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Electrochemical Polarization and Passivation of Iron in Acid Solutions

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Summary. The potentiodynamic polarization of the iron electrode in sulphuric acid solutions was studied. The formation of a passivating film on the electrode upon anodic oxidation in sulphuric acid solution depends on the concentration of the acid. Addition of Cl^- ions to sulphuric acid solutions raises the current densities along both the active and passive regions. The difference between the dissolution current in halogen-containing media and solutions devoid of these ions, i.e., the enhancing effect of Cl^- ions, Δi, varies with the aggressive ions concentration according to $\log \Delta i = a_5 + b_5 \log C_{agg}$. Organic carboxylates enhance the active dissolution of iron through their participation in the dissolution mechanism, while they inhibit pitting corrosion through competitive adsorption with Cl^- ions for adsorption sites on the metal surface.

Keywords. Iron; Polarization; Passivation; Pitting; Potentiodynamic.

Elektrochemische Polarisation und Passivierung von Eisen in sauren Lösungen

Zusammenfassung. Es wurde die potentiodynamische Polarisierung der Eisenelektrode in schwefelsauren Lösungen untersucht. Die Ausbildung eines passivierenden Films auf der Eisenelektrode nach der anodischen Oxidation hängt von der Säurekonzentration ab. Zugabe von Cl^--Ionen zur Schwefelsäurelösung erhöht die Stromdichten sowohl in den aktiven als auch den passiven Bereichen. Der entsprechende Lösungsstrom mit bzw. ohne diese Ionen, also der verstärkende Effekt der Cl^--Ionen variiert mit der Konzentration der aggressiven Ionen: $\log \Delta i = a_5 + b_5 \log c_{agg}$. Organische Carboxylate verstärken die aktive Lösung von Eisen durch ihre Teilnahme am Lösungsmechanismus, andererseits inhibieren sie Narben-Korrosion, da sie mit den Cl^--Ionen bezüglich möglicher Adsorptionsstellen an der Metalloberfläche konkurrieren.

Introduction

The nature of the passive film on an iron anode in H_2SO_4 has been studied by several authors. Herbsleb and Engell [1] proposed that a noncrystalline film is first produced, which transformed into a $FeSO_4 \cdot 7\,H_2O$ film as the potential is shifted more in the noble direction. Williamson and Hines [2] proposed a film of Fe_2O_3 to be responsible for the final passivity of mild steel in H_2SO_4 solutions. Cohen et. al. [3 – 5] are of the opinion that the film formed upon anodic polarization of iron in sulphuric acid has a duplex structure with Fe_3O_4 next to the metal and Fe_2O_3

on the outside. However, several recent studies have indicated that this passivating film is entirely ferric in nature, but its outer region is hydrated. Whatever the exact nature of this film, it behaves essentially as a ferric oxide. At potentials more negative than the reduction potential of this oxide film, the iron electrode can be protected by another passivating film [6]. Evidence from electron diffraction [5 – 7] and cathodic reduction studies [5, 8, 9] indicates this film to have a structure and properties similar to magnetite. However, some recent work [10,11] suggests that this film does not have a definite composition but that its essential feature is that it contains ferrous ions in increasing proportion as the potential becomes more negative. Although the active-passive behaviour of stainless steels is more pronounced than that of iron, it is of interest from the fundamental as well as the practical points of view to determine the extent of the chloride ions affect on the passive behaviour of iron. The aim of the present investigation is to study the active passive behaviour of iron in H_2SO_4 solutions containing chloride ions and the influence of addition of sodium salts of organic carboxylates with the help of electrochemical polarization measurements by the potentiodynamic technique.

Experimental Part

The cell was made of pyrex glass with a thermostating jacket and had a capacity of 250 ml. Seven ground glass standard joints on top of the cell permitted the insertion of the working electrode, the platinium counter electrode compartment, the reference electrode compartment, gas inlet and gas outlet, while the remaining two joints were used for insertion of a thermometer, and for filling the cell when needed. The potential of the working electrode was measured relative to a saturated calomel electrode over a salt bridge whose tip was drawn to almost touching proximity to the working electrode. The working electrode was in the form of a short rod arranged as to make the exposed area to solution remaining always 0.2 cm^2. It was polished with the finest grade emery paper, degreased with acetone, washed with bidistilled water, and dried immediately before use. The potential of the working electrode was controlled by a Wenking potentioscan, type POS 73. The current density-potential curves were recorded on a *X-Y* recorder, type Advance HR 2000. All measurements were made in unstirred solutions at room temperature (25 ± 0.5°C). Solutions of sulphuric were prepared from analytical grade quality and standardized by the usual standard methods.

Results and Discussion

The effect of addition of chloride ions on the potentiodynamic anodic polarization behaviour of the iron electrode traced in 0.05, 0.1 and 0.5 *N* H_2SO_4 solutions at a sweep rate of 1 mV/s have been investigated (see, for example, Fig. 1).

In the chloride free solutions the following observations were made in agreement with results of previous workers [12, 13]:

a. As the potential of the working electrode is shifted into the noble (positive) direction, an increase in the anodic current density is noted representing the active dissolution of the metal. This increase is fairly well represented by a Tafel type relationship [14]. At higher anodic displacements a deviation from linearity in the sense of lower current densities is noted. This indicates auto-inhibition of the anodic reaction by the dissolution product.

b. A region of current oscillations is observed covering a potential range which depends on the acid concentration. Both the frequency and amplitude of oscillations increase with the increase of the electrode potential in the noble direction. These oscillations in current are characteristic of the active passive transition.

c. At a certain definite potential (depending on the sulphuric acid concentration), which is more positive with increasing acid concentration, the current drops abruptly to low values indicating the onset of passivity. The electrode surface is considered now to be covered by a pore-free passivating oxide film of trivalent iron. These passivating potentials are commonly identified with the flade potential [13].

d. The current flowing along the passive region is commonly identified as the corrosion current and is used to counteract the chemical dissolution of the oxide by the electrolyte [13]. The constancy of these currents is attributed to the stability of the passivating oxide film on the iron surface.

The following observations were made in connection with the addition of increasing concentrations of Cl^- ions on the anodic behaviour of iron:

a. The dissolution current density flowing along the active region progressively increases with the increase in the concentration of the aggressive Cl^- ions, while the corrosion potential remains unaffected. This behaviour could be attributed to the adsorption of Cl^- ions on the bare metal surface at potentials less positive than those accepted for the onset of passivity with the catalysis of the dissolution reaction.

b. In solutions of lower Cl^- ion content, where the polarization curves still exhibit the same passivation features as in Cl^- free solutions, the flade potential, E_f, is practically independent of the Cl^- ion concentration. This reveals that the nature of the passivating film is basically the same in all solutions.

c. In presence of slightly higher Cl^- ion concentrations, the flade potential, E_f at which passivity onset takes place is shifted into the positive direction with increasing the Cl^- ion content. This indicates that the presence of these Cl^- ion

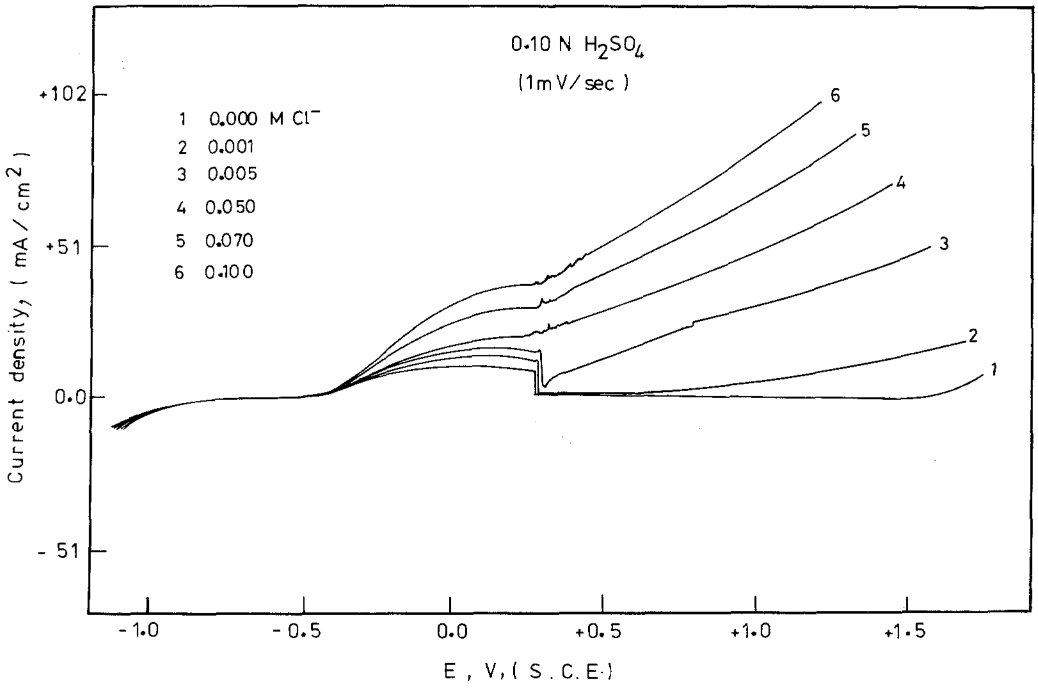

Fig. 1. The potentiodynamic anodic polarization of iron in 0.1 *N* H_2SO_4 solution at a sweep rate of 1 mV/s and effect of different concentration of Cl^- ions

concentrations causes the retardation of metal passivation. The variation of E_f with the logarithm of the Cl^- ion concentration in $0.5\,N$ H_2SO_4 may be seen in Fig. 2, where a straight line relationship is obtained up to a concentration of $0.05\,M$ Cl^- ion, obeying the form:

$$E_f = a_4 + b_4 \log C_{Cl^-} \tag{1}$$

where a_4 and b_4 are constants.

d. In relatively concentrated Cl^- ion solutions, however, passivity does not develop. The region of active/passive transition shifts towards more positive potentials, and the current oscillations become more violent. The iron electrode continues to dissolve up to a potential of +1.7 V in the noble direction. Examined after the polarization experiments, the electrode exhibited visible pits whose number per unit area increased with the Cl^- ion content of the solution.

e. In contrast to the behaviour of stainless steels, and in agreement with previous authors [15] the pitting of iron in H_2SO_4 solutions does not develop at a definite potential, but occurs along the whole passive range. The aggressive Cl^- ions raise the current flowing along the passive region as a whole until it virtually equals, or is higher than that corresponding to the active dissolution. In the presence of a particular Cl^- ion content the corrosion current increases steadily with the electrode potential.

In the present study we can see from the curves of Figs. 3 – 5 that $\log \Delta i$ (i. e. $i_{Cl^-} - i_O$) is linearly related to $\log C_{Cl^-}$ in solution of 0.05, 0.1, $0.5\,N$ H_2SO_4, according to the following equation:

$$\log \Delta i = a_5 + b_5 \log C_{Cl^-} \tag{2}$$

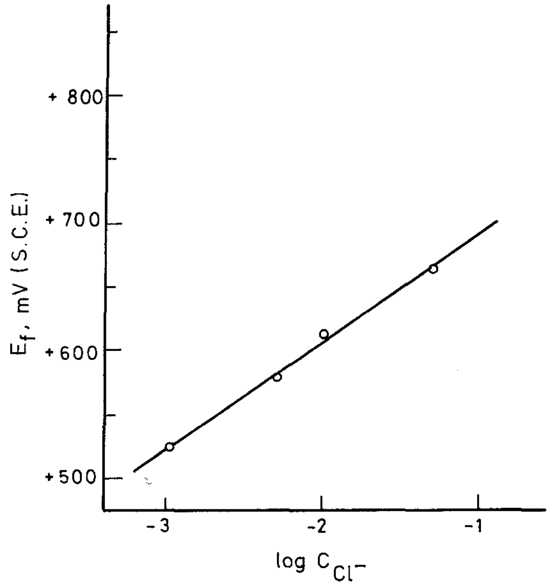

Fig. 2. The variation of the flade potential E_f with the logarithm of the Cl^- ion concentration in $0.5\,N$ H_2SO_4

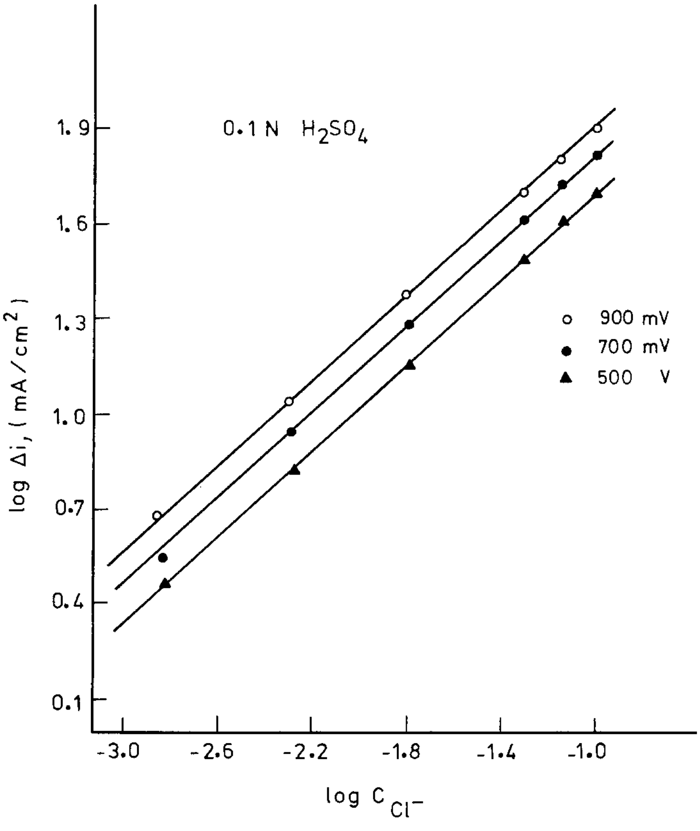

Fig. 3. The relation between log Δ*i* and the log of concentration of Cl^- ions in 0.05 *N* H_2SO_4

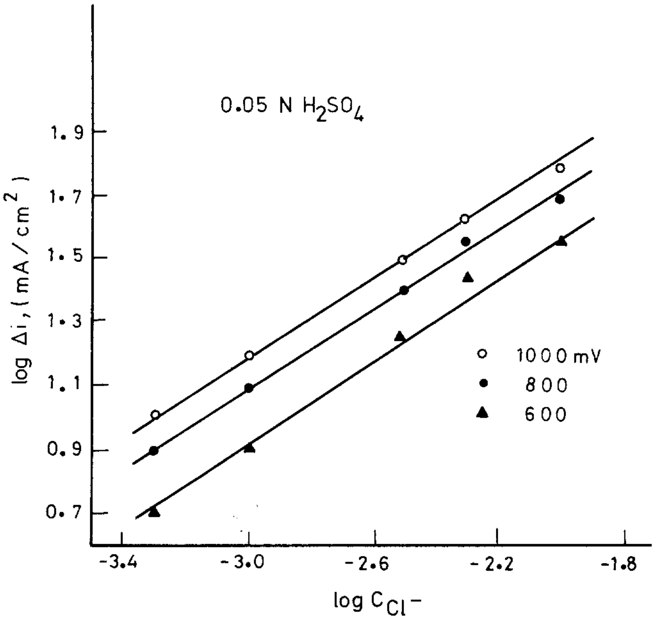

Fig. 4. The relation between log Δ*i* and the log of concentration of Cl^- ions in 0.1 *N* H_2SO_4

where a_5 and b_5 are constants. From the straight lines obtained at different potentials in 0.05, 0.1, and 0.5 N H_2SO_4 it is seen that the relationships are independent of the potential at which the current is measured. The slopes b_5 ($\partial \log \Delta i / \partial \log C_{Cl^-}$) of the straight lines obtained from Figs. 3 – 5 equal 0.62, 0.89, and 1.8. At the same time it was found that a tenfold increase in the concentration of Cl^- ions raises the dissolution current density by factors of 6.2, 8.9, and 18 respectively. It is evident from these values and previous results [16] that the current density varies with the concentration of the aggressive anion.

Influence of Organic Carboxylates on the Anodic Behaviour of Iron in H_2SO_4 Solutions Containing Cl^- Ions

The effect of increasing concentrations of the sodium salts of the organic carboxylic acids, acetic, propionic, citric, and succinic, on both the active dissolution and pitting corrosion of iron in two different concentrations of H_2SO_4 solutions in the presence of Cl^- ions in 0.1 N H_2SO_4 + 0.1 M Cl^- ion and in 0.05 N H_2SO_4 + 0.1 M Cl^- at sweep rate of 1 mV/s and at 25°C was examined (see, for example, Fig. 6).

Inspection of these curves reveals the following interesting features:

a. Addition of slightly lower concentrations of these carboxylic salts causes first the increase of the dissolution current density of iron in the active region markedly above that measured in additive-free solutions without any tendency of passivity to take place. The same enhancing effect is also noted in absence of Cl^- ions. This behaviour is readily understood, according to Shams El Din, when both the mechanism of anodic dissolution of iron, on one hand, and the catalytic properties of the organic carboxylates in acid solutions, on the other, are taken into consideration:

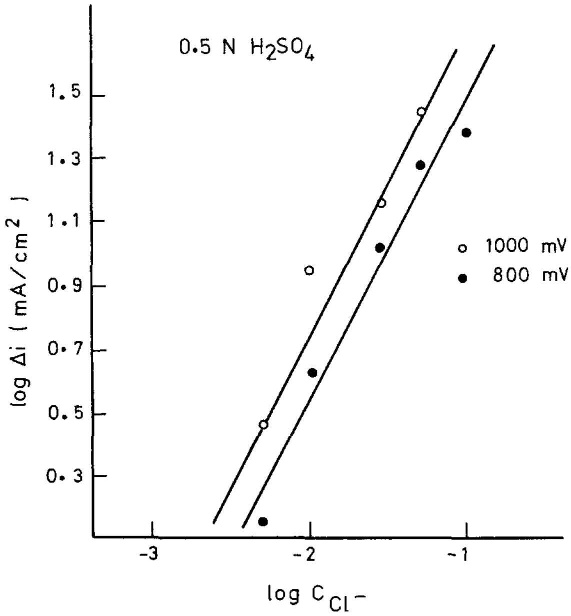

Fig. 5. The relation between log Δi and the log of concentration of Cl^- ions in 0.5 N H_2SO_4

It is well established that the overall anodic reaction, $Fe = Fe^{2+} + 2e$, occurs in a succession of steps involving the participation of H_2O dipoles, and the formation of various Fe-OH species in the double layer [14]. The dissolution of high purity iron, having low surface activity, and produced either by recrystallization under vacuum or by zone melting, is assumed to occur, at low overpotentials, by a "noncatalyzed" charge transfer mechanism [17, 18]. On the other hand, at high overpotentials and/or when the metal has a high surface activity (i. e. a high density of multi-dimensional crystal imperfections and dislocations, or strong deformationtion [14] dissolution follows a "surface-intermediate" mechanism [19, 12]. The elements of the two mechanisms are given according to the following equations:

$$Fe + H_2O = Fe(H_2O)_{ads} \tag{3}$$

$$Fe(H_2O)_{ads} = Fe(OH)^-{}_{ads} + H^+ \tag{4}$$

$$Fe(OH)^-{}_{ads} = [Fe(OH)]_{ads} + e^- . \tag{5}$$

i. Non-catalyzed mechanism:

$$[Fe(OH)]_{ads} \overset{rds}{\rightarrow} [Fe(OH)^+]_{ads} + e^- \tag{6}$$

$$[Fe(OH)^+]_{ads} + H^+ = Fe^{2+}_{aq} + H_2O . \tag{7}$$

ii. Surface intermediate mechanism:

$$[Fe(OH)]_{ads} + H_2O = [Fe(OH)_2]_{ads} + H^+ + e^- \tag{8}$$

$$[Fe(OH)_2]_{ads} + H^+ \overset{rds}{\rightarrow} [Fe(OH)]^+ + H_2O \tag{9}$$

$$[Fe(OH)_2]_{ads} + A^- \overset{rds}{\rightarrow} [Fe(OH)]^+ + A^- + OH^- . \tag{10}$$

In the non-catalyzed mechanism the rate determining step (rds) is the passage of $FeOH^+$ ions through the electrochemical double layer. The surface intermediate, dissolution of iron, on the other hand, involves the participation of $(Fe(OH)_2)$ ads, whose formation depends on the surface activity of the metal [21]. This intermediate is not to be confused with the non-pourous, passivating $Fe(OH)_2$ or $FeO \cdot H_2O$, but is to be looked upon as a primary adsorbate film [19, 22] which acts as a membrane inhibitor to the active dissolution of the metal [23]. It changes into a passivating film at high enough potentials, and leads to the abrupt drop in current. Dissolution of $(Fe(OH_2)$ ads, as the rate determining step, can occur through the participation of H^+ or of the anions A^-, present in solution by reactions (9) and (10). On the basis of the last reaction, one can account for the increase in the dissolution current density upon introducing Cl^- ion which acts as the anion A^- in reaction (10). The kinetics of iron dissolution and the various probable mechanism for the transition of the non-catalyzed into the surface-intermediate mechanism were recently considered, in detail, by Lorenz and coworkers [21].

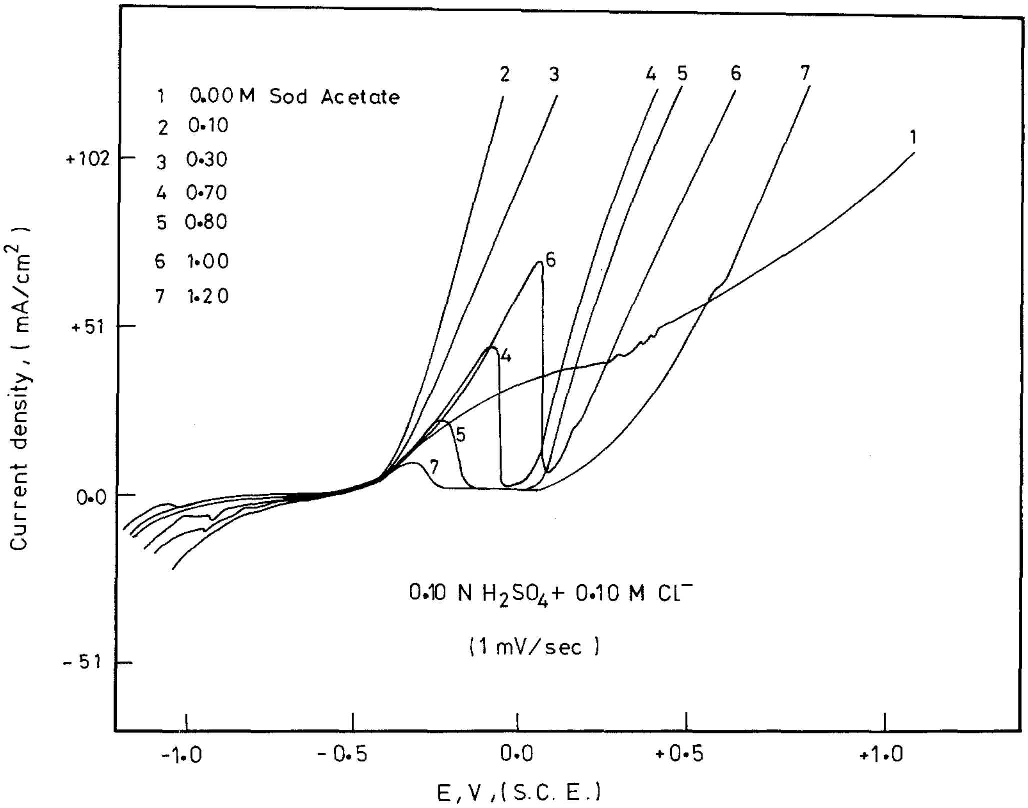

Fig. 6. The effect of addition of sodium acetate on the potentiodynamic anodic polarization behaviour of iron in 0.1 *N* H_2SO_4 and 0.1 *M* Cl^- ion at a sweep rate of 1 mV/s

Carboxylates in acid solutions are known to catalyze proton discharge and proton transfer reactions. This behaviour is related to the ability of the free proton to form the carboxylic acid with the -COO^- radicals, which then act either as a proton carrier to and from the reaction site [24] or as recipient for electrons [25].

By virtue of the nature of the Fe electrodes in the present investigation, as well as considering the highly anodic potentials, it is most likely that the dissolution of Fe follows the surface intermediate charge transfer mechanism, in which reaction (9) is one of the two alternative rate determining steps. It is assumed that the carboxylates adsorbed on the metal surface accelerate the process of proton transfer to $(Fe(OH)_2)_{ads}$ and lead to the observed increase in the rate of corrosion at one and the same potential. Reference to the curves of Fig. 6 and the other related figures reveals the interesting fact that the extent of catalysis of the metal dissolution is highest in the presence of low carboxylate concentrations and that it decreases progressively as more of these compounds are introduced into the solutions. This result shows that the additive exerts two counteracting effects, namely dissolution catalysis at lower concentrations and inhibition at higher ones. Inhibition is apparently due to surface blocking either by the carboxylates or the precipitated $FeSO_4 \cdot x H_2O$.

b. Depending on their concentration the carboxylates first reduce and later completely eliminate the current oscillations associated with the active/passive transition. Since these oscillations are due to the alternate formation and breakdown of the passivating film, it is easily concluded that carboxylates hinder the destruction of the film once it is formed. This can occur through the blocking of the surface and its isolation from the attacking solution by the carboxylates or by being incorporated into the film and causing therefore new properties.

As a result of hindrance of film destruction, the flade potential, E_f, shifts towards more negative (active) potentials with a subsequent marked decrease in the dissolution current density. The curves of Fig. 7a and b represent the variation of E_f with the logarithm of the carboxylate concentration in two solution compositions, whereby straight line relationships are obtained satisfying the relation:

$$E_f = a_6 - b_6 \log \mathrm{C}_{\text{carboxylate}} \tag{11}$$

where a_6 and b_6 are constants. At the same time, the curves of Fig. 8a and b represent the variation of the dissolution current density (mA/cm^2) vs. the concentration of the inhibitors on a double logarithmic scale. Straight lines are obtained following the relation:

$$\log i = a_7 - b_7 \log C_{\text{carboxylate}} \tag{12}$$

where a_7 and b_7 are also constants. The inhibiting action of these carboxylates decreases in the order: acetate < propionate < citrate < succinate.

c. The effect of carboxylates on the passivation current is of interest. Thus, lower concentrations of acetate and propionate when added to the low concentration of the acid and Cl^- ions (0.05 N H_2SO_4 + 0.01 M Cl^-), reduce slightly the current flowing along the whole passive range. Apparently these two additives compete

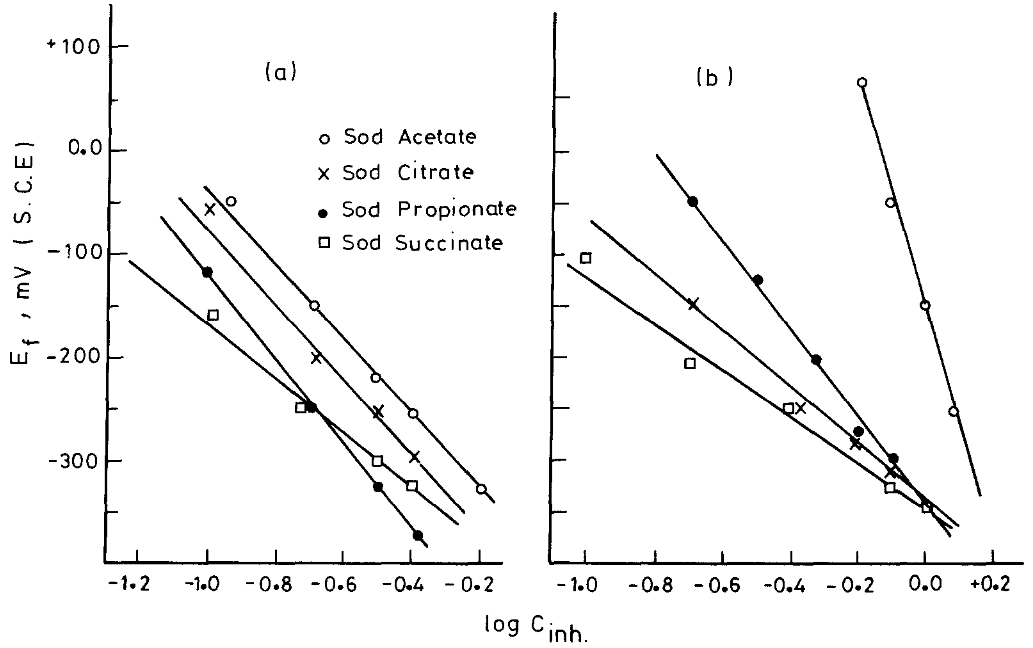

Fig. 7. The variation of the flade potential E_f with the concentration of organic carboxylates: a. 0.1 N H_2SO_4 + 0.1 M Cl^- ion. b. 0.05 N H_2SO_4 + 0.1 M Cl^- ion

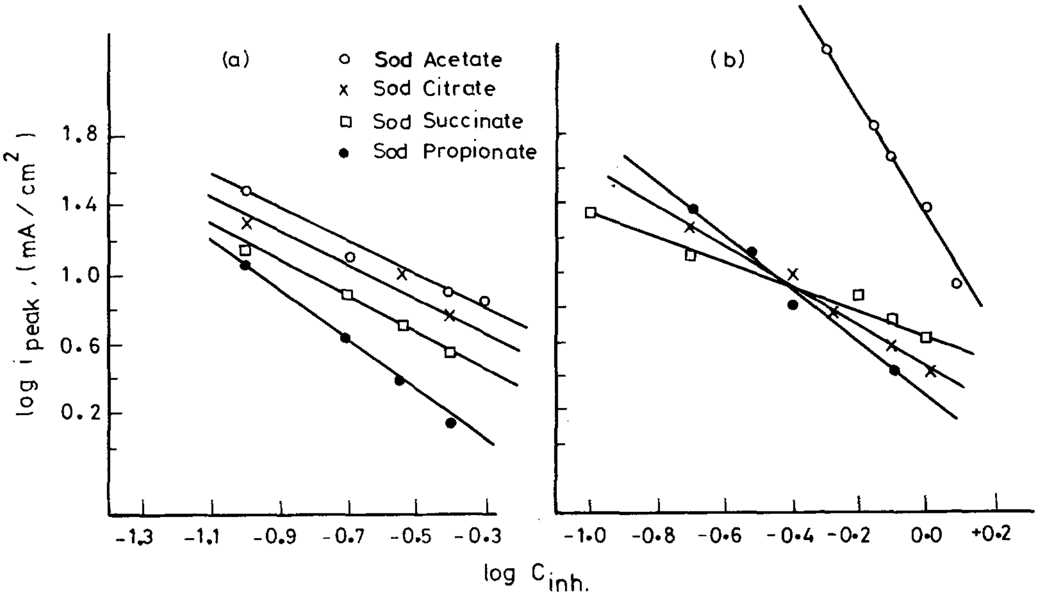

Fig. 8. The variation of the dissolution current density (mA/cm^2) with the concentration of the inhibitors: a. 0.1 *N* H_2SO_4 + 0.1 *M* Cl^- ion. b. 0.05 *N* H_2SO_4 + 0.1 *M* Cl^- ion

with both the Cl^- and HSO_4^- ions for adsorption sites on the passive metal surface and retard their corresponding destructive action. However, the other two anions, citrate and succinate, when added to the first solution, as well as the four anions when added to the concentrated solutions, do not cause the Cl^- ion to break down the passivating oxide film along the whole passive range but rather at specific definite pitting potential which is shifted into the noble direction as the inhibitor concentration is increased. Furthermore, when the passive film breaks down, the pitting corrosion currents increases linearly and steadily with increasing potential of the working electrode. The specification of the initiation of pitting corrosion at definite potentials in the passive region is entirely due to the increased strength of the passive film in the presence of these carboxylates. Pitting under these conditions results from the preferential competitive adsorption of Cl^- ions with the carboxylate anions as the potential of the working electrode becomes more noble. When the concentration of Cl^- ion reaches a certain critical value in the electrical double layer, it succeeds to destroy passivity and initiating pitting corrosion at a certain critical potential which is more noble with increasing carboxylate concentration.

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