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THE REDUCTION MECHANISM OF ALLYL ALCOHOL ON IRON SURFACE AND THE EFFECT ON THE CORROSION OF IRON

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ABSTRACT

In this study the corrosion of recrystallized pure iron in the sulphuric acid media and the reduction mechanism of allyl alcohol on the iron surface were investigated. For this purpose current potential curves were obtained by potentiodynamic method. The reduction of allyl alcohol on the iron surface was shown by using these curves.

INTRODUCTION

The corrosion rates of metals and alloys can be determined by electrochemical and nonelectrochemical methods. Electrochemical methods are:

1– Extrapolating the steady state cathodic and anodic Tafel lines to $E = E_{cor}$.

2– The linear polarization method by the help of Stern–Geary equation.

3– Measuring the polarization resistance, R_p, using the ac technique.

In both cases 2) and 3) the measued R_p values are related to the corrosion current density according to the Stern–Geary equation:

$$i_{cor} = \frac{b_a \cdot b_c}{2.303\ (b_a + b_c)} \cdot \frac{1}{R_p} = \frac{B}{R_p} \qquad (1)$$

Where b_a and b_c represent the anodic and cathodic Tafel slopes respectively. Non electrochemical methods include.

1– measuring the decrease of weight and

2– solution analysis.

In this study corrosion rates were obtained by extrapolating the cathodic and anodic Tafel lines to $E = E_{cor}$. The reduction of PA to ALA was shown in literature (Aksüt, A.A. et al, 1982; Aksüt, A.A., 1982 and Aksüt, A.A., 1983). In some studies PA is proposed to be reduced to the single bond (Poling, G.W., 1967; Tedeschi, R.J., 1975; Hausler R.H., 1977). Hence, in this study, it was investigated whether the reduction of allyl alcohol takes place on the iron surface or not and it was shown that allyl alcohol could be reduced up to the single bond.

EXPERIMENTAL

The investigations were carried out in the following systems Fe* / xM H_2SO_4 + yM Na_2SO_4 + zmM ALA**

using by purified nitrogen (passed through liquid nitrogen), rotating disc technique at a rotation frequency of 30 rps. Saturated calomel and Pt foil electrodes were used as reference and counter electrodes. The electrode was polished with sandpaper and washed with bidistilled water. The solution were also prepared by bidistilled water.

EXPERIMENTAL RESULTS

The current density–potential curves measured by linear potential sweep technique in deaerated 0.5M H_2SO_4 + zmM ALA (pH = 0.7), 0.05M H_2SO_4 + 0.45M Na_2SO_4 + zmM ALA (pH = 1.7) and 0.005M H_2SO_4 + 0.495M Na_2SO_4 + zmM ALA (pH = 2.7) solutions are given in Figs 1, 2 and 3 respectively. The potential sweep was started at $E = E_{cor}$ and then the curves were obtained first in cathodic and then anodic directions using a sweep rate of 1 mVs^{-1}. For each system at different pH values, cathodic Tafel slopes were obtained to be $b_c = -120 \mp 10$ mV in the ALA–free systems while $b_c = -200 \mp 20$ mV in the ALA containing systems. Anodic Tafel slopes were determined to be $b_a = 45 \mp 5$ mV for each system.

Figure 4 shows the variation of log i with respects to log C_{ALA} at constant potential and constant pH.In this figure the three lines are parallel to each other and the slope is approximately 0.26 – 0.28. At constant potential and constant C_{ALA} the variation of log i with pH

* The electrode kept at 1050°C for two hours recrystalliezed by cooloing with a rate of 150 °C/hour, having a purity of 99.999 %.

** Freshly distilled allyl alcohol.

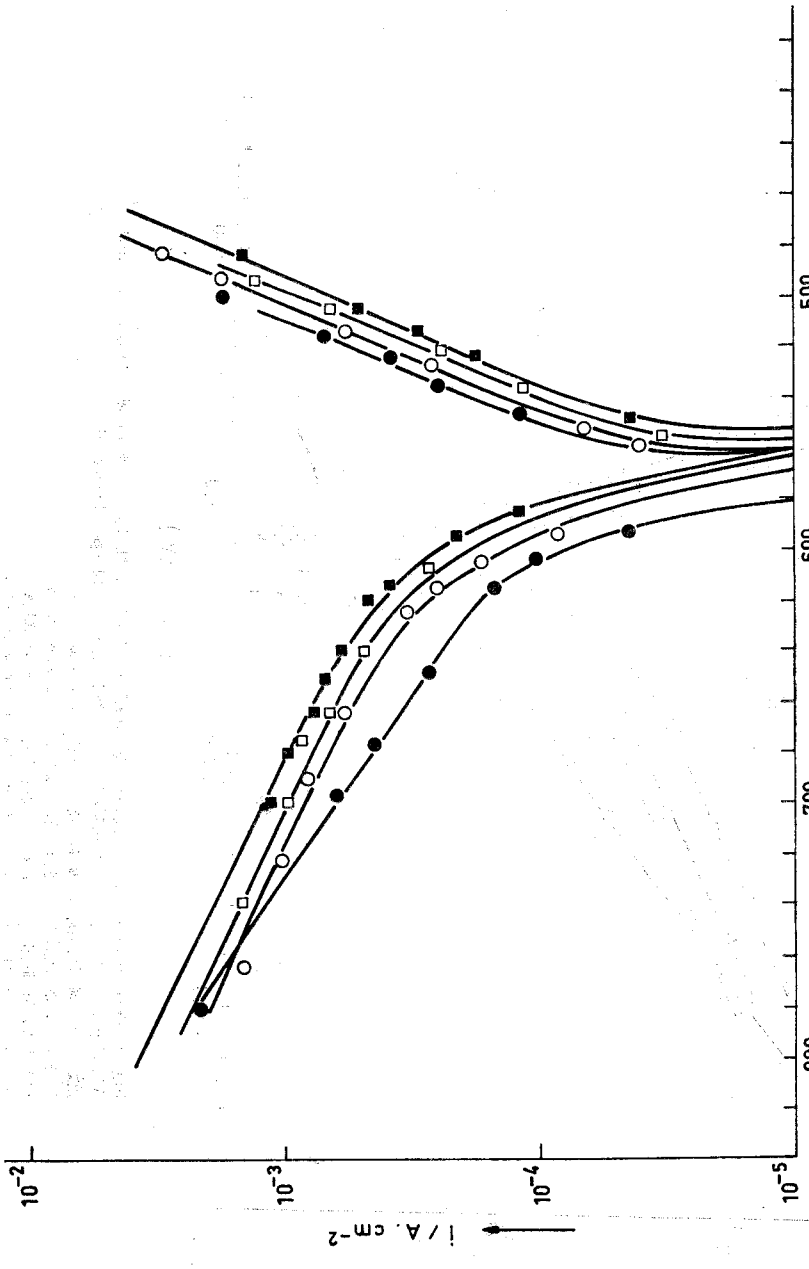

Fig. 1. Current - potential curves obtained in 0.5 M H_2SO_4 + zmM ALA (pH = 0.7). v = 1 mVs^{-1}. T = 298°K, v = 30 rps, deaerated
(●) 0.5 M H_2SO_4 + 0mM ALA; (○) 0.5 M H_2SO_4 + 1mM ALA;
(□) 0.5 M H_2SO_4 + 2mM ALA; (■) 0.5 M H_2SO_4 + 10mM ALA.

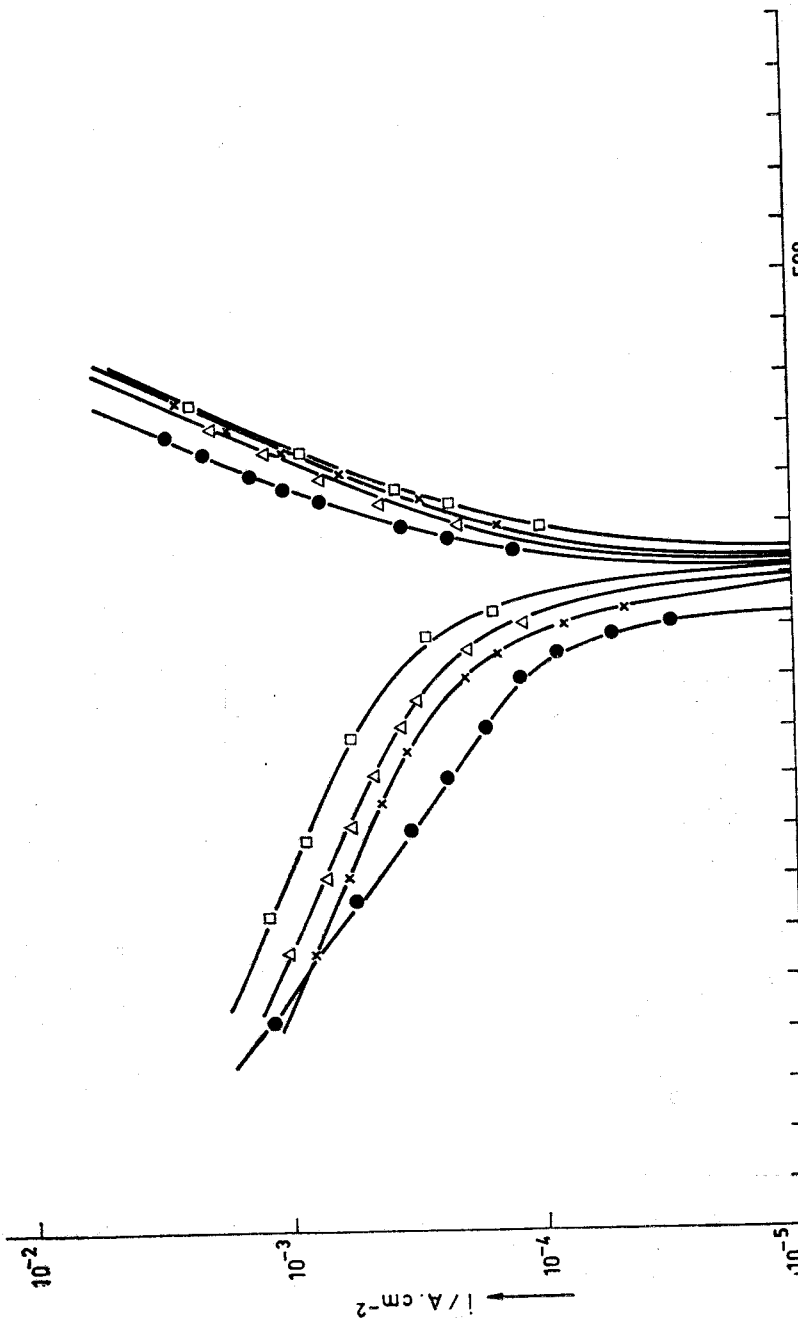

Fig. 2. Current - potential curves obtained in 0.05 M H_2SO_4 + 0.45 M Na_2SO_4 + zmM ALA (pH = 1.7). v = 1 mVs^{-1}, T = 298°K, ν = 30 rps, deaerated
(●) 0.05 M H_2SO_4 + 0.45 M Na_2SO_4 + 0mM ALA;
(×) 0.05 M H_2SO_4 + 0.45 M Na_2SO_4 + 1 mM ALA;
(Δ) 0.05 M H_2SO_4 + 0.45 M Na_2SO_4 + 2 mM ALA;
(□) 0.05 M H_2SO_4 + 0.45 M Na_2SO_4 + 10 mM ALA

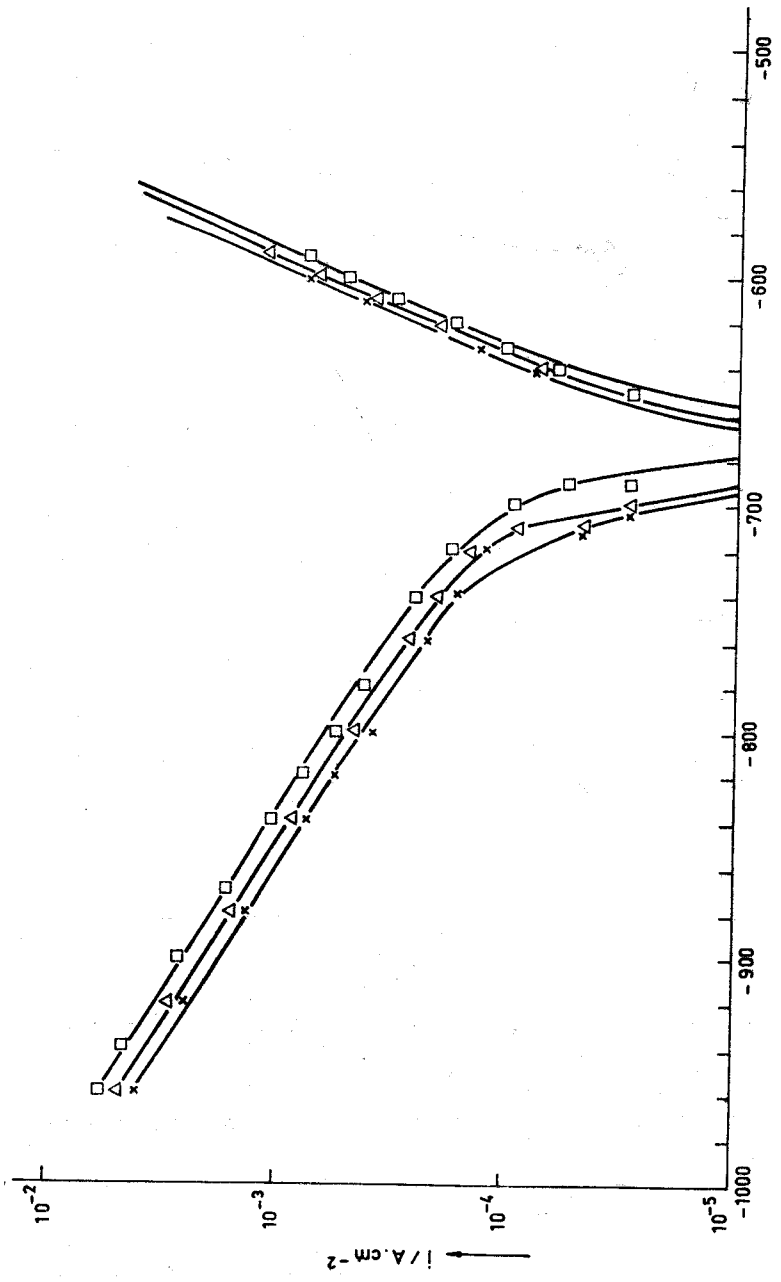

Fig. 3. Current - potential curves obtained in 0.005 M H_2SO_4 + 0.495 M Na_2SO_2 + zmM ALA (pH = 2,7). v = 1 mVs^{-1}. T = 293°K, v = 30 rps, deaerated
(×) 0.005 M H_2SO_4 + 0.495 M Na_2SO_4 + 1 mM ALA;
(Δ) 0.005 M H_2SO_4 + 0.495 M Na_2SO_4 + 2 mM ALA;
(□) 0.005 M H_2SO_4 + 0.495 M Na_2SO_4 + 10 mM ALA.

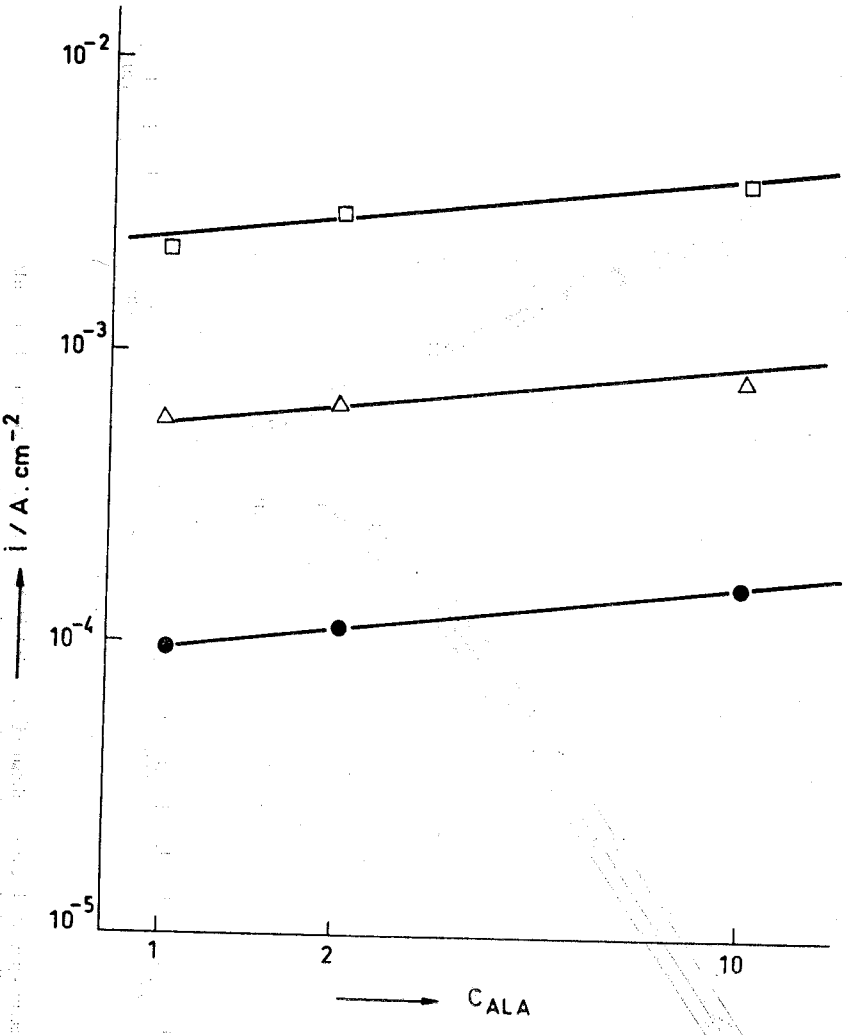

Fig. 4. The variation of log C_{ALA} with log i at constant potential. (□) pH = 0.7; (Δ) pH = 1.7; (●) pH = 2.7. T = 298°K, ν = 30 rps, deaerated

can be seen in Figure 5. The lines obtained are also parallel to each other and the slope is around 0.56 – 0.60.

DISCUSSION AND RESULTS

The reaction order can be calculated from the plot of log i vs log C_{ALA} at constant potential and constant pH (Fig. 4). The calculated reaction order according to ALA concentration is

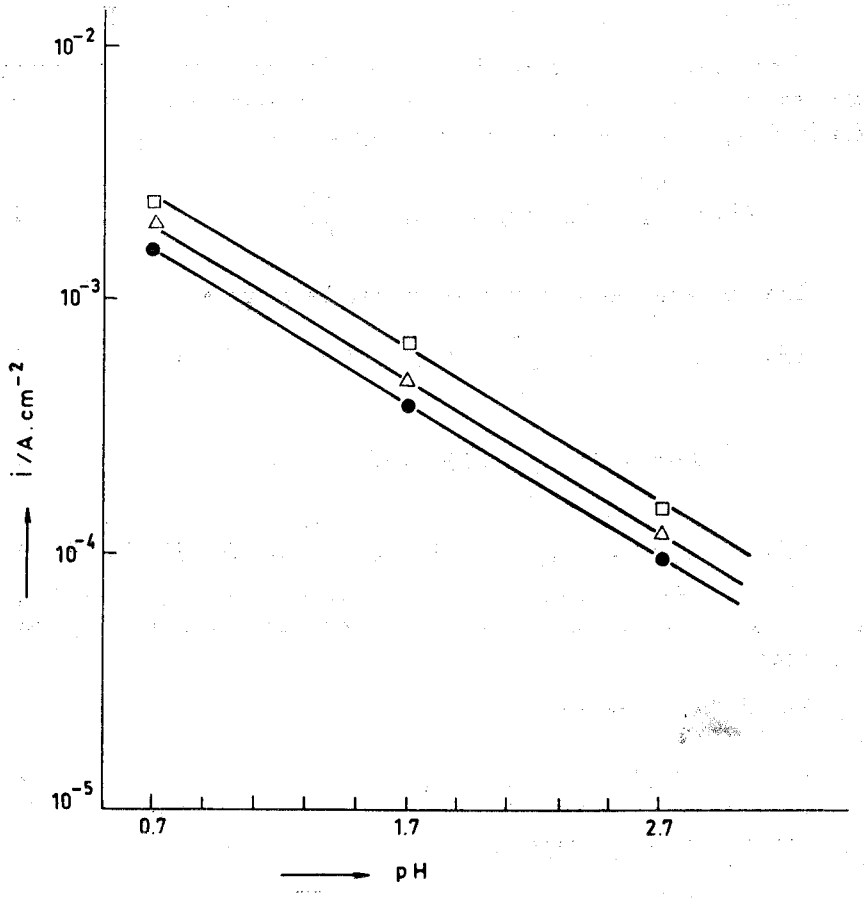

Fig. 5. The variation of log i with pH at constant C_{ALA}. (●) 1 mM ALA; (Δ) 2mM ALA; (□) 10 mM ALA. T = 298°K, ν = 30 rps, deaerated.

$$\left(\frac{\partial \log i}{\partial \log C_{ALA}}\right)_{E,pH} = 0.28$$

The reaction order according to the H^+ can be determined from the plot of log i vs pH at constant C_{ALA} and constant potential in the cathodic zone. From Fig. 5 this value was found to be.

$$\left(\frac{\partial \log i}{\partial pH}\right)_{E,C_{ALA}} = -0.56$$

According to these results it can be seen that ALA should be reduced to $CH_3CH_2CH_2OH$ according to the following equation.

$$CH_2{=}CH{-}CH_2OH + 2H^+ + 2\ e \longrightarrow CH_3CH_2CH_2OH$$

From these kinetic parameters, the following equation describing the reduction rate of ALA to propanol on iron electrodes in acidic media is obtained within the potential range studied.

$$i_- = -2F.k_-.C_{ALA}^{0,28}.C_{H+}^{0,56} \exp\left(-\alpha_{cath}\ \frac{FE}{RT}\right) \quad (2)$$

The following reaction mechanism can be proposed

$$CH_2 = CH{-}CH_2OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2 = CH{-}CH_2OH\ (ads) \quad (3)$$

$$2H^+ + 2e^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2H\ (ads) \quad (4)$$

$$CH_2 = CH{-}CH_2OH_{(ads)} + 2H_{(ads)} \xrightarrow{k_3} CH_3CH_2CH_2OH \quad (5)$$

The following equations can be written for reactions (3) and (4) at the Temkin adsorption conditions (CELDRAN, R and et al, 1981 and 1981).

For the 3 rd reaction:

$$e^{-\frac{r_{ALA}.\theta_{ALA}}{RT}} = K_1\ C_{ALA} \quad (6)$$

and for the 4 th reaction,

$$e^{-\frac{r_H\ .\ \theta_H}{RT}} = K_2\ C^2_{H+}\ \exp\left(-\frac{FE}{RT}\right) \quad (7)$$

From the rate determining step (5) the following equation can be written

$$v_3 = -k_3\ \theta_{ALA}\ \theta_H^2\ \exp\left[-\frac{\gamma\ (r_{ALA}.\ \theta_{ALA} + r_H.\ \theta_H)}{RT}\right] \quad (8)$$

Multiplying the right and left sides of (6) and (7) and raising to power γ: the following equation is obtained.

$$\exp\left[-\frac{\gamma\ (r_{ALA}.\ \theta_{ALA} + r_H.\ \theta_H)}{RT}\right] = (K_1K_2)^{\gamma}\ C_{ALA}^{\gamma}\ C_{H+}^{2\gamma} + \exp\left(-\frac{\gamma\ FE}{RT}\right) \quad (9)$$

From (8) and (9) the following equation is obtained for the reaction rate

$$i_{-} = -2\ FK\ C_{ALA}^{\gamma}\ C_{H+}^{2\gamma} + \exp\left(-\frac{\gamma\ FE}{RT}\right) \qquad (10)$$

where

$$K = k_3\ (K_1K_2)\quad \theta_{ALA}\ 0^2{}_{H+}$$

Equation (10) completely agrees with (2) if $\gamma = 0.28$. Under this condition, the cathodic Tafel slope is

$$\left(\frac{\partial\ E}{\partial\ \log\ i}\right)_{pH} = -\frac{2{,}303\ RT}{\gamma\ F} = -\ 207\ mV.$$

This value is in complete compliance with the experimental value obtained ($b_c = -\ 200\ \mp\ 20$ mV).

The variation of i_{cor} with log C_{ALA} at constant pH and with pH at constant C_{ALA} are given in Figs. 6 and 7 respectively.

These experimental data show that ALA is reduced to propanol according to the given reaction mechanism.

ÖZET

Bu çalışmada yeniden kristallendirilmiş saf demirin (% 99,999) allil alkol içeren sülfürik asit ortamındaki korozyonu, allil alkolün (ALA) redüksiyonu ve redüksiyon mekanizması incelenmiştir. Bu amaçla potansiyodinamik yöntemle ($dE/dt = 1$ mV/s) akım-potansiyel eğrileri elde edilmiştir. Bu eğrilerden ALA'ün demir yüzeyinde redüklendiği gösterilmiştir.

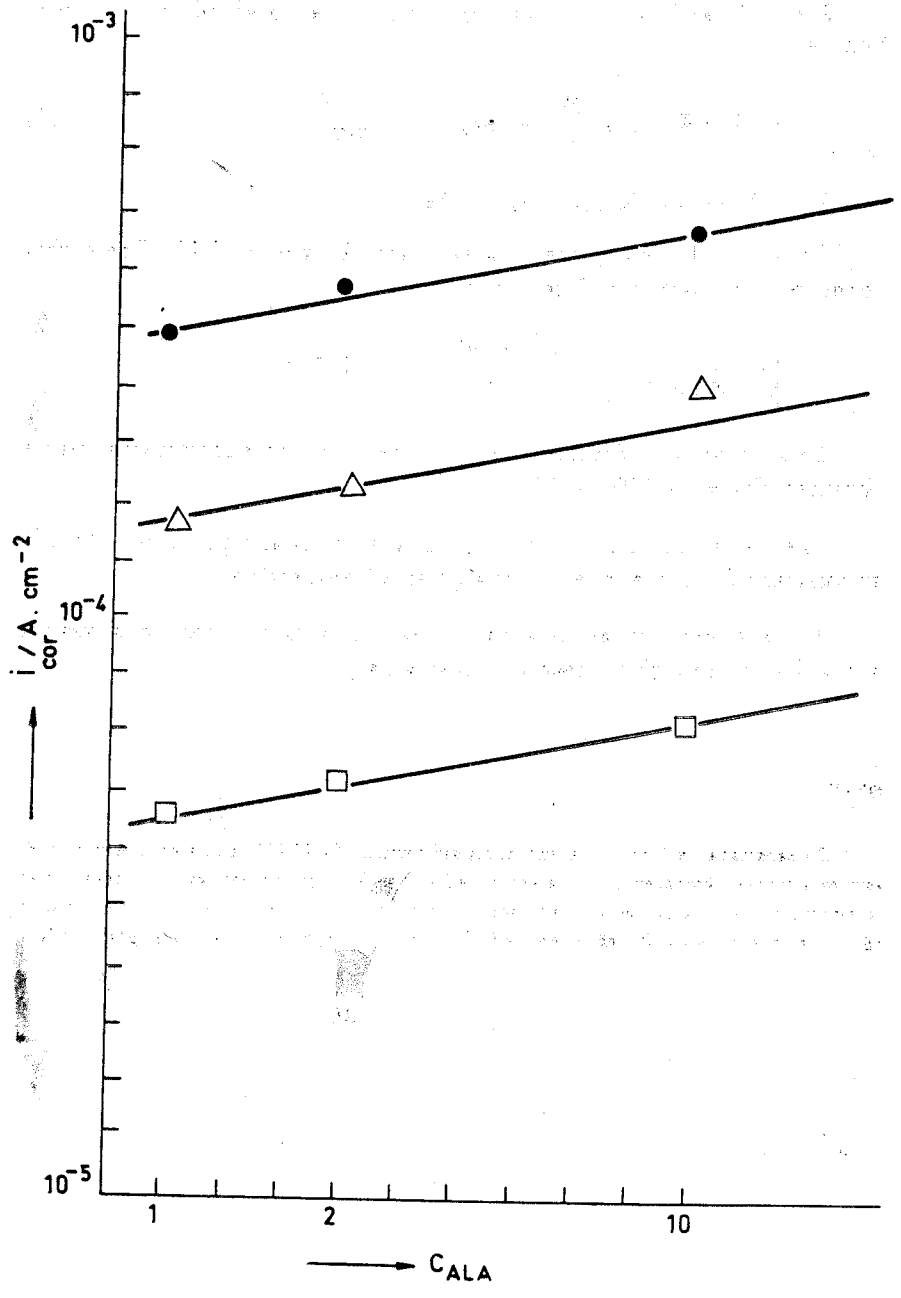

Fig. 6. The variation of log i_{cor} with log C_{ALA} at constant pH. (□) 1mM ALA; (Δ) 2mM ALA; (●) 10 mM ALA. T = 298°K, ν = 30 rps, deaerated.

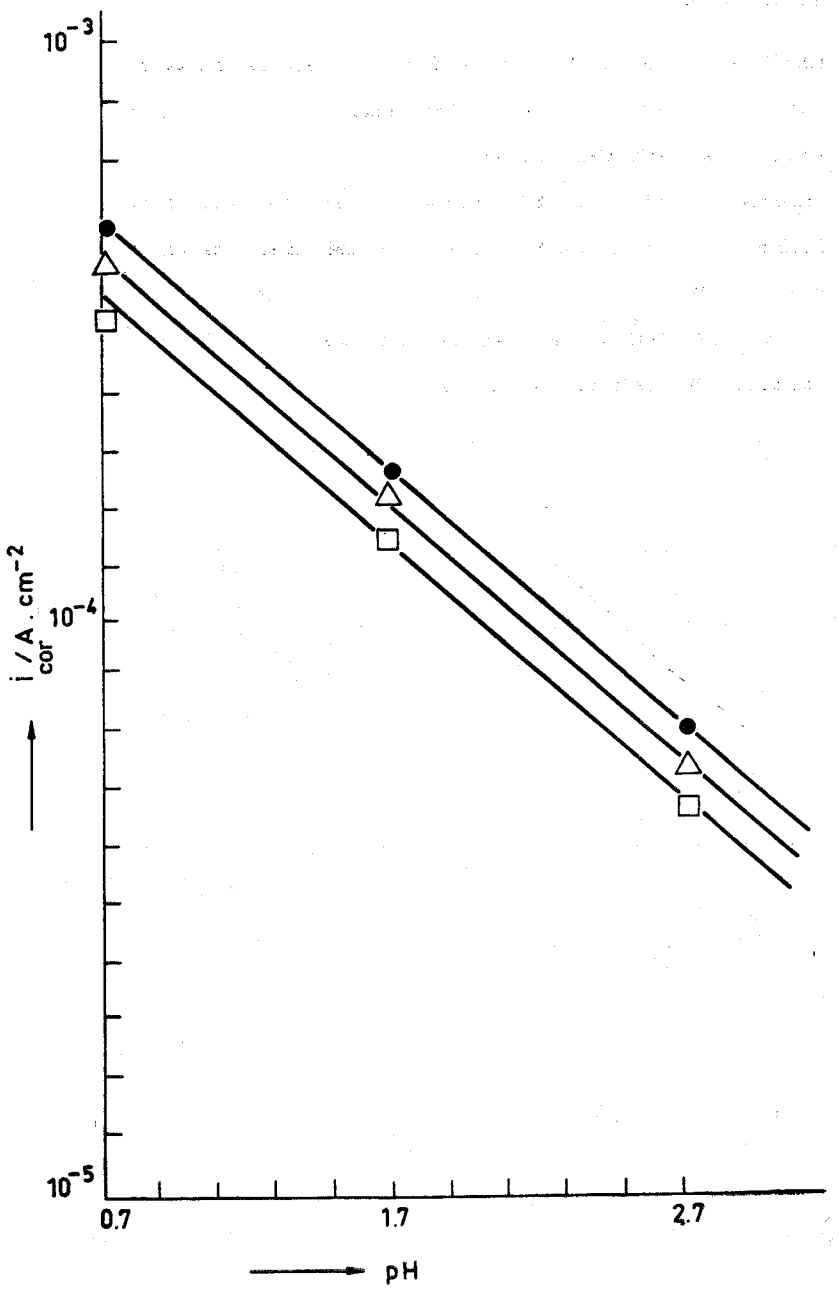

Fig. 7. The variation of log i_{cor} with pH at coastant C_{ALA}. (□) 1 mM ALA; (Δ) 2mM ALA; (●) 10 mM ALA. T = 298°K, ν = 30 rps, deaerated.

REFERENCES

AKSÜT, A.A., LORENZ, W.J. and MANSFELD, F., 1982. *Cor. Sci.* 22, 611.

AKSÜT, A.A., 1982. *Comm. Fac. Sci. Univ.* Ankara.

AKSÜT, A.A., 1983. Elec. Acta, 28, 1177.

CELDRAN, R. and GONZALEZ - VELASCO, J., 1981. *Elec. Acta*, 26, 525.

CELDRAN, R. and GONZALEZ - VELASCO, J., 1981. Elec. Acta, 26, 763.

HAUSLER, R.H., 1977. Corrosion, 33, 117.

POLING, G.W., 1967. *J. Electrochem. Soc.*, 114, 1209.

TEDESCHI, R.J. 1975. *Corrosion*, 3, 130.