

## ELECTROLYTIC DISSOLUTION OF IRON IN AQUEOUS CITRATE SOLUTIONS

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Analysis of polarization curves for electrolytic dissolution of an iron (steel) electrode in citrate solutions of various pH values and concentrations of citrate anions showed that the given medium promotes the electrolytic dissolution by shifting the corrosion potential of iron to more negative values. However, the catalytic formation of an iron(II) hydroxo complex cation in the active dissolution region according to the scheme proposed by Heusler remains the rate-determining step of the dissolution mechanism.

The electrolytic dissolution of iron and its technical alloys in citrate solutions has been used since long in isolation of various non-metallic phases from these alloys with the purpose of their identification by X-ray diffraction and microchemical analysis as a part of metallurgical research<sup>1</sup>. The electrolyte is a solution of citric acid more or less neutralized by an alkali hydroxide; usually an alkali metal halide and ascorbic acid are added to maintain the conductance and the reduction properties of the solution.

Since detailed physico-chemical studies of the mentioned process are lacking, the object of the present work is to fill up this gap.

### EXPERIMENTAL

Cyclic voltammetry with a steel disc electrode was used. Three sorts of steel were employed

- 1) Non-alloyed, medium carbon steel (steel I, containing only 0.70% C);
- 2) low-carbon manganese steel microalloyed with titanium (steel II, containing 0.11% C, 1.61% Mn, 0.12% Ti, and 0.016% S);
- 3) low-carbon manganese steel microalloyed with vanadium and niobium (steel III, containing 0.15% C, 1.40% Mn, 0.07% V, 0.01% Nb, and 0.013% S).

A cylinder was made of each of the given materials, 3 mm in diameter and 5–6 mm in height, which was pressed into a hollow Teflon cylinder so that their bases were coplanar, forming a disc electrode, which was then fixed to the shaft of the rotor, connected with a d.c. voltage source. The rotation rate was maintained at 200 rpm. The disc surface was ground with a fine emery paper (SIA, grade 2/0–6/0) and polished with a sateen cloth before every voltammetric record.

The electrolytic cell of 100 ml holding capacity contained the working, rotating, and counter electrodes (silver in 1M-KCl in a separate compartment), and a reference normal calomel electrode (NCE), and besides it was provided with an inlet and an outlet of argon to permit working in inert atmosphere.

The solutions were prepared from commercial reagent grade chemicals and redistilled water; their pH was measured with a pH meter OP-208 (Radelkis, Hungary) with a glass electrode. No iron salt was added. The temperature of measurement was 21–23°C.

The d.c. voltage source was a multipurpose polarograph of the type GWP 673 (Akademie der Wissenschaften, G.D.R. Berlin) in combination with an XY recorder ENDIM 620-00 serving to record the voltammetric curves. Triangular voltage pulses with a sweep rate 25 or 100 mV/min were applied from negative (–0.7 to –1.0 V) to positive potentials (–0.4 to 0.0 V) and back. The potential values are given with respect to NCE.

## RESULTS

The anodic portion of the voltammetric curves is shown in Fig. 1. The curves during polarization in the back direction showed a hysteresis, the current being higher than during forward polarization, therefore the back records will be disregarded in our discussion. All records were obtained under standard experimental conditions.

Three basic dependences were followed:

- 1) Dependence of the corrosion potential (corrosion current density) on pH of the electrolyte;
- 2) dependence of the anodic dissolution current on pH of the solution (at constant electrode potential and constant total analytical concentration of citrate ions);
- 3) dependence of the anodic dissolution current on the total concentration of citrate (at constant pH and constant electrode potential). The passivity region was studied only for orientation.

The values of the corrosion potential,  $E_c$ , were determined from the polarization curves involving also the cathodic portion after transformation into the Tafel form,  $\log |i| - E$ , by extrapolation (Fig. 2). The values of the corrosion current were determined analogously. The following relations were obtained for the corrosion potential  $E_c$  (V vs NCE) measured on the three materials (Fig. 3):

- for steel I,  $(E_c)_I = -0.41 - 0.057 \text{ pH}$ ,  
for steel II,  $(E_c)_{II} = -0.45 - 0.043 \text{ pH}$ ,  
for steel III,  $(E_c)_{III} = -0.46 - 0.045 \text{ pH}$ .

The error of the determination is  $\pm 0.01$  V. (The total concentration of citrate was  $0.25 \text{ mol l}^{-1}$  for steel II,  $0.20 \text{ mol l}^{-1}$  for steel III, and increased with pH from  $0.25$  to  $1.00 \text{ mol l}^{-1}$  for steel I.) These equations are valid in the pH range of citrate buffer solutions, i.e. 1.2–7; since they are only little different from one another, only steel I was used in further studies.

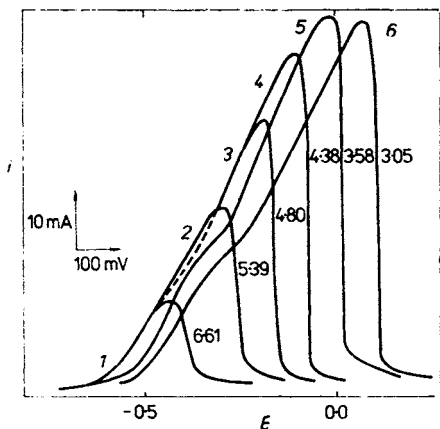


FIG. 1

Anodic portions of the polarization curves at various pH values; steel III (the corresponding value of pH is indicated at each curve)

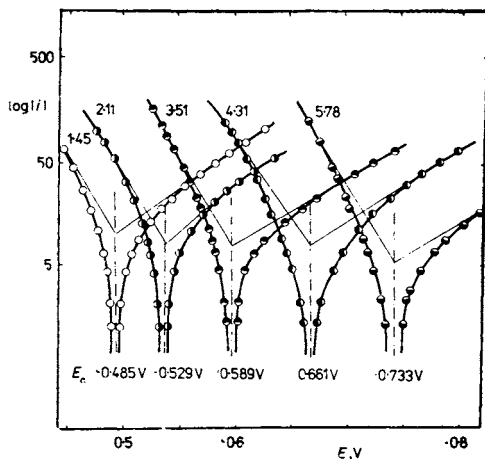


FIG. 2

Tafel plots of  $\log i$  vs  $E$  at various pH values; steel I (the corresponding value of pH is indicated at each curve)

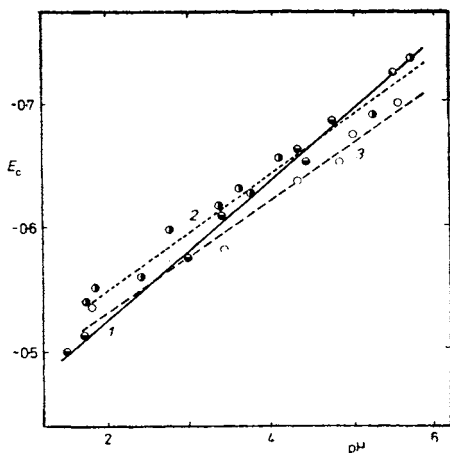


FIG. 3

Dependence of the corrosion potential  $E_c$  (V) on pH; 1 steel I (carbon steel, non-alloyed); 2 steel II (MnMoTi); 3 steel III (MnVNb)

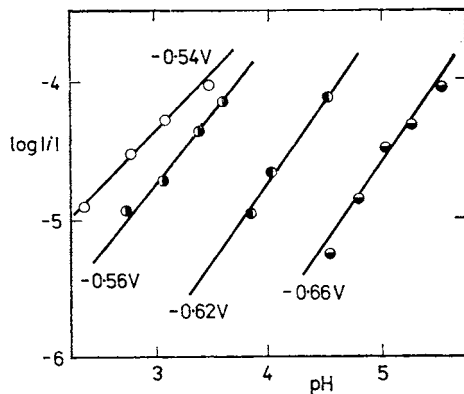


FIG. 4

Dependence of the current on pH at constant  $E$  for steel II and concentration of citrate  $0.25 \text{ mol l}^{-1}$

The dependence of the corrosion current density ( $\text{A cm}^{-2}$ ) on pH was found to be given for steel I by the equation  $j_c = 1.42 \cdot 10^{-4} - 1.3 \cdot 10^{-5} \text{ pH}$ .

The dependence of the current on pH at constant electrode potential and constant total concentration of citrate ions  $0.25 \text{ mol l}^{-1}$ , (Fig. 4) has the mean slope  $\Delta \log i / \Delta \text{pH} = 1.00 \pm 0.05$  corresponding to a linear dependence of the current on the concentration of hydroxyl ions.

The dependence of the anodic dissolution current on the electrolyte concentration at constant potential and pH was measured at  $\text{pH} = 3.00$ ,  $E = -0.52 \text{ V}$ , and  $\text{pH} = 5.00$ ,  $E = -0.66 \text{ V}$ . In both cases (Fig. 5) the current is nearly independent of the citrate concentration (although the experimental errors are higher than in the pH dependence).

In the passivity region, the following empirical relations were found between the Flade potential ( $\text{V vs NCE}$ ) and pH:  $(E_F)_I = 0.353 - 0.137 \text{ pH}$  for steel I and  $(E_F)_{II} = 0.488 - 0.140 \text{ pH}$  for steel II.

## DISCUSSION

The dependences of the corrosion potential on pH (Fig. 3) have approximately the same course, especially for the manganese steels II and III, which is apparently due to their similarity in chemical composition. The shift of the corrosion potential is obviously related with the shift of the hydrogen overpotential on iron and with the equilibrium potential of iron depending on the formation of Fe(II) citrate complexes. This follows from the comparison of the Tafel dependences at different pH values (Fig. 2), whose both branches are shifted but remain parallel and do not coincide either in the region of hydrogen evolution or in the region of iron dissolution. A quantitative evaluation of these dependences would be difficult because of the complexity of the intervening dissociation equilibria.

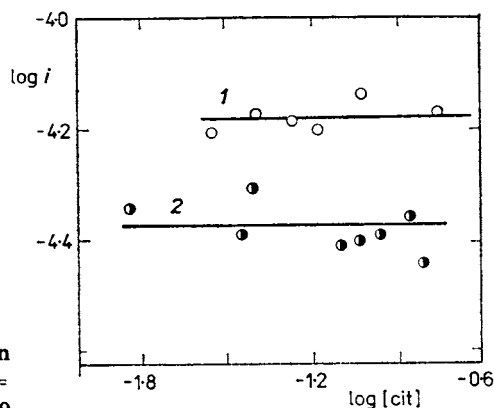
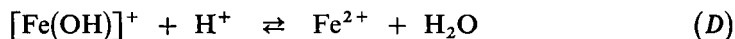
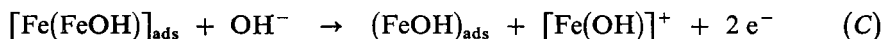
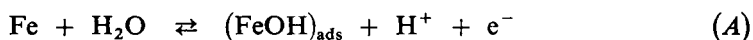


FIG. 5  
Dependence of the dissolution current on the citrate concentration for steel II; 1  $E = -0.52 \text{ V}$ ,  $\text{pH} 3.0$ ; 2  $E = -0.66 \text{ V}$ ,  $\text{pH} 5.0$

More information about the dissolution of iron in citrate solutions can be obtained from the dependence of the current density on pH (at constant total concentration of citrate ions and constant electrode potential) and from the dependence of the current density on the total citrate concentration (at constant pH and potential).

In the first case, a linear dependence with a slope equal very nearly to 1 was found in the studied potential range, evidence that the rate of the controlling reaction step is proportional to the concentration of hydroxyl ions. But there is no dependence on the citrate concentration in the second case. Thus, the catalytic dissolution scheme proposed by Heusler<sup>2</sup> seems suitable for the dissolution of iron in the citrate medium:



Here, reaction (C) is the rate-determining step of the whole reaction mechanism in contrast to that proposed by Bockris *et al.*<sup>3</sup>.

Citrate anions participate in the reaction mechanism only secondarily, reacting either with  $\text{Fe}^{2+}$  aq or with  $[\text{Fe}(\text{OH})]^+$  ions to give the citrate complexes  $[\text{Fe}(\text{HCit})]$  or  $[\text{Fe}(\text{Cit})]^-$ . If we consider the dissociation constants for  $[\text{Fe}(\text{OH})]^+$ ,  $K_{\text{OH}} = 1.3 \cdot 10^{-4}$ , for  $[\text{Fe}(\text{HCit})]$ ,  $K_{\text{HCit}} = 7.6 \cdot 10^{-3}$ , and for  $[\text{Fe}(\text{Cit})]^-$ ,  $K_{\text{Cit}} = 8.3 \cdot 10^{-4}$ , then at pH 5.00 and the total citrate concentration  $0.10 \text{ mol l}^{-1}$  the concentration ratio of the concurrent complexes will be  $c_{\text{Fe}(\text{HCit})}/c_{\text{Fe}(\text{OH})} \approx 10^6$ . In the case of the complex  $[\text{Fe}(\text{Cit})]^-$ , this ratio is still more favourable for the citrate complexes which are in a sufficient excess to influence the equilibrium electrode potential of iron and thus the shift of its corrosion potential with pH.

If the rate of iron dissolution is nevertheless limited by the concentration of hydroxyl, rather than citrate anions, it is necessary to assume that  $\text{OH}^-$  ions are accumulated at the interface probably as a result of their specific adsorption or of the dissociative adsorption of water, *e.g.* according to Eq. (A).

The influence of citrate anions or citric acid in electrolytic isolation of non-metallic phases from steels thus consists in that they prevent the formation of insoluble hydroxo compounds, at least in the potential range of active dissolution, and that they act as a good buffer in a rather broad pH interval. However, the existence of the passive region on the polarization curves at potentials more positive than the Flade potential at a given pH shows that even the citrate medium does not prevent the formation of insoluble hydroxo (or oxo) compounds of Fe(III), which are responsible for the formation of a passivating layer at the iron electrode surface.

## REFERENCES

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