calculations. Figure 19 shows the effect of the external pH on the pH profile inside the pit. For similar specimens, to reach the same degree of acidification it was necessary to change one order of magnitud the current density every time there was a change of one unit in the pH value. If the current density in the acid solution inside the pit follows a logarithmic law, this means that there will be also a logarithmic relation between the pitting potential and the concentration of the OH^- ions.

$$E_p = A' + B \log C_{OH^-} \qquad (IV)$$

Where A' and B' are constants, and C_{OH^-} is the OH^- ion concentration. B' should be equal to the Tafel slope in the pit-like solution.

There are other anions that interfere with pitting, acting as pitting inhibitors. For example, borate ion inhibits the pitting of zinc, as shown by Augustinski et al. (29). They reported that the pitting potential increased as a function of the logarithm of borate ion concentration.

Zinc borate is insoluble, so the presence of borate ions will produce a depletion of zinc ions inside the pit. From the solubility product of the zinc borate (24) it was possible to calculate the modifications introduced in the ionic concentration profiles. Figure 20 shows the result of such calculations for an external borate concentration of 10^{-1}M. In absence of borate ions the zinc reached the necessary degree of acidification with an X.i value of about 2×10^{-7} A/cm. In presence of 10^{-1}M borate the X.i value reached almost 1^{-4} A/cm.

Figure 21 shows the effect of various borate ion concentrations on the Zn diagram No effect should be expected for borate ion concentrations below 10^{-4}M For higher concentrations, an increase in one order of magnitud in the concentration of borates will produce an increase of about one order of magnitud in the current density. From this it was concluded that the relation between the pitting potential and the borate ion concentration should follow the same law as the relation between electrode potential and current density for the dissolution of the metal in the acid solution If the anodic dissolution of the metal in the pit-like solution follows a Tafel law, the pitting potential should be given by:

$$E_p = A'' + B'' \log C_{L^-} \qquad (V)$$

where A" and B" are constants, and C_{L^-} is the inhibiting anion concentration B" should be equal to the Tafel slope in the pit-like solution.

Sillen and Martell did not report the solubility product of the iron borate, nevertheless from the values for cobalt borate, and nickel borate, the solubility of iron borate was estimated as $10^{-8\ 6}$. The results of the calculations for iron are shown in Figure 22. As mentioned above, Vetter and Strehblow (18) used a borate ion concentration of 5×10^{-2}M. According to this diagram, such a concentration will produce a shift in the X i value of about 2 orders of magnitud From the Tafel slope for iron (50 to 75 mV) the estimated potential difference should be somewhere between 100 to 150 mV This estimation is in good agreement with the difference in pitting potentials found experimentally, which was between 120 to 180 mV, Figure 5.

When the concentration of the aggressive anion is changed over a wide range of values, the assumption of a supporting electrolyte does not apply any more. In this case the potential gradient inside the pit can not be ignored, and the following equations must be used:

$$\frac{i \cdot \nu_j}{n \cdot F} = D_j \left(\frac{dC_j}{dx} + Z_j \quad C_j \quad \frac{F}{R \cdot T} \quad \frac{d\phi}{dx} \right)$$

$$C_j = C_o \cdot e^{-(z_j \cdot F/R \cdot T)\phi}$$

$$\sum Z_i \cdot C_j = 0$$

The resolution of the equations for a system including the hydrolisis equilibria is quite complex. Nevertheless the resolution of a simpler system gave very useful information Assuming that we have dissolution of a trivalent metal, like aluminum, we have to solve the following four equations:

$$\frac{i}{3D_1 \cdot F} = \frac{dC_1}{dx} + 3 C_1 \frac{d\psi}{dx} \quad ;$$

$$\left(\text{where } \psi = \frac{F}{RT} \phi;\ C_1 = C_{Al^{3+}}\right);$$

$$C_2 = C_o \cdot e^{-\psi} \quad ; \ (\text{where } C_2 = C_{Na^+});$$

$$C_3 = C_o \cdot e^{+\psi}; \quad (\text{where } C_3 = C_{Cl^-});$$

$$3C_1 + C_2 - C_3 = 0$$

As for the boundary conditions, they were the same as in previous calculations.

For the case of aluminum in 1M NaCl solution it was found, Figure 23, that the considerations of potential gradients did not modify the diagram for the initial steps of pit growth So all the previous discussion is valid for pit initiation The effect becomes important for X.i values of the order of 10^{-2} or higher. Considering that most of the pitting cases studied in the literature showed current densities of the order of 1 A/cm^2, and that the size of the pits should be of the order of 10^{-2} cm, it can be safely assumed that most of the published literature on pitting potentials correspond to X.i values of about 10^{-2}. Doing the calculations for various NaCl concentrations it was found, Figure 24, that the potential gradient was higher the lower the salt concentration, and that the difference in potential, for each increase of one order of magnitud in the salt concentration was equal to -59 mV, or more precisely:

$$E_p = A - B \log C_{NaCl} \qquad (VI)$$

where A and B are constants, and C_{NaCl} is the NaCl concentration

And·

$$B = \frac{R.T}{F} \quad \ln 10 = 0.059 \text{ V}$$

Figure 25 shows some results found in the literature It was observed that for aluminum and for zirconium the potential gradient inside the pit accounts for all the variation of pitting potentials observed. As for stainless steel, more than a half of the pitting potential change is due to the potential gradient.

Another potential contribution to be considered, and which was not evaluated in the present work, is the ohmic drop inside the pit. The lower the salt concentration, the higher the ohmic drop This could explain the slopes higher than -59 mV reported in the literature.

It is concluded that the pitting potential is a value based on the corrosion potential of the metal in the acid solution (E_c^*), and it is increased by a potential gradient function of the salt concentration, plus an ohmic drop, plus a potential contribution function of the concentration of the inhibitor anions:

$$E_p = E_c^* + \phi_{f(C^o)} + \Gamma\Big)_{\Omega} + E_{f(Inh)} \qquad \text{(VII)}$$

As for the pitting inhibition potentials, like those reported by Leckie and Uhlig (20) and by Vetter and Strehblow (18) it is considered that such values are equal to the passivation potential of the metal in the pit-like solution:

$$E_i = E_F^* \qquad \text{(VIII)}$$

Several authors have reported pit initiation and pit protection potentials (30-32) Those potentials can also be explained with the present model. Figure 26

For pit initiation we have to apply a potential high enough to reach the X i=1 condition Figure 26 a).

If the potential is maintained constant, X will increase with an almost constant current density We will reach then the X i=2 value. Figure 26. b)

Now, if we reduce the electrode potential, the current

density will decrease Nevertheless the pit will remain active while the X.1 value is higher than 1 Only at X i = 1 (Figure 26 c), the pit will repassivate In this way the pit initiation potential will be higher than the pit protection potential The limit for the decrease of the pit protection potential will be given by the corrosion potential of the metal in the pit-like solution.

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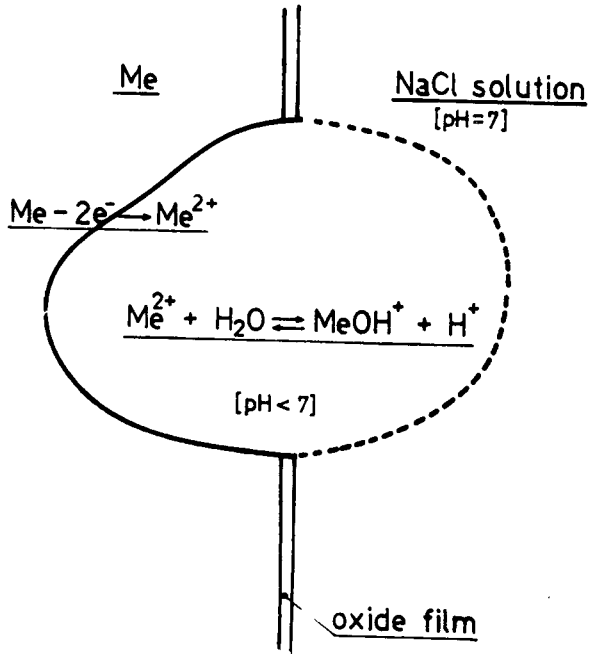


FIGURE 1

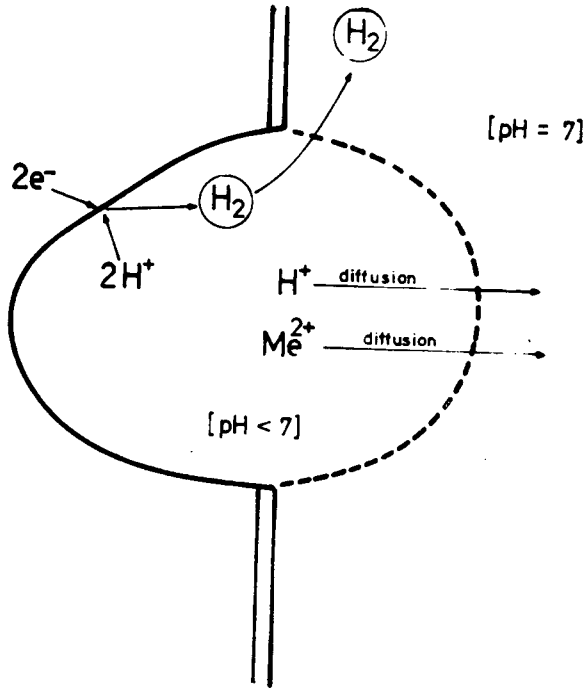


FIGURE 2

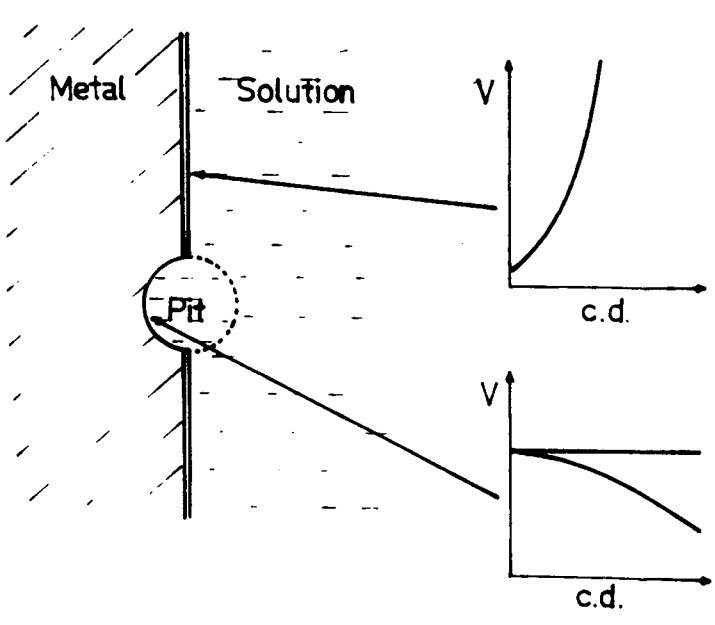
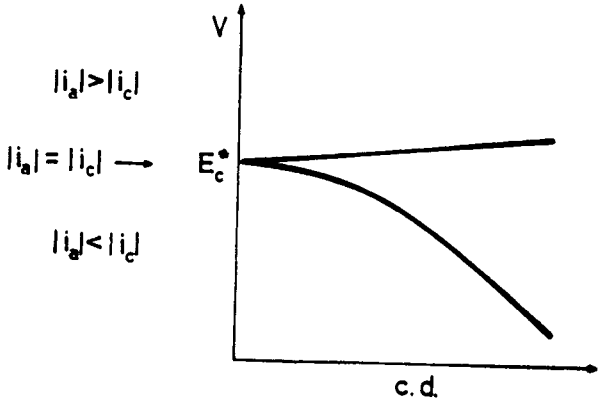


FIGURE 3



i_a : $Me = Me^{2+} + 2e^-$

i_c : $2H^+ + 2e^- = H_2$

FIGURE 4

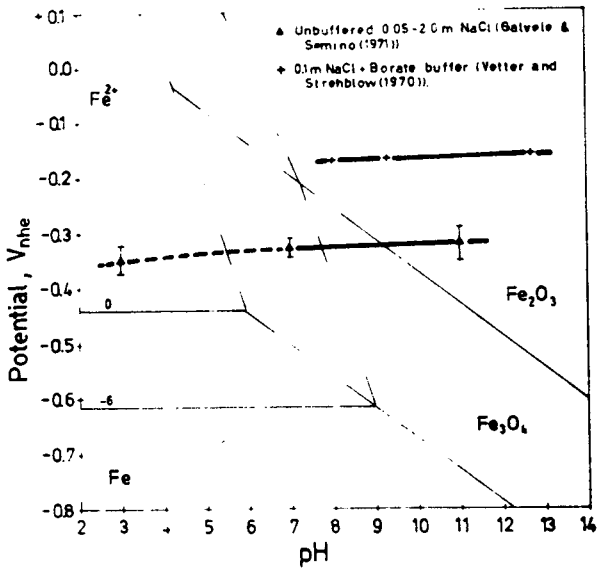


FIGURE 5

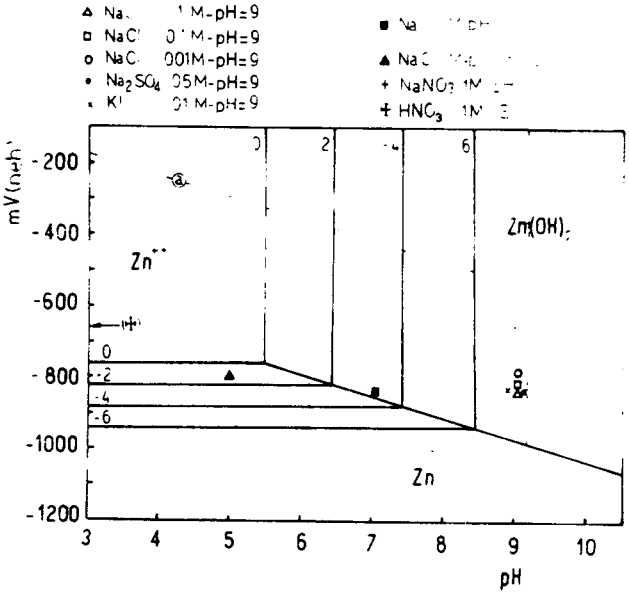


FIGURE 6

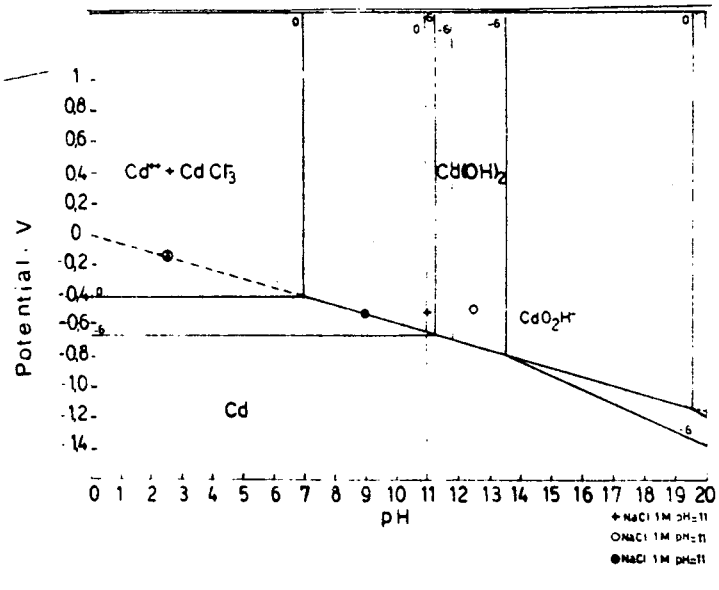


FIGURE 7

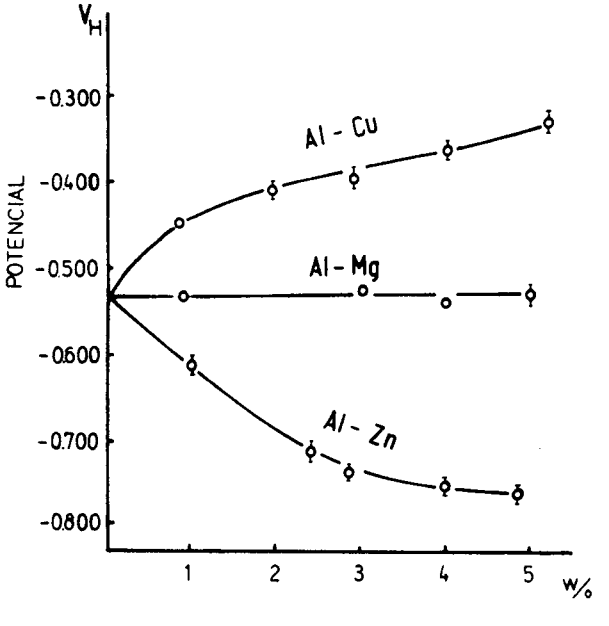


FIGURE 8

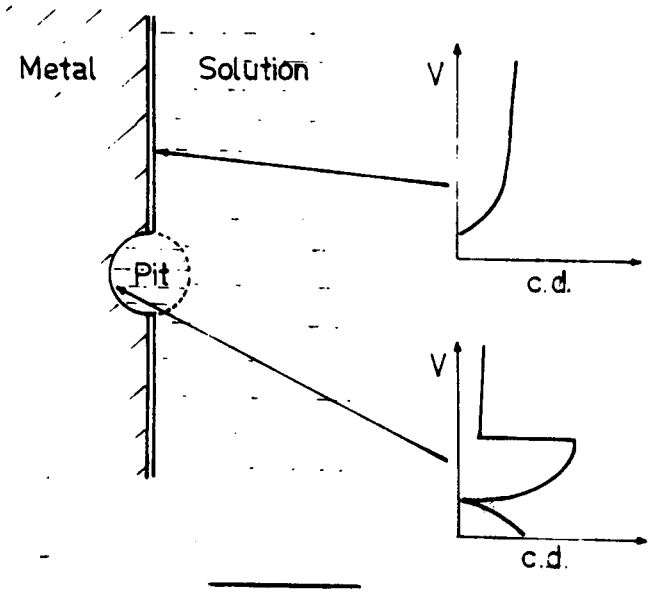


FIGURE 9

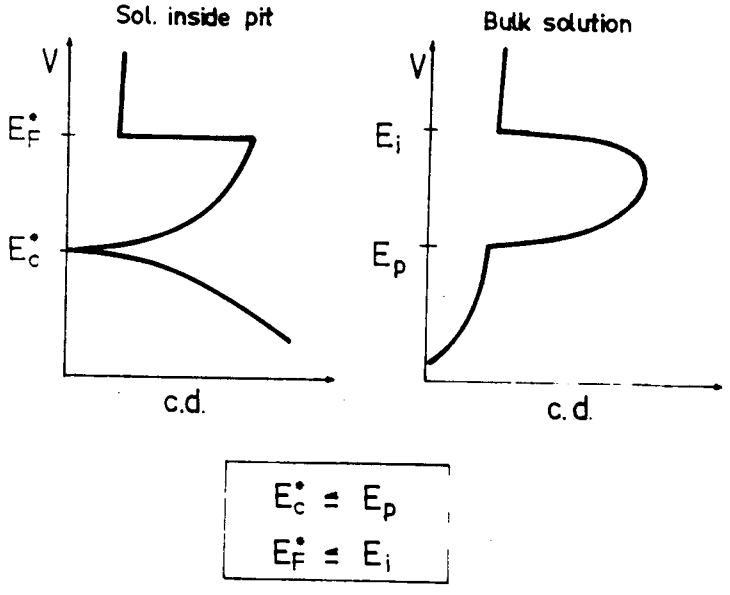


FIGURE 10

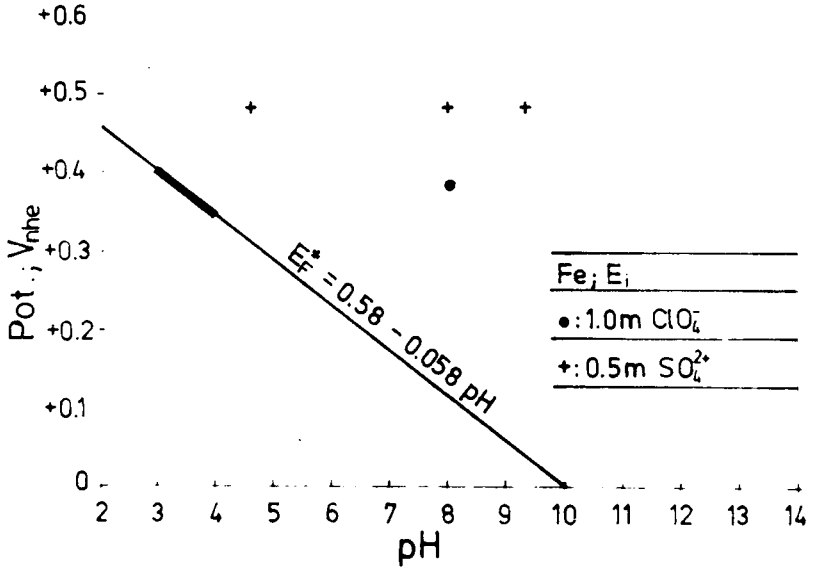


FIGURE 11

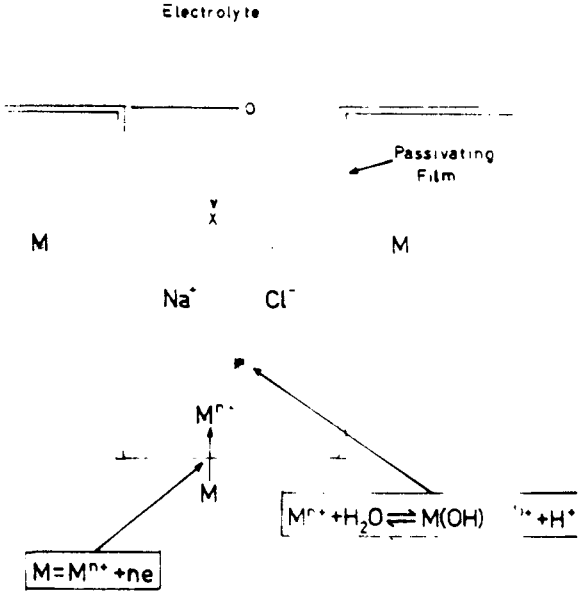


FIGURE 12

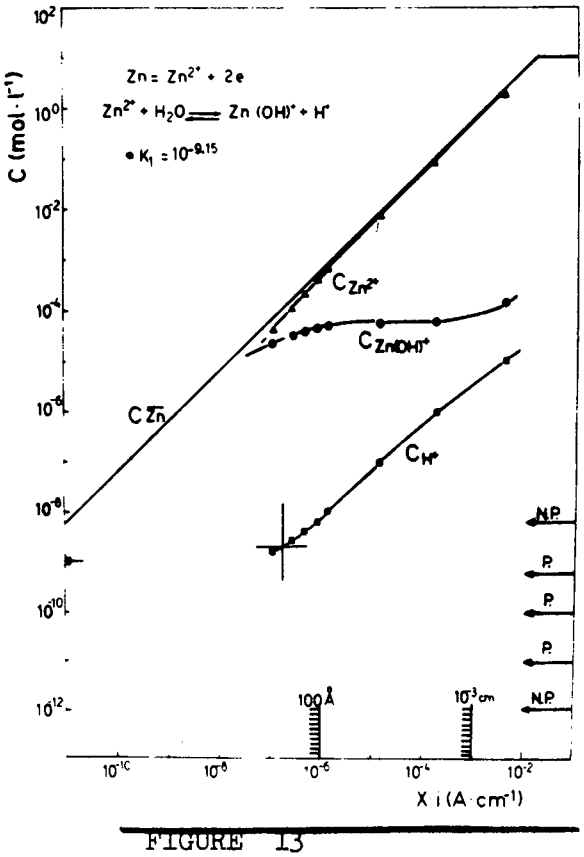


FIGURE 13

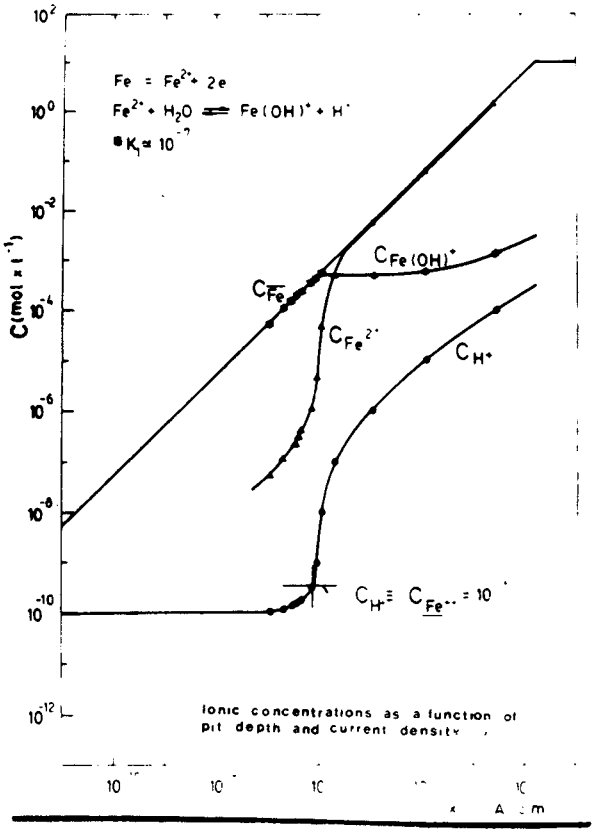


FIGURE 14

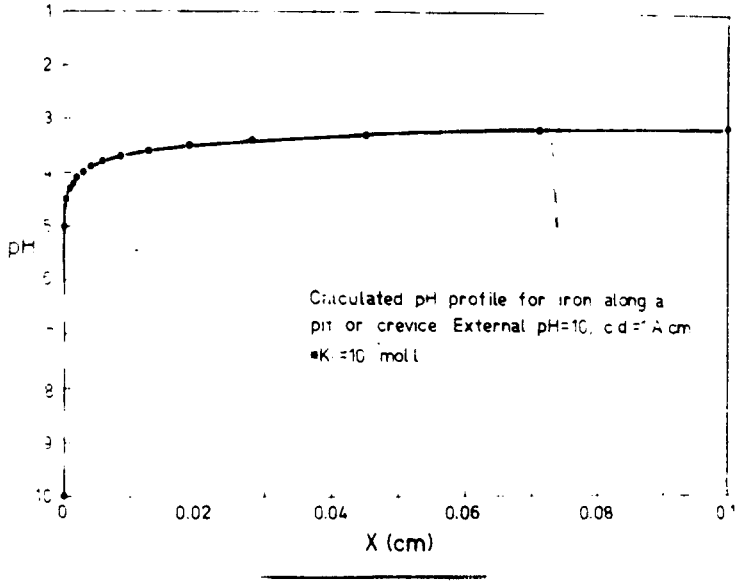


FIGURE 15

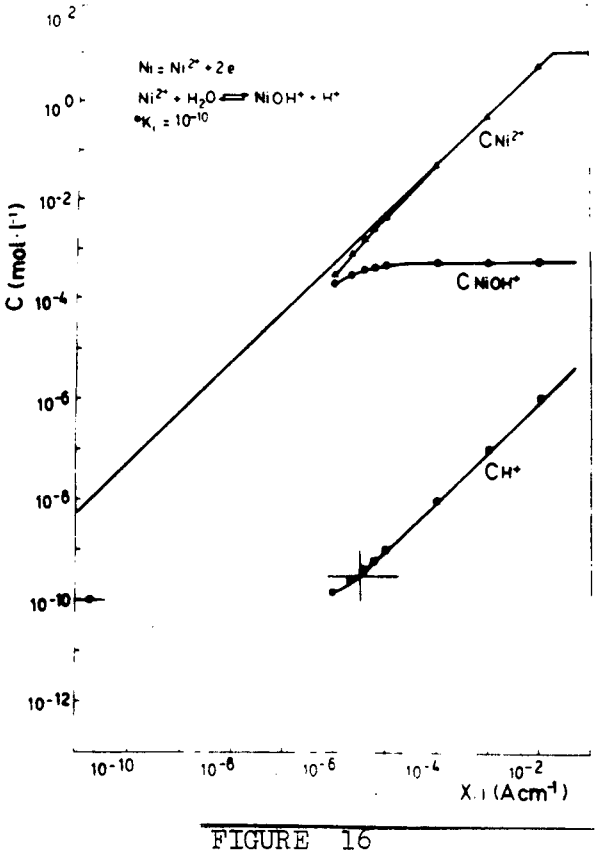


FIGURE 16

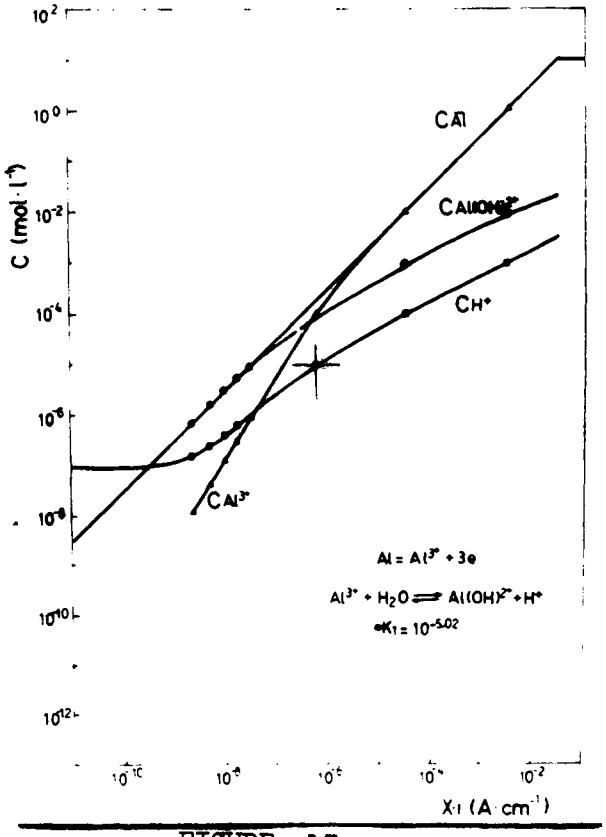


FIGURE 17

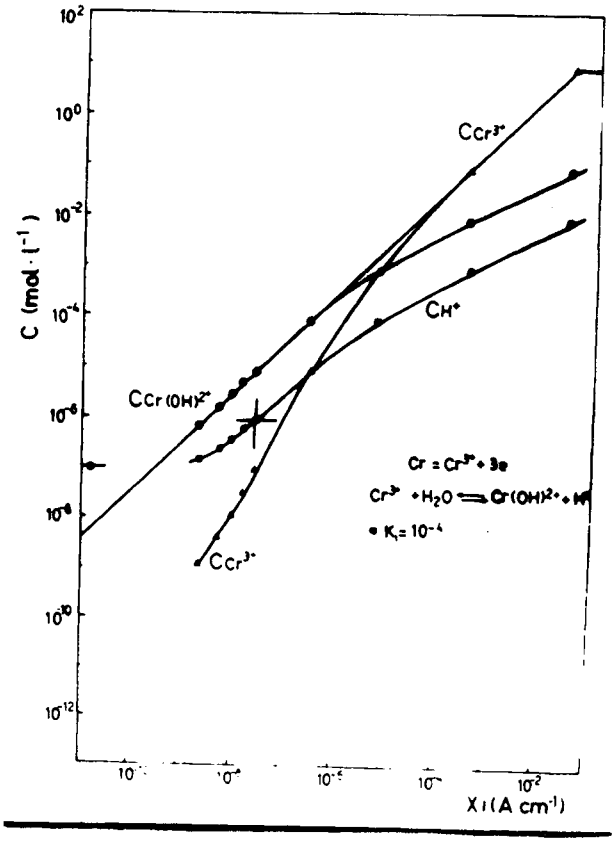


FIGURE 18

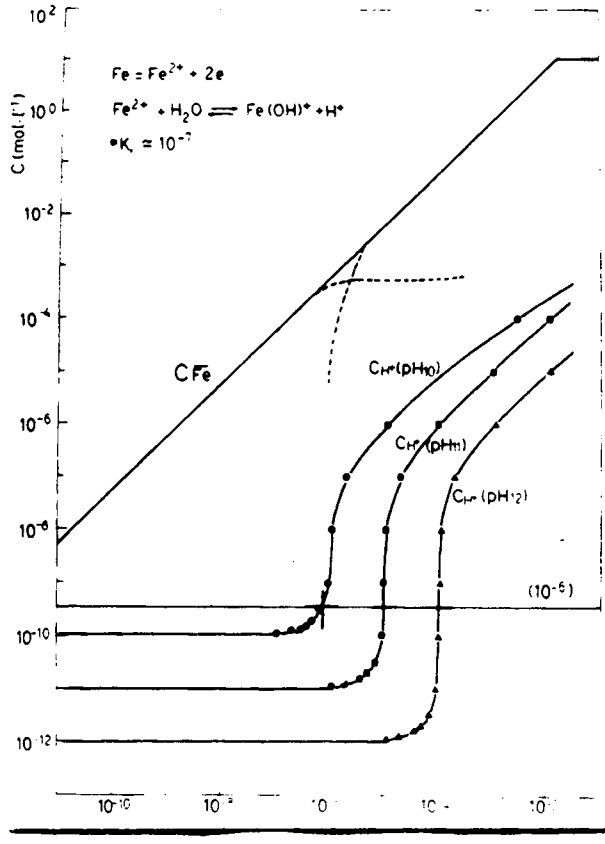


FIGURE 19

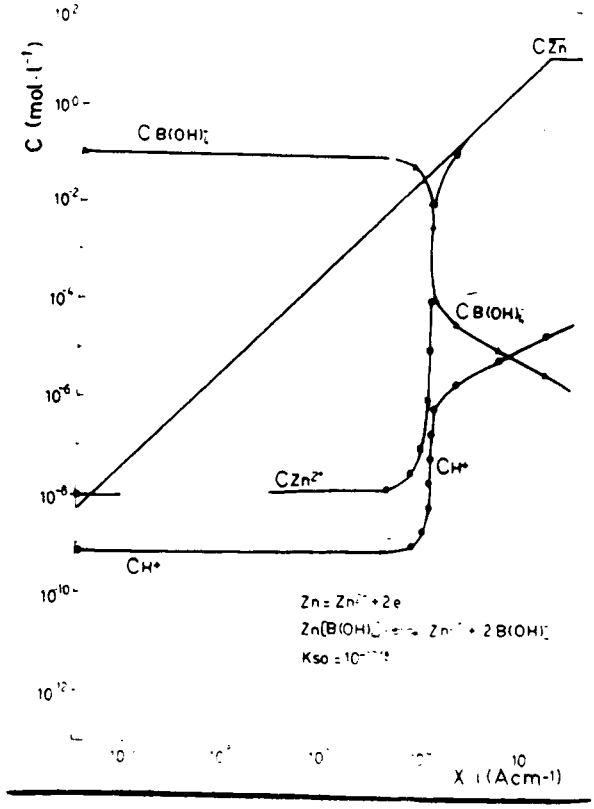


FIGURE 20

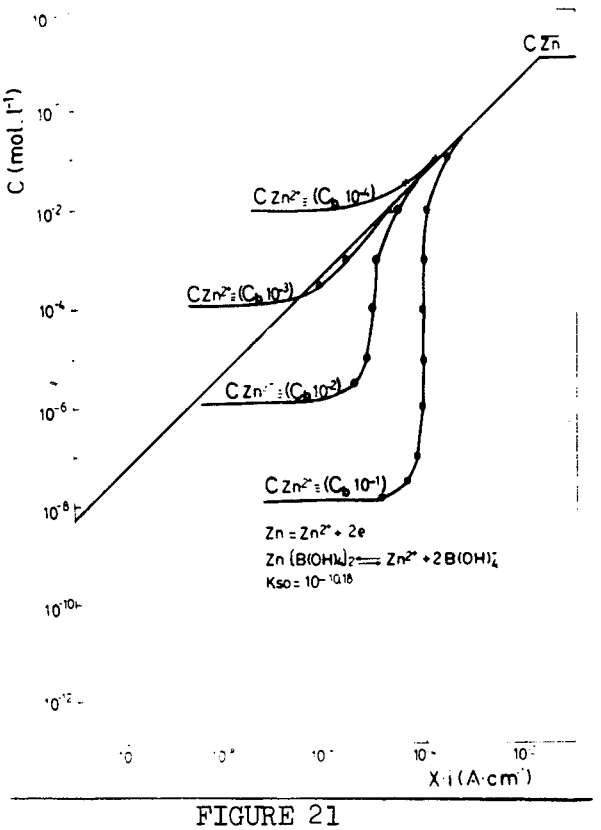


FIGURE 21

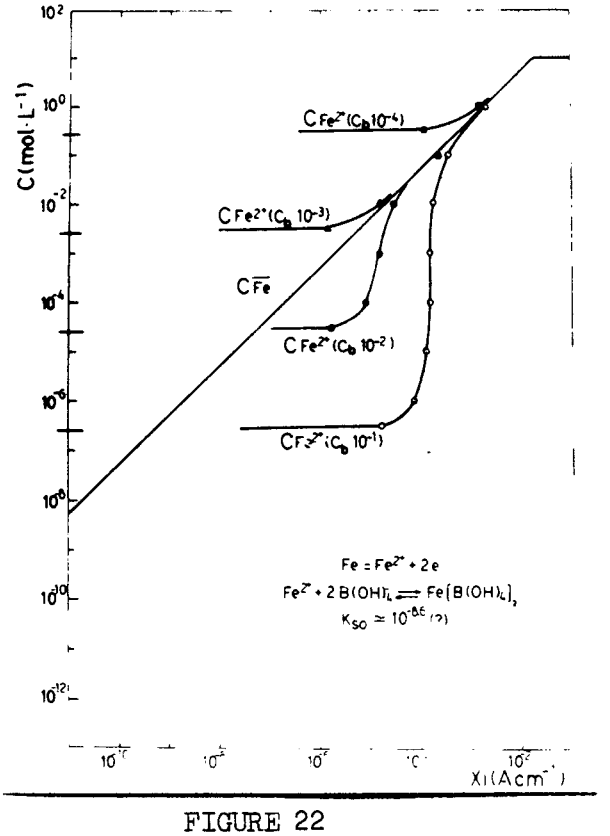


FIGURE 22

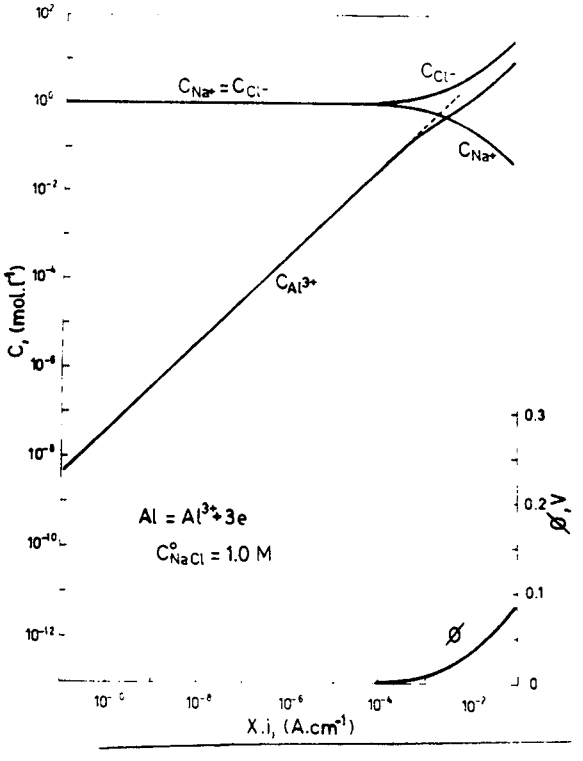


FIGURE 23

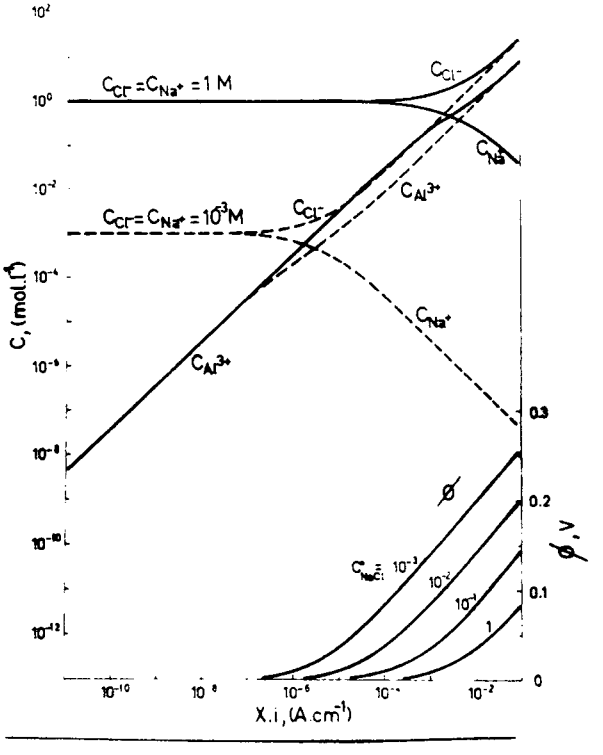


FIGURE 24

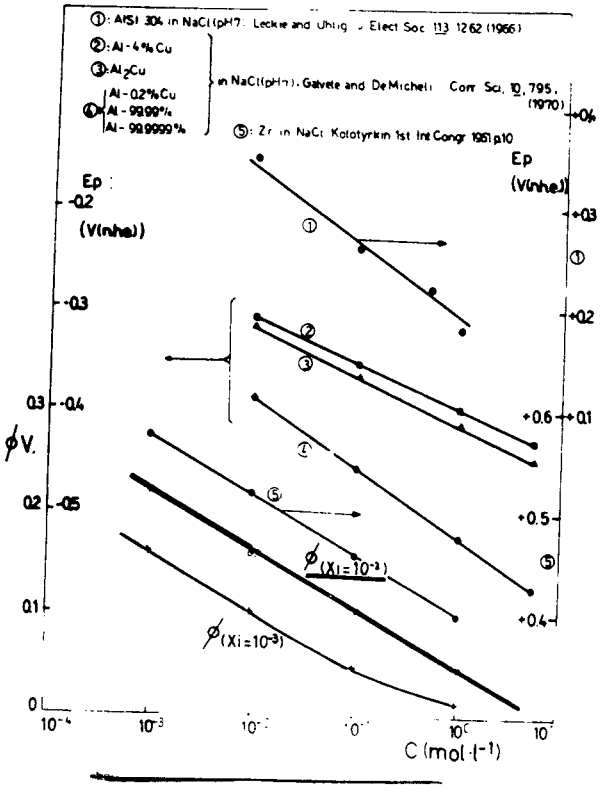


FIGURE 25

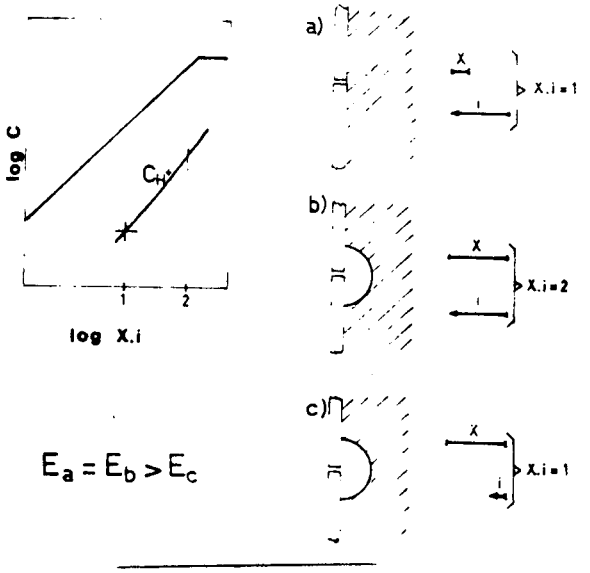


FIGURE 26