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The purpose of these studies is to obtain a better understanding of the role which antimony plays in accelerating the corrosion of tin. Tin-antimony alloys were prepared by electrodeposition and the corrosion rates were determined from polarization data obtained in deaerated 0.33M citric acid. The corrosion rates were linearly related to the antimony concentration in the alloy and could be described by the following equation:

$$\text{Corrosion rate in } A/cm^2 = 0.0003 + 0.000079X$$

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where X is the antimony concentration in the tin in ppm. Nitrite additions to the deaerated citric acid greatly accelerated the corrosion rate. The effect of nitrite could be described by the following equation:

$$\text{Corrosion rate in } A/cm^2 = 0.0003 + 0.021Y$$

where Y is the nitrite concentration in the citric acid in ppm. The nitrite results and the great effect of antimony on the corrosion rate were attributed to the fact that a partially oxidized surface serves as a remarkably effective catalyst for the cathodic hydrogen evolution on tin.

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Factors Affecting the Corrosion of Tin in the Presence of Reducible Inorganic and Organic Substances

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ABSTRACT

The purpose of these studies is to obtain a better understanding of the role which antimony plays in accelerating the corrosion of tin. Tin-antimony alloys were prepared by electrodeposition and the corrosion rates were determined from polarization data obtained in deaerated 0.33M citric acid. The corrosion rates were linearly related to the antimony concentration in the alloy and could be described by the following equation:

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where X is the antimony concentration in the tin in ppm. Nitrite additions to the deaerated citric acid greatly accelerated the corrosion rate. The effect of nitrite could be described by the following equation:

$$\text{Corrosion rate in A/m}^2 = 0.0003 + 0.021Y$$

where Y is the nitrite concentration in the citric acid in ppm. The nitrite results and the great effect of antimony on the corrosion rate were attributed to the fact that a partially oxidized surface serves as a remarkably effective catalyst for the cathodic hydrogen evolution on tin.

INTRODUCTION

Several isolated studies have shown that antimony has an accelerating effect on the corrosion of tin in aqueous solutions (1,2) and in oxidation reactions (3). A satisfying explanation of the effects of antimony has not been offered. It is also well known that nitrite and nitrate greatly accelerate the corrosion of tin (4,5,6). In the latter case there is a better understanding since it is well recognized that oxidizing species accelerate the cathodic reaction on tin. Much work has been done in understanding those factors which lead to increased tin corrosion under conditions simulating food storage in tinned containers (7,8,9,10,11). Albu-Yaron and Semel (12) have studied the effect of nitrate in terms of different stored food products.

The purpose of the research reported herein is to obtain a better understanding of the role which antimony plays in accelerating the corrosion of tin. Experiments were also carried out in nitrite solutions with the hope that experimental data with nitrite might assist in interpreting data obtained with antimony additions to tin.

EXPERIMENTAL

All measurements were carried out in 0.33M citric acid prepared from C.P. reagent grade and distilled water. Tin rods, 9.5 mm in diameter, and antimony rods, 12.7 mm in diameter, were used as electrodes in polarization work. Both materials were supplied by Alfa Products. Tin-antimony alloys were prepared by electrodeposition on the tin rods with an apparent surface area of 5 cm^2. The plating bath contained

$Na_2SnO_3 \cdot 3H_2O$	25 g/L
NaOH	4 g/L

Antimony additions were made from a solution of antimony chloride containing 1000 ppm antimony as determined by atomic absorption analysis. Plating conditions were 60°, stirred solution, 150-200 A/m^2, 3-4 hours. Plating baths containing low concentrations of antimony were prepared from a solution formed by dissolution of 99.999% tin.

The antimony content of the deposits was determined after the completion of the experiment by dissolving the plated metal in 40% HCl-10% HNO_3 solution. The dissolution process was halted when the crystal structure of the substrate became visible. The acid solutions containing the antimony were diluted to 50 ml, aliquots of which were delivered by means of a micropipet into the carbon rod assembly of a Model 360 Perkin-Elmer atomic absorption spectrophotometer. The total amount of antimony and a knowledge of the weight of the electrodeposited alloy allowed calculation of the concentration of antimony in the deposit.

Pure antimony electrodeposits were made from a potassium antimony citrate plating bath (13) at pH = 3.6 using lead as a substrate. The first deposits from each freshly formed bath were discarded since it was expected that such deposits would contain the majority of the depositable impurities. Excellent deposits were obtained at a current density of 250 A/m^2.

The apparatus used for polarization measurements was that described in ASTM standard G5-72. A Wenking potentiostat was used for potentiostatic measurements in nitrite solutions and with the tin-antimony alloys. Potentiodynamic experiments were performed with a Princeton Applied Research Model 350 Corrosion Measurement Console and a PAR Model K47 Corrosion Cell system. All potentials are referenced to the saturated calomel electrode (SCE). Scan rates were 0.1 mv/sec unless otherwise specified.

The citric acid solution as prepared had a pH of 1.8. Higher pH's were obtained by additions of sodium hydroxide. Deaeration of test solutions was accomplished by sparging with purified grade nitrogen which was dispersed through an ammonium vanadous chloride solution in order to remove traces of oxygen and then through 0.33M citric acid to rid the gas of spray and to equilibrate the nitrogen with water vapor.

Experiments were carried out in practically quiescent solutions. A very small stream of gas passed through a bubbler immersed near the top of the liquid level in the electrolytic cell.

RESULTS

Effect of Antimony on the Corrosion of Tin

The initial studies were carried out on tin-antimony alloys that were electroplated from commercial CP grade of $Na_2SnO_3 \cdot 3H_2O$. Antimony was added to the plating bath from the standard make-up solution and the amount of antimony in the resulting deposit was determined by atomic absorption. The relationship between the amount of antimony in the deposit and the amount of antimony in the solution was linear as shown in Figure 1. However, the curve also shows that the plating bath made up in this way contains appreciable amounts of antimony since the datum point for no purposely-added antimony is at 170 ppm. An estimate of the antimony concentration in the sodium stannate from the electroplating data yielded a value for the tin/antimony ratio of 1000/1. This value is very reasonable since a review of supplier's catalogs indicated that chemically pure sodium stannate typically contains 0.02% antimony. Further experiments were then conducted in plating baths in which the tin was introduced by dissolution of high purity tin.

Figure 2 shows typical cathodic polarization curves obtained in 0.33M citric acid at room temperature for pure tin, and tin alloys containing 350 and 850 ppm of antimony. The Tafel slope of the cathodic curve for pure tin was 0.12 v/decade and that for the anodic curve was approximately 0.04 v/decade. The value for the anodic curve is approximate only since the curve had a limited linear range and little attention was paid to the anodic curve since it was the same for all the alloys studied.

Data summarizing the corrosion rate, as determined from extrapolation of the cathodic polarization curve, as a function of the amount of antimony in the deposit are given in Figure 3. The corrosion rate was linear with respect to the amount of antimony in the tin up to a concentration of antimony of 1000 ppm (0.1%). The important effect of antimony in increasing the corrosion rate is shown by the fact that the corrosion rate was increased approximately 4 times for each 10 ppm antimony.

The question was next addressed as to the mechanism by which antimony had an effect on the corrosion rate of tin. Two possibilities were considered: (1) antimony metal is a better cathode than tin and the increase

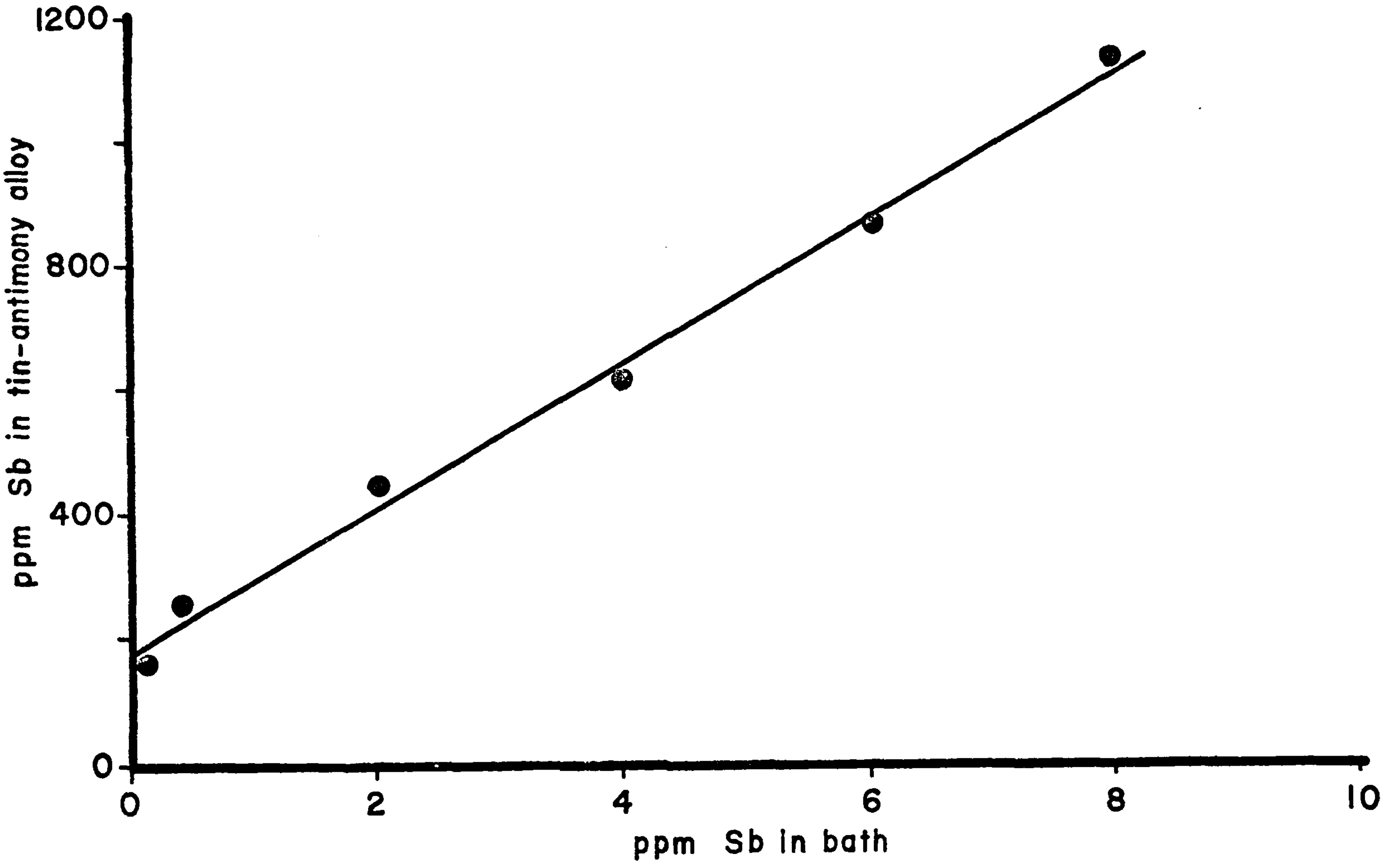

Figure 1. Antimony content of plotting bath versus antimony content in electrodeposit.

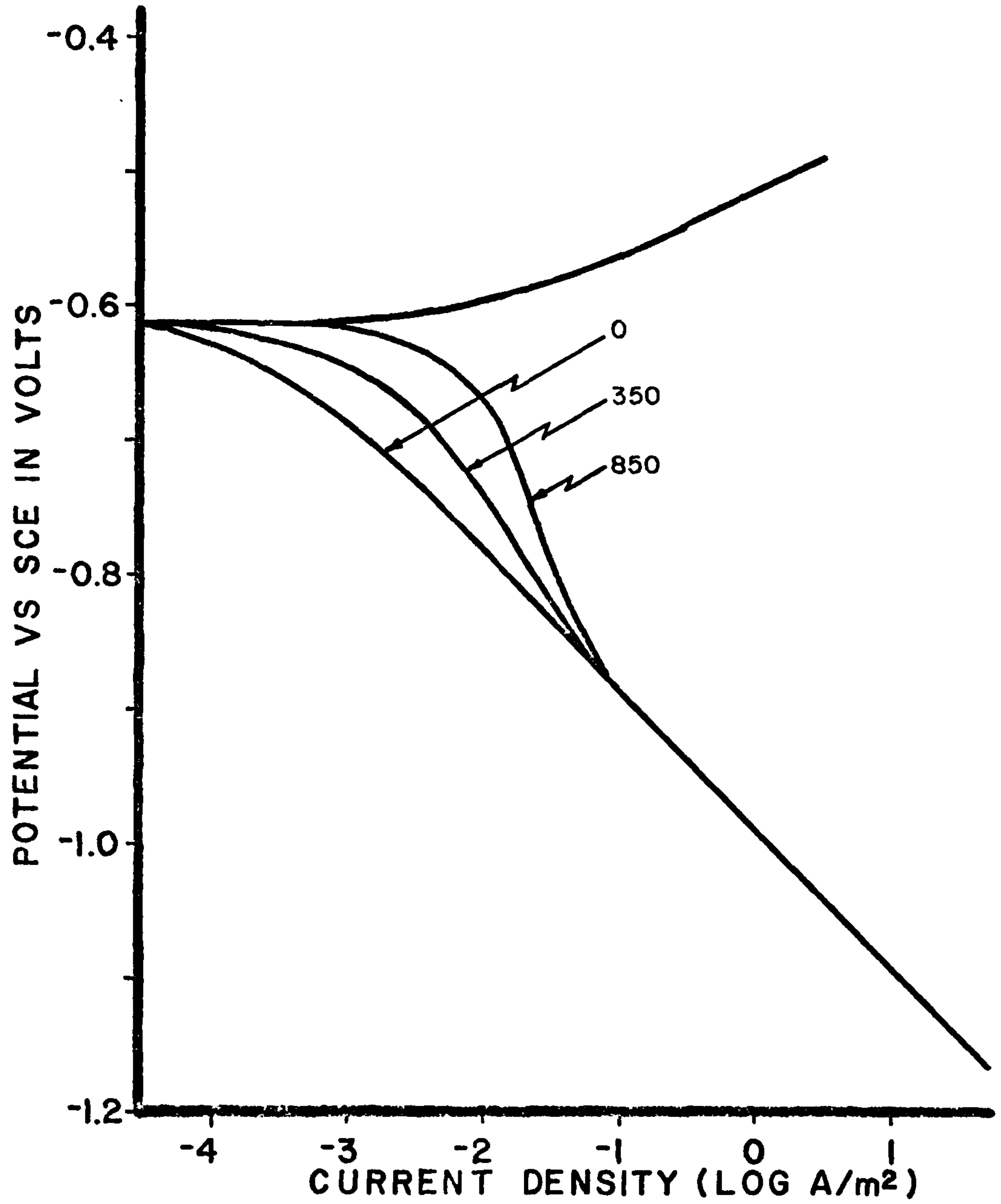

Figure 2. Anodic and cathodic polarization curves for pure tin and tin-antimony alloys in deaerated 0.33M citric acid. Numbers by curves indicate antimony concentration in the tin in ppm. Anodic curve was not changed by antimony additions to tin.

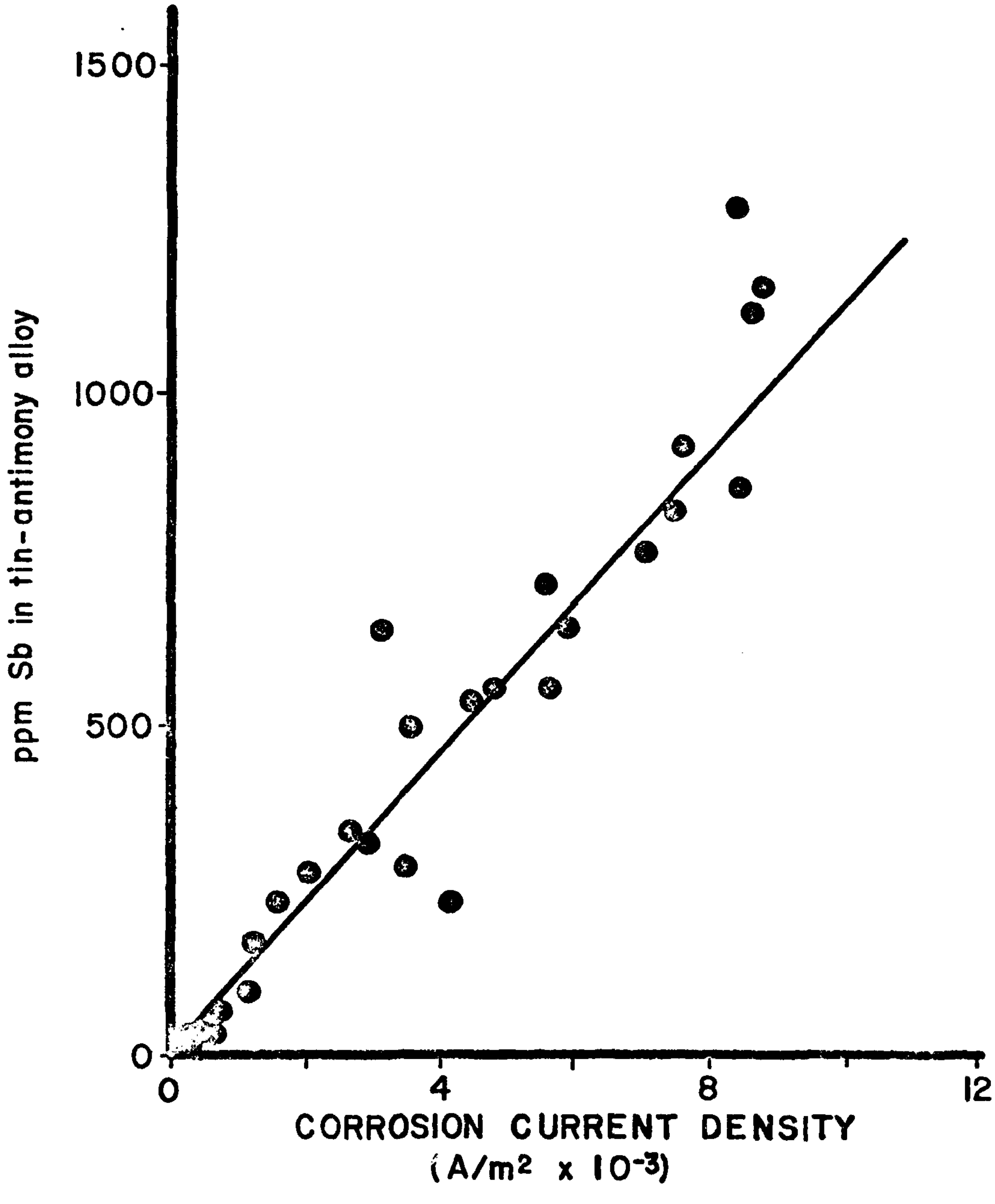

Figure 3. The corrosion rate of tin-antimony alloys in deaerated 0.33M citric acid as calculated from polarization curves.

in corrosion rate is simply in terms of the effect of antimony in increasing the rate of the cathodic reaction; and (2) the corroding surface consists of a thin oxide film on tin and the antimony increases the rate by influencing the catalytic properties of the oxide. Information related to the second question will be presented later in the report.

The cathodic polarization curves were considered to be made up of the sum of the cathodic properties of the two components, pure tin and the antimony additive. Figure 4 shows the method by which the antimony contribution was identified separately from the tin. It was assumed that the contribution of antimony to the total cathodic current was limited by a diffusion step, presumably the removal of the hydrogen product from the vicinity of the antimony atom. Under such an assumption, the limiting current density could be calculated by the method outlined in the schematic drawing in Figure 4 in which the current density due to antimony was obtained by subtracting the cathodic current density due to pure tin from the total cathodic current density. The results of such calculations are shown in Figure 5. There is considerable scatter in the data, but the results are not seriously inconsistent with the assumption made.

The following experiment was carried out to determine if antimony concentrated at the surface during the corrosion reaction. Two identical electrodeposits were prepared, each containing approximately 1000 ppm antimony. The first was analyzed using Auger spectroscopy for antimony content in the surface without any corrosion and the second was analyzed after being subjected to anodic dissolution at 0.2 A/m^2. Within the limits of experimental error, the two specimens were found to have the same surface concentration of antimony. This analytical information combined with the facts that antimony corrodes at a significant rate in the citric acid electrolyte and that the surface of the tin-antimony alloys retained their appearance during dissolution indicate that antimony does not concentrate on the surface of tin during the corrosion process.

Effect of Nitrite on the Corrosion of Tin

Although much work has been done by others on the effect of nitrite on the corrosion of tin, the experiments reported herein were performed in

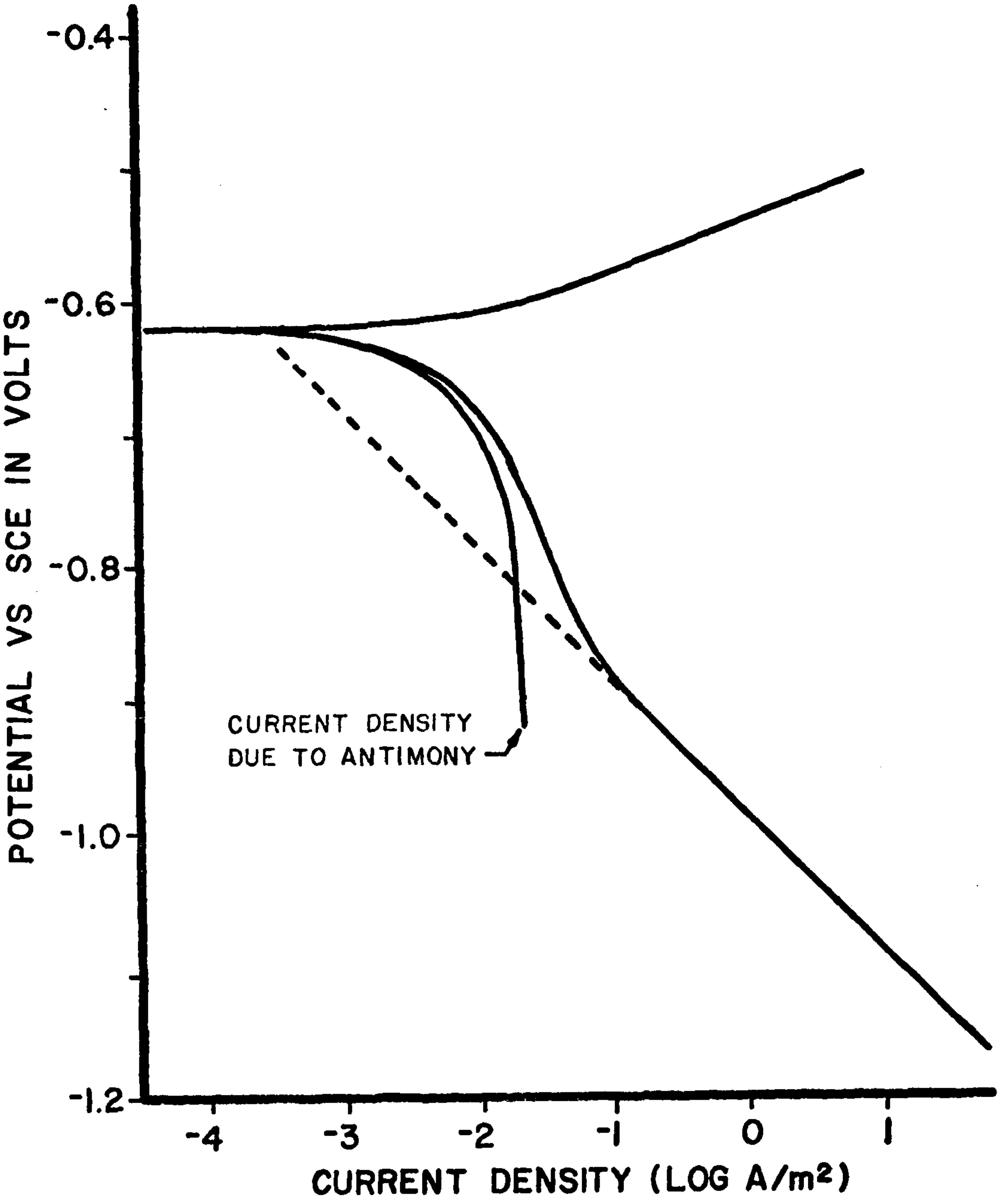

Figure 4. Schematic representation of the method used to calculate the contribution of the antimony to the measured polarization curve.

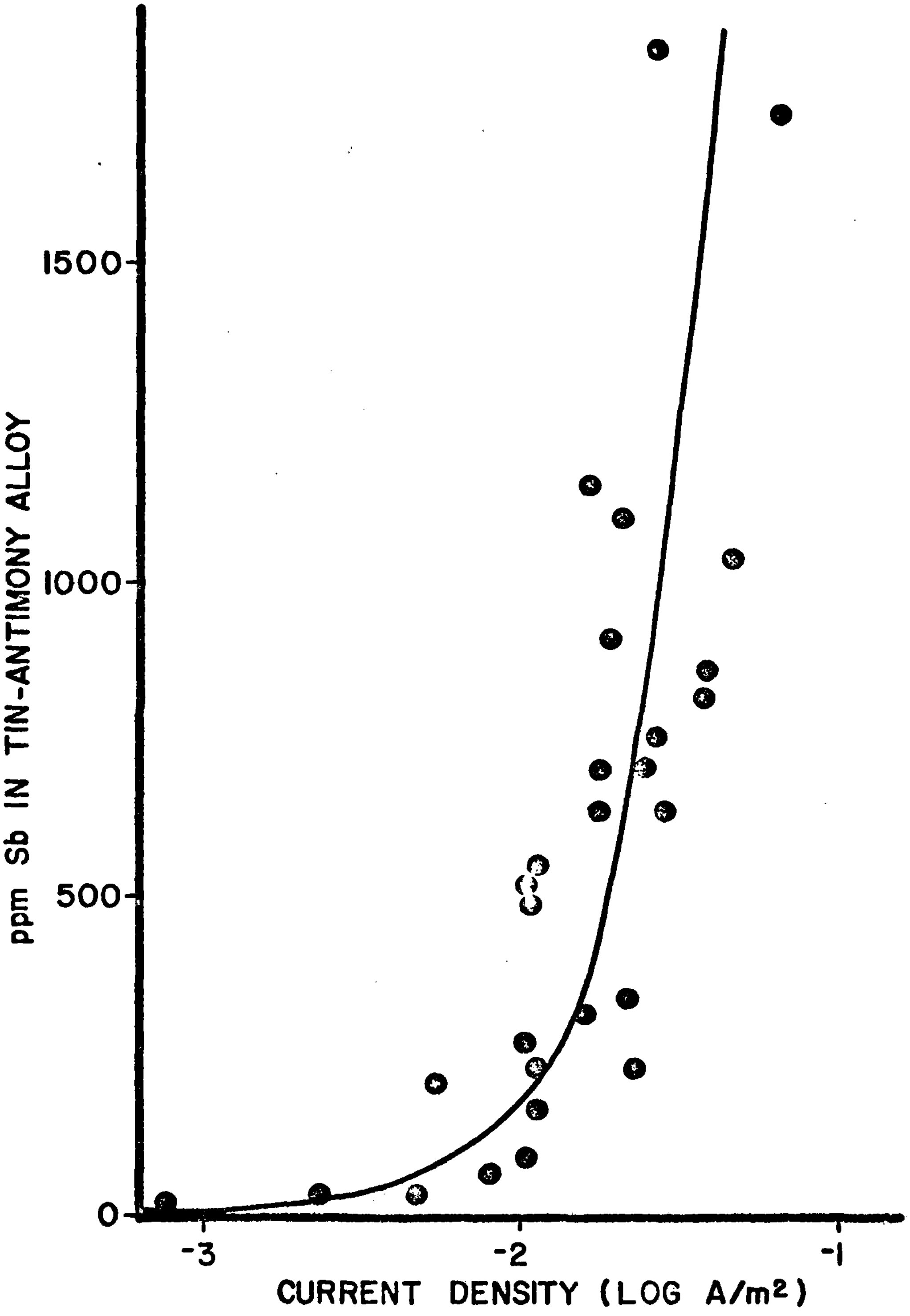

Figure 5. Limiting current density in A/m^2 due to antimony calculated by the method shown in Figure 4.

order to generate specific kinds of information that might be useful in understanding better the influence of the oxide film on tin in controlling corrosion behavior.

Cathodic polarization curves obtained in deaerated 0.33M citric acid in the presence of different concentrations of nitrite are summarized in Figure 6. The curves were similarly shaped at and below 75 ppm NO_2^- with a limiting density that increased with increasing concentration of nitrite in the solution. Above 75 ppm NO_2^- the limiting current density decreased at high cathodic polarizations. The values of the corrosion rate obtained by extrapolation to the corrosion potential are summarized as a function of nitrite concentration in Table I and the values are plotted in Figure 7.

A plot of the corrosion potential vs. the logarithm of the corrosion rate for all the nitrite experiments is given in Figure 8. A plot of the anodic polarization curve is given for comparision. Data are also summarized in Figure 9 in which the corrosion potential is plotted vs. the concentration of nitrite.

Table I

Effect of Nitrite on Tin Corrosion

Nitrite ppm	Corrosion Rate in A/m^2
0	0.00031
5	.067
8	.10
10	.125
12	.17
20	.34
50	.88
75	1.35
100	1.90
200	4.10
300	6.10
500	10.00
1000	21.00

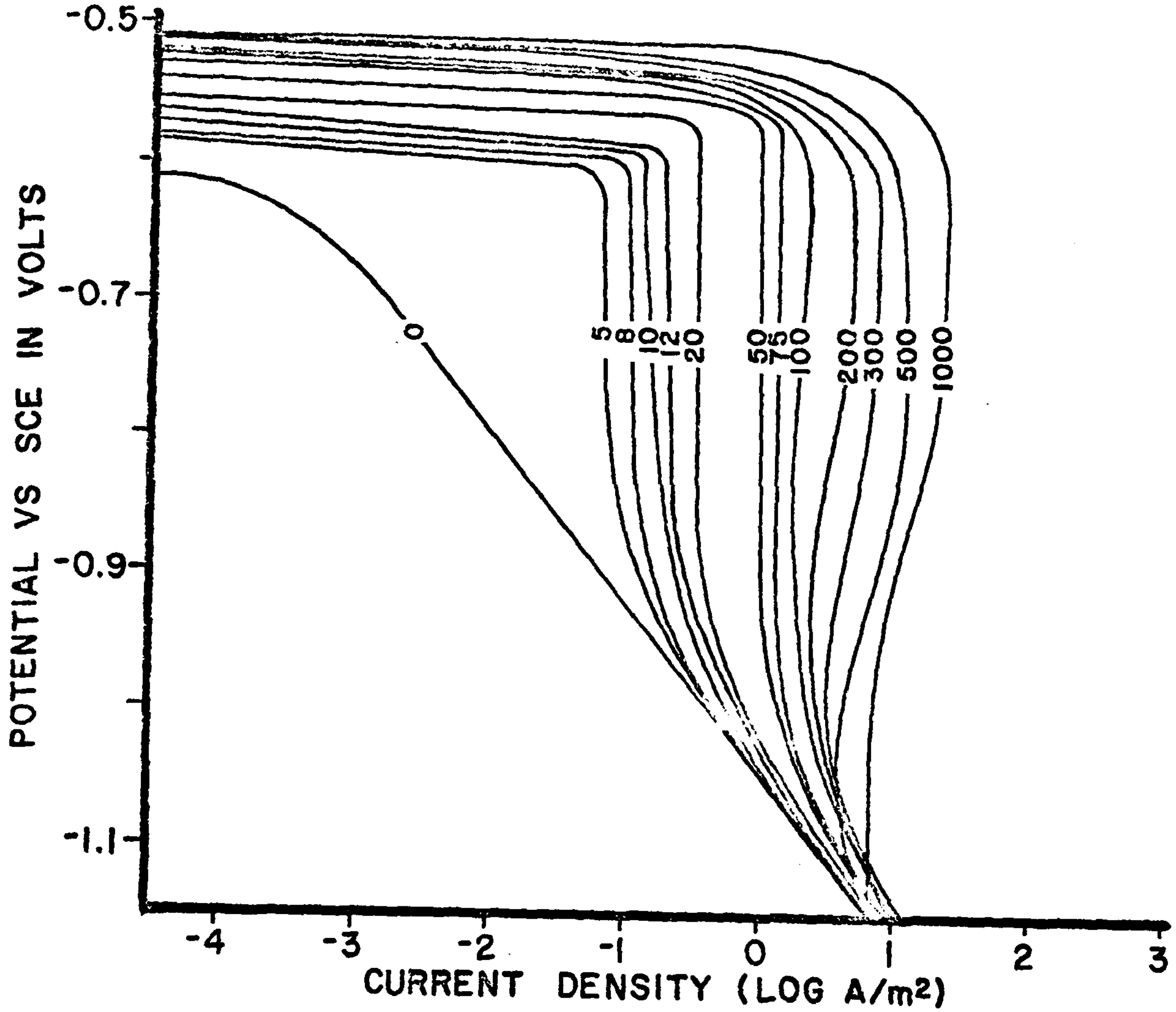

Figure 6. Cathodic polarization curves of pure tin in deaerated 0.33M citric acid containing 0-1000 ppm nitrite.

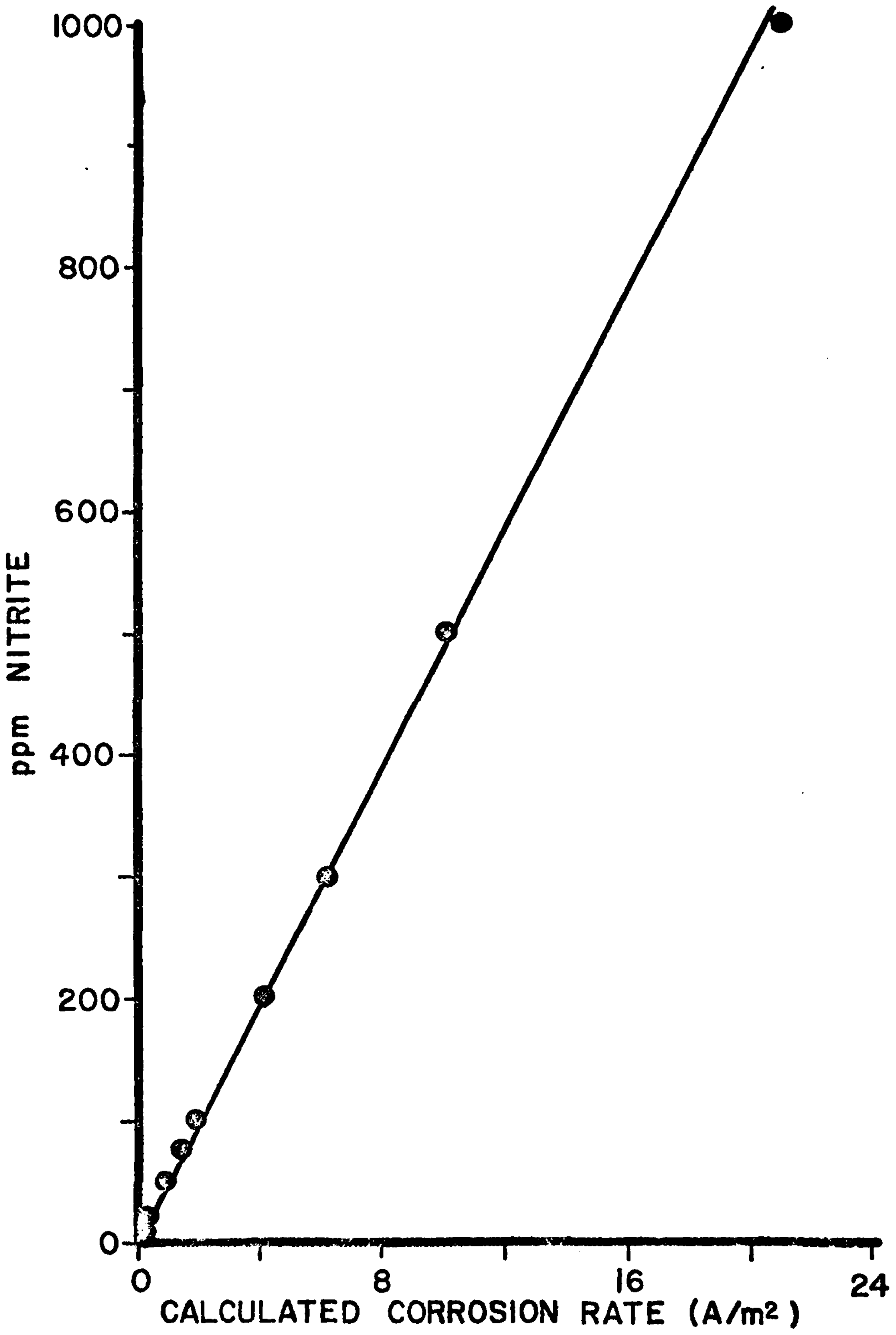

Figure 7. Calculated corrosion rate of tin in deaerated 0.33M citric acid as a function of the nitrite concentration in the solution.

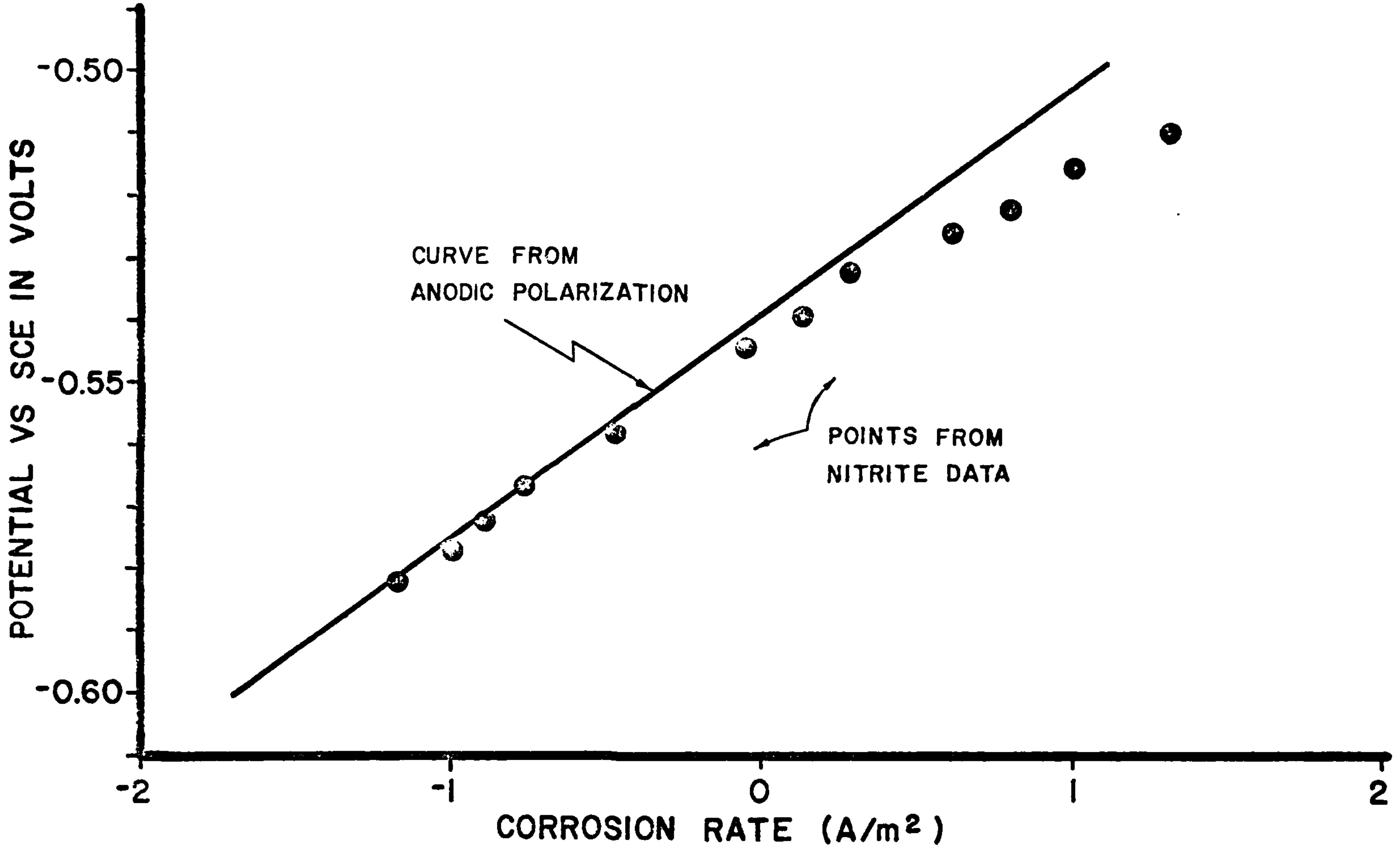

Figure 8. Comparison of the anodic polarization curve for tin in deaerated 0.33M citric acid with the polarization curve as calculated from extrapolation of polarization curves obtained in nitrite solutions back to corrosion potential.

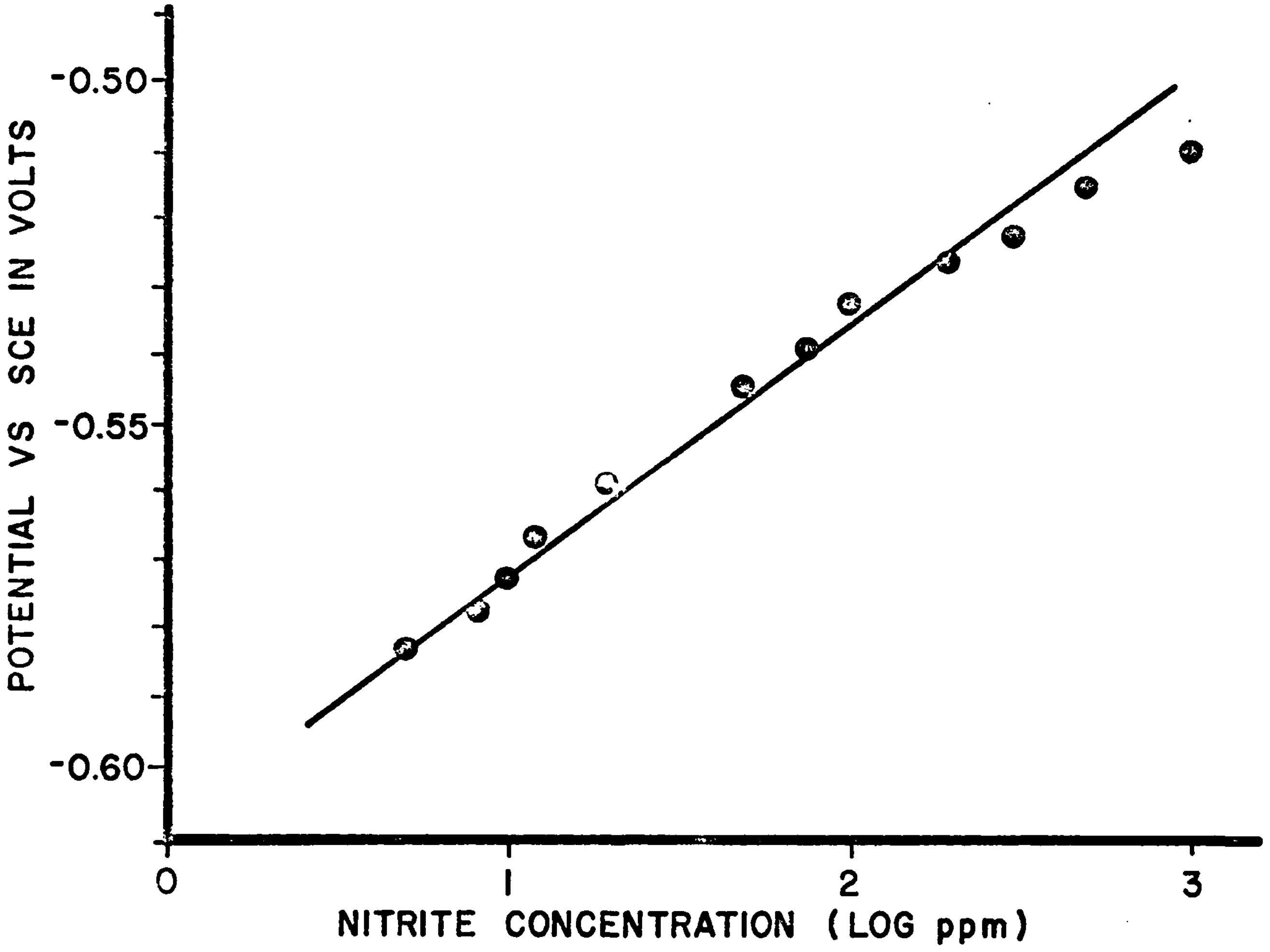

Figure 9. The relationship between the corrosion potential of tin in deaerated 0.33M citric acid and the concentration of nitrite in the solution.

Electrochemical Measurements on Tin and Antimony

Reference polarization curves in deaerated 0.33M citric acid are given in Figure 10 for tin and in Figure 11 for antimony. In both cases the electrode was polarized from the most cathodic potential (-0.9 v. in the case of tin and -0.9 v. in the case of antimony) in the anodic direction at a scan rate of 0.1 mv./sec. The cathodic curve for tin was normal and over the whole range the potential was appoximately linearly related to the logarithm of the current. The cathodic curve for antimony, however, exhibited a "shoulder" at potentials close to the corrosion potential. This shoulder was tentatively associated with an oxide on the antimony and the higher current in the shoulder region was associated with the sum of the currents due to the hydrogen evolution reaction and that associated with reduction of the continuously-forming oxide. Many attempts were made without success to obtain for antimony a typical, Tafel-like cathodic polarization curve. The curve with the minimum shoulder, shown in Figure 12, was the closest to the ideal. Note the discontinuity in the curve labeled "A" in Figure 12.

The effect of scan direction on the cathodic polarization curve is shown in Figure 13. The effects of scan rate and scan direction on the cathodic polarization behavior of antimony are summarized in Figures 14 and 15. Polarization curves obtained at scan rates of 1, 3, and 10 mv./sec. are given in Figure 14. The most striking feature is the increase in the current density associated with the plateau with increase in scan rate. The areas under the shoulder in each of these curves correspond to approximately 100 μ coulombs of charge. Over this scanning range, the charge associated with the shoulder was independent of scan rate.

Figure 15 shows the cathodic polarization curves for antimony obtained when the scan was made in the anodic direction from a starting potential of -0.9 to -0.95 v. The curve obtained at the lowest scan rate, 0.1 mv./sec., is similar to that given in Figure 11. It appears that scan rates of 0.1 mv./sec. allow steady-state conditions whether the scan is in the anodic or cathodic directions. The curve obtained at 1 mv./sec. shows a lower corrosion potential than that obtained when antimony is measured in the absence of polarization. There is a discontinuity at point "A" at approximately the same potential as that equivalent to a corrosion potential obtained with the highest scan rate, 3 mv./sec. The anodic curve exhibited a discontinuity at point "B",

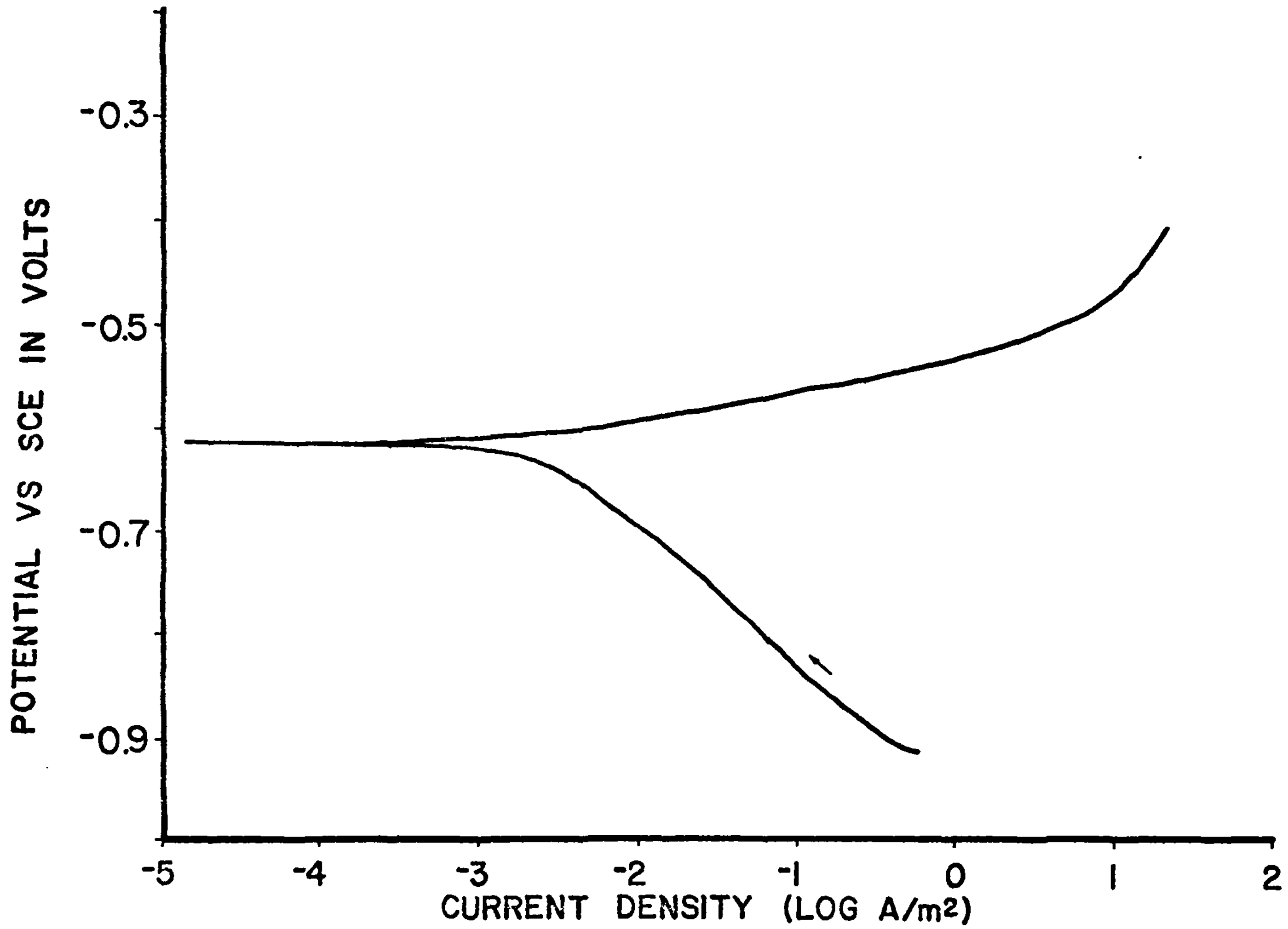

Figure 10. Cathodic and anodic polarization curves for tin in deaerated 0.33M citric acid when polarization was carried out in the anodic direction from a starting potential of 0.91 v. Scan rate = 0.1 mv/sec.

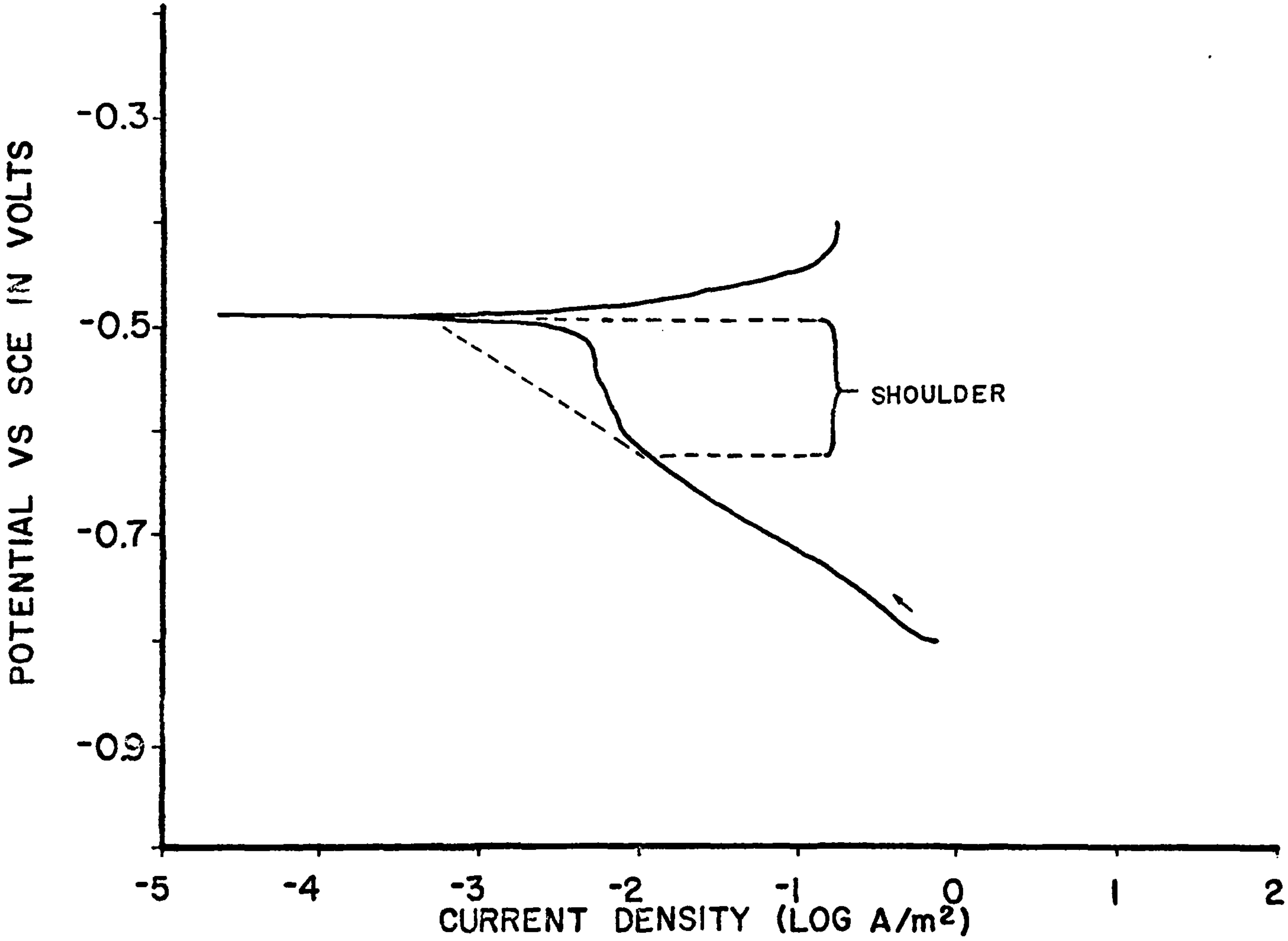

Figure 11. Cathodic and anodic polarization curves for antimony in deaerated 0.33M citric acid when polarization was carried out in the anodic direction from a starting potential of 0.9 v. Scan rate = 0.1 mv/sec.

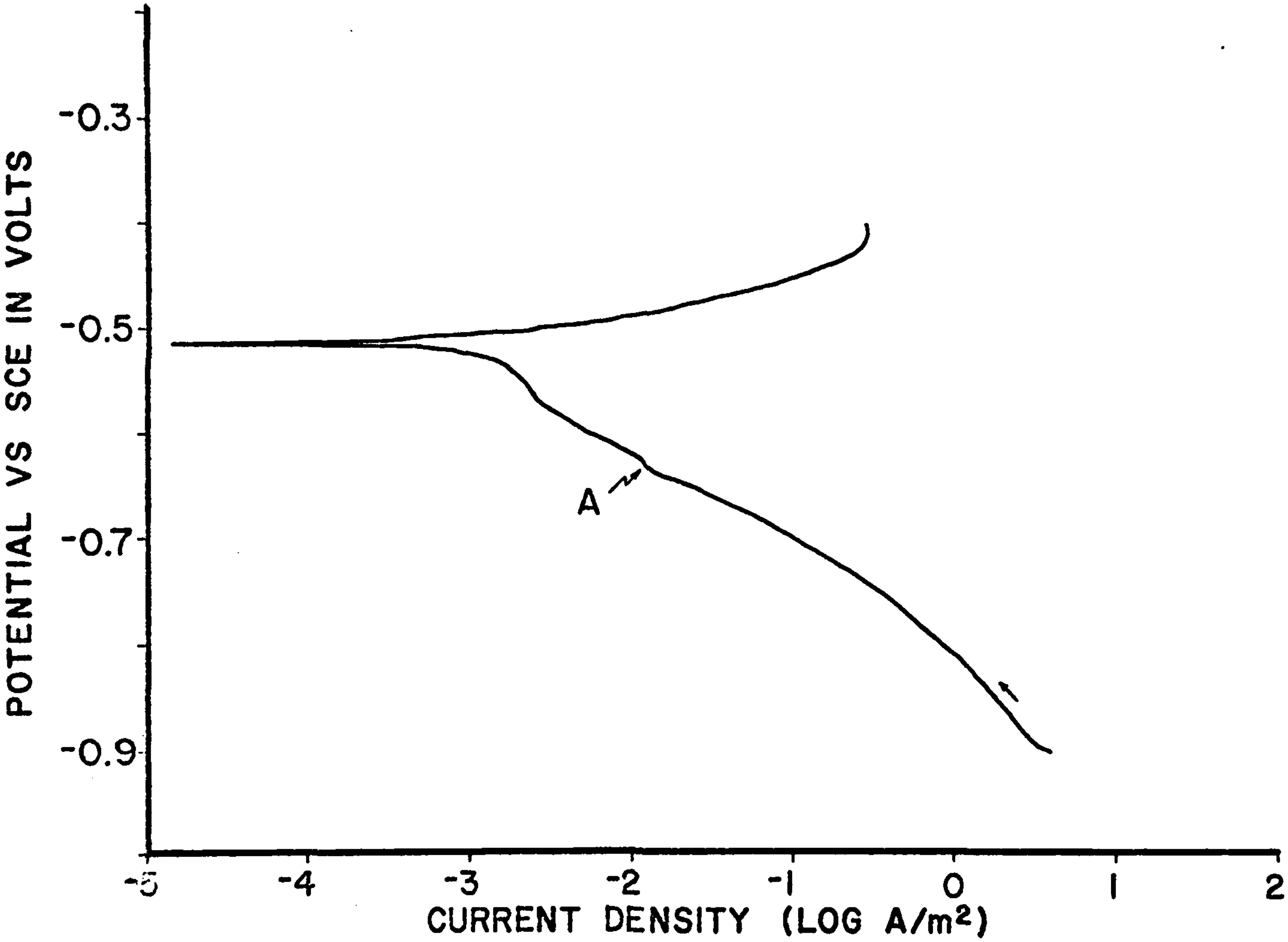

Figure 12. The cathodic polarization curve of antimony in deaerated 0.33M citric acid which exhibited the minimum shoulder in the vicinity of the corrosion potential. Scan rate = 0.2 mv/sec.

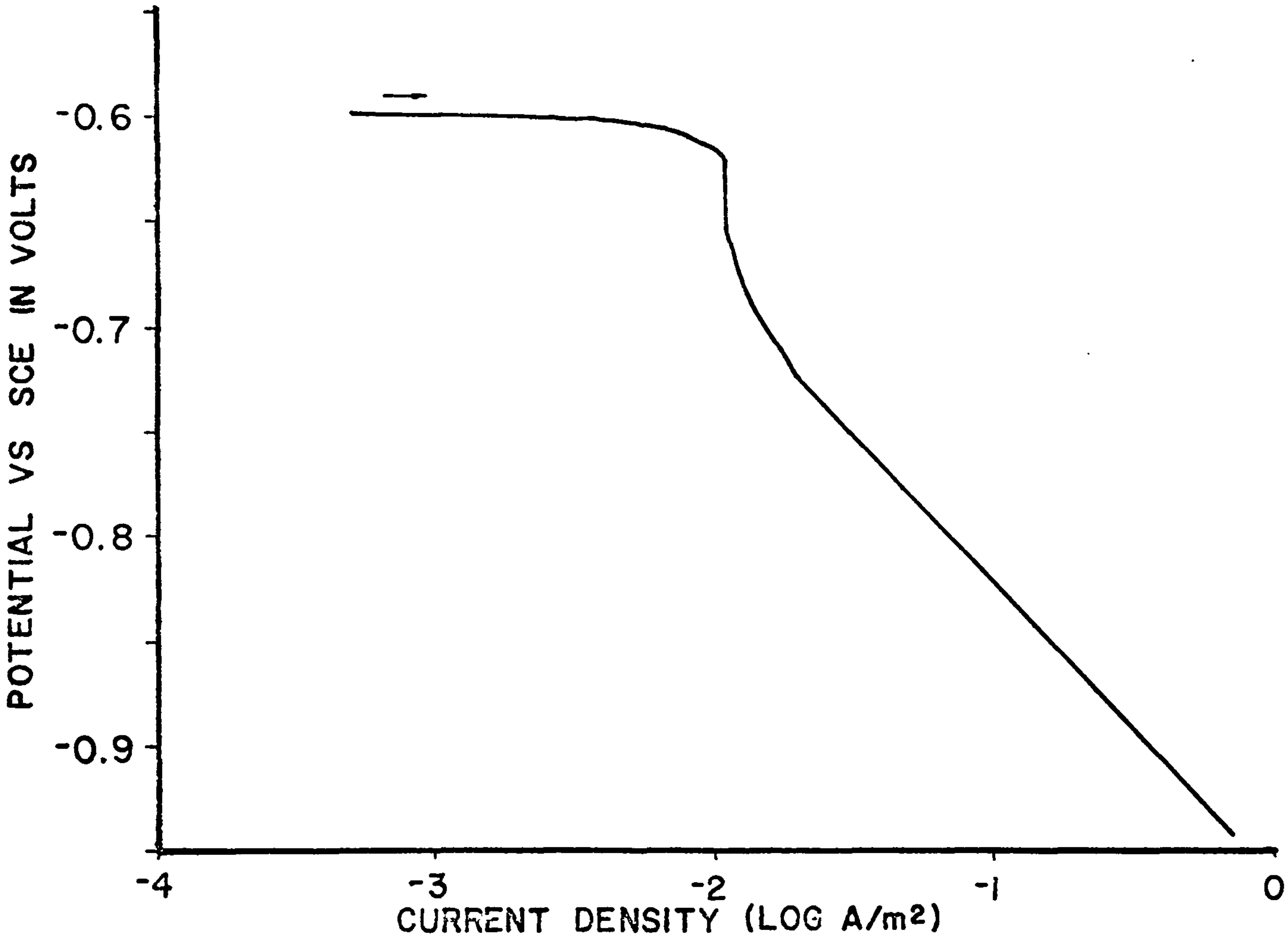

Figure 13. Cathodic polarization curve for tin in deaerated 0.33M citric acid when scan is in the cathodic direction. Compare curve with Figure 10. Scan rate = 0.1 mv/sec.

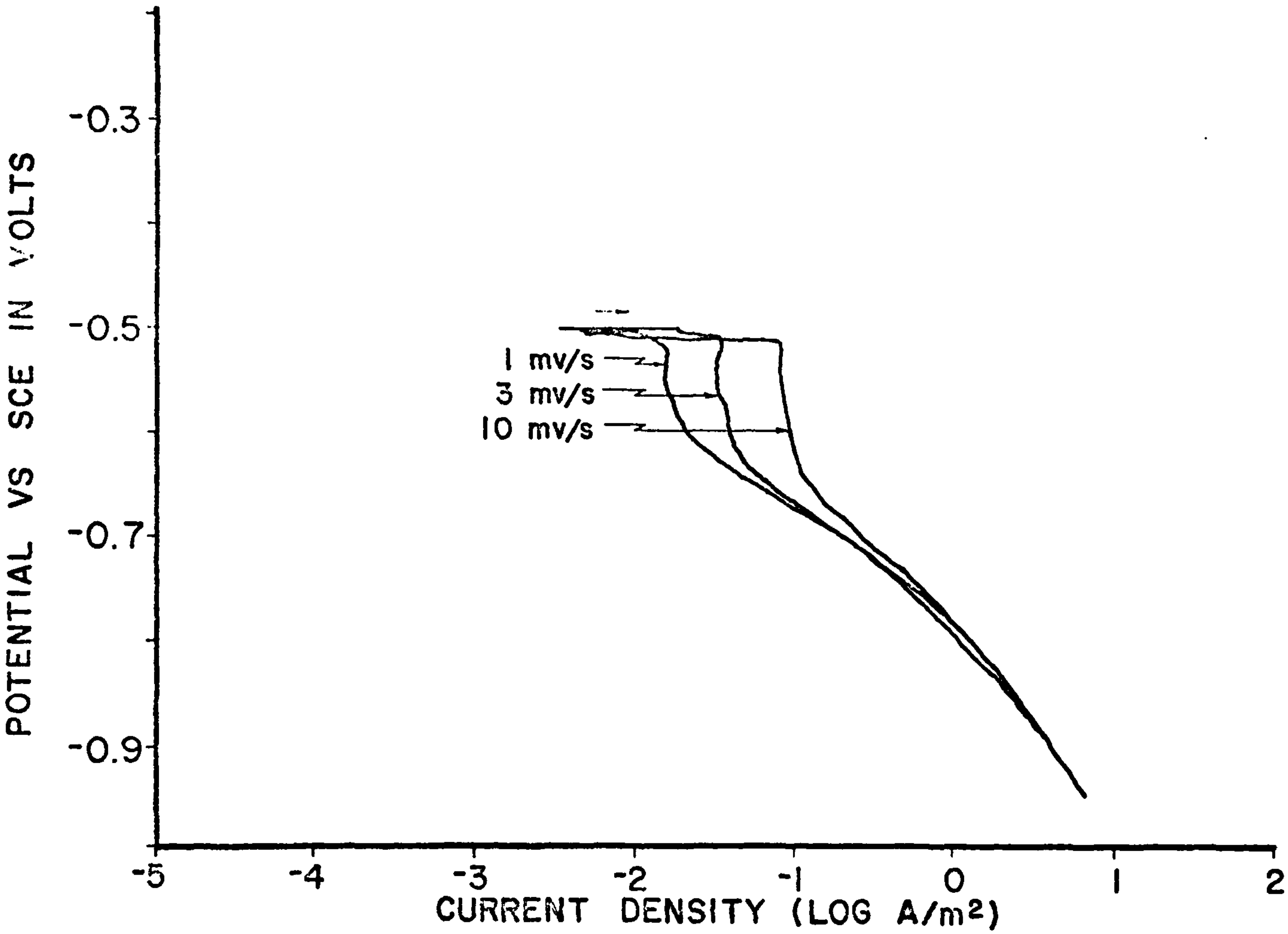

Figure 14. The effect of scan rate on the polarization curve for antimony in deaerated 0.33M citric acid. Scans made in the cathodic direction.

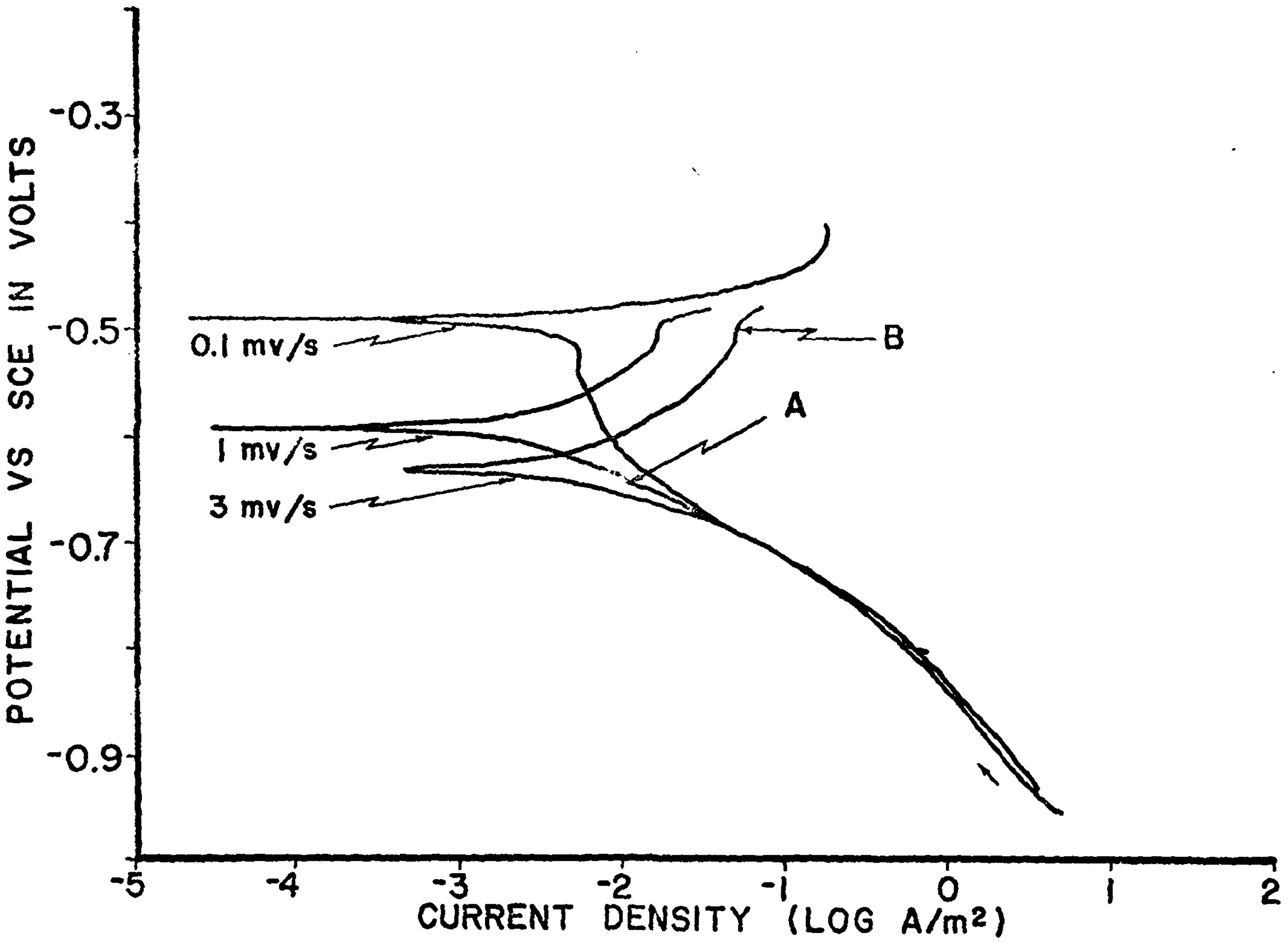

Figure 15. The effect of scan rate on the polarization curve for antimony in 0.33M citric acid. Scans made in the anodic direction.

equivalent to the corrosion potential at the slowest scan rate. The curve obtained at the highest scan rate exhibited no shoulder and the corrosion potential was at the most negative value.

The next objective of the research was to determine the significance of the observed polarization curves to the corrosion of tin containing small amounts of antimony. Figure 16 shows a set of polarization curves for an electrodeposited antimony electrode obtained in deaerated 0.33M citric acid at pH 1.8. Curve a represents the first curve taken in the cathodic direction. Curve b represents a second polarization curve taken a few moments after the completion of curve a and after the electrode had equilibrated at -0.95 v. In other words, the electrode was previously polarized to a potential of approximately -0.95 v. and, presumably, any surface oxide had been reduced by the cathodic treatment. The shoulder area was very small in the second polarization. Curve c was taken shortly after curve b with the direction of polarization in the anodic direction. A slight shoulder is apparent and the corrosion potential is at a slightly more negative potential than when the antimony was first introduced into the solution. Curve d shows the effect of a fast scan rate in the anodic direction. The shoulder is missing because the corrosion potential is at a much more negative value.

Air was bubbled through the solution and curve e was obtained. Under these conditions the corrosion potential is at a less negative value and the shoulder region occupies a considerable area. Finally, curve f was obtained after anodic treatment at +0.5 v. for 2 minutes in the presence of oxygen in solution. The corrosion potential is at a much less negative value and the shoulder region now exhibits the classic appearance of a reduction peak. It should be noted that the peak in the shoulder region is at a potential of approximately -0.5 v. in curves a, e, and f.

A set of polarization curves obtained in deaerated 0.33M citric acid at pH 3.8 is shown in Figure 17. The same general behavior is observed at pH 3.8 as at pH 1.8 but the peak in the shoulder region is at a more negative potential. Curves a, b, d, e, and f are analogous to curves a, b, c, d, and e, respectively, in Figure 16. Curve c, of Figure 17, was obtained under similar conditions as b, except at a fast scan rate.

Figures 14-16 summarize the observations about the polarization behavior of antimony. Different values of the corrosion potential are obtained depending

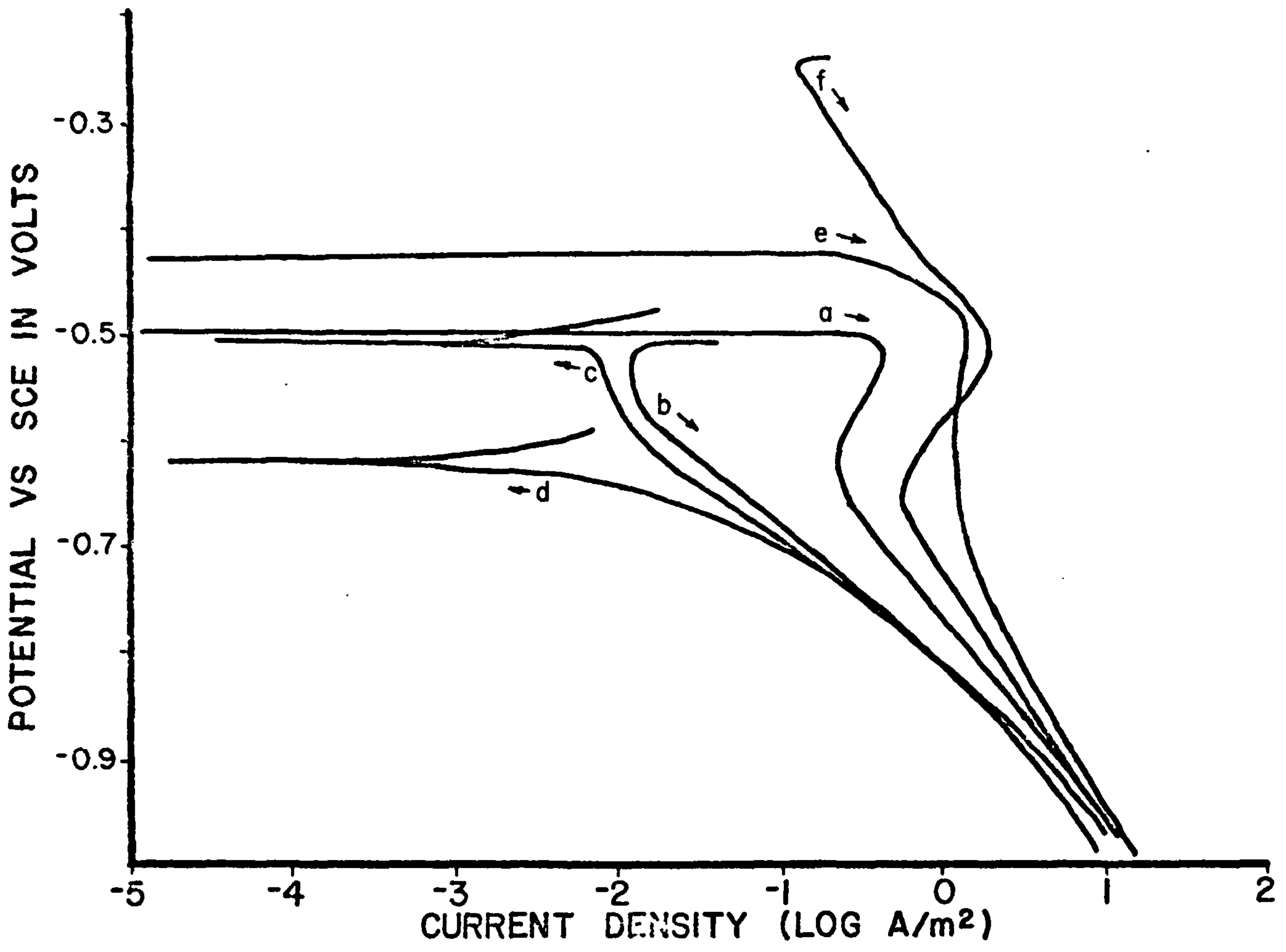

Figure 16. Series of polarization curves for antimony in deaerated 0.33M citric acid. See text for details.

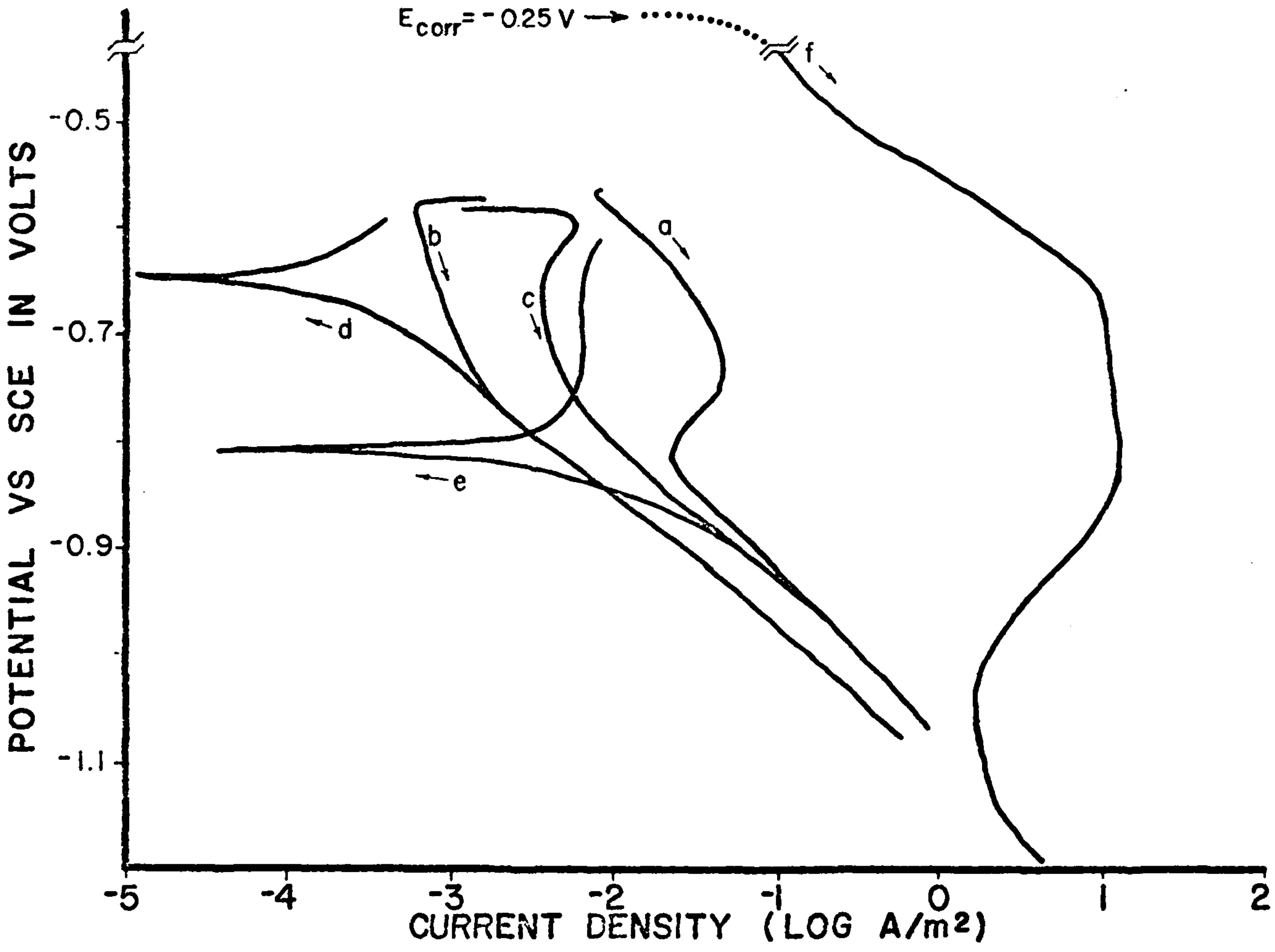

Figure 17. Series of polarization curves for antimony in 0.33M citric acid adjusted to pH 3.8. See text for details.

on the rate of potential change during data collection. A rapid scan rate of 3 mv./sec. leads to a corrosion potential of -0.62 v. A slow scan rate of 0.1 mv./sec. leads to a corrosion potential of -0.506 v. An antimony sample immersed in deaerated solution for the first time, with its air-formed oxide, attains a corrosion potential of approximately -0.5 v. When the antimony is allowed to remain in the solution overnight in the presence of dissolved oxygen, the polarization curve labeled f in Figure 16 is obtained. These results are interpreted by the diagram in Figure 18. It is suggested that at potentials more negative than -0.62 v. the antimony is essentially oxide-free because the cathodic reaction keeps the surface free of oxide. In the region between -0.51 and -0.62, the antimony is partially covered with oxide, the actual amount decreasing with increase in the extent of negative polarization. In the region between -0.50 and -0.51, the antimony is covered with an oxide one to several layers in thickness. At potentials more positive than -0.50 v., the antimony is covered with a thick oxide film. The stoichiometry of the oxides over the whole potential range is not known.

DISCUSSION

The results reported herein firmly establish the fact that antimony when present in tin in concentrations of the order of ppm considerably increases the corrosion rate at room temperature in deaerated 0.33M citric acid. The effect of antimony on the corrosion rate of tin is linearly related to the concentration of antimony in the tin as shown in Figure 3. The equation that describes this effect is:

$$\text{Corrosion rate in A/m}^2 = 0.0003 + 0.000079\ X,$$

where X is the concentration of antimony in the tin in ppm. This equation suggests that the corrosion rate of pure tin, 0.0003 A/m^2, is equivalent to the increased rate caused by the presence of 4 ppm of antimony. Stated in another way, the presence of 4 ppm of antimony in tin doubles the corrosion rate of tin in 0.33 M citric acid at room temperature. This calculation assumes, of course, that the corrosion rate for unalloyed tin is that for pure tin. It is probable, however, that the tin actually used had traces of antimony and that the corrosion rate of pure tin is less than 0.0003 A/m^2.

The Auger spectroscopic studies proved that antimony did not concentrate on the surface of tin during corrosion. The lack of any change in color of the surface during the corrosion process was confirming evidence that antimony did not concentrate at the surface during corrosion. The linear relationship between the corrosion rate and antimony concentration is also circumstantial evidence that the antimony concentration at the surface is linearly related to the antimony concentration in the alloy. Superposition of the cathodic polarization curves for pure tin (Figure 10) and for pure antimony (Figure 11) indicates that at the corrosion potential of tin (-0.61 v.) the antimony is approximately 10 times more effective as a cathode than pure tin in 0.33M citric acid at room temperature.

If it is assumed, as the evidence indicates, that antimony has its influence on the cathodic reaction and if it is further assumed that the contribution of antimony to the cathodic reaction is correctly expressed by the above equation, it may be calculated that the cathodic current density on the antimony is 79 A/m^2, or in more familiar terms, .0079 A/cm^2. This calculated current density may be compared with an actual current density of approximately 10^{-6} A/cm^2 obtained on bulk antimony at the corrosion potential of tin as judged from Figure 12. Thus, antimony in tin at low concentrations is approximately 8000 times more effective in catalyzing the cathodic reaction than antimony in the bulk state. The conclusion appears inescapable that the cathodic activity of antimony atoms is greatly increased when the atoms are present on the surface of a tin substrate.

It is well known that nitrite is an accelerator for the corrosion of tin in fruit acids (4,5,6). This acceleration is attributed to the fact that the nitrite facilitates the cathodic reaction by providing an oxidizing agent to remove the hydrogen generated in the cathodic reaction. Reactions such as the following have been hypothesized:

$$NO_2^- + 2H^+ + e^- = NO + H_2O$$

or

$$NO_2^- + 7H^+ + 6e^- = 2H_2O + NH_3$$

Experimental data accumulated during this research was not directed towards an understanding of the nitrite reaction, but rather towards the effect of nitrite on the tin surface.

The effect of nitrite on the corrosion rate of tin may be described by the following equation:

$$\text{Corrosion rate in A/m}^2 = 0.0003 + 0.021\ Y$$

where Y is the concentration of nitrite in solution in ppm.

One of the interesting observations made in the work with nitrite is the shape of the polarization curve at nitrite concentrations in excess of 100 ppm. At highly negative cathodic potentials the current density decreased from its maximum value before it approached the Tafel line characteristic of the reaction, $2H^+ + 2e^- = H_2$, on tin. The curve has the shape of a "cathodic passivity curve" described previously by Clarke and Bernie (14). The tentative interpretation of this behavior is that at potentials up to approximately 200 mv. negative of the corrosion potential the surface of the tin is partially covered with a thin oxide resulting from the oxidizing character of the nitrite. At more negative potentials, the oxide film does not form because of the strong reducing character of the tin electrode. If this interpretation is correct, it suggests that the partially oxided tin surface is a better cathode than the clean tin surface.

The polarization curve experiments were designed largely to provide evidence related to the reason for the accelerating effect of antimony on the corrosion of tin. When tin is polarized from an initial cathodic potential of -0.9 v., the polarization curve exhibits normal Tafel-like behavior. However, when tin is first immersed in the solution and the cathodic polarization curve is determined from the corrosion potential in the negative direction (Figure 13), there is a shoulder region just negative to the corrosion potential. This shoulder does not occur on successive scans when the electrode is immediately polarized from the corrosion potential. The shoulder apparently represents a reducible form of tin oxide, which does not reform rapidly in the citric acid solution at room temperature.

Antimony showed a behavior during determination of the cathodic polarization curve much different from that of tin. The shoulder could not be eliminated when polarization was in the anodic direction (Figure 11). The magnitude of the shoulder was a function of scan rate (Figure 14), but the number of coulombs associated with the shoulder, 100 μ-coulombs/cm^2, was independent of the scan rate. It is thus concluded that a thin oxide film forms on the surface of antimony very rapidly when the metal is immersed in 0.33M citric acid.

The critical question from the standpoint of our interests is whether or not antimony has any residual oxide film on the surface at the corrosion potential of tin. Unfortunately, the question cannot be answered unequivocally. Studies of the electrochemistry of antimony reported in the literature do not provide an answer (15-27). Superposition of the cathodic polarization curves for tin (Figure 10) and that for antimony (Figure 12) indicates that point A in Figure 12 occurs at a slightly more negative potential than the corrosion potential of tin. As will be pointed out later, it is concluded that point A represents the potential at which an oxide film begins to form on antimony.

The following explanation is offered for the great effect of antimony on the corrosion of tin. The corrosion of tin in acidic solutions is controlled by

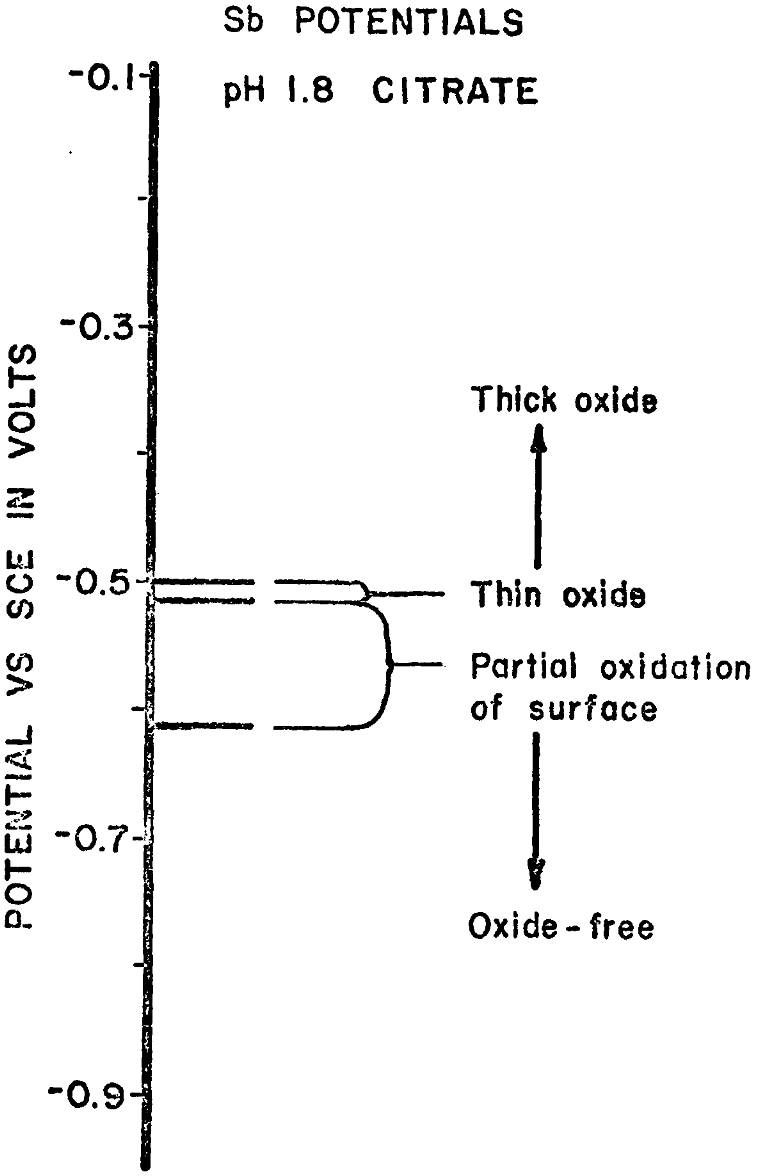

Figure 18. Proposed chemical state of antimony surface in deaerated 0.33M citric acid as a function of potential.

the cathodic reaction, $2H^+ + 2e^- = H_2$. Evidence for this statement comes from our own past research (1) and from many observations made with respect to the iron/tin couple as used in food containers (9,10,11). The reaction may be depolarized by (a) contact of tin with a metal having a high exchange current density for the hydrogen evolution reaction, (b) dissolved oxygen, (c) oxidizing agents such as nitrite, (d) hydrogen acceptors such as certain enzymes and unsaturated organic compounds, and (e) metallic impurities in the tin.

It is hypothesized that the antimony atoms are homogeneously distributed throughout the tin and that their lifetime on the surface is identical to that of a tin atom. In other words, the antimony does not aggregate on the surface and does not redeposit to any significant extent because of its very low concentration (as a result of corrosion) in the large volume of corrosive medium. The polarization curves of tin and antimony lead to the view expressed previously that the antimony is partially oxidized at the corrosion potential of tin. Thus, a single antimony atom at the tin surface, surrounded by tin atoms, would be expected to have a probability of participating in a reaction such as the following:

$$\text{Sb(at tin surface)} + H_2O = \text{SbO(at tin surface)} + H_2.$$

The oxygen, being weakly bonded to the antimony, would then serve as a catalyst for removal of reduced hydrogen atoms on the surface of tin atoms in the immediate vicinity of the antimony atom. The antimony would be free for an additional reaction. A somewhat similar hypothesis has been offered by Anson (28) in explaining the greater reversibility of the iodate reduction reaction on partially oxidized platinum electrodes. Alternatively, it might be considered that the Sb-O complex, surrounded by tin atoms, may serve as a catalyst for the hydrogen evolution reaction. In either event, the antimony atoms are much more effective as catalysts for the hydrogen evolution reaction when they are surrounded by tin atoms as opposed to bulk antimony where each atom is surrounded by antimony atoms.

ADMINISTRATIVE DETAILS

Public Disclosure of Results

(1) "Corrosion of Tin — Effect of Antimony in Deoxygenated Citric Acid", E. M. Ibrahim, R. D. Granata, and H. Leidheiser, Jr., 14th Middle Atlantic Regional Meeting, American Chemical Society, Valley Forge, Pennsylvania, April 23-25, 1980.

(2) "Comparative Behavior of Cathodic Corrosion Reactions on Metals and Oxide-Covered Metals", R. D. Granata, E. M. Ibrahim, and H. Leidheiser, Jr., Electrochemical Society Meeting, Hollywood, Florida, October 8, 1980.

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