

MICHIGAN STATE UNIVERSITY LIBRARIES  
3 1293 00852 3643



RETURNING MATERIALS:  
Place in book drop to  
remove this checkout from  
your record. FINES will  
be charged if book is  
returned after the date  
stamped below.

SEP 26 1994

EFFECT OF SURFACTANTS UPON CORROSION  
INHIBITION OF HIGH-STRENGTH 7075-T6  
ALUMINUM ALLOY

By  
Freddy Castellanos

A THESIS  
Submitted to  
Michigan State University  
in partial fulfillment of the requirements  
for the degree of  
MASTER OF SCIENCE

Department of Metallurgy, Mechanics and Material Science

1985

## ABSTRACT

### EFFECT OF SURFACTANTS UPON CORROSION INHIBITION OF HIGH-STRENGTH 7075-T6 ALUMINUM ALLOY

By

Freddy Castellanos

A potentiodynamic polarization technique has been used to investigate the effectiveness of various surfactants and borax-nitrite formulations upon the corrosion inhibition of 7075-T6 aluminum alloy in chloride-containing solutions.

Small additions of surface-active agents provide effective protection against general corrosion to Al 7075-T6 in the presence of low chloride concentrations. The passive film formed by these surfactants and the borax-nitrite inhibitor, however, does not provide good protection against attack at high chloride concentrations.

Most of the surface-active agents evaluated behaved similarly in the extent of protection to Al 7075-T6 against general corrosion, when used with and without inhibitor. Furthermore, these surfactants interacted synergistically with the borax-nitrite inhibitor formulations to give a better protection to this alloy. The effectiveness of these surfactants in the corrosion inhibition of high-strength 7075-T6 aluminum alloy is discussed from the results of the anodic polarization measurements.

## ACKNOWLEDGMENT

The author wishes to express his appreciation to his major professor, Dr. Robert Summitt, for his counsel and encouragement during the investigation and for his helpful suggestions on the manuscript.

## TABLE OF CONTENTS

|  | page |
|--|------|
| LIST OF TABLES .....                           | iv   |
| LIST OF FIGURES .....                          | v    |
| I.    INTRODUCTION .....                       | 1    |
| II.   THEORETICAL BACKGROUND .....             | 3    |
| III.  APPARATUS AND EXPERIMENTAL PROCEDURE ... | 13   |
| IV.   EXPERIMENTAL RESULTS .....               | 24   |
| V.    DISCUSSION .....                         | 50   |
| VI.   CONCLUSIONS .....                        | 53   |
| REFERENCES .....                               | 54   |

## LIST OF TABLES

| Table |   | Page |
|-------|---|------|
| 1     | Inhibitors Formulations .....             | 19   |
| 2     | Surface-Active Agents .....               | 20   |
| 3     | Chemical Analysis of Al 7075-T6 .....     | 21   |
| 4     | Mechanical Properties of Al 7075-T6 ..... | 22   |

## LIST OF FIGURES

| Figure |  | Page |
|--------|--|------|
| 1      | Theoretical Electrochemical System with Two<br>Oxidation-Reduction Reactions .....   | 7    |
| 2      | Corrosion Cell for Polarization Measurements...  | 14   |
| 3      | Experimental Arrangement .....   | 15   |
| 4      | Anodic Polarization of Al 7075-T6 in 1.0 wt. %<br>NaCl Solution without Inhibitor .....                                      | 25   |
| 5      | Anodic Polarization of Al 7075-T6 in 0.02 wt.%<br>NaCl Solution without Inhibitor .....                                      | 26   |
| 6      | Effect of Increasing Chloride Concentration<br>upon Anodic Polarization of Al 7075-T6 without<br>Inhibitor .....             | 27   |
| 7      | Anodic Polarization of Al 7075-T6 in 0.58 wt. %<br>NaCl Solution with Inhibitor Formulation I ....                           | 28   |
| 8      | Anodic Polarization of Al 7075-T6 in 0.02 wt. %<br>NaCl Solution with Inhibitor Formulation I ....                           | 29   |
| 9      | Effect of Increasing Chloride Concentration<br>upon Anodic Polarization of Al 7075-T6 with<br>Inhibitor Formulation I .....  | 30   |
| 10     | Anodic Polarization of Al 7075-T6 in 0.58 wt. %<br>NaCl Solution with Inhibitor Formulation II ...                           | 32   |
| 11     | Anodic Polarization of Al 7075-T6 in 0.02 wt. %<br>NaCl Solution with Inhibitor Formulation II ...                           | 33   |
| 12     | Effect of Increasing Chloride Concentration<br>upon Anodic Polarization of Al 7075-T6 with<br>Inhibitor Formulation II ..... | 34   |

| Figure   | Page |
|--|------|
| 13 Effect of Surfactant upon Anodic Polarization of Al 7075-T6 in 0.02 wt.% NaCl Solution with Inhibitor Formulation II .....  | 35   |
| 14 Effect of Surfactant upon Anodic Polarization of Al 7075-T6 in 0.02 wt.% NaCl Solution with Inhibitor Formulation III ..... | 36   |
| 15 Anodic Polarization of Al 7075-T6 in 0.02 wt.% NaCl, 0.01 wt.% Zonyl FSA Solution without Inhibitor .....                   | 38   |
| 16 Anodic Polarization of Al 7075-T6 in 0.02 wt.% NaCl, 0.01 wt.% Hamposyl L-30 Solution without Inhibitor .....               | 39   |
| 17 Anodic Polarization of Al 7075-T6 in 0.02 wt.% NaCl, 0.01 wt.% Polystep B-12 Solution without Inhibitor .....               | 40   |
| 18 Effect of Surfactant upon Anodic Polarization of Al 7075-T6 in 0.02 wt.% NaCl Solution without Inhibitor .....              | 41   |
| 19 Anodic Polarization of Al 7075-T6 in 1.0 wt.% NaCl, 0.01 wt.% Hamposyl C Solution without Inhibitor .....                   | 43   |
| 20 Anodic Polarization of Al 7075-T6 in 1.0 wt.% NaCl, 0.01 wt.% Hamposyl O Solution without Inhibitor .....                   | 44   |
| 21 Anodic Polarization of Al 7075-T6 in 1.0 wt.% NaCl, 0.01 wt.% Hamposyl L-30 Solution without Inhibitor .....                | 45   |

| Figure   | Page |
|--|------|
| 22 Anodic Polarization of Al 7075-T6 in 1.0 wt.%<br>NaCl, 0.01 wt.% Zonyl FSA Solution without<br>Inhibitor .....                    | 46   |
| 23 Effect of Surfactant Concentration upon<br>Anodic Polarization of Al 7075-T6 in 1.0 wt.%<br>NaCl Solution without Inhibitor ..... | 48   |
| 24 Effect of Surfactant upon Anodic Polarization<br>of Al 7075-T6 in 0.02 wt.% NaCl Solution with<br>Inhibitor Formulation IV .....  | 49   |

## I. INTRODUCTION

### A. General Introduction

This study evaluates the effects of various surface-active agents on the corrosion inhibition by borax-nitrite in aqueous corrosion of aluminum alloys. A potentiodynamic polarization technique was used to investigate the effectiveness of the various surfactants and borax-nitrite formulations when a 7075-T6 high strength aluminum alloy was exposed to chloride-containing solutions. This electrochemical technique accelerates the corrosion process, thus, the data may be obtained in a short time.

Several surfactants were tested with relation to their effect on general corrosion. As a result, some additions have been found to provide protection to 7075-T6 aluminum alloy.

### B. General Background

Aluminum owes much of its wide range of applications to its good corrosion resistance. However, high strength aluminum alloys, like all other alloys, are subject to corrosion in chloride-containing solutions. Corrosion may be prevented in a number of ways. One way is to isolate the metal from the aggressive environment by coating the surface of the metal. Anodic and cathodic protection by external polarization also is used to reduce the corrosion rate of

metals. Another way is to use inhibitors.

Inhibitors may be grouped as anodic and cathodic types. The cathodic inhibitor retards the reaction at the cathode and permits the metal to stay at a negative potential (very close to the corrosion potential). The anodic inhibitor suppresses the reaction at the anode and promotes the formation of protective oxide films.

Cathodic inhibitors are usually less effective than the anodic type in terms of reduction in corrosion rate. Anodic inhibitors, when used in sufficient quantity are very effective. It is known that two or more inhibitors acting together can act synergistically, having a greater effect than would be expected from the effects observed when they act separately<sup>(1)</sup>.

Several studies have shown that a variety of inhibitors are effective in reducing the corrosion of aluminum and its alloys<sup>(2)-(8)</sup>. Borax-nitrite based inhibitor formulations have been found to be effective as corrosion inhibitors for aluminum alloys<sup>(9)-(11)</sup>. The use of surface-active agents as corrosion inhibitors for aluminum and its alloys also has been studied<sup>(12),(13)</sup>.

A program was conducted to determine whether addition of small amounts of surfactants to a borax-nitrite based inhibitor formulation was effective in corrosion inhibition of 7075-T6 aluminum alloy. This study is similar to that performed by Khobaib<sup>(2)</sup> and others<sup>(12)</sup>.

## II. THEORETICAL BACKGROUND

### A. The Basic Electrode Equation: The Butler-Volmer Equation

One of the most important trends in electrochemical kinetics consists of the development of equations which describe the potential-current relationships of an electrode. An understanding of the nature and shape of polarization curves is important in practical studies of corrosion phenomena. Since corroding systems are not at equilibrium our interest is in electrode kinetics. Excellent reviews of the electrode kinetics are given by Bockris<sup>(14),(15)</sup> and others<sup>(16)-(23)</sup>.

#### 1. Electrode Reactions

When an inert metal is immersed in a solution containing an oxidation-reduction system, electron-transfer reactions may occur. Electron transitions take place from the metal or electrode to the oxidized component of the system and from the reduced component to the metal. We will designate the forward reaction



as the cathodic reaction, and the reverse reaction as the anodic reaction. The rate of the cathodic reaction can be written as

$$v_c = K_c C_1 \exp(-\beta F \Delta \phi / RT), \quad (1)$$

and similarly, the rate of the anodic reaction can be written

$$v_a = K_a C_2 \exp ((1-\beta) F \Delta \phi / RT), \quad (2)$$

where  $K_c$  and  $K_a$  are the rate constants for the cathodic and anodic reactions, respectively, and are independent of potential and concentration. The quantities  $C_1$  and  $C_2$  are the concentrations of the reacting ions at the immediate surface of the electrode,  $\Delta \phi$  is the potential difference between the electrode or metal and a reference electrode, e.g., hydrogen or saturated calomel electrode (SCE),  $\beta$  is a factor greater than zero but less than unit, called the symmetry factor,  $F$  and  $R$  are the Faraday constant and gas constant, respectively, and  $T$  is the absolute temperature. These rates may be expressed in terms of current density as

$$i_c = -Fv_c, \quad (3)$$

and

$$i_a = Fv_a, \quad (4)$$

where  $v$  and  $F$  have the units moles/cm<sup>2</sup>-sec and amperes times second per mole, respectively, then the units of  $i$  are amperes per square centimeter. The above equations also can be written as

$$i_c = -FK_c C_1 \exp (-\beta F \Delta \phi / RT), \quad (5)$$

and

$$i_a = FK_a C_2 \exp ((1-\beta) F \Delta \phi / RT). \quad (6)$$

Anodic currents are positive and cathodic currents negative.

The net current density for the reactions will be

$$i = i_a + i_c. \quad (7)$$

## 2. The Exchange-Current Density

At equilibrium the rates of the cathodic and anodic reactions become equal, thus, there is no net current. The currents corresponding to these reactions are equal in magnitude and opposite in direction,

$$i_o = FK_c C_1 \exp(-\beta F\Delta\phi^0/RT) = FK_a C_2 \exp((1-\beta)F\Delta\phi^0/RT), \quad (8)$$

where  $i_o$  is defined as the exchange-current density and the equilibrium potential will be

$$\Delta\phi^0 = RT/F(1-2\beta) \ln K_c C_1 / K_a C_2. \quad (9)$$

## 3. The Polarized electrode

If the potential difference between the electrode and the reference electrode is changed from the equilibrium value, the cathodic current density and anodic current density are unequal to each other. Thus, there is a net current density and the magnitude of this will depend on the change in the potential difference introduced. The net current density can be written

$$i = i_o \left( \exp((1-\beta)F(\Delta\phi - \Delta\phi^0)/RT) - \exp(-\beta F(\Delta\phi - \Delta\phi^0)/RT) \right), \quad (10)$$

where  $\Delta\phi$  is different from  $\Delta\phi^0$  and is defined as the non-equilibrium potential difference. The difference  $\Delta\phi - \Delta\phi^0$  is defined as the overpotential  $\eta$ , and measures how much the potential difference has departed from the equilibrium potential value, thus

$$\eta = \Delta\phi - \Delta\phi^{\circ} \quad (11)$$

Equation (10) can be written

$$i = i_0 \left( \exp \left( \frac{(1-\beta)F\eta}{RT} \right) - \exp \left( -\frac{\beta F\eta}{RT} \right) \right) \quad (12)$$

Equation (12) is a fundamental equation in electrode kinetics known as the Butler-Volmer equation<sup>(15),(22),(23)</sup>. At positive overvoltage  $i$  is positive, so that the net current is anodic, and at negative overvoltage,  $i$  is negative, therefore, the net current is cathodic. If the electrochemical reaction occurs at large anodic overvoltage, i.e., at  $\eta \gg RT/F$ , the second term of equation (12) can be neglected, then, it becomes

$$i = i_0 \exp \left( \frac{(1-\beta)F\eta}{RT} \right) \quad (13)$$

If the electrochemical reaction occurs at large cathodic overvoltage, i.e., at  $\eta \ll RT/F$ , the first term in Equation (12) can be neglected, thus

$$i = i_0 \exp \left( -\frac{\beta F\eta}{RT} \right) \quad (14)$$

Equations (13) and (14) can be written as

$$\eta = -\frac{RT}{(1-\beta)F} \ln i_0 + \frac{RT}{(1-\beta)F} \ln i \quad (15)$$

for anodic polarization, and

$$\eta = \frac{RT}{\beta F} \ln i_0 - \frac{RT}{\beta F} \ln i \quad (16)$$

for cathodic polarization.

Both Equations (15) and (16) can be reduced to the form of the Tafel equation

$$\eta = a + b \log i, \quad (17)$$

where  $a$  and  $b$  are the Tafel coefficient and Tafel slope, respectively. Figure 1 shows the relationships between

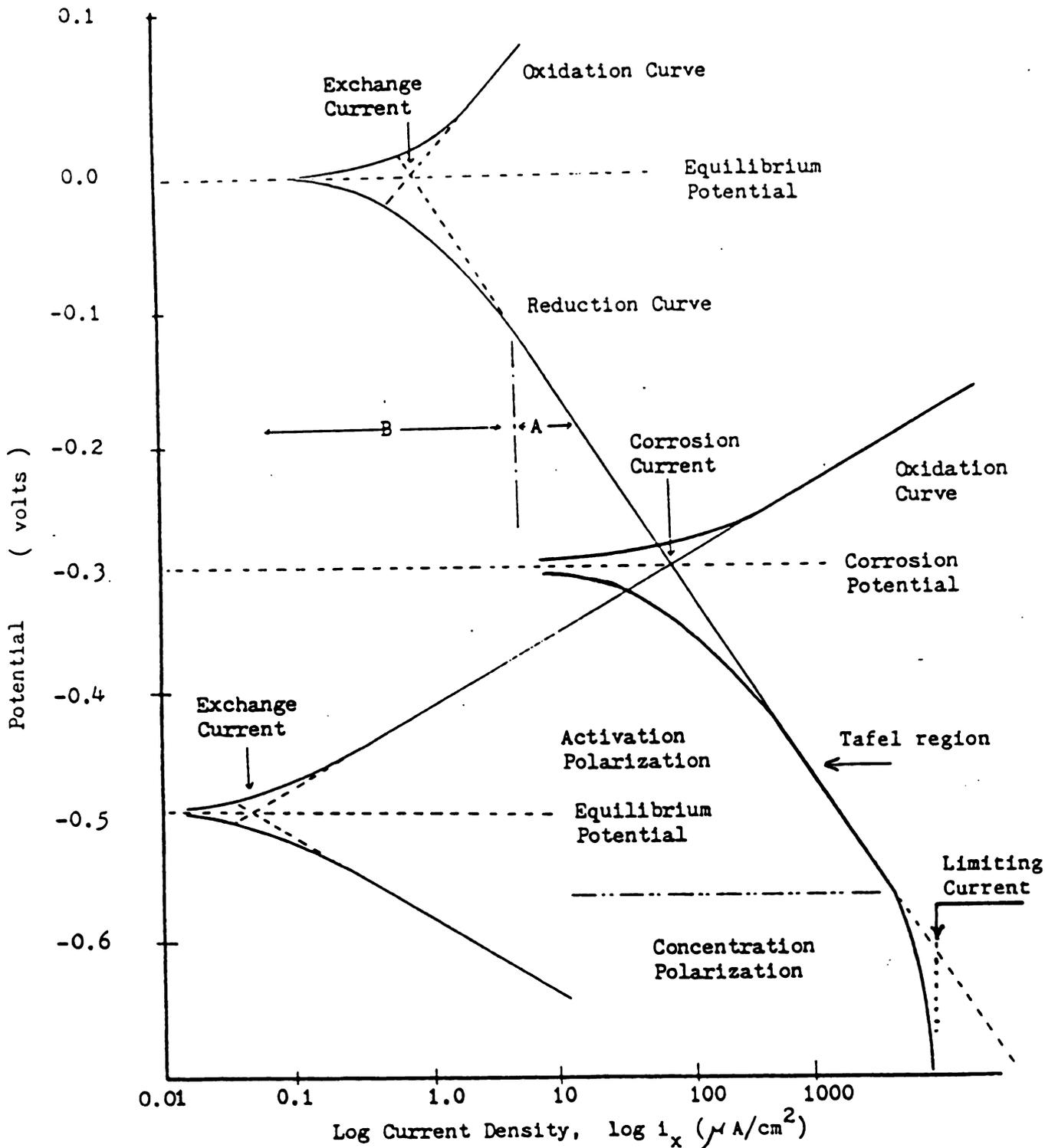


FIGURE 1 THEORETICAL ELECTROCHEMICAL SYSTEM WITH TWO OXIDATION - REDUCTION REACTIONS

the overvoltage and the exchange-current density for these values as  $\eta$  vs  $\log i$ . Note the deviation from Tafel slope that exists at low overvoltages.

a. Concentration Polarization

Concentration polarization occurs at high overvoltages when the reaction rate is so large that the species being oxidized or reduced cannot reach the surface at a sufficiently rapid rate. Thus, the concentration of the reactants in the vicinity of the electrode will change and the rate then is controlled by the rate at which the reacting ions can diffuse to the surface of the electrode. The change in potential resulting from concentration polarization is given by<sup>(24),(25)</sup>

$$\eta_c = RT/nF \ln (1-i/i_L), \quad (18)$$

where  $i_L$  is the limiting current density for the cathodic reaction, representing the maximum rate of reduction possible for a given system, and  $i$  is the applied current density.

The equation expressing the limiting current density  $i_s$ <sup>(24)</sup>

$$i_L = nDFC_0/x, \quad (19)$$

where  $D$  is the diffusion coefficient of the reacting ions (ions being reduced),  $C_0$  is the concentration of the reacting ions in the bulk solution,  $n$  is the number of unit charges transported per ion in the diffusion process,  $F$  is the Faraday constant, and  $x$  is the thickness of the diffusion layer of electrolyte next to the electrode surface. In stirred

solutions,  $x$  is independent of the concentration gradient between the bulk solution and the surface. On the other hand, in unstirred solutions,  $x$  is not totally independent of the concentration gradient, but only varies slightly with it. Petrocelli<sup>(26)</sup> and others<sup>(27),(28)</sup> have presented extensive discussions on concentration polarization.

#### 1. Concentration Changes

The concentration changes in the vicinity of the electrode are caused by mass transfer, which results either from differences in electrical or chemical potential, or from movement of a volume of solution. Three processes are of importance in the mass transfer process<sup>(24),(30)</sup>:

i. Migration, i.e., the movement of reacting ions toward the surface of the electrode under the influence of an electrical field.

ii. Convection, i.e., the movement of liquid containing the substance of interest in solution, which can result either from mechanical stirring or convection caused by a thermal or density gradient.

iii. Diffusion, i.e., the movement of species under the influence of a chemical potential concentration gradient.

#### b. Resistance Polarization

Resistance polarization occurs in the case that the

electrolyte near the electrode has an appreciable resistance. In this case the passage of current will give rise to a potential difference which obeys Ohm's law; this ohmic potential difference contributes to the total overvoltage measured. Ohmic resistance is dependent on the conductivity of the solution and on the experimental arrangement. The resistance polarization is given by<sup>(24),(29)</sup>

$$\eta_r = i K_r, \quad (20)$$

where  $i$  is the applied current density, and  $K_r$  is the solution resistance, a function of applied current if the conductance of the solution adjacent to the electrode interface changes.

## B. Corrosion Reaction

When an electrode is placed in a solution containing an oxidation-reduction system and the electrode material takes part in the reaction so that the whole system is not in oxidation-reduction equilibrium, the measured potential difference between the metal or electrode and the reference electrode on open circuit is called the corrosion potential. Then, there will be a cathodic current density, whereby the oxidized system is being reduced and an anodic current density dissolving the metal, and the two currents will be of the same magnitude on open circuit. This open-circuit current density is called the corrosion current density, given by

$$i_a = i_c = i_{\text{corr}}. \quad (21)$$

Substituting the Butler-Volmer equation for each reaction,

$$\begin{aligned} & i_{\text{oa}} \left( \exp\left(\frac{(1-\beta_1)F(\Delta\phi^* - \Delta\phi_1)}{RT}\right) - \right. \\ & \quad \left. \exp\left(-\beta_1 F(\Delta\phi^* - \Delta\phi_1)/RT\right) \right) \\ = & i_{\text{oc}} \left( \exp\left(\frac{(1-\beta_2)F(\Delta\phi^* - \Delta\phi_2)}{RT}\right) - \right. \\ & \quad \left. \exp\left(-\beta_2 F(\Delta\phi^* - \Delta\phi_2)/RT\right) \right), \end{aligned} \quad (22)$$

where  $\Delta\phi^*$  is the corrosion potential (potential difference between the metal and the reference electrode), and it lies between  $\Delta\phi_1$  and  $\Delta\phi_2$ . The subscript 1 refers to the anodic reaction and the subscript 2 to the cathodic reaction. Given the values of  $i_{\text{oa}}$ ,  $i_{\text{oc}}$  and  $\Delta\phi_1, \Delta\phi_2$ , one can compute the corrosion potential,  $\Delta\phi^*$ . The net current density is given by

$$\begin{aligned} i = & i_{\text{corr}} \left( \exp\left(\frac{(1-\beta_1)F(\Delta\phi - \Delta\phi^*)}{RT}\right) - \right. \\ & \quad \left. \exp\left(-\beta_2 F(\Delta\phi - \Delta\phi^*)/RT\right) \right). \end{aligned} \quad (23)$$

This equation resembles the Butler-Volmer equation for a single reaction, where the corrosion potential and corrosion current density have replaced the equilibrium potential and the exchange-current density, respectively. For the anodic reaction, i.e.,  $i_a > i_c$ , the current  $i$  is

$$i = i_{\text{corr}} \exp\left(\frac{(1-\beta_1)F(\Delta\phi - \Delta\phi^*)}{RT}\right), \quad (24)$$

and, if  $i_c < i_a$  (cathodic reaction), Equation (23) becomes

$$i = i_{\text{corr}} \exp\left(-\beta_2 F(\Delta\phi - \Delta\phi^*)/RT\right). \quad (25)$$

Equations (24) and (25) can be written as

$$\begin{aligned} \Delta\phi - \Delta\phi^* = & RT/(1-\beta_1)F \ln i \\ & - RT/(1-\beta_1)F \ln i_{\text{corr}}, \end{aligned} \quad (26)$$

and

$$\Delta\phi - \Delta\phi^* = -RT/\beta_2 F \ln i + RT/\beta_2 F \ln i_{\text{corr}}. \quad (27)$$

Both, Equations (26) and (27) can be reduced to the form of the Tafel equation. Extrapolation of Tafel branches to their intersection at the corrosion potential gives the corrosion current density and is shown in Figure 1. Hence, the Tafel extrapolation technique may be used to determine anodic and cathodic Tafel slopes and the corrosion current density.

### III. APPARATUS AND EXPERIMENTAL PROCEDURE

It is well known that corrosion processes can be explained in terms of electrochemical reactions, for this reason, electrochemical techniques often are employed to evaluate general corrosion. One such technique is the polarization method which permits studies of the kinetics of corrosion phenomena and their reaction mechanisms.

The measured current during polarization experiments is related to the reactions taking place. The procedure is to polarize a working electrode anodically or cathodically with respect to a reference electrode, and to measure the current associated with the potential change. Figure 2 shows a cell for polarization measurements. After sufficient data have been obtained a polarization curve relating current to potential is plotted. Information regarding to corrosion behavior of different materials in different solutions are obtained from the polarization curves. They also can be used to evaluate the effectiveness of corrosion inhibitors and surface-active agents, to calculate corrosion rates, and to detect changes of corrosion with time.

#### A. Equipment

The experimental arrangement used in this investigation is shown in Figure 3. the measurements were conducted by means of a potentiostat/galvanostat, corrosion cell, and electrome-

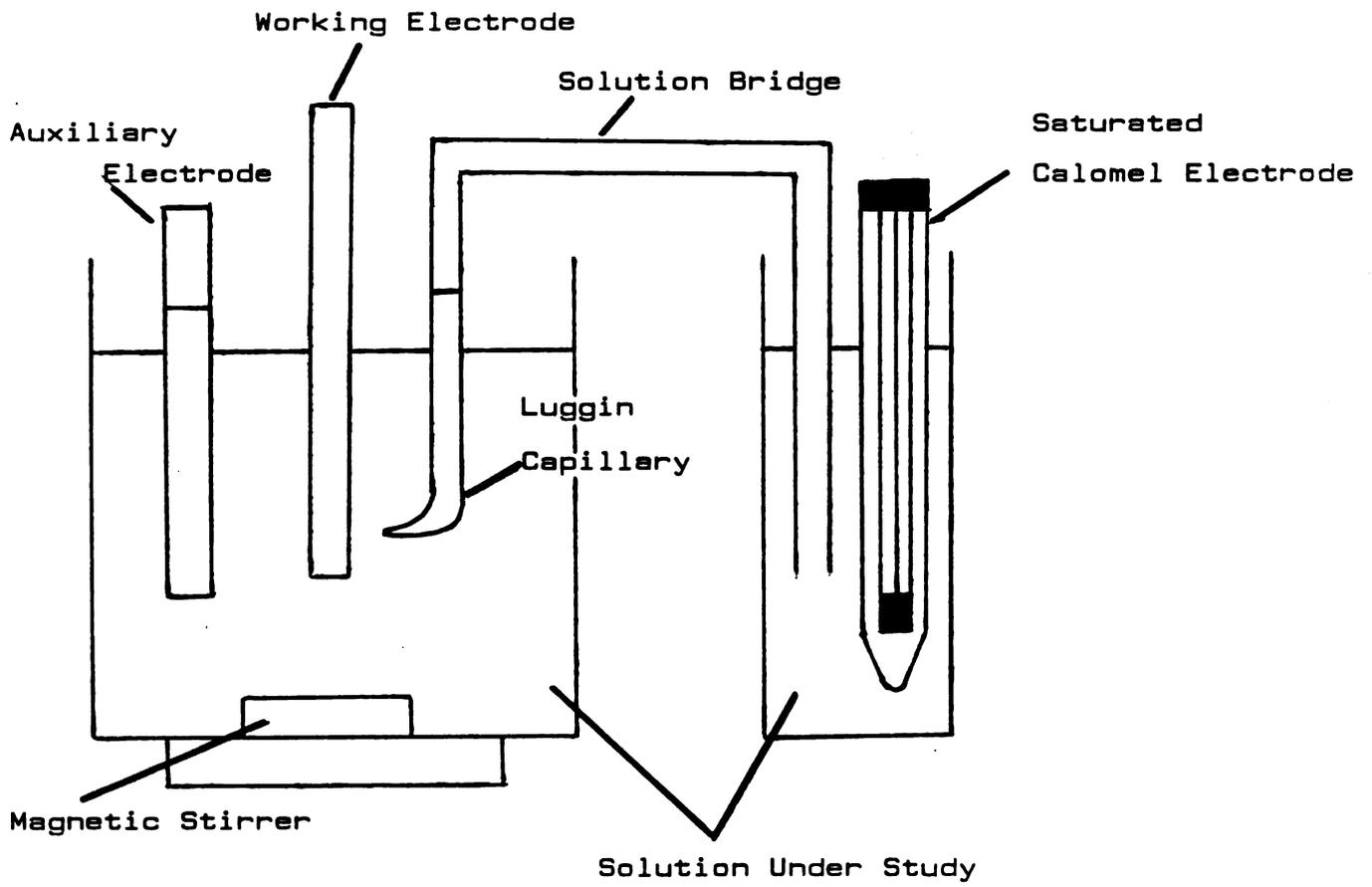


FIGURE 2 CORROSION CELL FOR POLARIZATION MEASUREMENTS.

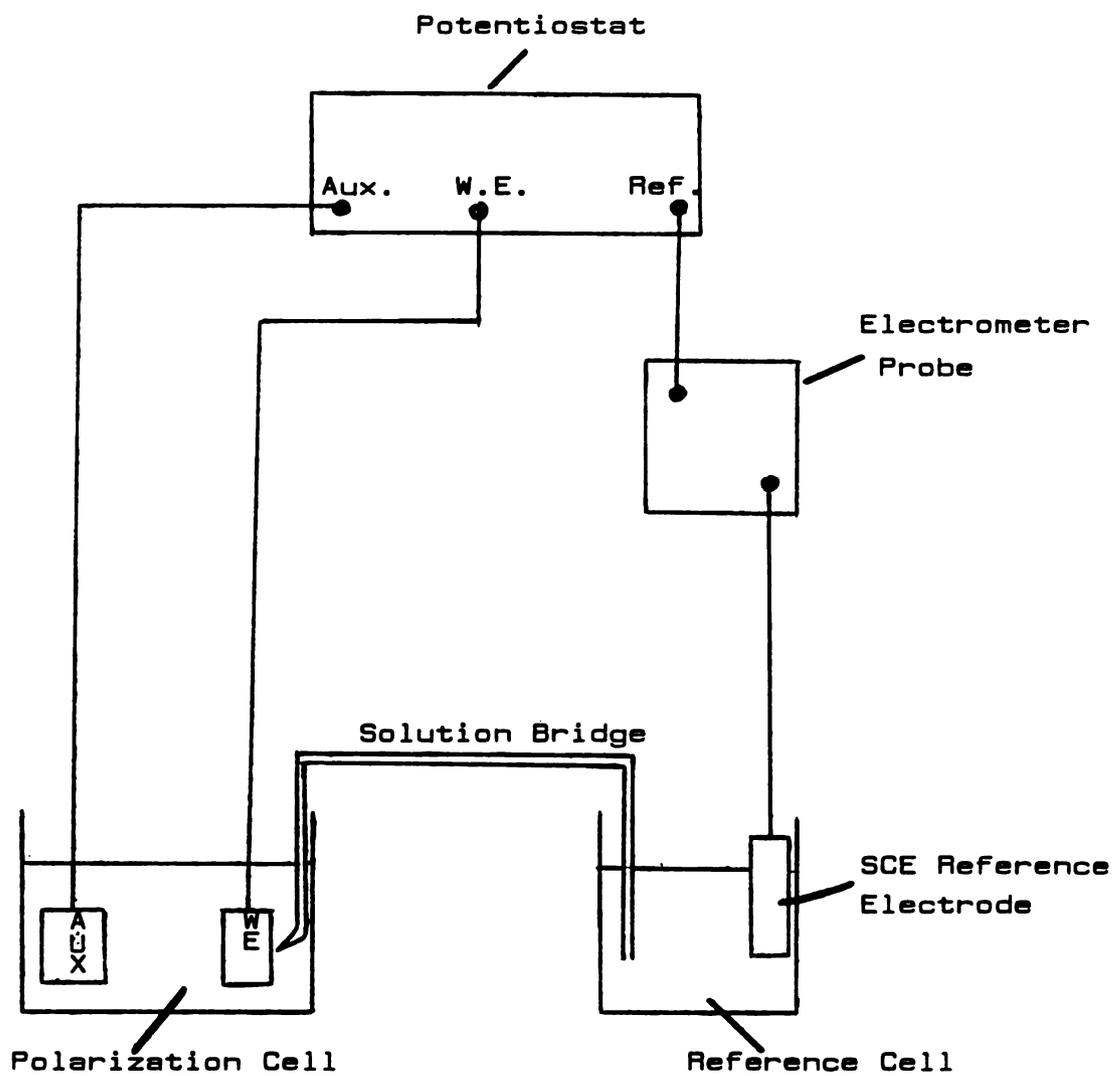


FIGURE 3 EXPERIMENTAL ARRANGEMENT.

ter probe.

## 1. Cell

The test cell used was a glass beaker containing the solution in which the working electrode, the auxiliary electrode, a Luggin capillary with salt bridge connection to the reference electrode and a thermometer were inserted.

## 2. Electrodes

### a. Working Electrodes

The working electrodes for this investigation were rectangular pieces, with width and thickness of 0.31 mm and 0.16 mm, respectively.

### b. Auxiliary Electrode

A platinum screen electrode was employed as the auxiliary electrode to transfer current to or from the working electrode. After using the platinum-screen counter electrode, no material is retained on its surface which might contaminate subsequent experiments.

### c. Reference Electrode

A saturated calomel electrode (SCE) was used as the reference electrode. A solution bridge from the Luggin capillary

to another beaker containing the reference electrode made the electrical connection between this electrode and the solution. This liquid junction was used to avoid contamination of the test solution.

### 3. Potentiostat

The potentiostat maintains the working electrode at a constant potential with respect to the reference electrode. A Princeton Applied Research (PAR) Model 173 was the potential controller for this investigation. Additional details are presented elsewhere<sup>(31)</sup>.

### 4. Electrometer Probe

In conjunction with the PAR Model 173 potentiostat, a PAR Model 178 electrometer probe was utilized to monitor the potential at the reference electrode.

## B. Solutions

All solutions were prepared using distilled water just before each experiment. Concentrations are expressed throughout on a weight percentage basis. All tests were conducted in unstirred solutions at room temperature.

The specimens were tested in solutions with different concentrations of sodium chloride with and without inhibitors.

and commercial surface-active agents. The inhibitors and surface-active agents are listed in Tables 1 and 2, respectively.

### C. Specimens

#### 1. Material

For all the measurements bare rectangular sheets of high strength 7075-T6 aluminum alloys were employed. The chemical analysis and mechanical analysis for this Al alloy are given in Tables 3 and 4, respectively.

#### 2. Specimen Preparation

The working electrodes were mechanically polished up to 600 emery paper followed by cleaning in acetone, degreasing thoroughly in petroleum ether, then rinsing in distilled water, and finally drying in a stream of air.

### D. Experimental Technique

Before the corrosion cell was assembled, it and its components were cleaned using detergent followed by rinsing in distilled water. The solution under study was poured into the glass vessel and the working electrode, counter electrode, thermometer and Luggin capillary were immersed. Then the so-

TABLE 1

Inhibitor Concentrations, weight per cent.

|                     | <u>I</u> | <u>II</u> | <u>III</u> | <u>IV</u> |
|---------------------|----------|-----------|------------|-----------|
| Sodium Borate       | 0.35     | 0.35      | 0.35       | 0.198     |
| Sodium Nitrate      | 0.1      | 0.22      | 0.22       | 0.124     |
| Sodium Nitrite      | 0.05     | 0.11      | 0.11       | 0.061     |
| Sodium Metasilicate | 0.01     | 0.01      | 0.01       | 0.006     |
| Pentahydrate        |          |           |            |           |
| Sodium Hexameta-    | 0.002    | 0.002     | 0.002      | 0.0013    |
| phosphate           |          |           |            |           |
| Mercaptobenzo-      | 0.001    | 0.001     |            | 0.0006    |
| thiazole (MBT)      | ————     | ————      | ————       | ————      |
| SUM                 | 0.513    | 0.693     | 0.692      | 0.3909    |

TABLE 2

## Surface-Active Agents

| <u>Name</u>                              | <u>Class</u> | <u>Type</u>       | <u>Form</u>     | <u>Source</u>             |
|--|--------------|-------------------|-----------------|---------------------------|
| Hamposyl C                               | Anionic      | Sarcosinate       | Liquid          | W.R. Grace & Co.          |
| Hamposyl O                               | Anionic      | Sarcosinate       | Liquid          | W.R. Grace & Co.          |
| Hamposyl L-30                            | Anionic      | Sarcosinate       | Liquid          | W.R. Grace & Co.          |
| Polystep B-12                            | Anionic      | Ethoxylate        | Liquid          | Stepan Chemical Co.       |
|  |              | Sulfate           |                 |                           |
| Zonyl FSA                                | Anionic      | Fluorosurfac-     | Liquid          | Du Pont                   |
|  |              | tant              |                 |                           |
| 4-(4-Methyl-1-Piperi-<br>diny1)-Pyridine | Cationic     | Tertiary<br>Amine | Liquid          | Reilly Tar & Chemical Co. |
| 1,3-Di-(4-Piperidy1)-<br>Propane         | Cationic     | Alkyl<br>Amine    | Flaked<br>Solid | Reilly Tar & Chemical Co. |

TABLE 3

Chemical Analysis of Al 7075-T6<sup>(31)</sup>

| Element | Zn   | Mg   | Cu   | Cr   | Mn |
|---------|------|------|------|------|----|
| WT. %   | 5.52 | 2.76 | 1.41 | 0.23 | 0  |

TABLE 4

Mechanical Properties of Al 7075-T6<sup>(31)</sup>

|          | Tensile Strength<br>(psi) | Yield Strength<br>(psi) | Hardness<br>(Rockwell) |
|----------|---------------------------|-------------------------|------------------------|
| Specimen | 72,000                    | 66,000                  | 76R <sub>B</sub>       |
| Handbook | 83,000                    | 73,000                  | 85R <sub>B</sub>       |

lution bridge junction from the Luggin capillary to the reference electrode, which was immersed in another beaker containing the same type of solution under investigation, was connected. The Luggin capillary was employed in order to minimize errors in the measurements of potentials caused by IR drop through the electrolyte.

The experimental instrumentation set-up is shown in Figure 3. All experiments were carried out in accordance with the ASTM Standard G5-82, "Standard Recommended Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements."

Specimens were immersed in the solution for three hours before the commencement of the polarization. The potential attained by the working electrode after this equilibration period was taken as the corrosion potential. Then, the corrosion potential was changed anodically (the potential was increased) at a rate of 10 mv per minute for about three hours, and the corresponding current, between the working electrode and the counter electrode, recorded during this time. All potentials are reported with reference to the saturated calomel electrode (SCE) as specified.

#### IV. EXPERIMENTAL RESULTS

##### A. Effect of Chloride Concentration

Figures 4 and 5 show the anodic polarization of 7075-T6 Aluminum alloy for concentrations of 1.0 wt. % and 0.02 wt. % of NaCl without inhibitor, respectively. Figure 6 shows the effect of increasing chloride concentration upon the anodic polarization of Al 7075-T6. From these figures it can be seen that the corrosion potential of Al 7075-T6 depends on the solution concentration, i.e., the higher the concentration of chloride ions, the lower the corrosion potential. Additionally, the current density is dependent upon the chloride concentration; increasing current densities corresponds to increasing concentration of chloride ions. These results agree with those obtained before<sup>(31)</sup>. The corrosion current density for the anodic profile corresponding to 1.0 wt. % NaCl may be obtained by means of the Tafel extrapolation technique; it was found to be about  $10,000 \mu\text{A}/\text{cm}^2$ . The same cannot be said for the anodic polarization of Al 7075-T6 in 0.02 wt. % NaCl solution due to the absence of a long enough linear region.

Figures 7 and 8 show the anodic polarization behavior of Al 7075-T6 in 0.58 wt. % NaCl and 0.02 wt. % NaCl solutions, both solutions containing inhibitor formulation I. The difference in the amount of passivation is significant. In fact, a complete breakdown of passivity occurs at high chloride concentrations. In Figure 9, it can be seen the

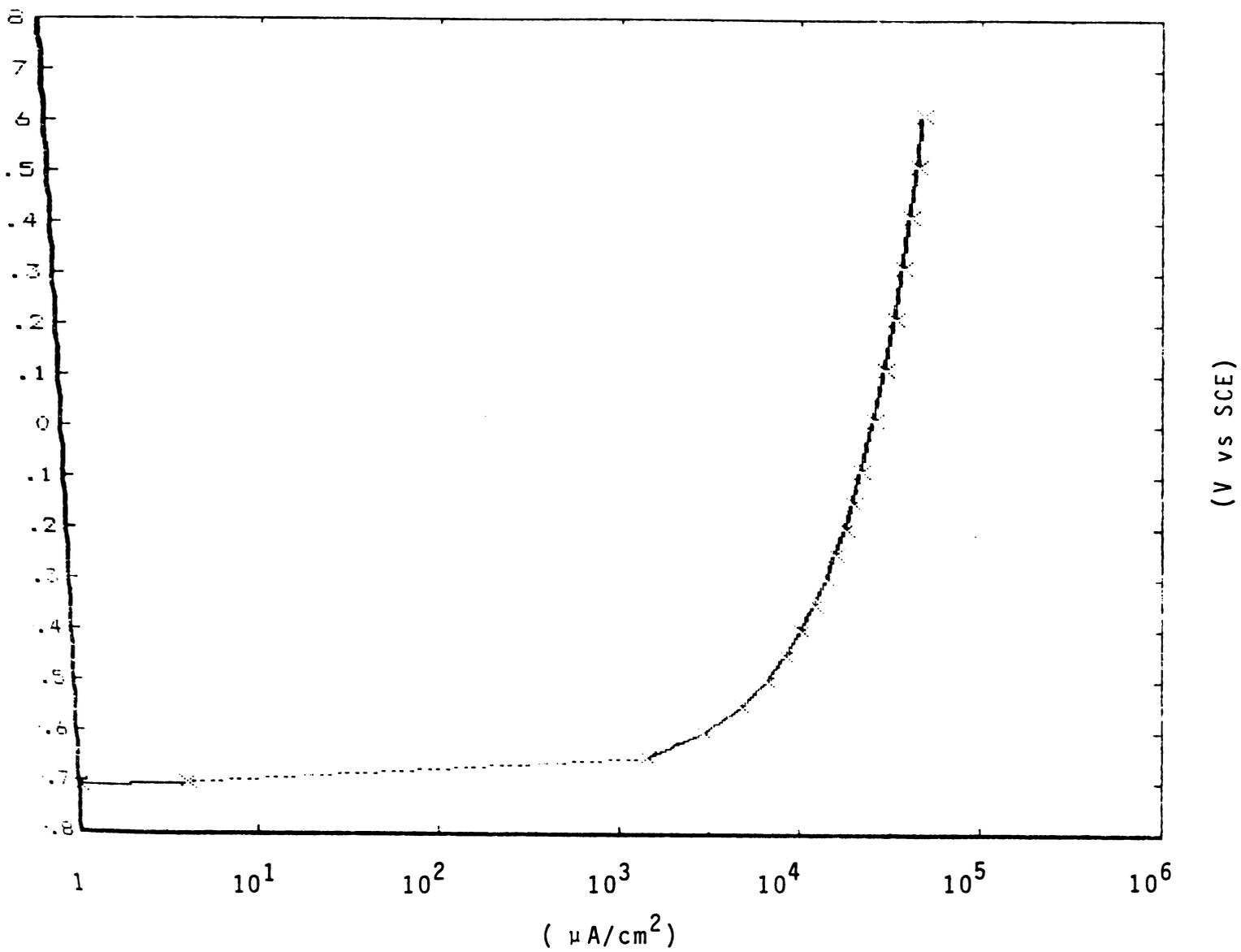


FIGURE 4 ANODIC POLARIZATION OF AL 7075-T6 IN 1.0 WT.% NaCl SOLUTION WITHOUT INHIBITOR

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100

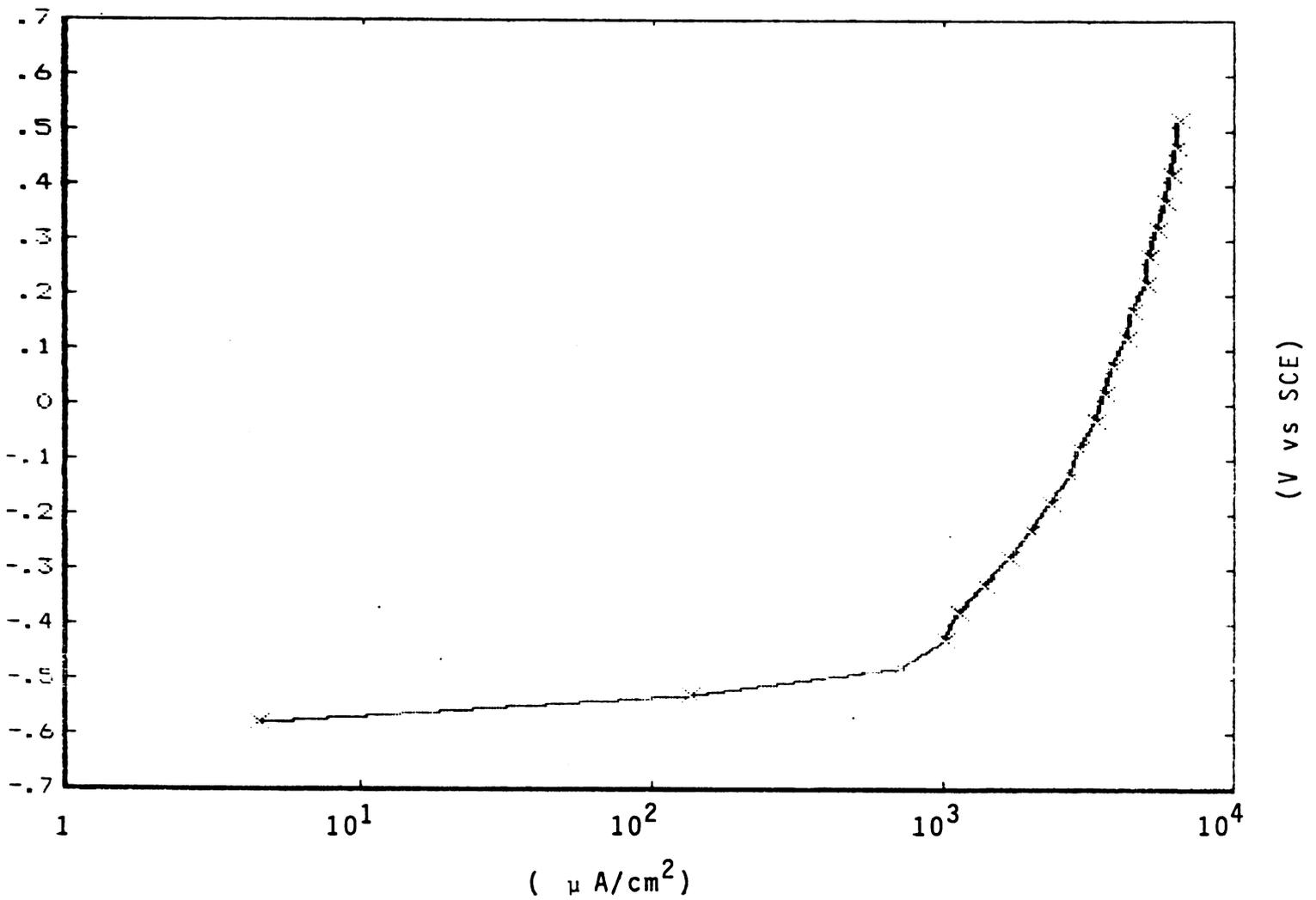


FIGURE 5 ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NaCl SOLUTION WITHOUT INHIBITOR

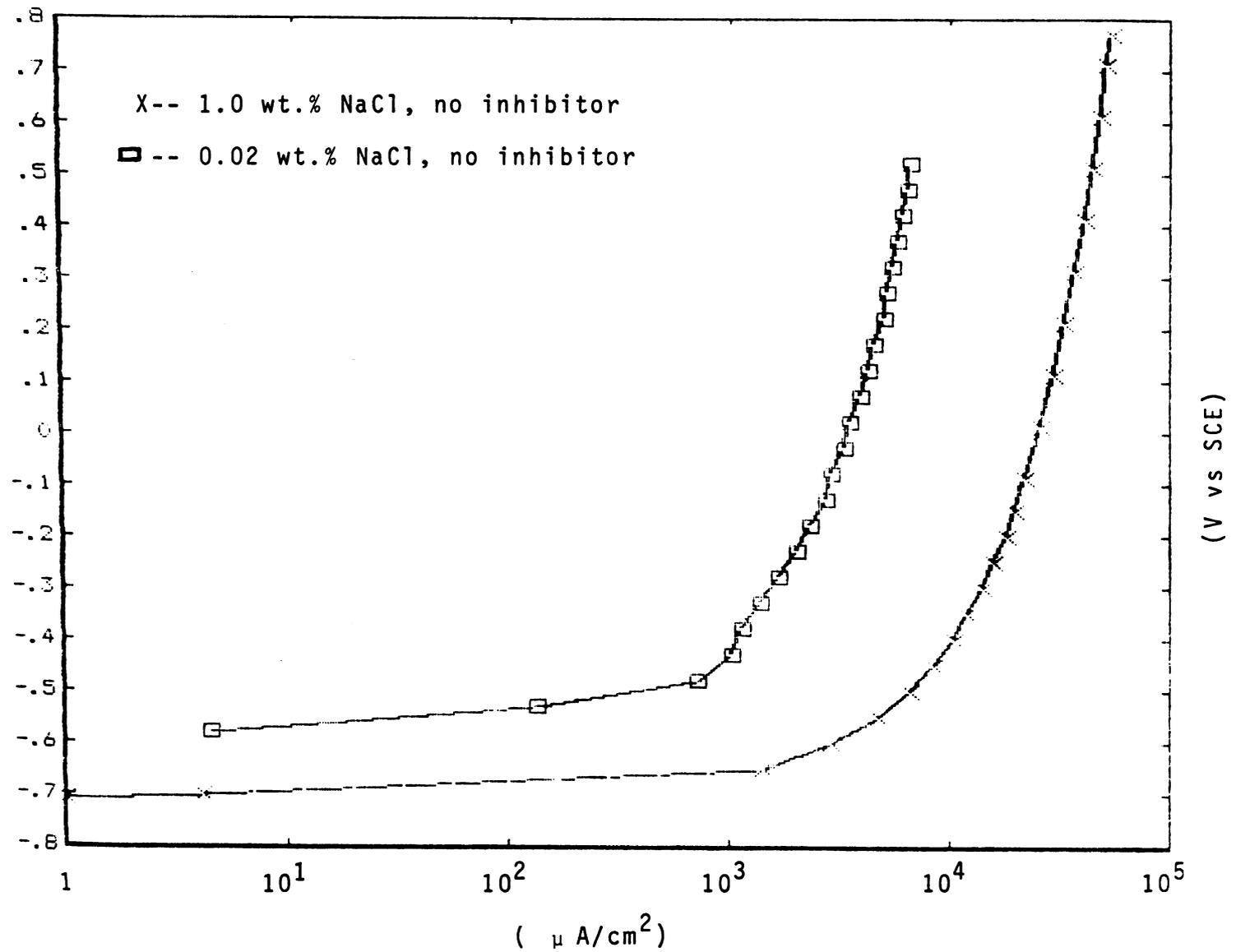


FIGURE 6 EFFECT OF INCREASING CHLORIDE CONCENTRATION UPON ANODIC POLARIZATION OF AL 7075-T6 WITHOUT INHIBITOR

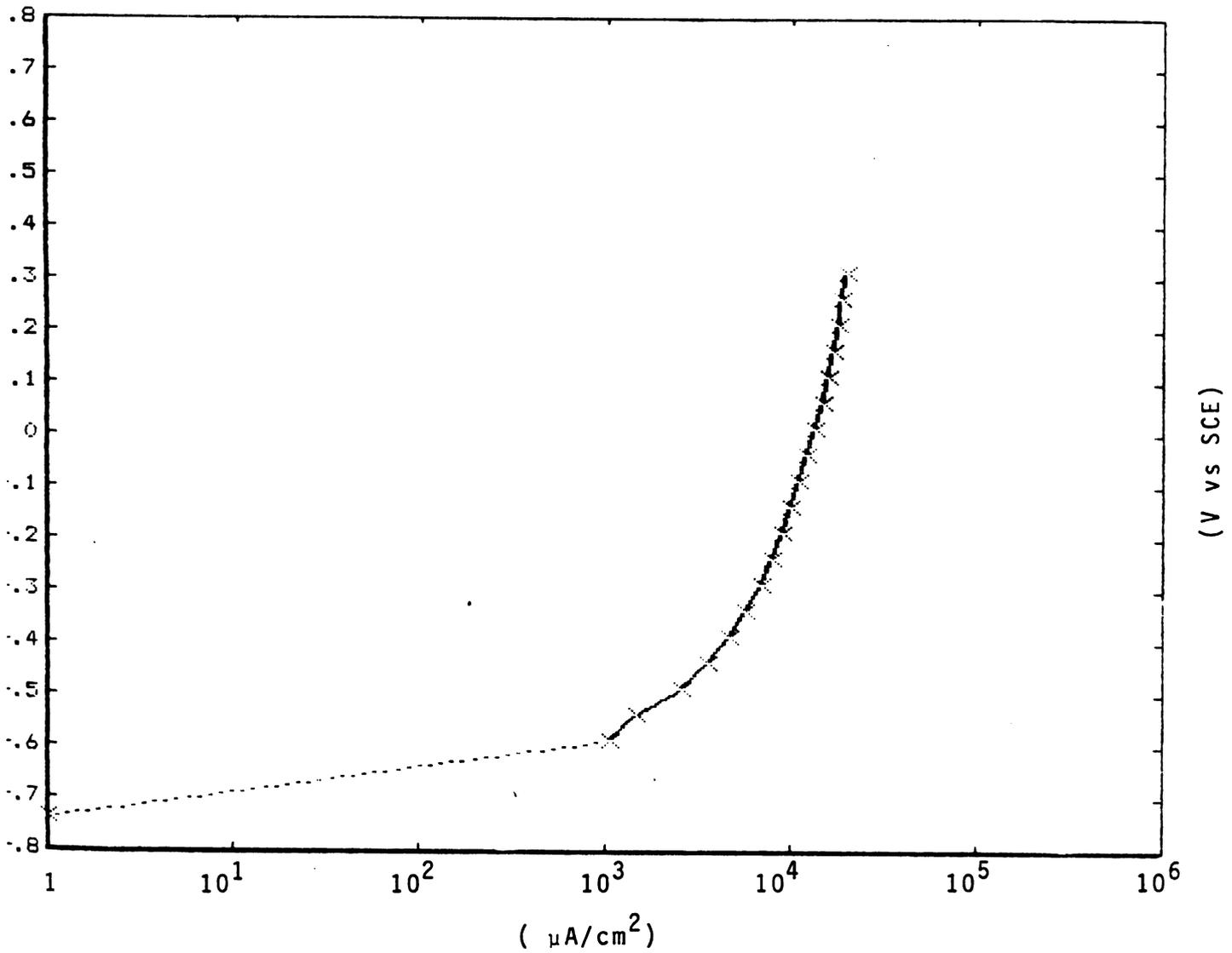


FIGURE 7 ANODIC POLARIZATION OF AL 7075-T6 IN 0.58 WT.% NaCl SOLUTION WITH INHIBITOR FORMULATION I

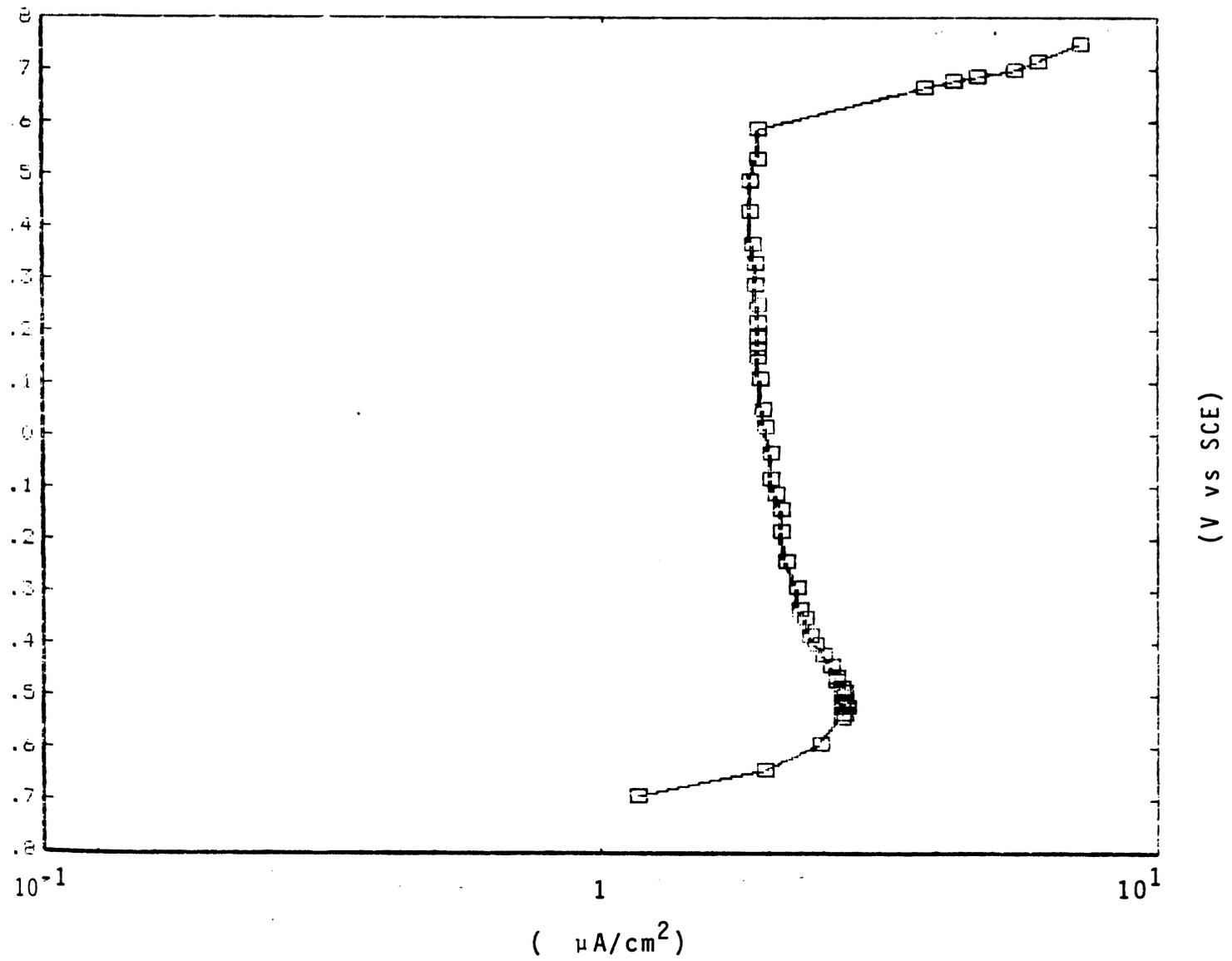


FIGURE 8 ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NaCl SOLUTION WITH INHIBITOR FORMULATION I

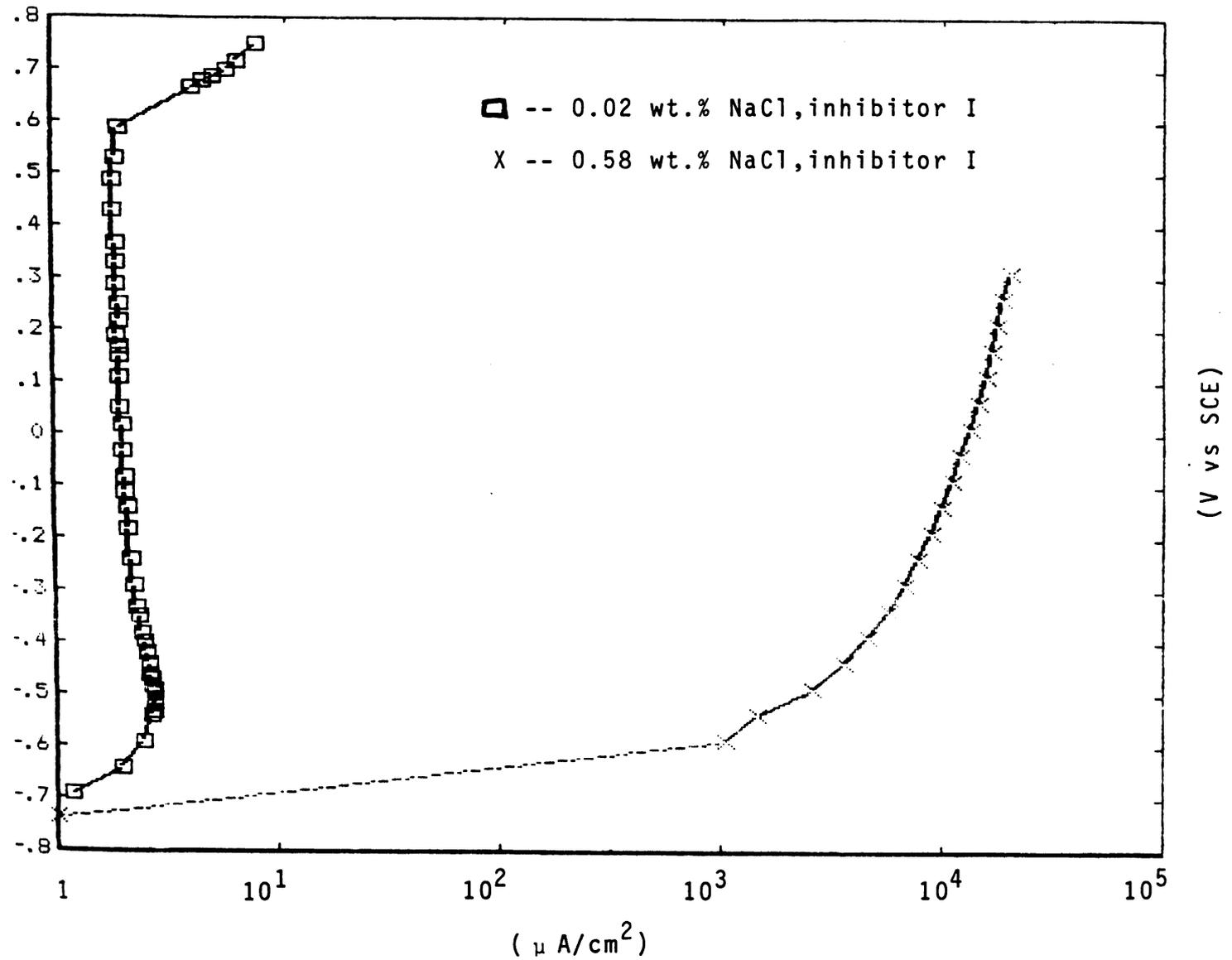


FIGURE 9 EFFECT OF INCREASING CHLORIDE CONCENTRATION UPON ANODIC POLARIZATION OF AL 7075-T6 WITH INHIBITOR FORMULATION I

effect of increasing chloride concentration upon the breakdown of the passivity. It has been found<sup>(12)</sup> that a loss of passivity, using a borax-nitrate based inhibitor formulation, occurs above about 4.8 wt. % of NaCl.

Figures 10 and 11 show the anodic profiles of this alloy for the same concentrations of chloride ions (0.02 wt. % and 1.0 wt. % , respectively), but in solutions containing inhibitor formulation II. In this inhibitor formulation the concentration of nitrate and nitrite was increased with respect to the inhibitor formulation I. As it is known, nitrate is used to prevent corrosion of aluminum<sup>(32)</sup> and aluminum alloys<sup>(12),(33)</sup>, in the presence of chloride-containing solutions. From Figure 12 it can be observed that there is a very small change in the degree of passivity, even though, the increase in nitrate and nitrite concentrations was small.

#### B. Effect of Inhibitors and Surfactants

Figures 13 and 14 show the effect of small additions of Polystep B-12 surfactant upon the anodic polarization of 7075-T6 aluminum alloy. As can be noticed from Figure 13, the corrosion potential has been moved in the active direction, by the addition of surfactant, from -0.689 volts to -0.726 volts. The corrosion potential was somewhat altered by the addition of Polystep B-12 to the inhibitor formulation II. The same cannot be concluded for the addition of this surfactant to

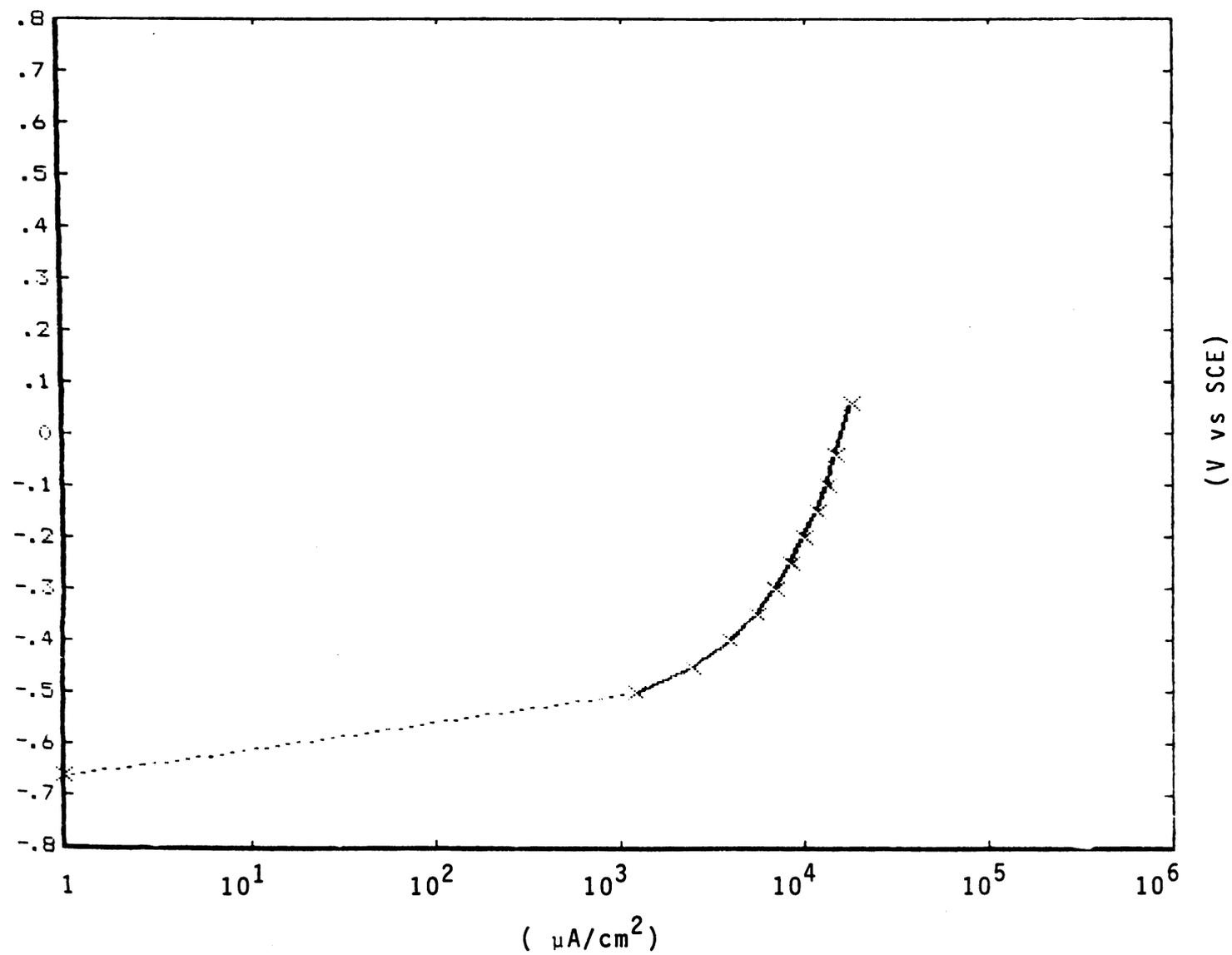


FIGURE 10 ANODIC POLARIZATION OF AL 7075-T6 IN 0.58 WT.% NaCl SOLUTION WITH INHIBITOR FORMULATION II

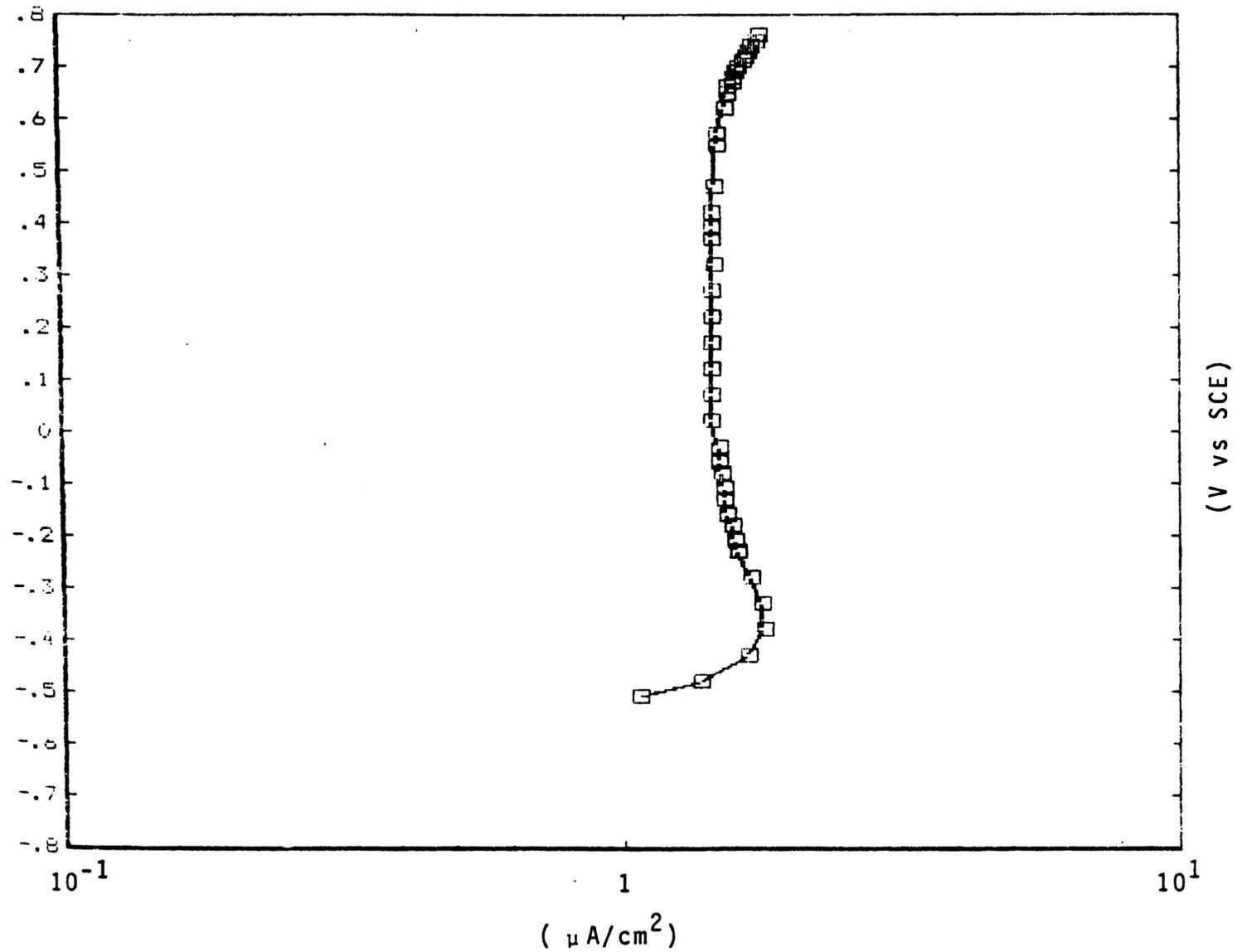


FIGURE 11 ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NaCl SOLUTION WITH INHIBITOR FORMULATION II

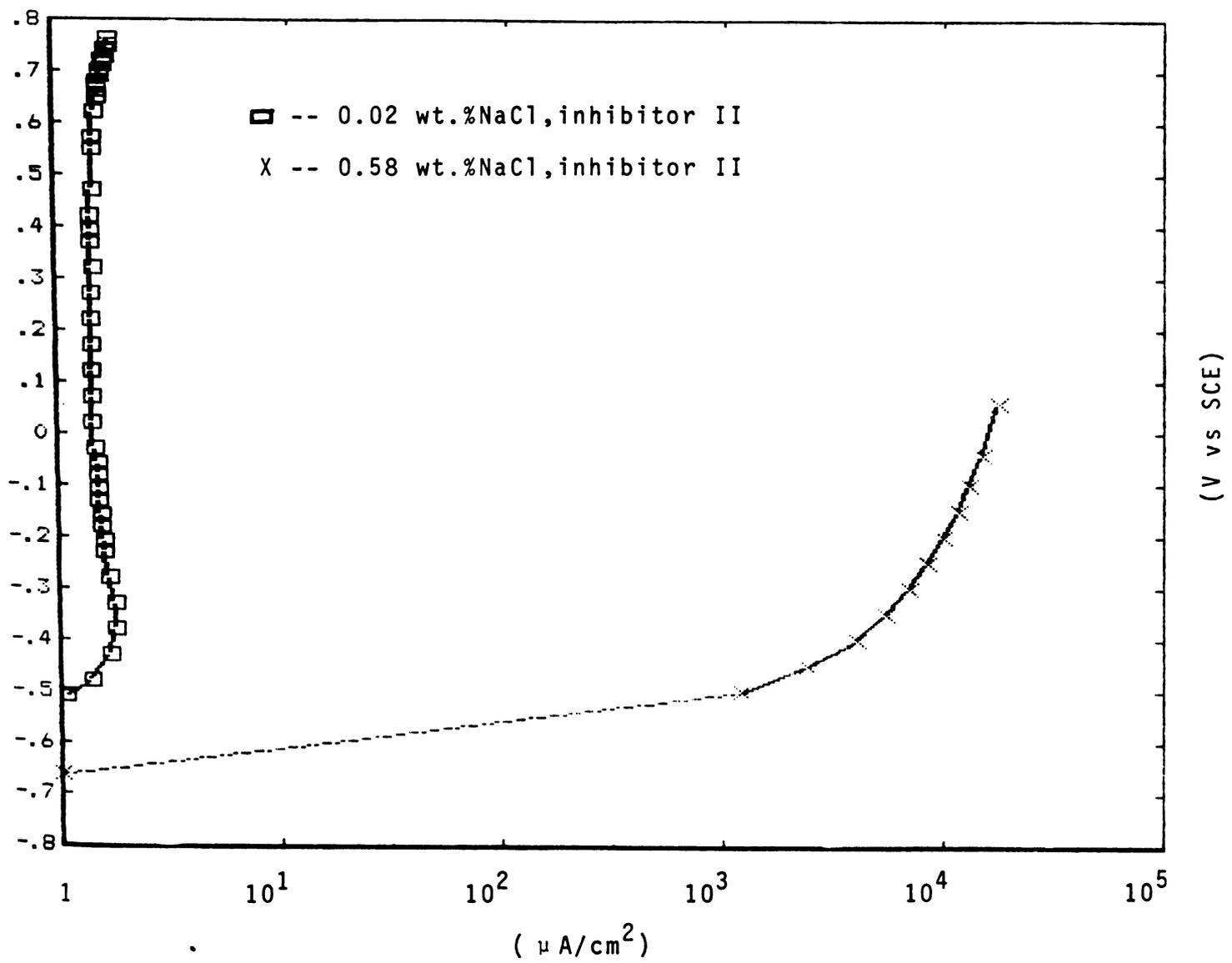


FIGURE 12 EFFECT OF INCREASING CHLORIDE CONCENTRATION UPON ANODIC POLARIZATION OF AL 7075-T6 WITH INHIBITOR FORMULATION II

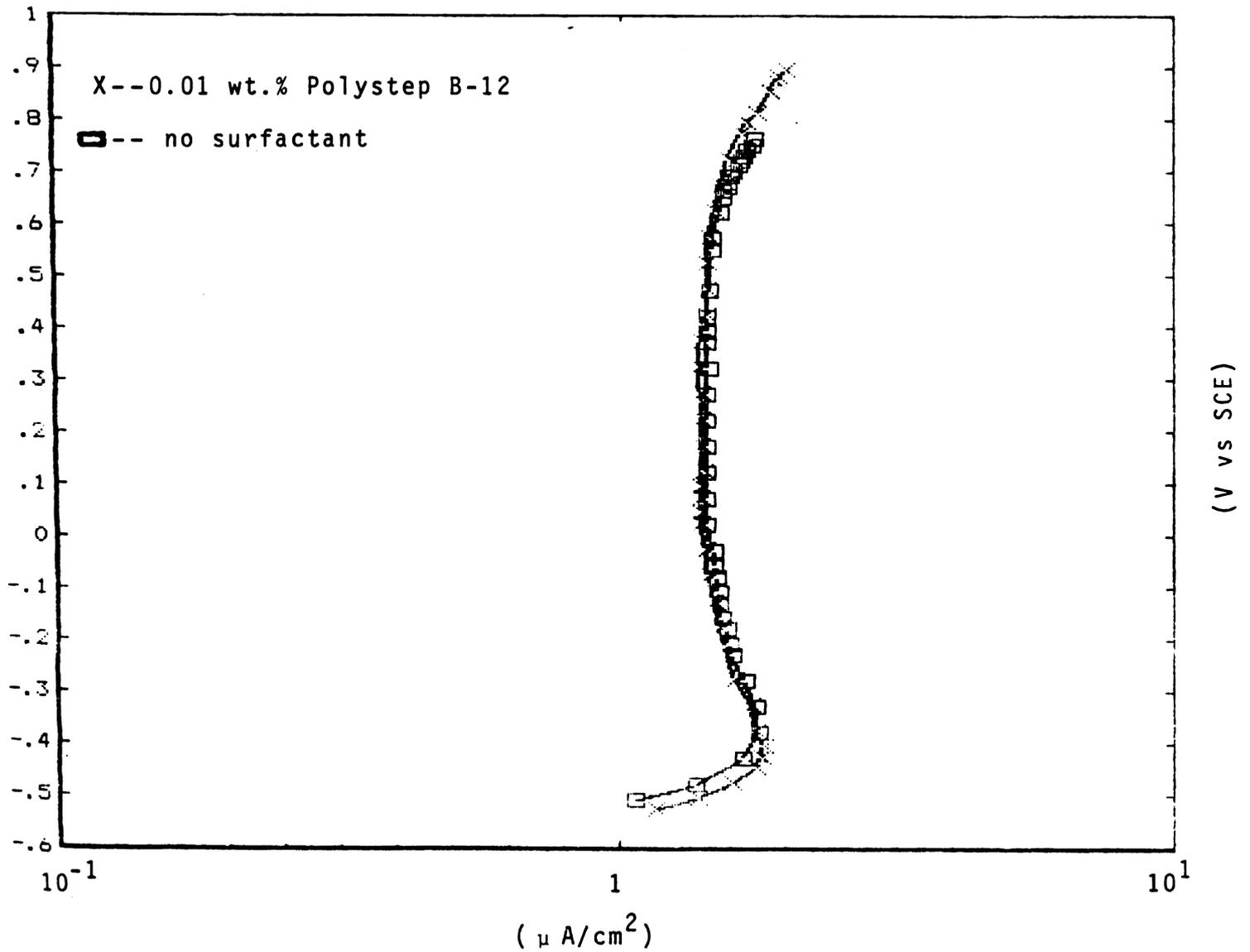


FIGURE 13 EFFECT OF SURFACTANT UPON THE ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NaCl SOLUTION WITH INHIBITOR FORMULATION II

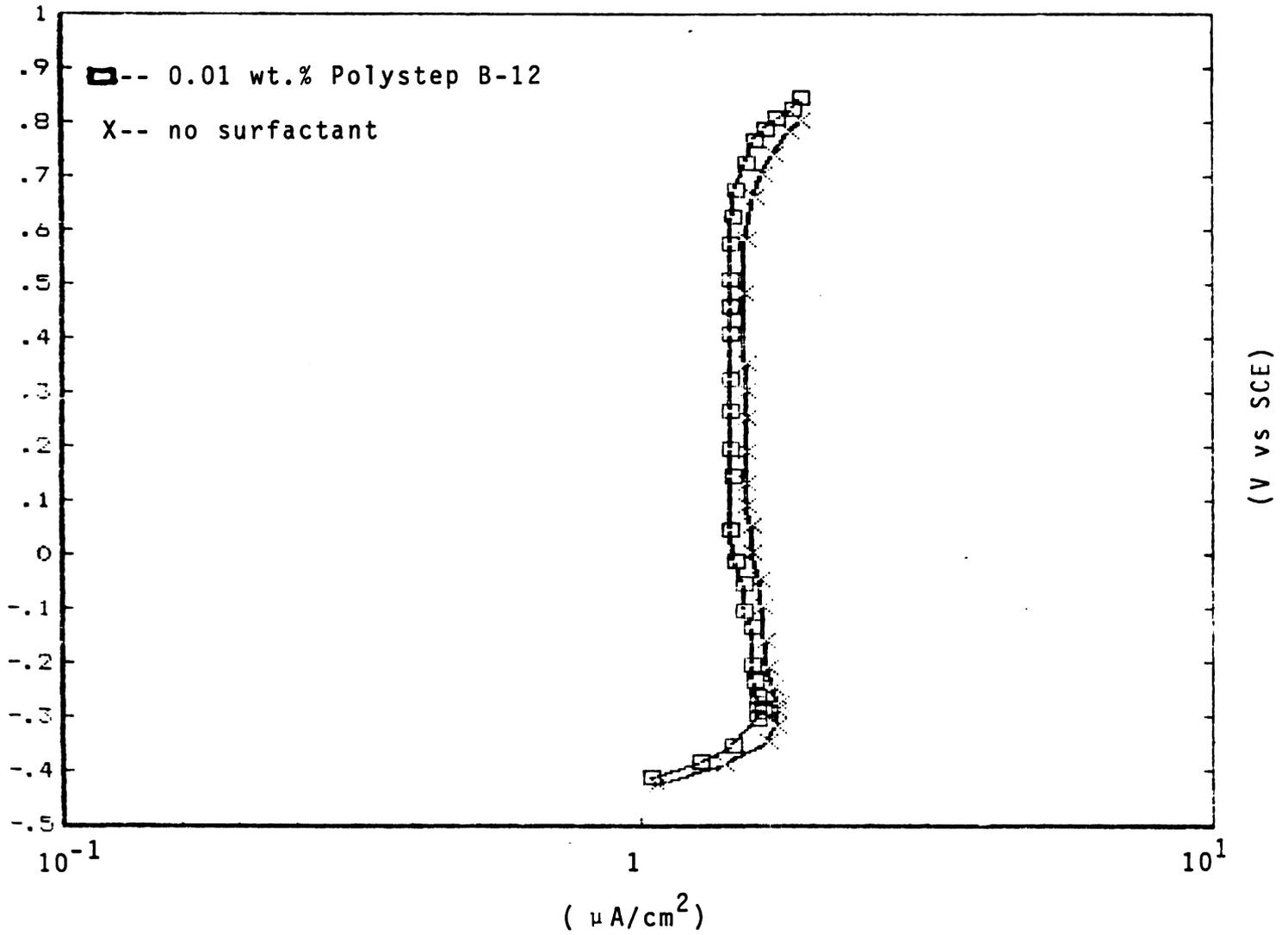
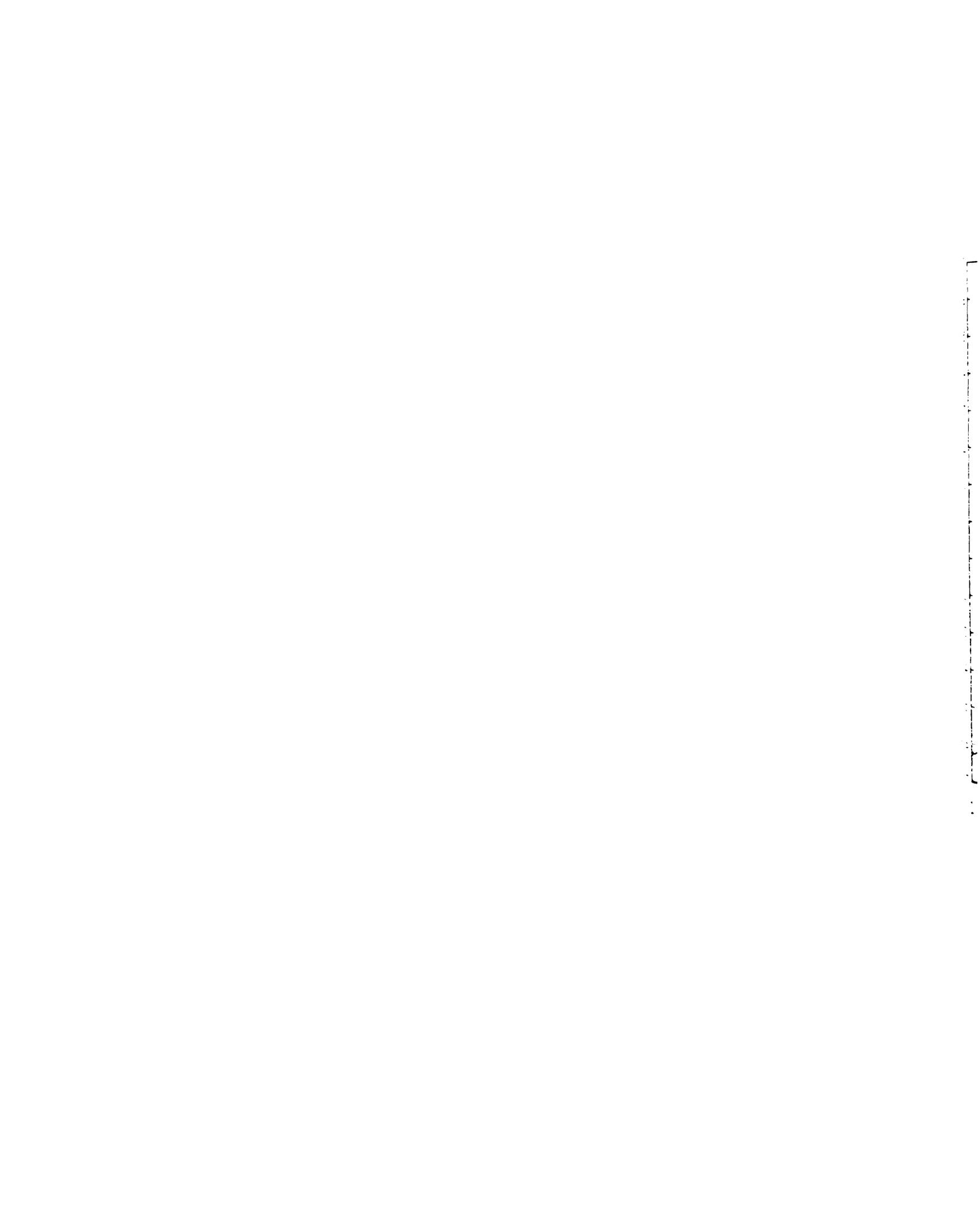


FIGURE 14 EFFECT OF SURFACTANT UPON ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NaCl SOLUTION WITH INHIBITOR FORMULATION III

inhibitor formulation III. In this case, from the anodic profiles, it is evident that the corrosion potential is almost the same for both solutions, it is about -0.525 volts. It must be pointed out that formulation III does not have MBT like the other inhibitor formulations. However, the addition of Polystep B-12 demonstrated the ability for a little increase in passivation against chloride attack at low concentrations of chloride ions.

Figures 15, 16 and 17 show the anodic polarization of Al 7075-T6 in 0.02 wt. % NaCl solution without inhibitor for different surfactants. Zonyl FSA, Hamposyl L-30 and Polystep B-12, respectively. In Figure 18 is shown the effect of small additions of surfactants (Zonyl FSA), in anodic polarization behavior of 7075-T6 aluminum alloy, to 0.02 wt. % NaCl solution with no inhibitor. The anodic profiles shown in Figures 15, 16 and 17 contain no discontinuities. It is evident that a film was formed but no passivation occurred as a result of absence of inhibitor formulation. This suggests that the surfactants have a synergistic effect. The corrosion potential of the corroding Al alloys was independent of the addition of different surfactants to the solution, as well as, the corrosion current density. The corrosion current density corresponding to these anodic profiles was found to be about  $150 \mu\text{A}/\text{cm}^2$ . Comparing Figures 15, 16 and 17, one can say that these surfactants have the same effect on the anodic polarization behavior of Al 7075-T6 in solutions with



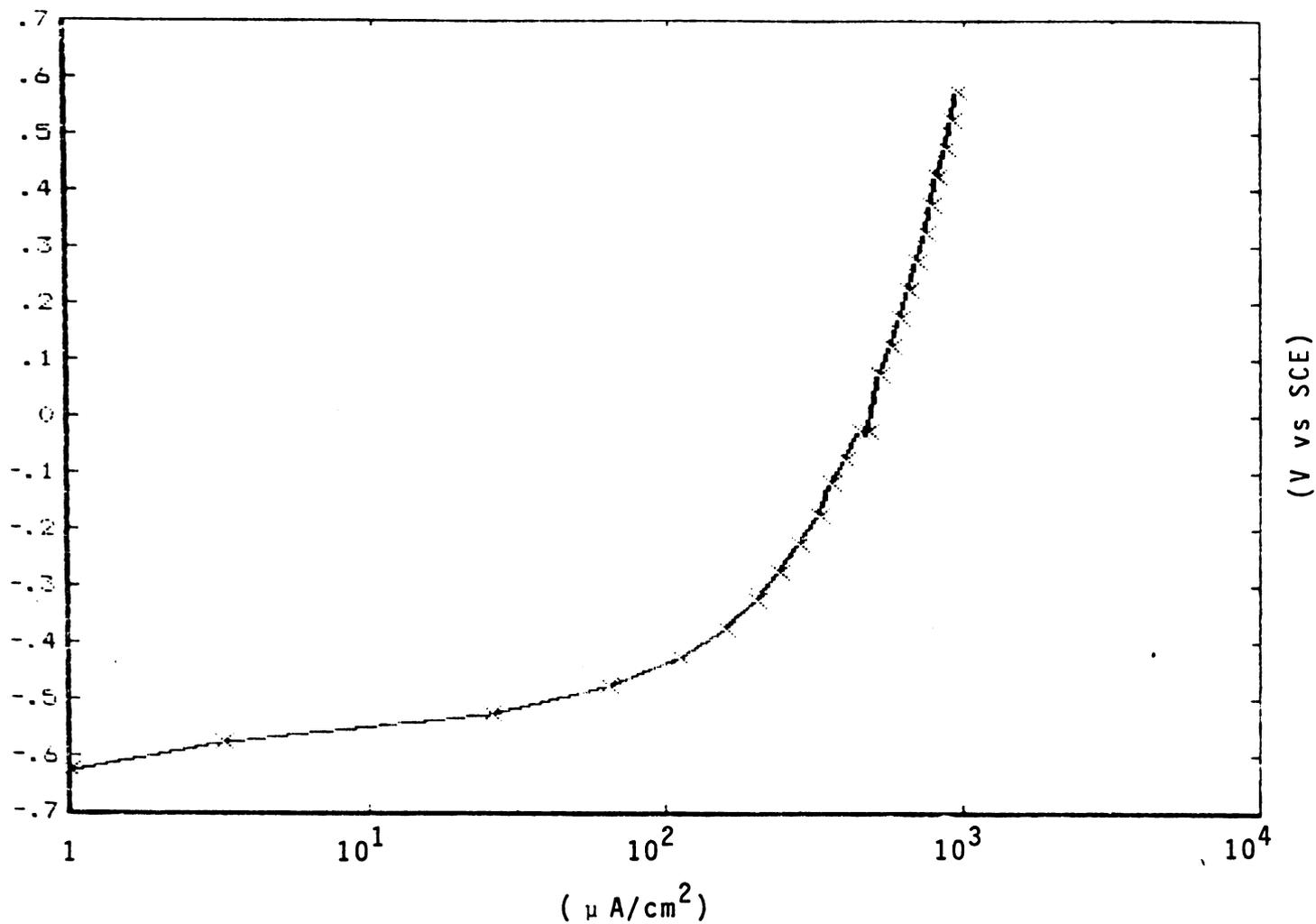


FIGURE 15 ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NaCl,  
0.01 WT.% ZONYL FSA SOLUTION WITHOUT INHIBITOR

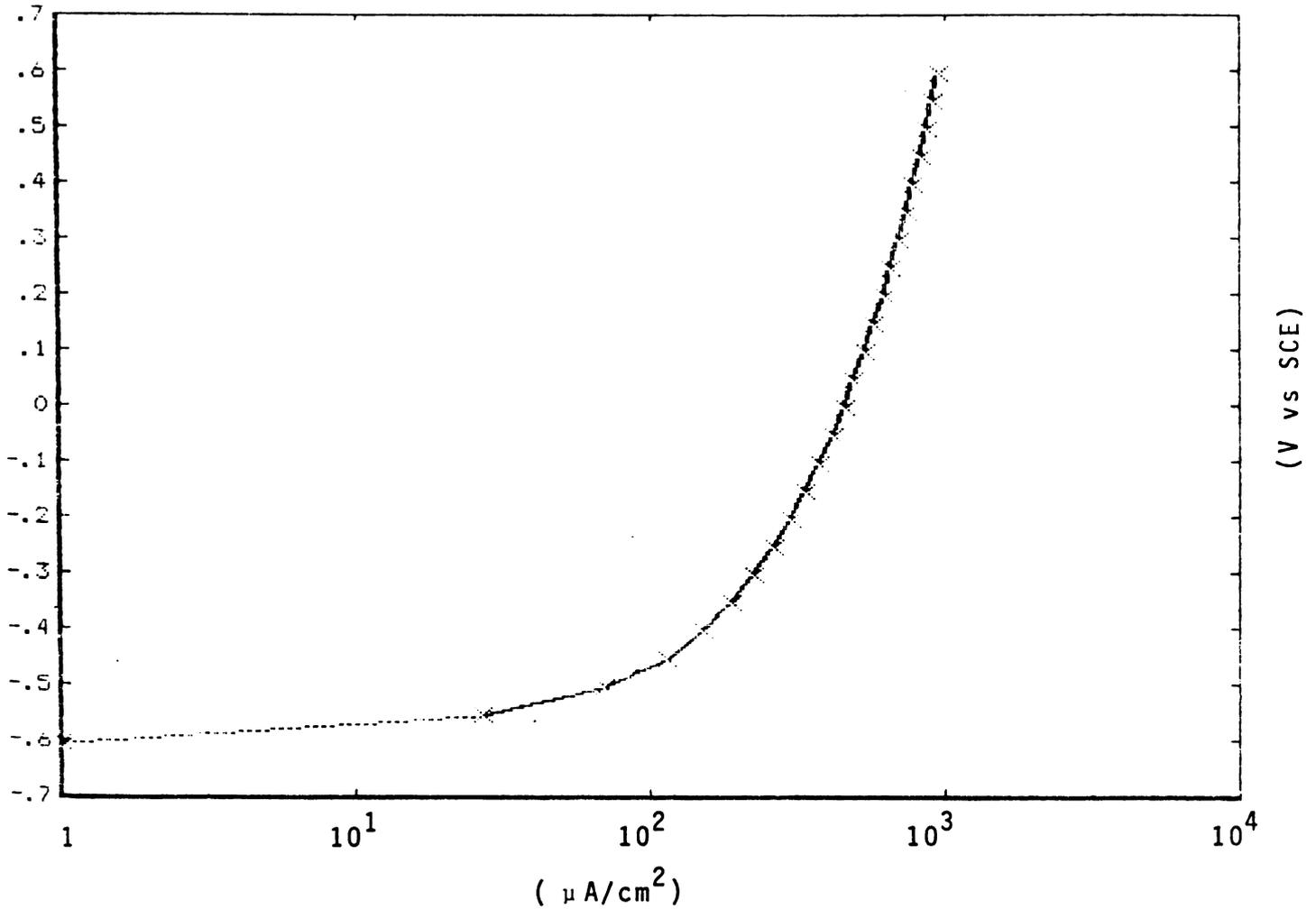


FIGURE 16 ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NaCl,  
0.01 WT.% HAMPOSYL L-30 SOLUTION WITHOUT INHIBITOR

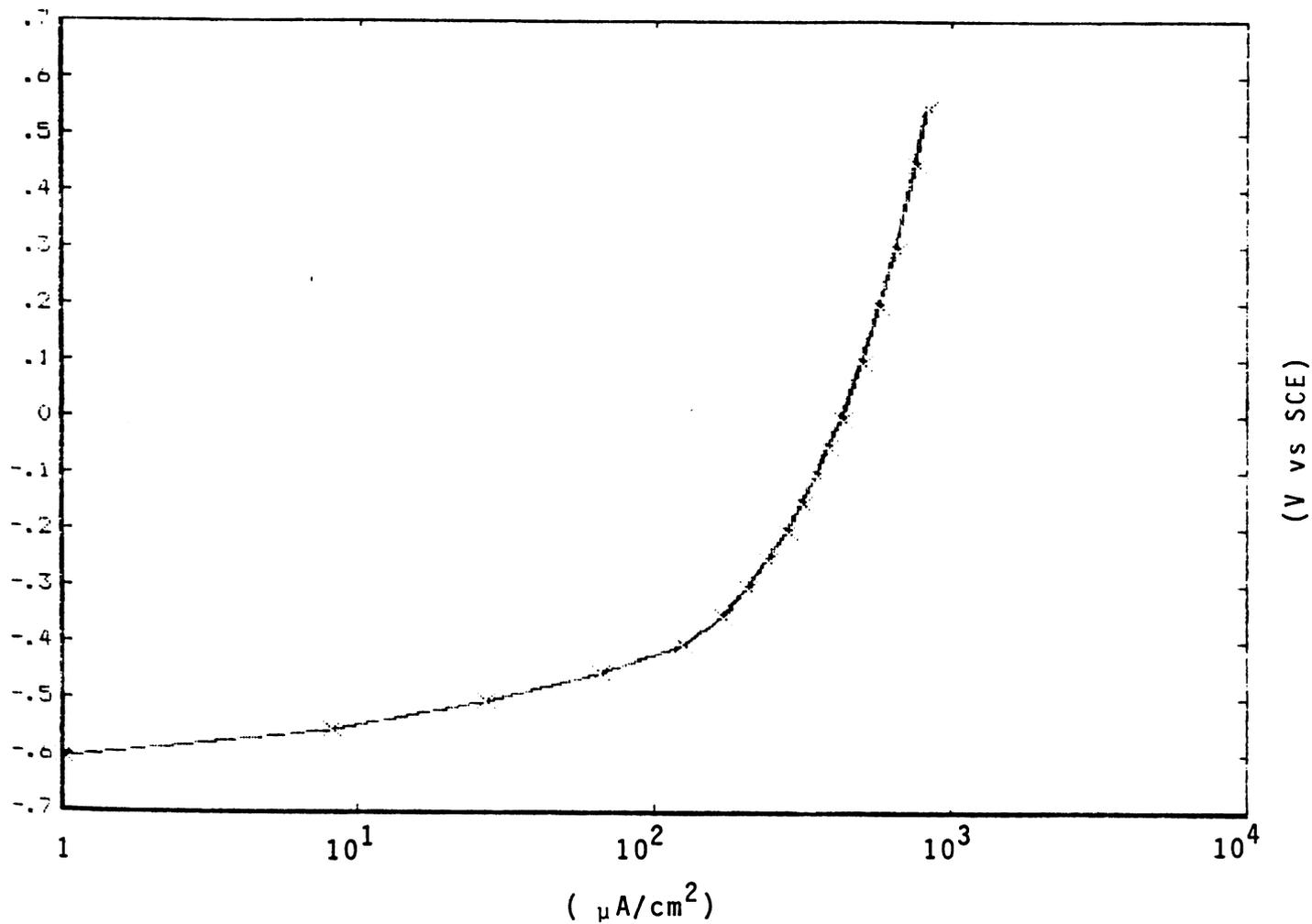


FIGURE 17 ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NaCl,  
0.01 WT.% POLYSTEP B-12 SOLUTION WITHOUT INHIBITOR

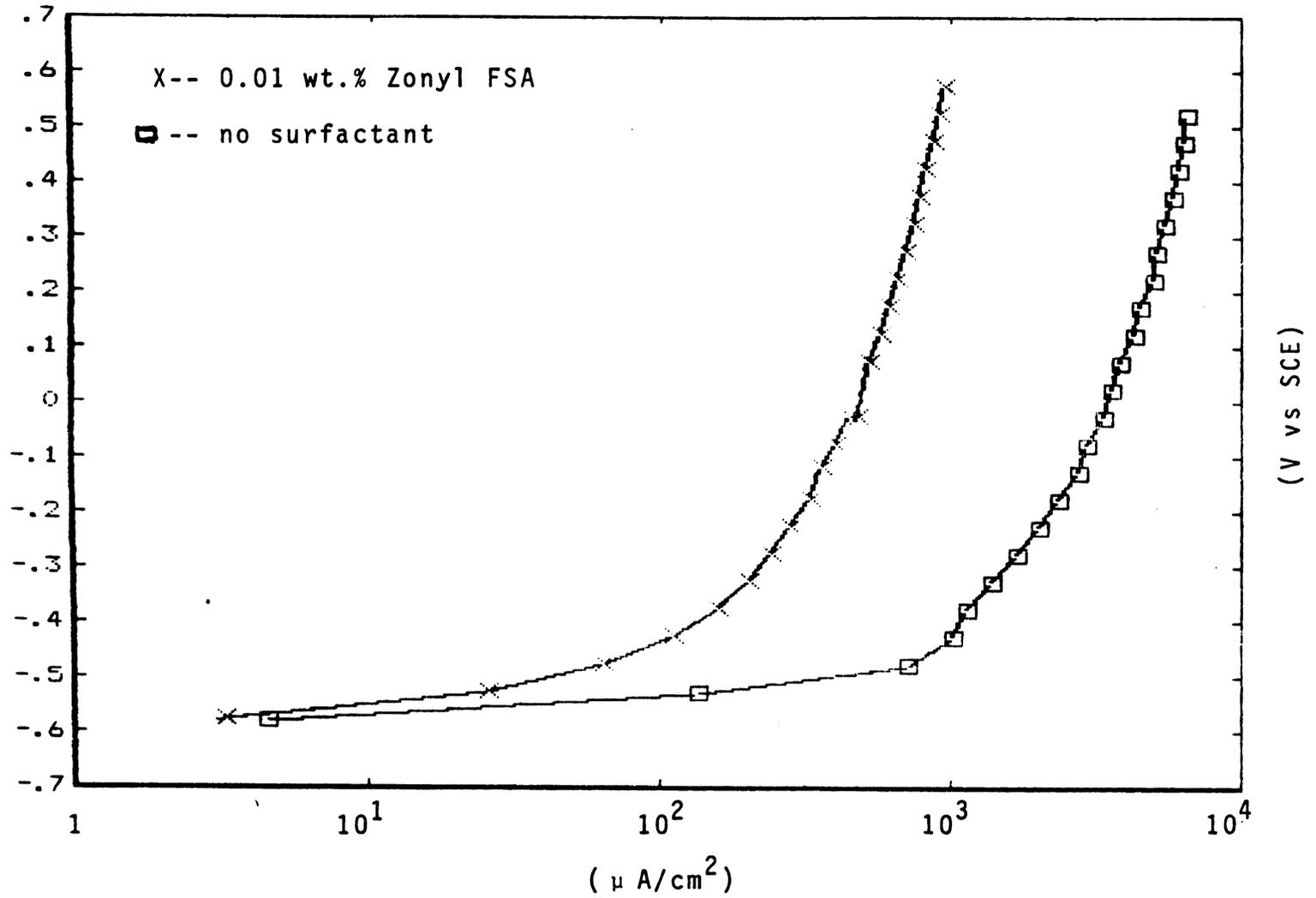


FIGURE 18 EFFECT OF SURFACTANT UPON ANODIC POLARIZATION OF AL 7075-T6 IN 0.02 WT.% NA CL SOLUTION WITHOUT INHIBITOR

low concentrations of chloride ions without inhibitor. The anodic profiles in Figure 18 show that the corrosion current density is decreased when small amounts of these surfactants were added to the solution. By means of the Tafel extrapolation technique it was found that the corrosion current density was reduced from about  $1500 \mu\text{A}/\text{cm}^2$  to about  $150 \mu\text{A}/\text{cm}^2$ . The corrosion potential was independent of the addition of these surfactants.

Figures 19, 20, 21 and 22 show the anodic polarization behavior of Al 7075-T6 in 1.0 wt. % NaCl solution without inhibitor for different surfactants. The anodic polarization behavior of the corroding aluminum alloys in these solutions containing small addition of surfactants is similar to that with low concentration of chloride ions. Again, the anodic profiles show no discontinuities associated with film formation and no passivation. The corrosion potential seems to be independent of additions of different surfactants to solutions without inhibitor. Comparing these figures to Figure 4, it may be also noticed that at high concentrations of chlorides ions, the corrosion current density is independent of the addition of these surfactants. However, the addition of Hamposyl C slightly reduced the corrosion current density, and it may be suggested that this surfactant provides better protection to 7075-T6 Al alloy than that rendered by the other at the same  $\text{Cl}^-$  concentration. Obviously, at this concentration of  $\text{Cl}^-$  ions, the values of the corrosion current

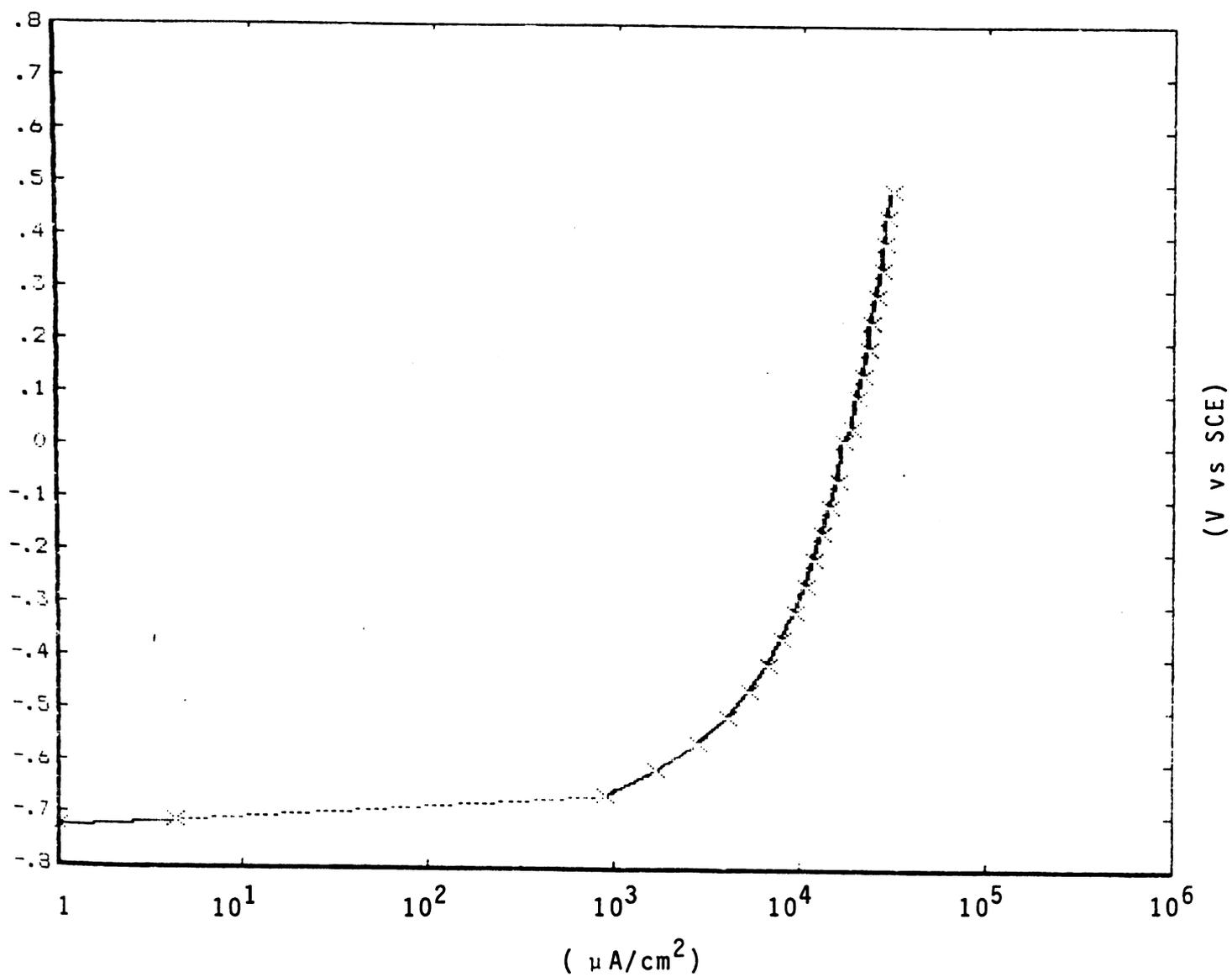


FIGURE 19 ANODIC POLARIZATION OF AL 7075-T6 IN 1.0 WT.% NaCl,  
0.01 WT.% HAMPOSYL C SOLUTION WITHOUT INHIBITOR

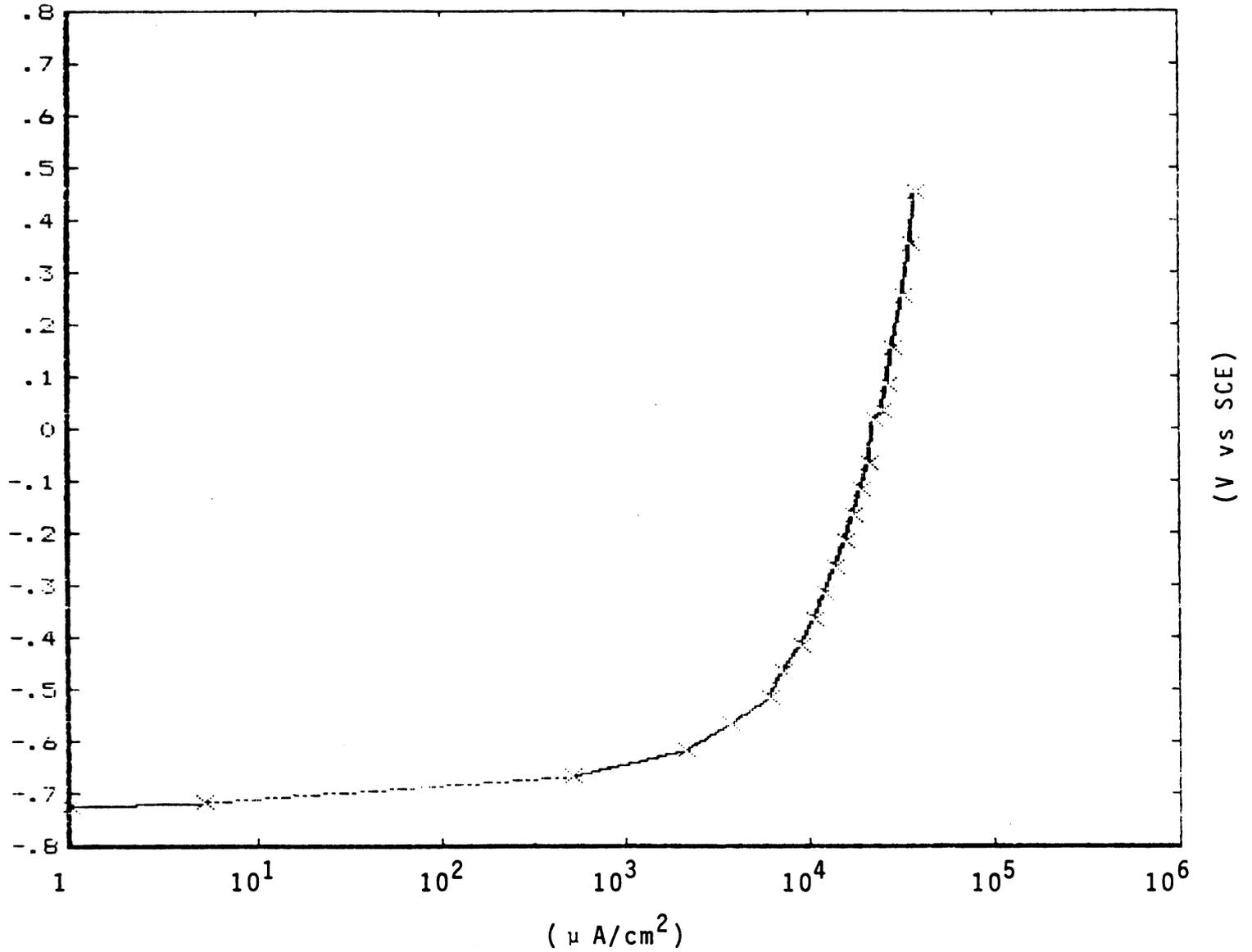


FIGURE 20 ANODIC POLARIZATION OF AL 7075-T6 IN 1.0 WT.% NaCl,  
0.01 WT.% HAMPOSYL 0 SOLUTION WITHOUT INHIBITOR

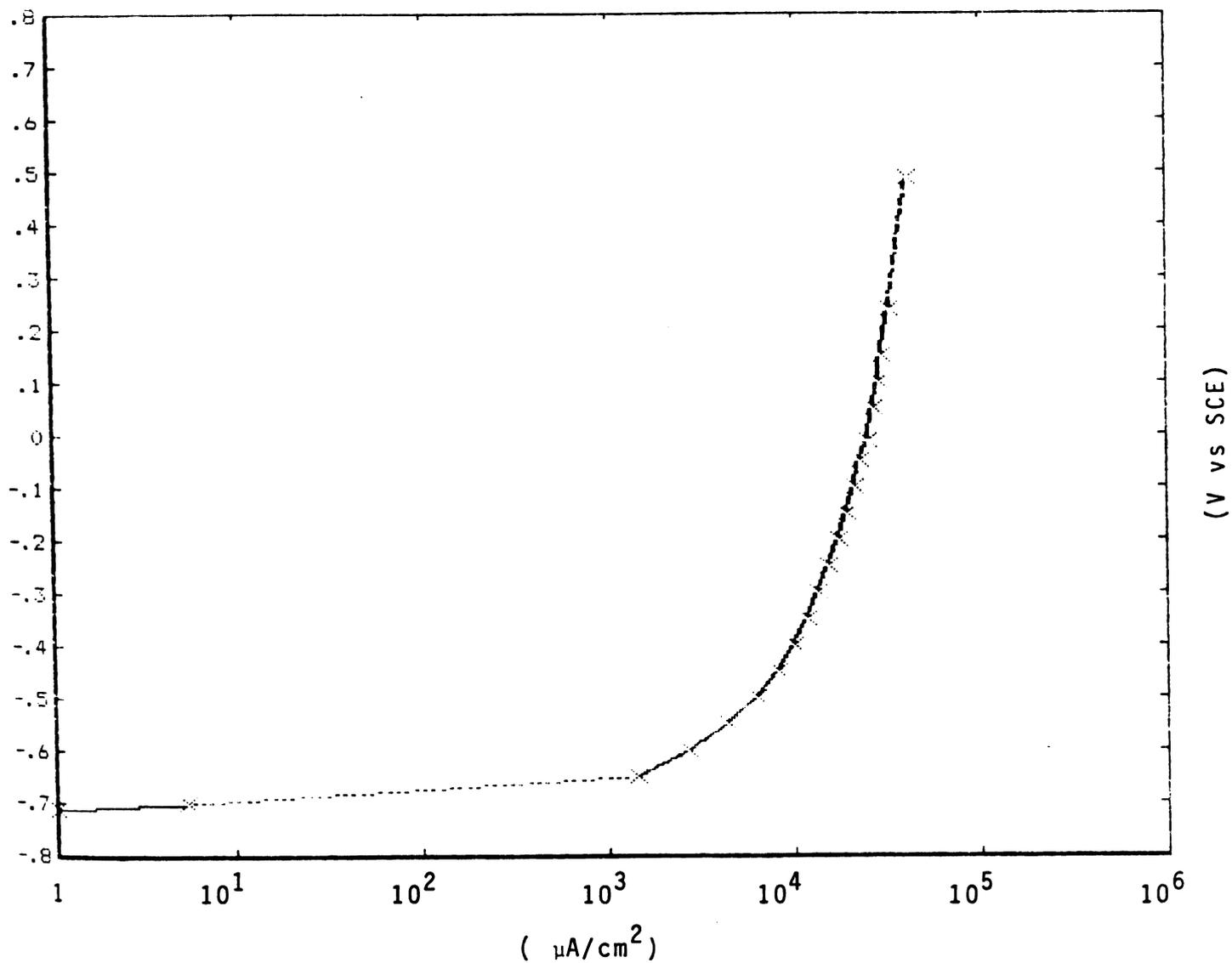


FIGURE 21 ANODIC POLARIZATION OF AL 7075-T6 IN 1.0 WT.% NAACL,  
0.01% HAMPOSYL L-30 SOLUTION WITHOUT INHIBITOR

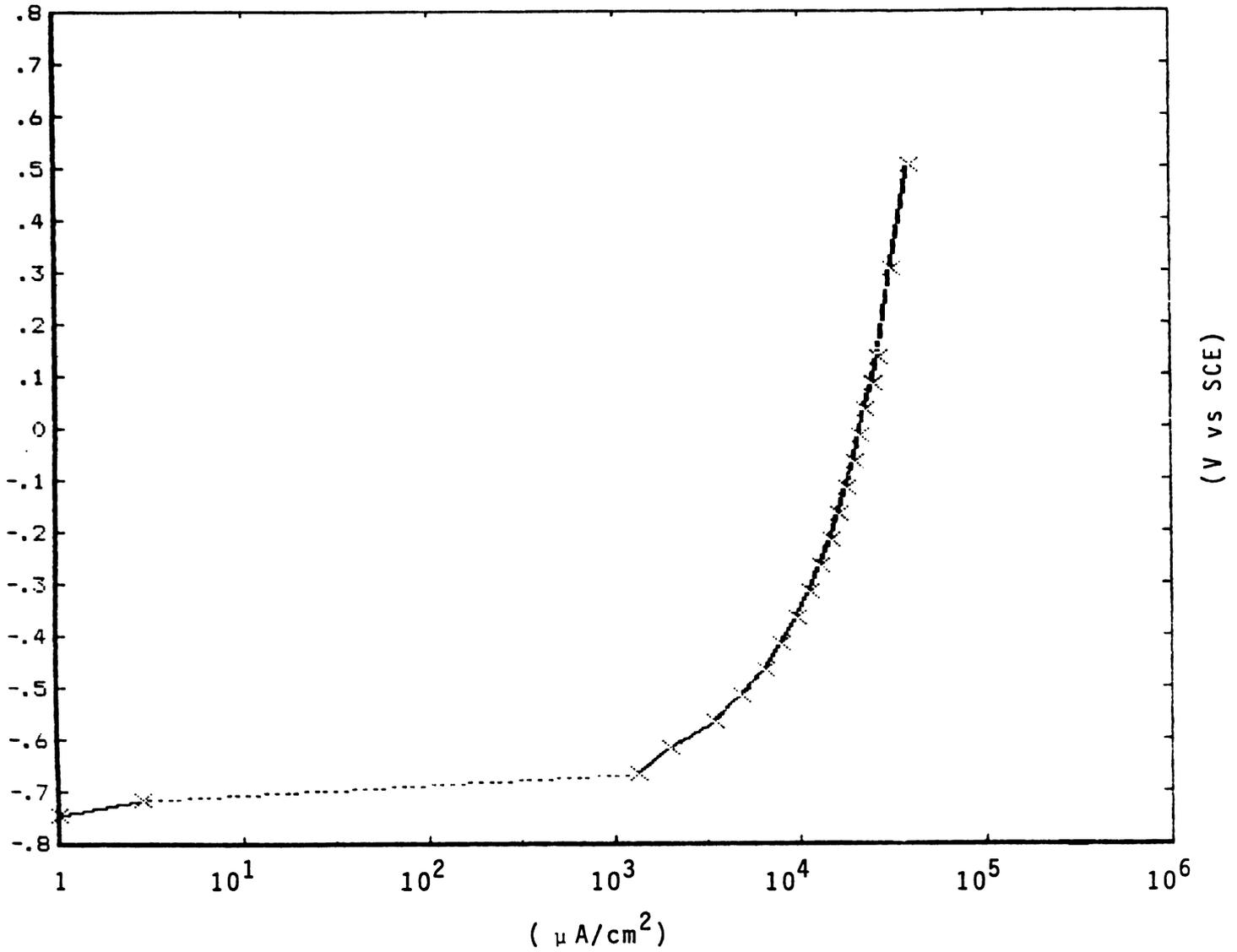


FIGURE 22 ANODIC POLARIZATION OF AL 7075-T6 IN 1.0 WT.% NaCl,  
0.01 WT.% ZONYL FSA SOLUTION WITHOUT INHIBITOR

densities are greater than those with 0.02 wt. % of NaCl.

In Figure 23 are shown the anodic polarization curves of 7075-T6 Al alloy in 1.0 wt. % NaCl solution without inhibitor for different concentrations of Hamposyl 0 surfactant. In these experiments there was no change in corrosion potential, nevertheless, there was a slight reduction in corrosion current density when the concentration of surfactant was doubled. It suggests that by increasing the surfactant concentration, better protection could be achieved.

Figure 24 shows the anodic profiles of Al 7075-T6 in 0.02 wt. % NaCl solution with inhibitor formulation IV for different surfactants. One can notice that when the surfactants were used with inhibitor, the inhibition was very good. In these tests the corrosion potential was dependent on the added surfactant. The shape of the curves suggests passivation against chloride attack. All the surfactants tested exhibited similar effects but did not increase the amount of passivation against chloride attack, with the exception of 1,3-Di-(4-Piperidyl)Propane, which caused a decrease in the passivation. It is suggested that this surfactant may have a synergistic effect that is negative with respect to passivation against chloride attack.

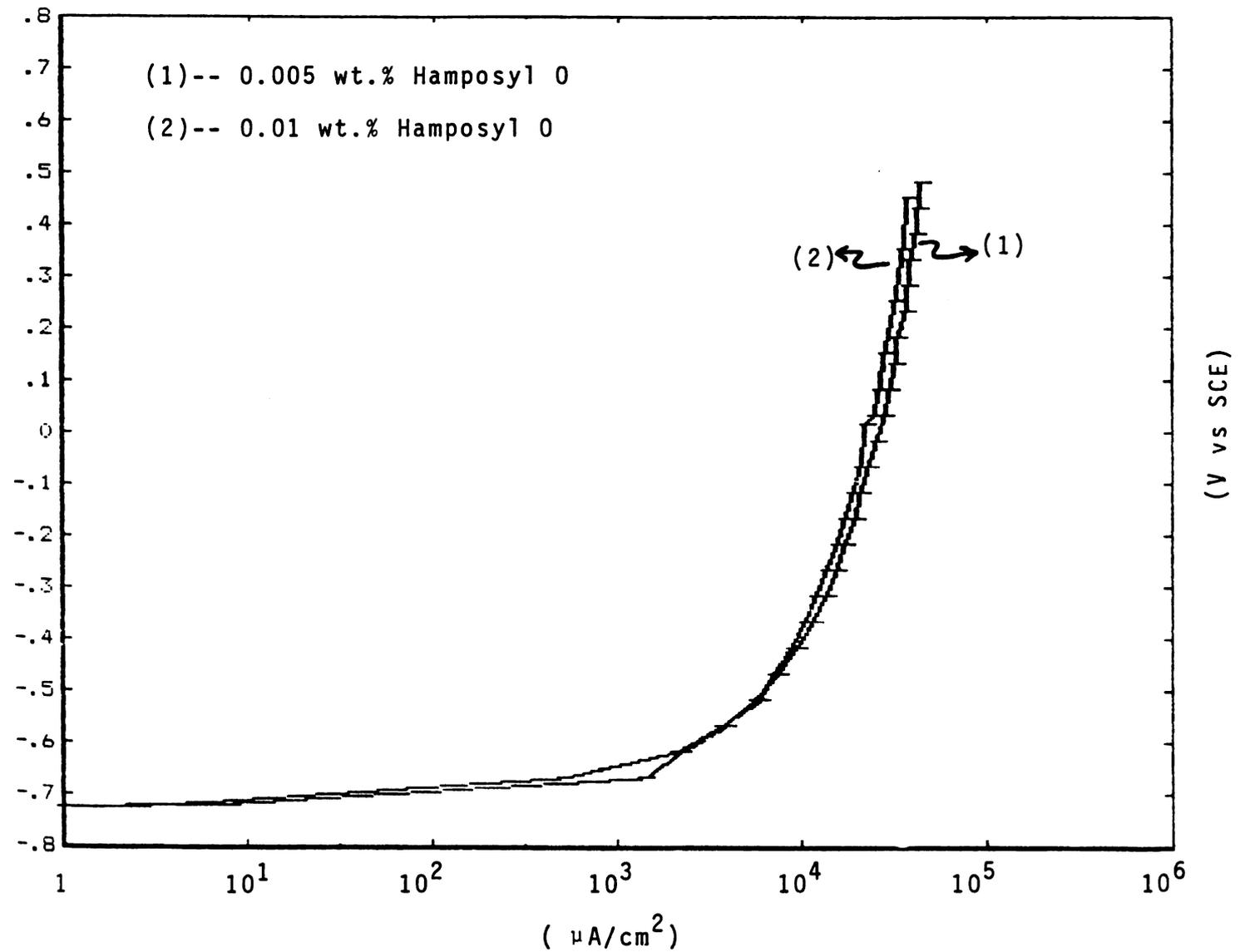


FIGURE 23 EFFECT OF SURFACTANT CONCENTRATION UPON ANODIC POLARIZATION OF AL 7075-T6 IN 1.0 WT.% NaCl SOLUTION WITHOUT INHIBITORS

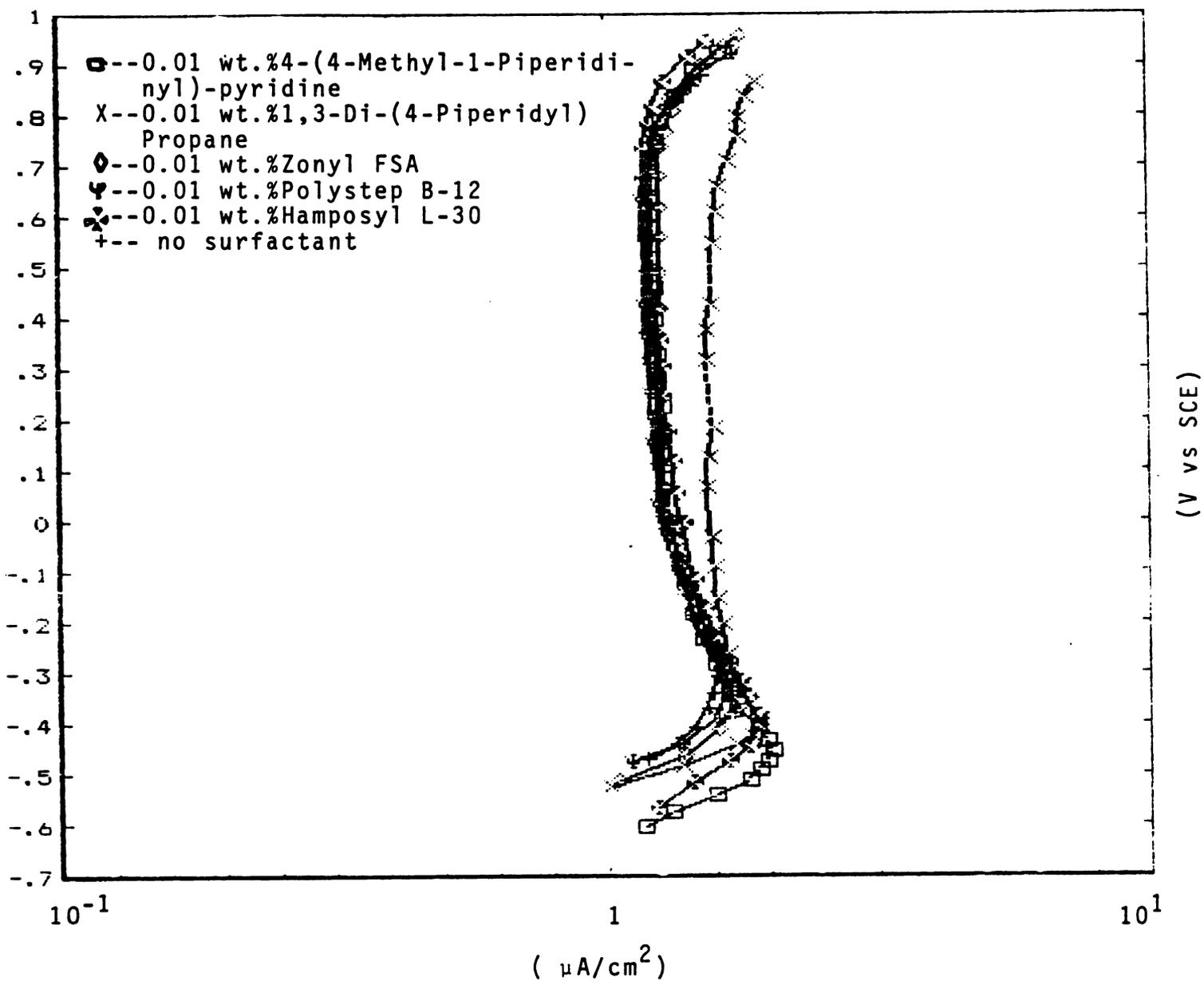


FIGURE 24 EFFECT OF SURFACTANT UPON ANODIC POLARIZATION OF  
 AL 7075-T6 IN 0.02 WT.% NA CL SOLUTION WITH  
 INHIBITOR FORMULATION IV

## V. DISCUSSION

Since the corrosion rates are so much smaller for aluminum and its alloys in neutral and near-neutral salt solutions than in markedly acid or basic solutions, it is not easy to evaluate the usefulness of the surface-active agents used in this study

After evaluating the anodic polarization behavior of corroding 7075-T6 Al alloys for different combinations of inhibitor formulations, surfactant type and concentration, and chloride concentration, it was found that almost all of the surfactants used in this investigation showed similar effects in the extent of protection of Al 7075-T6 against chloride attack.

These surfactants when used with the inhibitor formulations provided good protection to this Al alloy in chloride-containing solutions at low concentrations of  $\text{Cl}^-$  ions. However, when the chloride concentration was increased the addition of surfactants did not provide sufficient protection to Al 7075-T6 to general corrosion. There was evidence of film formation but no passivation. This suggests that the passive film formed, by the different tested surfactants combined with the borax-nitrite inhibitor, is ineffective to protect this alloy when the chloride ions are present in high concentrations.

The effectiveness of these surfactants when used without inhibitor formulation was very poor at low and high concen-

trations of chloride ions. It can be suggested that the surfactants evaluated in this study have a synergistic effect. Similar results were obtained by Khobaib<sup>(12)</sup> with other surface-active agents.

Although, the effectiveness rendered by these surfactants was very poor in the absence of the borax-nitrite inhibitor, it could be suggested, from the analysis of Figure 23, that this weak protection can be improved by increasing the concentration of surfactant. From this figure one can say that the increase in surfactant concentration did not passivate the Al alloy but slightly reduced the corrosion current density, i.e., a film was formed on the specimen surface. Then, it can be expected that when used in higher concentrations and combined with the inhibitor formulation better protection could be achieved.

The study of the inhibition mechanism of the surfactants was not within the scope of this research. However, some studies have been done in this field. A mechanism of inhibition by anodic surfactants for aluminum is suggested by Vermilyea<sup>(13)</sup>. He suggests that anodic surface-active agents become attached to the  $Al_2O_3$  surface by the inorganic group, forming a hydrophobic surface, preventing access of water to the surface and hence preventing dissolution of the  $Al_2O_3$ . According to Khobaib<sup>(12)</sup>, it seems that surfactants interfere in the dissolution

reaction by interacting synergistically with the passive film provided by the borax-nitrite formulation resulting in a stronger protective film.

## VI. CONCLUSIONS

- (1) Almost all the surfactants evaluated in this study showed similar effects in the extent of protection against chloride attack to Al 7075-T6. Most of them behaved similarly when used with and without inhibitor formulation and at low and high chloride concentrations.
- (2) The protection rendered by these surface-active agents when used alone was very poor. It suggests that the surface-active agents used in this work interact synergistically with the borax-nitrite inhibitor formulation to give a better protection to 7075-T6 Al alloy against general corrosion.
- (3) The passive film formed by these surfactants and the borax-nitrite inhibitor is still weak and does not provide good protection to this Al alloy against chloride attack at high chloride concentrations.
- (4) Small additions of surface-active agents to the inhibitor formulation have been found to provide effective protection against general corrosion to Al 7075-T6 in the presence of low  $\text{Cl}^-$  concentrations.
- (5) According to Figure 23, one can suggest that increasing the concentration of surfactant and combining them with the inhibitor formulations, an improvement in protection of this alloy in chloride-containing solutions could be achieved.

## VII. REFERENCES

1. U.R. Evans, "The Corrosion and Oxidation of Metals", Second Supplementary Volume, Edward Arnold Publishers, Ltd., 1976
2. M. Khobaib, "Development of Corrosion Inhibitors", AFML-TR-79-4127, Air Force Wright Aeronautical Laboratories, Wright-Patterson AFB, OH, Sept. 1979
3. M.N. Desai, S.M. Desai, C.B. Shah and M.H. Gandhi, Brit. Corr. J. 6, 269 (1971)
4. M.N. Desai, G.J. Shah, D.K. Shah and M.H. Gandhi, Anticorrosion. 19, 16 (1972)
5. M.N. Desai and S.M. Desai, Corr. Sci. 10, 233 (1970)
6. K. Schwabe and C. Michels, Corr. Sci. 8, 285 (1968)
7. R.B. Mears and G.G. Elderidge, Trans. Electrochem. Soc. 83, 403 (1943)
8. G.G. Eldredge and R.B. Mears, Ind. Eng. Chem. 37, 736 (1945)
9. J. Green and D. Boies, "Corrosion-Inhibiting Compositions", U.S. Patent No. 2,815,328, Dec. 3, 1957
10. J.T. Bregman and D. Boies, Corrosion. 14, 275 (1958)
11. C. Nathan, "Corrosion Inhibitors", NACE, Houston, TX 1974
12. M. Khobaib, L. Quackenbush and C.T. Lynch, NACE. 39, 253 (1983)
13. D.A. Vermilyea, J.F. Brown and D.R. Ochar, J. Electrochem. Soc. 117, 783 (1970)

14. J. O'M. Bockris, Chem. Revs. 43, 525 (1948)
15. J. O'M. Bockris, "Modern Aspects of Electrochemistry", Academic Press, New York, (1954)
16. M. Stern and A.L. Geary, J. Electrochem. Soc. 104, 56 (1957)
17. J.V. Petrocelli, ibid. 97, 10 (1950)
18. J.A.V. Butler, "Electrocapillarity", Chemical Publishing Co. New York, (1940)
19. J. O'M. Bockris and E.C. Potter, J. Electrochem. Soc. 99, 169 (1952)
20. M. Stern, ibid. 102, 609 (1955)
21. M. Stern, ibid. 104, 559 (1957)
22. J.A.V. Buttler, Proc. Roy. Soc. A157, 423 (1936)
23. J.A.V. Buttler, Trasn. Faraday Soc. 28, 379 (1932)
24. J.N. Agar and F.P. Bowden, Proc. Roy. Soc. 169A, 206, (1938)
25. H.H. Uhlig, "Corrosion and Corrosion Control", 2nd Ed. John Willey 1971
26. J.V. Petrocelli, J. Electrochem. Soc. 98, 187 (1951)
27. C.W. Tobias, M. Eisenberg and C.R. Wilke, ibid. 99, 395C (1952)
28. C.R. Wilke, M. Eisenberg and C.W. Tobias, ibid. 100, 513 (1953)
29. S. Barnatt, ibid. 99, 549 (1952)
30. J. Newman, "Electrochemical Systems", Prentice-Hall, Englewood Cliffs, N.J. 1973

31. H. Omura, "Effect of Multi-Functional Inhibitors on the Electrochemistry within a Corrosion Crack", Ph.D. Thesis, Michigan State University, 1984
32. Callender, Engineering. 70, 340 (1925)
33. H. Leckie and U.H. Uhlig, J. Electrochem. Soc. 113, 1262 (1966)

MICHIGAN STATE UNIV. LIBRARIES



31293008523643