BRONZE IMMERSION PLATING ON MILD STEEL

IN CYANTDE-FREE SOLUTIONS:

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DECLARATION:

I hereby declare that this thesis contains the report of my research work and has not been presented in any previous application for a Higher Degree. Information from other sources has been acknowledged by means of reference.

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CERTIFICATION:

This thesis entitled 'Bronze Immersion Plating on Mild Steel in Cyanide-free Solutions' by Dogara Bijimi, meets the regulations governing the award of the Degree of Doctor of Philosophy of Ahmadu Bello University and is approved for its contribution to Engineering Literary presentation.

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To my Late Mother, Hawwa.

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ABSTRACT:

Bronze immersion plating on mild steel was successfully carried out in cyanide-free solutions. The plating solutions contained cupric and stannous chloride:; (hydrated) of various proportions; the most common being 4-10 g/L $CuCl_2.2H_20$ and 8-20 g/L $SnCl_2.2II_20$. The plating took place in aqueous, non aqueous and akamu media. Non aqueous media comprised of methanol, ethanol, propanol and butanol. The plating was performed at a temperature of 25°C. The addition of NaCl, KC1 and $BaCl_2$ promotes plating rate approximately in that order. Similarly, the addition of thiourea, I,-cysteine and sodium dithionate to the plating solutions enhances coating thickness growth. However, the addition of IIC1 to the plating solutions retards plating rate.

The immersion plated substrates were later electroplated in aqueous medium, non aqueous media (alcohols), mixed aqueous (water/alcohols, water/ acetone),99% acetone and 37% formaldehyde containing hydrated cupric and stannous chlorides of 100 g/L each. The plating rate favours lower molecular weight alcohols, aqueous, mixed water/acetone and 37% formaldehyde media approximately in that order compared to akamu and 99% acetone. The addition of nitric, acetic and formic acids to plating solution also promotes plating rate.

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CHAPTER ONE

1.0 GENERAL INTRODUCTION:

Some Steel tubes used in the oil industry are often internally and/or externally immersion plated for the purpose of resisting corrosion. Straight runs of tubes are continuously passed through the process of automation in a bronze immersion plating bath.

In the automobile industry, Carburretor parts, bushings and some connecting rod bearings of internal combustion engines are either made from bronze or are bronze plated. Bronze provides good castings and can easily be machined.

In Marine, oil and gas industries, bronze and bronze plated valves and fittings are widely used for corrosion resistant purposes.

Nowadays, bronze immersion plating covers ornamentals, ash trays, office pins and clips. The plating imparts decorative appearance in addition to corrosion resistance.

However, bronze immersion plating finds its widest application in electrical, electronic and printed circuit industry as well as being a good base for electroplating.

Bronze immersion plating solutions containing cyanide as a complexing agent is well known in the literature (Gabe,1978). However, its toxicity makes its continous use as a complexant unsafe. Therefore, other simple solutions have to be developed as alternatives to cyanide baths.

In this work, chloride baths have been tried and have been found to be effective. The baths contained cupric and stannous chlorides of various proportions according to their effectiveness identified in accordance with the literature (Chemicals, 1952 and Britton, 1952) in addition to the results of several trial runs.

The solubilities of cupric and stannous chlorides (hydrated) in the plating media have been the guiding factors for their choice as plating media. Effort was therefore made in this work to obtain solubility results for cupric and stannous chlorides (hydrated) in all the media so chosen.

The Addition of NaCl, KCl and $BaCl_2$ to the immersion plating solutions was done and their respective effects observed.

HCl was added to most of the plating solutions and its effect was also noted.

In general, although, NaCl, KCl and $BaCl_2$ are only slightly soluble in pure alcohols, their various additions to alcohols containing hydrated cupric and stannous chlorides promote plating rates. However, the addition of HCl retards plating rates.

This work also covers immersion plating and subsequent electroplating from solutions containing cupric and stannous chlorides of various compositions.

This work has exploited many plating media (solvents). They include aqueous, mixed aqueous, non aqueous and akamu (which is a colloidal solution made from maize). Non-aqueous media include alcohols (metahnol, ethanol, propanol and butanol) for bronze immersion plating and aqueous, alcohols, akamu, acetone, mixed water/acetone and formaldehyde for bronze electroplating. However, immersion plating in palm and groundnut oils was discontinued because of the difficulty encountered in rinsing the deposits with running water.

The most common bronze immersion plating solutions in this work contained 4-10 g/L $CuCl_2.2H_2O$ and 8-20 g/L $SnCl_2.2H_2O$. The immersion plating took place at a controlled temperature of 25°C. Sodium dithionate, L-cysteine and thiourea were respectively added to the immersion plating solutions and their effects on plating rate have been observed.

The effects of cupric ion concentration and HCl addition on plating rate have also been noted.

The immersion plated substrates were later electroplated from solutions containing 100 g/L $SnCl_2.2H_2O$ and 100 g/L $CuCl_2.2H_2O$. Acids effects (nitric, acetic and formic) on plating rate were observed.

However, while the addition of sodium dithionate, L-cysteine and thiourea promotes plating rate during bronze immersion plating, the addition of HCl retards plating rate.

Similarly, the addition of nitric, acetic and formic acids to bronze electroplating solutions promotes plating rate.

1.1 PRINCIPLE OF IMMERSION PLATING:

Immersion plating covers displacement plating, contact plating and chemical plating (Burns and Bradley, 1954).

Displacement plating which is also known as dip plating takes place when a base metal is immersed in a solution containing the salt of a noble metal. This results in a chemical exchange reaction with the subsequent deposition of the more noble metal on the surface of the less noble substrate.

Chemical plating results from chemical reduction reaction taking place in the plating bath. The coating continues to catalyse the reaction with the resultant build-up of the coating thickness (Metell, 1949 and Subestre, 1972).

For example,

(i) $Fe + Cu^{2+} \longrightarrow Cu + Fe^{2+}$ ..... (1.1)

(ii) $Fe + Sn^{2+} \longrightarrow Sn + Fe^{2+}$ ..... (1.2)

Contact plating uses the principle of potential difference between two metals immersed in a solution containing the metal salt to be plated. The differential potential generated in solution provides the internal current to carry out the plating reaction. Usually a more base (or reactive) metal is required to be immersed in solution in contact with the metal to be plated if the metal by itself cannot initiate the plating process.

For example, in contact tin plating, a metal which by itself could not initiate the plating process is immersed in a solution of tin salt in contact with more active metal, such as aluminium, and hence becomes plated. An ordinary sodium stannate bath operated at a temperature of 80°C could be well suitable for contact plating (Wilson and Wright, 1951).

1.2 ADVANTAGES OF IMMERSION PLATING:

The following are the advantages of immersion plating:

(i) The processes are relatively simple.

(ii) The processes are relatively cheaper. They require the use of simple solutions.

1.3 LIMITATION OF IMMERSION PLATING:

There are three observed limitations of immersion plating:

(i) unless solutions of complex ions are sometimes used in specific manner, the coating are normally noble to the substrates; hence, making it non sacrificial in times of corrosion.

(ii) As immersion plating continues, the substrates becomes less accessible to drive the reaction forward; hence, limiting the coating thickness.

(iii) Non metallic substrates ordinarily connot be plated.

1.4 BRONZE IMMERSION PLATING:

The literature does not contain much work on bronze immersion plating in cyanide-free baths despite its potential application in the electronic, printed-circuit, food packaging industries in addition to being a good surface for electroplating. Conventionally, bronze plating is done in cyanide baths. However, cyanide is hazardous and potent to man. Given the level of technology in the third world and the maintenance culture of the existing technology, it becomes necessary to discourage the use of cyanide baths and to develop other simplier but effective bronze plating baths free from cyanide.

Consequently, this work has limited the bronze immersion plating to simple solutions containing no cyanide complexes.

1.5 CHANGES IN IONIC CONCENTRATION DURING PLATING:

Ions and molecules in solutions are always in constant motion. They move by the process of diffusion, electrostatic attraction, electrostatic repulsion, mechanical forces, thermally enduced motion or Convection forces.

If concentration gradient exist in solution, ions will diffuse

from the more concentrated regime to the dilute regime. The rate at which the transfer occurs is directly proportional to the difference in concentration between the two concentration regimes.

In plating, diffusion of ions occurs according to the relationship,

$$D = K\ (C-C_O) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1.3)$$

where D is the diffusion rate of ions onto a plating surface, C is the concentration of reactants, C_O is the equilibrium concentration at the plating surface and K is the proportionality constant.

If however a potential is applied to the plating surface, C_O will be diminishing while the diffusion rate will be increasing simultaneously.

However, irrespective of the plating medium, ionic diffusion from bulk solution to plating sites on substrates surface during immersion plating and/or subsequent electroplating may be expressed in terms of Fick's Law and Nernst diffusion equation (Gabe, 1980):

$$\text{Fick's Law:}\quad J\ \left(= \frac{dN}{dt}\right) = -D\,\frac{dC}{dx} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (1.4).$$

$$\text{Nernst:}\quad \frac{i}{nF} = -D\,\left(\frac{C_O - C_b}{\delta}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (1.5)$$

$$i_l = \frac{nFDC_b}{\delta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (1.6)$$

where C_o and C_b are surface and bulk concentrations respectively, J is the flux in moles/sec and $-\frac{dC}{dx}$ is the uni-directional concentration gradient, normally defined graphically, N is in moles, δ is the diffusion layer, n is the number of electrons and F is the Faraday constant.

Fick's Law is more related to immersion plating because it does not require an external current to accomplish plating. As earlier stated, the plating rate during immersion plating may be related to ionic diffusion rate or mass transport, and is proportional to the concentration gradient of the metallic ions in solution.

For the subsequent electroplating which requires an external current, the flux is essentially a current density, hence, Nernst equation is applicable.

1.6 CHEMICAL AND ELECTROCHEMICAL PROCESSES OCCURRING DURING PLATING:

Before delving further into plating, it may be necessary to appreciate some of the salient chemical and electrochemical processes that occur during plating.

1.6.1 ELECTRODE-SOLUTION INTERFACE:

The electrode solution interface behaves very much like a capacitor.

If E is the potential across the capacitor, and q is the charge,

then $q = E. C_p$ 1.7

where C_p is the capacitance.

When a potential is applied across a capacitor, charge will accumulate on the metal plates and current will flow according to,

$$i = -\frac{dq}{dt} \quad \text{..... 1.8}$$

where i is the instantaneous current. However, for a given applied potential E for time t, the instantaneous current can be calculated from the relationship,

$$i = \frac{E}{R_e} . e^{-t/R_e {}_dC_p} \quad \text{..... 1.9}$$

where R_e is the external resistance, and ${}_dC_p$ is the differential capacitance across the double layer.

The applied potential E_p, is the sum total of the potential drops across the resistor and across the capacitor,

ie $E_p = E_{R_e} + E_{c_p}$

or $E_p = iR_e + \frac{q}{{}_dC_p}$ 1.10

combining equations 1.8 and 1.10 we get,

$$\frac{dq}{dt} = \frac{E_p}{R_e} - \frac{q}{R_e {}_dC_p}$$

.../7

$$\text{or} \quad \frac{dq}{dt} = \frac{1}{R_e} \left(E_p - \frac{q}{dC_p}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 1.11$$

A charge on a capacitor may consist of an excess of electrons on one plate, and the deficiency of electrons on the other. Since the electrode - solution behaves like a capacitor,

$$q_s = -q_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1.12$$

where q_s is the charge in the solution, and q_m is the charge on the electrode.

When the circuit is charged by a constant current, i, like in the case of electroplating, we then have the relationship,

$$q = \int i dt$$

$$\text{And} \quad E_p = iR_e + \frac{i}{dC_p} \int_0^t dt \quad \ldots\ldots\ldots\ldots \quad 1.13$$

By integration we get,

$$E_p = i\,(R_e + t/_dC_p) \quad \ldots\ldots\ldots\ldots\ldots \quad 1.14$$

A charge q_s in solution is the sum total of excess of cations and ions in the vicinity of the electrode surface, while q_m is the sum total of excess or deficiency of electrons. It is this whole array of charged particles and oriented dipoles that are present at the metal - solution interface that is known as the electrical double - layer.

1.6.2 THE DOUBLE LAYER:

The double layer is made up of layers of atoms, molecules or other adsorbed species. The inner layer called the Helmholtz layer is compact, and the locus of the adsorbed species (atoms, ions, etc.) is called the inner Helmholtz plane (IHP) and is approximately a monolayer thick. The locus of the nearest solvated ions to the compacted layer is called the outer Helmholtz plane (OHP). Electrostatic forces control the interaction between the charged metal surface and the solvated ions. The diffused

layer extends from the outer Helmholtz plane to the bulk of the solution (Fig. 1.1).

The thickness of the double-layer may be equal or less than ($\lesssim$)10Å or 100nm. The thickness of the diffuse layer depends upon the concentration of ions in solution, but it is rarely greater than 300Å for concentration over and above 0.01M. (Bard and Foulkner, 1980).

The concentration profiles across the double-layer are shown in Figures 1.1a and 1.1b respectively.

In electroplating, the current required for the overall conversion of the dissolved oxidised species to a reduced form is governed by:

(i) rate of chemical reactions taking place during electroplating.

(ii) rate of mass transfer, eg ions from bulk solution to the electrode surface where they are reduced.

(iii) rate of electron transfer at the electrode surface.

(iv) rate of reactions taking place directly at the electrode surface, eg absorption and crystallisation of ions during electroplating.

At the attainment of steady-state current, all the reaction rates in solution are the same. However, the magnitude of the steady-state current is always limited due to rate determining steps caused by inherently sluggish reactions.

A fast reaction step is characterised by a small resistance, conversely a slow reaction is characterised by a high resistance. However, the resistances are related to the electrode potential and the current in the circuit.

ie $E = iR_T$ 1.15

where E is the electrode potential and R_T the total resistance. If however, an external current is applied to the system,

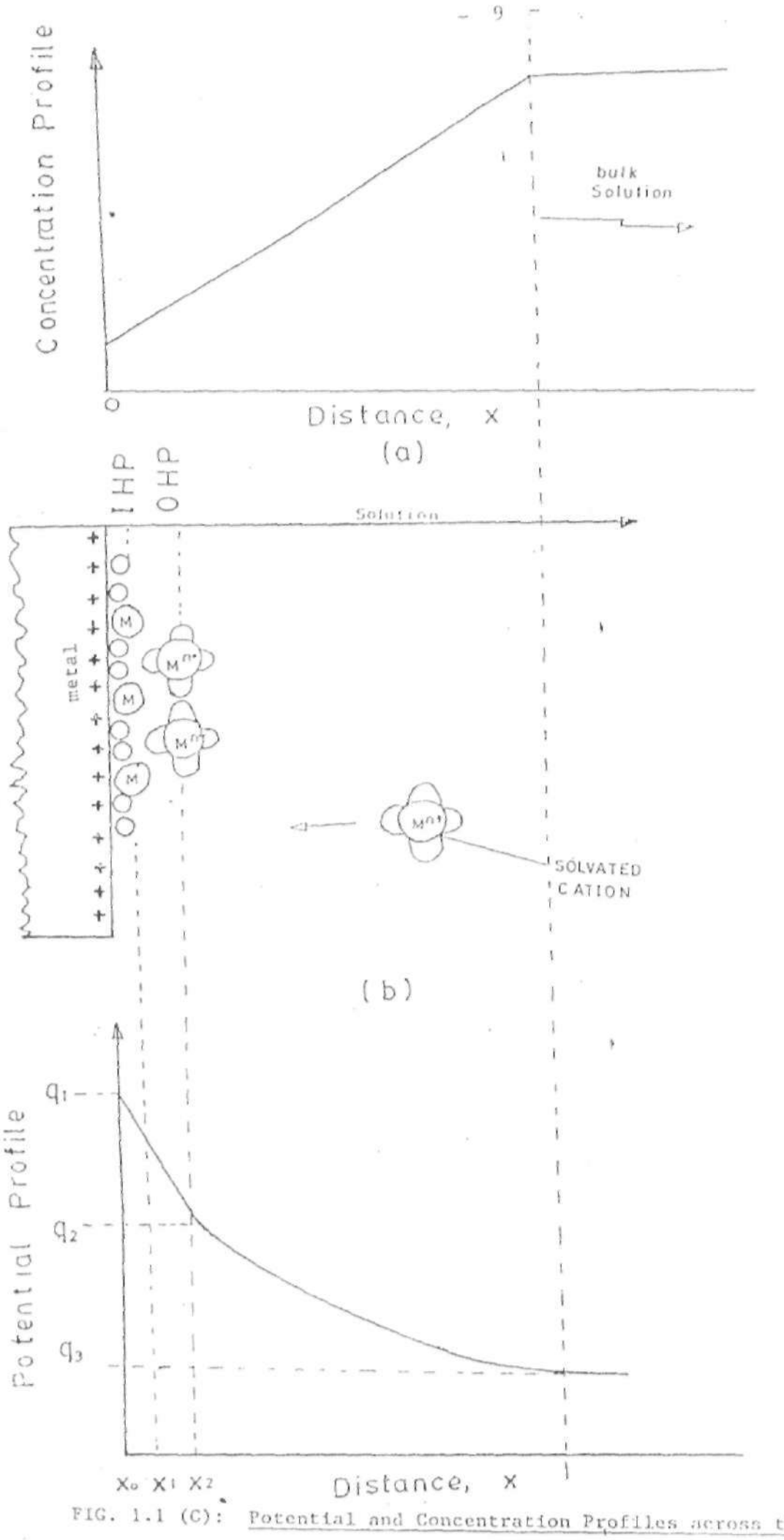


FIG. 1.1 (C): Potential and Concentration Profiles across the double layer.

Then $E_p = E + iR_T$ 1.16

where E_p is the applied voltage.

If however, there is a mass transfer overpotential in the system,

then $E_p = E_q + iR_T + \theta_j$ 1.17

where θ_j is the mass transfer overpotential, E_q is the equilibrium potential.

It should be noted that the mass transfer overpotential θ_j is clearly the deviation of the potential from equilibrium.

1.1.3 ELECTRODE PROCESSES:

In an electrochemical cell, the electrode where an oxidation reaction occurs is called the anode, conversely an electrode where a reduction reaction takes place is called the cathode.

Figure 1.2 is a model of electron transfer in a typical electrochemical system. The transfer is taking place in the bulk of the solution signifying an oxidation-reduction reaction.

Figure 1.3 is another model describing a typical galvanic cell. The cathode is at a higher potential than the anode, hence the flow of electric current is from cathode to anode, while the flow of electrons from anode to cathode. The species undergoing reduction withdraws electrons from the cathode, thereby leaving a net positive charge on it. Conversely, the species undergoing oxidation dump electrons at the anode, thereby giving it a net negative charge. From the foregoing, the cathode is much more at a higher energy level than the anode.

However, in electrolysis the reverse is the case. The anode is made positive relative to the cathode. Anions have to be induced to move to the anode in order to be oxidised and cations have to be drawn to the cathode in order to be reduced (Fig. 1.4).

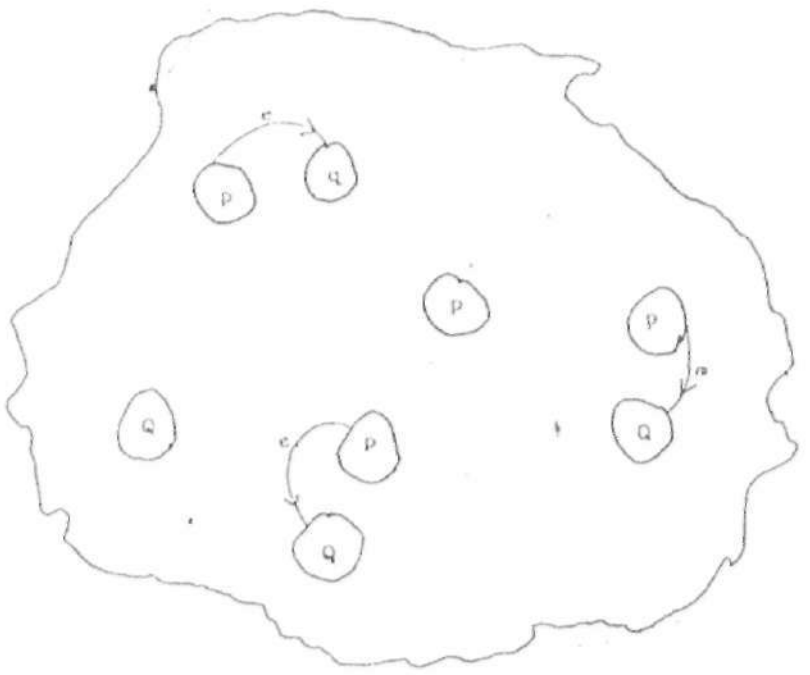


Fig 1·2 A model of electron in an electrochemical system.

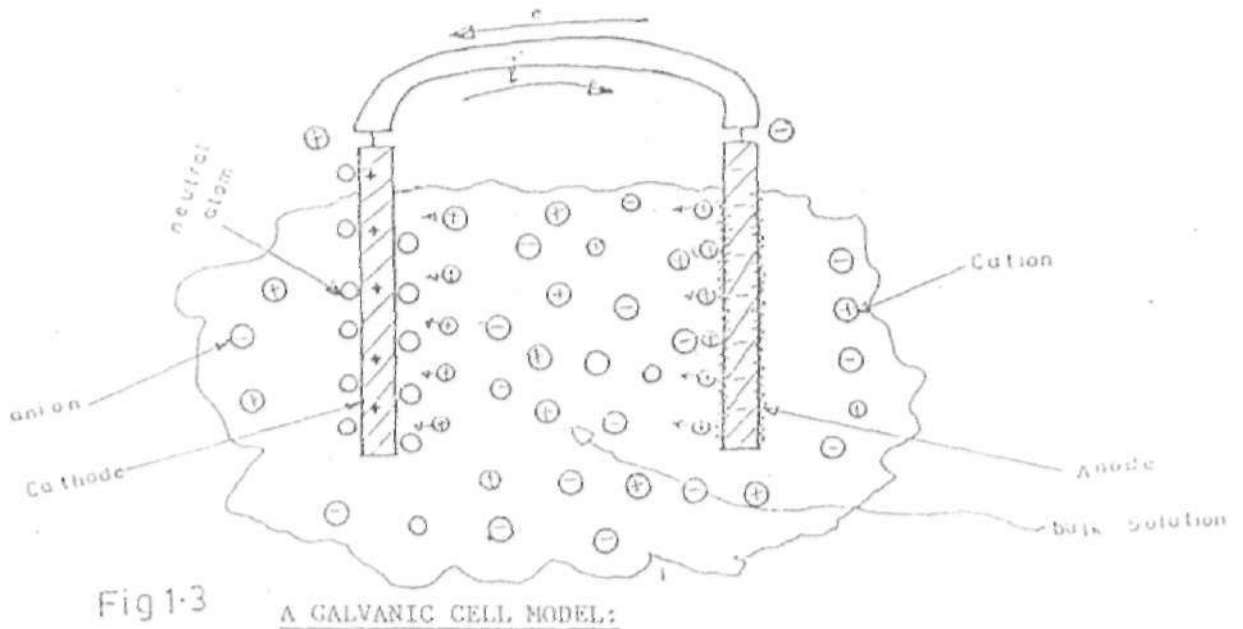


Fig 1·3 A GALVANIC CELL MODEL:

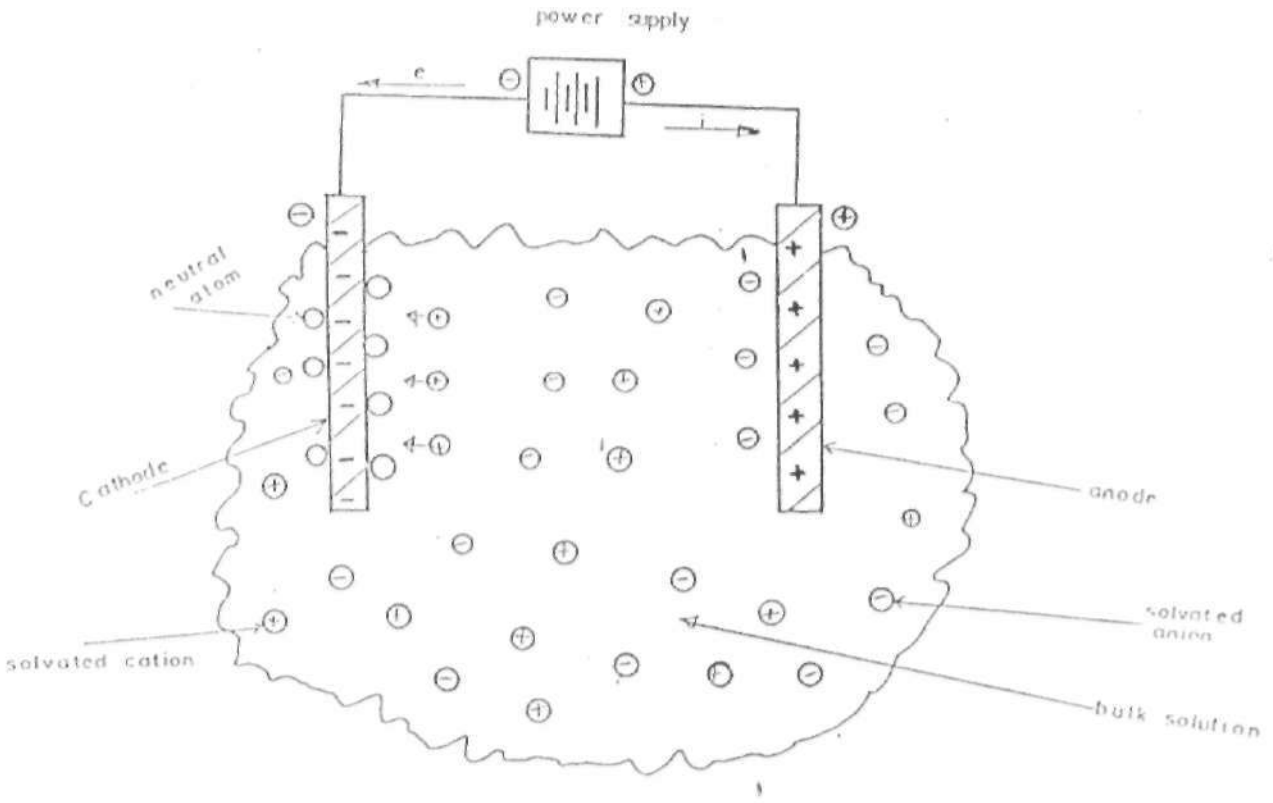


Fig 1.4 ELECTROLYTIC CELL MODEL

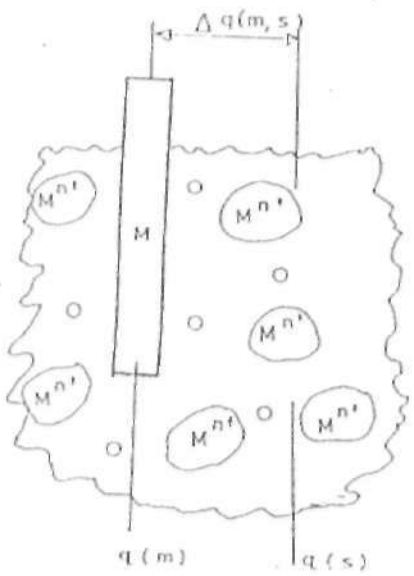


Fig 1.5 Electrical Potentials at the Interface of an electrode-electrolyte system.

Galvanic cells are mostly used for the conversion of chemical energy into electricity. Commercial usage of galvanic cells are limited to rechargeable primary cells, eg car battery and fuel cells. However, an electrolytic cell is one being imposed by an external voltage to drive the reactions forward. The external voltage so imposed is usually by far greater than the reversible or equilibrium potential of the cell of interest. The electrolytic cell model is employed commercially for electroplating, electrorefining, electrolytic synthesis, etc.

As can be seen from the two models (Figs. 1.2 and 1.3), both galvanic and electrolytic cells are very similar. However, apart from the fact that the electrolytic cell is being imposed with an applied voltage, its cathode is negative with respect to the anode. Conversely, in a galvanic cell, the cathode is positive with respect to the anode.

1.6.4 VARIABLES AFFECTING REACTION RATES:

Electrode reaction rates are affected by the following variables.

1.6.4.1 ELECTRODE:

(i) It is necessary to know the material from which the electrode is made.

(ii) We have to know the total surface area of the electrode.

(iii) We need to know the surface finish of the electrode.

(iv) The geometry of the electrode has to be specified.

1.6.4.2 SOLUTION:

(i) We need to know the concentration of the major electroactive species in the bulk solution.

(ii) We need to know the concentration of other secondary species in the bulk solution.

(iii) The solvent to be used must be specified.

1.6.4.3 MASS TRANSFER:

(i) We need to know the rate of mass transfer.

(ii) Is the mass transfer diffusion control or convection control?

(iii) What is the rate of diffusivity?

(iv) What are the surface concentrations?

(v) We need to know the process and the rate of adsorption at the electrode surface.

1.6.4.4 ELECTRICAL PROPERTIES:

(i) We need to know all the electrical properties and their variables.

(ii) What is the potential at which the process is taking place?

(iii) What is the magnitude of the current flowing through the circuit?

(iv) What about the quantity of electricity that is produced with respect to time?

1.6.4.5 EXTERNAL CONDITIONS:

The most important external variables of interest include:

(i) Variation in time,

(ii) temperature variation,

and (iii) pressure variation.

1.6.5 ELECTROCHEMICAL POTENTIAL ACROSS THE DOUBLE LAYER:

The linkage between the electrode potential E, and the concentration of participants in the electrochemical process may be represented by the simple reaction.

$$O + ne \rightleftharpoons R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1.18$$

where O represents oxidation process and R is a reduction process, eg. electroplating and ne is the number of electrons that took part in the reaction.

Reaction 1.18 above can be represented by the popular Nernst equation,

eg. $E = E^{\ominus} + \frac{RT}{nF} \text{ Ln } \frac{[O]}{[R]}$ 1.19

where E is the electrode potential, $E^{\ominus}$ is the standard potential, n is the valency and F is the Faraday constant ($F = 96,485 \text{ Cmol}^{-1}$).

The Nernst equation is only applicable to reversible processes. However, it must be noted that a given system may behave reversibly in one experiment and irreversibly in another.

The equilibrium potential of equation 1.19 can be written in terms of the concentration of the species or participants in solution,

ie $E = E^{\ominus} + \frac{RT}{nF} \text{ Ln. } \frac{C_{O*}}{C_{R*}}$ 1.20

where C_{O*} and C_{R*} are bulk concentrations.

Now, it must be noted that the Gibbs function μ relates to both chemical and electrochemical potentials according to,

$\bar{\mu}_i = \mu_i + nFq$ 1.21

where $\bar{\mu}_i$ is the electrochemical potential, μ_i the chemical potential according to equation 1.21 and q is the electric potential.

CHAPTER TWO

2.0 LITERATURE REVIEW:

2.1 TIN, COPPER AND BRONZE IMMERSION PLATING:

Immersion plating practice can be dated as far back as 1939 or more. At that time, copper and brass were successfully tinned (Blum and Hogaboom, 1967). The plating solution contained tin chloride, sodium hydroxide and sodium cyanide.

However, Pavlish and Sullivan (1949) patented an immersion plating process. The solution contained tin chloride, thiourea and hydrochloric acid.

A similar plating process was patented about the same period as mentioned above. The process contained tin chloride, thiourea and sulphuric acid (Braley, 1942).

Several other solutions reported to have greater effectiveness were patented thereafter. For example, an alkaline solution containing potassium stannate, potassium cyanide and potassium hydroxide was patented (Lowenheim and Forman, 1956). It was claimed that the solution produced faster deposition with greater coating stability.

Another solution was reported by Drobne and Ceresa (1959). The solution was made up of stannous chloride, thiourea and citric acid or a few other organic acids. The plating was said to be effective.

Tin plating of lead and lead alloy by immersion was reported to be very effective. Coating thickness up to 5μm was said to have been obtained within 30 minutes (Burns and Bradley, 1954).

A high quality plating was reported in the literature (Chemicals, 1952) from an immersion plating solution containing tin chloride, hydrochloric acid, thiourea and sodium hypophosphite. A definite improvement in deposition rate was reported. Although, the addition of sodium hypophosphite was

.../2

said to have improved the deposition rate, its actual role in the plating could not be exactly determined.

Drobne and Ceresa (1959) reported that the surface to be immersion plated must be well polished to mirror finish (bright) if bright deposits are required. The thickness of tin coating on a bright copper substrate could be of the order of 3μm if immersed in the solution for an hour.

Immersion plating of tin on aluminium and its alloys, the so-called aluminium tinning has received wide acceptance in the plating industry (Chemicals, 1960), particularly the immersion plating of tin onto aluminium alloy pistons for internal combustion engines. The purpose of tinning the piston is to produce a self lubricating surface, thereby reducing wear during its working life. The pistons could be tinned by immersion in 45 - 70 g/L sodium or potassium stannate for about 3 - 4 minutes at 50 - 75°C. The ultimate plating thickness could be as high as 5μm while still remaining a mat white finish.

The addition of acetic acid helped to control the rise in the level of free alkali as the plating progresses, while stannate periodic addition or temperature rise or both could control tin content in the solution; Chemicals (1952).

A process using polyphosphates in addition to alkali stannate on the immersion tinning of aluminium was reported to have better control of the free akali and longer bath's life because plain sodium stannate is most stable in solution; Britton (1952).

Other solutions of interest reported in the literature include stannous sulphate used with hydrofluoric acid; stannous fluoborate solution; stannous fluosilicate solution and stannous chloride solution containing ammonium alum were all said to be effective. Chemicals (1952).

An important bronze immersion plating solution, the so-called liquor finish for steel was reported by Chemicals (1952). The solution comprised of the following:

7.5 g/L Stannous sulphate

7.5 g/L Copper sulphate

10-30 g/L Sulphuric Acid (conc).

The 'liquor finish' was said to have imparted decorative and lubricity properties during wire drawing. The plating was operated at room temperature. Different coating colours were produced by the variation of copper sulphate concentration in solution.

Saubestre (1970) on similar plating on copper, steel, gold, silver, platinum, cobalt, nickel, rhodium and palladium from copper baths containing 3.6 g/L copper sulphate, 25 g/L sodium potassium tartrate, 3.6 g/L sodium hyroxide and 10 g/L formaldehyde, operated at a temperature of 22°C produced plating rates up to 0.5 μmh^{-1}.

The coatings were said to be widely used as undercoats for electroplating, but were also used in the metalizing of printed-circuit boards. Complexing or chelating agents such as tartrate ion, amines and glycolic acid were reportedly used to hold the copper in solution prior to plating.

The stoichiometry of the reaction was given as:

$$Cu^{2+} + 2HCHO + 4OH^{-} \longrightarrow Cu^{o} + H_2 + 2H_2O + HCO_2^{-} \quad \ldots\ldots 2.1$$

It was reported that the mechanism of copper deposition is similar to that of nickel and involves a hydride ion originating from formaldehyde:

$$2H^{+} + Cu^{2+} \longrightarrow H_2 + Cu^{o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.2$$

However, it was reported that the copper baths were not very stable because of spontaneous decomposition arising from competing reactions from bulk solutions according to:

$$2Cu^{2+} + HCHO + 2OH^{-} \longrightarrow Cu_2O + HCOO + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots 2.3$$

However, in order to prevent such decompsition, the use of stabilizers

such as thiourea, mercapto-benzothiazole, cyanide, vanadium pentoxide, methyl butanol, etc were proposed.

Krochler and Creighton (1944) reported that white tinning of steel was obtained from solutions containing 0.8-2.5 g/L stannous sulphate, 5-15 g/L sulphuric acid. The steel immersion plating was operated between 90-100°C for about 5-20 minutes.

Blum and Hogaboom (1967) reported that tin deposits could be applied to small articles such as pins by tumbling them in suitable solution with zinc which generates sufficient current without the application of an external souce. The articles could be immersed in hot solution containing stannous chloride, a cream of tartar and ammonium alum. It was reported that it is also possible to immerse the articles in fused salts of stannous chloride.

Wilson and Wright (1953) as with as Blums and Bradley (1954) reported that a method for contact tinning which could be applied to different base metals is to hang the work in the conventional stannate tin plating bath in contact with aluminium. This can be done by suspending the work on aluminium wires.

Articles could be immersion plated from a sodium stannate bath by coupling the articles to an aluminium surface before the immersion (Lowenheim, 1964).

Another contact type immersion plating is that applied to awkwardly placed areas which makes the normal direct immersion plating unsuitable and the coating unduly thin (Shipley,1967). In such a case, aluminium is used for the contact tinning to produce relatively thicker deposits without the use of external current. This is thus a case of a metal which by itself could not initiate an immersion plating process being immersed in a solution containing tin salt in contact with a more reactive metal

such as aluminium.

It has also been found that stannate solution for electrodeposition could equally be used for immersion plating on steel when the appropriate contact is made with a reactive metal of interest. The solution should be operated at a temperature of about 80°C (Kohan, 1959).

Britton (1952) reported that bronze immersion plating from solutions containing 38-42 g/L stannous chloride, 7.5-8.5 g/L cupric chloride, 16-18 g/L sodium cyanide produced dense and adherent coatings.

Oguta and Mikio (1975) studied the immersion plating of copper on iron from copper sulphate baths in the absence of complexing agents. The galvanic displacement,

$$Fe + Cu^{2+} = Fe^{2+} + Cu^{o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.4$$

was studied. It was found that poorly adherent copper deposits were obtained on iron in highly concentrated copper sulphate solution. $FeSO_4$ or Fe_2O_3 codeposited with the copper because of high accumulation of Fe^{2+} at the interface. Well adherent deposits were obtained by the use of diluted solutions, eg. 0.01M $CuSO_4$.Fe^{2+} was removed into bulk solution by diffusion. The conditions for obtaining adherent deposits were 0.0025-0.03M $CuSO_4$ at pH about 2.5. The plating took place at a room temperature with an immersion time between 0.5-1.5 minutes. The deposits were said to be suitable as base for electroplating from ordinary pyrophosphate baths.

Costain, (1972) added a complexing amine and a conjugated unsaturated nitrile or oxime to a copper immersion plating solution on steel substrate. The cupric chloride plating solution contained some small amount of HCl. Thin but firmly adherent coatings were obtained which could not be detached when bent through 180°C.

Some electroless copper plating solutions of importance that have

been reported in the literature (Saubestre, 1972) are:

(i) 3.6 g/L $CuSO_4$ ($CuSO_4 5H_2O$)
25 g/L Sodium potassium tartrate
3.8 g/L Sodium hydroxide
10 g/L Formaldehyde
22°C (Operating Temperature).

(ii) 5 g/L Copper sulphate
25 g/L Sodium potassium tartrate
7 g/L Sodium hydroxide
10 g/L Formaldehyde (HCHO)
22°C (Operating Temperature).

(iii) 30 g/L Copper sulphate
100 g/L Sodium potassium tartrate
50 g/L Sodium hydroxide
32 g/L Formaldehyde
25°C (Operating Temperature).

(iv) 30 g/L Copper sulphate
140 g/L Sodium potassium tartrate
42 g/L Sodium hydroxide
25 g/L Sodium carbonate
17 g/L "Versene T"
167 g/L Formaldehyde
25°C (Operating Temperature).

(v) 13 g/L Copper sulphate
66 g/L Sodium potassium tartrate
20 g/L Sodium hydroxide
0.013 g/L Mercaptobenzothiazole
38 g/L Formaldehyde
25°C (Operating Temperature).

.../7

It was reported that the coatings obtained from the above solutions were bright and dense, and were good surfaces for electroplating.

2.2 BRONZE ELECTROPLATING:

Gabe (1978) reported that bronze plating baths containing 80 g/L Na_2SnO_3, 10-15 g/L NaOH, 10-20 $Cu(CN)_2$ and 20-25 g/L NaCN produced coatings of integrity. Bronze or copper/tin metals were used as anodes. A current density range of 1-4 A/dm^2 was applied to the plating baths whose temperature was maintained at 65°C.

A typical bronze plating solution may comprise the following (Ollard and Smith, 1954):

Potassium stannate ($K_2Sn(OH)_6$		60 g/L
Tin metal	-	19-26g/L
Potassium hydroxide (KOH)		4-11g/L
copper cyanide (CuCN)		40g/L
Free potassium cyanide		34g/L
Temperature range		60° - 70°C.

The use of brightener, addition and wetting agents are advisable for the above formulation.

Although in bronze plating, bronze anodes are rarely used, they can however, be used at very low current densities (Gabe, 1978).

Temperature increase favours tin deposition, and this in turn raises the tin content of the deposit. Hydroxyl ion in the bath complexes tin while the cyanide ion complexes copper in solution making the metal ions more stable in solution. It follows that lower hydroxyl ions favours tin deposition, and lower cyanide ion favours copper deposition (Canning, 1970).

A temperature range of 68° - 71°C has been suggested during electroplating of tin-copper if a golden colour is desirable. That also means that the

tin content and free potassium cyanide are at the upper and lower points respectively. (Canning, 1970).

Bronze plating, the so-called speculum plating which enables the co-deposition of tin-copper alloy onto iron, steel, tinplate, bronze, brass, nickel, copper and lead castings has been reported in the literature (Brenner, 1963). The resultant coatings are decorative, and also often have protective values.

The deposits are fairly hard, resistant to corrosion and abrasion. The coatings are quite suitable for domestic and indoor applications. Articles obtained from speculum plating replaced silver in the field of table-ware.

Many solutions are known for optimum results: eg (i) solution containing 40-45% tin and 45-60% copper; (ii) solution containing 42% tin and 58% copper.

However, the following composition makes up a good plating bath (Brenner, 1963).

Sodium stannate	38-42 g/L
Copper cyanide	7.5-8.5g/L
Sodium cyanide	16-18 g/L
Caustic soda	14-16 g/L

It is advisable that each ingredient be fully dissolved in solution before the next is added. The plating should be done between 65-67°C.

Ageing of the solution is important in order not to have excessive tin deposits. The ageing time is normally an hour, but it could be accelerated by the addition of ammonia in order to drastically reduce the time. A typical solution is as follows (Brenner, 1963):

Sodium stannate	94 g/L
Single copper cyanide	11 g/L
Sodium cyanide	28 g/L
Caustic Soda	13 g/L
Ammonia	1 ml/L

.../9

Electroplating can be done in a steel tank lined with reinforced glass for commercial purposes. An electrical, gas or steam heating coil may be employed for controlling the temperature of the bath. A direct current equipment may also be used in order to supply the necessary plating currents (Graham, 1962).

Very thin speculum coatings could provide well compacted and non porous surfaces which could have good corrosion resistance. Coating thickness for general engineering application are: 13μm on brass, copper, etc and 25μm on steel (Gabe, 1978).

If the cathode current density is known, the thickness of the coating and hence the plating time could be calculated. For example, if the cathode current density is 2.3 A/m^2, coating thickness of about 13μm is obtainable within 20 minutes or 25μm within 40 minutes of plating (Gabe, 1978).

However, for most practical application, the cathode current density of between 1.4 to 2.3 A/m^2 is recommended for optimum result. This will give a cathode efficiency of 60%.

Alloy anodes do not give correct solution composition, hence two separate anodes are used; viz: (i) copper anode having a sufficient surface area to generate current density between 0.5 A/m^2 to 1 A/m^2. (ii) Tin anode must be filmed in order to ensure that it dissolves as stannic ions. The filming is done by the use of iron sheet as cathode to provide a large current density so that as soon as the anode touches the solution it receives a high current density and is thus filmed. A pale or greenish yellow colour is an indication that the tin anode has been completely filmed (Gabe, 1978).

The tin anode must never be defilmed. This is achieved by its prior withdrawal from the bath before switching off the circuit and unloading the work. If however, an unfilmed anode is used the tin anode will dissolve

as stannite ion thereby producing dark and rough deposits (Gabe, 1978).

It has been well established that tin-copper can be codeposited in all proportion from stannate cyanide solutions. However, some commercial tin-copper alloy plating of remarkable importance are the alloys in the range 50 to 70% tin and 30% to 40% copper. The colour is golden yellow when the tin content is between 14 - 15% (Canning, 1970).

Bronze coatings are superior undercoats for chromium plating as compared to copper coatings because of their superior corrosion resistance. This was more glaring in early 1950s when metallic nikel was scarce and could not be used as the traditional undercoat for chromium plating. Tin-copper coatings were therefore found to be good subtitute for nikel coatings in chromium plating. However, in terms of cost, bronze is more expensive than copper, but it is superior to copper in terms of rate of plating, hardness of deposits in addition to corrosion resistance (Graham, 1962).

Raub and Muller (1967) reported that a bright bronze plating bath for commercial use was introduced in 1955. The bath contained 30 to 60% tin, copper cyanide, sodium or potassium cyanide, sodium or potassium pyrophosphate, tin salts and potassium or sodium fluoride in an appropriate proportion. The optimum pH range should be between 8.5 - 9.0.

However, Vegramyam and Solovena (1962) reported that an important bronze plating bath contained 40% tin, copper, cyanide, sodium or potassium pyrophosphate. For optimum efficiency, the pH range was maintained between 11- 12. The coatings were said to be adherent and provided a good base for electroplating.

CHAPTER THREE

3.1 EXPERIMENTAL:

3.1.1 POWER SOURCE:

The electrical power source was a 6289A D.C Power Supply (Hewlett Packard). The current and voltage range were 0 - 1.5A and 0 - 40V respectively. The instrument provided the electroplating current density of the immersion plated substrates.

3.1.2 VOLTAGE AND CURRENT METERS:

A Multi-Range Meter (PHYWE 07021.01) was used to measure the applied voltage, while a Current Meter (HUA-2) was used to measure the electroplating current of the immersion plated substrates.

3.1.3 THE BATH:

The plating bath consisted of a 500 ml culture vessel, closed by a lid. The bath was held in position by a clip. The openings on top of the lid recieved the specimens to be immersion plated and a thermometer for temperature control.

Electroplating was also performed using the same culture vessel. The only modification was the careful insertion of jointed copper and tin foils into the plating bath to form the consumable anode. The anode was designed with a tongue sticking out to recieve electrical connection. However, before the insersion, the anode was abraded and pickled in a hot mixture of 10% HNO_3 and 10% HCl for about 5 minutes to remove oxide particles and other unwanted second phases.

3.1.4 SPECIMENS:

The specimens (substrates) were mild steel sheets containing 0.2% carbon. They were cut accordingly to the dimension: 1x5 cm^2 to give a total surface area of 10 cm^2.

3.1.4.1 SPECIMENS PREPARATION:

The mild steel specimens were mirror polished using 100, 200 and 300 grit in that order, before being rinsed in running water, dried and stored in a desiccator prior to immersion plating in order to prevent oxidation or surface contamination.

3.1.5 SOLUTION AND PROCEDURE:

3.1.5.1 IMMERSION PLATING SOLUTION:

The solvents used in this investigation to dissolve the salts included: water, methanol. ethanol, propanol, butanol and akamu. The choice of the solvents was based upon their attractive solubilities as obtained in this work. For the purpose of this investigation, the solvents have been referred to as plating media.

Different solution compositions for immersion plating were prepared. The formulations were based upon literature survey (Chemicals, 1952), solubility results and optimum plating conditions after many trial runs. The solutions so prepared for immersion plating comprised the following compositions:

(i) $SnCl_2 2H_2O$ = 20/ g/L

$CuCl_2 2H_2O$ = 10 g/L

HCl = 0-20 ml/L (0 ~ 2.32×10^{-1}M)

(ii) $SnCl_2 2H_2O$ = 8 g/L

$CuCl_2 2H_2O$ = 8 g/L

HCl = 0-20 ml/L (0 ~ 2.32×10^{-1}M)

(iii) $SnCl_2 2H_2O$ = 8 g/L

$CuCl_2.2H_2O$ = 6 g/L

HCl = 0-20 ml/L (0 ~ 2.32×10^{-1}M)

.../3

(iv) $SnCl_2.2H_2O$ = 8 g/L

$CuCl_2.2H_2O$ = 4 g/L

HCl = 0-20 ml/L (0 - $2.32x10^{-1}$M).

NaCl, KCl, and $BaCl_2$ were added at various concentrations, but between 0-20 g/L into the plating solutions and their effects on plating rate were observed.

Reducing agents such as sodium dithionate, L-cysteine and thiourea were added to various plating solutions of concentration between 0-20 g/L and their effects on plating rate were noted.

Other plating media eg. 25%, 50% and 75% alcohols were prepared by the addition of distilled water, and their various solubilities and effects on plating rate were observed.

3.1.5.2 ELECTROPLATING SOLUTIONS FOR IMMERSION PLATED SPECIMENS:

Electroplating of immersion plated substrates took place in different media, including 50% water/acetone, 99% acetone and 37% formaldehyde.

The cyanide-free plating solutions comprised of:

100 g/L $SnCl_2.2H_2O$

100 g/L $CuCl_2.2H_2O$

50-60 ml/L HCl ($5.8 - 7.0x10^{-1}$M)

Current density = 10 - 30 A/m^2

Nitric, acetic and formic acids of concentrations 0-20 g/L were independently added to the electroplating solutions at various stages and their effects on plating rate were also observed.

3.1.6 COATING STRIPPING:

Some immersion plated samples were stripped in acid solution containing 100 ml/L HCl and 30 ml/L HNO_3. The stripping solution was maintained at 80°C, and the actual stripping took place within 2 minutes. The stripped

samples were rinsed in running water, and finally dipped in diluted (50%) ammonia and dried before replating.

3.1.7 PROCEDURE:

3.1.7.1 IMMERSION PLATING:

The substrates (specimens) were inserted in the plating bath containing the plating solution through an aluminium stock (handle) well fitted to the central opening of the plating bath's lid. The specimens were removed, rinsed in running water, dried and weighed using electronic Mettler P163 balance while some of the coating thickness were measured by an elcometer.

3.1.7.2 ELECTROPLATING:

Electrical connections were made between the D.C power source and the plating bath via the multi-range meter (which measured the bath voltage and the current meter which measured the plating current. After all the connections were completed and the specimens inserted centrally in the bath solution via the aluminium handle, the current was gradually applied from power source to the desired steady state values as recorded in the current meter.

After the plating, the specimens were removed when the power supply had been switched off. The specimens were rinsed in running water, dried and reweighed, and the thickness also measured using electronic mettler balance and an elcometer respectively.

CHAPTER FOUR

4.0 RESULTS:

The results presented in this chapter cover the work done on:

(i) Solubility of hydrated stannous chloride in aqueous solution, 'akamu' (pap), alcohols, mixed alcohols, groundnut and palm oils.

(ii) Solubility of hydrated copper chloride in pure and mixed alcohols.

(iii) Bronze immersion plating in aqueous, non-aqueous, mixed aqueous media and 'akamu'.

(iv) Bronze electroplating of immersion plated substrates.

4.1 SOLUBILITY OF HYDRATED STANNOUS CHLORIDE IN DIFFERENT SOLVENTS:

The solubility of hydrated stannous chloride was examined in aqueous, mixed aqueous, non-aqueous, vegetable oils and 'akamu' media. Non-aqueous media include alcohols (methanol, ethanol, propanol and butanol) and vegetable oils such as groundnut and palm oils. Mixed aqueous is water/ethanol media of various proportions (eg. 25%, 50% and 75% ethanol).

4.1.1 THEORETICAL SOLUBILITY CURVE FOR HYDRATED STANNOUS CHLORIDE:

Figure 4.1 shows a calculated solubility curve for stannous chloride (hydrated) in aqueous system. The theoretical curve was plotted based upon the results obtained from the formula, (Atkins, 1982),

$$\ln x_B = -\left[\frac{H_m}{R}\right]\left(\frac{1}{T} - \frac{1}{T^*}\right) \quad \ldots\ldots 4.1$$

where x_B is the mole fraction in solution, H_m is the enthalpy at melting point and R is the gas constant. T^* is the temperature at boiling point. The curve shows an increase in solubility with respect to temperature.

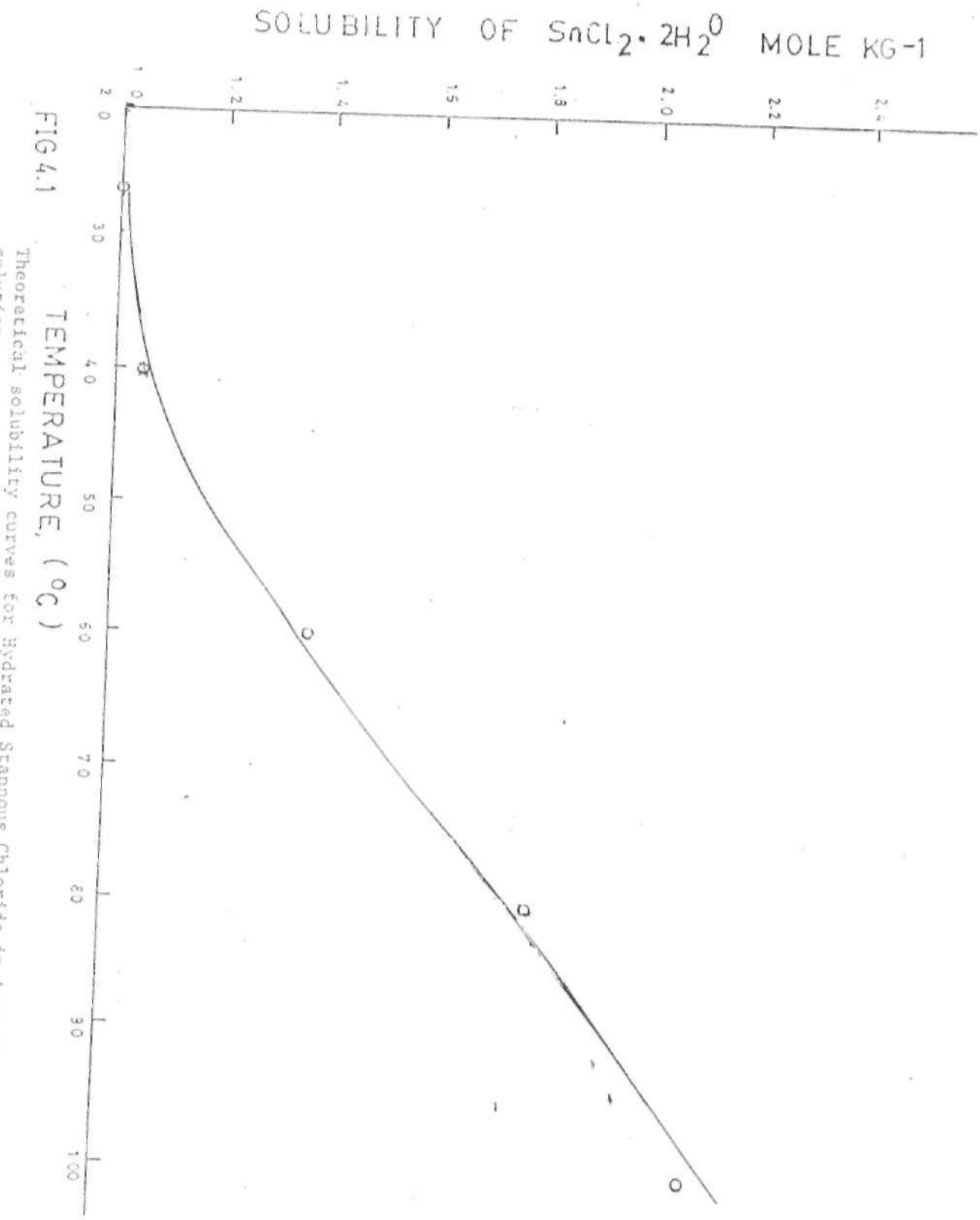


FIG 4.1 Theoretical solubility curves for Hydrated Stannous Chloride in Aqueous solution.

4.1.2 SOLUBILITY OF STANNOUS CHLORIDE IN 'AKAMU' (PAP), AQUEOUS, GROUNDNUT AND PALM OILS MEDIA:

Figure 4.2 shows the effects of solvents (media) and temperature on solubility of hydrated stannous chloride. The solubility increases with temperature. The solubility is highest in 'akamu' medium and least in groundnut oil. In akamu, the solubility varies between 2 to 4 mol kg^{-1} for a temperature change of 40°C. In aqueous solution, the solubility varies between 1.60 to 3.75 mol kg^{-1} for a temperature change of 50°C. In palm oil, the solubility varies between 2.25 to 3.75 mol kg^{-1} for a temperature change of 40°C, but in higher temperature range.

Similarly, in groundnut oil, the solubility varies between 2.45 to 3.09 mol kg^{-1} for a temperature change of 50°C, but also in the higher temperature range.

In Fig. 4.2, if S is the solubility of hydrated stannous chloride in mol kg^{-1} and T is the temperature in °C, the linear relationship for the curves is,

$$S = mT + k \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.2$$

where m is the slope and k is the intercept.

For curve (a), m = 0.05 mol kg^{-1} $(°C)^{-1}$ and k = 0.73 mol kg^{-1}

$$S = 0.05 \text{ [mol kg}^{-1} (°C)^{-1}\text{] T (°C)} + 0.73 \text{ mol kg}^{-1} \quad \ldots\ldots\ldots 4.3$$

For curve (b), m = 0.043 mol kg^{-1} $°C^{-1}$ and k = 0.05 mol kg^{-1}

$$S = 0.043 \text{ [mol kg}^{-1} (°C)^{-1}\text{] T (°C)} + 0.5 \text{ mol kg}^{-1} \quad \ldots\ldots\ldots 4.4$$

Similarly for curve (c), m = 0.033 mol kg^{-1} $°C^{-1}$ and k = -0.2 mol kg^{-1}.

$$S = 0.033 \text{ [mol kg}^{-1} (°C)^{-1}\text{] T (°C)} - 0.2 \text{ mol kg}^{-1} \quad \ldots\ldots\ldots 4.5$$

For curve (d), m = 0.04 mol kg^{-1} $°C^{-1}$ and k = -0.17 mol kg^{-1}

$$S = 0.04 \text{ [mol kg}^{-1} (°C)^{-1}\text{] T (°C)} - 0.17 \text{ mol kg}^{-1} \quad \ldots\ldots\ldots 4.6$$

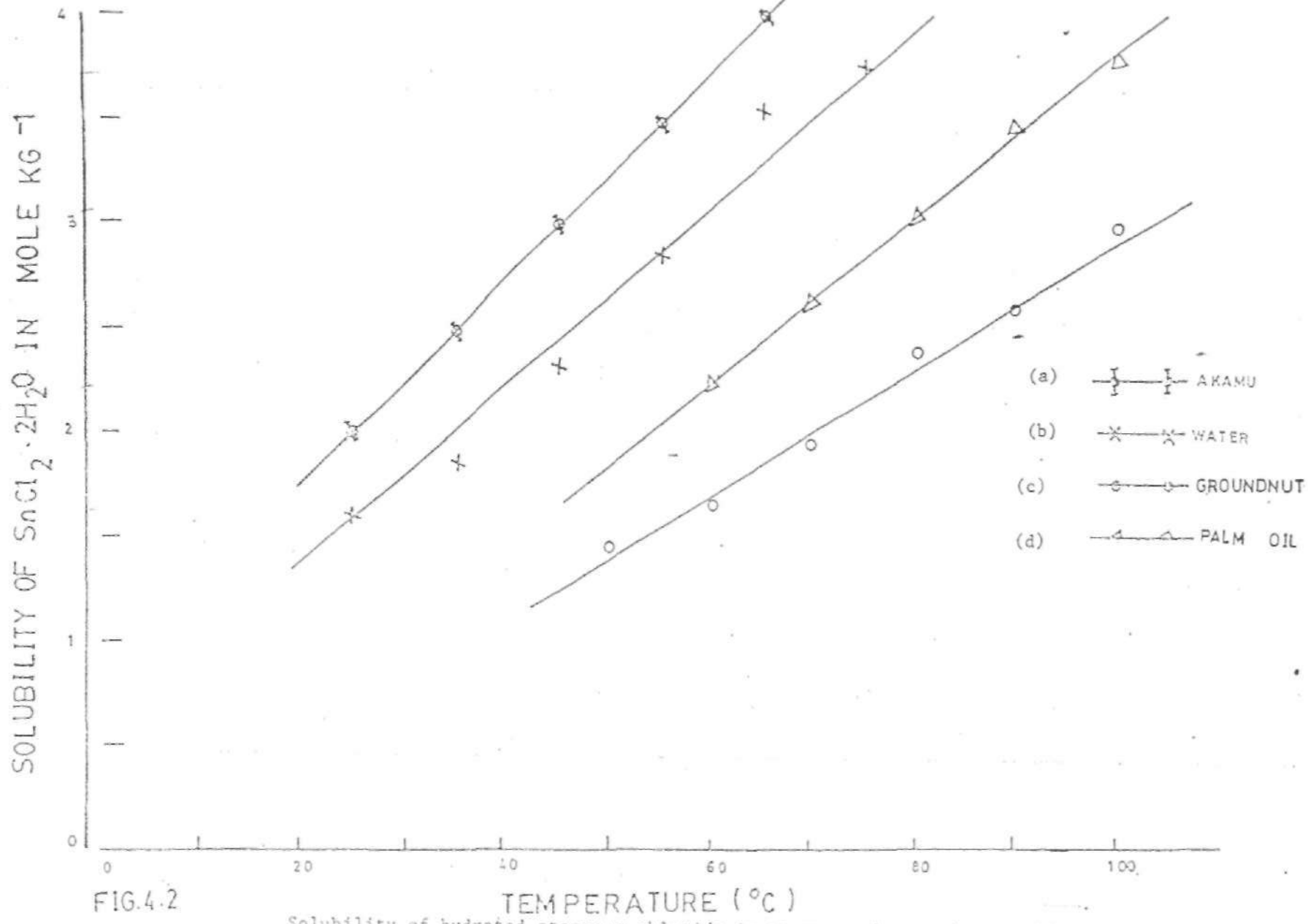


FIG.4.2

Solubility of hydrated stannous chloride in aqueous, akamu and vegetable oils.

4.1.3 SOLUBILITY OF HYDRATED STANNOUS CHLORIDE IN ALCOHOLS:

Figure 4.3 show the effect of temperature on solubility of stannous chloride in alcohols (methanol, ethanol, propanol and butanol). The solubility increases with corresponding increase in temperature. Stannous chloride is more soluble in methanol compared to propanol and butanol media. The solubility varies between 1.60 to 3.15 mol kg^{-1} in methanol medium with respect to the corresponding temperature change. In ethanol, the solubility varies between 1.00 to 2.25 mol kg^{-1} with respect to the corresponding change in temperature. However, the solubilities in propanol and butanol are about the same. They vary between 0.9 to 1.45 mol kg^{-1} for a temperature change of 25°C.

Generally, the solubility of stannous chloride in alcohols increases with temperature. However, the solubilityresults are not reliable at boiling points. The boiling points of methanol, ethanol and propanol are 64.7°C, 78.4°C and 90°C respectively (Dean, 1972).

In Fig. 4.3, the linear relationship are:-

Curve (a), $m = 0.064$ mol kg^{-1} $°C^{-1}$ and $k = 1.6$ mol kg^{-1}

$S = 0.064$ [mol kg^{-1} $(°C)^{-1}$] T (°C) + 1.6 mol kg^{-1} 4.7

For curve (b), $m = 0.05$ mol kg^{-1} $°C^{-1}$ and $k = 1.0$ mol kg^{-1}

$S = 0.05$ [mol kg^{-1} $(°C)^{-1}$] T (°C) + 1 mol kg^{-1}.....4.8

For curve (c), $m = 0.025$ mol kg^{-1} $°C^{-1}$ and $k = 0.8$ mol kg^{-1}

$S = 0.025$ [mol kg^{-1} $(°C)^{-1}$] T (°C) + 0.8 mol kg^{-1}..... 4.9

For curve (d), $m = 0.033$ mol kg^{-1} $°C^{-1}$ and $k = 0.75$ mol kg^{-1}

$S = 0.033$ [mol kg^{-1} $(°C)^{-1}$] T (°C) + 0.75 mol kg^{-1} 4.10

4.1.4 SOLUBILITY OF HYDRATED STANNOUS CHLORIDE IN WATER/ETHANOL MEDIA:

Figure 4.4 shows the effect of temperature on solubility of stannous choride (hydrated) in mixed/ethanol media. The solubility increases with temperature in all the media (25%, 50% and 75% water/ethanol). The addition of ethanol to water between 25% to 75% does not have a marked effect on solubility.

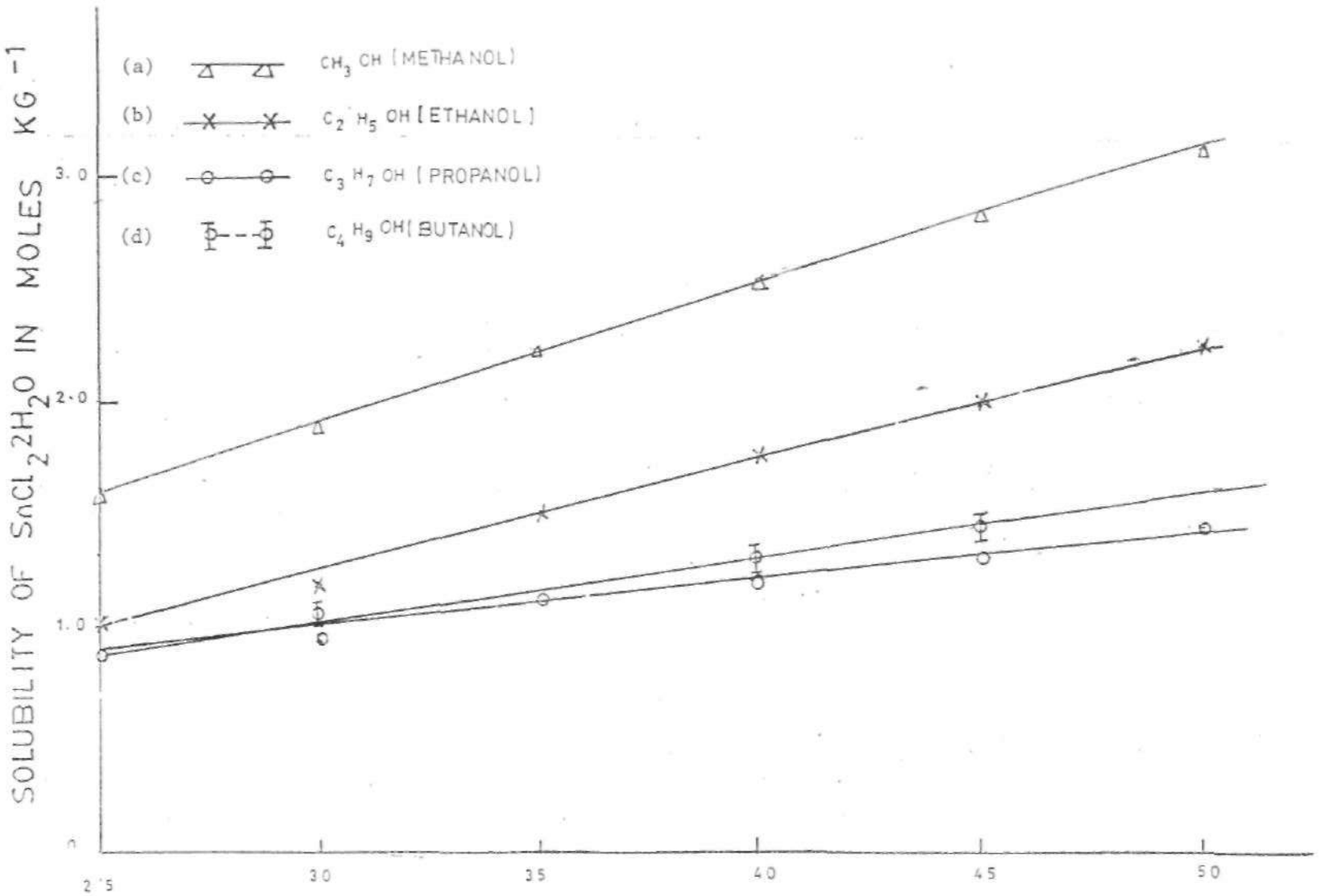


FIG 4.3

Solubility of hydrated stannous chloride in alcohols.

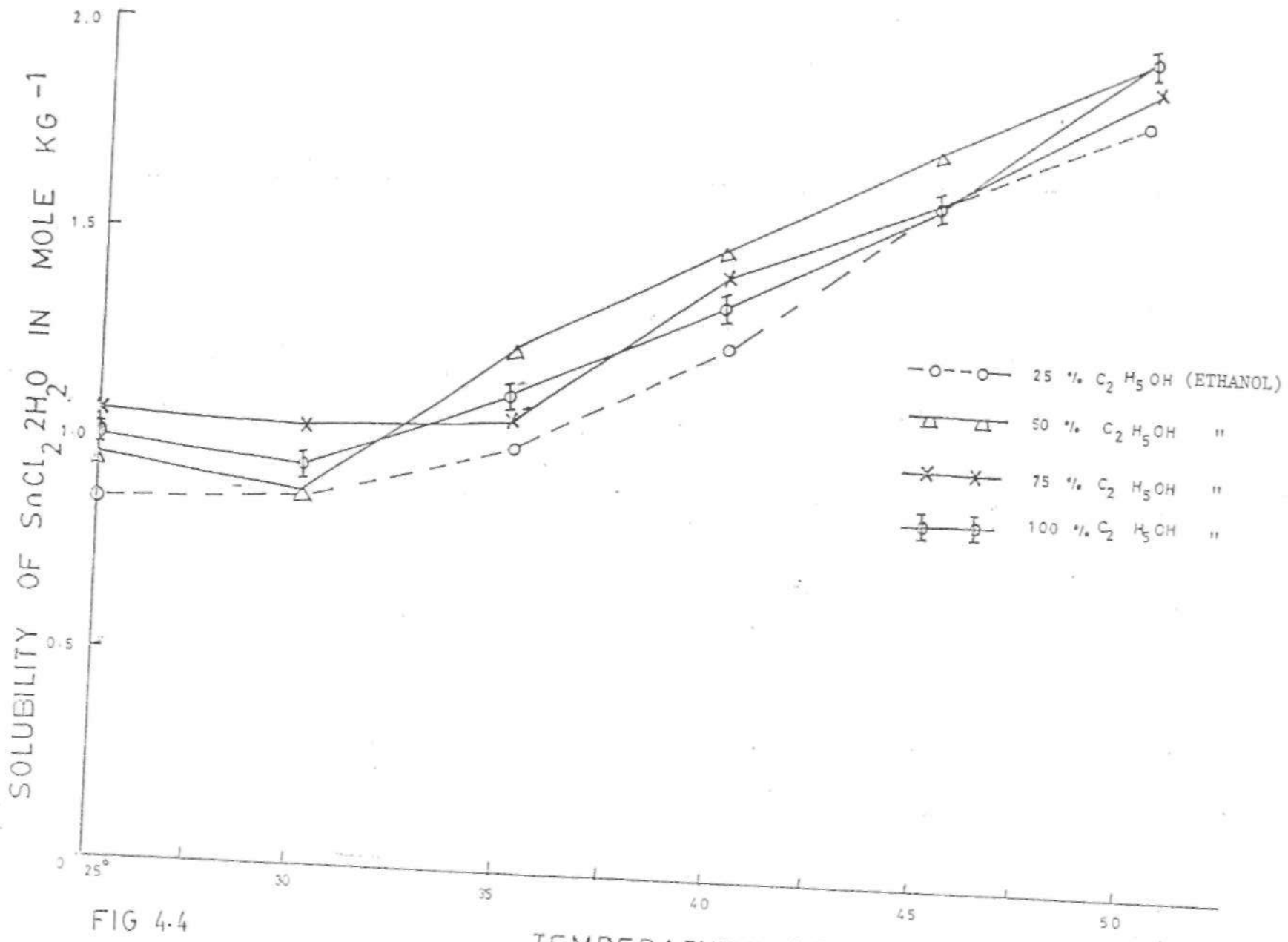


FIG 4.4

Solubility of hydrated stannous chloride in mixed alcohols.

4.2.1 SOLUBILITY OF HYDRATED CUPRIC CHLORIDE IN ALCOHOLS:

Figure 4.5 shows the effect of temperature on solubility of hydrated cupric chloride in alcohols (methanol, ethanol, propanol and butanol). The solubility is highest in methanol solvent, followed by ethanol; whereas, the solubilities in propanol and butanol are about the same, and are lower than the figures obtained in methanol and ethanol. The solubility varies between 3 to 6.5 mol kg^{-1} for a temperature change of 25°C in methanol. In ethanol, the solubility varies between 0.5 to 1.5 mol kg^{-1} for a temperature variation of 20°C. As earlier observed, the solubility results are not reliable at boiling points of the alcohols.

However, worthy of note is the fact that cupric chloride (hydrated) is extremely soluble in alcohols as attested in this work.

In Fig. 4.5, the linear relationship for curve (a) which has $m = 0.05$ mol kg^{-1} $°C^{-1}$ and $k = 3.0$ mol kg^{-1} is

$$S = 0.05 \text{ [mol kg}^{-1} (°C)^{-1}\text{]} T (°C) + 3 \text{ mol kg}^{-1} \quad \ldots\ldots\ldots\ldots 4.11$$

For curve (b), $m = 0.03$ mol kg^{-1} $°C^{-1}$ and k 0.25 mol kg^{-1}

$$S = 0.03 \text{ [mol kg}^{-1} (°C)^{-1}\text{]} T \quad (°C) + 0.25 \text{ mol kg}^{-1} \quad \ldots\ldots\ldots 4.12$$

For curve (c), $m = 0.008$ mol kg^{-1} $°C^{-1}$ and $k = 0.15$ mol kg^{-1}

$$S = 0.008 \text{ [mol kg}^{-1} (°C)^{-1}\text{]} T \quad (°C) + 0.15 \text{ mol. kg}^{-1} \quad \ldots\ldots\ldots 4.13$$

For curve (d), $m = 0.044$ mol kg^{-1} $°C^{-1}$, $k = -0.3$ mol. kg^{-1}

$$S = 0.044 \text{ [mol kg}^{-1} (°C)^{-1}\text{]} T \quad (°C) - 0.3 \text{ mol. kg}^{-1} \quad \ldots\ldots\ldots 4.14$$

4.2.2 SOLUBILITY OF HYDRATED CUPRIC CHLORIDE IN WATER/ETHANOL MEDIA:

Figure 4.6 shows the effect of temperature on solubility of hydrated cupric chloride in water/ethanol media. The solubility increases with the corresponding increase in temperature irrespective of media composition (eg. 25%, 50% and 75% ethanol).

In Fig. 4.6, the linear relationships are:-

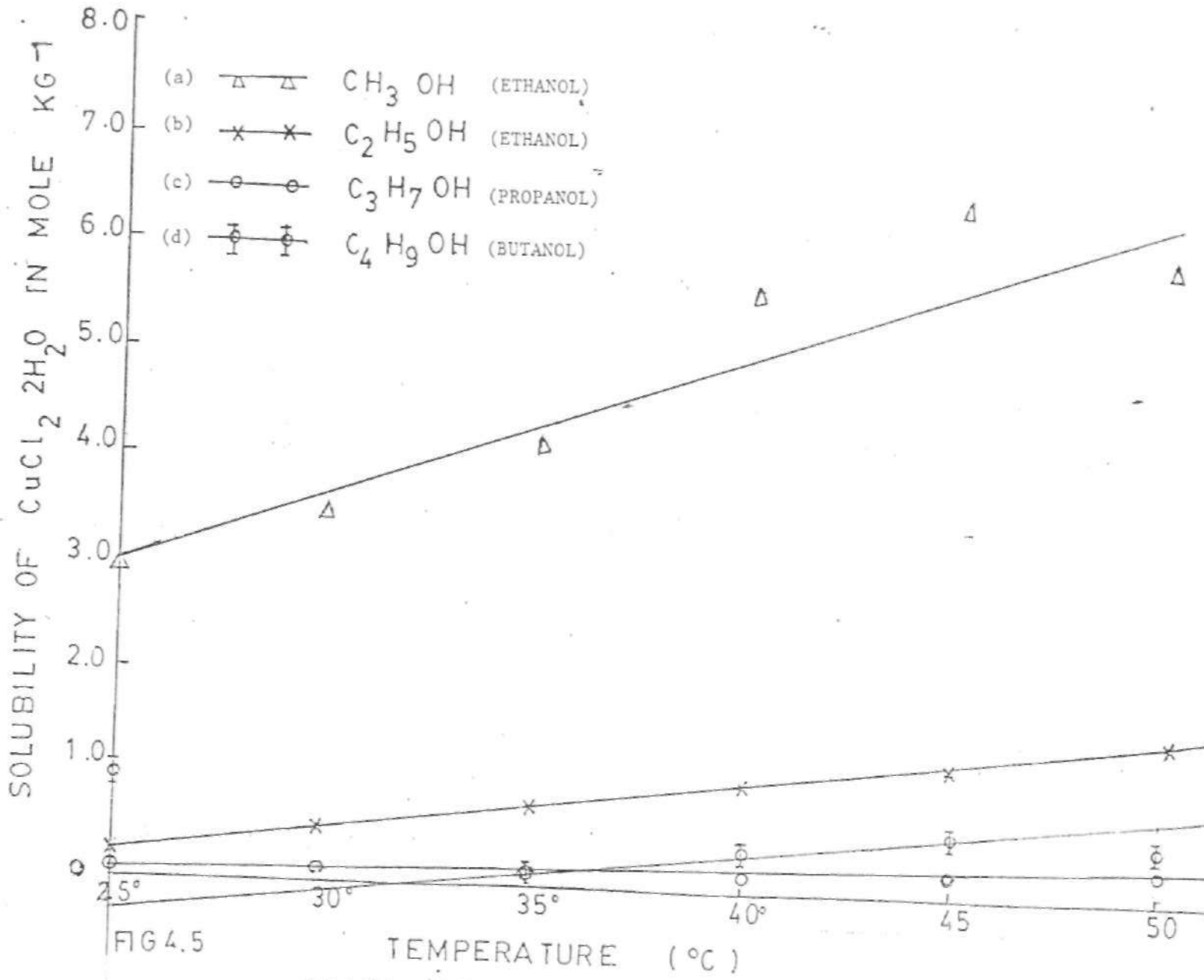


FIG 4.5

Solubility of hydrated cupric chloride in alcohols.

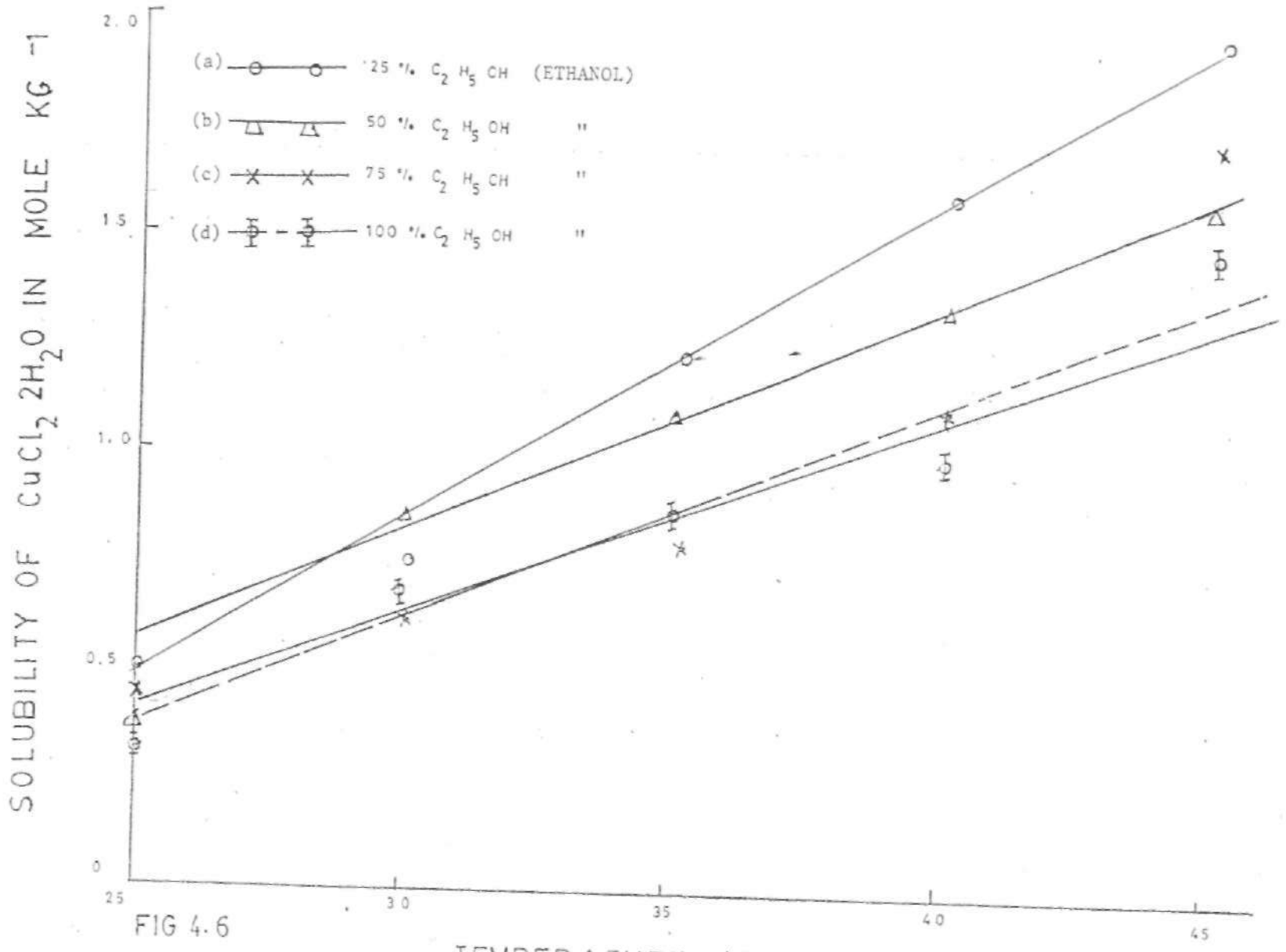


FIG 4.6

Solubility of cupric chloride in mixed alcohols.

For curve (a), m = 0.73 mol kg^{-1} $°C^{-1}$ and k = 0.5 mol. kg^{-1}

$$S = 0.73\ [\text{mol kg}^{-1}\ (°C)^{-1}]\ T\ (°C) + 0.5\ \text{mol. kg}^{-1} \quad \ldots\ldots 4.15$$

For curve (b), m = 0.053 mol kg^{-1} $°C^{-1}$ and k = 0.55 mol. kg^{-1}

$$S = 0.053\ [\text{mol kg}^{-1}\ (°C)^{-1}]\ T\ (°C) + 0.55\ \text{mol. kg}^{-1} \quad \ldots\ldots 4.16$$

For curve (c), m = 0.04 mol kg^{-1} $°C^{-1}$ and k = 0.15 mol. kg^{-1}

$$S = 0.04\ [\text{mol kg}^{-1}\ (°C)^{-1}]\ T\ (°C) + 0.15\ \text{mol. kg}^{-1} \quad \ldots\ldots 4.17$$

And for curve (d), m = 0.05 mol kg^{-1} $°C^{-1}$ and k = 0.10 mol. kg^{-1}

$$S = 0.05\ [\text{mol kg}^{-1}\ (°C)^{-1}]\ T\ (°C) + 0.1\ \text{mol. kg}^{-1} \quad \ldots\ldots 4.18$$

The solubility results in all the mixed solvents are about the same, showing high solubility. Consequently, hydrated cupric chloride is very soluble in pure and water/alcohol media. The high solubility of hydrated cupric chloride in aqueous and non-aqueous media makes it difficult to determine the end-point of titration.

4.3 BRONZE IMMERSIION PLATING IN DIFFERENT MEDIA:

Figures 4.7 to 4.79 and Tables 1 to 73 (appendix 1) show the results of work done on bronze immersion plating from solutions containing cupric and stannous chloridesof different compositions in different media under similar or different conditions.

4.3.1 EFFECTS OF VARIOUS SALTS AND HCl ON PLATING RATE IN AQUEOUS MEDIUM:

Figures 4.7 to 4.10 and Tables 1 - 4 (appendix 1) show that the addition of salts (NaCl, KCl and $BaCl_2$) to immersion plating solution increases plating rate in aqueous media. The plating solution contained 20 g/l $SnCl_2.2H_2O$, 10 g/L $CuCl_2.2H_2O$, 0-20 ml/L HCl and was operated at a temperature of 25°C.

Higher plating rate is observed when potassium chloride is added than the addition of sodium chloride. The effects of KCl and $BaCl_2$ are about the

same order in increasing plating rate. However, HCl addition limits plating rate.

In Fig. 4.7, the linear relationship for curve (a) which has a slope $m = 0.019$ mg cm^{-2} g^{-1} L and intercept $k = 0.2$ mg cm^{-2} is,

$$w = 0.019 \text{ (mg } cm^{-2} g^{-1} \text{ L) } C_{Na} \text{ (g } L^{-1}) + 0.2 \text{ mg } cm^{-2} \quad \ldots\ldots\ldots 4.19$$

where w is the weight gain in $mg.cm^{-2}$, and C_{Na} is the concentration of NaCl in solution.

In Fig. 4.9, the linear relationship for curve (a) which has $m = 0.027$ mg cm^{-2} g^{-1} L and $k = 0.25$ mg cm^{-2} is,

$$w = 0.027 \text{ (mg } cm^{-2} g^{-1} \text{ L) } C_{K} \text{ (g } L^{-1}) + 0.25 \text{ mg.cm}^{-2} \quad \ldots\ldots\ldots 4.20$$

where C_K is the concentration of KCl.

In Fig. 4.10, the linear relationship for curve (a) which has $m = 0.027$ mg cm^{-2} g^{-1} L and $k = 0.1$ mg cm^{-2} is,

$$w = 0.027 \text{ (mg } cm^{-2} g^{-1} \text{ L) } C_{Ba} \text{ (g } L^{-1}) + 0.1 \text{ mg.cm}^{-2} \quad \ldots\ldots\ldots 4.21$$

where C_{Ba} is the concentration of $BaCl_2$.

Hence, the plating rate (weight gain) can be found from the equation by simply varying the concentration of $BaCl_2$ in solution.

4.3.2 EFFECTS OF STRIPPING ON PLATING RATE:

Figure 4.8 and Table 4.2 (appendix 1) show the effects of coating stripping and sodium chloride addition on bronze immersion plating in aqueous solution containing 20 g/L $SnCl_2.2H_2O$ and 10 g/L $CuCl_2.2H_2O$, operated at 25°C. The results show coating rate enhancement when the initial coatings are stripped and subsequently replated.

In Fig. 4.8 , the linear relationships are:-

Curve (a), $m = 0.007$ mg cm^{-2} g^{-1} L and $k = 0$,

$$w = 0.007 \text{ (mg } cm^{-2} g^{-1} \text{ L) } C_{Na} \text{(g } L^{-1}) \quad \ldots\ldots\ldots\ldots\ldots 4.22$$

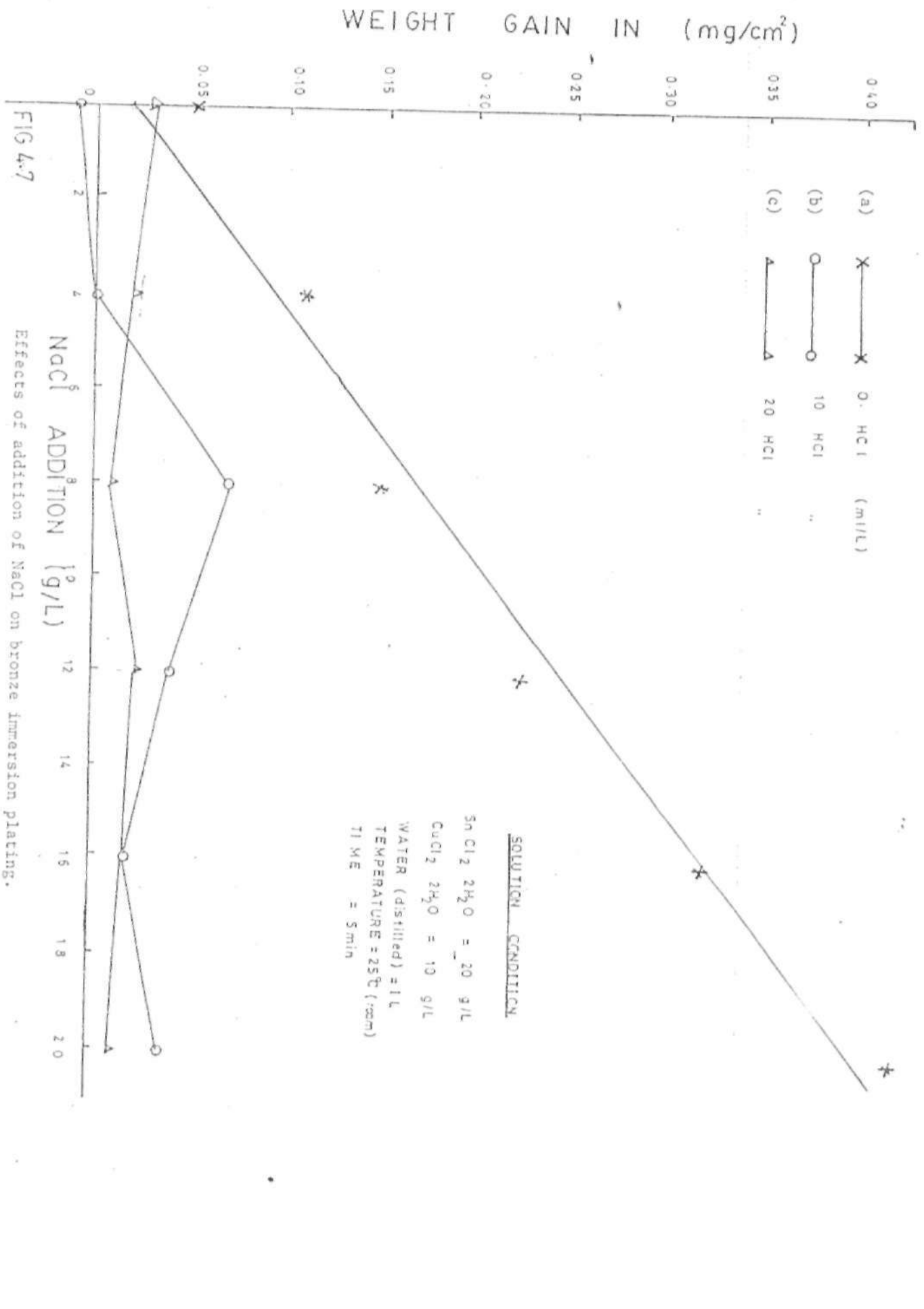


FIG 4.7 Effects of addition of NaCl on bronze immersion plating.

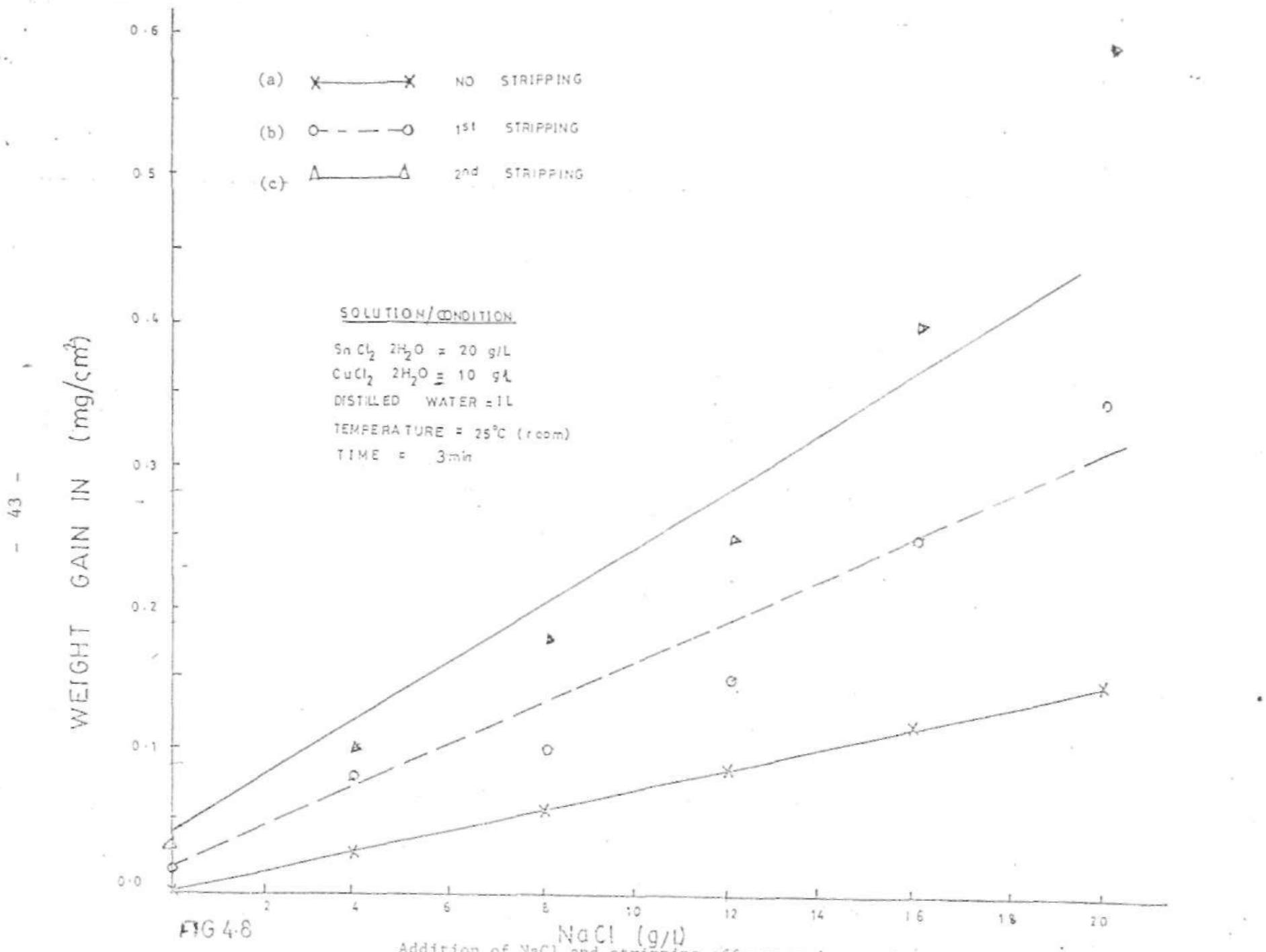


FIG 4.8

Addition of NaCl and stripping effects on bronze immersion plating

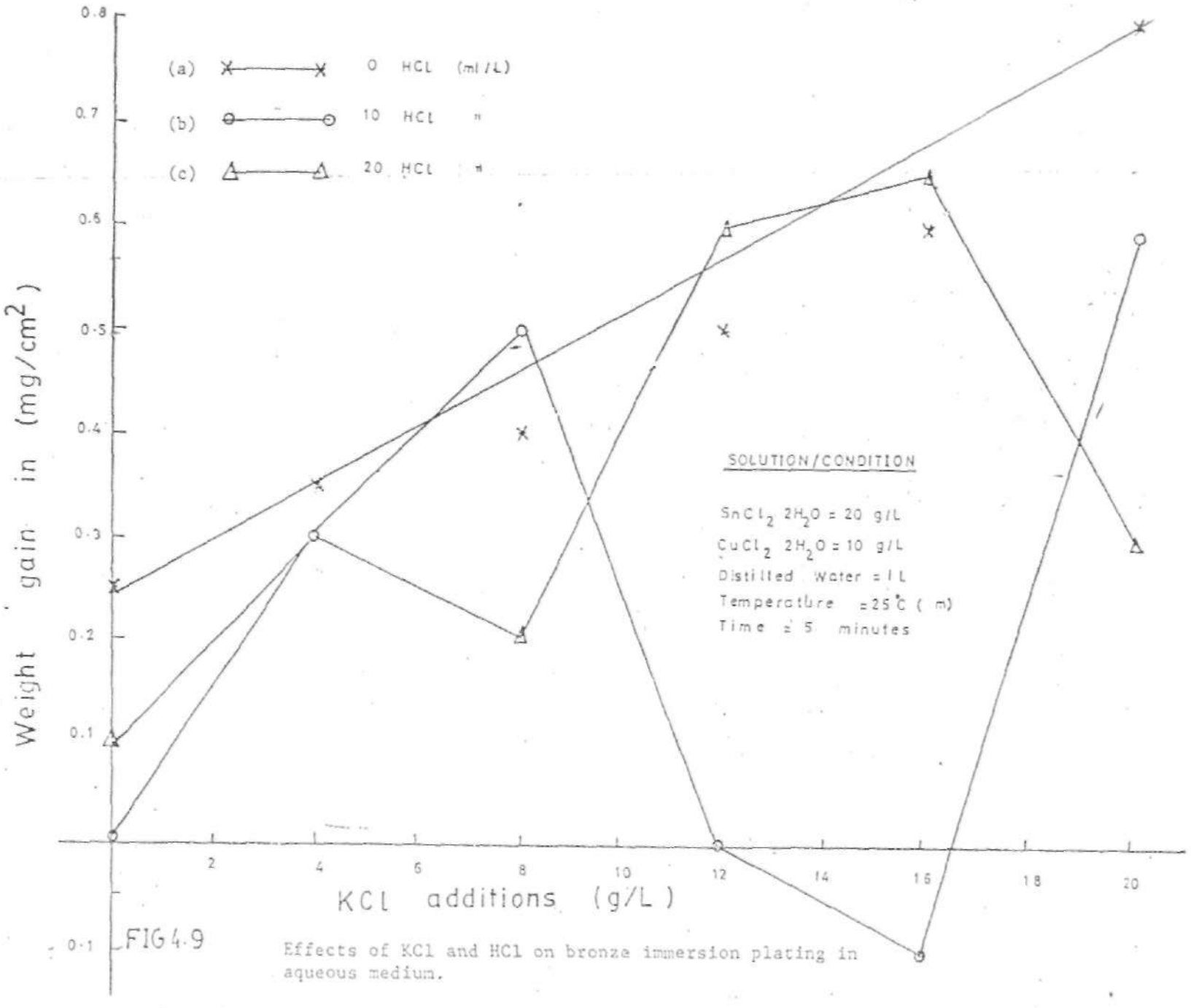


FIG 4.9 Effects of KCl and HCl on bronze immersion plating in aqueous medium.

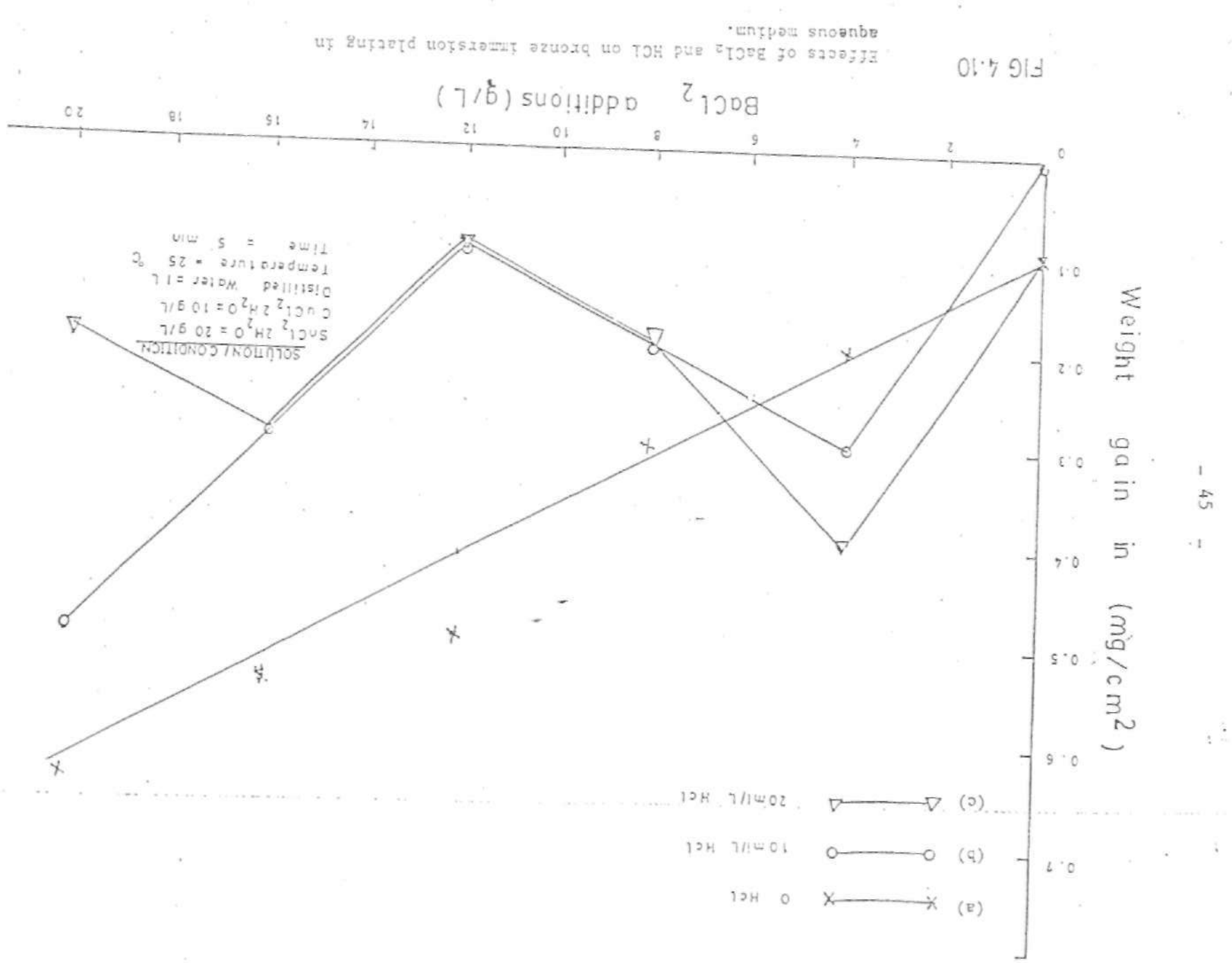


FIG 4.10 Effects of $BaCl_2$ and HCl on bronze immersion plating in aqueous medium.

For curve (b), $m = 0.014$ mg $cm^{-2}.g^{-1}.L$ and $k = 0.02$ mg cm^{-2}.,

$$w = 0.014 \text{ (mg cm}^{-2}\text{ g}^{-1}\text{ L)}.\ C_{Na}\ (g\ L^{-1}) + 0.02 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots\ 4.23$$

For curve (c), $m = 0.19$ mg cm^{-2} g^{-1} L and $k = 0.04$ mg cm^{-2},

$$w = 0.19 \text{ (mg cm}^{-2}\text{ g}^{-1}\text{ L)}\ C_{Na}\ (g\ L^{-1}) + 0.04 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots\ 4.24$$

4.3.3 EFFECTS OF SALTS AND HCl ON PLATING RATE IN METHANOL MEDIUM:

Figures 4.11 to 4.13 and Tables 5 - 7 (appendix 1) show that the addition of salts (NaCl, KCl and $BaCl_2$) to immersion plating solution increases plating rate in methanol media. The plating solution contained 20 g/L $SnCl_2.2H_2O$, 10 g/L $CuCl_2.2H_2O$, 0-2 ml/L HCl and was operated at a temperature of 25°C.

The effects of NaCl, KCl and $BaCl_2$ are about the same in increasing plating rate. However, the addition of HCl retards plating rate.

In Fig. 4.11, the linear relationship for curve (a) which has $m = 0.047$ mg cm^{-2} g^{-1} L and $k = 0.07$ mg cm^{-2} is,

$$w = 0.047 \text{ (mg cm}^{-2}\text{ g}^{-1}\text{ L)}\ C_{Na}\ (g\ L^{-1}) + 0.07 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots\ 4.25$$

In Fig. 4.12, the linear relationship for curve (a) which has $m = 0.025$ mg cm^{-2} g^{-1} L and $k = 0.2$ mg cm^{-2} is,

$$w = 0.025 \text{ (mg.cm}^{-2}\text{ g}^{-1}\text{ L)}\ C_{K}\ (g\ L^{-1}) + 0.2 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots\ 4.26$$

3.3.4 SALTS AND HCl, EFFECTS ON PLATING RATE IN PROPANOL MEDIUM:

Figures 4.14, 4.15 and 4.16 and Tables 8-10 (appendix 1) show the effects of NaCl, KCl and $BaCl_2$ and HCl on bronze immersion plating in propanol containing 20 g/L $SnCl_2.2H_2O$ and 10 g/L $CuCl_2.2H_2O$. The three salts are all effective in enhancing plating in this medium. NaCl and KCl are of the same order in increasing plating rate and the difference between the three salts on plating rate is not much. However, the addition of HCl in the plating solution decreases plating rate as earlier observed. An optimum weight gain of about 0.8 mg/cm^2 was obtained in this medium with respect to the corresponding addition of NaCl.

In Fig. 14, the linear relationship for curve (a) which has $m = 0.04$ mg $cm^{-2}.\ g^{-1}.L$ and $k = 0$ is,

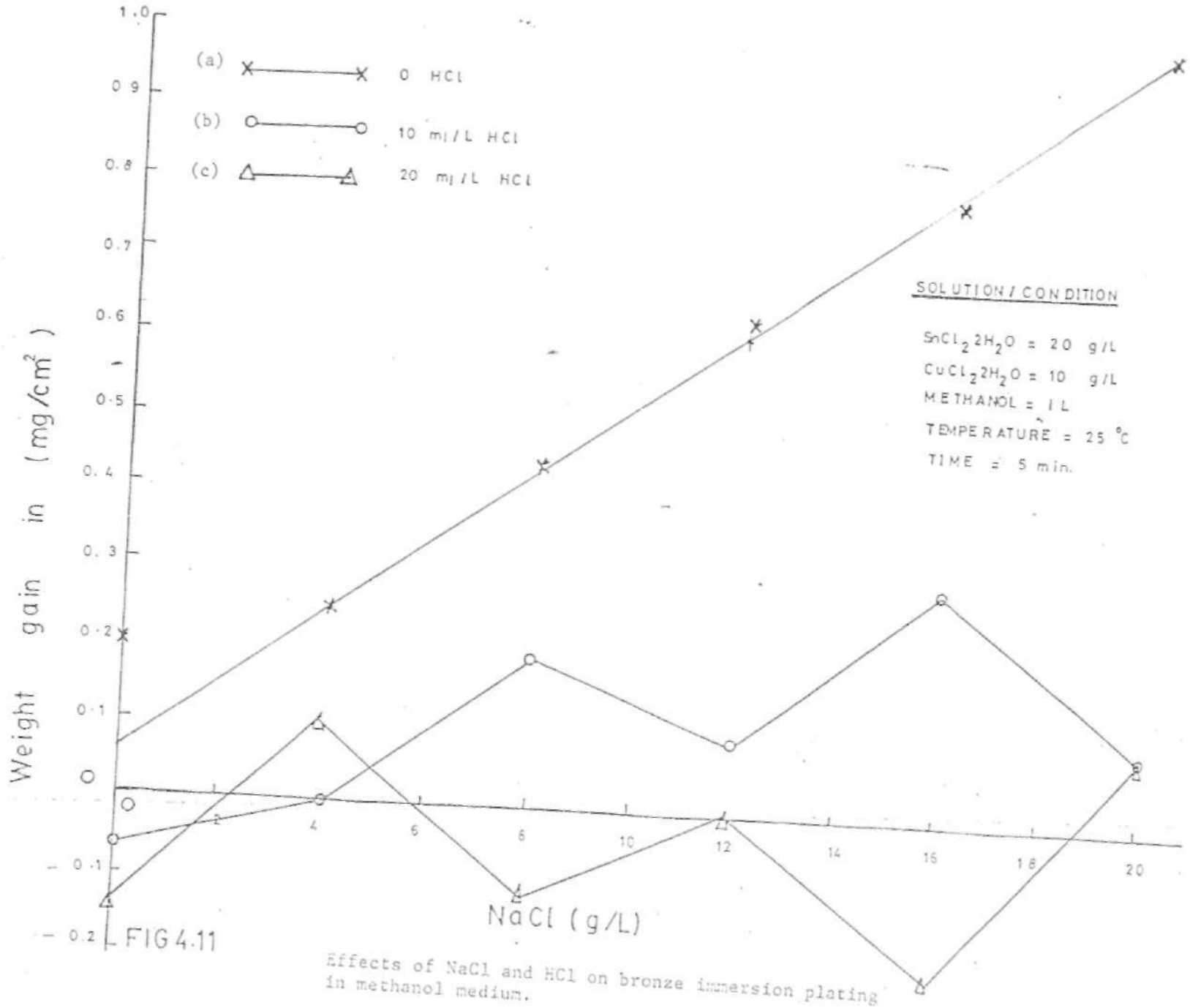


FIG 4.11

Effects of NaCl and HCl on bronze immersion plating in methanol medium.

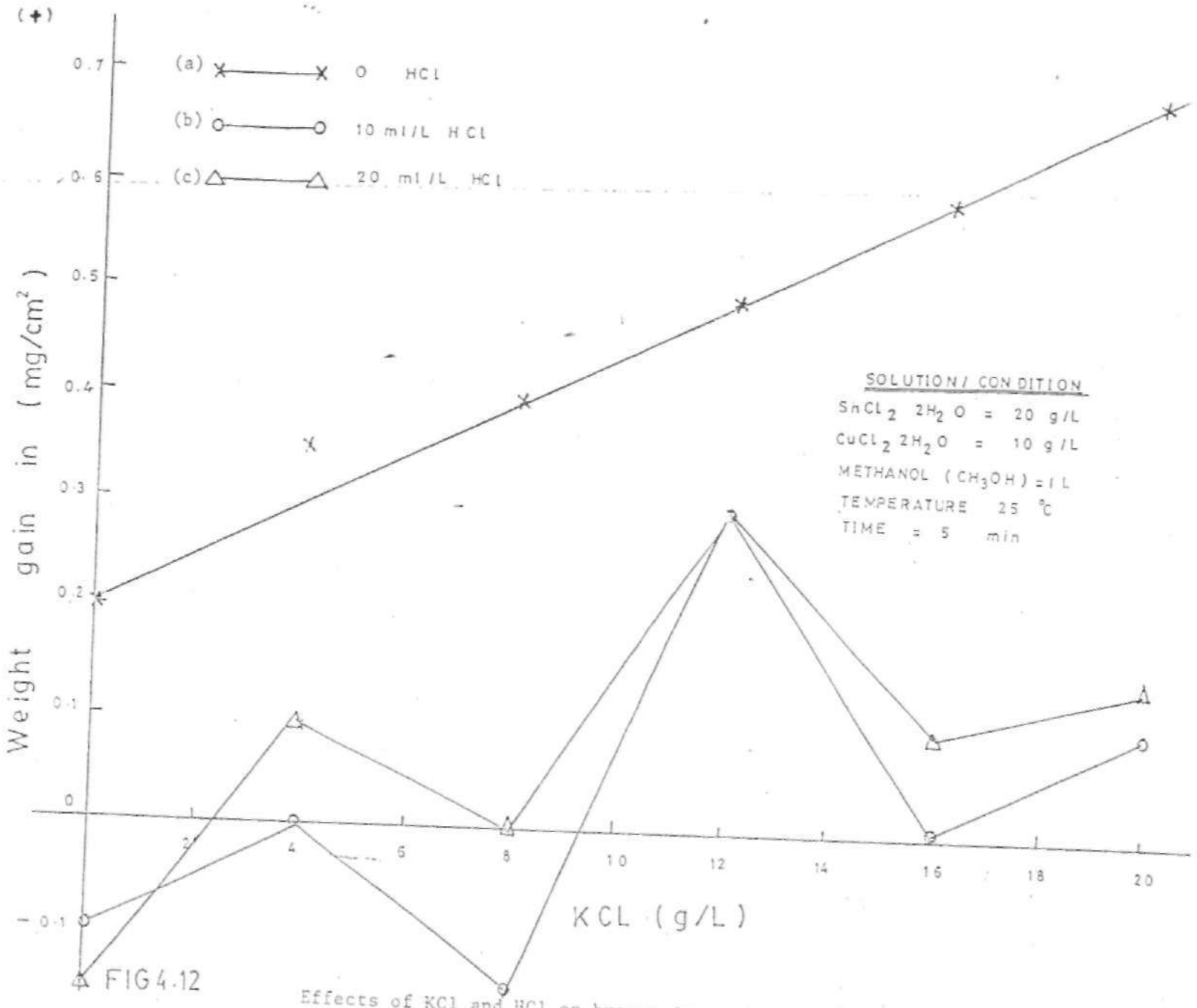


FIG 4.12

Effects of KCl and HCl on bronze immersion plating in methanol medium.

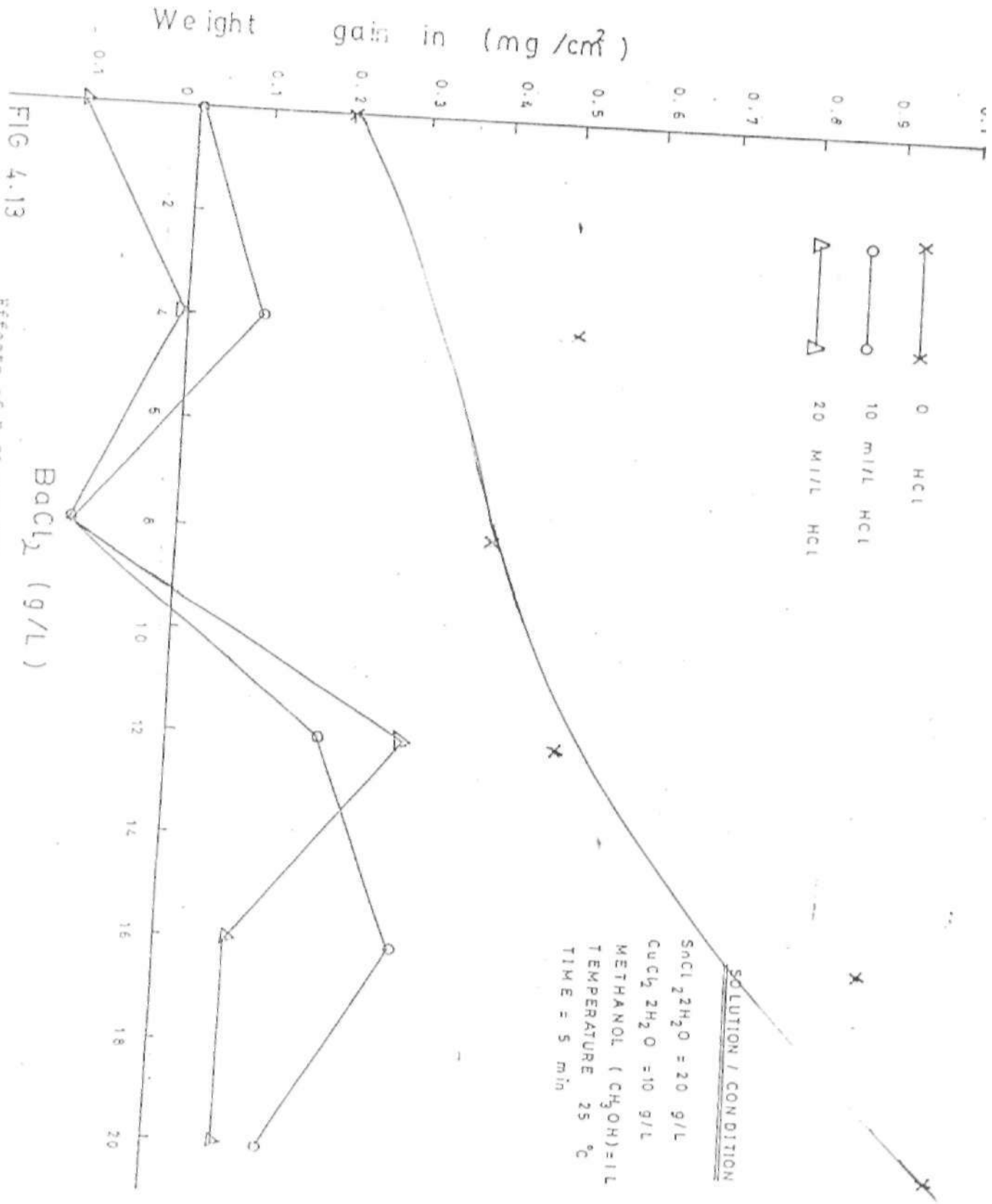


FIG 4.13 Effects of $BaCl_2$ and HCl on bronze immersion plating in methanol medium.

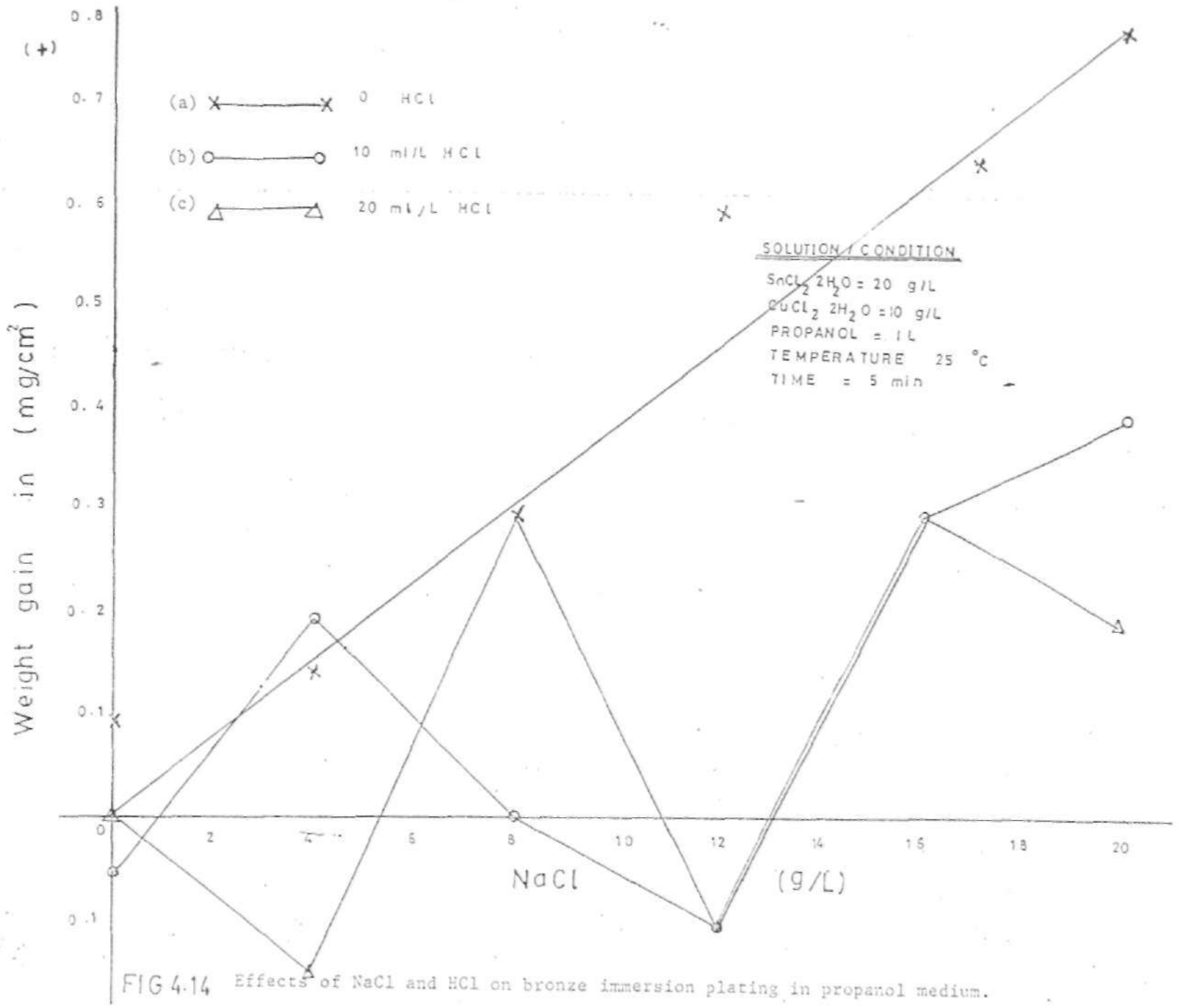


FIG 4.14 Effects of NaCl and HCl on bronze immersion plating in propanol medium.

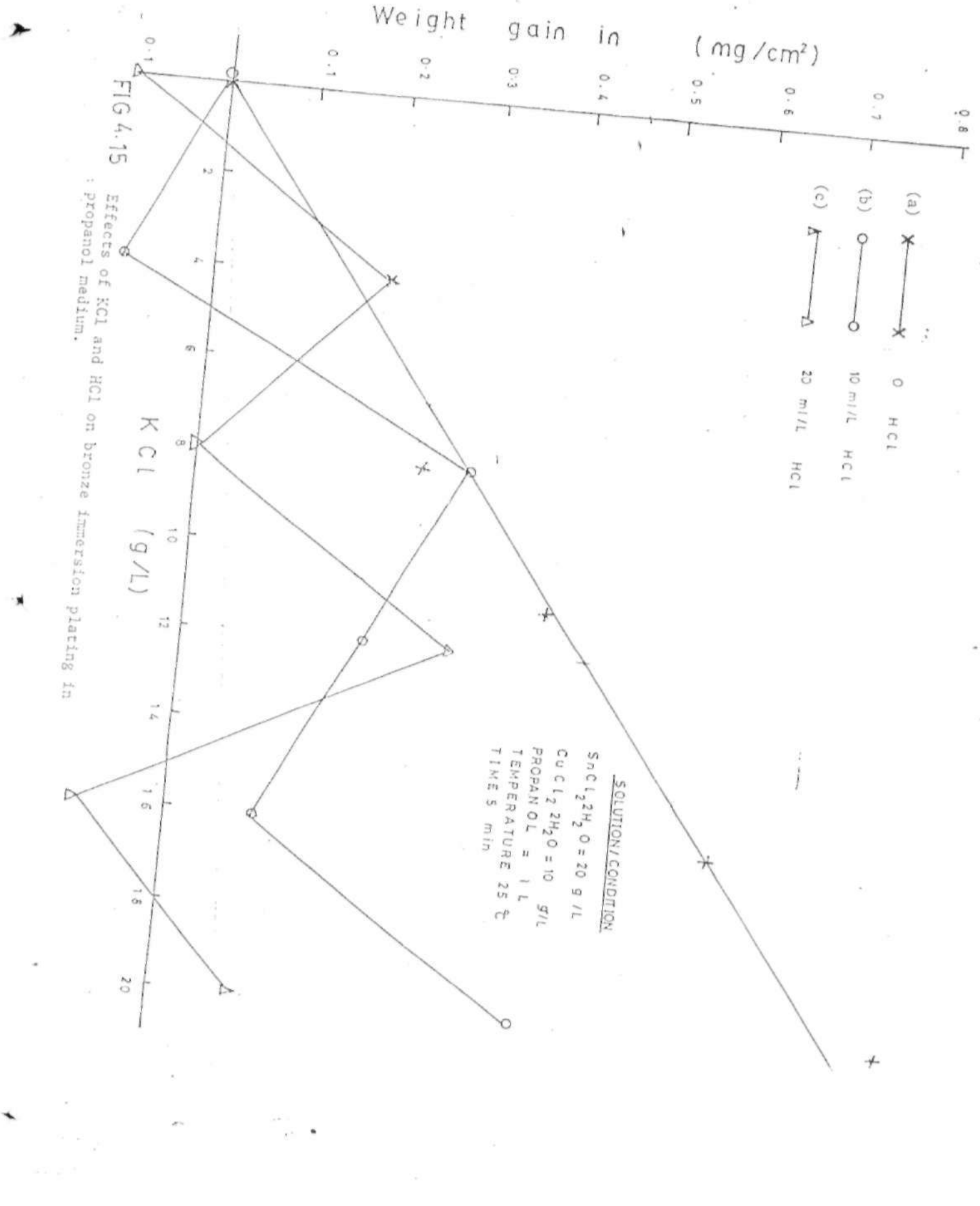


FIG 4.15 Effects of KCl and HCl on bronze immersion plating in : propanol medium.

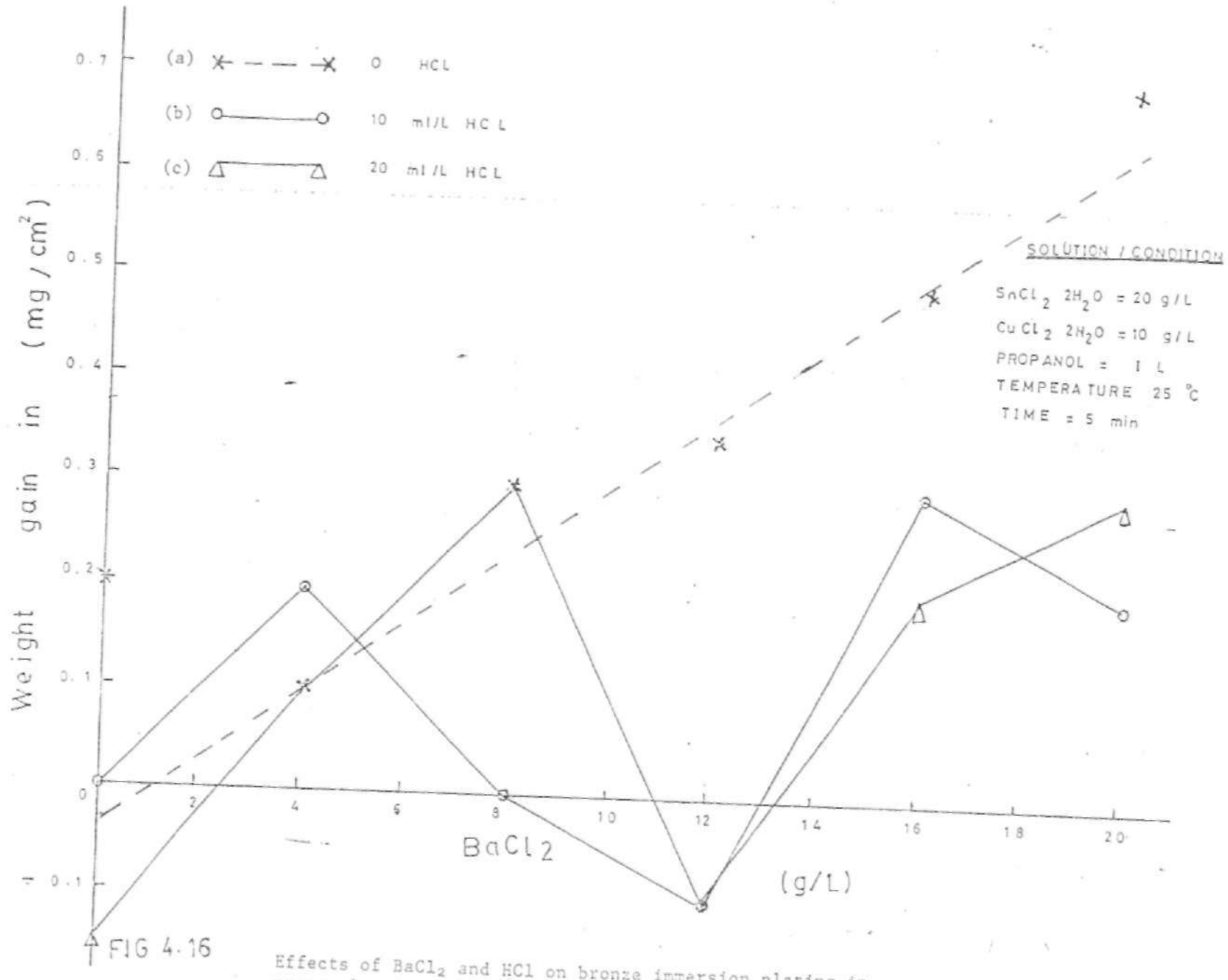


FIG 4.16

Effects of $BaCl_2$ and HCl on bronze immersion plating in propanol medium.

$$w = 0.04 \text{ (mg.cm}^{-2}\ g^{-1}\ L)\ C_{Na}\ (g\ L^{-1}) \quad \ldots\ldots 4.27$$

In Fig. 4.15, the linear relationship for curve (a) which has $m = 0.038$ mg cm^{-2} g^{-1} L and $k = 0$ is,

$$w = 0.038 \text{ (mg cm}^{-2}\ g^{-1}\ L)\ C_{K}\ (g\ L^{-1}) \quad \ldots\ldots 4.28$$

In Fig. 4.16, the linear relationship for curve (a) which has $m = 0.034$ mg.cm^{-2} g^{-1} L and $k = -0.035$ mg cm^{-2}. is,

$$w = 0.034 \text{ (mg cm}^{-2}\ g^{-1}\ L)\ C_{Ba}\ (g\ L^{-1}) - 0.035 \text{ mg cm}^{-2} \quad \ldots\ldots 4.29$$

4.3.5 ADDED SALTS AND HCl EFFECTS ON PLATING RATE IN BUTANOL MEDIUM:

Figures 4.17, 4.18 and 4.19 and Tables 11-13 (appendix 1) show the effects of NaCl, KCl and $BaCl_2$ and HCl on bronze immersion plating in butanol containing 20 g/L $SnCl_2.2H_2O$ and 10 g/L $CuCl_2.2H_2O$. The three salts, that is NaCl, KCl and $BaCl_2$ are about the same order in increasing plating rate in this medium. There is no much difference between them in plating rate enhancement.

In Fig. 17, the linear relationship for curve (a), which has $m = 0.033$ mg.cm^{-2} g^{-1} L and $k = 0.05$ mg cm^{-2} is,

$$w = 0.033 \text{ (mg cm}^{-2}\ g^{-1}\ L)\ C_{Na}\ (g\ L^{-1}) + 0.05 \text{ mg cm}^{-2} \quad \ldots\ldots 4.30$$

In Fig. 18, the linear relationship for curve (a) which has $m = 0.025$ mg cm^{-2} g^{-1} L and $k = 0.1$ mg cm^{-2} is,

$$w = 0.025 \text{ (mg cm}^{-2}\ g^{-1}\ L)\ C_{K}\ (g\ L^{-1}) + 0.1 \text{ mg cm}^{-2} \quad \ldots\ldots 4.31$$

In Fig. 19, the equation for curve (a) which has $m = 0.028$ mg cm^{-2} g^{-1} L and $k = 0.085$ mg.cm^{-2} is,

$$w = 0.028 \text{ (mg cm}^{-2}\ g^{-1}\ L)\ C_{Ba}\ (g\ L^{-1}) + 0.085 \text{ mg cm}^{-2} \quad \ldots\ldots 4.32$$

4.3.6 EFFECTS OF SALTS AND HCl ON PLATING RATE IN 'AKAMU' MEDIUM:

Figures 4.20 - 4.22 and Tables 14 - 16 (appendix 1) show the effects of NaCl, KCl and $BaCl_2$ and HCl on bronze immersion plating in akamu containing 20 g/L $SnCl_2.2H_2O$ and 10 g/L $CuCl_2.2H_2O$.

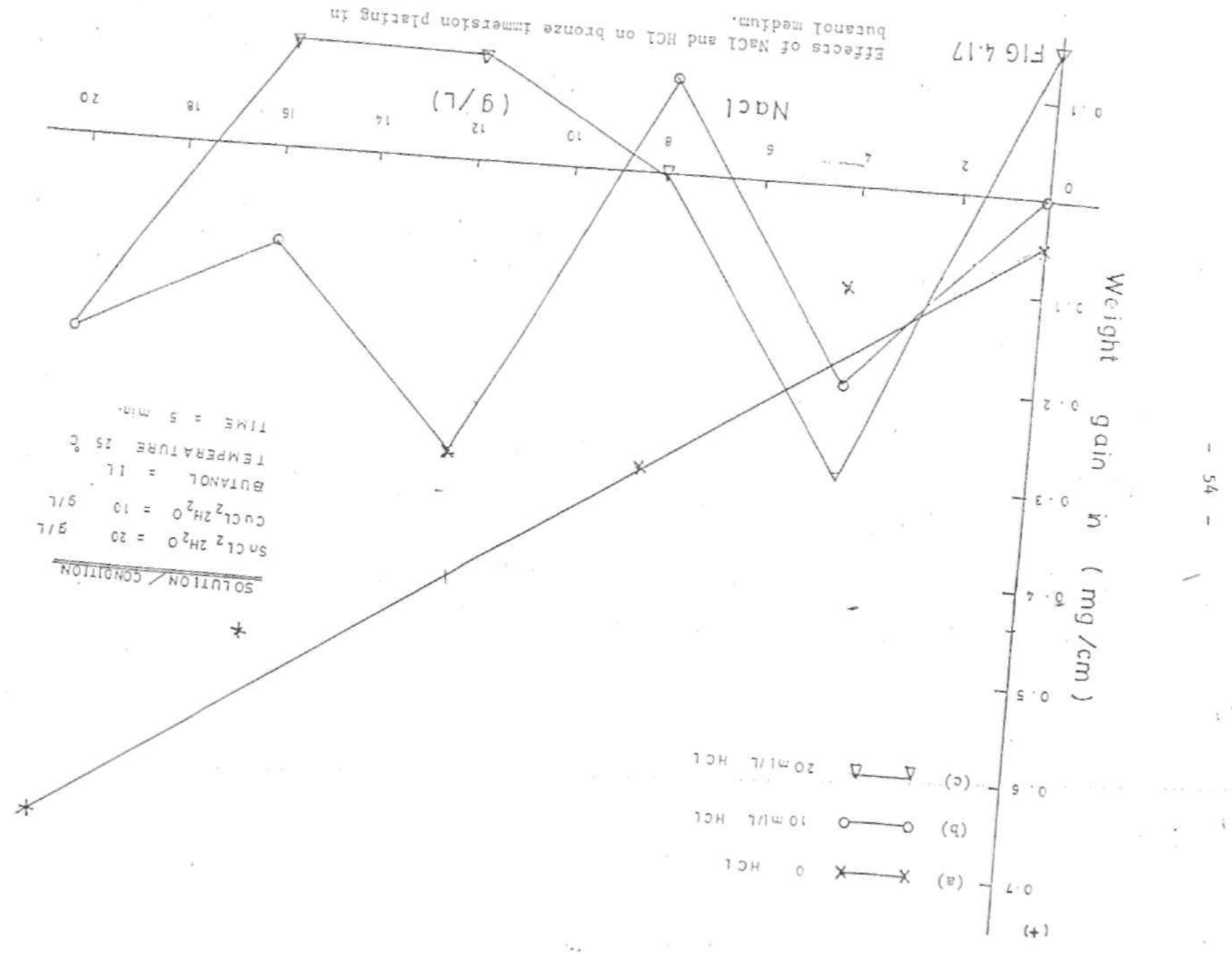


FIG 4.17 Effects of NaCl and HCl on bronze immersion plating in butanol medium.

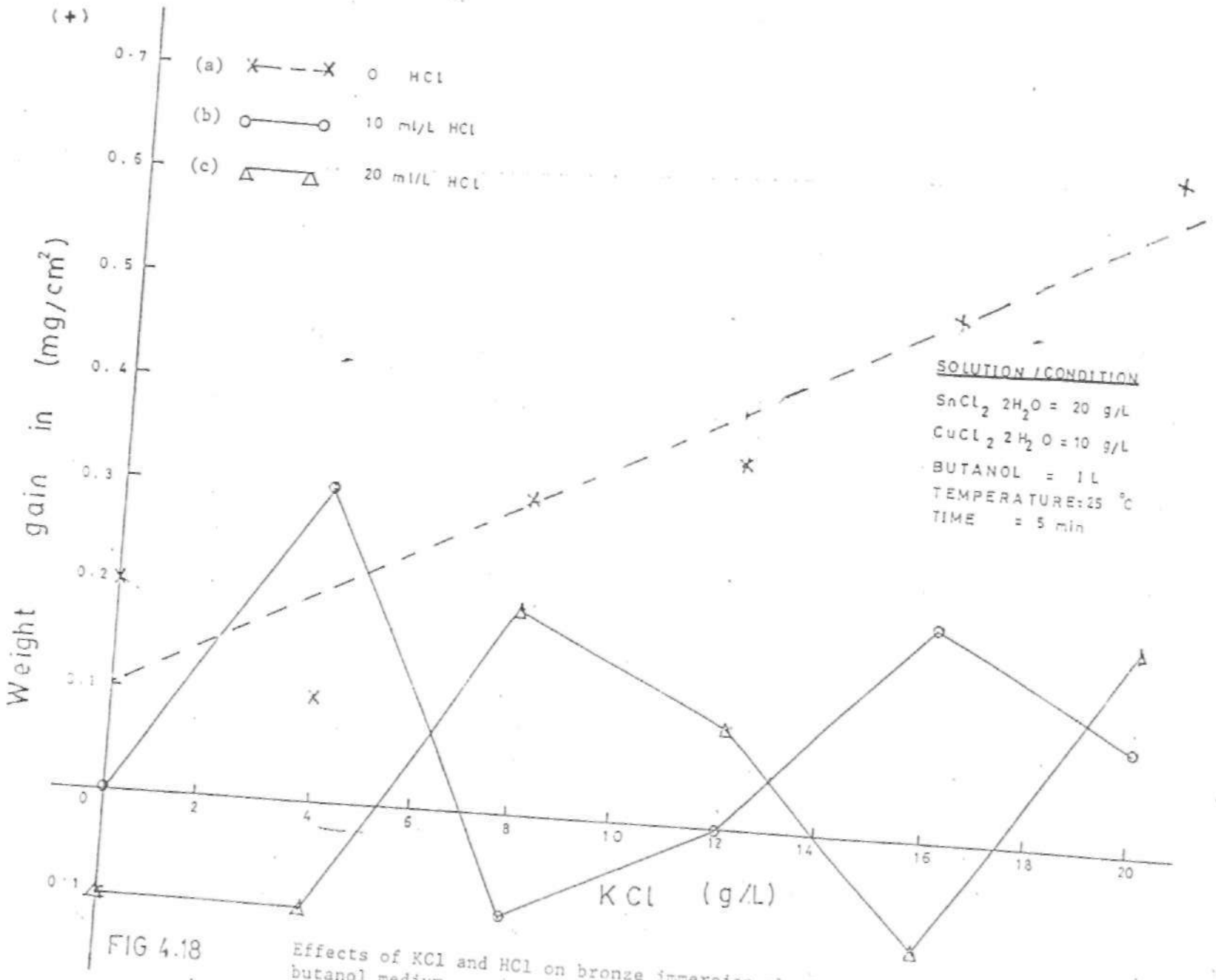


FIG 4.18 Effects of KCl and HCl on bronze immersion plating in butanol medium.

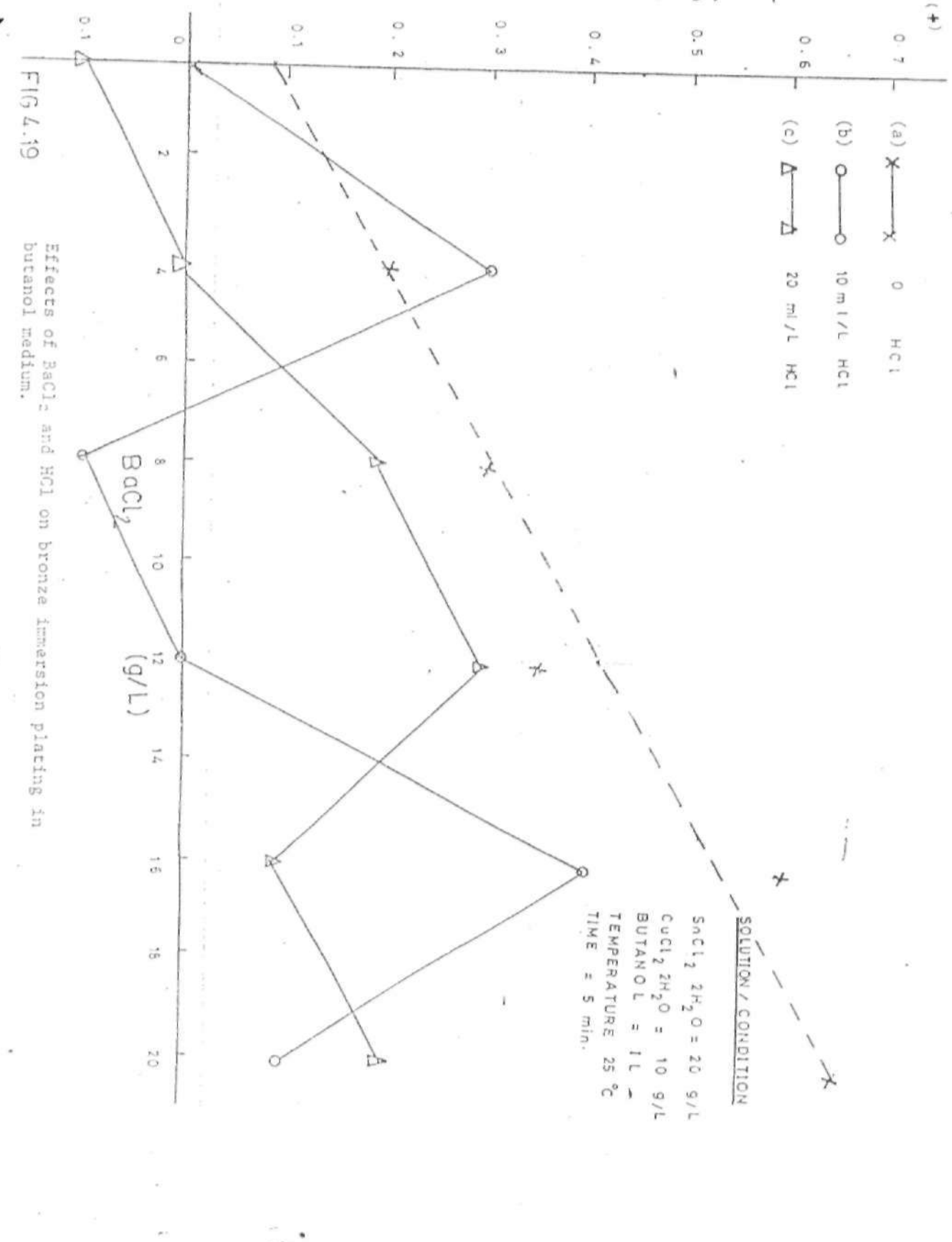


FIG 4.19 Effects of $BaCl_2$ and HCl on bronze immersion plating in butanol medium.

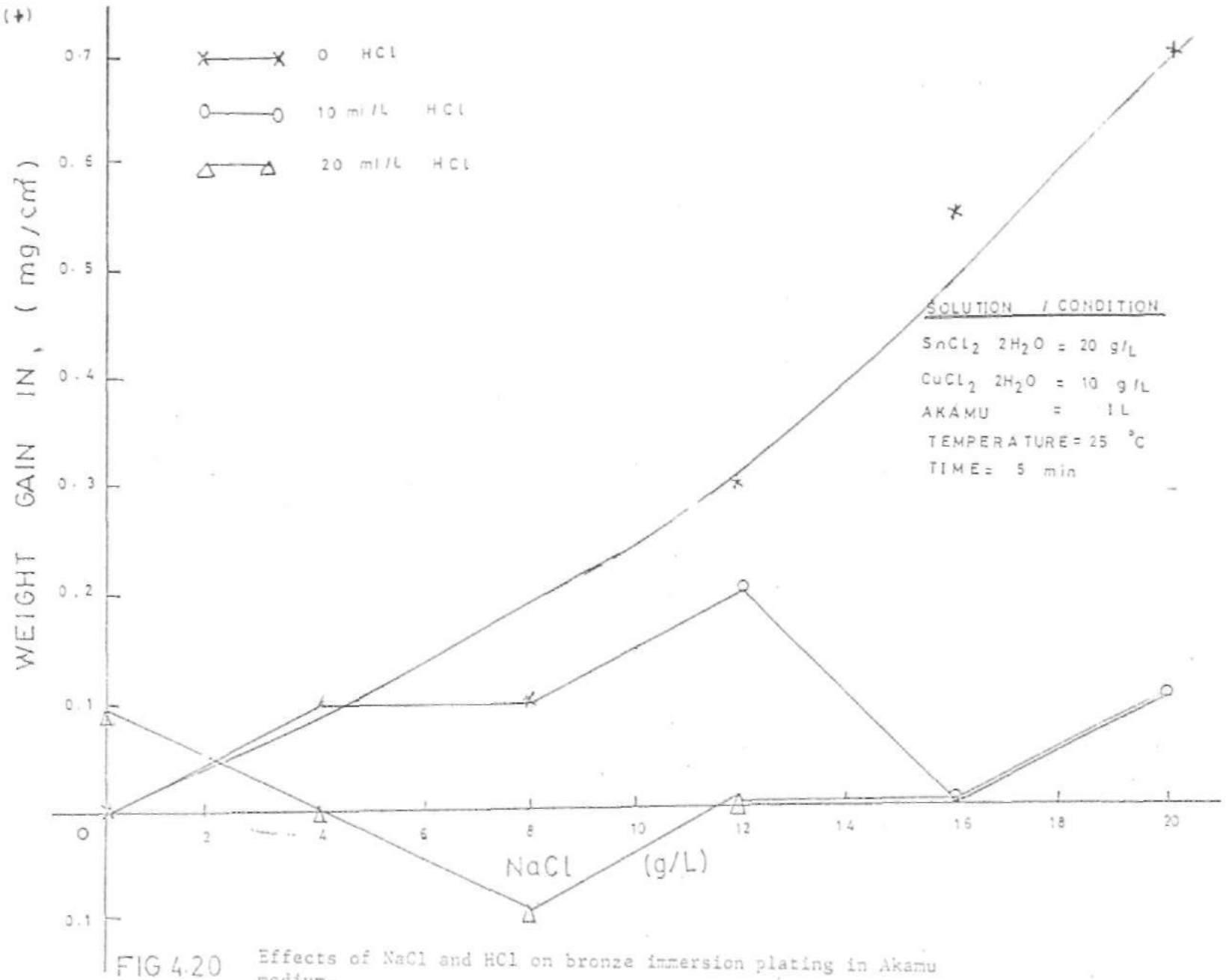


FIG 4.20 Effects of NaCl and HCl on bronze immersion plating in Akamu medium.

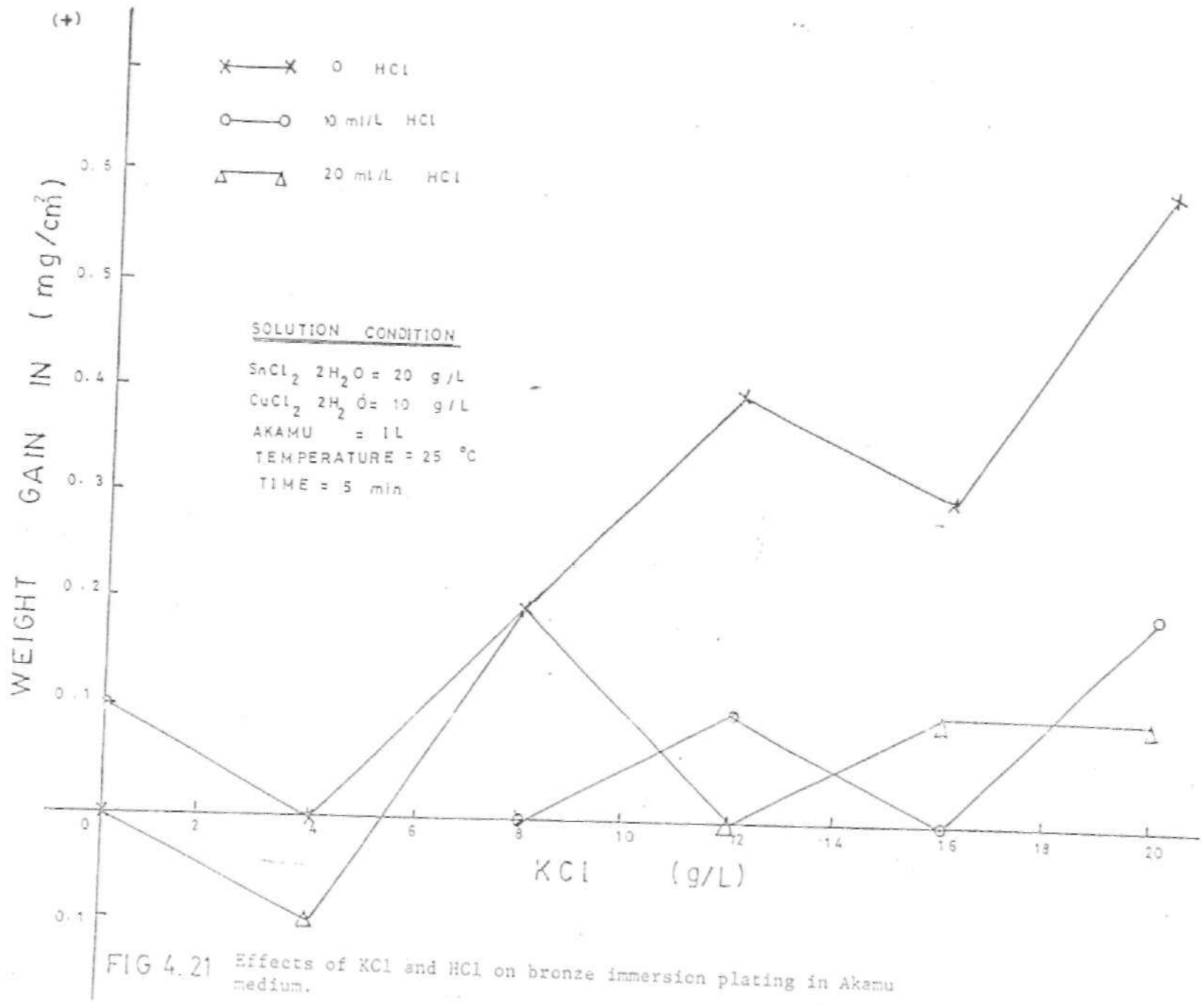


FIG 4.21 Effects of KCl and HCl on bronze immersion plating in Akamu medium.

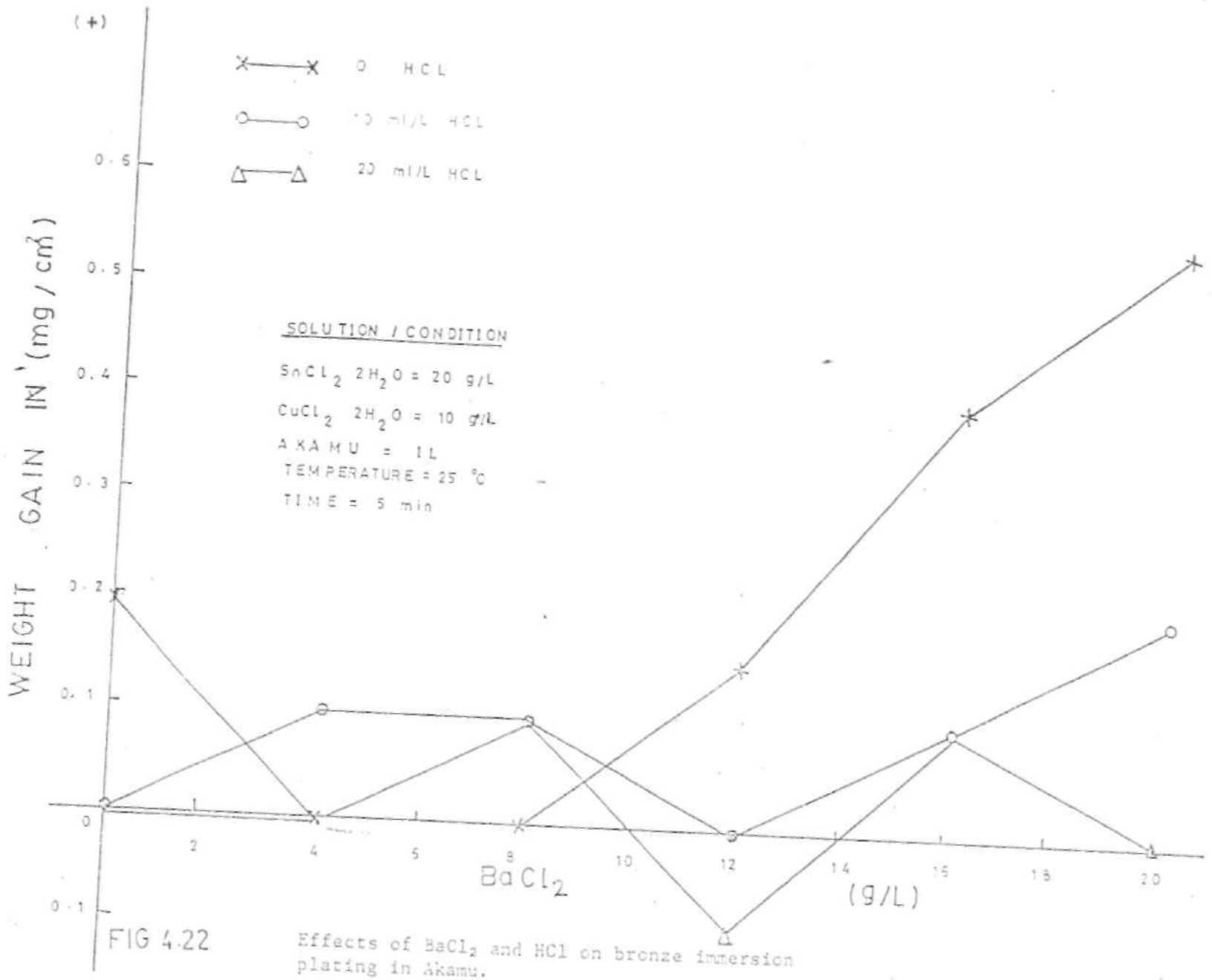


FIG 4.22 Effects of $BaCl_2$ and HCl on bronze immersion plating in Akamu.

The salts are all effective in enhancing plating rate; although, the effect of NaCl > KCl > $BaCl_2$. It is however, noted that the difference in plating rate enhancement between the three salts is not remarkable.

As earlier observed, the addition of HCl in the plating solution decreases plating rate. Almost similar trend to what is observed in aqueous solution apart from actual obtainable values. Relatively lower values are obtained in akamu medium.

4.3.7 MEDIA AND SODIUM CHLORIDE EFFECTS ON PLATING RATE (COATING THICKNESS:)

Figures 4.23 - 4.27 and Tables 17 - 21 (appendix 1) show the effects of plating media (eg. aqueous, methanol, propanol, butanol and 'akamu') respectively on plating rate (coating thickness) versus the addition of sodium chloride in plating solutions containing 20 g/L $SnCl_2.2H_2O$, 10 g/L $CuCl_2.2H_2O$ and $0-2.32\times10^{-1}$M(0-20 ml/L) HCl.

Greater coating thickness is obtained in methanol (up to 1.1μm) followed by propanol, butanol, 'akamu' and aqueous solution in that order of ranking with respect to NaCl level in solution.

The addition of NaCl enhances coating thickness growth in all the media, while the addition of HCl decreases plating rate.

In Fig. 4.24, the equation for curve (a) which has $m = 0.046\ \mu m\ g^{-1}.L$ and $k = 0.05\ \mu m$

$$t = 0.046\ (\mu m\ g^{-1}L)\ C_{Na}\ (g\ L^{-1}) + 0.05\ \mu m \quad \ldots\ldots\ldots\ldots\ldots\ 4.33$$

where t is coating thickness in μm.

In Fig. 4.25, the equation for curve (a) which has $m = 37.92\ m\mu m\ g^{-1}\ L$ and $k = 100 m\mu m$ is,

$$t = 37.92\ (m\mu m\ g^{-1}\ L)\ C_{Na}\ (g\ L^{-1}) + 100\ m\mu m \quad \ldots\ldots\ldots\ldots\ldots\ 4.34$$

where t is the coating thickness in mμm.

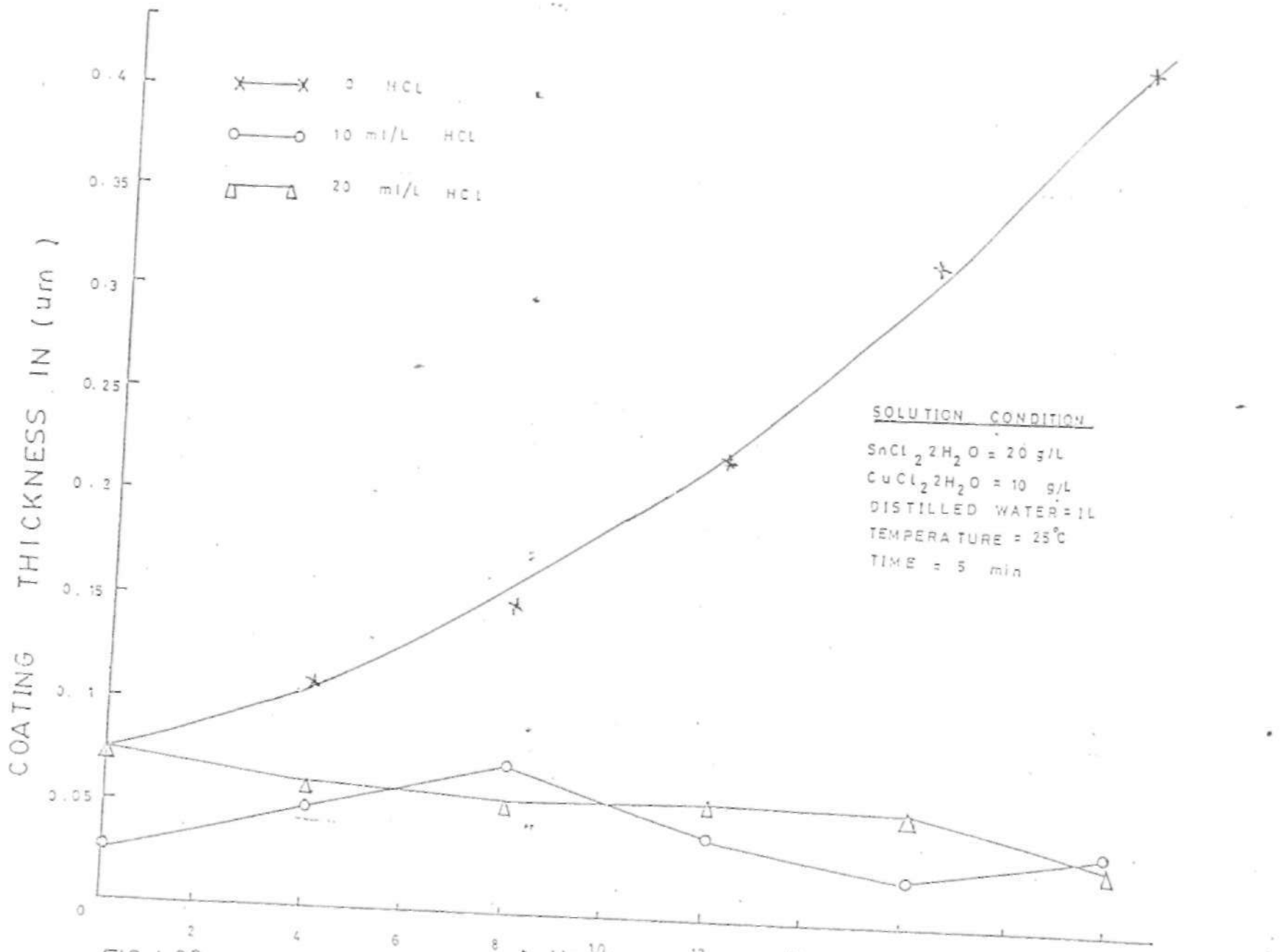


FIG 4.23 Effects of NaCl and HCl on bronze immersion plating in aqueous medium.

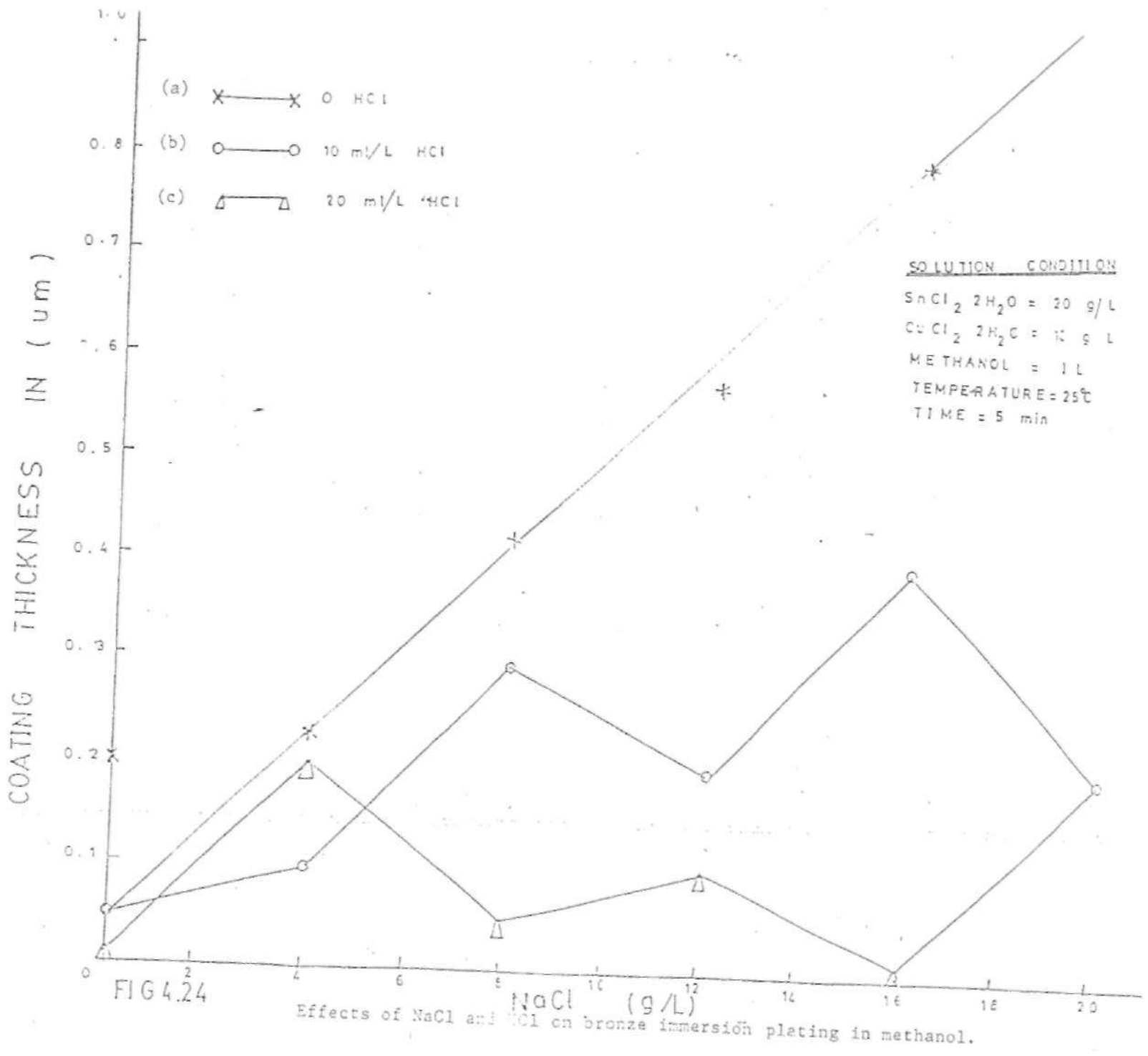


FIG 4.24 Effects of NaCl and HCl on bronze immersion plating in methanol.

FIG 4.25
Effects of NaCl and HCl on bronze immersion plating in propanol medium.

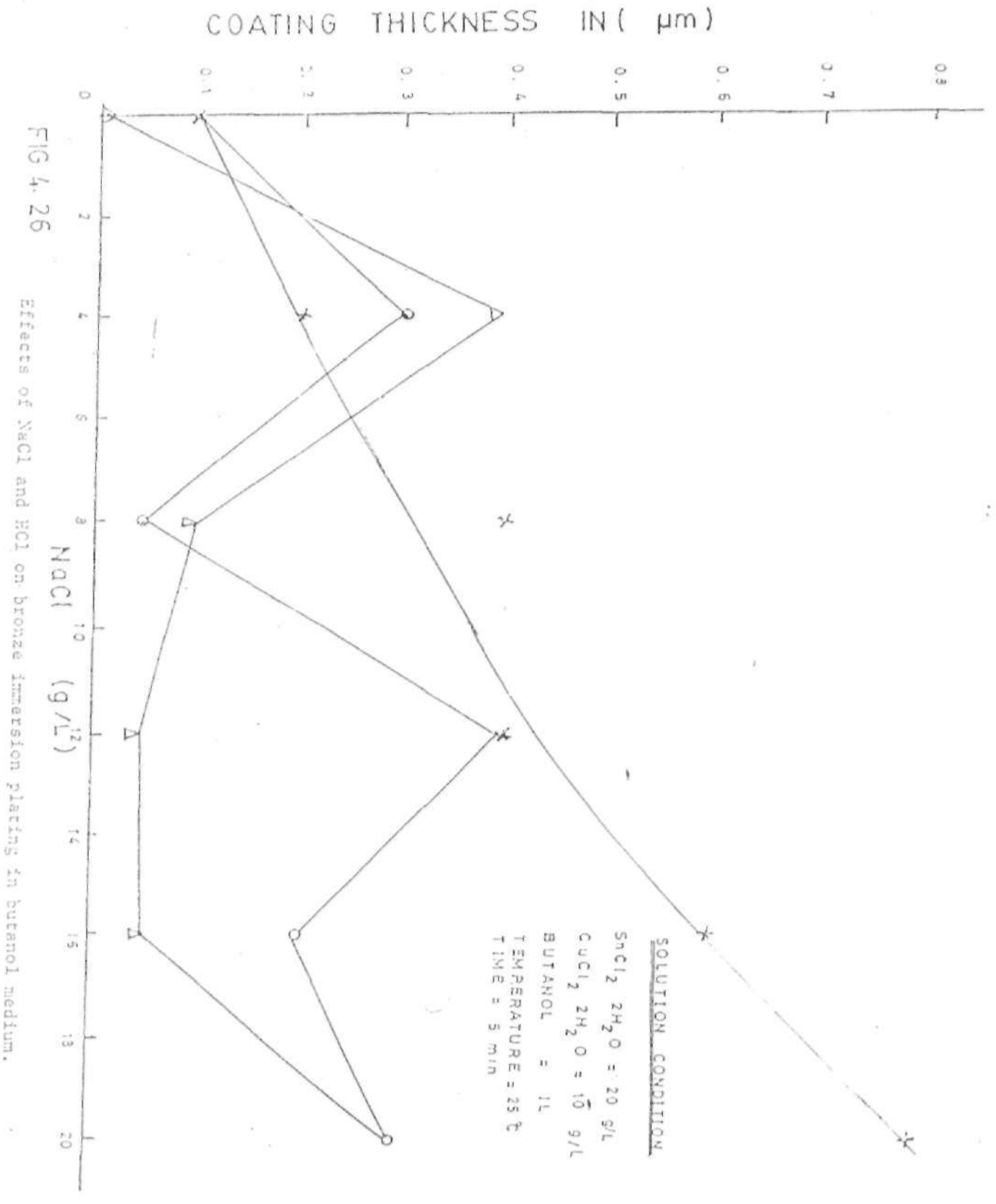


FIG 4.26 Effects of NaCl and HCl on bronze immersion plating in butanol medium.

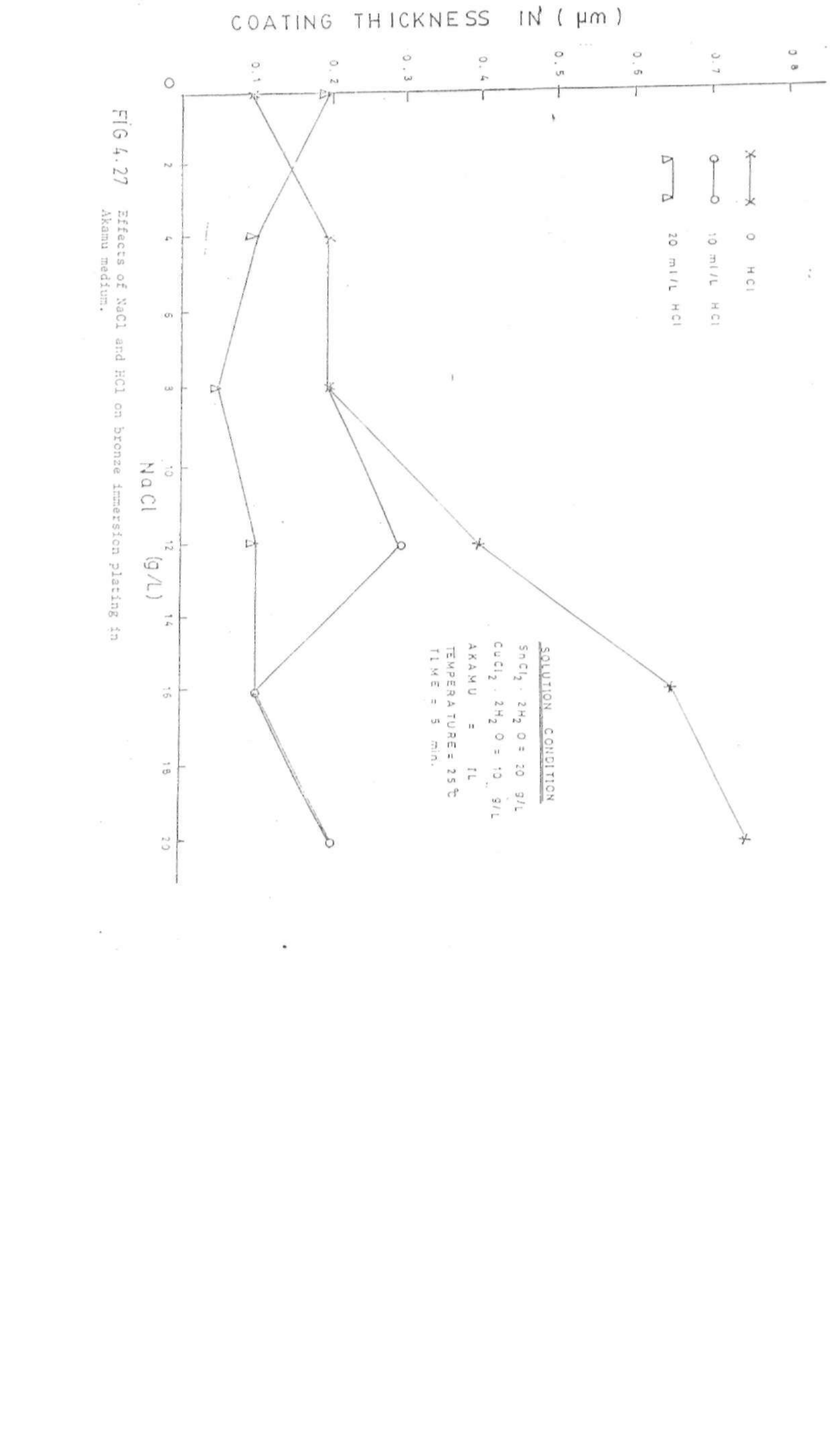


FIG 4.27 Effects of NaCl and HCl on bronze immersion plating in Akamu medium.

4.3.8 MEDIA AND KCl EFFECTS ON PLATING RATE:

Figures 4.28 - 4.29 and Tables 22 - 23 (appendix 1) show the effects of plating media: methanol, ethanol, propanol, aqueous, butanol and 'akamu' versus KCl addition on plating rate (coating thickness) in solutions containing 20 g/L $SnCl_2.2H_2O$ and 10 g/L $CuCl_2.2H_2O$.

The addition of KCl into the plating solution promote plating rate (higher coating thickness growth) in lower molecular weight alcohols (eg. methanol, ethanol and propanol in that order of effectiveness) than in higher molecular weight alcohols (eg. butanol) and 'akamu'.

4.3.9 PLATING RATES IN DIFFERENT MEDIA:

Figures 4,30, 4.31 and Tables 24 - 25 (appendix 1) show the rates of and the effects of plating media on coating thickness growth in solutions containing 20 g/L $SnCl_2.2H_2O$ and 10 g/L $CuCl_2.2H_2O$ and operated at 25°C.

The coating thickness increases with plating time before reaching steady state condition after which the thickness remains fairly constant. The increase in coating thickness with plating time is fairly linear at the initial stages but approaches steady value after about 2 to 3 minutes of plating. However, in most cases, the coating thickness is hardly over 1.0μm after about 5 minutes of plating.

4.3.10 MEDIA, HCl AND SODIUM DITHIONATE EFFECTS ON PLATING RATE (COATING THICKNESS):

Figures 4.32, 4.34, 4.36, 4.38, 4.40, 4.42 and Tables 26, 28, 30, 32 34 and 36 (appendix 1) show the effects of media (aqueous, methanol, ethanol, propanol and 'akamu' respectively) and the addition of sodium dithionate on plating rate (or gain in coating thickness) in bronze immersion plating solutions containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$, operated at a temperature of 25°C for 5 minutes.

In all the results, the addition of HCl retards plating rate. Conversely, plating rate is promoted in acid-free solution irrespective of plating media (solvents).

In Fig. 4.34, the equation for curve (a) which has $m = 0.23$ mg cm^{-2} g^{-1} L and $k = 1.5$ mg cm^{-2} is,

$$w = 0.23 \text{ (mg cm}^{-2} \text{ g}^{-1} \text{ L)} \; C_{SD} \text{ (g L}^{-1}\text{)} + 1.5 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots\ldots \; 4.35$$

where C_{SD} is the concentration of sodium dithionate.

In Fig. 4.36, the linear equation for curve (a) which has $m = 0.025$ mg cm^{-2} g^{-1} L and $k = 0.18$ mg cm^{-2} is,

$$w = 0.025 \text{ (mg cm}^{-2} \text{ g}^{-1} \text{ L)} \; C_{SD} \text{ (g L}^{-1}\text{)} + 0.18 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots\ldots \; 4.36$$

In Fig. 4.38, the linear equation for curve (a) which has $m = 0.023$ mg.cm^{-2} g^{-1} L and $k = 0.08$ mg cm^{-2} is,

$$w = 0.023 \text{ (mg cm}^{-2} \text{ g}^{-1} \text{ L)} \; C_{SD} \text{ (g L}^{-1}\text{)} + 0.08 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots\ldots \; 4.37$$

In Fig. 4.40, the linear relationship for curve (a) which has $m = 0.0167$ mg cm^{-2} g^{-1} L and $k = 0.075$ mg cm^{-2} is,

$$w = 0.0167 \text{ (mg.cm}^{-2} \text{ g}^{-1} \text{ L)} \; C_{SD} \text{ (g L}^{-1}\text{)} + 0.075 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots \; 4.38$$

In Fig. 4.42, the linear equation for curve (a) which has $m = 0.083$ mg cm^{-2}. g^{-1}.L and $k = 0.055$ mg cm^{-2} is,

$$w = 0.083 \text{ (mg cm}^{-2} \text{ g}^{-1} \text{ L)} \; C_{SD} \text{ (g.L}^{-1}\text{)} + 0.055 \text{ mg cm}^{-2} \quad \ldots\ldots\ldots 4.39$$

3.4.11 MEDIA, CONCENTRATION AND SODIUM DITHIONATE EFFECTS ON PLATING RATE:

Figures 4.33, 4.35, 4.37, 4.39, 4.41, 4.43 and Tables 27, 29, 31, 33 35 and 37 (appendix 1) show the effects of media (aqueous, methanol, propanol, butanol and 'akamu' respectively) concentration and the addition of sodium dithionate on plating rate from bronze immersion plating solution containing:

(i) 8 g/L $SnCl_2.2H_2O$

4 g/L $CuCl_2.2H_2O$

(ii) 8 g/L $SnCl_2.2H_2O$

6 g/L $CuCl_2.2H_2O$

(iii) 8 g/L $SuCl_2.2H_2O$

8 g/L $CuCl_2.2H_2O$

Plating favours lower molecular weight alcohols. The addition of sodium dithionate also enhances plating rate.

Higher concentrations of Cu^{2+} in solution promote plating rate.

In Fig. 4.33, the equation for the linear curves are:

Curve (a), m = 0.012 mg cm^{-2} g^{-1} L and k = 0.03 mg cm^{-2}

$w = 0.012\ (mg.cm^{-2}\ g^{-1}\ L)\ C_{SD}\ (g\ L^{-1}) + 0.03\ mg\ cm^{-2}$ 4.40

Curve (b), m = 0.0133 mg.cm^{-2} g^{-1} L and k = 0.07 mg cm^{-2}

$w = 0.0133\ (mg.cm^{-2}\ g^{-1}\ L)\ C_{SD}\ (g\ L^{-1}) + 0.07\ mg\ cm^{-2}$ 4.41

Curve (c), m = 0.009 mg.cm^{-2}. g^{-1}.L and k = 0.213 mg.cm^{-2}

$w = 0.009\ (mg.cm^{-2}.\ g^{-1}.L)\ C_{SD}\ (g.L^{-1}) + 0.213\ mg.cm^{-2}$ 4.42

In Fig. 4.35, the equation for the linear curves are:

Curve (a), m = 0.02 mg cm^{-2} g^{-1} L and k = 0.04 mg cm^{-2}.

$w = 0.02\ (mg\ cm^{-2}\ g^{-1}\ L)\ C_{SD}\ (g\ L^{-1}) + 0.04\ mg\ cm^{-2}$ 4.43

Curve (b), m = 0.028 mg cm^{-2} g^{-1} L and k = 0.09 mg cm^{-2}

$w = 0.028\ (mg\ cm^{-2}\ g^{-1}\ L)\ C_{SD}\ (g\ L^{-1}) + 0.09\ mg\ cm^{-2}$ 4.44

For curve (c), m = 0.029 mg cm^{-2} g^{-1} L and k = 0.215 mg cm^{-2}

$w = 0.029\ (mg\ cm^{-2}\ g^{-1}\ L)\ C_{SD}\ (g\ L^{-1}) + 0.215\ mg\ cm^{-2}$ 4.45

In Fig. 4.37, the equations for the linear curves are:

Curve (a), $m = 0.029$ mg cm^{-2} g^{-1} L and $k = 0.15$ mg cm^{-2}

$w = 0.029$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.15 mg cm^{-2}..... 4.46

Curve (b), $m = 0.025$ mg cm^{-2} g^{-1} L and $k = 0.09$ mg cm^{-2}

$w = 0.025$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.09 mg cm^{-2}..... 4.47

Curve (c), $m = 0.012$ mg cm^{-2} g^{-1} L and $k = 0.05$ mg cm^{-2}

$w = 0.012$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.05 mg cm^{-2}..... 4.48

In Fig. 4.39, the equation for the linear curves are:-

Curve (a), $m = 0.021$ mg.cm^{-2} g^{-1} L and $k = 0.1$ mg cm^{-2}

$w = 0.021$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.1 mg cm^{-2}..... 4.49

Curve (b), $m = 0.011$ mg cm^{-2} g^{-1} L and $k = 0.09$ mg cm^{-2}

$w = 0.011$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.09 mg cm^{-2}..... 4.50

Curve (c), $m = 0.007$ mg cm^{-2} g^{-1} L and $k = 0.065$ mg cm^{-2}

$w = 0.007$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.065 mg cm^{-2}..... 4.51

In Fig. 4.41, the equation for the linear curves are:

Curve (a), $m = 0.017$ mg cm^{-2} g^{-1} L and $k = 0.07$ mg cm^{-2}

$w = 0.017$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.07 mg cm^{-2}..... 4.52

Curve (b), $m = 0.016$ mg cm^{-2} g^{-1} L and $k = 0.04$ mg cm^{-2}

$w = 0.016$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.04 mg cm^{-2}..... 4.53

And Curve (c), $m = 0.0125$ mg cm^{-2} g^{-1} L and $k = 0.025$ mg cm^{-2}

$w = 0.0125$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.025 mg cm^{-2}..... 4.54

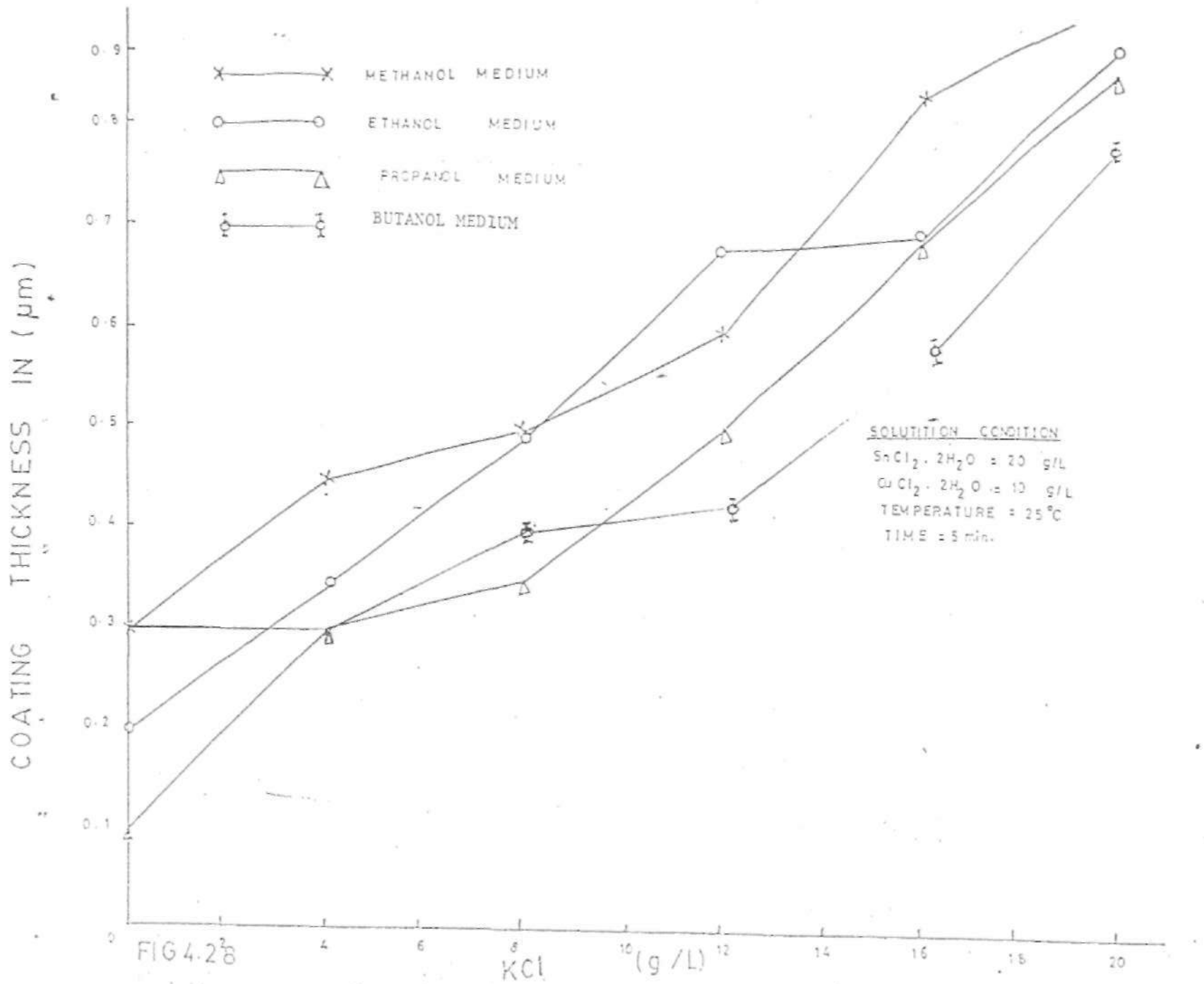


FIG 4.28

Comparison of the effect of KCl on bronze immersion plating in different media.

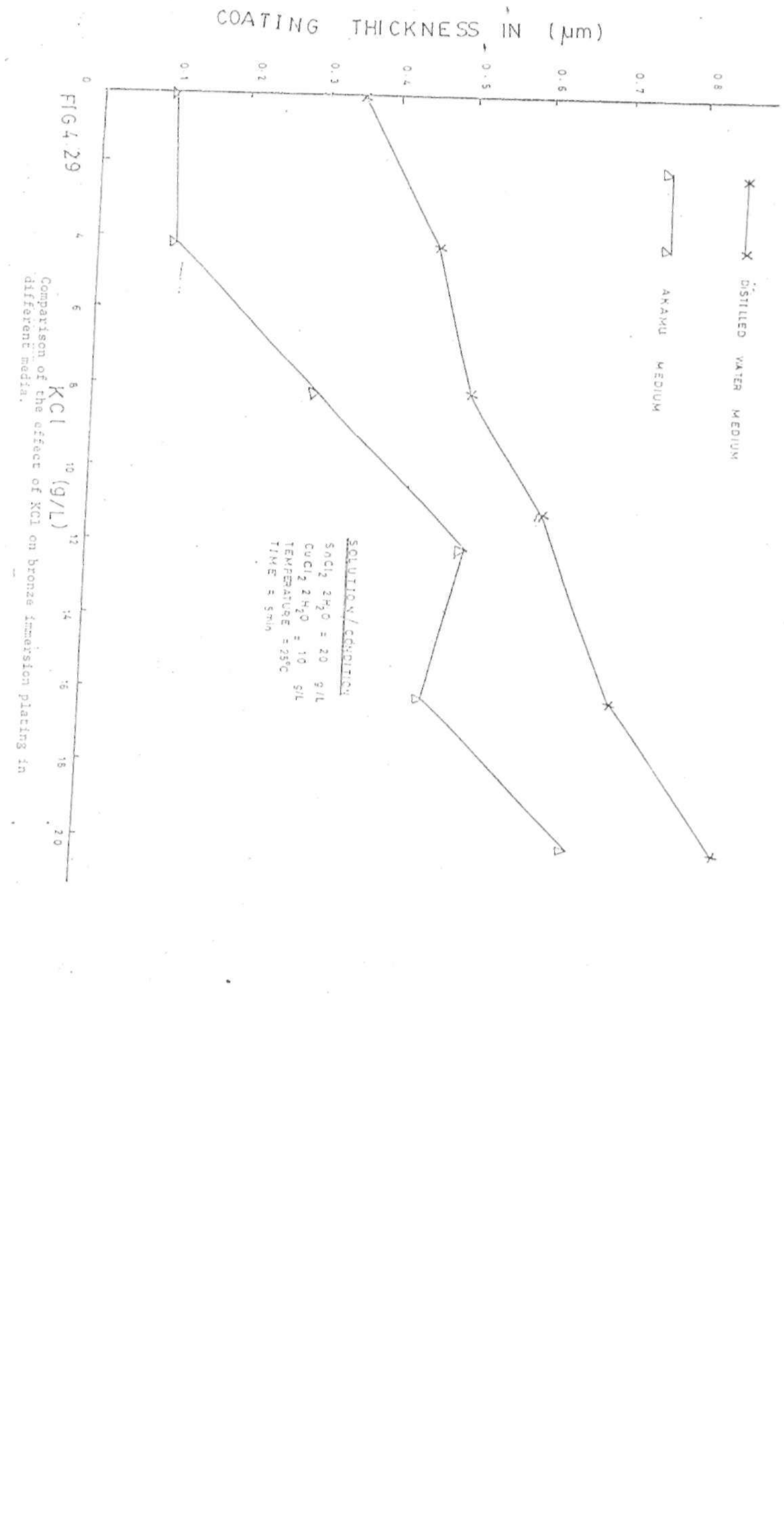


FIG 4.29 Comparison of the effect of KCl on bronze immersion plating in different media.

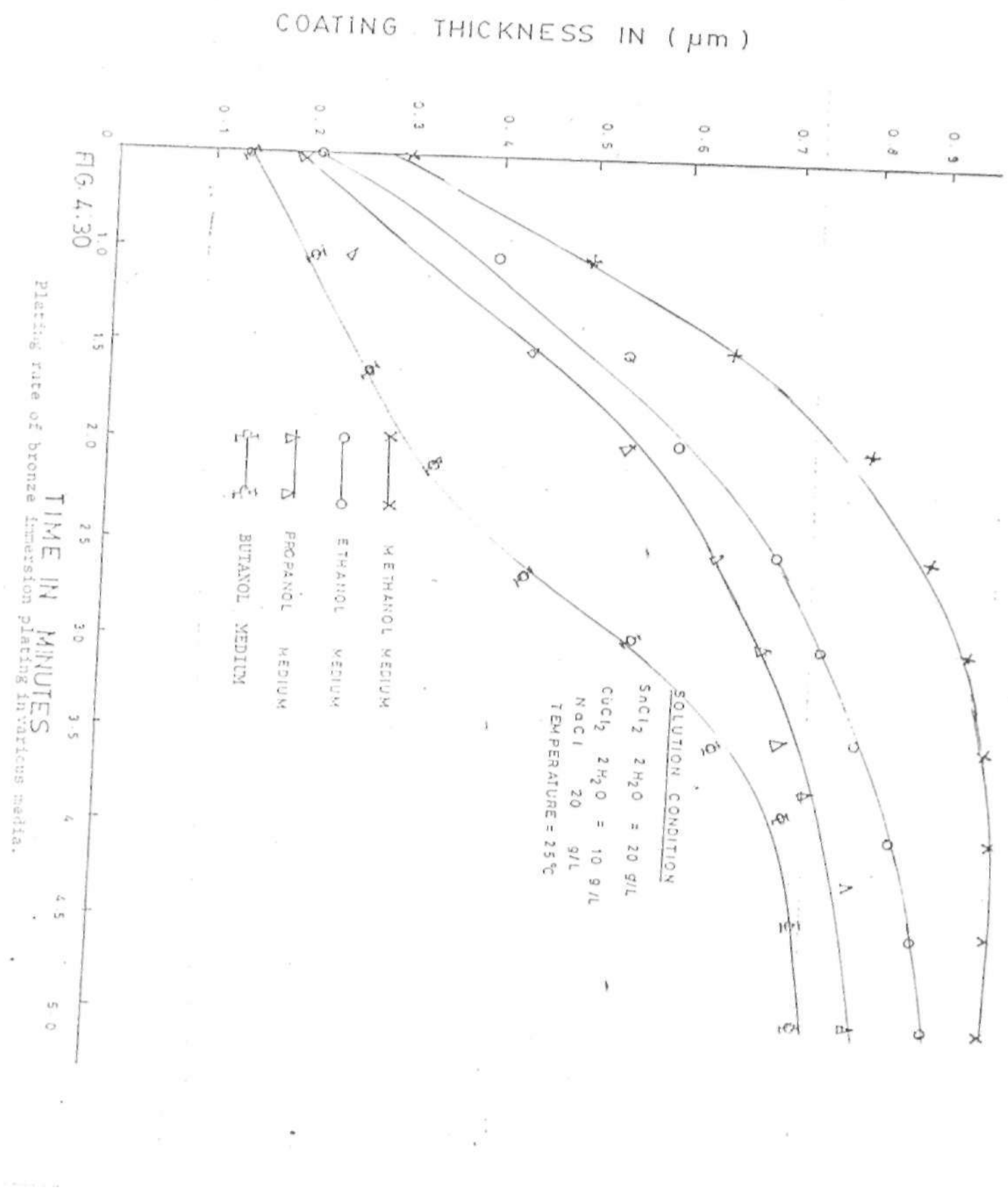

COATING THICKNESS IN (μm)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
1.0 1.5 2.0 2.5 3.0 3.5 4 4.5 5.0
TIME IN MINUTES
Plating rate of bronze from immersion plating in various media.
SOLUTION CONDITION
SnCl2 2H2O = 20 g/L
CuCl2 2H2O = 10 g/L
NaCl 20 g/L
TEMPERATURE = 25°C
METHANOL MEDIUM
ETHANOL MEDIUM
PROPANOL MEDIUM
BUTANOL MEDIUM

FIG. 4.30

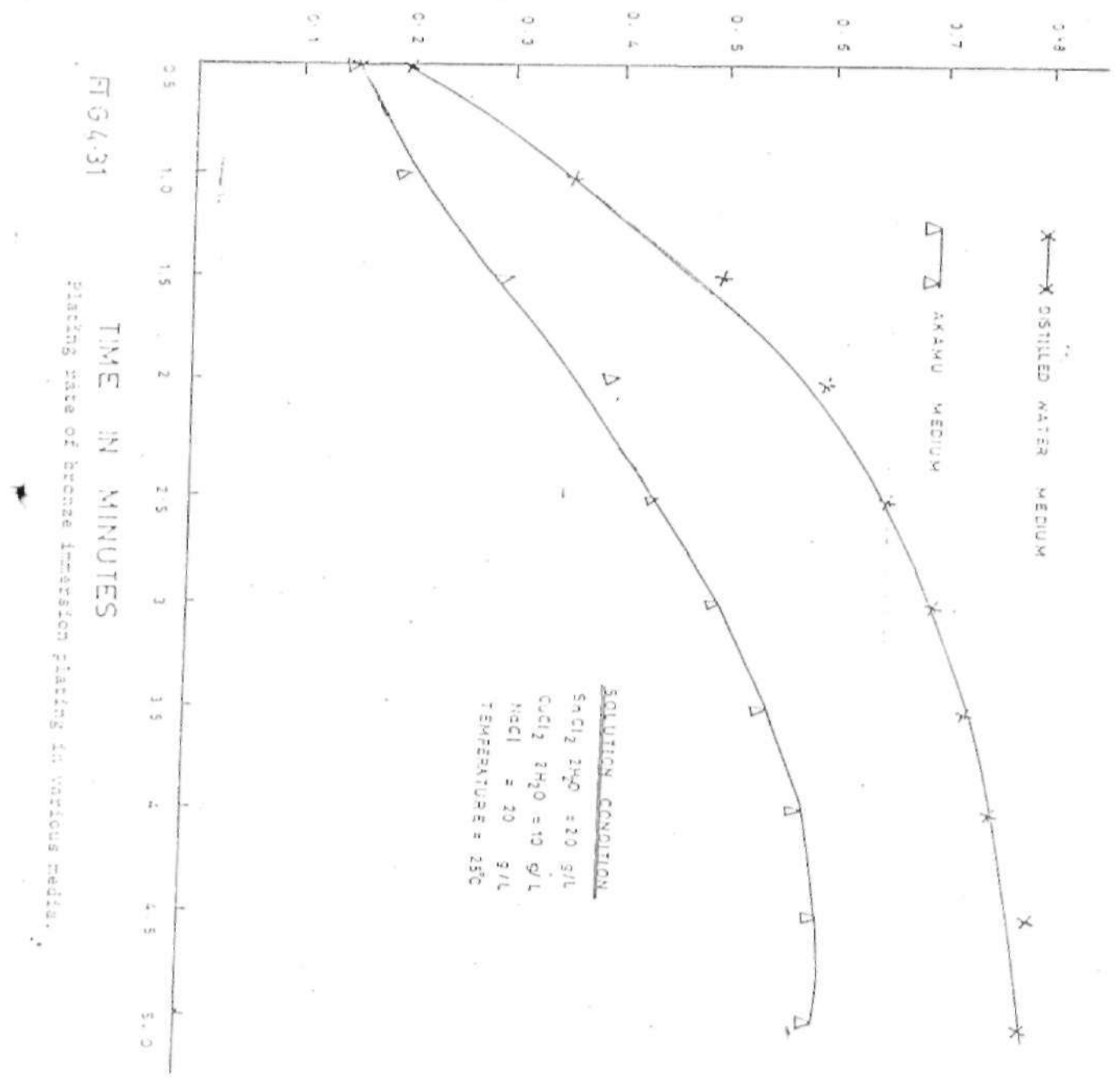


FIG 4.31 Plating rate of bronze immersion plating on various media.

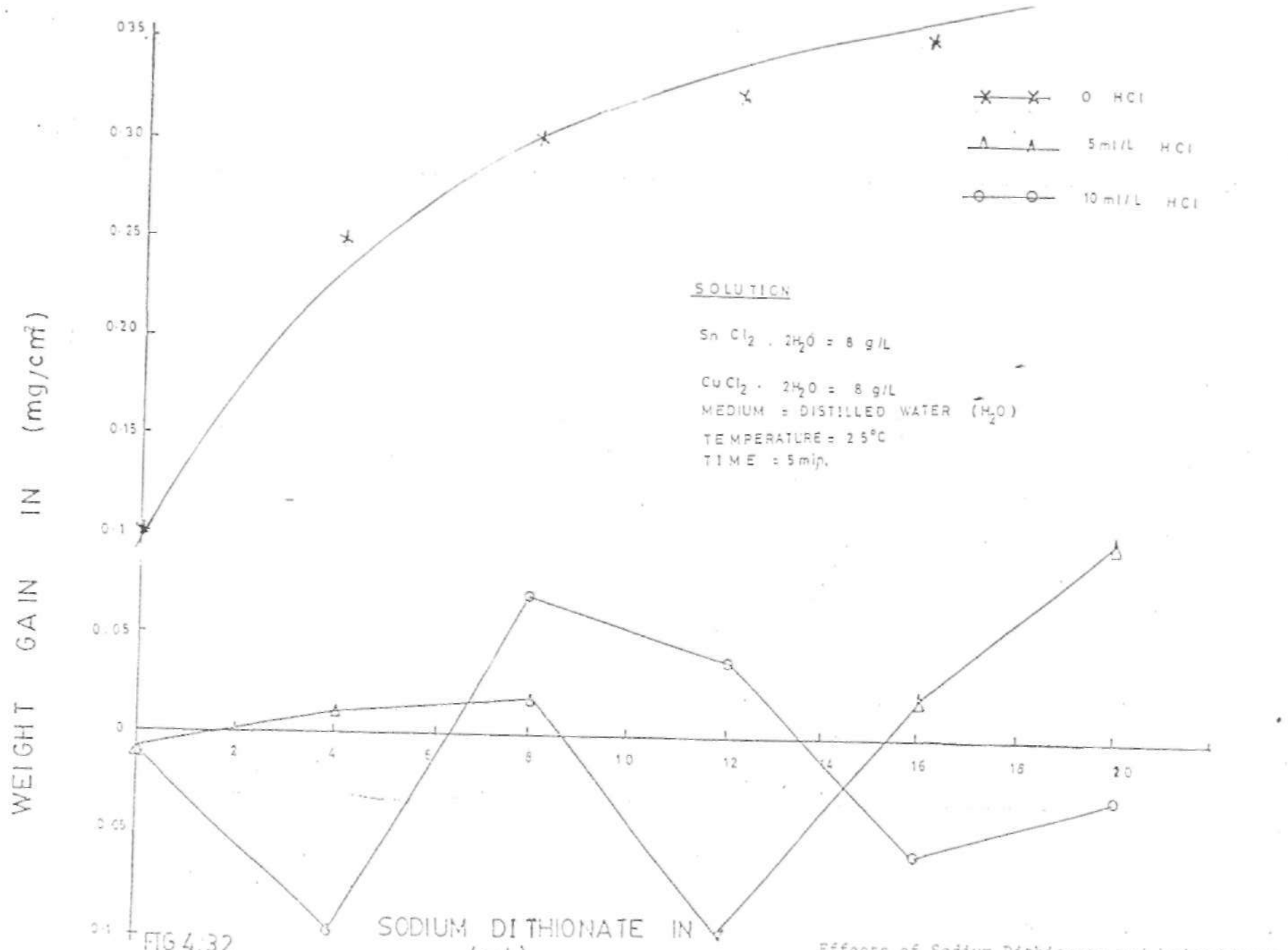


FIG 4.32

Effects of Sodium Dithionate and hydrochloric acid on weight gain during bronze immersion plating in H_2O.

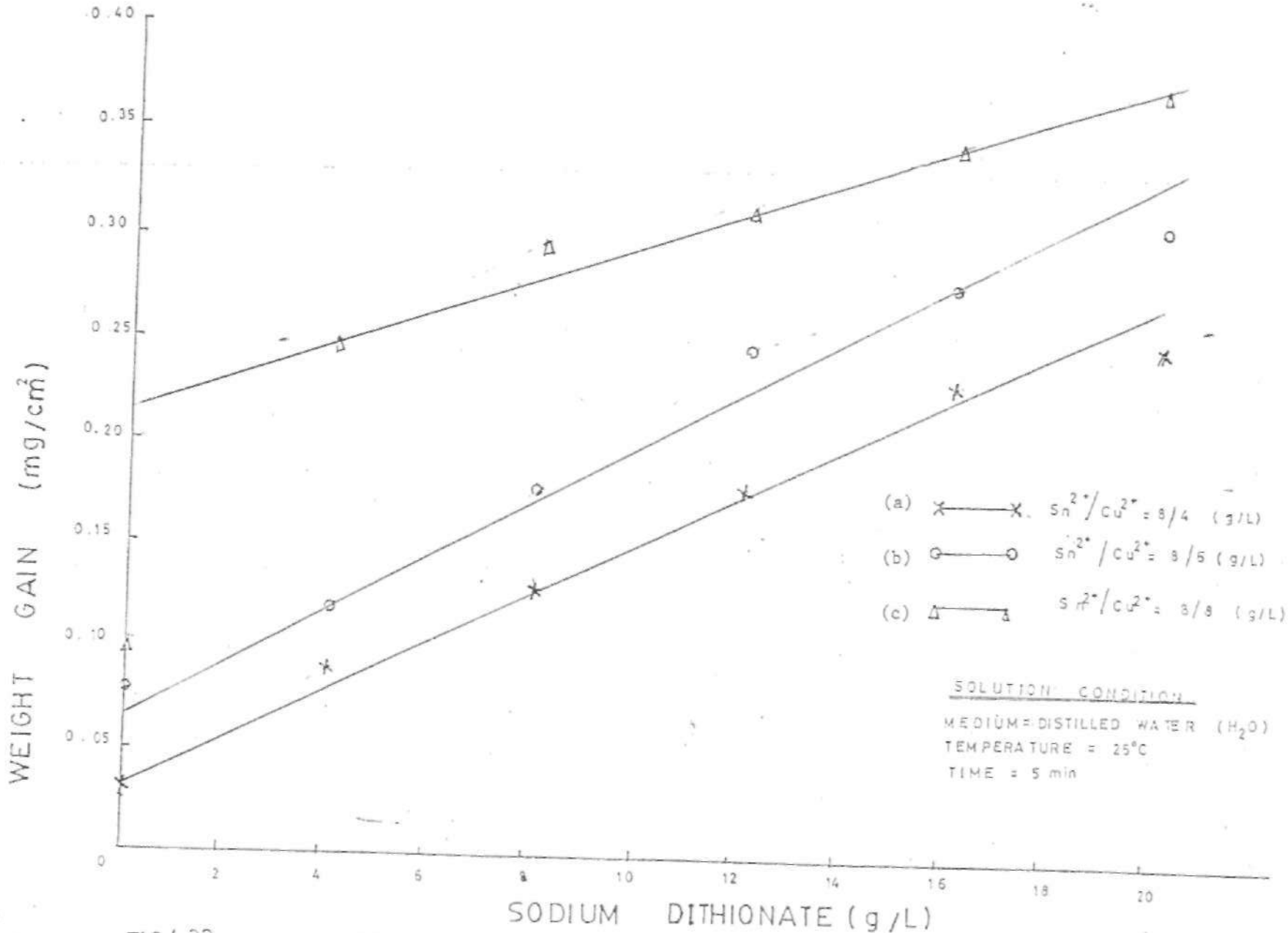


FIG 4.33 Effects of concentration and dithionate on bronze immersion plating in aqueous solution.

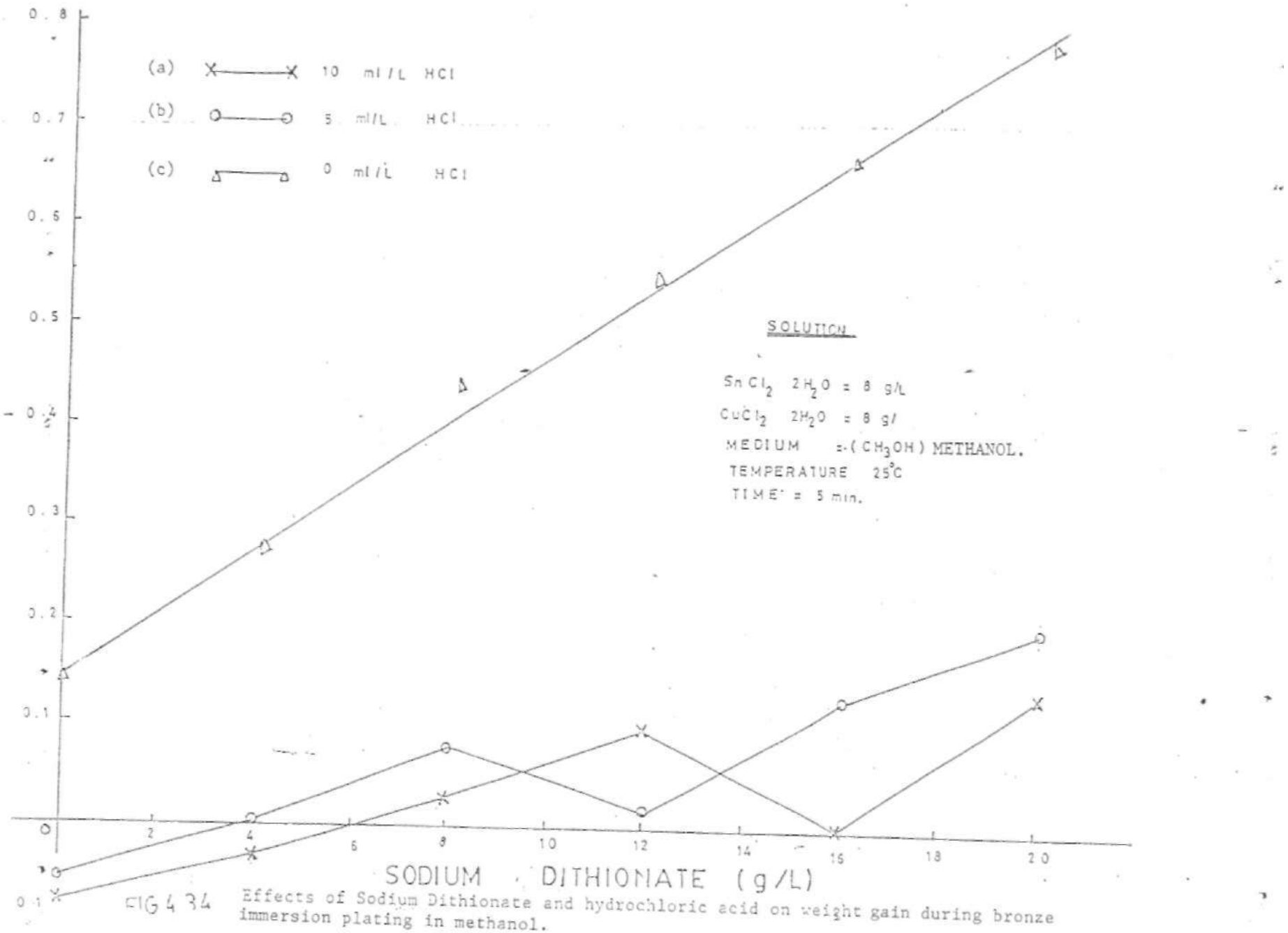


FIG 4.34 Effects of Sodium Dithionate and hydrochloric acid on weight gain during bronze immersion plating in methanol.

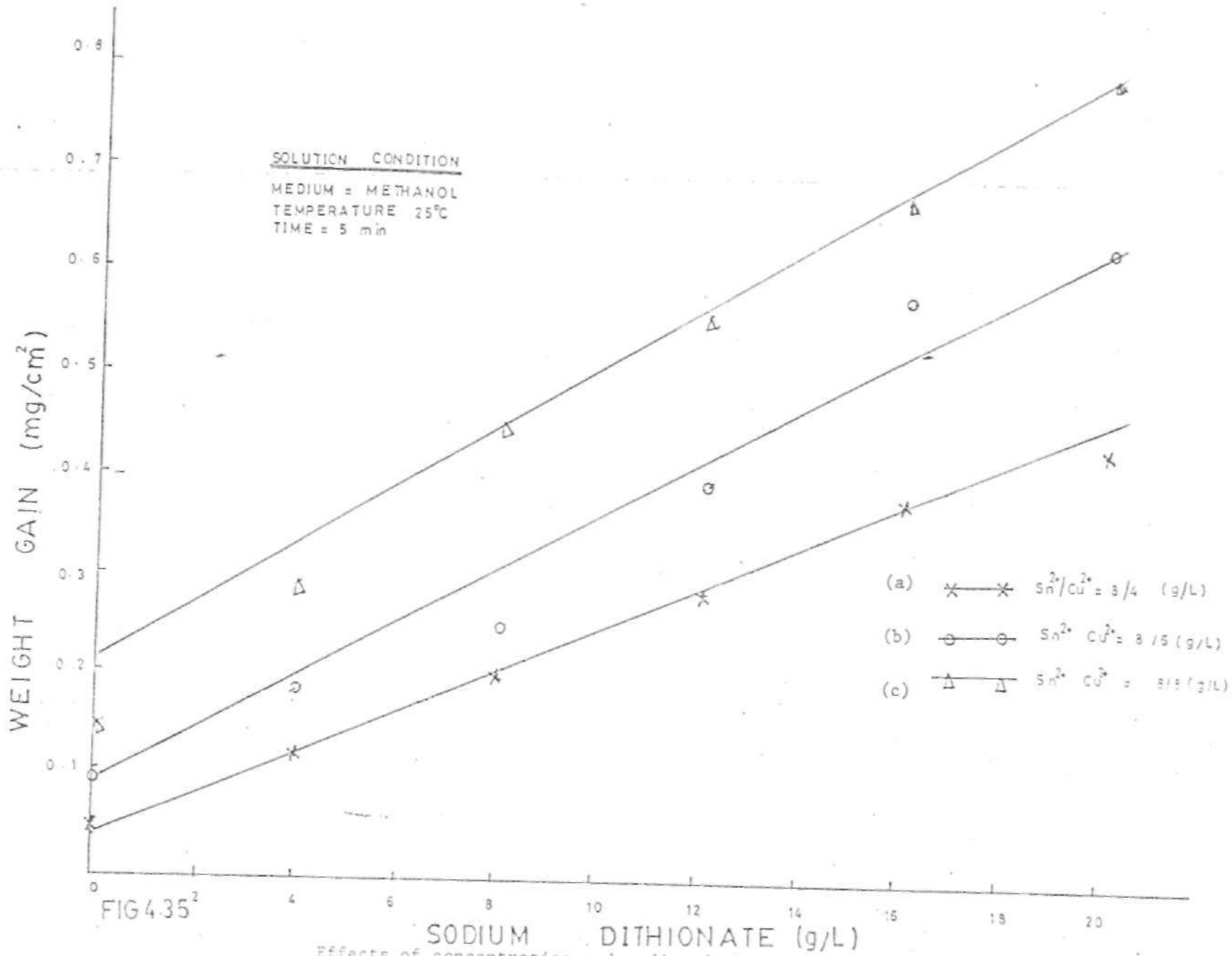


FIG 4.35

Effects of concentration and sodium dithionate on bronze immersion plating in methanol.

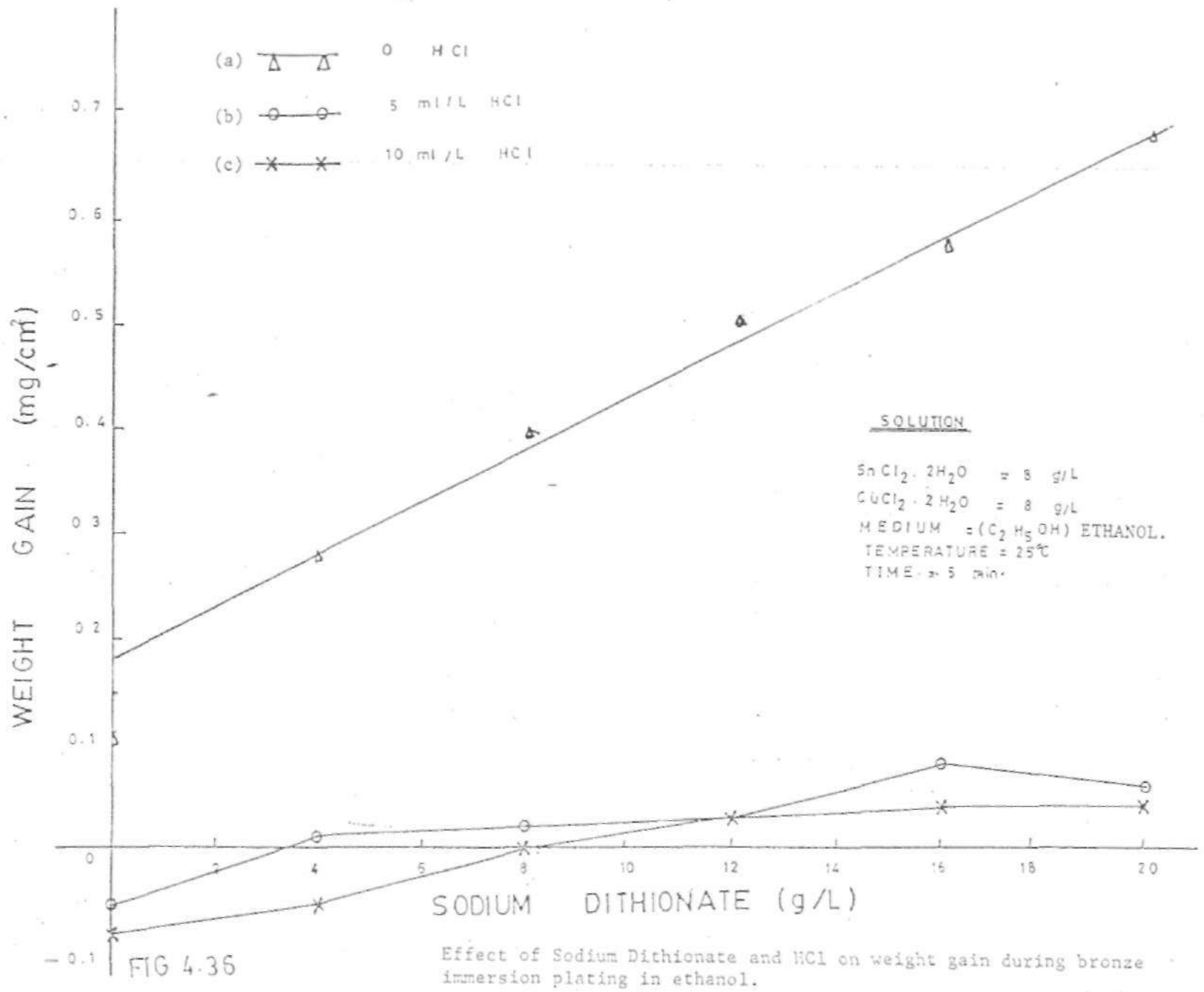


FIG 4.36

Effect of Sodium Dithionate and HCl on weight gain during bronze immersion plating in ethanol.

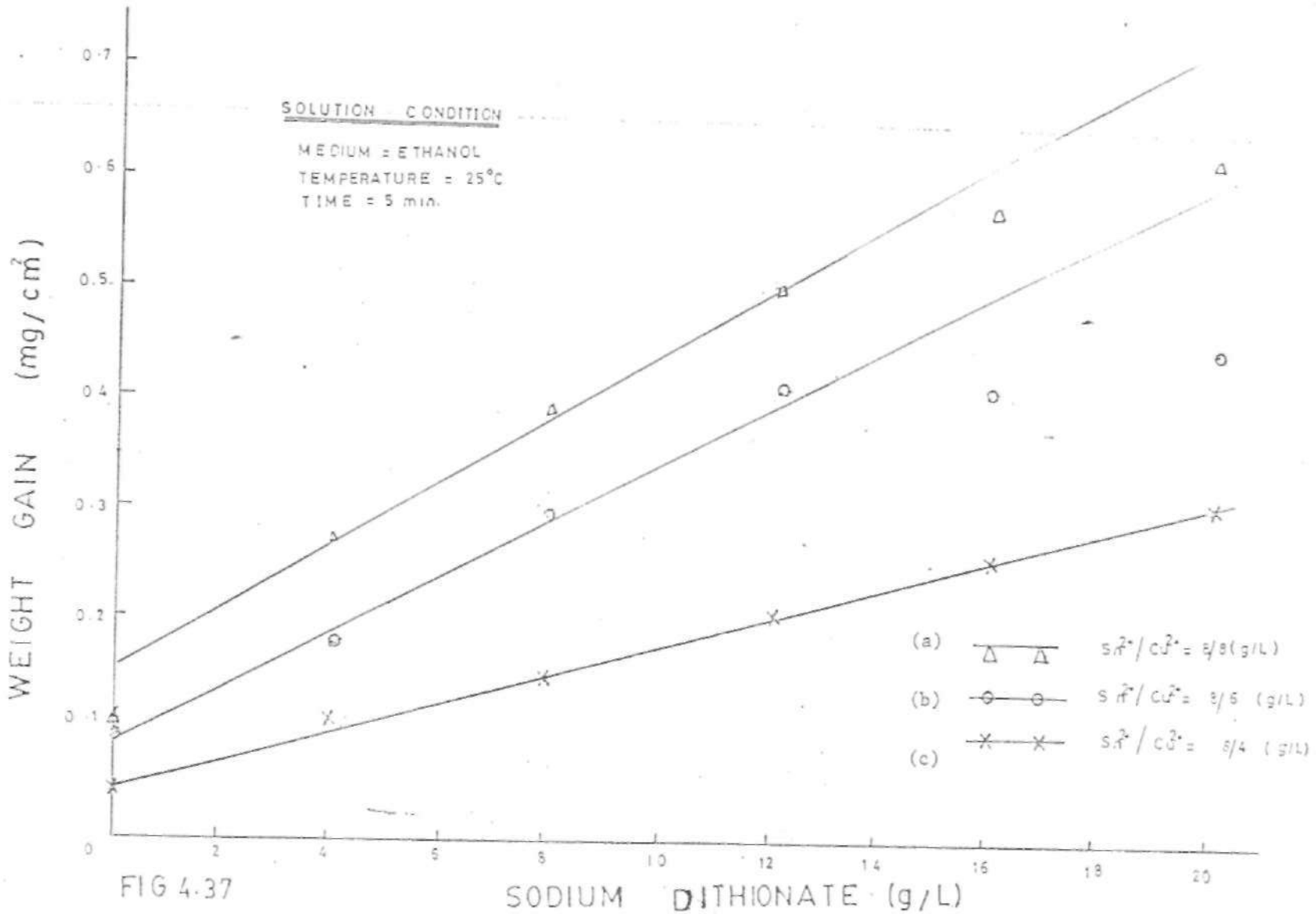
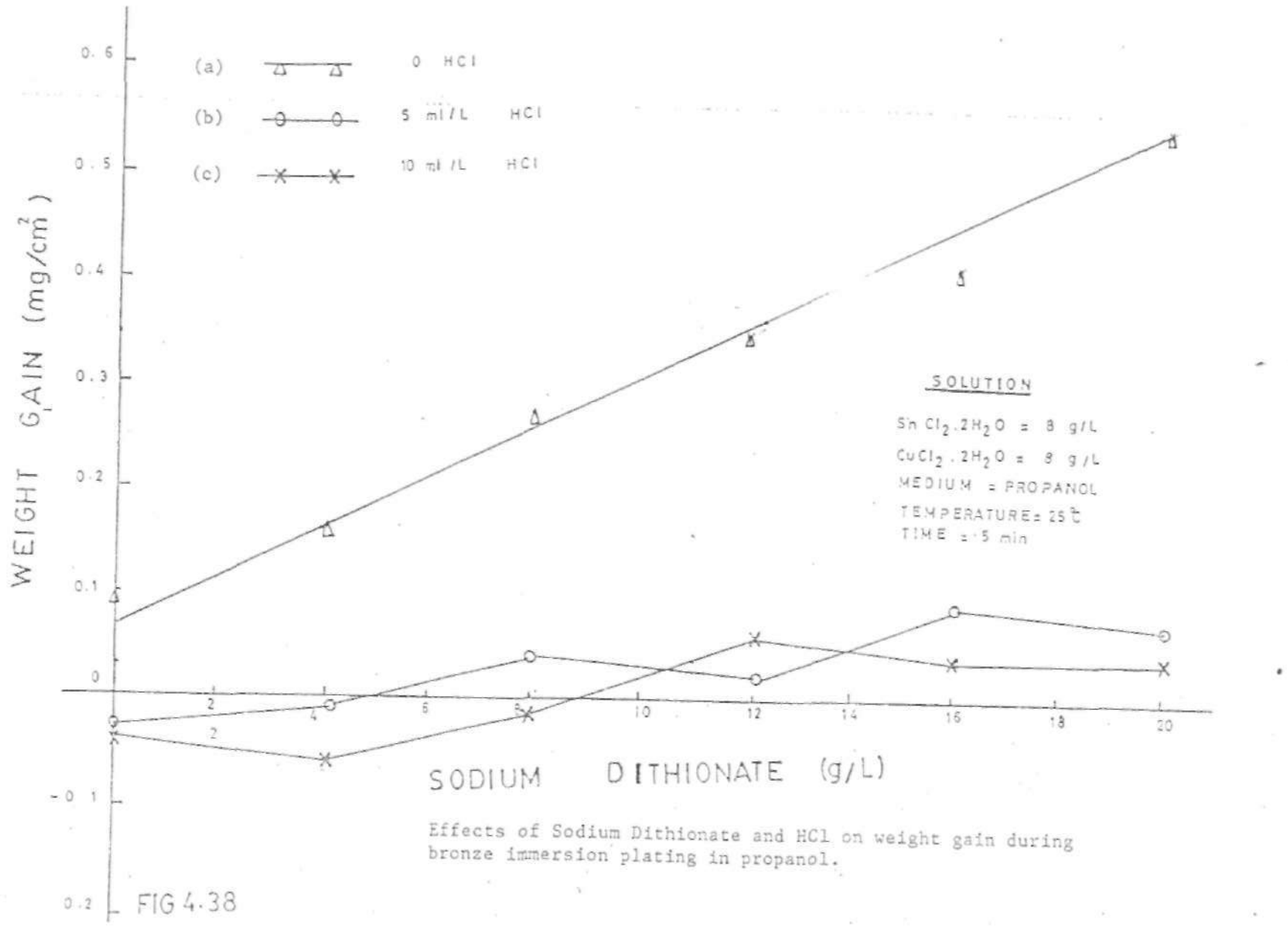


FIG 4.37

Effects of concentration and Sodium Dithionate on bronze immersion plating in ethanol.



Effects of Sodium Dithionate and HCl on weight gain during bronze immersion plating in propanol.

FIG 4.38

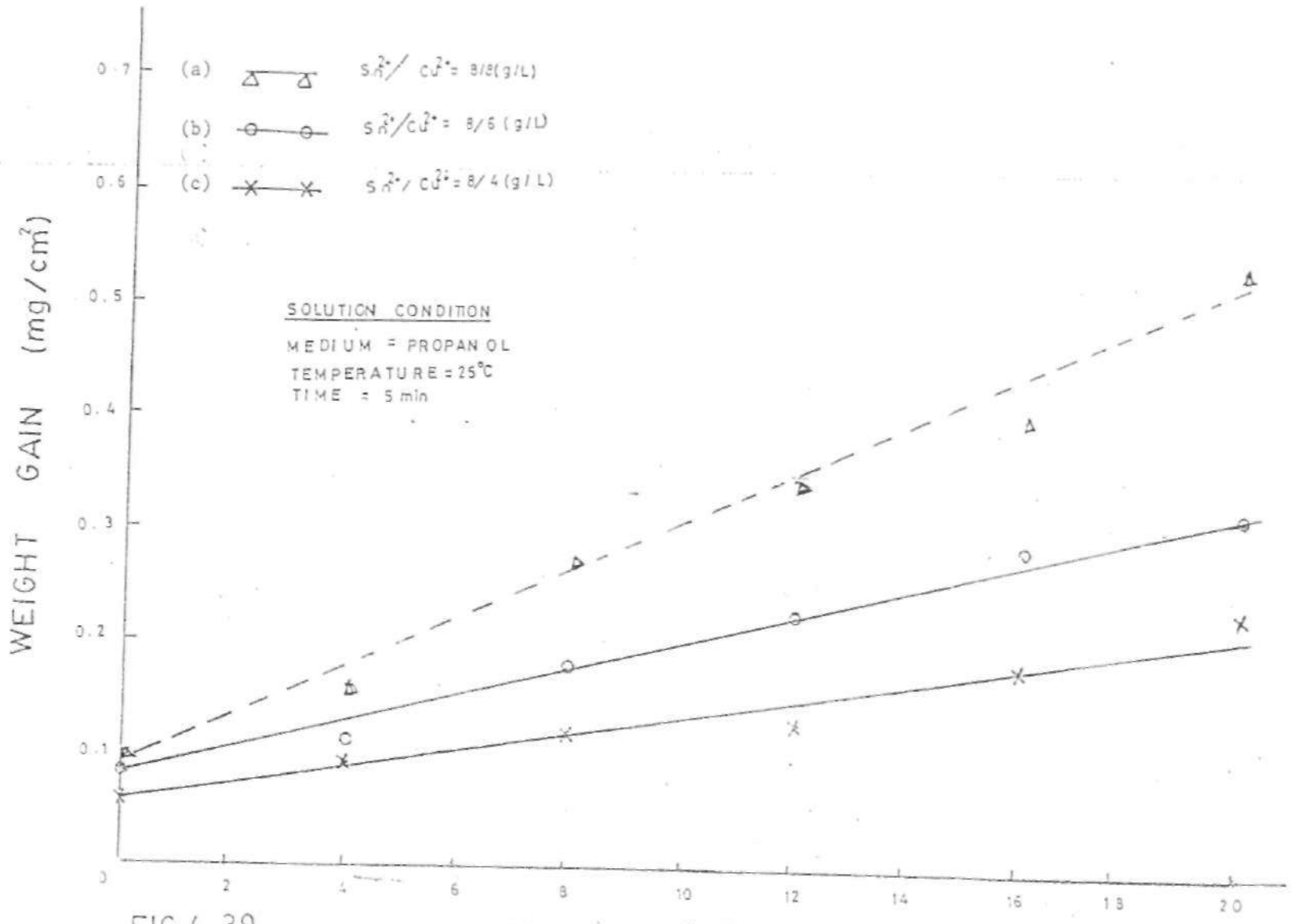


FIG 4.39

Effects of Sodium Dithionate and concentration on bronze immersion plating in propanol.

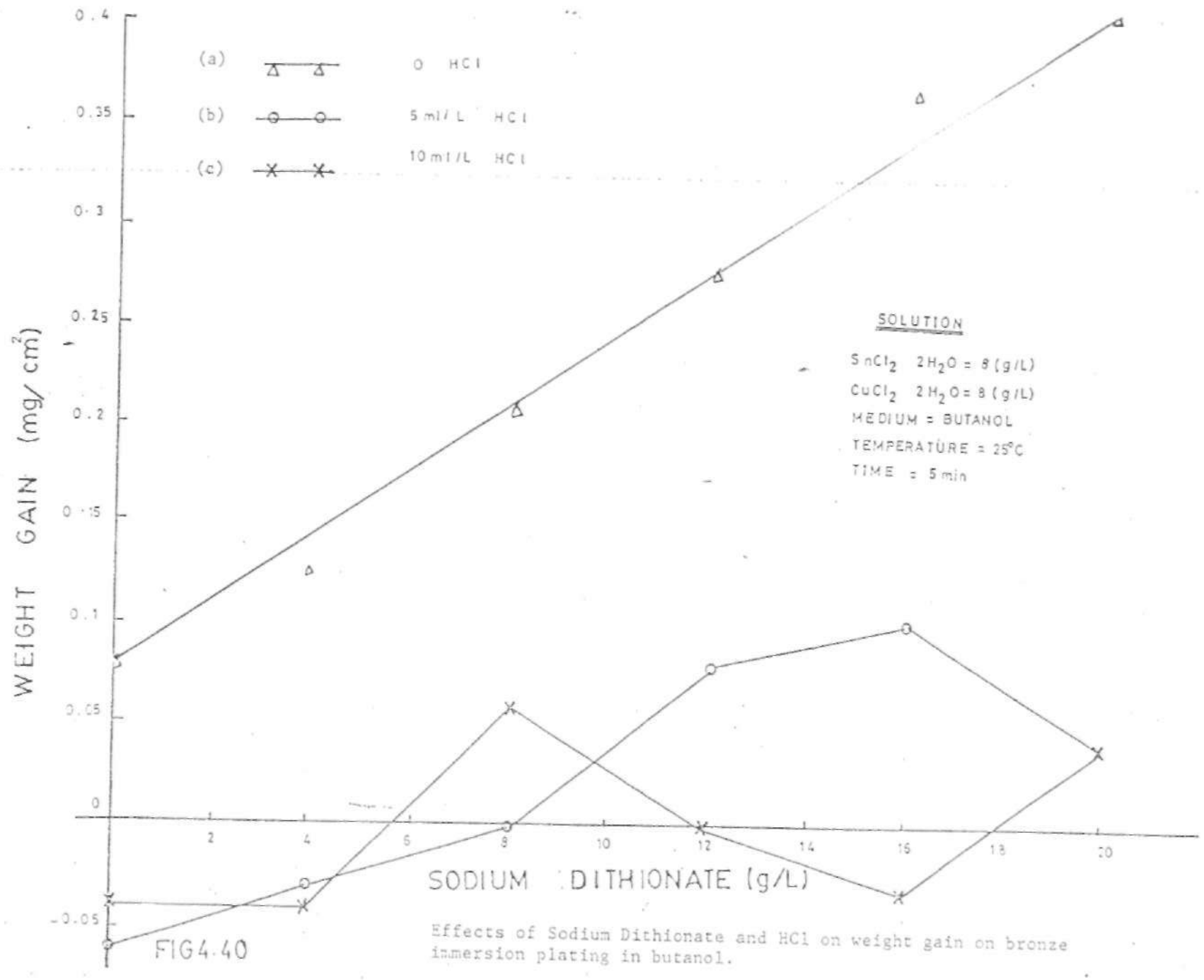


FIG4.40

Effects of Sodium Dithionate and HCl on weight gain on bronze immersion plating in butanol.

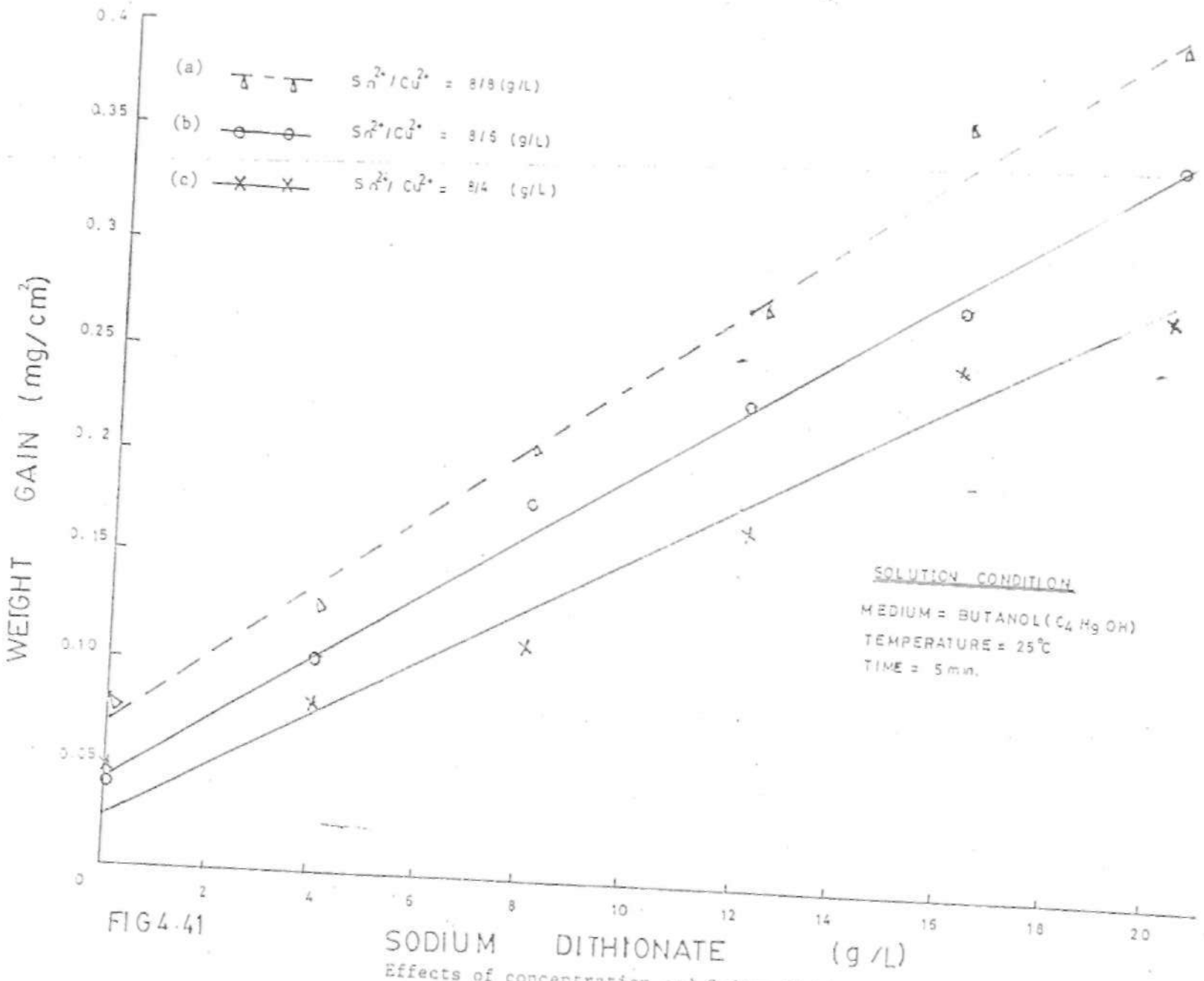


FIG 4.41

Effects of concentration and Sodium Dithionate on bronze immersion plating in butanol.

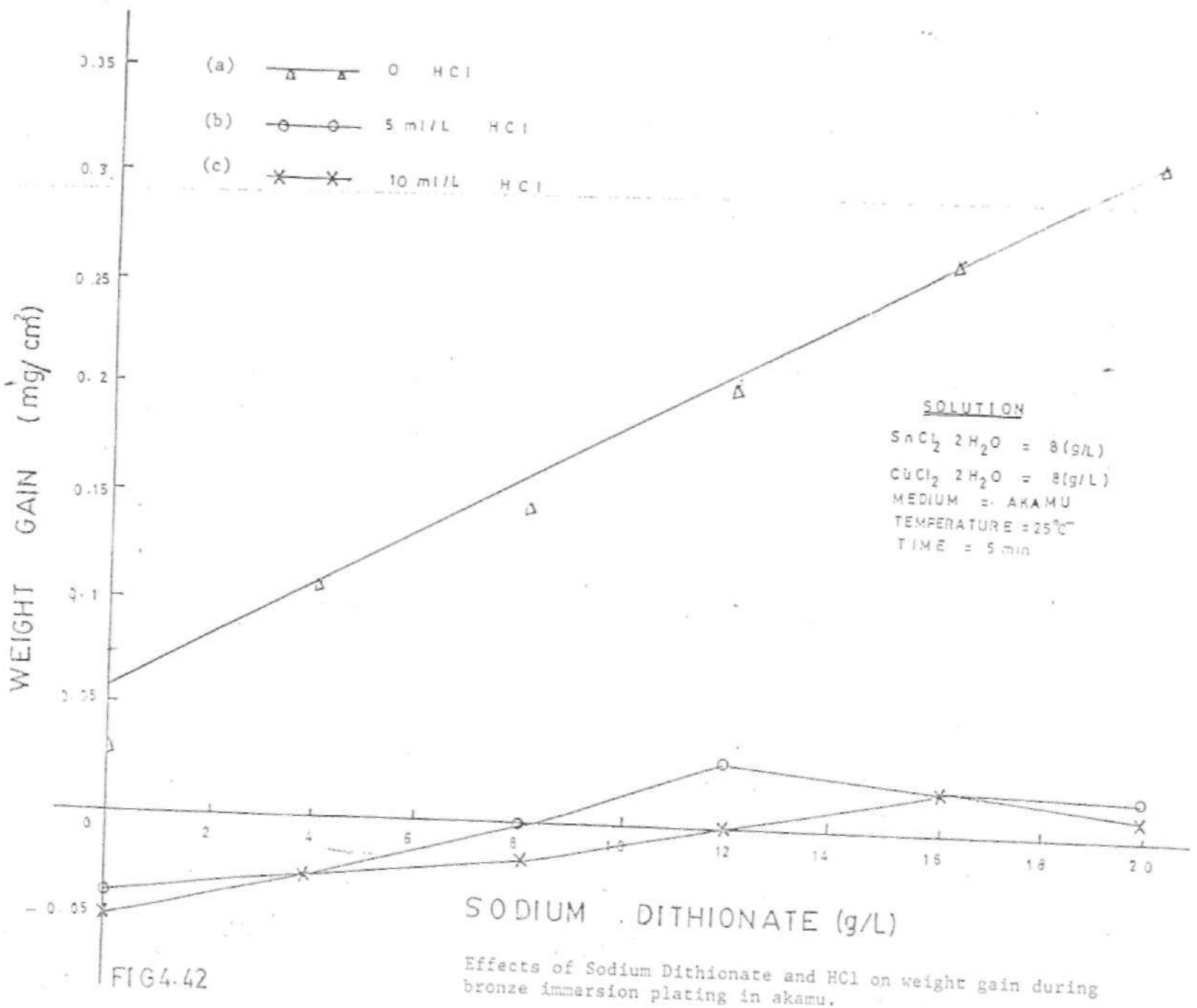


FIG4.42

Effects of Sodium Dithionate and HCl on weight gain during bronze immersion plating in akamu.

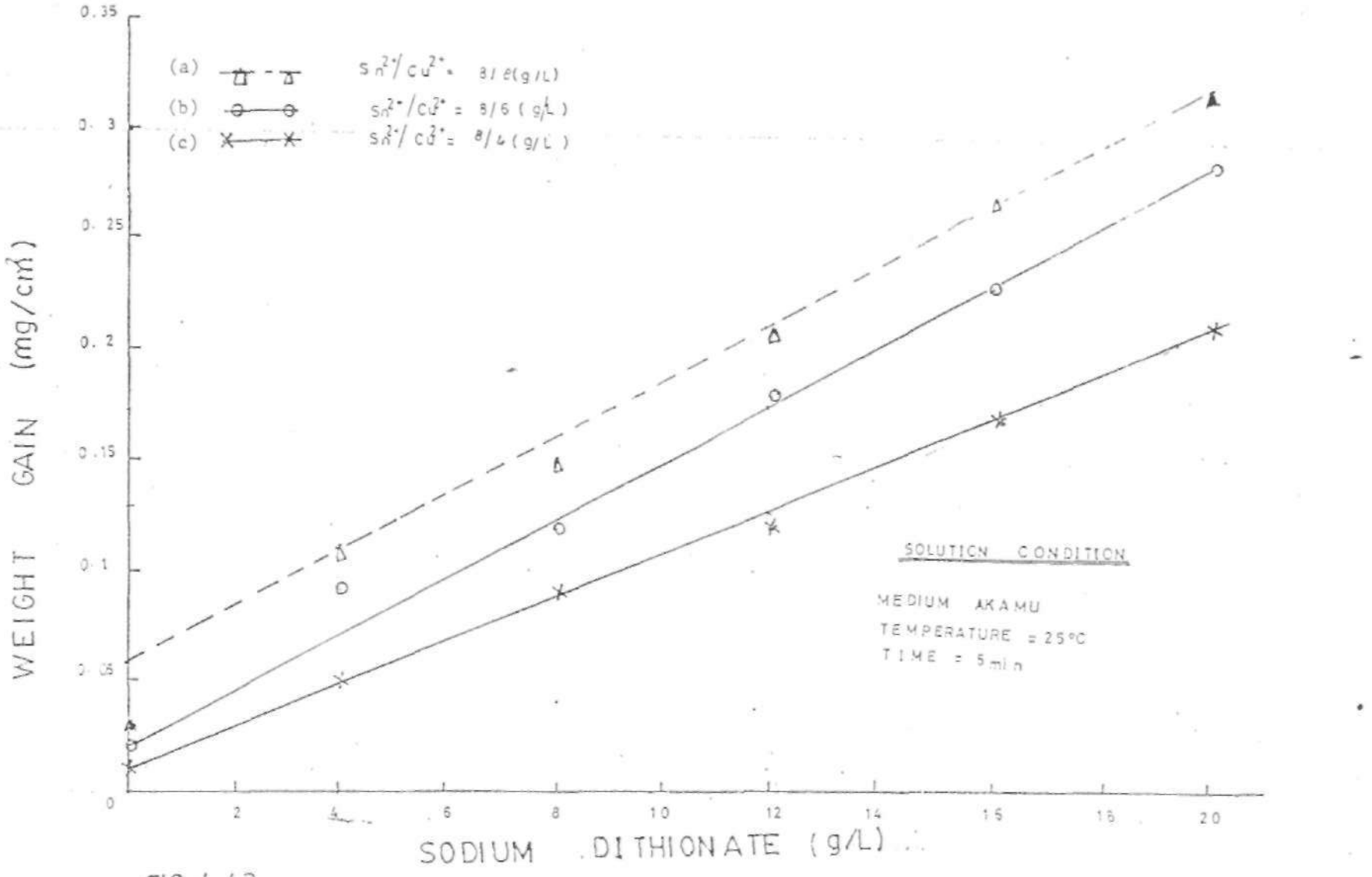


FIG 4.43

Effects of concentration and Sodium Dithionate on bronze immersion plating in akamu.

In Fig. 4.43, the equations for the linear curves are:

Curve (a), $m = 0.013$ mg cm^{-2} g^{-1} L and $k = 0.06$ mg cm^{-2}

$w = 0.013$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.06 mg cm^{-2} 4.55

Curve (b), $m = 0.013$ mg cm^{-2} g^{-1} L and $k = 0.02$ mg cm^{-2}

$w = 0.013$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.02 mg cm^{-2} 4.56

Curve (c), $m = 0.01$ mg cm^{-2} g^{-1} L and $k = 0.015$ mg cm^{-2}

$w = 0.01$ (mg cm^{-2} g^{-1} L) C_{SD} (g L^{-1}) + 0.015 mg cm^{-2} 4.57

4.3.12 MEDIA, HCl AND L-CYSTEINE EFFECTS ON COATING THICKNESS:

Figures 4.44, 4.46, 4.48, 4.50, 4.52, 4.54 and Tables 38,40, 42, 44, 46 and 48 (appendix 1) show the effects of media (aqueous, methanol, ethanol, propanol, butanol and 'akamu' respectively) and L-cysteine addition on coating thickness in bronze immersion plating solutions containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$, operated at a temperature of 25°C for 5 minutes.

The addition of HCl retards coating thickness growth in all the results. Conversely, plating in HCl-free solutions promotes the gain in coating thickness irrespective of plating medium.

Similarly, L-cysteine addition promotes coating thickness growth in acid-free solutions.

In Fig. 4.44, the equation for the linear curves are:

Curve (b), $m = 2.92$ mμm g^{-1} L and $k = 65$ mμm

$t = 2.92$ (mμm g^{-1} L) C_{LC} (g L^{-1}) + 65 mμm 4.58

where C_{LC} is the concentration of L-cysteine in solution, and t is the coating thickness in mμm.

Curve (c), m = 2.92 mμm g^{-1} L and k = 35 mμm

$t = 2.92\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 35\ m\mu m$ 4.50

In Fig. 4.46, the equations for the linear curves are:

Curve (b), m = 16.67 mμm g^{-1} L and k = 40 mμm.

$t = 16.67\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 40\ m\mu m$ 4.60

Curve (c), m = 4.167 mμm g^{-1} L and k = 30 mμm.

$t = 4.165\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 30\ m\mu m$ 4.61

In Fig. 4.48, the equations for the linear curves are:

Curves (a), m = 28.33 mμm g^{-1} L and k = 90 mμm

$t = 28.33\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 90\ m\mu m$ 4.62

Curve (b), m = 10.83 mμm g^{-1} L and k = 30 mμm.

$t = 10.83\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 30\ m\mu m$ 4.63

Curve (c), m = 8.92 mμm g^{-1} L and k = 18 mμm.

$t = 8.92\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 18\ m\mu m$..... 4.64

In Fig. 4.50, the equations for the linear curves are:

Curve (a), m = 24.58 mμm g^{-1} L and k = 80 mμm.

$t = 24.58\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 80\ m\mu m$ ..... 4.65.

Curve (b), m = 9.17 mμm g^{-1} L and k = 40 mμm.

$t = 9.17\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 40\ m\mu m$ 4.67

Curve (c), m = 3.33 mμm g^{-1} L and k = 20 mμm.

$t = 3.33$ (mμm g^{-1} L) C_{LC} ($g.L^{-1}$) + 20 mμm 4.67

In Fig. 4.52, the equations for the linear curves are:

Curve (a), m = 20.4 mμm g^{-1} L and k = 80 mμm.

$t = 20.4$ (mμm g^{-1} L) C_{LC} ($g\ L^{-1}$) + 80 mμm 4.68

Curve (b), m = 10.8 mμm g^{-1}.L and k = 25 mμm.

$t = 10.8$ (mμm. g^{-1}.L) C_{LC} ($g\ L^{-1}$) + 25 mμm 4.69

Curve (c), m = 2.9 mμm g^{-1} L and k = 20 mμm.

$t = 2.9$ (mμm g^{-1} L) C_{LC} ($g\ L^{-1}$) + 20 mμm 4.70

In Fig. 4.54, the equations for the linear curves are:

Curve (a), m = 14.08 mμm g^{-1} L and k = 55 mμm.

$t = 14.08$ (mμm g^{-1} L) C_{LC} ($g\ L^{-1}$) + 55 mμm 4.71

Curve (b), m = 9.6 mμm. g^{-1}.L and k = 45 mμm.

$t = 9.6$ (mμm g^{-1} L) C_{LC} ($g\ L^{-1}$) + 45 mμm 4.72

Curve (c), m = 1.67 mμm g^{-1} L and k = 40 mμm.

$t = 1.67$ (mμm g^{-1} L) C_{LC} ($g\ L^{-1}$) + 40 mμm 4.73

4.3.13 MEDIA, CONCENTRATION AND L-CYSTEINE EFFECTS ON COATING THICKNESS:

Figures 4.45, 4.47, 4.49, 4.51, 4.53, 4.55 and Tables 39, 41, 43, 45, 47 and 49 (appendix 1) show the effects of media (aqueous, methanol, ethanol, propanol, butanol and 'akamu' respectively), solution concentration and L-cysteine on coating thickness from bronze immersion plating solutions containing:

(i)	8 g/L	$SnCl_2.2H_2O$
	4 g/L	$CuCl_2.2H_2O$
(ii)	8 g/L	$SnCl_2.2H_2O$
	6 g/L	$CuCl_2.2H_2O$
(iii)	8 g/L	$SnCl_2.2H_2O$
	8 g/L	$CuCl_2.2H_2O$

From the results, plating favours lower molecular weight alcohols as earlier observed. The addition of L-cysteine range of concentration in the plating solutions promotes thickness growth.

Plating rate (coating thickness) increases with corresponding increase in Cu^{2+} concentration in solution.

In Fig. 4.45, the equations for the linear curves are:

Curve (b), m = 9.17 mμm. g^{-1} L and k = 60 mμm.

$t = 9.17\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 60\ \text{mμm}$ 4.74

Curve (c), m = 1.25 mμm. g^{-1} L and k = 65 mμm.

$t = 1.25\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 65\ \text{mμm}$ 4.75

In Fig. 4.47, the equations for the linear curves are:

Curve (b), m = 24.58 mμm g^{-1} L and k = 80 mμm.

$t = 24.58\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 80\ \text{mμm}$ 4.76

Curve (c), m = 16.67 mμm. g^{-1} L and k = 25 mμm.

$t = 16.67\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 25\ \text{mμm}$ 4.77

In Fig. 4.49, the equations for the linear curves are:

Curve (a), m = 28.08 mμm g^{-1} L and k = 80 mμm.

$t = 28.08\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 80\ m\mu m$ 4.78

Curve (b), m = 14.58 mμm g^{-1} L and k = 45 mμm.

$t = 14.58\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 45\ m\mu m$ 4.79

Curve (c), m = 8.75 mμm g^{-1} L and k = 40 mμm.

$t = 8.75\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 40\ m\mu m$ 4.80

In Fig. 4.51, the equations for the linear curves are:

Curve (a), m = 24.17 mμm g^{-1} L and k = 80 mμm.

$t = 24.17\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 80\ m\mu m$ 4.81

Curve (b), m = 14.17 mμm g^{-1} L and k = 50 mμm.

$t = 14.17\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 50\ m\mu m$ 4.82

Curve (c), m = 10 mμm g^{-1} L and k = 40 mμm.

$t = 10\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 40\ m\mu m$ 4.83

In Fig. 4.53, the equations for the linear curves are:

Curve (a), m = 20 mμm g^{-1} L and k = 80 mμm.

$t = 20\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 80\ m\mu m$ 4.84

Curve (b), m = 10 mμm g^{-1} L and k = 60 mμm.

$t = 10\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 60\ m\mu m$ 4.85

Curve (c), m = 9.4 mμm g^{-1} L and k = 37 mμm.

$t = 9.4\ (m\mu m\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 37\ m\mu m$ 4.86

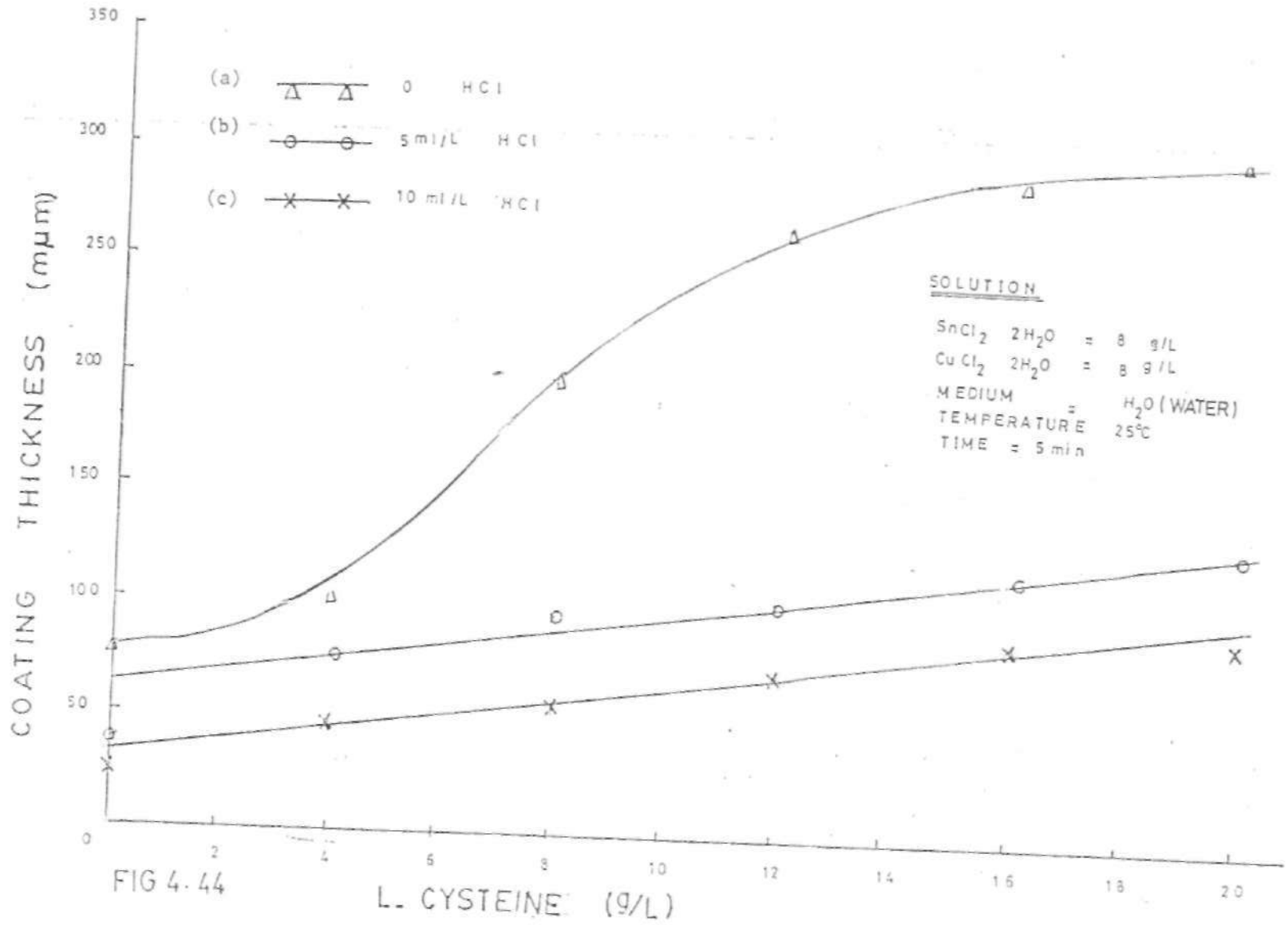


FIG 4.44

Effects of L-cysteine and HCl on bronze immersion plating in distilled water.

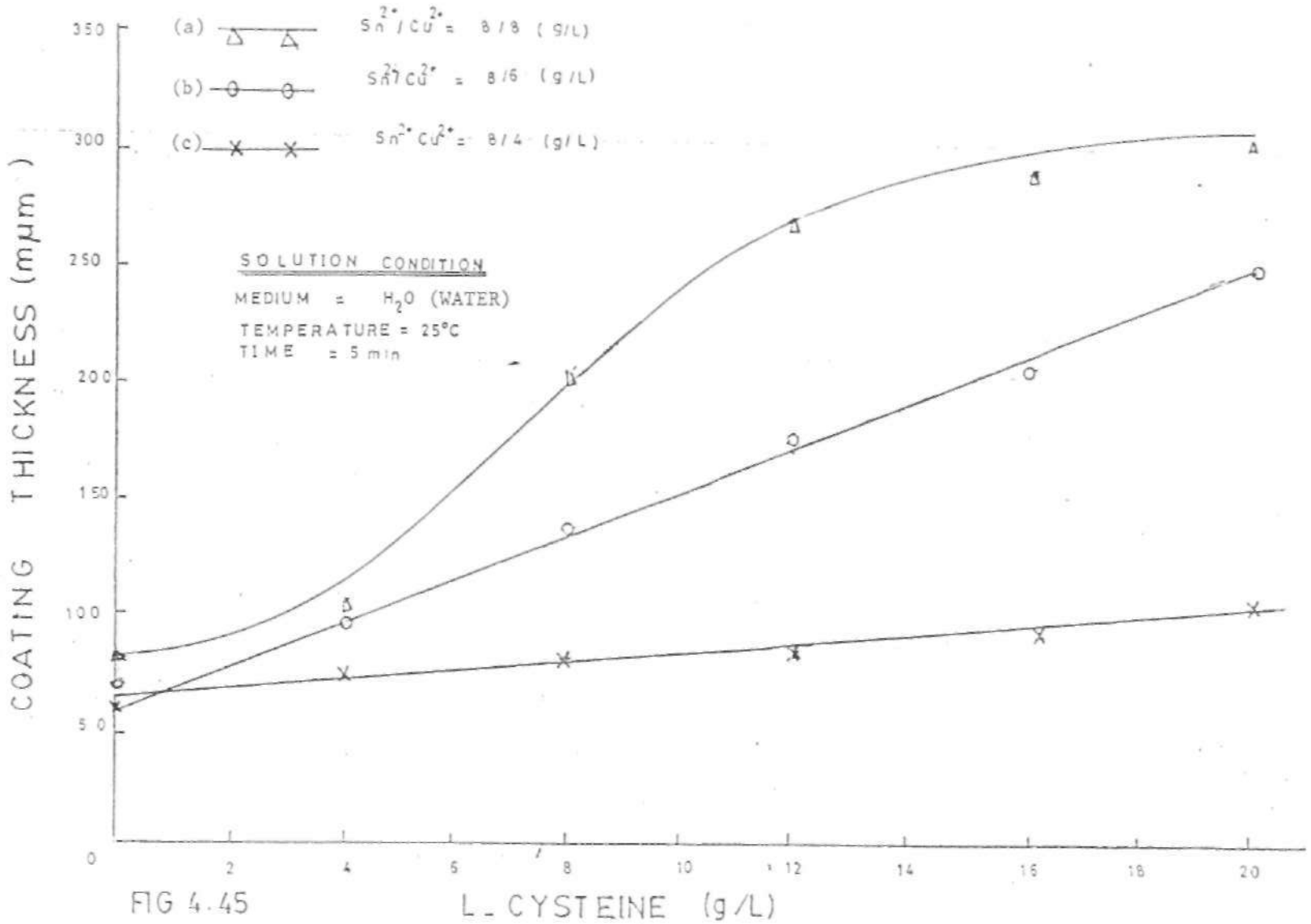


FIG 4.45

Effects of concentration and L-cysteine on bronze immersion plating in distilled water.

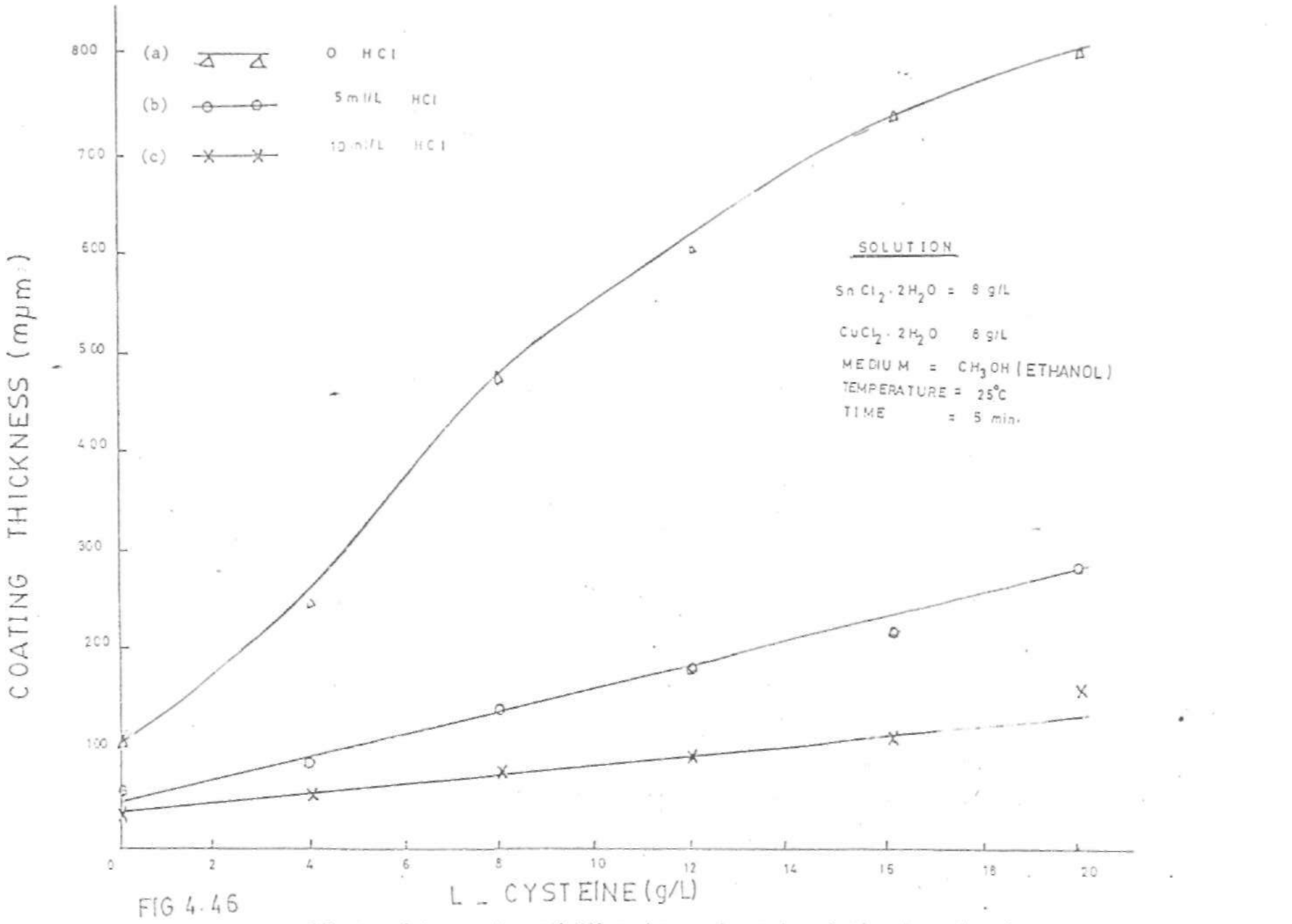


FIG 4.46

Effects of L-cysteine and HCl on bronze immersion plating in methanol.

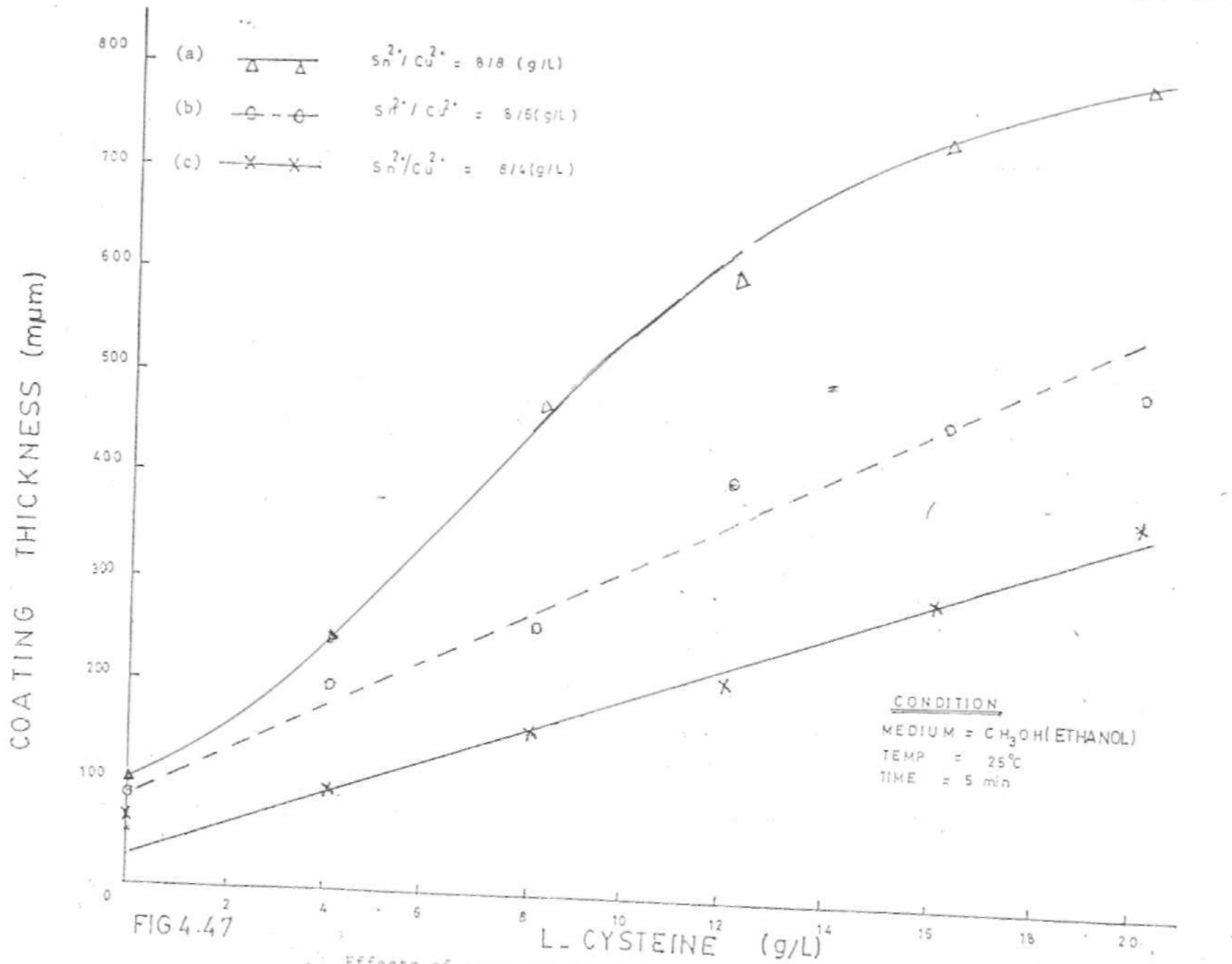


FIG 4.47

Effects of concentration and L-cysteine on bronze immersion plating in methanol

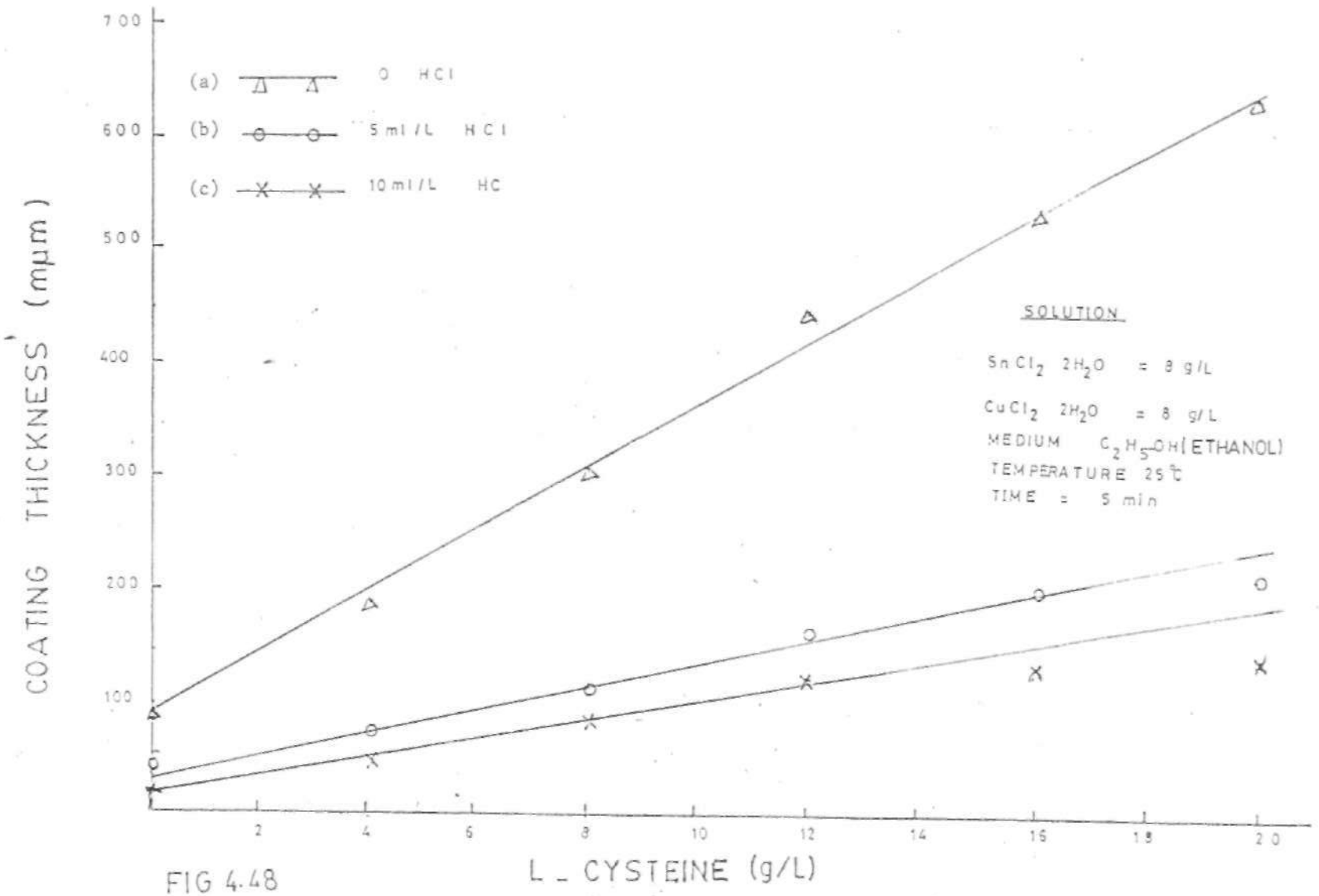


FIG 4.48

Effects of L-cysteine and HCl on bronze immersion plating in ethanol.

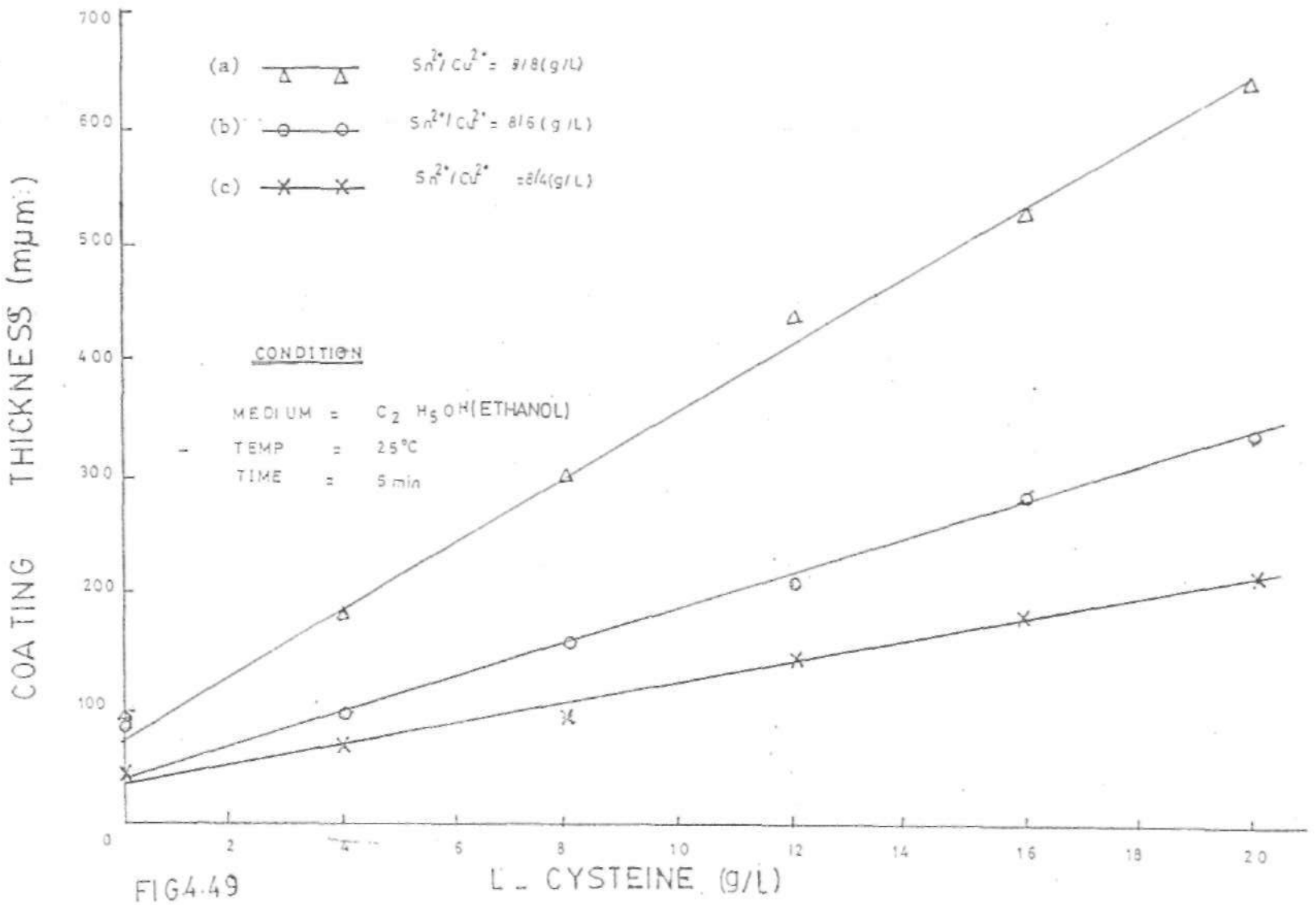


FIG4.49

Effects of concentration and L-cysteine on bronze immersion plating in ethanol.

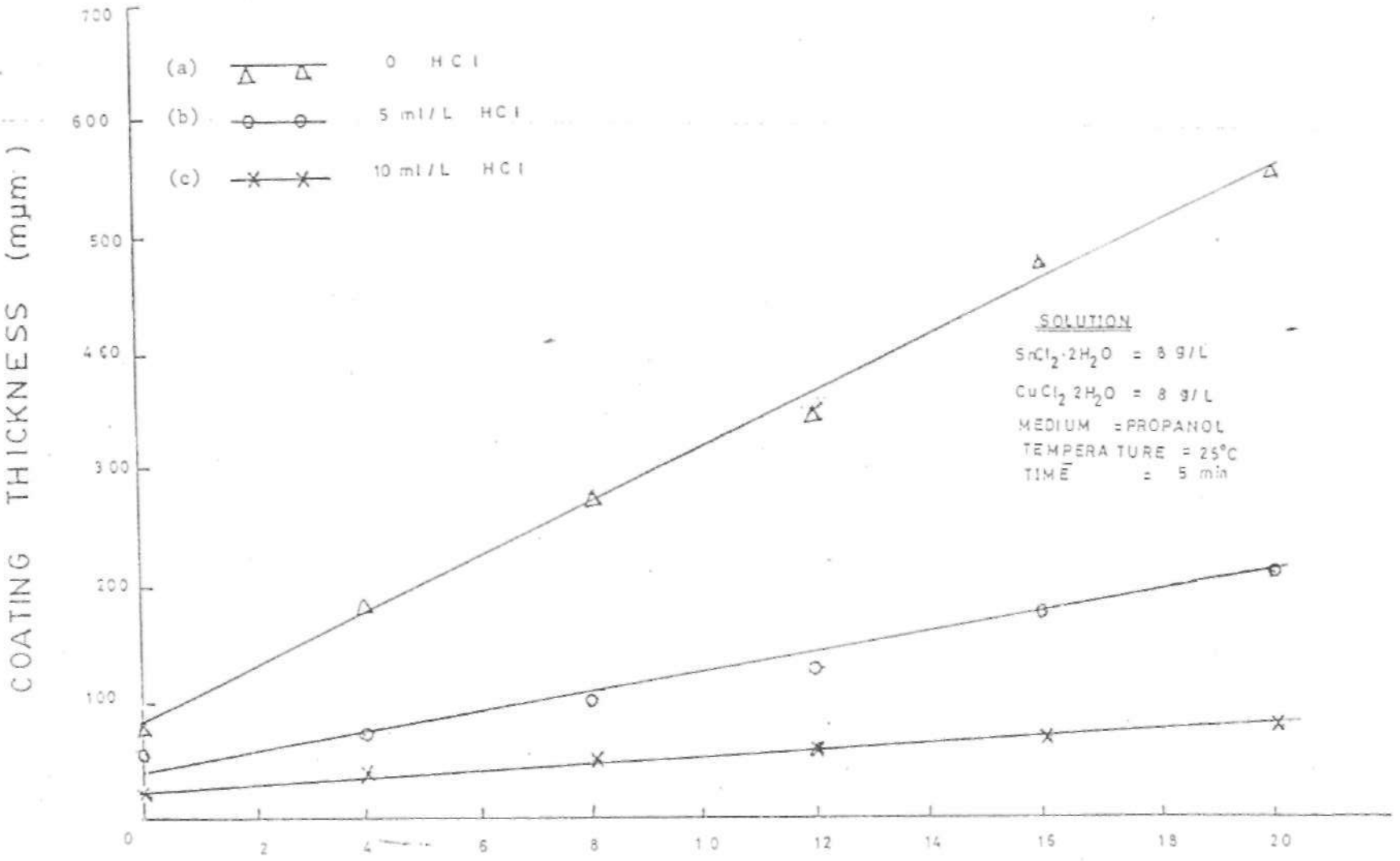


FIG 4.50

Effects of L-cysteine and HCl on bronze immersion plating in propanol.

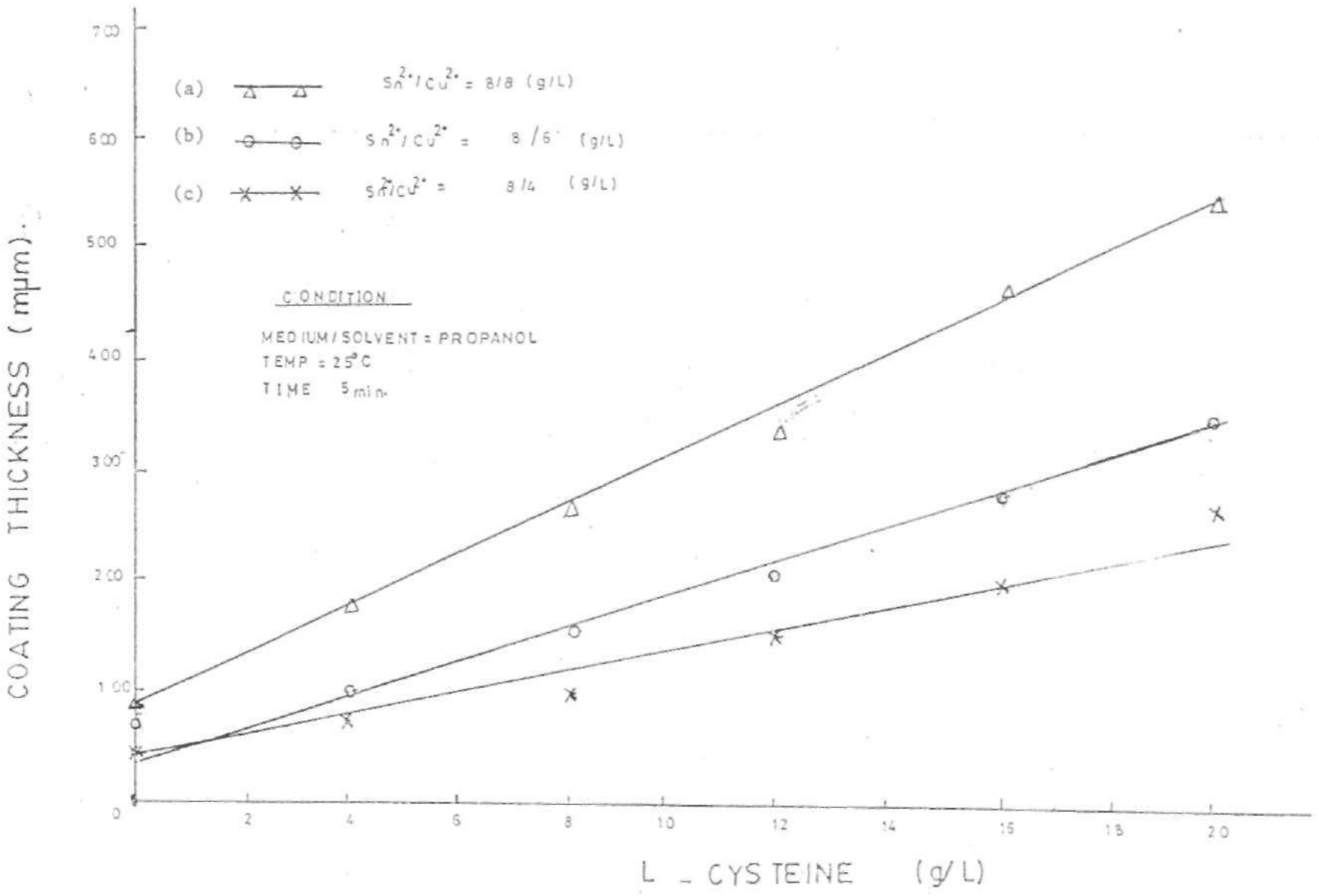


FIG4.51 Effects of concentration and L-cysteine on bronze immersion plating in propanol.

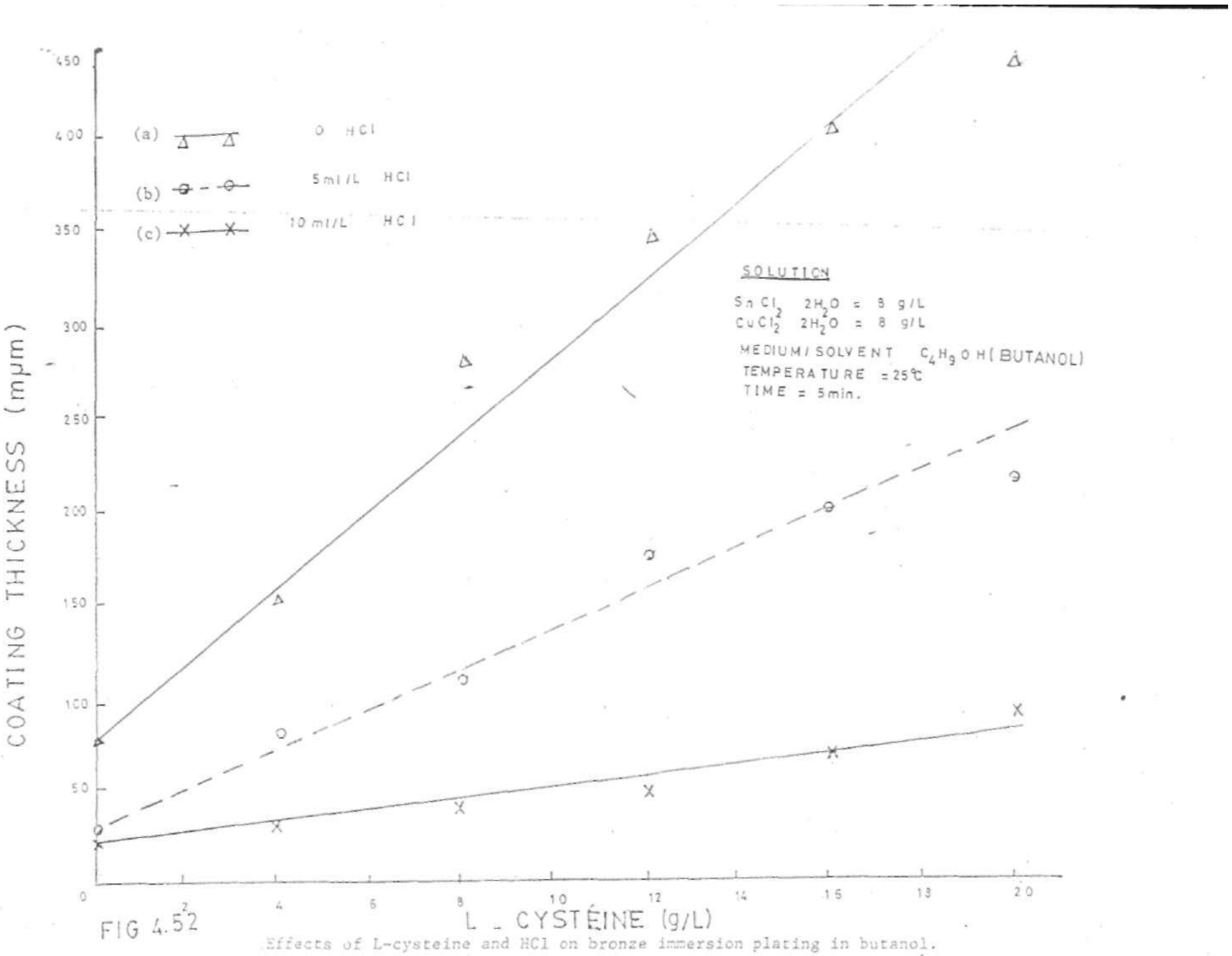


FIG 4.52

Effects of L-cysteine and HCl on bronze immersion plating in butanol.

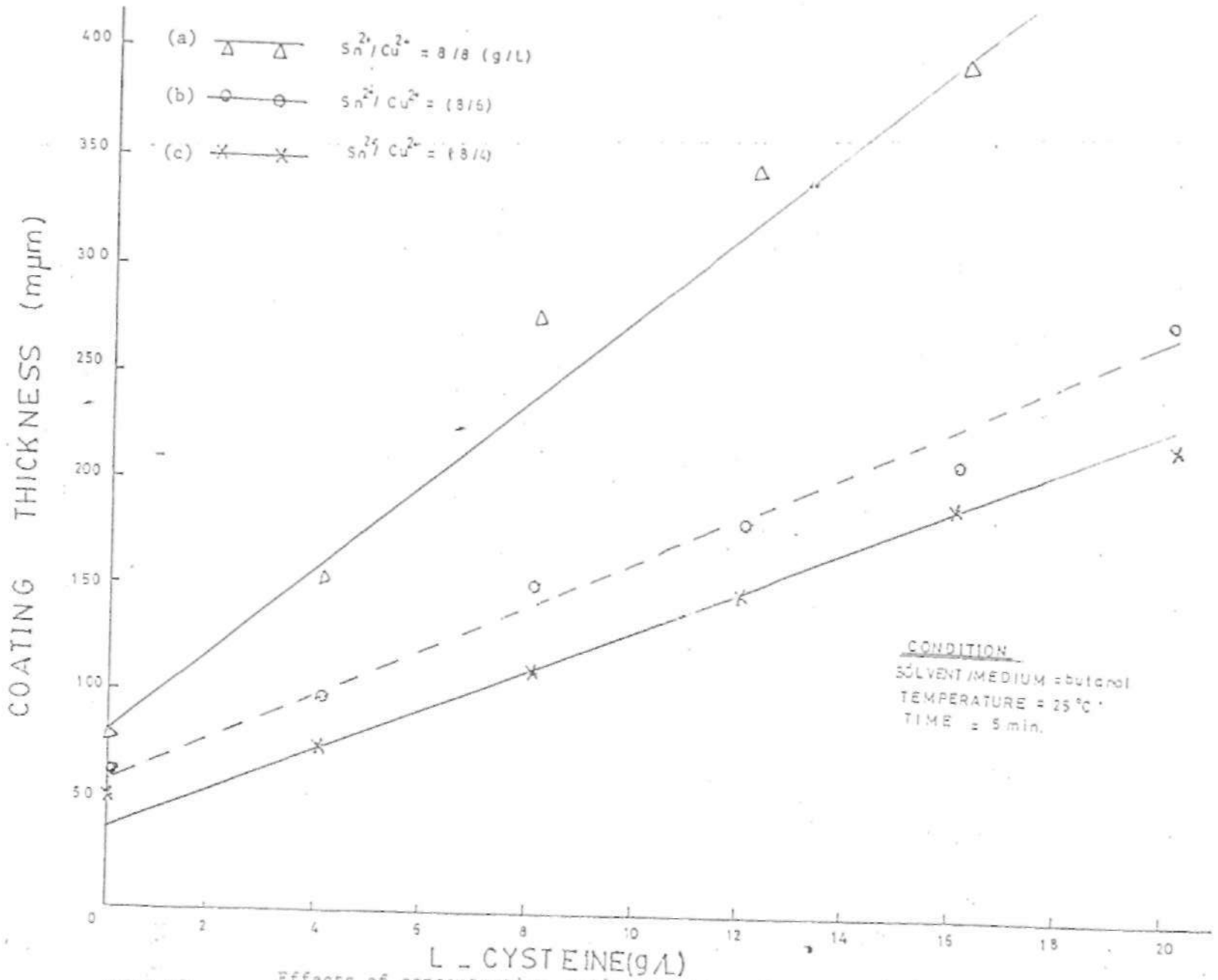


FIG 4.53 Effects of concentration and L-cysteine on bronze immersion plating in butanol.

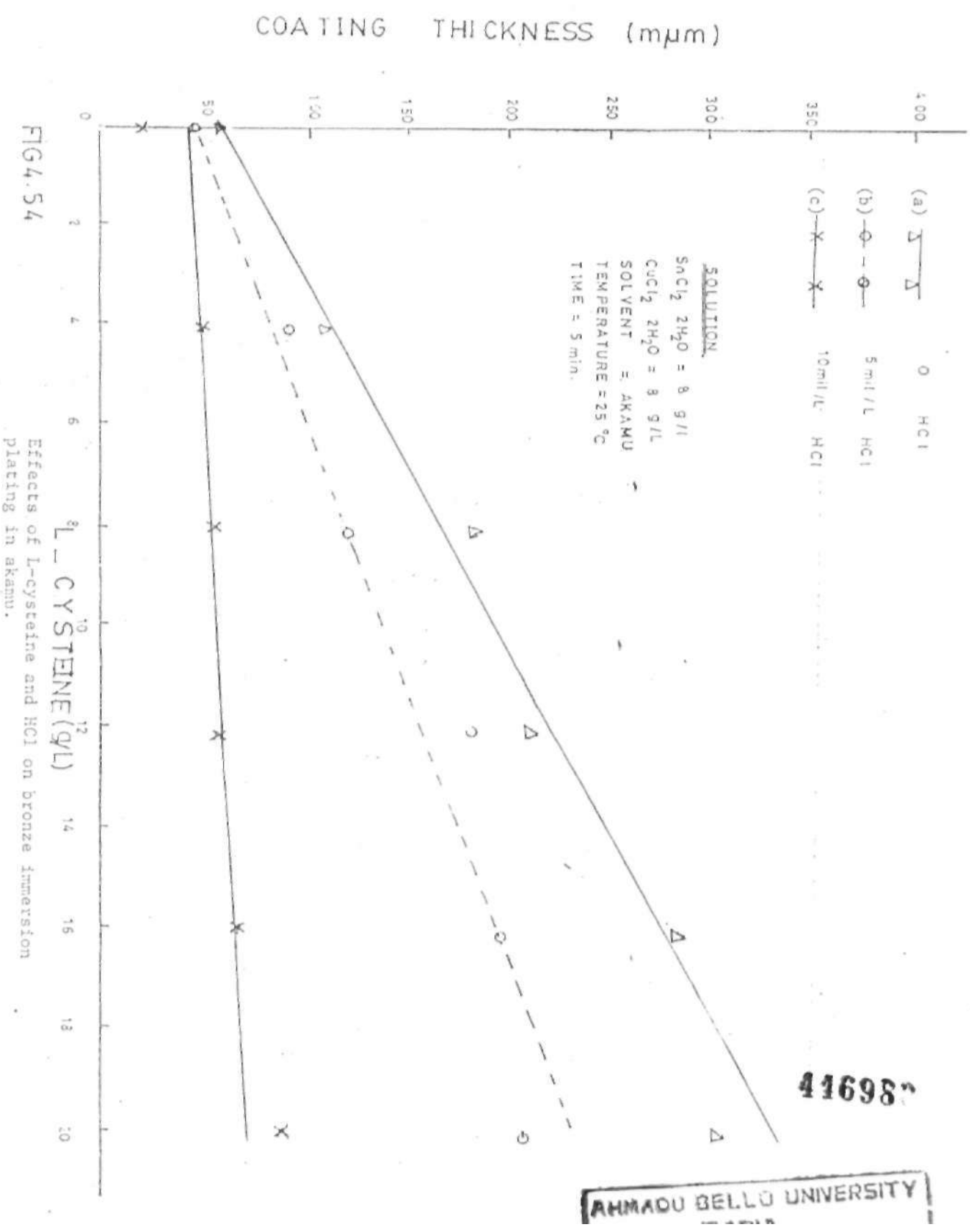


FIG 4.54

Effects of L-cysteine and HCl on bronze immersion plating in akamu.

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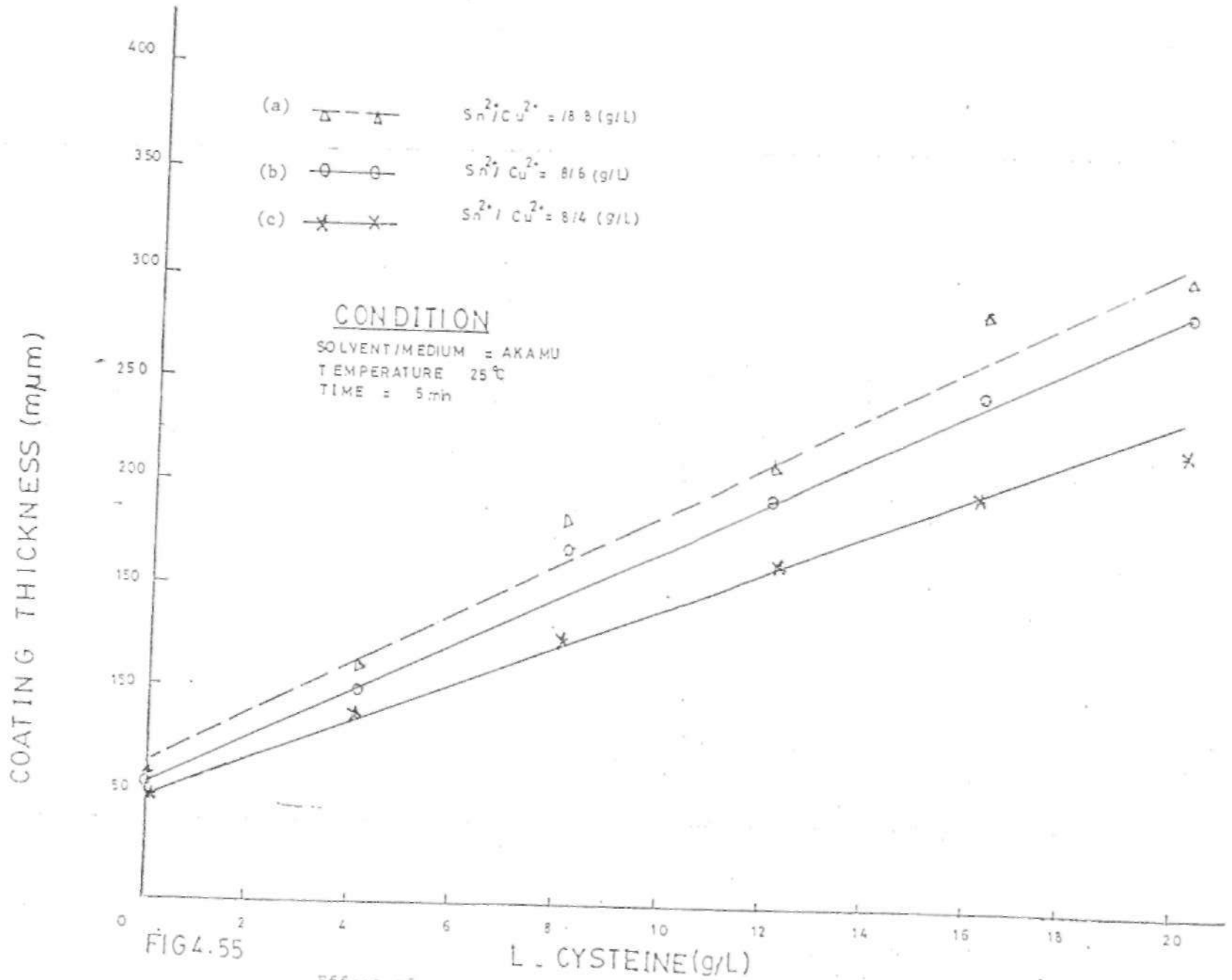

FIG4.55

Effect of concentration and L-ctsteine on bronze immersion plating in Akamu.

In Fig. 4.55, the equations for the linear curves are:

Curve (a), m = 12.33 mμm g^{-1} L and k = 62 mμm.

$t = 12.33\ (\text{mμm}\ g^{-1}.L)\ C_{LC}\ (g\ L^{-1}) + 62\ \text{mμm}$ 4.87

Curve (b), m = 11.25 mμm g^{-1} L and k = 50 mμm.

$t = 11.25\ (\text{mμm},\ g^{-1}\ L)\ C_{LC}\ (g.L^{-1}) + 50\ \text{mμm}$ 4.88

Curve (c), m = 9.58 mμm g^{-1} L and k = 45 mμm.

$t = 9.58\ (\text{mμm}.\ g^{-1}.L)\ C_{LC}\ (g.L^{-1}) + 45\ \text{mμm}$ 4.89

4.3.14 MEDIA, HCl, AND THIOUREA EFFECTS ON COATING THICKNESS:

Figures 4.56, 4.58, 4.60, 4.62, 4.64, 4.66 and Tables 50, 52, 54, 56, 58 and 60 (appendix 1) show the effects of media (aqueous, methanol, ethanol, propanol, butanol and 'akamu' respectively) and thiourea addition on coating thickness in bronze immersion plating solution containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$, operated at a temperature of 25°C for 5 minutes.

From all the Figures, the addition of HCl retards the gain in coating thickness; whereas, plating in HCl-free solutions promotes coating thickness growth irrespective of plating medium. Also, the addition of thiourea promotes coating thickness growth in all the acid-free solutions.

In Fig. 4.56, the equations for the linear curves are:

Curve (a), m = 31.25 mμm g^{-1} L and k = 165 mμm.

$t = 31.25\ (\text{mμm}\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 165\ \text{mμm}$ 4.90

where C_{TH} is the concentration of thiourea in solution.

Curve (b), m = 7.5 mμm g^{-1} L and k = 80 mμm.

$t = 7.5\ (\text{mμm}\ g^{-I}\ L)\ C_{TH}\ (g\ L^{-1}) + 80\ \text{mμm}$ 4.91

Curve (c), m = 6.25 mμm. g^{-1} L and k = 50 mμm.

$t = 6.25\ (\text{mμm. } g^{-1}\text{ L})\ C_{TH}\ (\text{g } L^{-1}) + 50\ \text{mμm}$ 4.92

In Fig. 4.58, the equations for the linear curves are:

Curve (a), m = 35.4 mμm g^{-1}.L and k = 250 mμm.

$t = 35.4\ (\text{mμm } g^{-1}\text{ L})\ C_{TH}\ (\text{g } L^{-1}) + 250\ \text{mμm}$ 4.93

Curve (b), m = 12.5 mμm g^{-1}.L and k = 100 mμm.

$t = 12.5\ (\text{mμm } g^{-1}\text{ L})\ C_{TH}\ (\text{g } L^{-1}) + 100\ \text{mμm}$ 4.94

Curve (c), m = 6.25 mμm. g^{-1} L and k = 100 mμm.

$t = 6.25\ (\text{mμm. } g^{-1}\text{.L})\ C_{TH}\ (\text{g } L^{-1}) + 100\ \text{mμm}$ 4.95

In Fig. 4.60, the equations for the linear curves are:

Curve (a), m = 28.75 mμm g^{-1} L and k = 120 mμm.

$t = 28.75\ (\text{mμm } g^{-1}\text{ L})\ C_{TH}\ (\text{g } L^{-1}) + 120\ \text{mμm}$ 4.96

Curve (b), m = 12.5 mμm g^{-1} L and k = 80 mμm.

$t = 12.5\ (\text{mμm } g^{-1}\text{ L})\ C_{TH}\ (\text{g } L^{-1}) + 80\ \text{mμm}$ 4.97

Curve (c), m = 7.9 mμm g^{-1} L and k = 70 mμm.

$t = 7.9\ (\text{mμm. } g^{-1}\text{ L})\ C_{TH}\ (\text{g } L^{-1}) + 70\ \text{mμm}$ 4.98

In Fig. 4.62, the equations for the linear relationship are:

Curve (a), m = 12.75 mμm g^{-1} L and k = 160 mμm.

$t = 12.75\ (\text{mμm } g^{-1}\text{ L})\ C_{TH}\ (\text{g } L^{-1}) + 160\ \text{mμm}$ 4.99

Curve (b), m = 12.08 mμm g^{-1}.L and k = 80 mμm.

$t = 12.08\ (\text{mμm } g^{-1}\text{ L})\ C_{TH}\ (\text{g } L^{-1}) + 80\ \text{mμm}$ 4.100

Curve (c), m = 6.25 mμm g^{-1} L and k = 40 mμm.

t = 6.25 (mμm g^{-1} L) C_{TH} (g L^{-1}) + 40 mμm 4.101

In Fig. 4.64, the equations for the linear curves are:

Curve (a), m = 15.83 mμm g^{-1} L and k = 80 mμm.

t = 15.83 (mμm. g^{-1} L) C_{TH} (g L^{-1}) + 80 mμm 4.102

Curve (b), m = 11.67 mμm. g^{-1}.L and k = 50 mμm.

t = 11.67 (mμm. g^{-1} L) C_{TH} (g L^{-1}) + 50 mμm 4.103

Curve (c), m = 8.08 mμm g^{-1} L and k = 40 mμm.

t = 8.08 (mμm. g^{-1} L) C_{TH} (g L^{-1}) + 40 mμm 4.104

In Fig. 4.66, the equations for the linear curves are:

Curve (a), m = 8.42 mμm. g^{-1} L and k = 62 mμm.

t = 8.42 (mμm. g^{-1} L) C_{TH} (g L^{-1}) + 62 mμm 4.105

Curve (b), m = 5.83 mμm g^{-1} L and k = 50 mμm.

t = 5.83 (mμm g^{-1} L) C_{TH} (g L^{-1}) + 50 mμm 4.106

Curve (c), m = 12.25 mμm g^{-1} L and k = 40 mμm.

t = 12.25 (mμm g^{-1} L) C_{TH} (g L^{-1}) + 40 mμm 4.107

4.2.15 MEDIA, CONCENTRATION AND THIOUREA EFFECTS ON COATING THICKNESS:

Figures 4.59, 4.61, 4.63, 4.65, 4.67 and Tables 53, 55, 57, 59 and 61 (appendix 1) show the effects of media (distilled water, methanol, ethanol, propanol, butanol and 'akamu' respectively), solution concentration and thiourea addition on bronze immersion plating solutions containing:

(i) 8 g/L $SnCl_2.2H_2O$

4 g/L $CuCl_2.2H_2O$

(ii) 8 g/L $SnCl_2.2H_2O$

6 g/L $CuCl_2.2H_2O$

(iii) 8 g/L $SnCl_2.2H_2O$

8 g/L $CuCl_2.2H_2O$

The addition of thiourea in the plating solution promotes coating thickness growth.

The plating rate also increases with the corresponding increase in cupric ion concentration in solution.

In Fig. 4.57, the equations for the linear curves are:

Curve (a), $m = 22.1$ mμm g^{-1} L and $k = 280$ mμm.

$t = 22.1$ (mμm g^{-1} L) C_{TH} (g L^{-1}) + 280 mμm 4.108

Curve (b), $m = 20.8$ mμm g^{-1} L and $k = 100$ mμm.

$t = 20.8$ (mμm g^{-1} L) C_{TH} (g L^{-1}) + 100 mμm 4.109

Curve (c), $m = 12.5$ mμm g^{-1} L and $k = 80$ mμm.

$t = 12.5$ (mμm g^{-1} L) C_{TH} (g L^{-1}) + 80 mμm 4.110

In Fig. 4.59, the equations for the linear curves are:

Curve (a), $m = 36.67$ mμm g^{-1} L and $k = 220$ mμm.

$t = 36.67$ (mμm g^{-1} L) C_{TH} (g L^{-1}) + 220 mμm 4.111

Curve (b), $m = 16.67$ mμm g^{-1} L and $k = 180$ mμm.

$t = 16.67$ (mμm g^{-1} L) C_{TH} (g L^{-1}) + 180 mμm 4.112

Curve (c), m = 20 mμm g^{-1} L and k = 80 mμm.

$t = 20\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 80\ m\mu m$ 4.113

In Fig. 4.61, the equations for the linear curves are:

Curve (a), m = 26.25 mμm g^{-1} L and k = 165 mμm.

$t = 26.25\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 165\ m\mu m$ 4.114

Curve (b), m = 14.17 mμm g^{-1} L and k = 150 mμm.

$t = 14.17\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 150\ m\mu m$ 4.115

Curve (C), m = 12.08 mμm g^{-1} L and k = 90 mμm.

$t = 12.08\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 90\ m\mu m$ 4.116

In Fig. 4.63, the equations for the linear curves are:

Curve (a), m = 14.75 mμm g^{-1} L and k = 148 mμm.

$t = 14.75\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 148\ m\mu m$ 4.117

Curve (b), m = 11.92 mμm g^{-1} L and k = 115 mμm.

$t = 11.92\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 115\ m\mu m$ 4.118

Curve (c), m = 11.4 mμm g^{-1} L and k = 75 mμm.

$t = 11.4\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 75 m\mu m$ 4.119

In Fig. 4.65, the equations for the linear curves are:

Curve (a), m = 15.83 mμm g^{-1} L and k = 75 mμm.

$t = 15.83\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 75\ m\mu m$ 4.120

Curve (b), m = 13.75 mμm g^{-1} L and k = 60 mμm.

$t = 13.75\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 60\ m\mu m$ 4.21

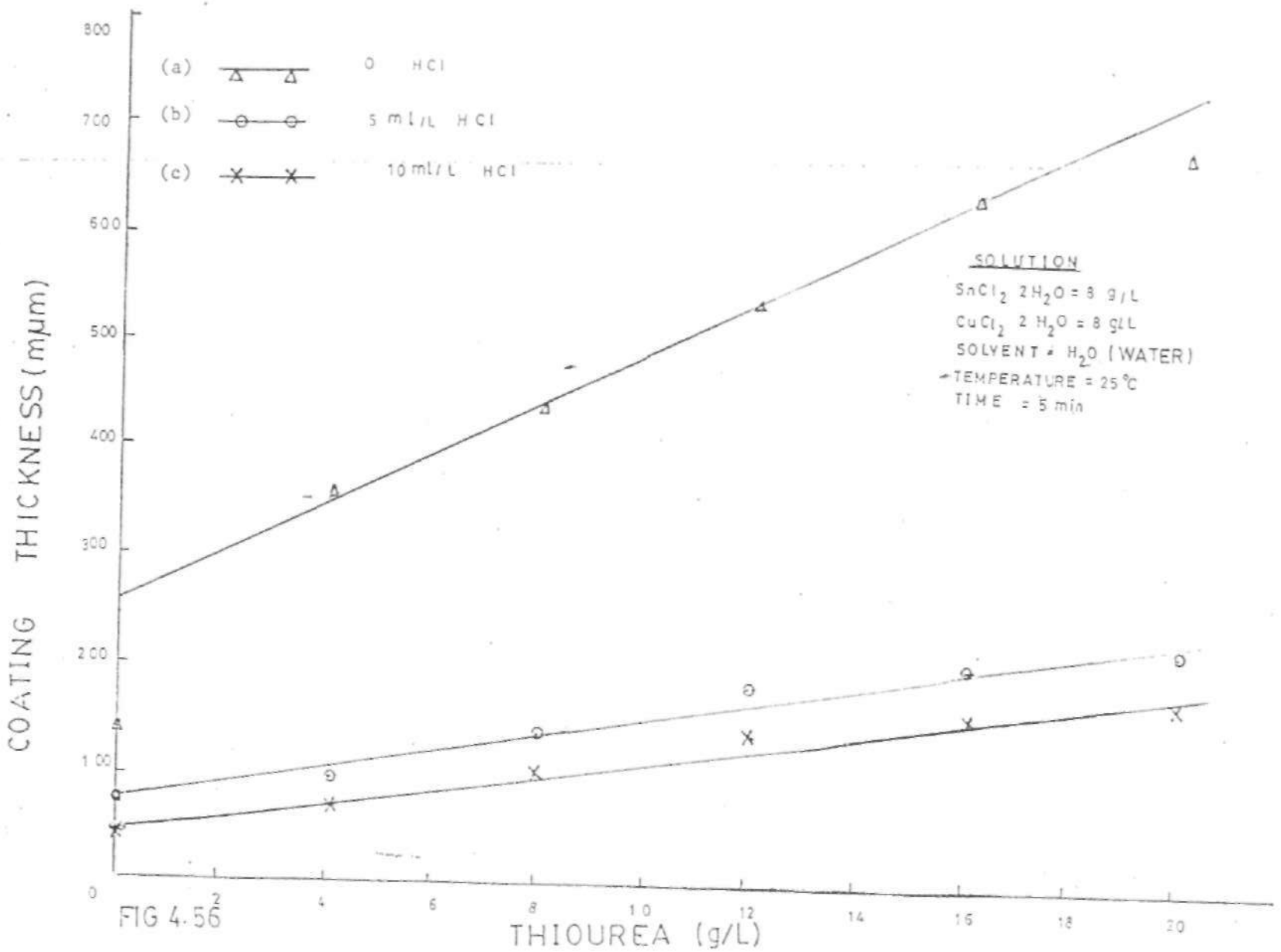

FIG 4.56

Effects of thiourea and HCl on bronze immersion plating in distilled water.

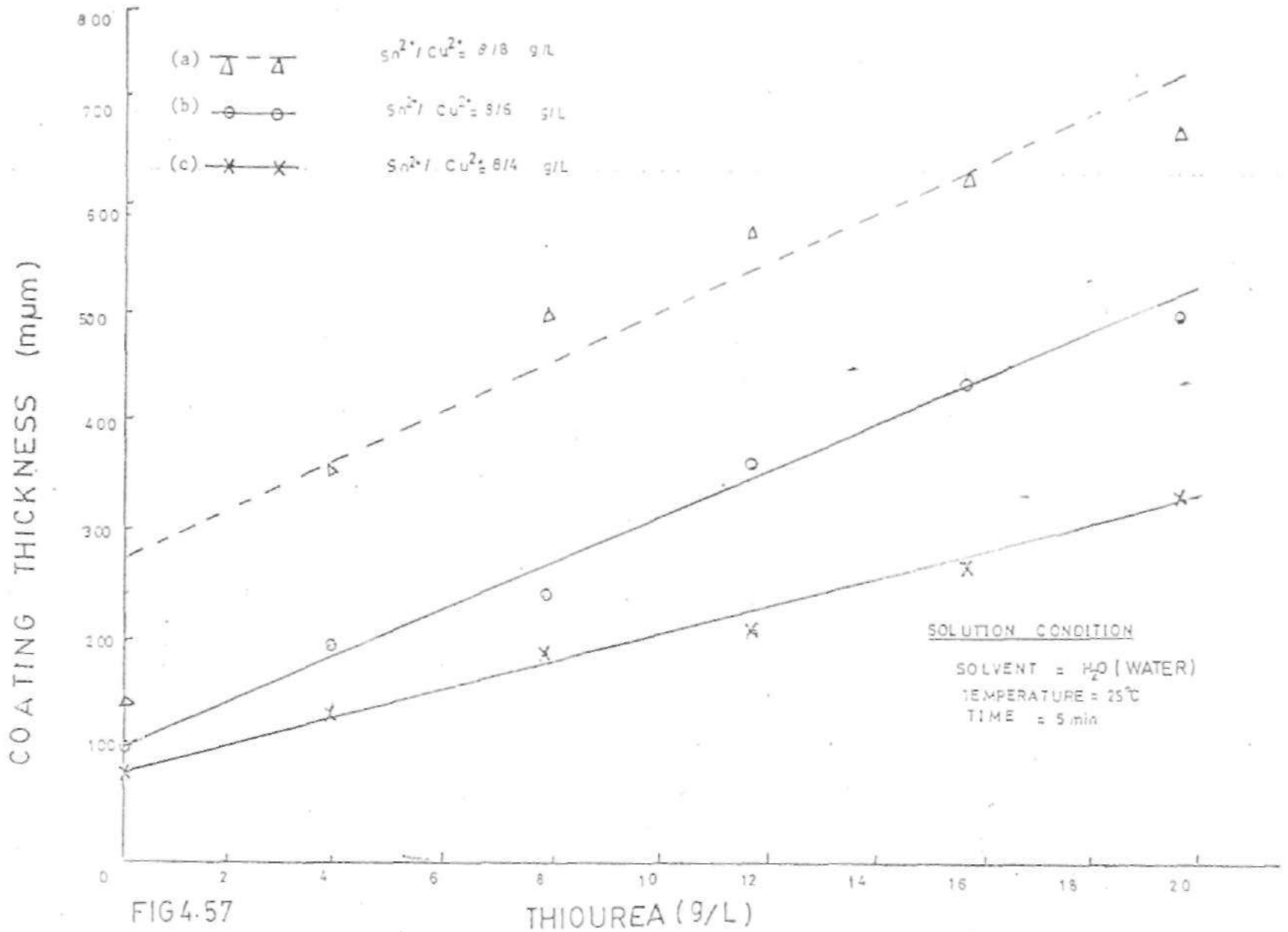

FIG 4.57

Effects of concentration and thiourea on bronze immersion plating in distilled water.

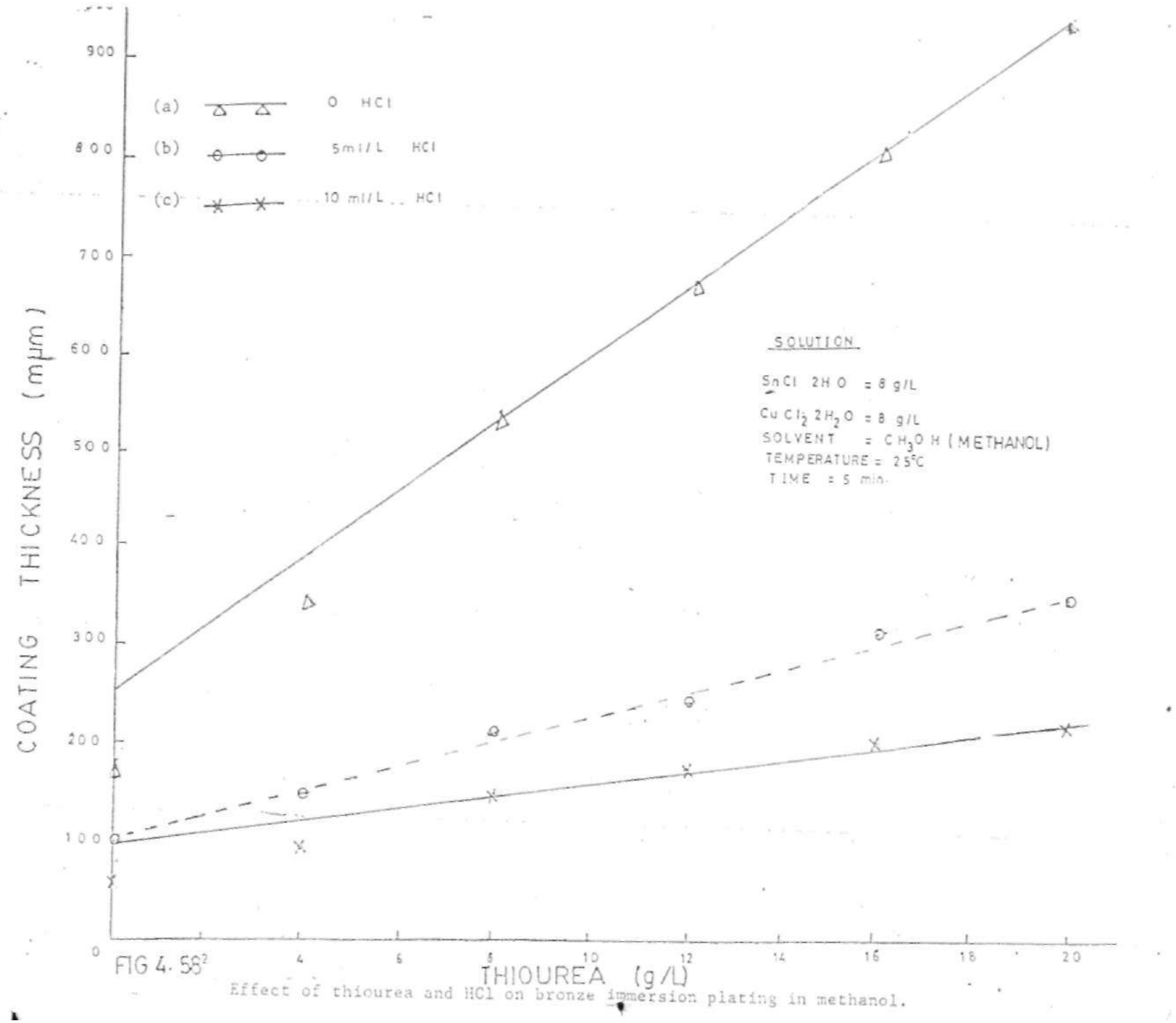

FIG 4.58

Effect of thiourea and HCl on bronze immersion plating in methanol.

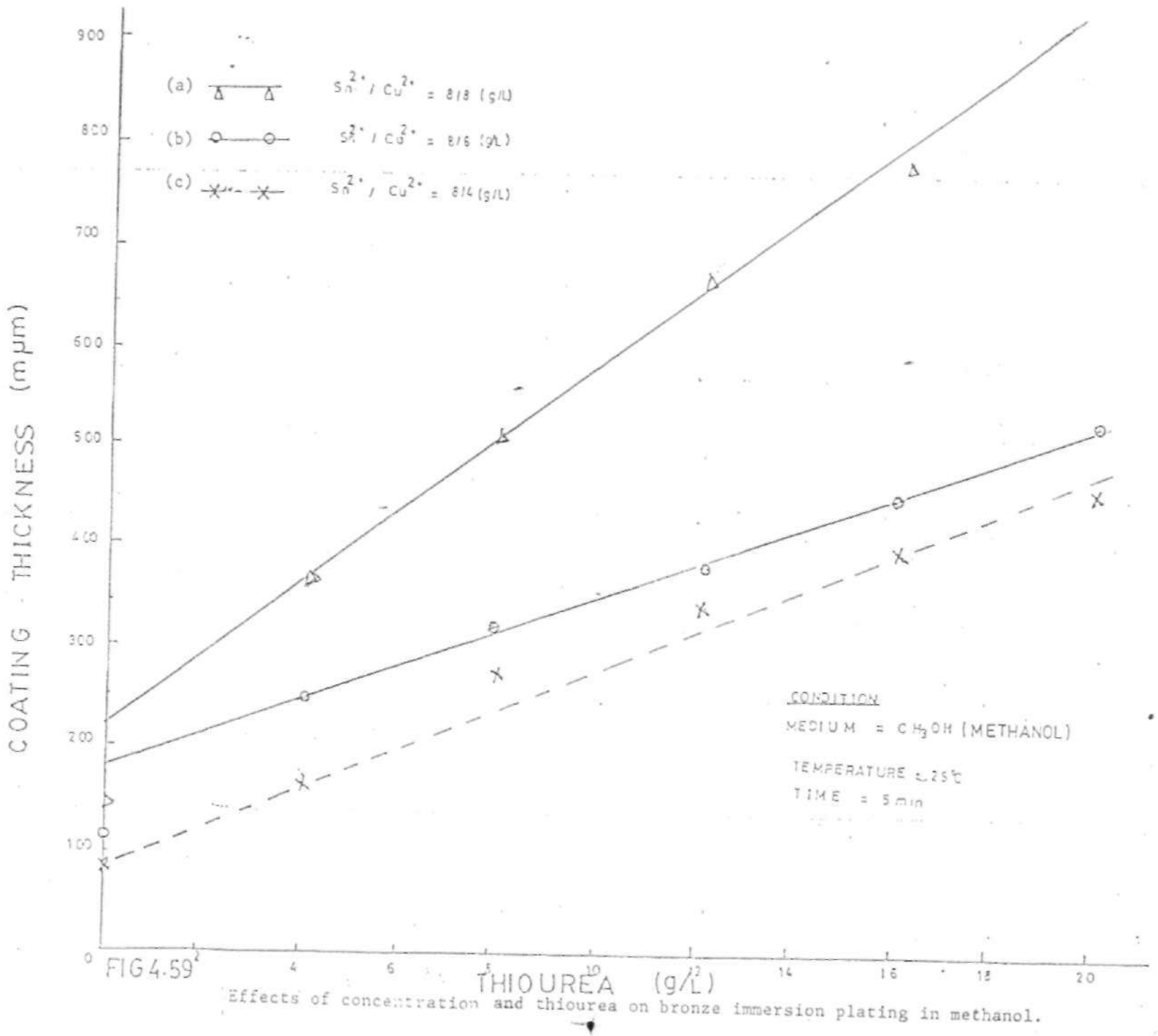

FIG 4.59 Effects of concentration and thiourea on bronze immersion plating in methanol.

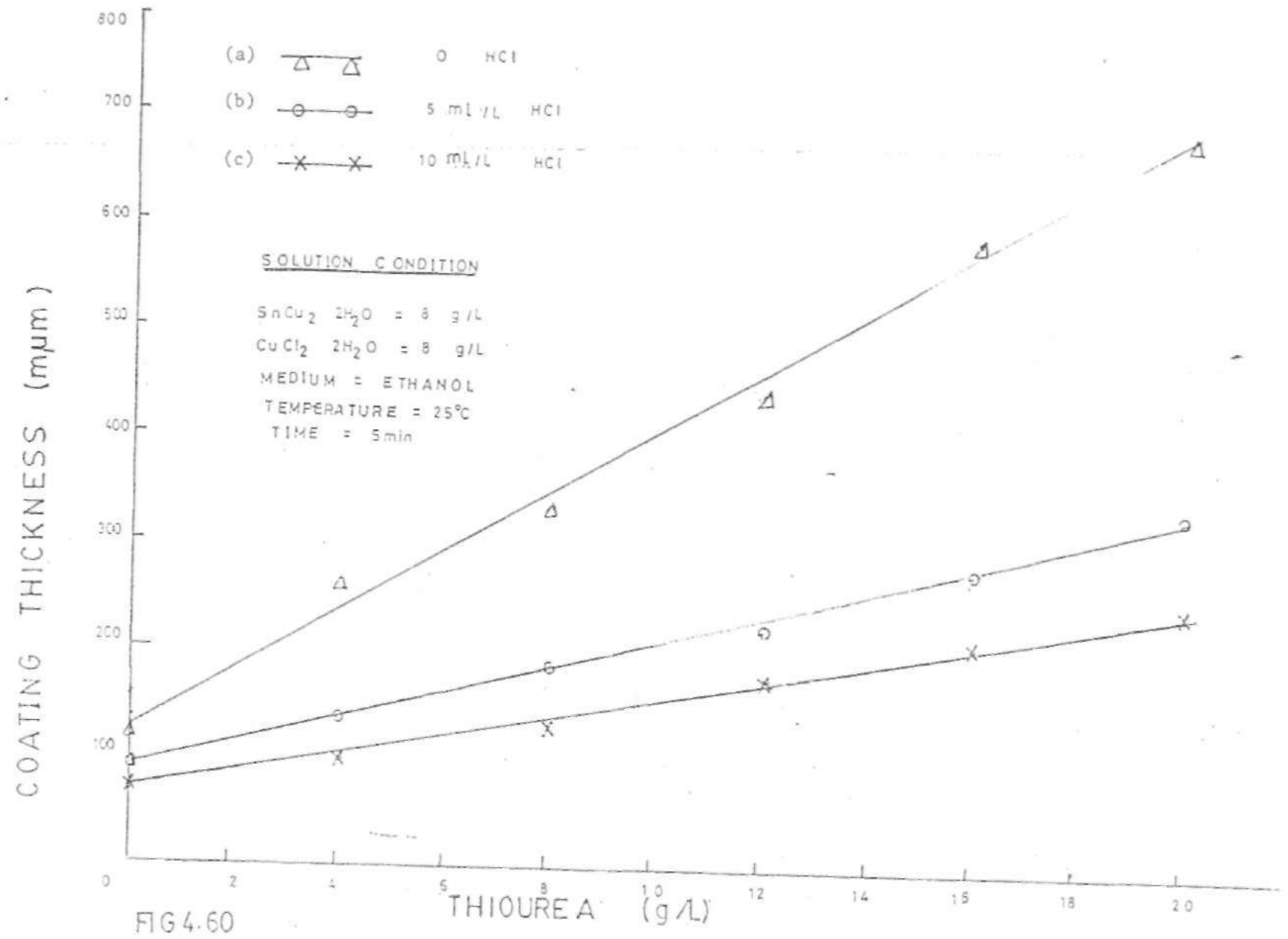

FIG 4.60

Effects of Thiourea and HCl on bronze immersion plating in ethanol.

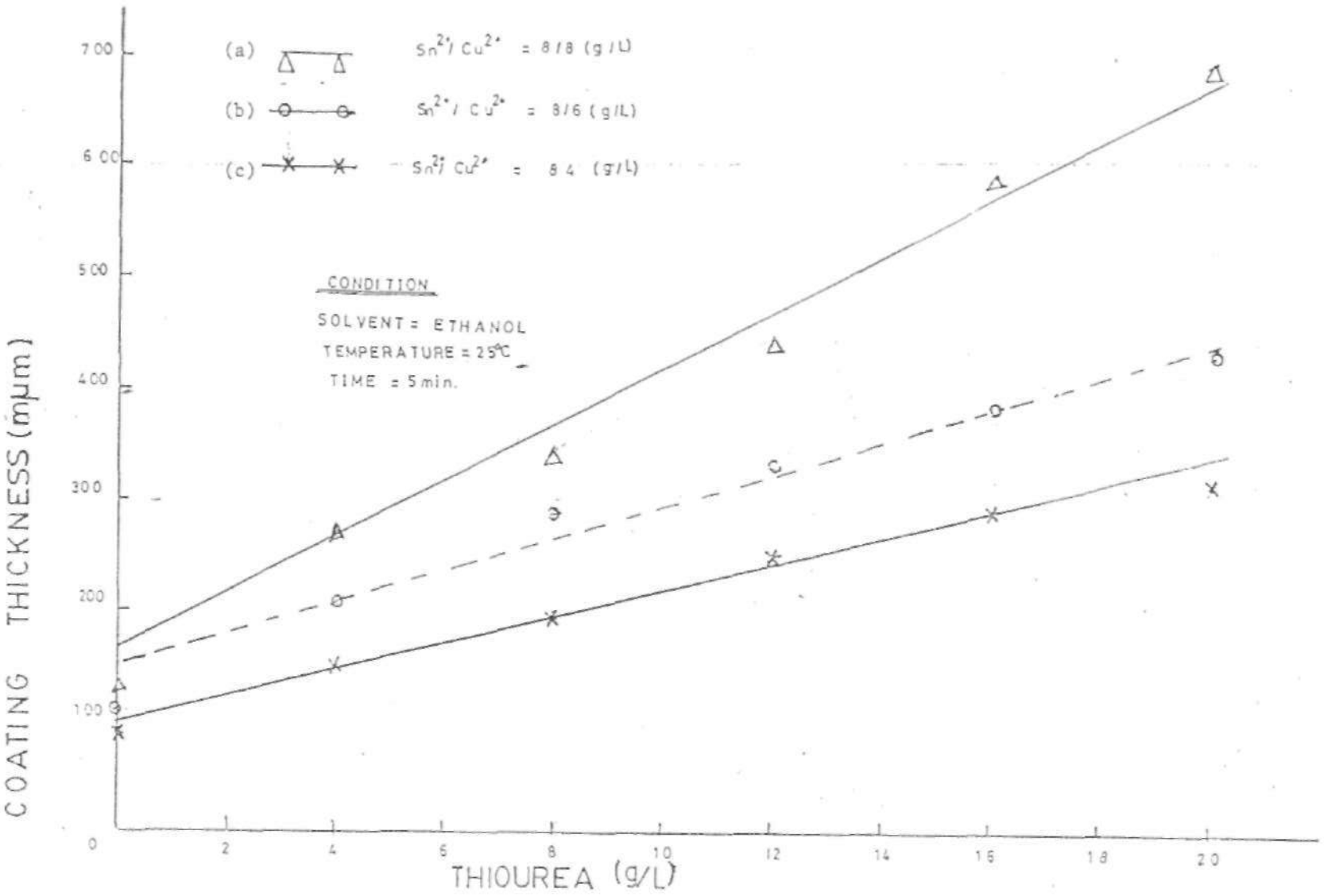

FIG4.61 Effects of thiourea and concentration on bronze immersion plating in ethanol medium.

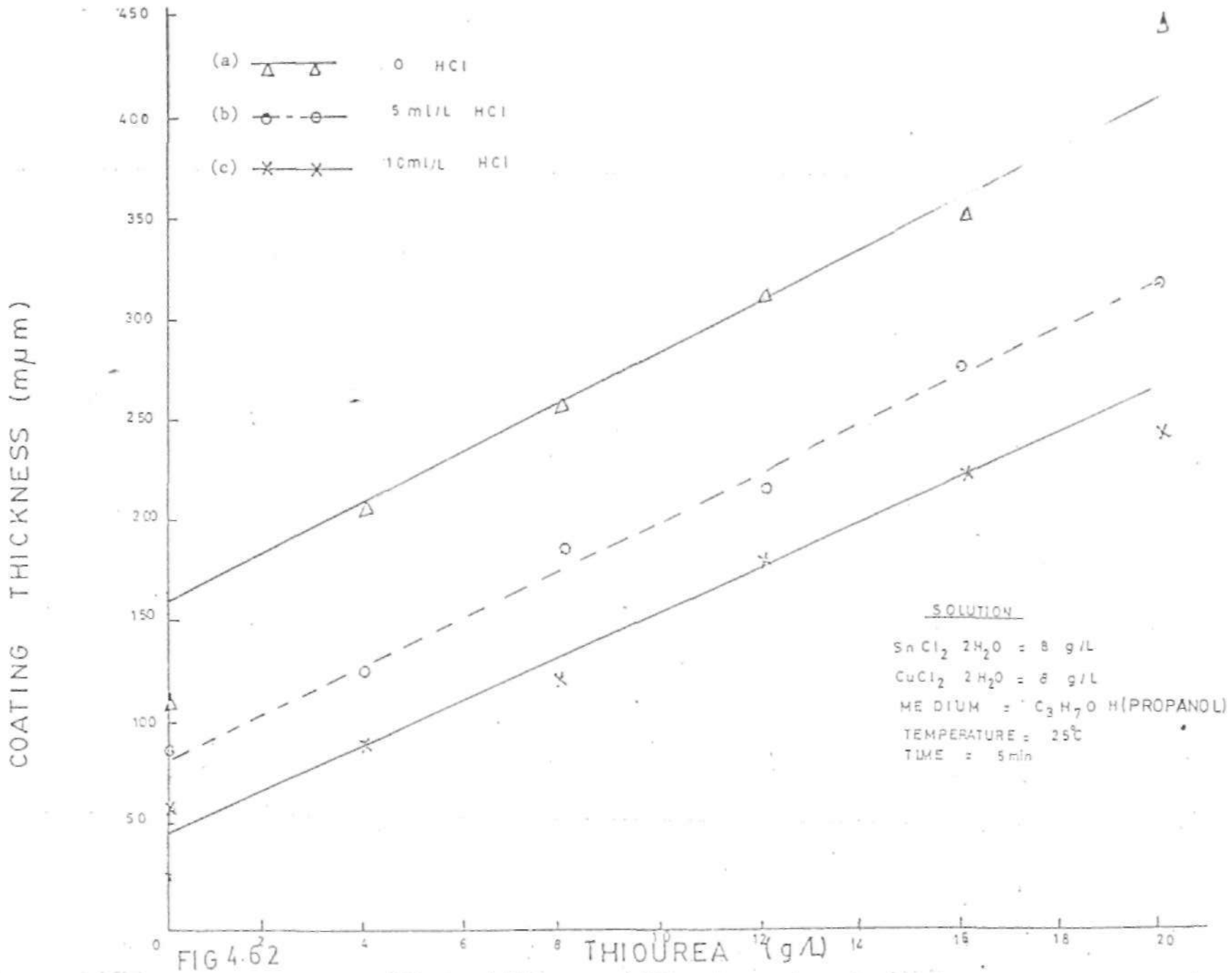

FIG 4.62

Effects of Thiourea and HCl on bronze immersion plating in propanol.

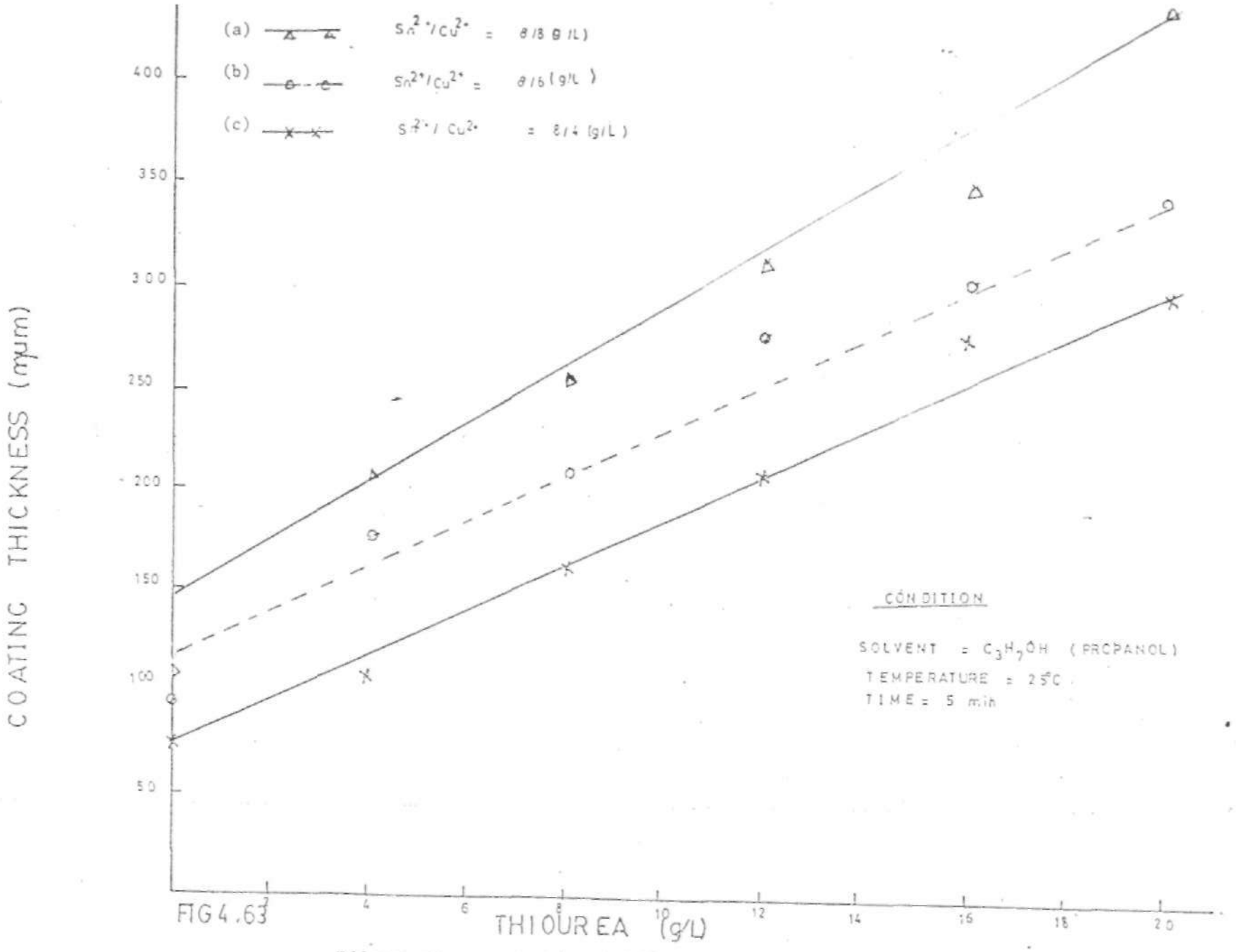

FIG 4.63

Effects of concentration and Thiourea on bronze immersion plating in propanol.

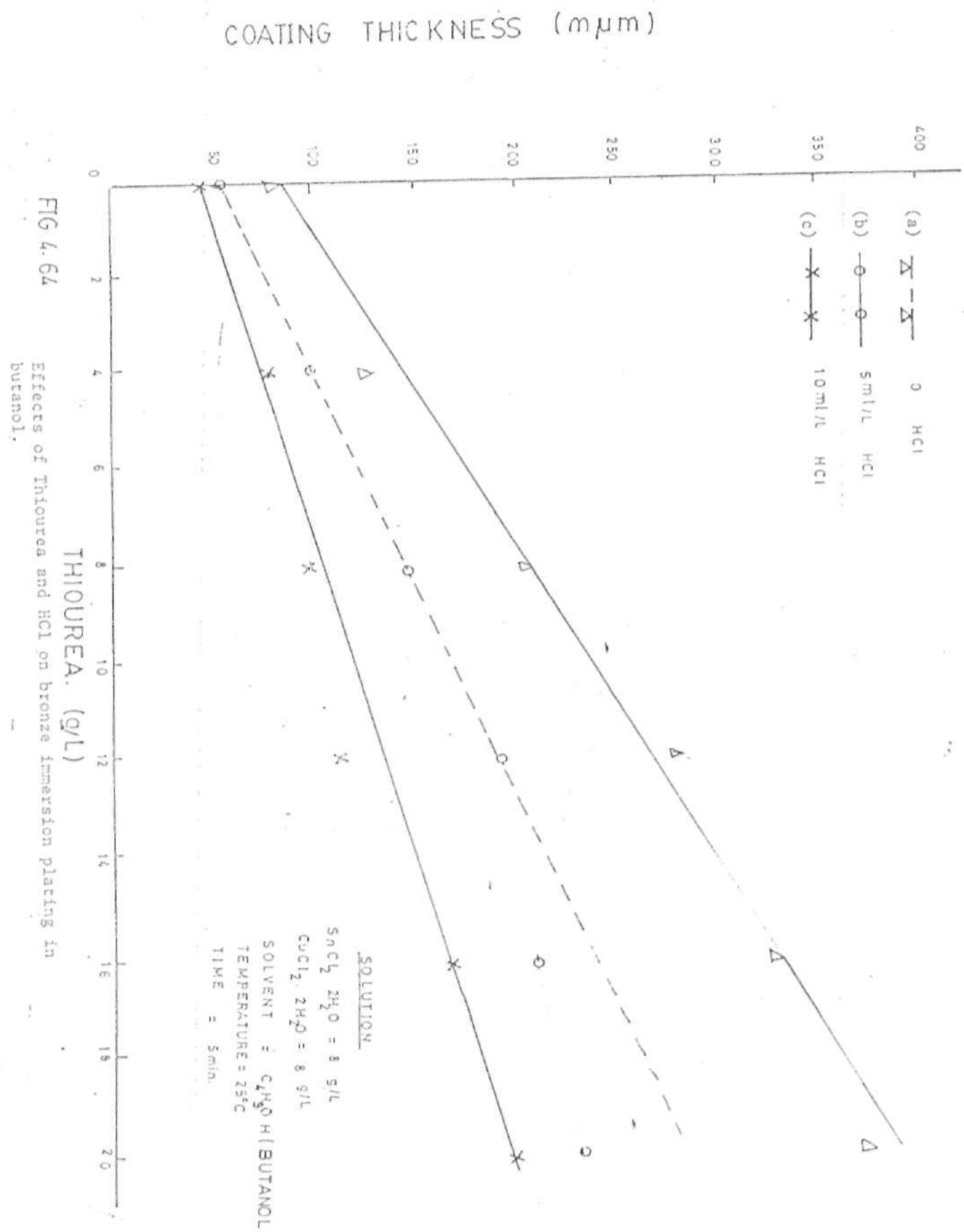

FIG 4.64 Effects of Thiourea and HCl on bronze immersion plating in butanol.

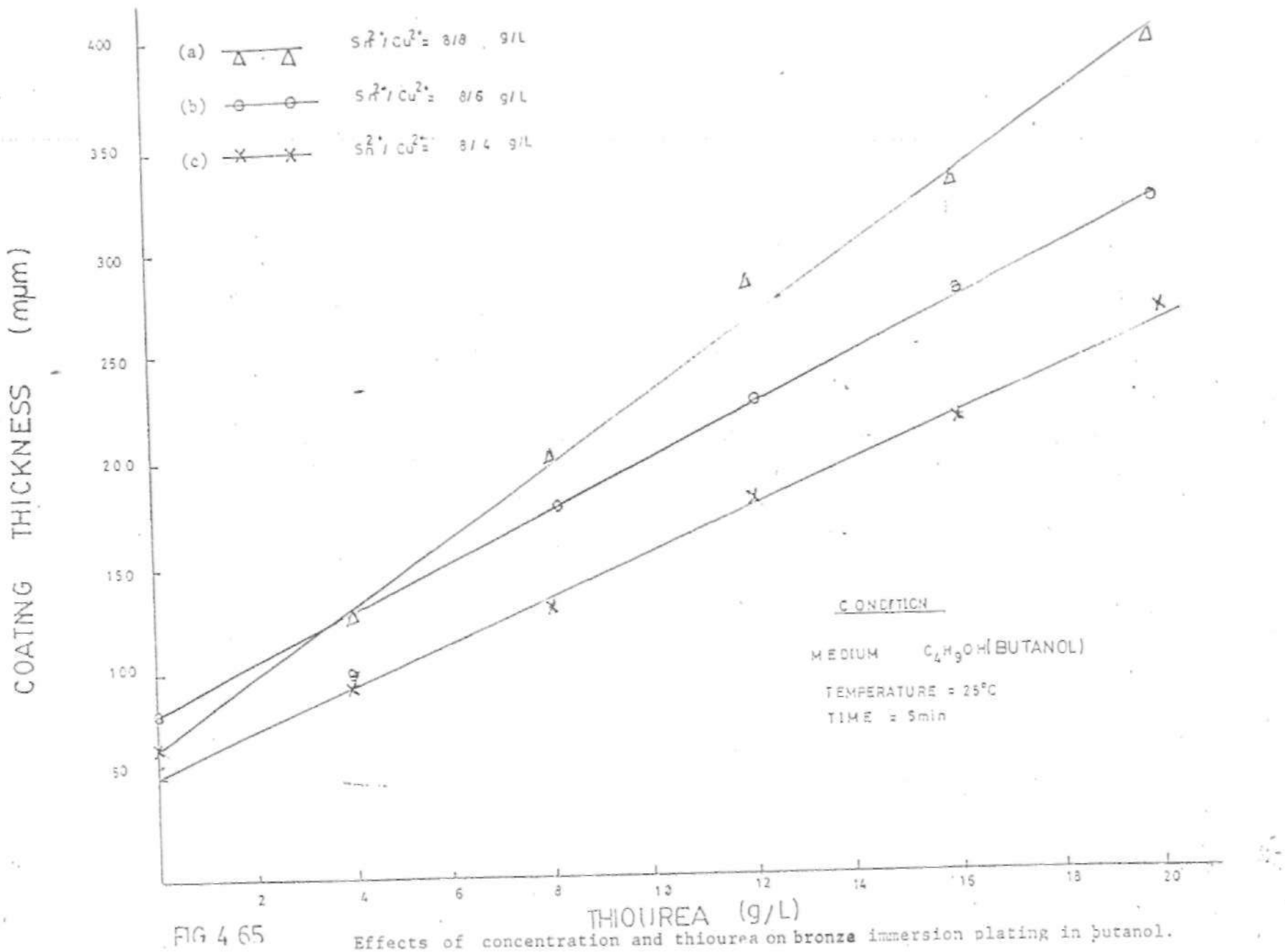

FIG 4.65 Effects of concentration and thiourea on bronze immersion plating in butanol.

COATING THICKNESS (μm)

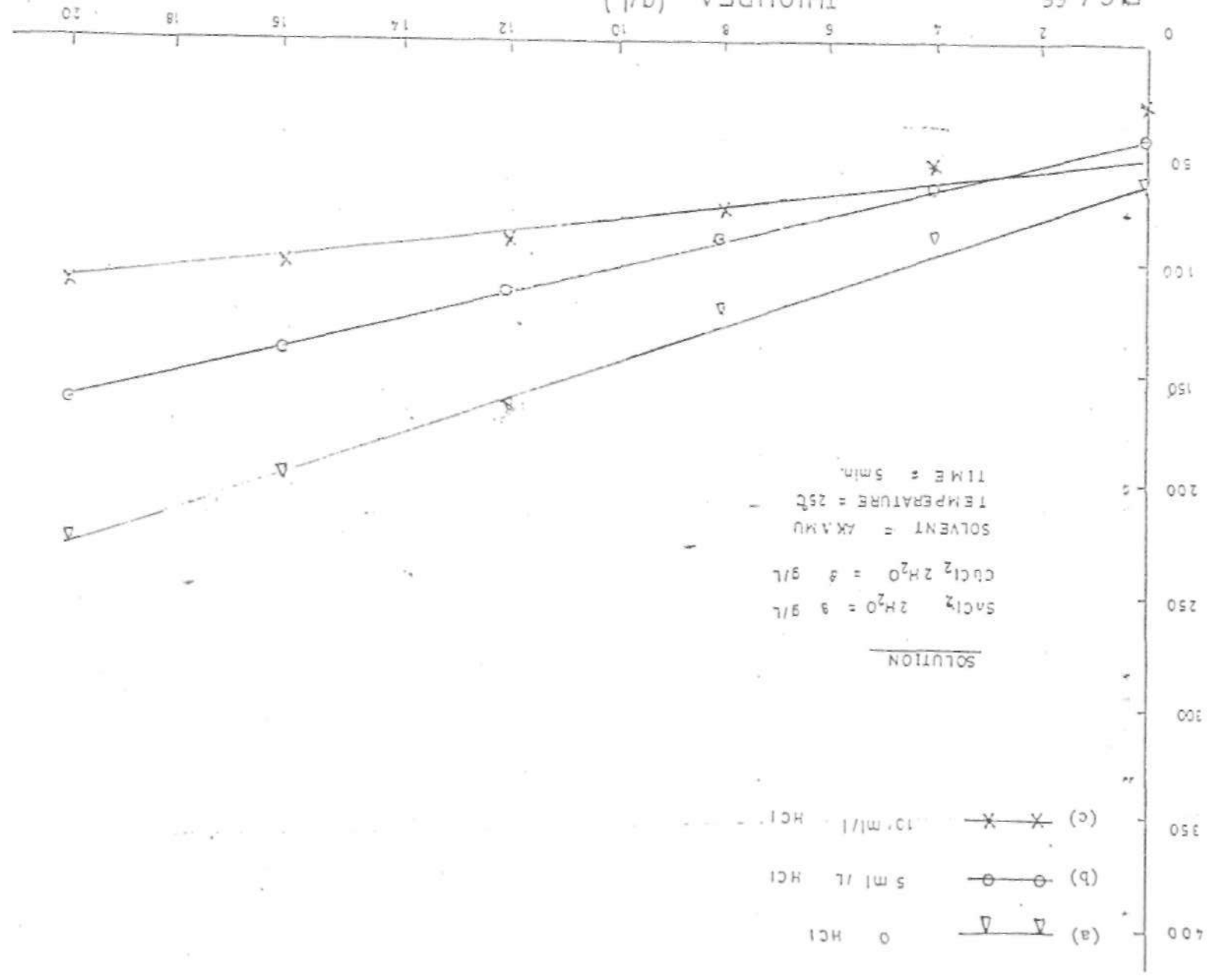

FIG 4.66 Effects of thiourea and HCl on bronze immersion plating in akamu.

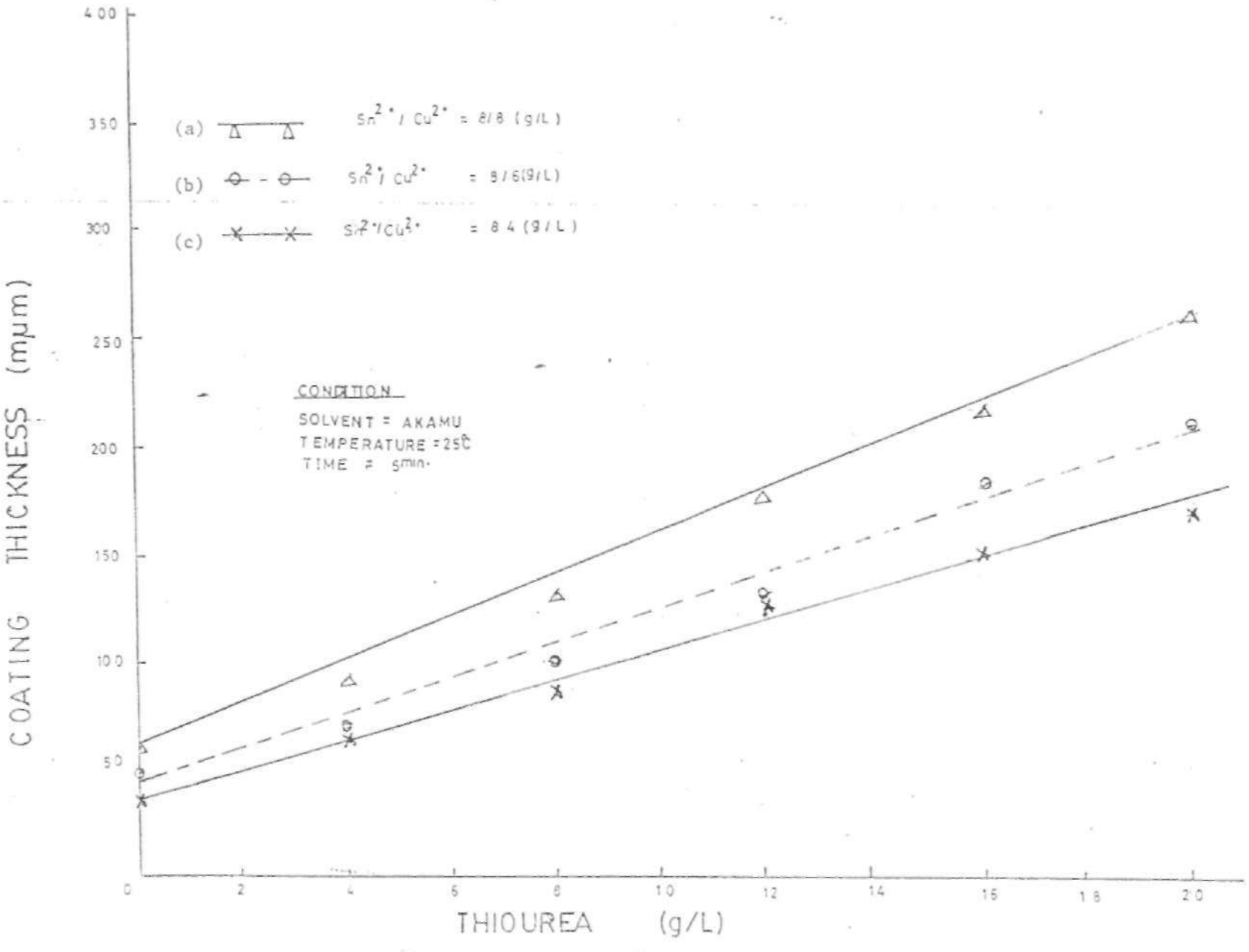

FIG 4.67 Effects of concentration and Thiourea on bronze immersion plating in akamu.

Curve (c), m = 11.25 mμm g^{-1} L and k = 45 mμm.

t = 11.25 (mμm g^{-1} L) C_{TH} (g L^{-1}) + 45 mμm 4.22

In Fig. 4.67, the equations for the linear curves are:

Curve (a), m = 10.42 mμm g^{-1} L and k = 60 mμm.

t = 10.42 (mμm g^{-1} L) C_{TH} (g L^{-1}) + 60 mμm 4.123

Curve (b), m = 8.33 mμm g^{-1} L and k = 45 mμm.

t = 8.33 (mμm g^{-1} L) C_{TH} (g L^{-1}) + 45 mμm 4.124

Curve (c), m = 7.92 mμm g^{-1} L and k = 35 mμm.

t = 7.92 (mμm g^{-1} L) C_{TH} (g L^{-1}) + 35 mμm 4.125

4.3.16 MEDIA, CONCENTRATION AND SODIUM DITHIONATE EFFECTS ON COATING THICKNESS:

Figures 4.68 - 4.71 and Tables 62 - 65 (appendix 1) show the effects of alcohol concentrations in aqueous solutions (ie. 25%, 50% and 75% alcohol) and sodium dithionate on coating thickness in acid-free solutions containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$, operated at 25°C, for a period of 5 minutes.

From the results it can be seen that higher alcohol concentrations in solution favour coating thickness growth with respect to the corresponding addition of sodium dithionate.

In Fig. 4.68, the equations for the linear curves are:

Curve (a), m = 21.25 mμm g^{-1} L and k = 310 mμm.

t = 21.25 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 310 mμm 4.126

Curve (b), m = 20 mμm g^{-1} L and k = 280 mμm.

t = 20 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 280 mμm 4.127

Curve (c), m = 28.75 mμm g^{-1} L and k = 75 mμm.

t = 28.75 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 75 mμm 4.128

In Fig. 4.69, the equations for the linear curves are:

Curve (a), m = 21.7 mμm g^{-1} L and k = 80 mμm.

t = 21.7 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 80 mμm 4.129

Curve (b), m = 21.7 mμm g^{-1} L and k = 99.5 mμm.

t = 21.7 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 99.5 mμm 4.130

Curve (c), m = 28.58 mμm g^{-1} L and k = 77 mμm.

t = 28.58 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 77 mμm 4.131

In Fig. 4.70, the equations for the linear curves are:

Curve (a), m = 13.33 mμm g^{-1} L and k = 60 mμm.

t = 13.33 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 60 mμm 4.132

Curve (b), m = 16.67 mμm g^{-1} L and k = 100 mμm.

t = 16.67 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 100 mμm 4.133

Curve (c), m = 16.25 mμm g^{-1} L and k = 130 mμm.

t = 16.25 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 130 mμm 4.134

In Fig. 4.71, the equations for the linear curves are:

curve (a), m = 13.75 mμm g^{-1} L and k = 50 mμm.

t = 13.75 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 50 mμm 4.135

Curve (b), m = 17.5 mμm g^{-1} L and k = 85 mμm.

t = 17.5 (mμm g^{-1} L) C_{SD} (g L^{-1}) + 85 mμm 4.136

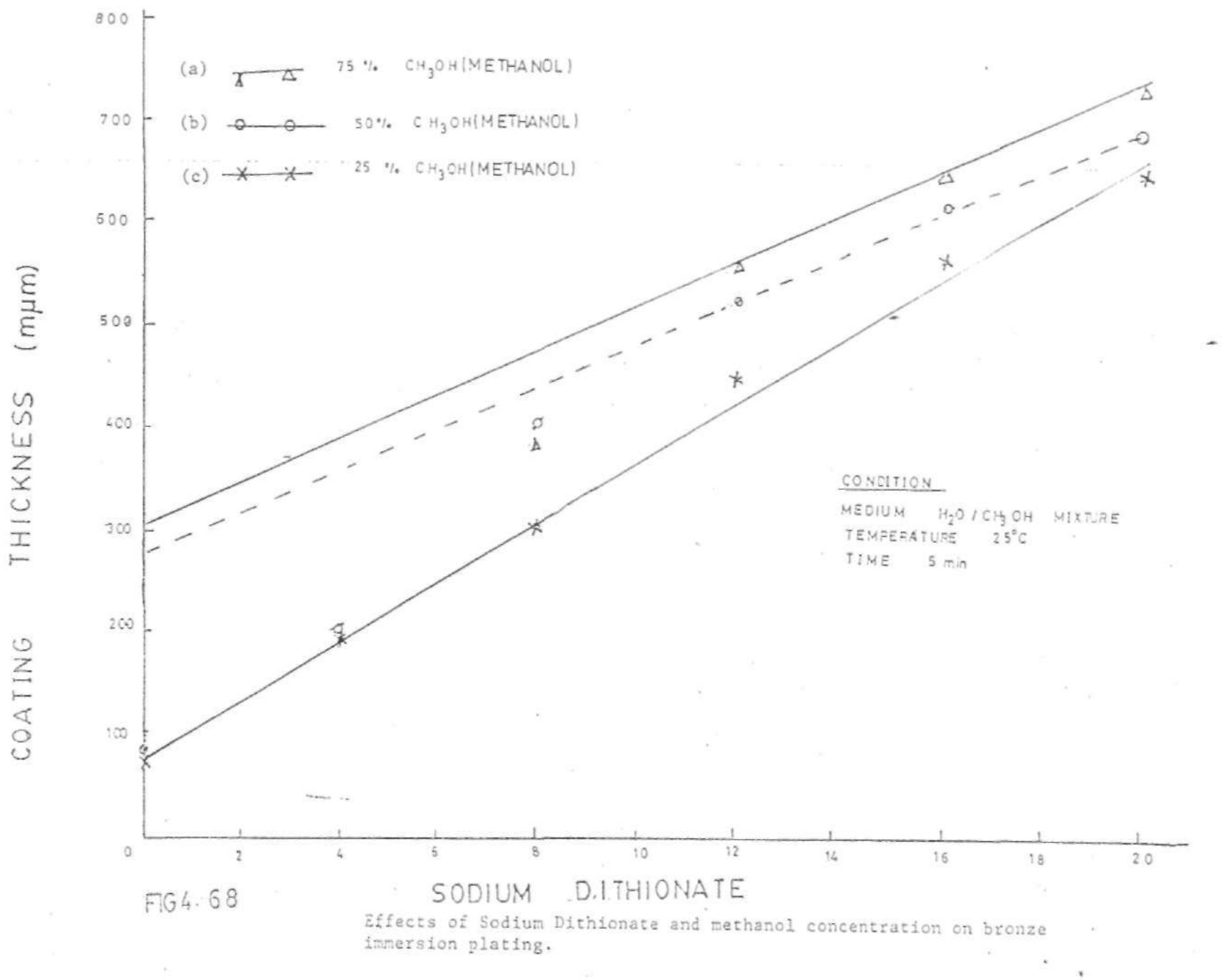

FIG4·68

Effects of Sodium Dithionate and methanol concentration on bronze immersion plating.

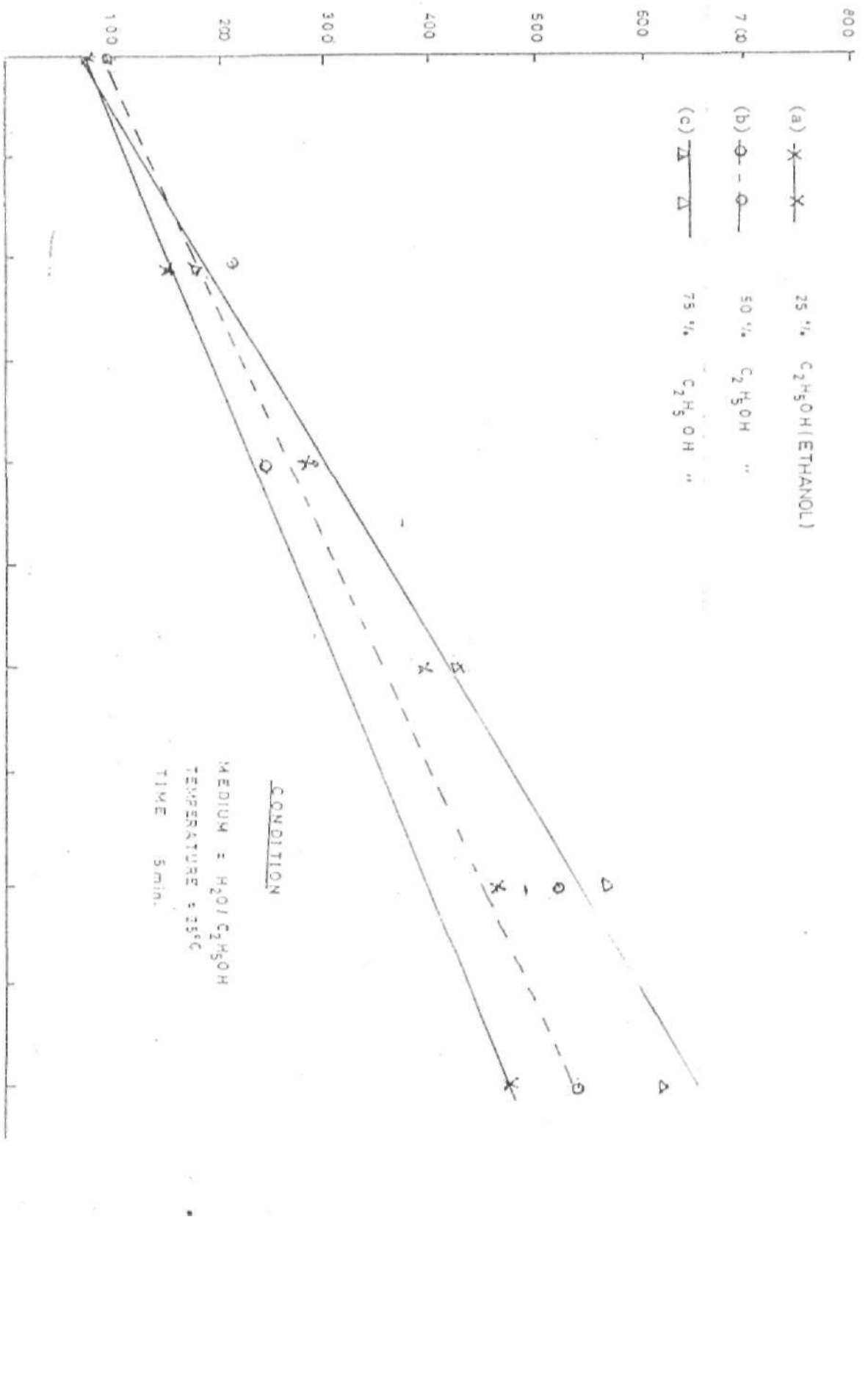

FIG.4.69 Effects of Sodium Dithionate and ethanol concentration on bronze immersion plating.

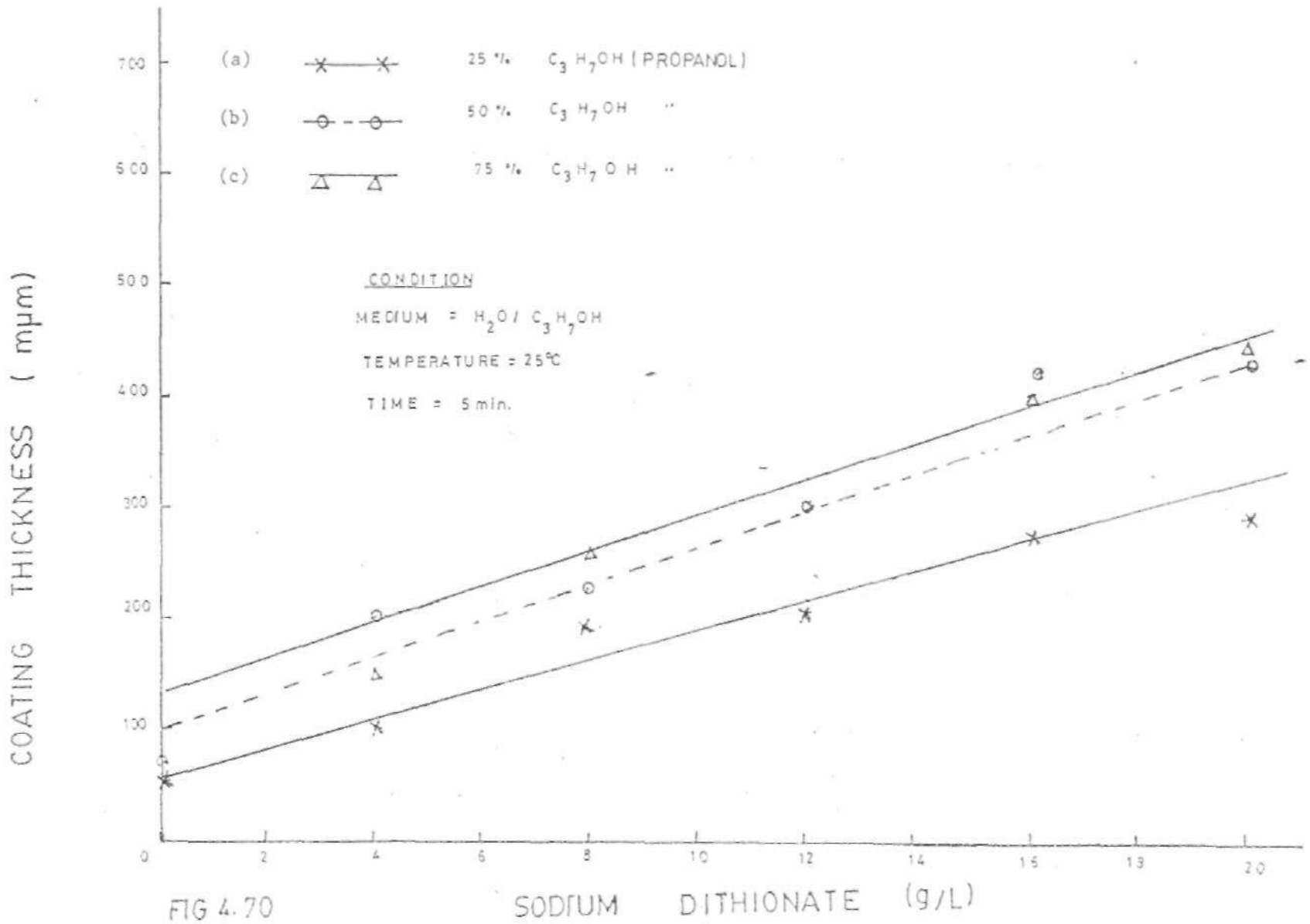

FIG 4.70

Effects of Sodium dithionate and propanol concentration on bronze immersion plating.

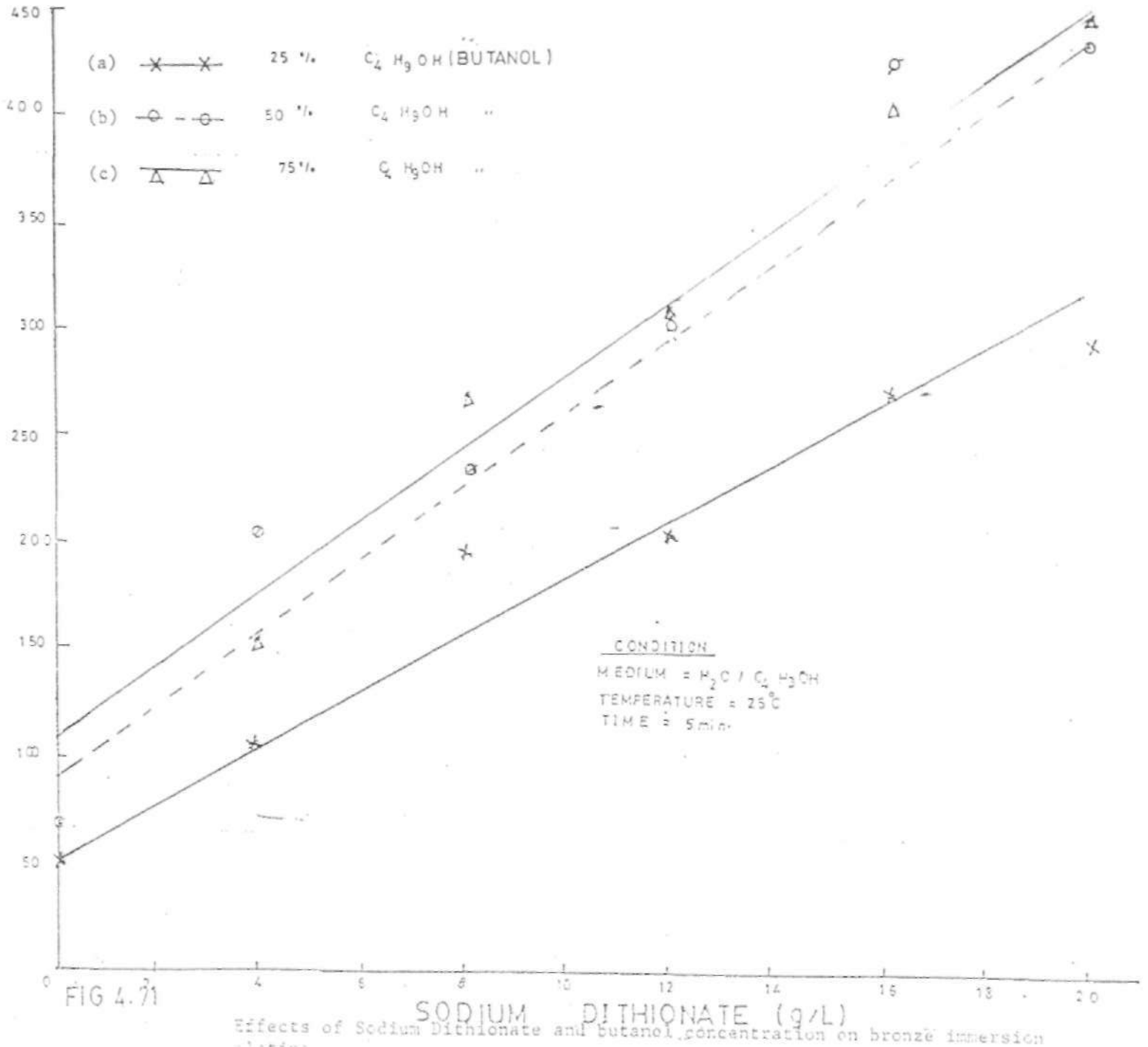

FIG 4.71

Effects of Sodium Dithionate and butanol concentration on bronze immersion
-tion

Curve (c), m = 17.5 mμm g^{-1} L and k = 110 mμm.

$t = 17.5\ (\text{mμm}\ g^{-1}\ L)\ C_{SD}\ (g\ L^{-1}) + 110\ \text{mμm}$ 4.137

4.3.17 MEDIA, CONCENTRATION AND L-CYSTEINE EFFECTS ON COATING THICKNESS:

Figures 4.72 - 4.75 and Tables 66 - 69 (appendix 1) show the effects of alcohol concentration in aqueous solution (25%, 50% and 75% alcohol) and L-cysteine on coating thickness in acid-free solutions containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$, operated at 25°C for a period of 5 minutes.

The figures show the relative growth of coating thickness in higher alcohol concentrations with respect to the corresponding level of L-cysteine addition in the plating solution.

in Fig. 4.72, the equations for the linear curves are:

Curve (a), m = 15.42 mμm. g^{-1} L and k = 30 mμm.

$t = 15.42\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g.L^{-1}) + 30\ \text{mμm}$ 4.138

Curve (b), m = 27.1 mμm. g^{-1} L and k = 50 mμm.

$t = 27.1\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 50\ \text{mμm}$ 4.139

Curve (c), m = 24.17 mμm. g^{-1} L and k = 170 mμm.

$t = 24.17\ (\text{mμm}.\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 170\ \text{mμm}$ 4.140

In Fig. 4.73, the equations for the linear curves are:

Curve (a), m = 15.4 mμm g^{-1} L and k = 40 mμm.

$t = 15.4\ (\text{mμm}.\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 40\ \text{mμm}$ 4.141

Curve (b), m = 22.1 mμm g^{-1} L and k = 55 mμm.

$t = 22.1\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 55\ \text{mμm}$ 4.142

Curve (c), m = 31.25 mμm g^{-1} L and k = 75 mμm.

$t = 31.25\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 75\ \text{mμm}$ 4.143

In Fig. 4.74, the equations for the linear curves are:

Curve (a), m = 17.5 mμm g^{-1} L and k = 40 mμm.

$t = 17.5\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 40\ \text{mμm}$ 4.144

Curve (b), m = 18 mμm g^{-1} L and k = 99 mμm.

$t = 18\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 99\ \text{mμm}$ 4.145

Curve (c), m = 22.5 mμm. g^{-1}.L and k = 100 mμm.

$t = 22.5\ (\text{mμm}.\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 100\ \text{mμm}$ 4.146

In Fig. 4.75, the equations for the linear curves are:

Curve (a), m = 10.25 mμm. g^{-1} L and k = 40 mμm.

$t = 10.25\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 40\ \text{mμm}$ 4.147

curve (b), m = 14.17 mμm g^{-1} L and k = 50 mμm.

$t = 14.17\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 50\ \text{mμm}$ 4.148

Curve (c), m = 16.08 mμm. g^{-1} L and k = 95 mμm.

$t = 16.08\ (\text{mμm}\ g^{-1}\ L)\ C_{LC}\ (g\ L^{-1}) + 95\ \text{mμm}$ 4.149

4.3.18 MEDIA, CONCENTRATION AND THIOUREA EFFECTS ON COATING THICKNESS:

Figures 4.76 - 4.79 and Tables 70 - 73 (appendix 1) show the effects of alcohol concentration in aqueous solutions (25%, 50% and 75% alcohol) and thiourea on coating thickness in acid-free solution containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$, operated at 25°C for a period of 5 minutes.

Coating thickness growth is promoted in higher alcohol concentrations in accordance with the corresponding level of added thiourea.

In Fig. 4.76, the equations for the linear curves are:

Curve (a), m = 23.75 mμm g^{-1} L and k = 0

$t = 23.75\ (m\mu m.\ g^{-1}\ L)\ C_{TH}\ (g.L^{-1})$ 4.150

Curve (b), m = 31.67 mμm g^{-1} L and k = 70 mμm.

$t = 31.67\ (m\mu m.\ g^{-1}.L)\ C_{TH}\ (g.L^{-1}) + 70\ m\mu m$ 4.151

Curve (c), m = 28.33 mμm g^{-1} L and k = 180 mμm.

$t = 28.33\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 180\ m\mu m$ 4.152

In Fig. 4.77, the equations for the linear curves are:

Curve (a), m = 17.08 mμm g^{-1} L and k = 60 mμm.

$t = 17.08\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 60\ m\mu m$ 4.153

Curve (b), m = 23.33 mμm g^{-1} L and k = 70 mμm.

$t = 23.33\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g.L^{-1}) + 70\ m\mu m$ 4.154

Curve (c), m = 24.17 mμm g^{-1} L and k = 90 mμm.

$t = 24.17\ (m\mu m.\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 90\ m\mu m$ 4.155

In Fig. 4.78, the equations for the linear curves are:

Curve (a), m = 5 mμm g^{-1} L and k = 110 mμm.

$t = 5\ (m\mu m.\ g^{-1}.L)\ C_{TH}\ (g\ L^{-1}) + 110\ m\mu m$ 4.156

Curve (b), m = 12.75 mμm g^{-1} L and k = 100mμm.

$t = 12.75\ (m\mu m.\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 100\ m\mu m$ 4.157

Curve (c), m = 13.33 mμm g^{-1} L and k = 130 mμm.

$t = 13.33\ (m\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 130\ m\mu m$ 4.158

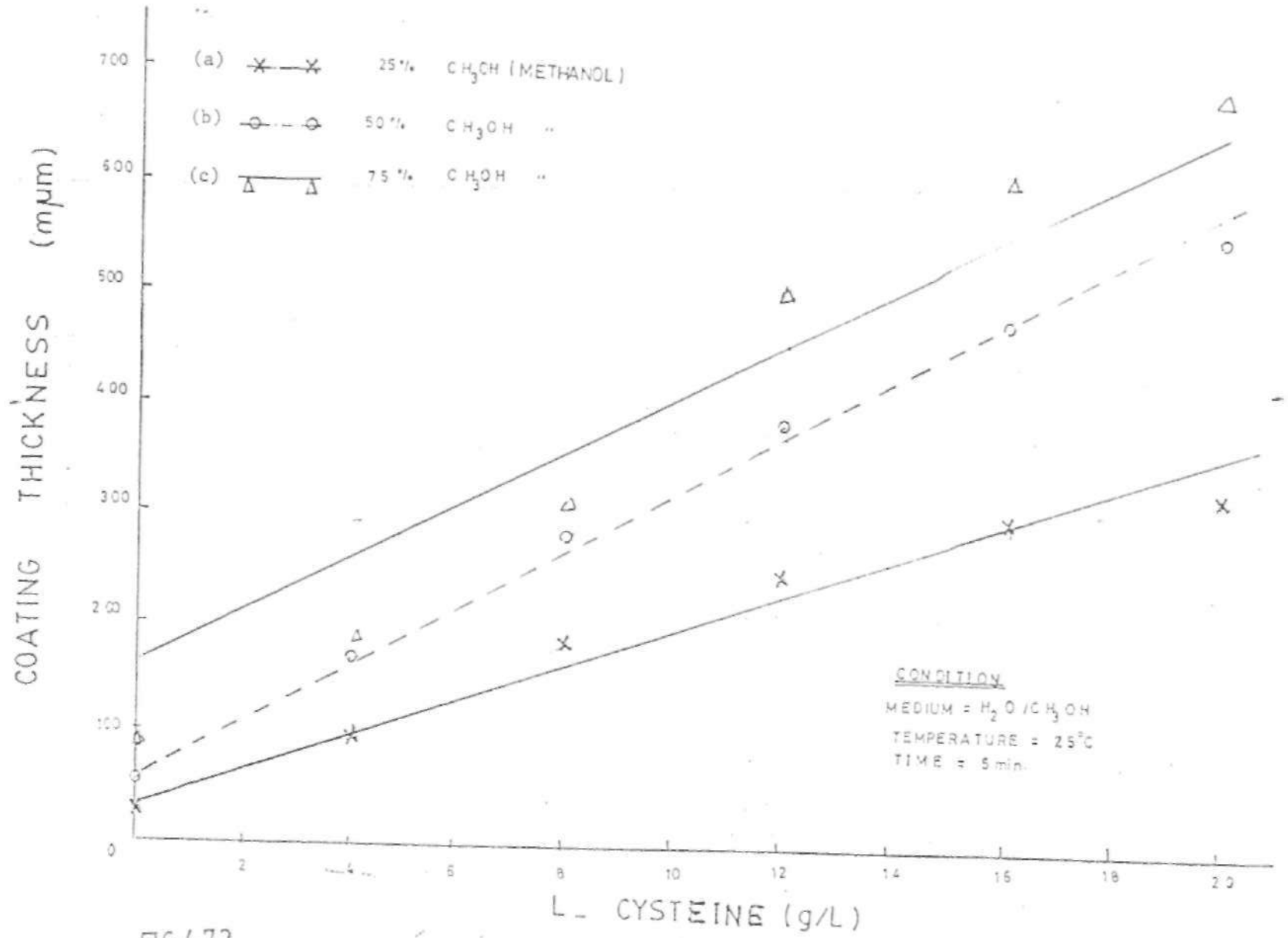

FIG 4.72

Effects of L-cysteine and methanol concentration on bronze immersion plating.

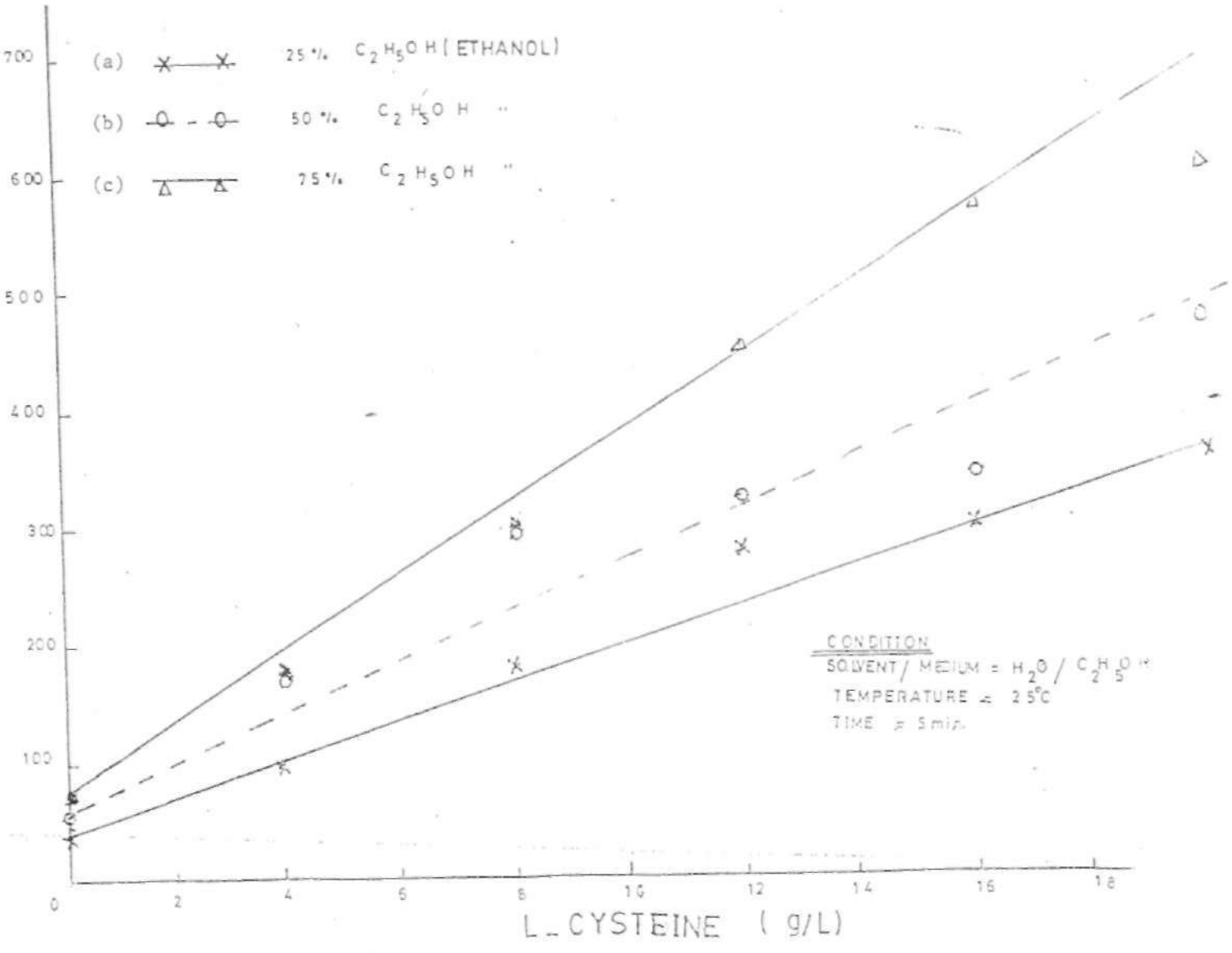

FIG 4.73 Effects of L-cysteine and ethanol concentration on bronze immer plating.

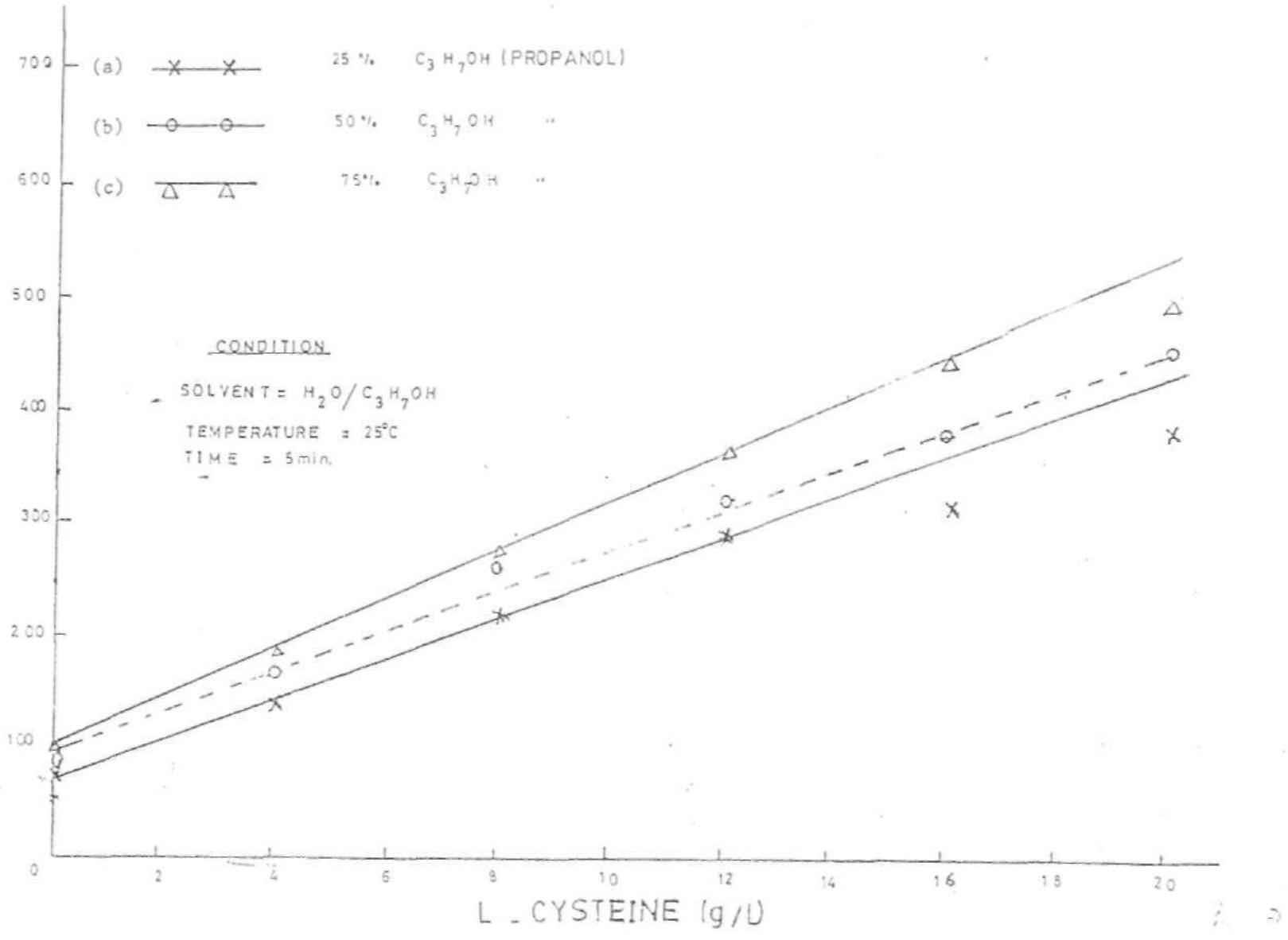

FIG 4.74 Effects of L-cysteine and propanol concentration on bronze immersion plating.

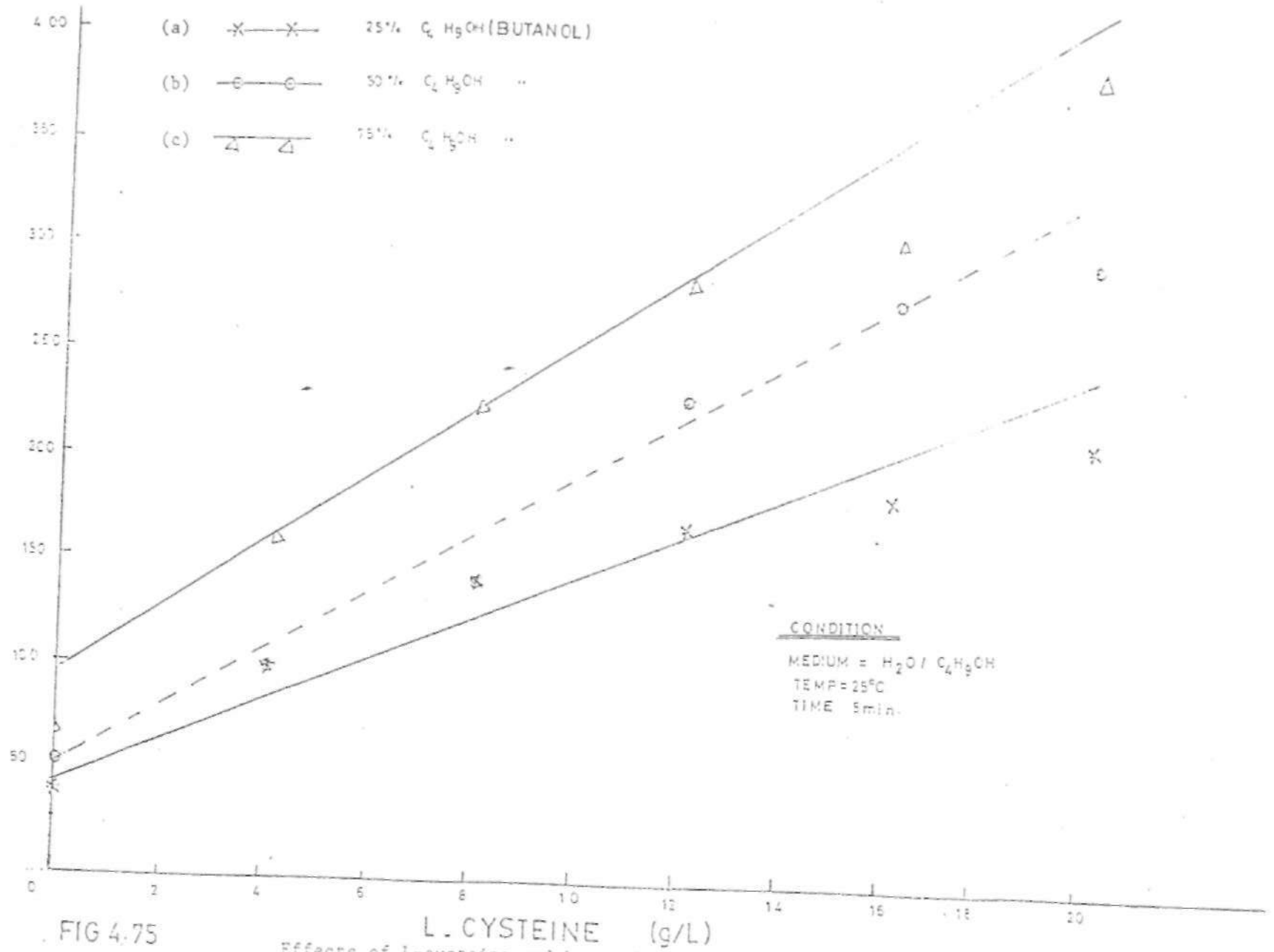

FIG 4.75

Effects of L-cysteine and butanol concentration on bronze immersion plating

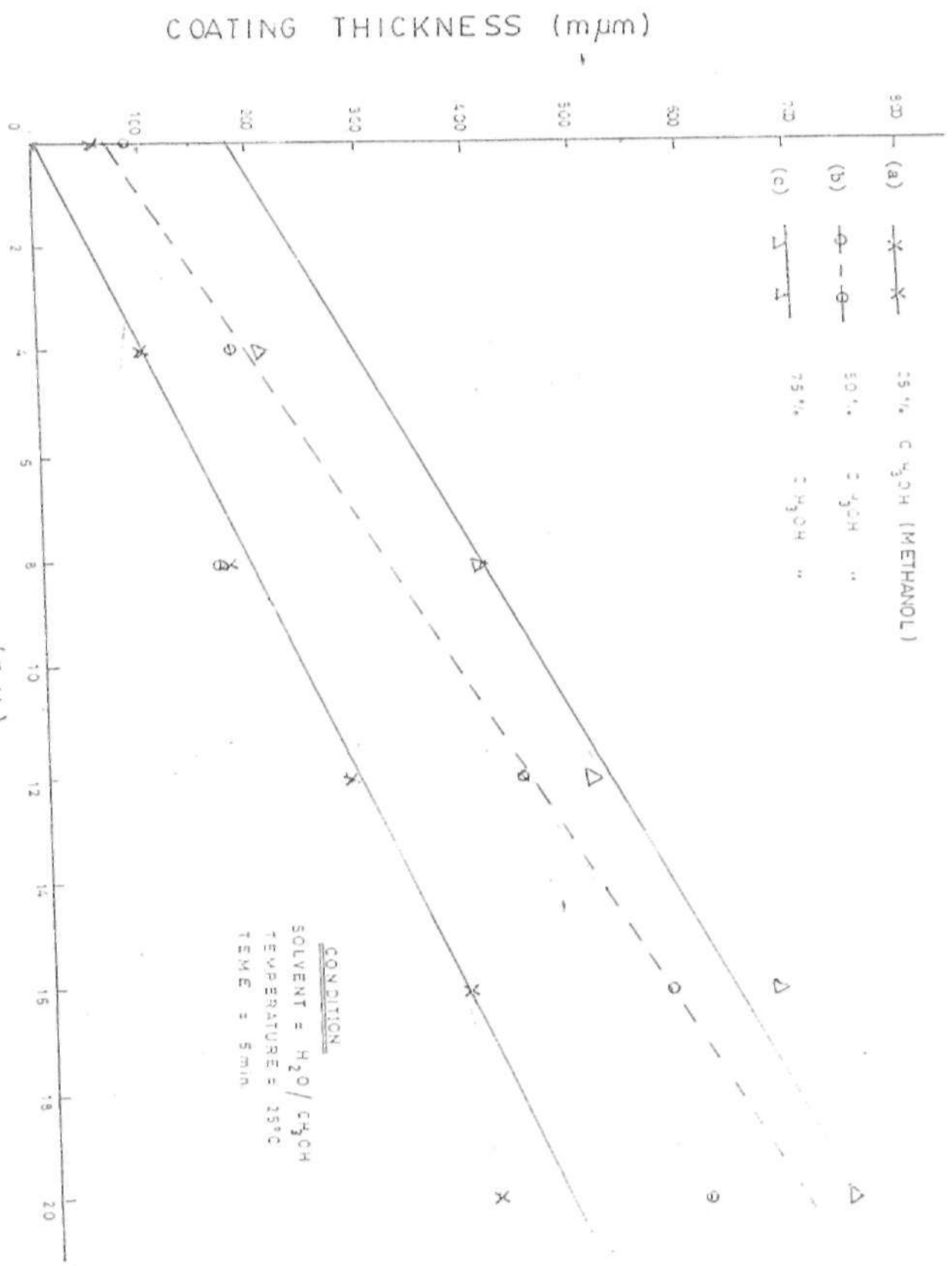

FIG 4.76 Effects of thiourea and methanol concentration on bronze immersion plating.

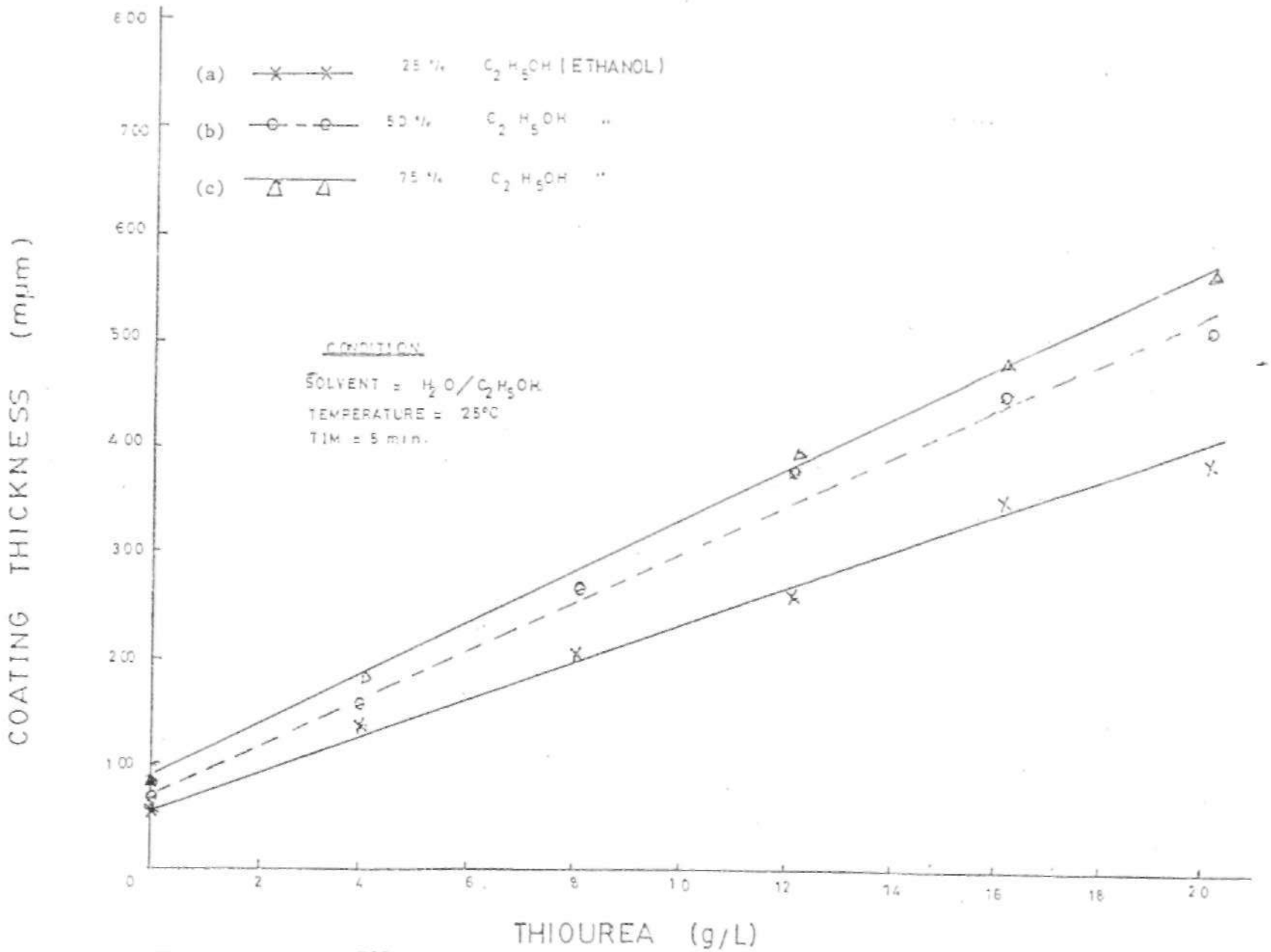

FIG 4.77 Effects of thiourea and ethanol on bronze immersion plating.

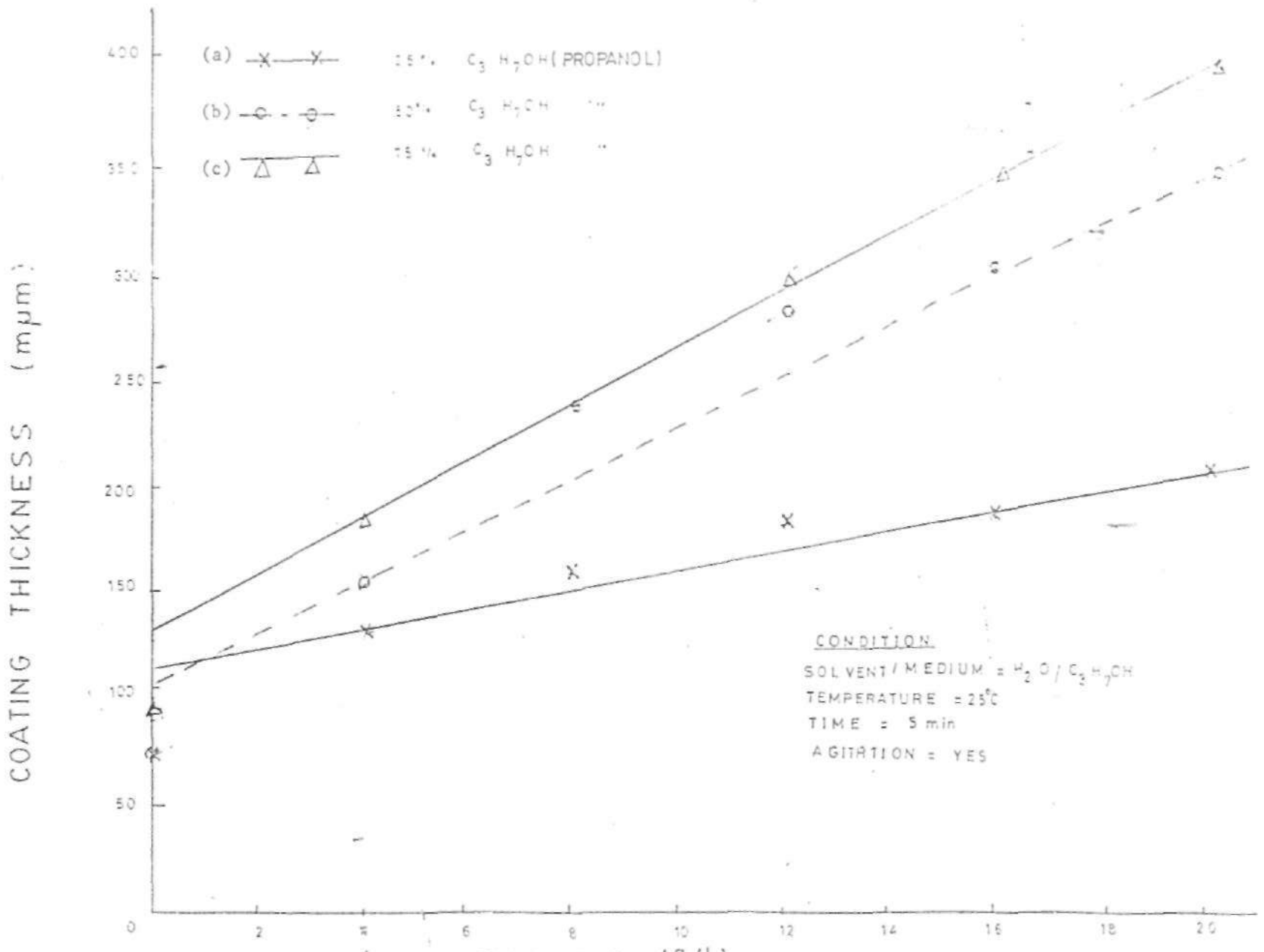

FIG 4.78 Effects of thiourea and propanol on bronze immersion plating.

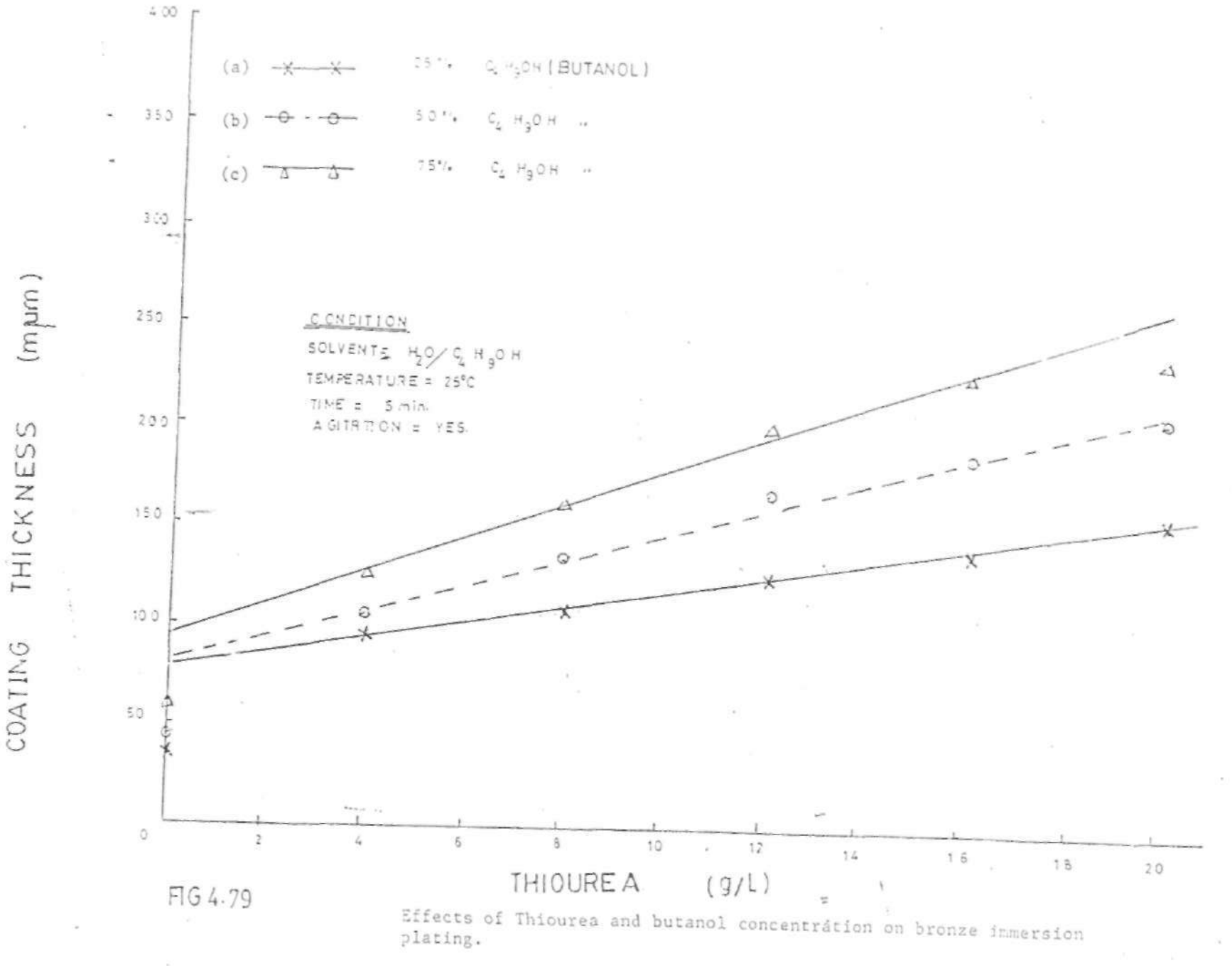

FIG 4.79

Effects of Thiourea and butanol concentration on bronze immersion plating.

In Fig. 4.79, the equations for the linear curves are:

Curve (a), $m = 6.67\ \mu m\ g^{-1}\ L$ and $k = 70\ \mu m$.

$t = 6.67\ (\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 70\ \mu m$ 4.159

Curve (b), $m = 6.92\ \mu m\ g^{-1}\ L$ and $k = 75\ \mu m$.

$t = 6.92\ (\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 75\ \mu m$ 4.160

Curve (c), $m = 8.75\ \mu m\ g^{-1}\ L$ and $k = 90\ \mu m$.

$t = 8.75\ (\mu m\ g^{-1}\ L)\ C_{TH}\ (g\ L^{-1}) + 90\ \mu m$ 4.161

4.4.1 CURRENT DENSITY, PLATING TIME AND HCl EFFECTS ON BRONZE ELECTROPLATING IN DIFFERENT MEDIA:

Figures 4.80 - 4.91 and Tables 74 - 85 (appendix 2) show the effects of current density, plating time and HCl on bronze electroplating of immersion plated steel substrates in aqueous, methanol, ethanol, propanol, butanol and 'akamu' media respectively containing 100 g/L $SnCl_2.2H_2O$, 100 g/L $CuCl_2.2H_2O$, 5.8 - 7 $X10^{-1}$M (50 - 60 ml/L) HCl, by applying a current density range of 10 - 30 A/m^2 for a period of 30 minutes at a temperature of 35°C.

In Fig. 4.80, the equations for the linear curves are;

Curve (a), $m = 0.012\ \mu m\ (min)^{-1}$ and $k = 2\ \mu m$.

$t = 0.012\ (\mu m\ min^{-1})\ J\ (min) + 2\ \mu m$ 4.162

where J is the plating time.

Curve (b), $m = 0.26\ \mu m\ (min)^{-1}$ and $k = 4.3\ \mu m$.

$t = 0.26\ (\mu m.\ min^{-1})\ J\ (min) + 4.3\ \mu m$ 4.163

Curve (c), $m = 0.36\ \mu m\ (min)^{-1}$ and $k = 6.3\ \mu m$.

$t = 0.36\ (\mu m\ min^{-1})\ J\ (min) + 6.3\ \mu m$ 4.164

In Fig. 4.81, the equations for the linear curves are:

Curve (a), $m = 0.087\ \mu m\ (min)^{-1}$ and $k = 4.4\ \mu m$.

$t = 0.087\ (\mu m\ min^{-1})\ J\ (min) + 4.4\ \mu m$ 4.165

Curve (b), $m = 0.087\ \mu m\ (min)^{-1}$ and $k = 9.7\ \mu m$.

$t = 0.087\ (\mu m.\ min^{-1})\ J\ (min) + 9.7\ \mu m$ 4.166

Curve (c), $m = 0.197\ \mu m\ (min)^{-1}$ and $k = 10.5\ \mu m$.

$t = 0.197\ (\mu m.\ min^{-1})\ J\ (min) + 10.5\ \mu m$ 4.167

In Fig. 4.82, the equations for the linear curves are:

Curve (a), $m = 0.133\ \mu m\ (min)^{-1}$ and $k = 5\ \mu m$.

$t = 0.133\ (\mu m\ min^{-1})\ J\ (min) + 5\ \mu m$ 4.168

Curve (b), $m = 0.29\ \mu m\ (min)^{-1}$ and $k = 7\ \mu m$.

$t = 0.29\ (\mu m.\ min^{-1})\ J\ (min) + 7\ \mu m$ 4.169

Curve (c), $m = 0.25\ \mu m\ (min)^{-1}$ and $k = 12\ \mu m$.

$t = 0.25\ (\mu m.\ min^{-1})\ J\ (min) + 12\ \mu m$ 4.170

In Fig. 4.83, the equations for the linear curves are:

Curve (a), $m = 0.10\ \mu m\ (min)^{-1}$ and $k = 6\ \mu m$

$t = 0.1\ (\mu m.\ min^{-1})\ J\ (min) + 6\ \mu m$ 4.171

Curve (b), $m = 0.14\ \mu m\ (min)^{-1}$ and $k = 9.9\ \mu m$.

$t = 0.14\ (\mu m\ min^{-1})\ J\ (min) + 9.9\ \mu m$ 4.172

Curve (c), $m = 0.31\ \mu m\ (min)^{-1}$ and $k = 11.8\ \mu m$.

$t = 0.31\ (\mu m.\ min^{-1})\ J\ (min) + 11.8\ \mu m$ 4.173

In Fig. 4.84, the equations for the linear curves are:

Curve (a), $m = 0.08\ \mu m\ (min)^{-1}$ and $k = 4.7\ \mu m$

$t = 0.08\ (\mu m.\ min^{-1})\ J\ (min) + 4.7\ \mu m$ 4.174

Curve (b), $m = 0.2\ \mu m\ (min)^{-1}$ and $k = 7.5\ \mu m.$

$t = 0.2\ (\mu m\ min^{-1})\ J\ (min) + 7.5\ \mu m$ 4.175

Curve (c), $m = 0.2\ \mu m\ (min)^{-1}$ and $k = 12\ \mu m.$

$t = 0.2\ (\mu m\ min^{-1})\ J\ (min) + 12\ \mu m$ 4.176

In Fig. 4.85, the equations for the linear curves are:

Curve (a), $m = 0.11\mu m\ (min)^{-1}$ and $k = 4.4\ \mu m.$

$t = 0.11\ (\mu m\ min^{-1})\ J\ (min) + 4.4\ \mu m$ 4.177

Curve (b), $m = 0.28\ \mu m\ (min)^{-1}$ and $k = 6.5\ \mu m.$

$t = 0.28\ (\mu m\ min^{-1})\ J\ (min) + 6.5\ \mu m$ 4.178

Curve (c), $m = 0.17\ \mu m\ (min)^{-1}$ and $k = 12.5\ \mu m.$

$t = 0.17\ (\mu m\ min^{-1})\ J\ (min) + 12.5\ \mu m$ 4.179

In Fig. 4.86, the equations for the linear curves are:

Curve (a), $m = 0.133\mu m\ (min)^{-1}$ and $k = 2\ \mu m.$

$t = 0.133\ (\mu m\ min^{-1})\ J\ (min) + 2\ \mu m$ 4.180

Curve (b), $m = 0.31\mu m\ (min)^{-1}$ and $k = 4.6\ \mu m.$

$t = 0.31\ (\mu m\ min^{-1})\ J\ (min) + 4.6\ \mu m$ 4.181

Curve (c), $m = 0.37\ \mu m\ (min)^{-1}$ and $k = 5.1\ \mu m.$

$t = 0.37\ (\mu m\ min^{-1})\ J\ (min) + 5.1\ \mu m$ 4.182

In Fig. 4.87, the equations for the linear curves are:

Curve (a), $m = 0.133\ \mu m\ (min)^{-1}$ and $k = 2.5\ \mu m$.

$t = 0.133\ (\mu m.\ min^{-1})\ J\ (min) + 2.5\ \mu m$ 4.183

Curve (b), $m = 0.39\ \mu m\ (min)^{-1}$ and $k = 4.6\ \mu m$.

$t = 0.39\ (\mu m\ min^{-1})\ J\ (min) + 4.6\ \mu m$ 4.184

Curve (c), $m = 0.4\ \mu m\ (min)^{-1}$ and $k = 6\ \mu m$.

$t = 0.4\ (\mu m.\ min^{-1})\ J\ (min) + 6\ \mu m$ 4.185

In Fig. 4.88, the equations for the linear curves are:

Curve (a), $m = 0.08\ \mu m\ (min)^{-1}$ and $k = 2.2\ \mu m$.

$t = 0.08\ (\mu m.\ min^{-1})\ J\ (min) + 2.2\ \mu m$ 4.186

Curve (b), $m = 0.19\ \mu m\ (min)^{-1}$ and $k = 3.5\ \mu m$.

$t = 0.19\ (\mu m.\ min^{-1})\ J\ (min) + 3.5\ \mu m$ 4.187

Curve (c), $m = 0.46\ \mu m\ (min)^{-1}$ and $k = 3.5\ \mu m$.

$t = 0.46\ (\mu m\ min^{-1})\ J\ (min) + 3.5\ \mu m$ 4.188

In Fig. 4.89, the equations for the linear curves are:

Curve (a), $m = 0.16\ \mu m\ (min)^{-1}$ and $k = 1.8\ \mu m$.

$t = 0.16\ (\mu m\ min^{-1})\ J\ (min) + 1.8\ \mu m$ 4.189

Curve (b), $m = 0.37\ \mu m\ (min)^{-1}$ and $k = 2\ \mu m$.

$t = 0.37\ (\mu m.\ min^{-1})\ J\ (min) + 2\ \mu m$ 4.190

Curve (c), $m = 0.61\ \mu m\ (min)^{-1}$ and $k = 2.9\ \mu m$.

$t = 0.61\ (\mu m\ min^{-1})\ J\ (min) + 2.9\ \mu m$ 4.191

In Fig. 4.90, the equations for the linear curves are:

Curve (a), m = 0.08 μm $(min)^{-1}$ and k = 1 μm.

t = 0.08 (μm min^{-1}) J (min) + 1 μm 4.192

Curve (b), m = 0.16 μm $(min)^{-1}$ and k = 2.2 μm.

t = 0.16 (μm min^{-1}) J (min) + 2.2 μm 4.193

Curve (c), m = 0.35 μm $(min)^{-1}$ and k = 3 μm.

t = 0.35 (μm min^{-1}) J (min) + 3 μm 4.194

In Fig. 4.91, the equations for the linear curves are:

Curve (a), m = 0.09 μm $(min)^{-1}$ and k = 2.25 μm.

t = 0.09 (μm min^{-1}) J (min) + 2.25 μm 4.195

Curve (b), m = 0.133 μm $(min)^{-1}$ and k = 4 μm.

t = 0.133 (μm min^{-1}) J (min) + 4 μm 4.196

Curve (c), m = 0.23 μm $(min)^{-1}$ and k = 4.8 μm.

t = 0.23 (μm min^{-1}) J (min) + 4.8 μm 4.197

4.4.2 MEDIA AND ACIDS EFFECTS ON COATING THICKNESS DURING BRONZE ELECTROPLATING:

Figures 4.92 - 4.94 and Tables 86 - 88 (appendix 2) show the effects of plating media (aqueous, methanol and 'akamu' respectively) and acids (nitric, acetic and formic) on coating thickness (plating rate) on bronze electroplating from solutions containing 100 g/L $SnCl_2.2H_2O$ and 100 g/L $CuCl_2.2H_2O$, operated at a temperature of 35°C by applying a current density of 35 A/m^2 on already immersion plated steel substrates.

In Fig. 4.92, the equations for the linear curves are:

Curve (a), m = 0.48 μm $(min)^{-1}$ and k = 4.75 μm.

t = 0.48 (μm min^{-1}) J (min) + 4.75 μm 4.98

Curve (b), m = 0.48 μm $(min)^{-1}$ and k = 2 μm.

t = 0.48 (μm min^{-1}) J (min) + 2 μm 4.199

Curve (c), m = 0.47 μm $(min)^{-1}$ and k = 1.65 μm.

t = 0.47 (μm min^{-1}) J (min) + 1.65 μm 4.200

4.4.3 ACETONE AND FORMALDEHYDE EFFECTS ON COATING THICKNESS DURING BRONZE ELECTROPLATING:

Figures 4.95 - 4.96 and Tables 89 - 90 (appendix 2) show the effects of 50% water/acetone, 99% acetone and 37% formaldehyde on coating thickness growth during bronze electroplating from solutions containing 100 g/l $SnCl_2.2H_2O$ and 100 g/L $CuCl_2.2H_2O$, operated at a temperature of 35°C by applying current densities of 20 A/m^2 and 30 A/m^2 respectively on already immersion plated steel substrates.

In Fig. 4.95, the equations for the linear curves are:

Curve (a), m = 0.31 μm $(min)^{-1}$ and k = 3.2 μm.

t = 0.31 (μm min^{-1}) J (min) + 3.2 μm 4.201

Curve (b), m = 0.35 μm $(min)^{-1}$ and k = 1.8 μm.

t = 0.35 (μm min^{-1}) J (min) + 1.8 μm 4.202

Curve (c), m = 0.18 μm $(min)^{-1}$ and k = 1.6 μm.

t = 0.18 (μm min^{-1}) J (min) + 1.6 μm 4.203

In Fig. 4.96, the equations for the linear curves are:

Curve (a), m = 0.07 μm $(min)^{-1}$ and k = 3.2 μm.

$t = 0.07\ (\mu m.\ min^{-1})\ J\ (min) + 3.2\ \mu m$ 4.204

Curve (b), m = 0.15 μm $(min)^{-1}$ and k = 2 μm.

$t = 0.15\ (\mu m.\ min^{-1})\ J\ (min) + 2\ \mu m$ 4.205

Curve (c), m = 0.08 μm $(min)^{-1}$ and k = 1.6 μm.

$t = 0.08\ (\mu m.\ min^{-1})\ J\ (min) + 1.6\ \mu m$ 4.206

4.5.1 CURRENT DENSITY, PLATING TIME AND HCl EFFECTS ON BRONZE ELECTROPLATING IN DIFFERENT MEDIA:

The following deductions can be made from Figures 4.80 - 4.91.

(i) Coating thickness increases with the corresponding increase in plating time.

(ii) Coating thickness growth is initially linear, but tends towards steady values after about 30 minutes of plating.

(iii) Coating thickness increases slightly with HCl addition between $5.8 - 7 \times 10^{-1}$M (50 - 60 ml/L).

(iv) Coating thickness increases with current density (between 10 - 30 A/m^2).

(v) Coating Thickness up to 15.5μm have been obtained in aqueous medium, 18.2μm in methanol, 16μm in ethanol, 14.2μm in propanol, 14μm in butanol and 10μm in 'akamu' medium within 30 minutes of plating when 7×10^{-1}M HCl is added to the plating solution with the application of a current density of 30 A/m^2.

(vi) Lower molecular weight alcohols promote higher plating rate compared to higher molecular weight alcohols and aqueous medium. However, the rate in aqueous medium is greater than in higher alcohols (propanol and butanol) and in 'akamu' medium.

(vii) Lower current density plating ($\bar{<}$ 10 A/m^2) produces brighter and dense coatings irrespective of media.

(viii) Plating in 'akamu' produces bright and dense thin coatings.

(ix) High current density ($\bar{>}$ 30 A/m^2) plating produces thicker coatings. The coatings may be dull and sometimes burnt or non adherent.

4.5.2 MEDIA AND ACIDS EFFECTS ON COATING THICKNESS DURING BRONZE ELECTROPLATING:

A similar pattern to that of section 4.5.1 has been observed as different acids are added to the electroplating media (Figures 4.92 - 4.94) resulting to the following deductions.

(i) Nitric acid addition to plating solution promote higher plating rate compared to acetic and formic acids. The high solubility of cupric and stannous chloride in nitric acid may account for the above observed effect.

(ii) As earlier observed, the plating rate is initially spontaneous but gradually approaches steady values after about 25 minutes.

(iii) The effects of acetic and formic acids are about the same in promoting plating rate.

(iv) Coating thikcness is higherin methanol (up to 17μm) as against 15μm obtained in aqueous medium with respect to plating time when nitric acid is added (Figure 4.93).

(v) Coating thickness is least in akamu (10μm with respect to plating time).

4.5.3 ACETONE AND FORMALDEHYDE EFFECTS ON COATING THICKNESS DURING BRONZE ELECTROPLATING:

The following conclusions can be made (Figures 4.95 - 4.96).

(i) Coating thickness increases with plating time irrespective of plating medium.

(ii) Coating thickness growth favours plating in 50% water/acetone and 37% formaldehyde than 99% acetone. The reason for this is that cupric and stannous chlorides are more soluble in mixed acetone, formaldehyde than in 99% acetone. That is more ions are present in solution for plating in mixed acetone than in 99% acetone because of the relative difference in solubility of the solvents.

(iii) As earlier observed, the plating rate is initially spontaneous, but gradually approaches steady values in about 25 minutes of plating. This is expected because more plating sites are available on the substrate initially to receive the deposits. However, the exposed surface diminishes with time as plating progresses; hence, limiting the plating rate.

(iv) As earlier observed, coating thickness growth increases with current density.

(v) The application of 10 A/m^2 current density produces coating thickness of 6μm with respect to plating time; whereas, a current density of 20 A/m^2 produces coating thickness up to 10μm with respect to plating time in 50% acetone medium. However, the coatings are brighter and dense at lower current densities ($\leq$ 10 A/m^2) compared to higher current densities as earlier observed.

4.5.4 GENERAL COMMENT ON THE ELECTROPLATING RESULTS:

This research is aimed at producing a bronze strike deposit in cyanide-free baths which serves as a basis for further conventional electroplating in simple, non-complexed baths. The above results show that this objective has been achieved to a large extent.

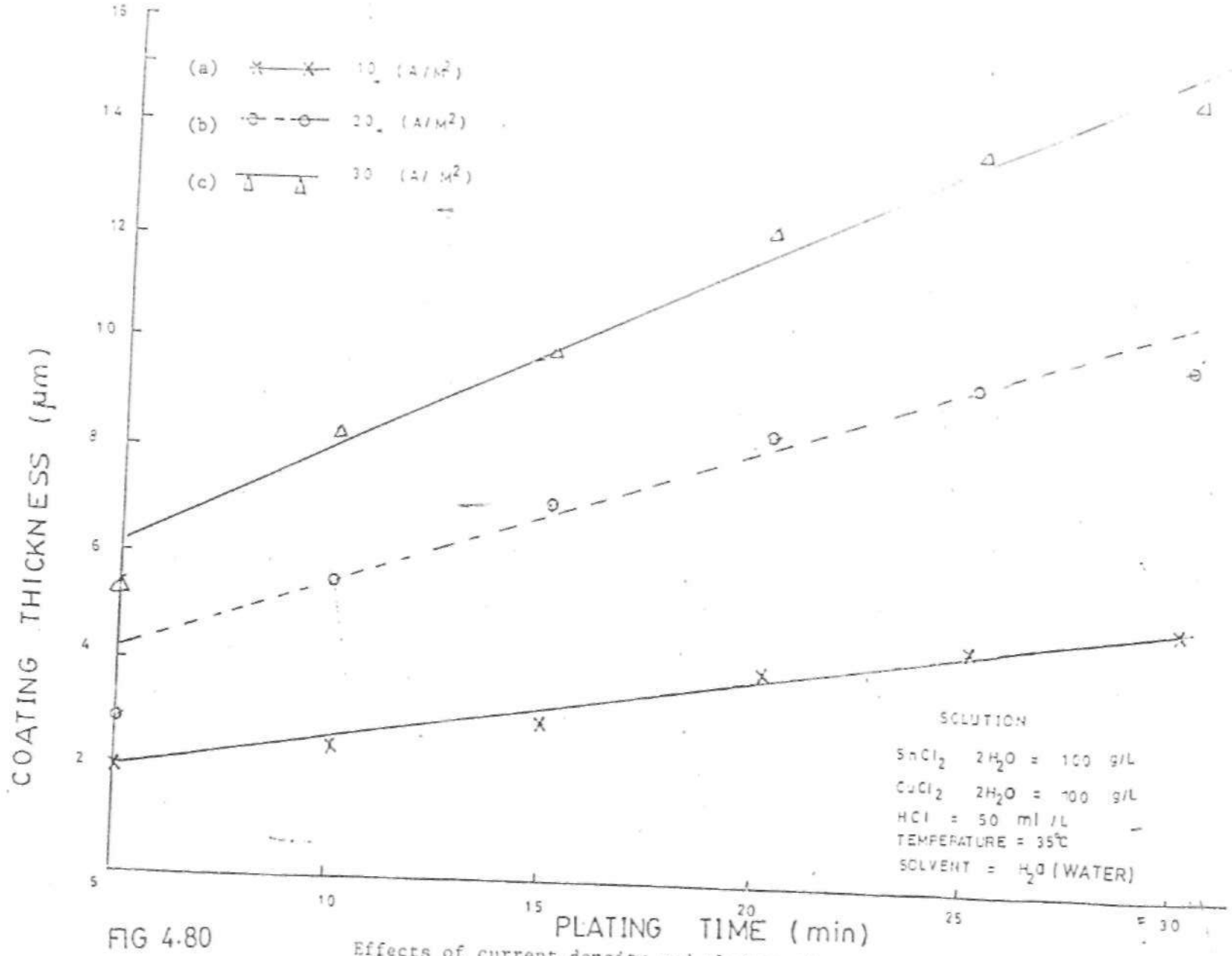

FIG 4.80

Effects of current density and plating time on bronze electroplating in distilled water of immersion plated substrate.

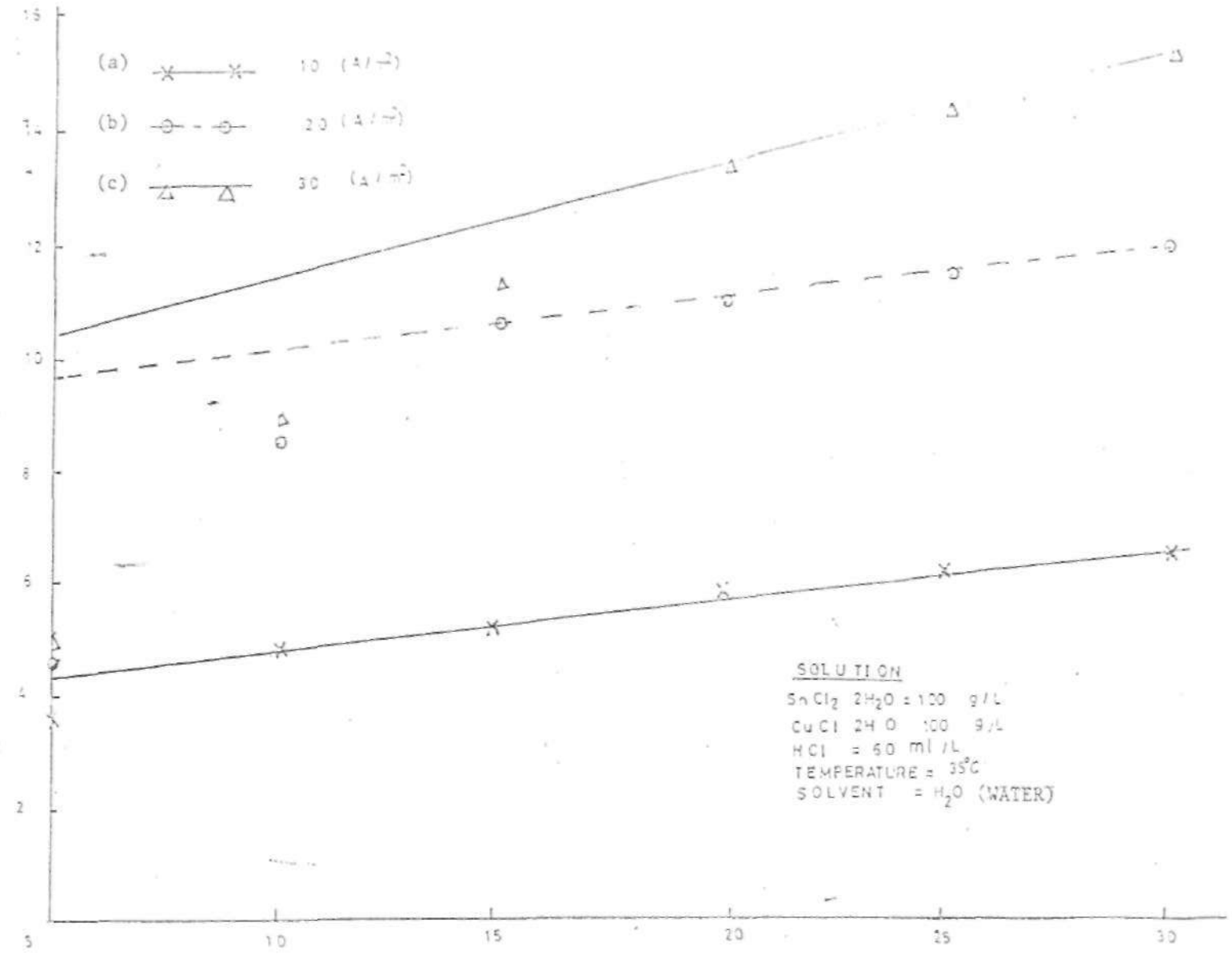

FIG. 4.81 Effects of current density and plating time on bronze electroplating in distilled water of immersion plated substrate.

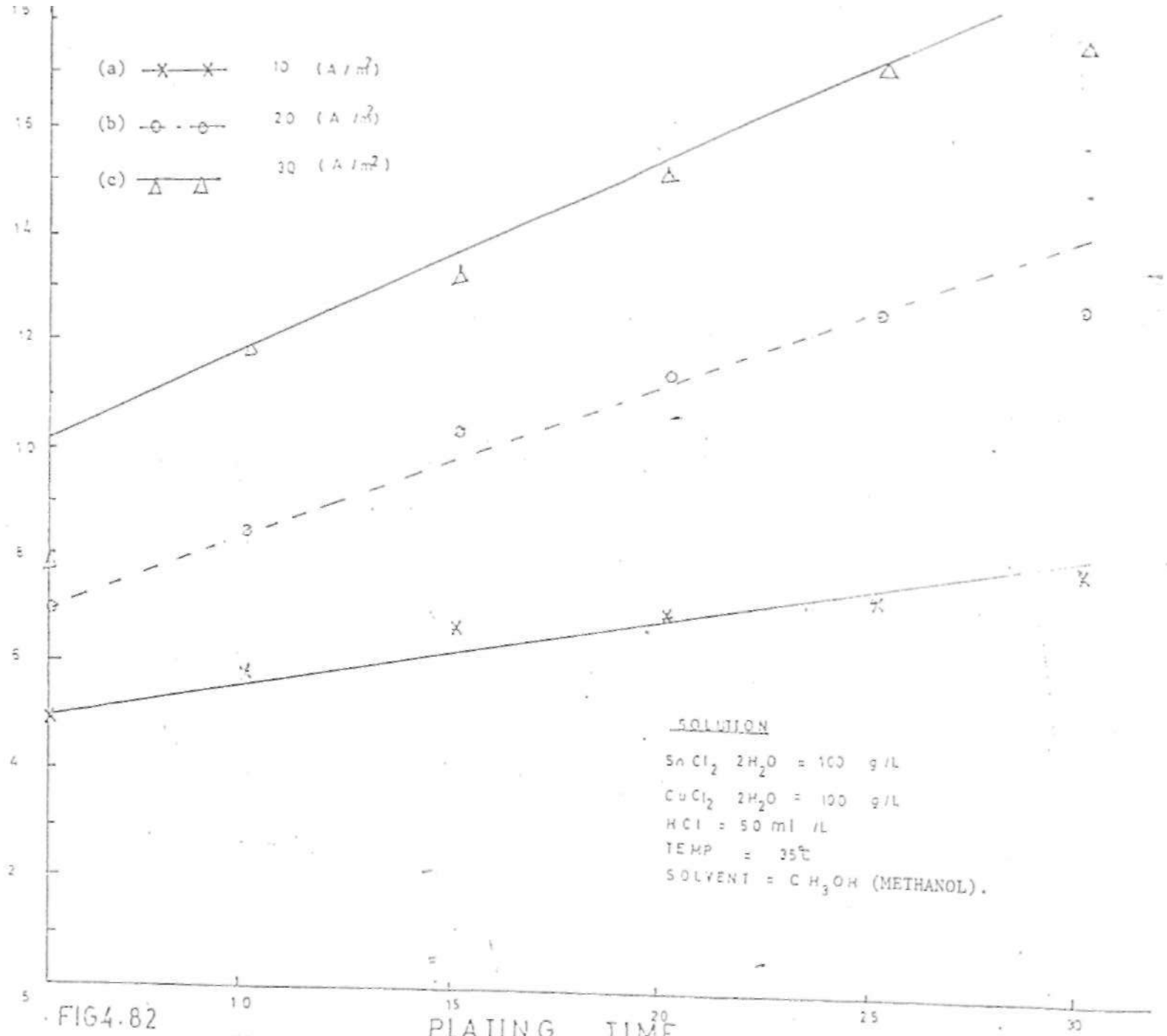

FIG4.82

Effects of current density and plating time on bronze electroplating in methanol of immersion plated substrate.

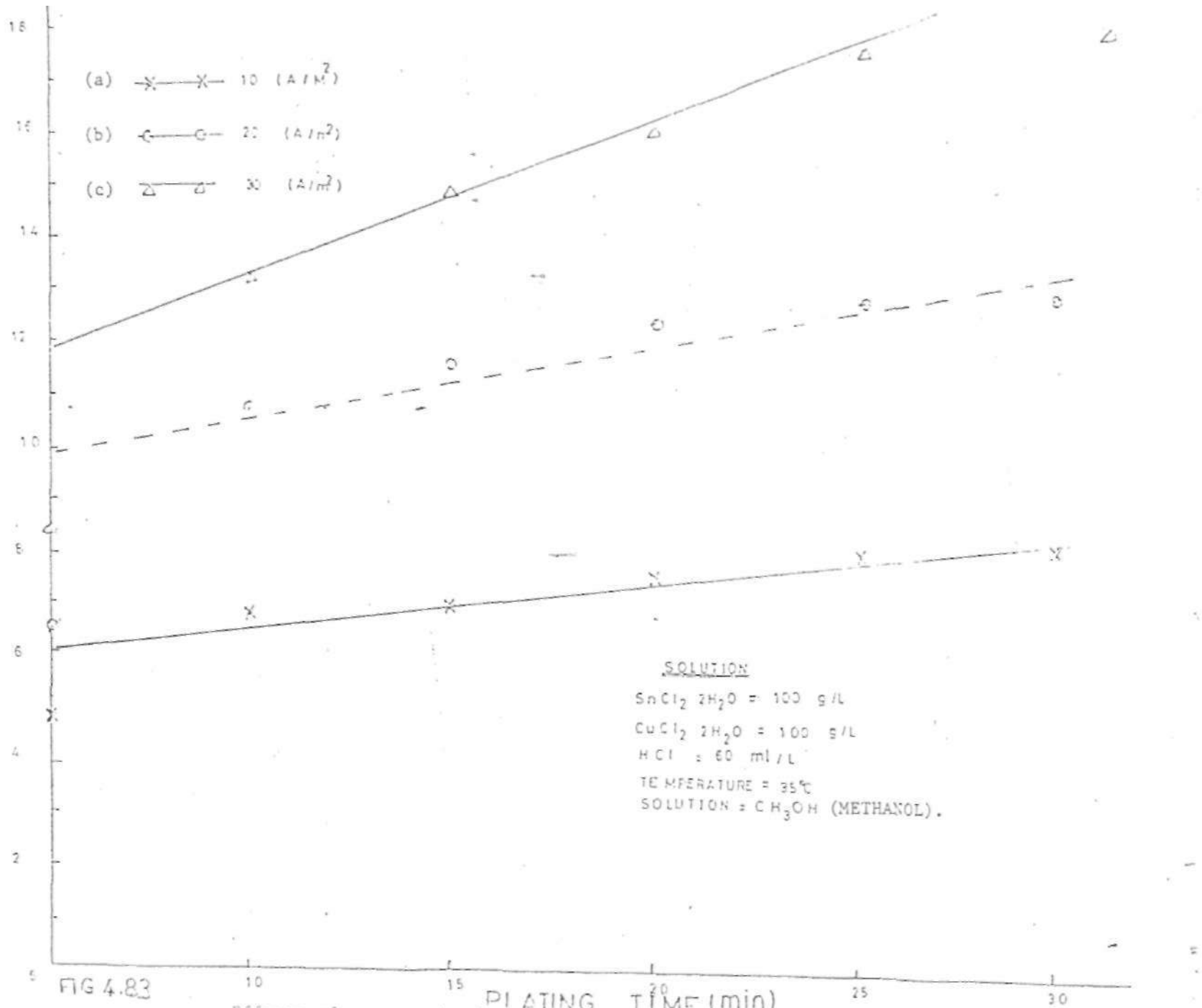

FIG 4.83 Effects of current density and plating time on bronze electroplating in methanol of immersion plated substrate.

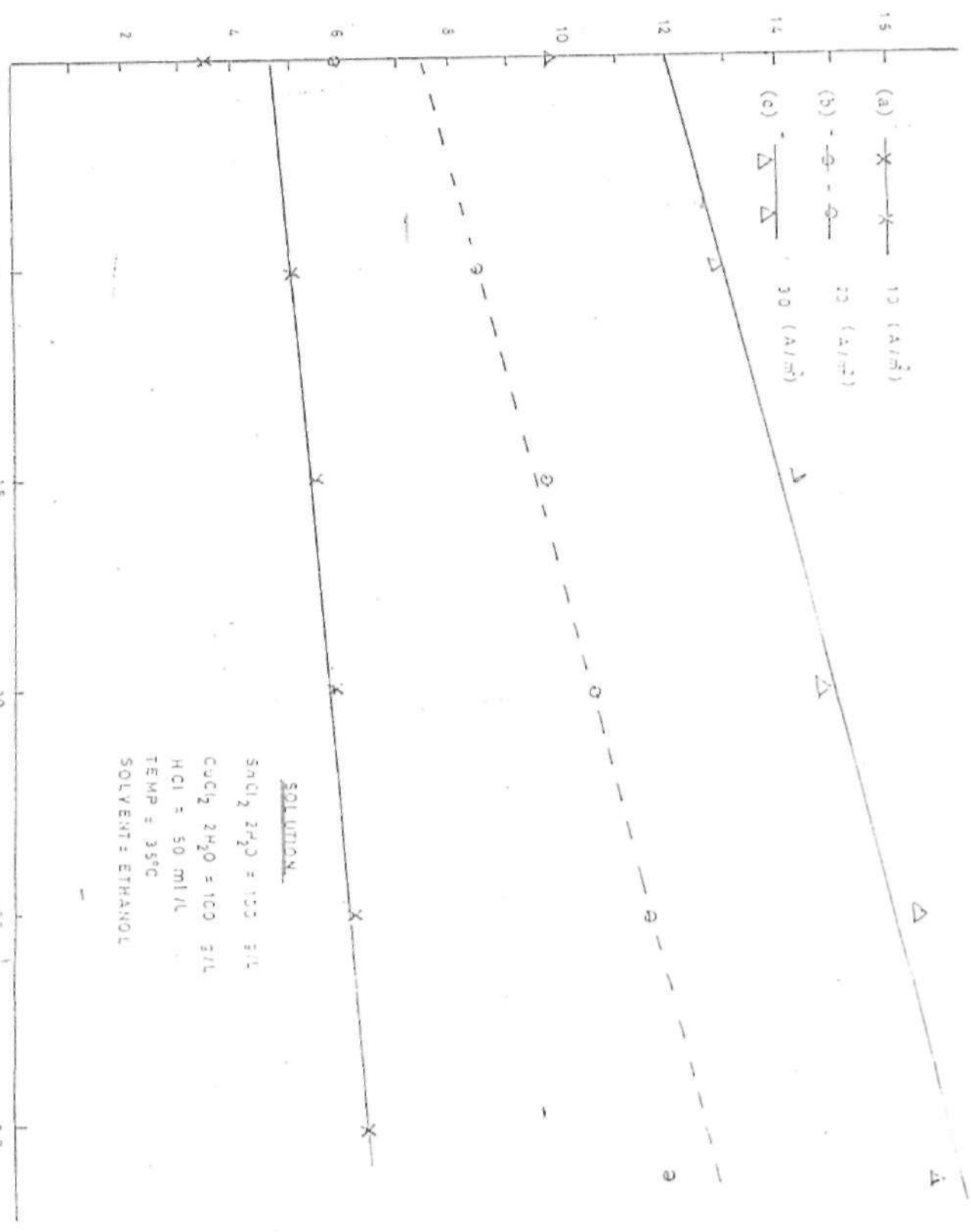

FIG 4.84 Effects of current density and plating time on bronze electroplating in ethanol of immersion plated substrate.

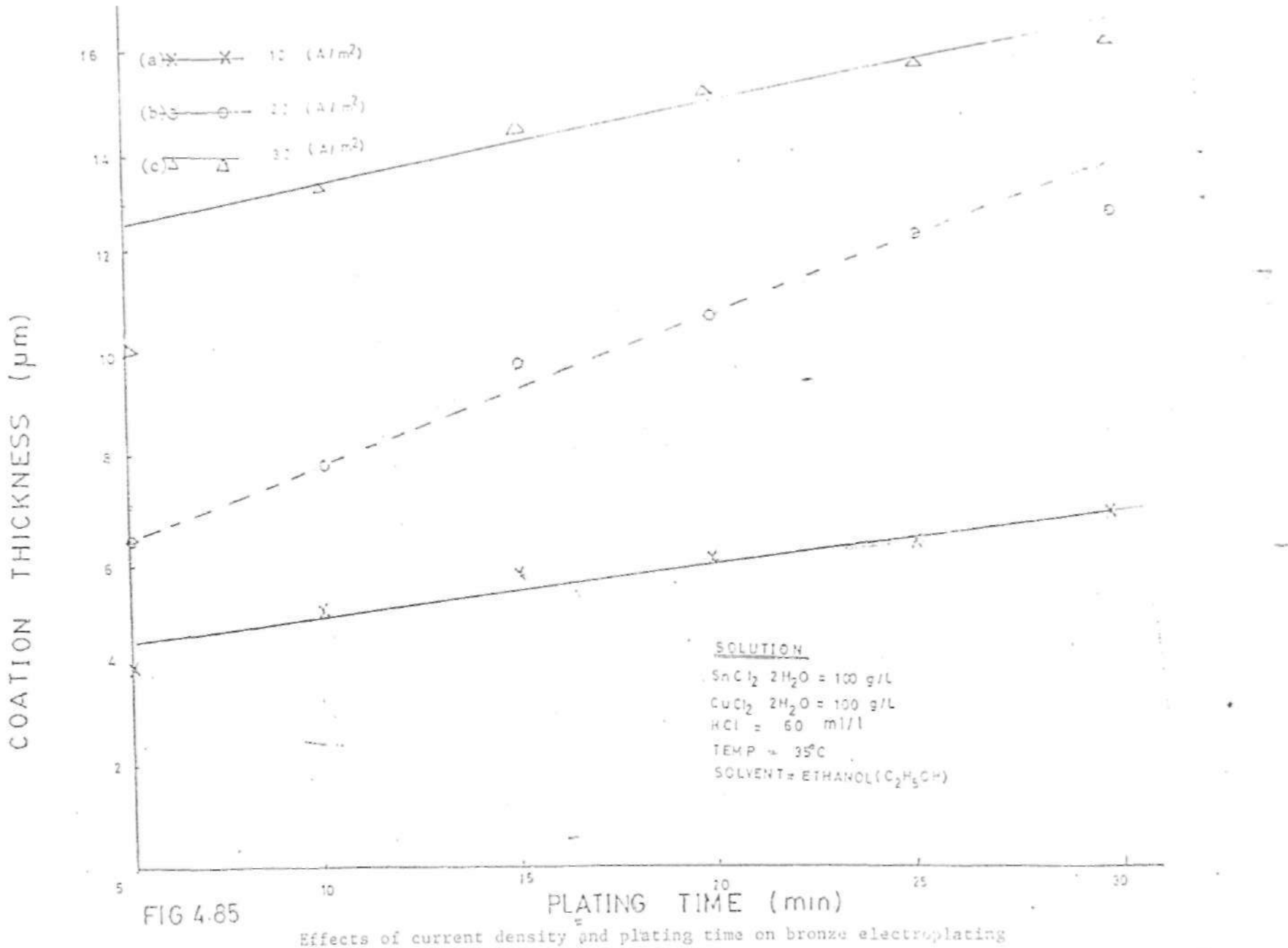

FIG 4.85

Effects of current density and plating time on bronze electroplating in ethanol of immersion plated substrate.

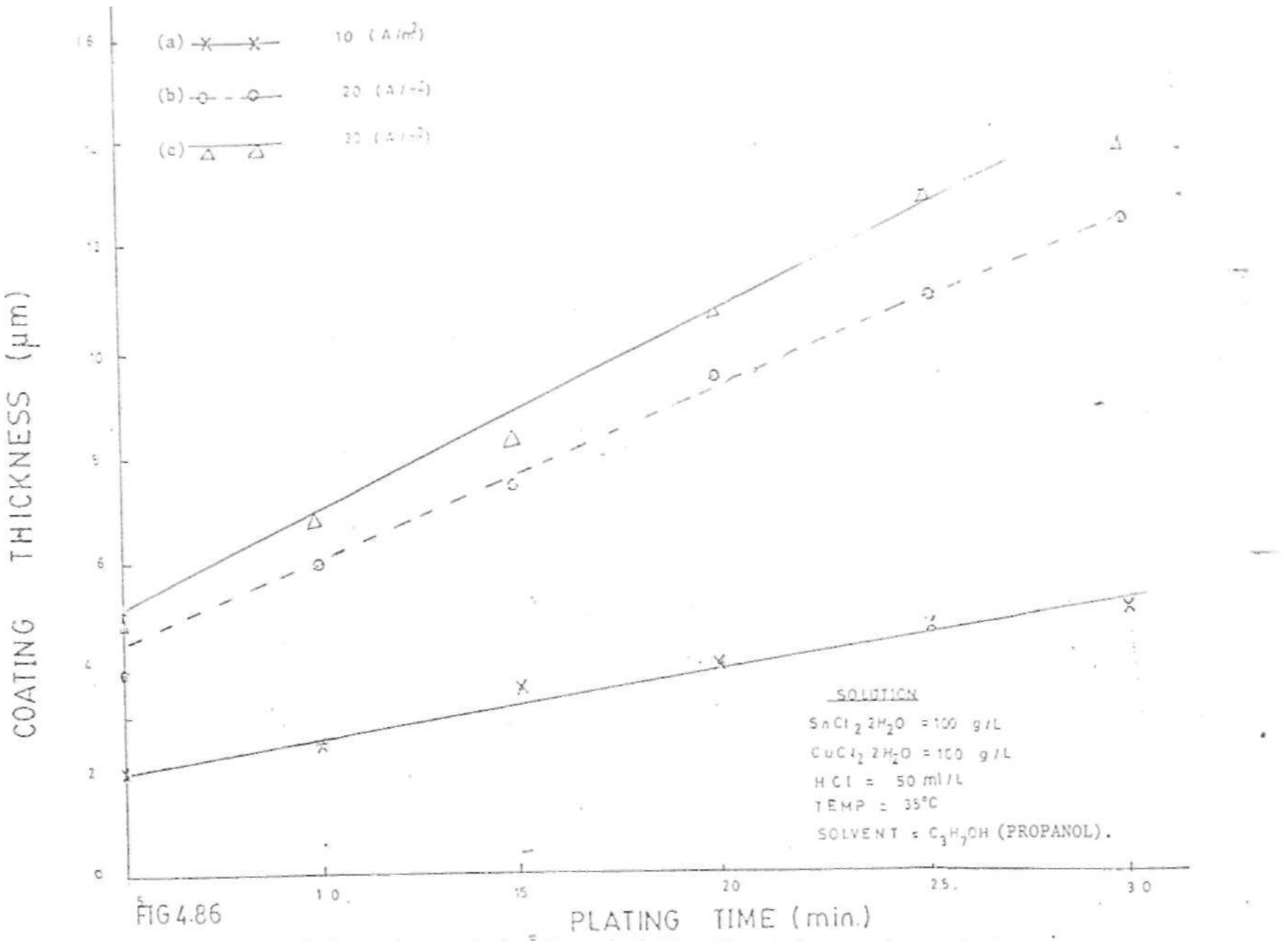

FIG 4.86

Effect of current density and plating time on bronze electroplating of immersion plated substrate in propanol.

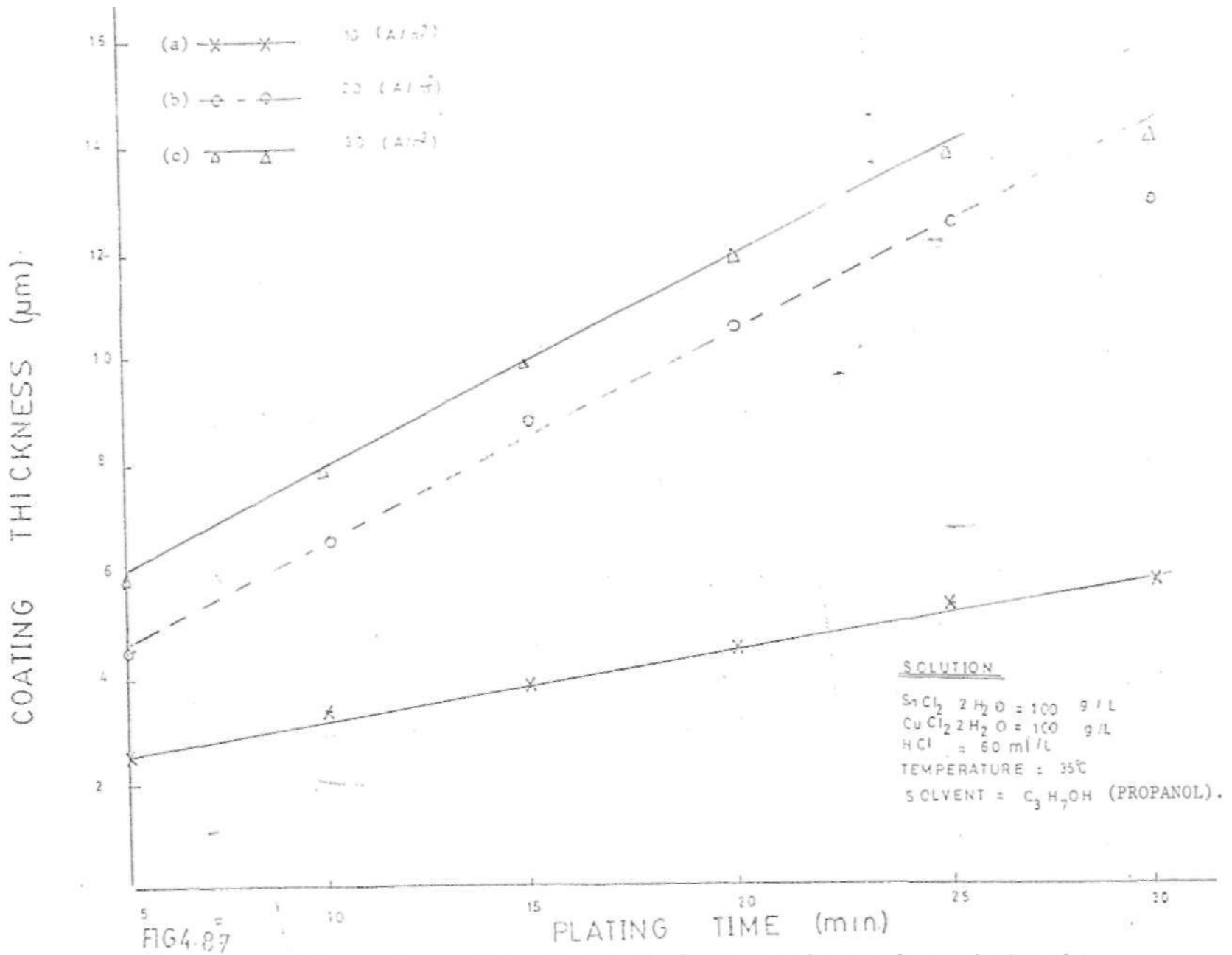

FIG4.87

Effects of current density and plating time on bronze electroplating of immersion plated substrate in propanol.

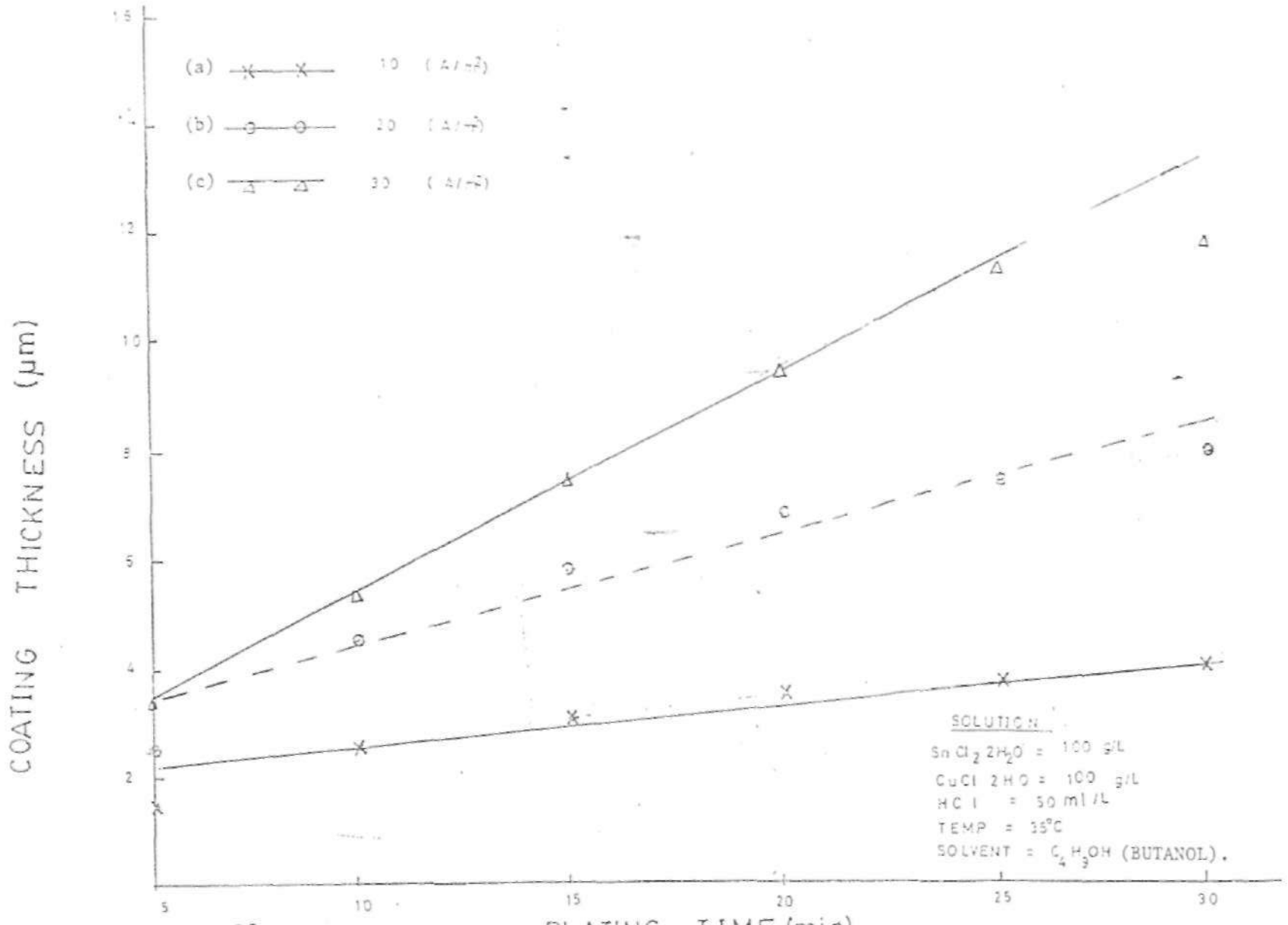

FIG 4.88

Effects of current density and plating time on bronze electroplating in butanol of immersion plated substrate.

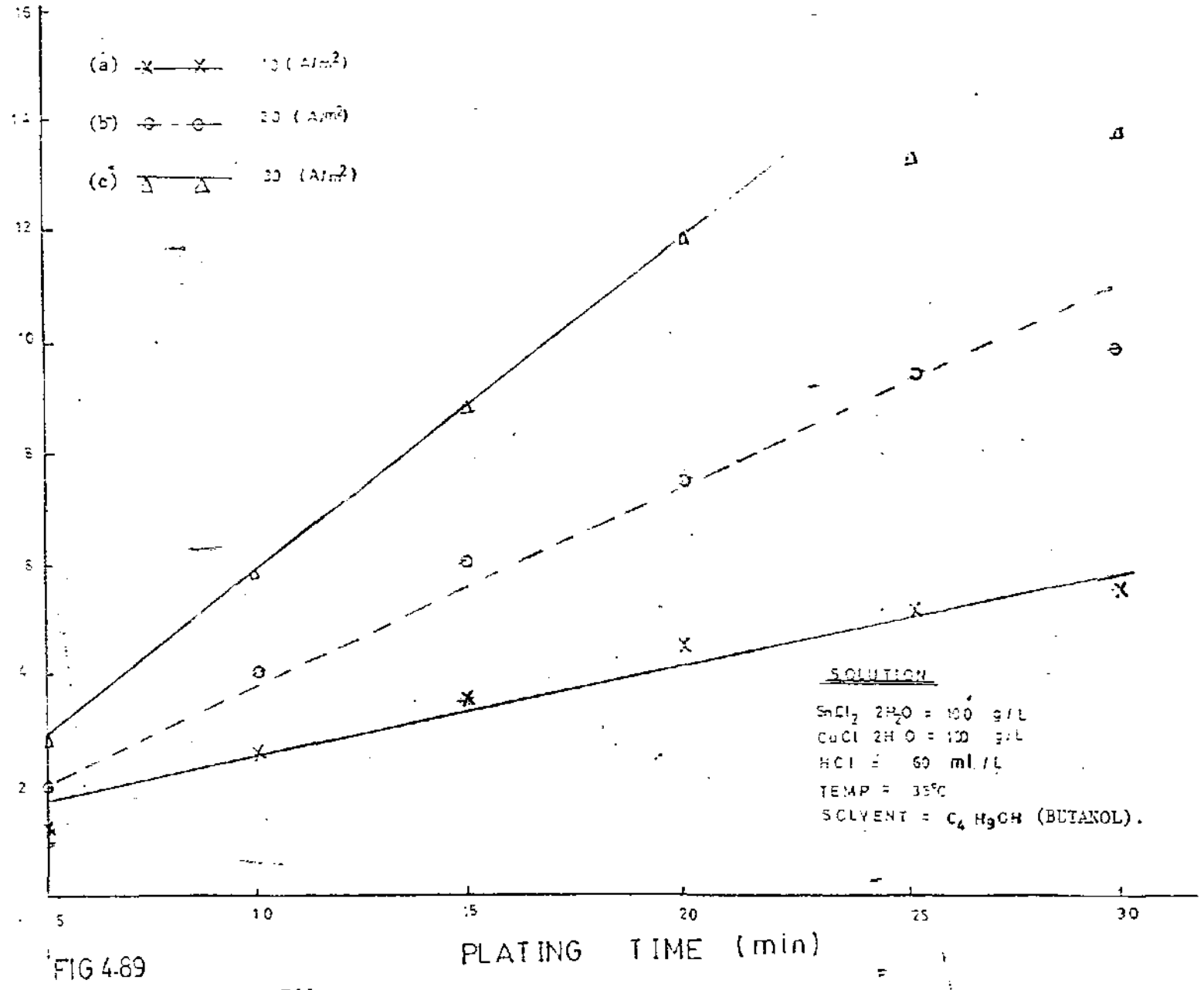

FIG 4-89

Effects of current density and plating time on bronze electroplating in butanol of immersion plated substrate.

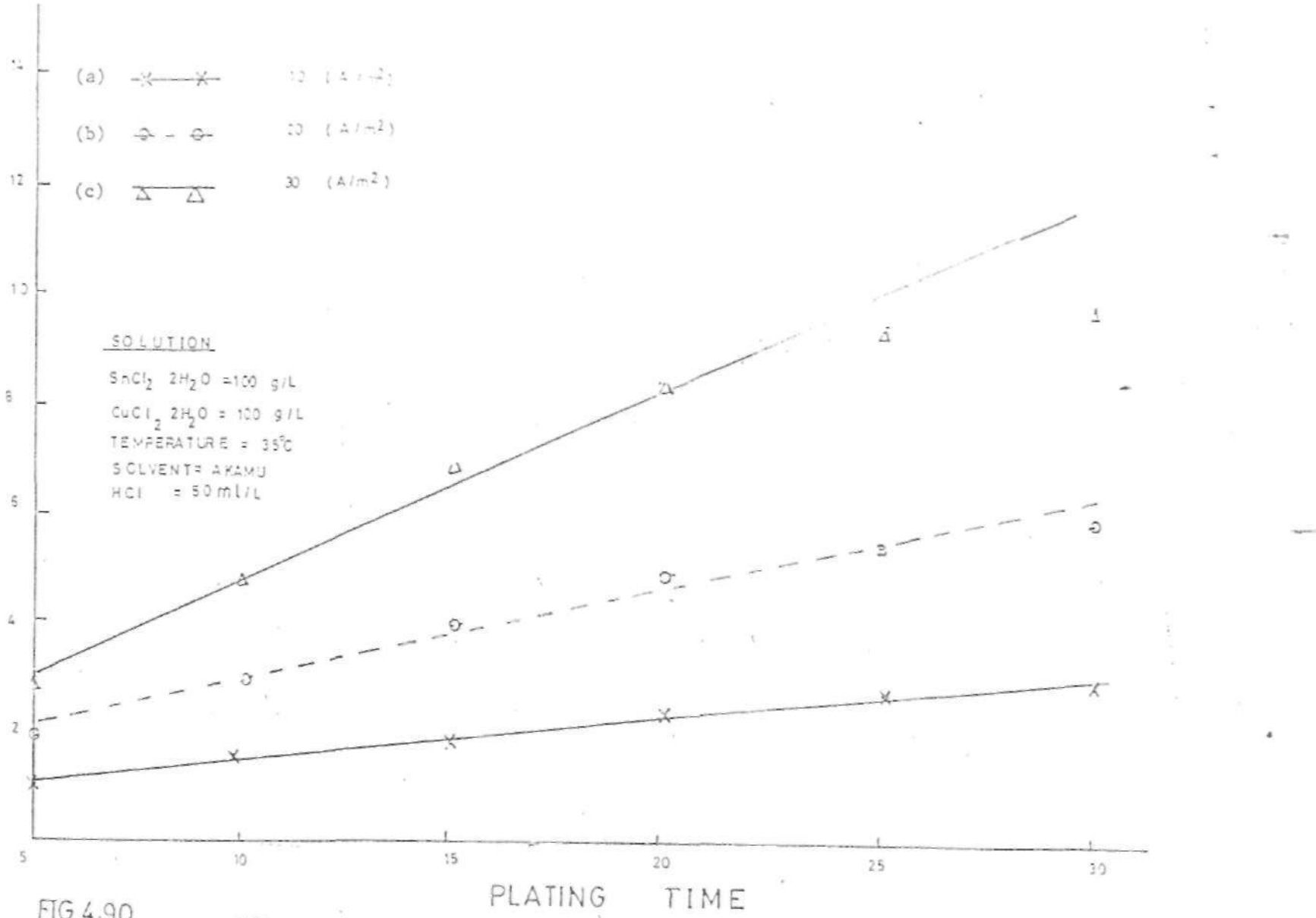

FIG 4.90

Effects of current density and plating time on bronze electroplating in akamu of immersion plated substrate..

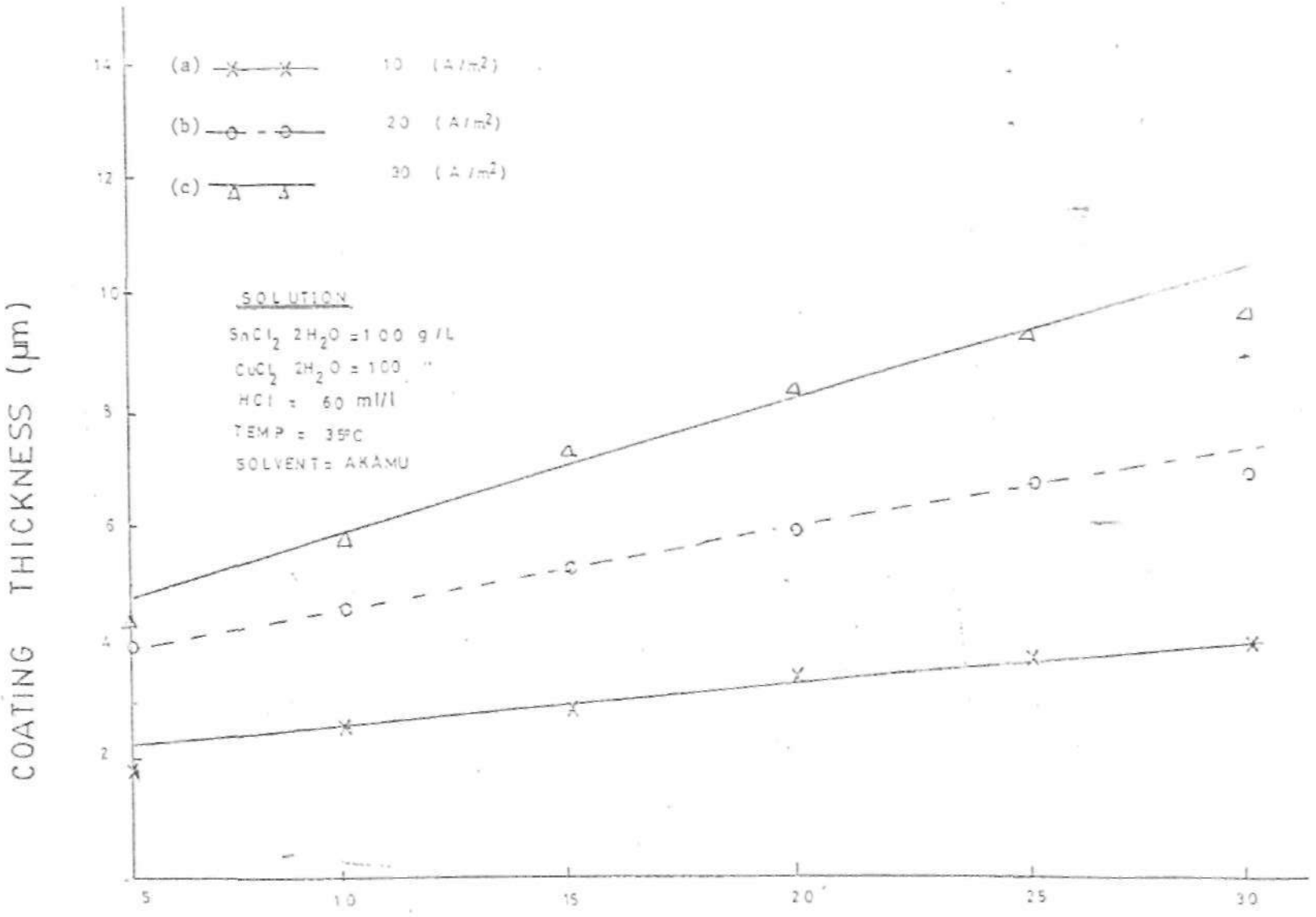

FIG4·91

Effects of current density and plating time on bronze electroplating in akamu of immersion plated substrate.

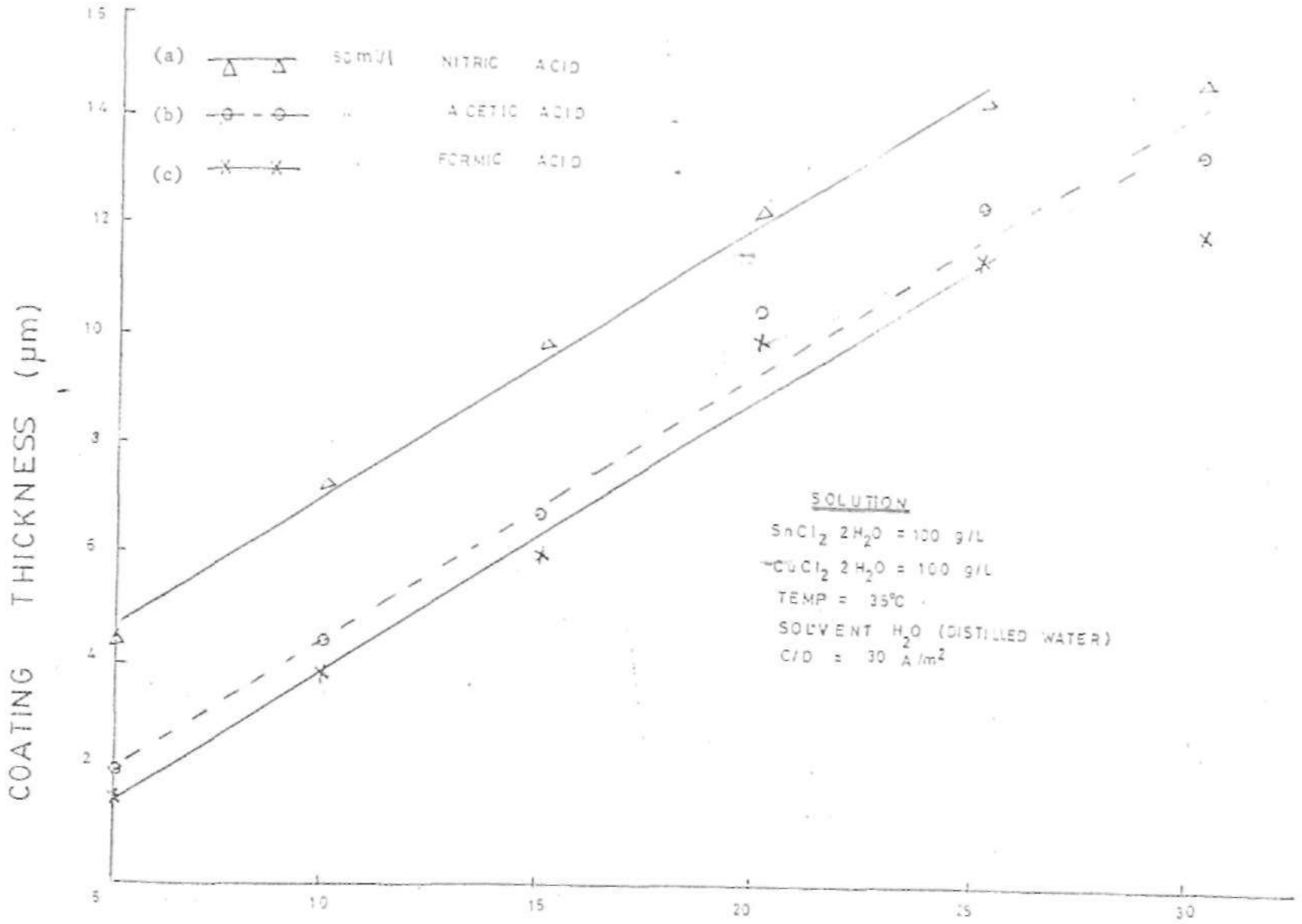

FIG4.92

Acids effects on bronze electroplating in distilled water of immersion plated substrate.

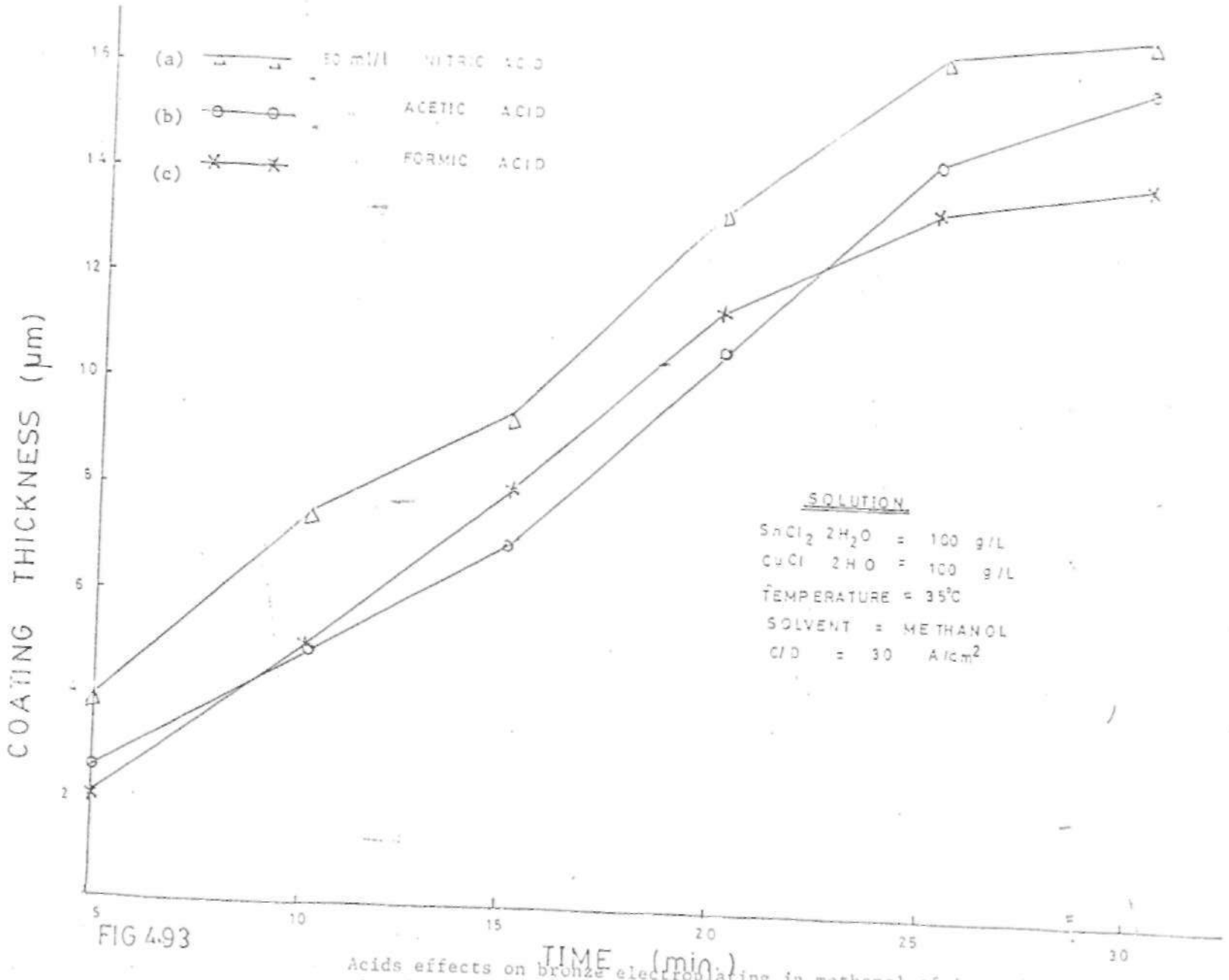

FIG 4.93

Acids effects on bronze electroplating in methanol of immersion plated substrate.

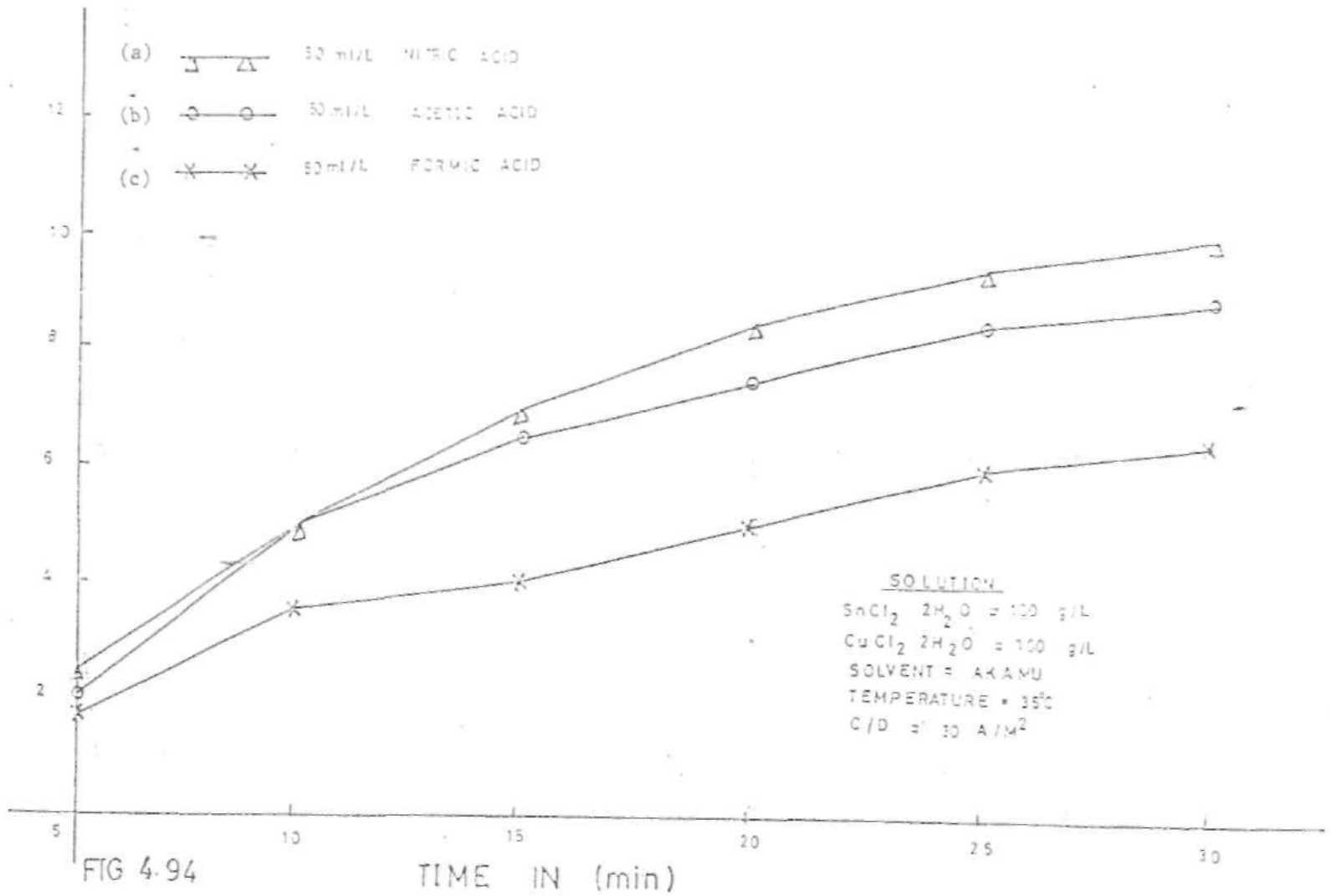

FIG 4.94

Acids Effects on bronze electroplating in akamu containing 100 g/L $SnCl_2.2H_2O$, 100 g/L $CuCl_2.2H_2O$ of immersion plated substrate.

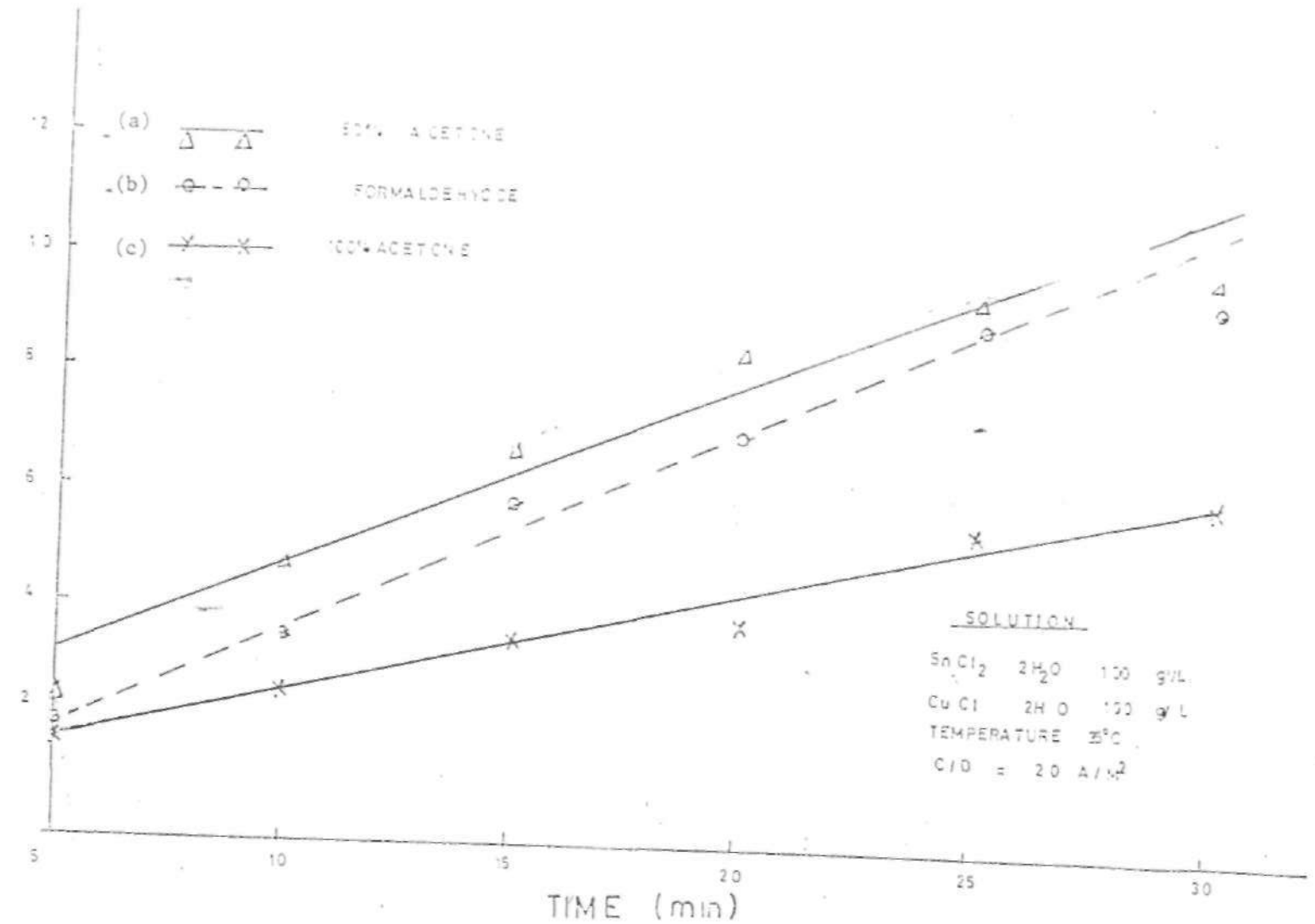

FIG 4.95

Acetone and Formaldehyde effects on bronze electroplating of immersion plated substrate by applying a current density of $20A/M^2$.

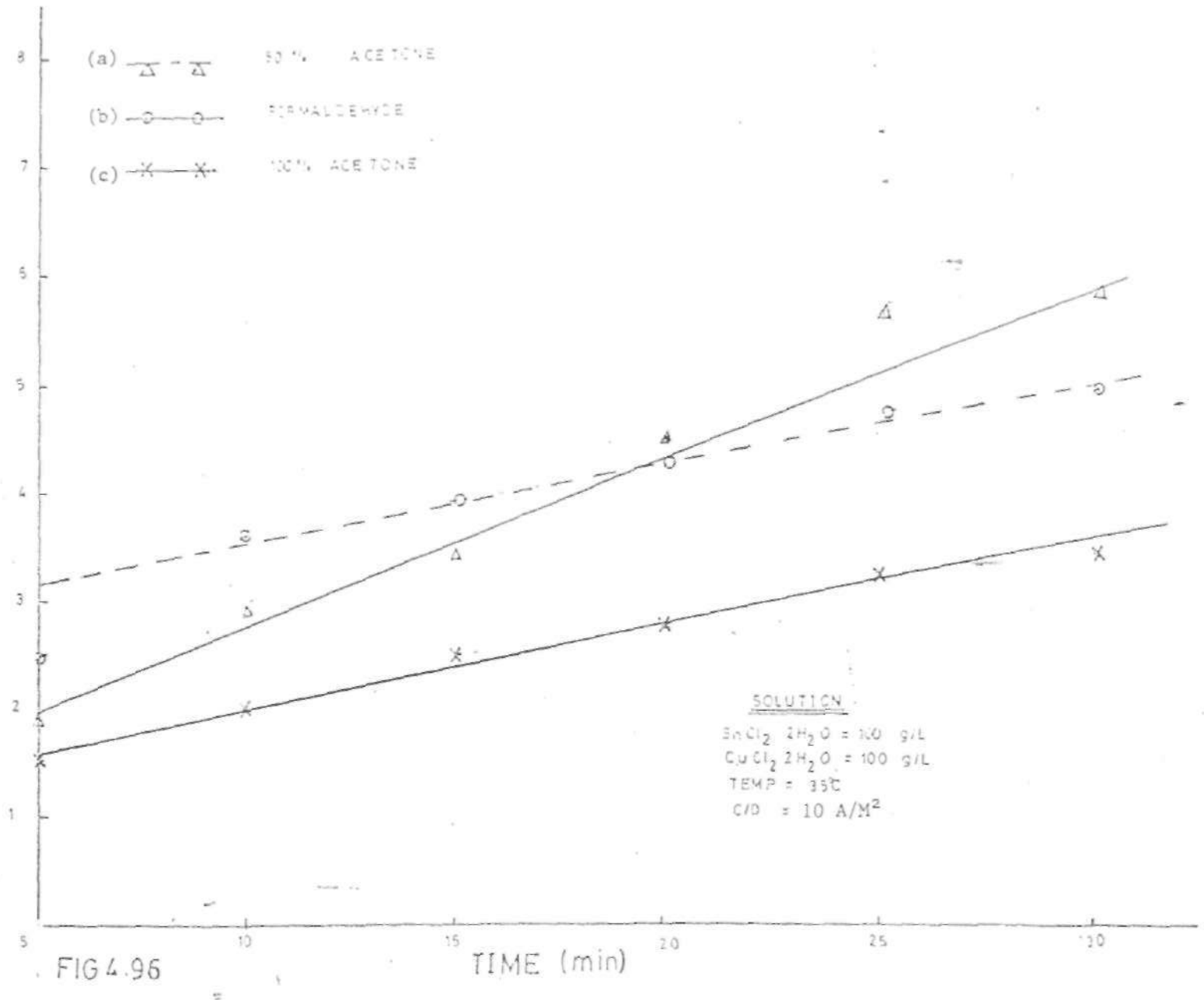

FIG 4.96

Effect of media (acetone, mixed acetone and formaldehyde) on bronze electroplating by applying current density of 10 A/M^2.

CHAPTER FIVE:

5.0 DISCUSSION:

5.1 CHOICE OF PLATING MEDIA:

This work is the first attempt made so far to present such a large volume of work covering different plating media on bronze immersion plating from cyanide-free solutions. The chosen plating media which include aqueous, alcohols and 'akamu' is based upon the solubility of cupric and stannous chlorides in them. Both cupric and stannous chlorides (hydrated) have been found to be respectively soluble in distilled water, methanol, ethanol, propanol, butanol and 'akamu' as expressed in Figures 4.1 - 4.4. The solubilities in alcohols are however, limited to lower temperatures (<100°C) because of their relatively lower boiling points.

5.2 EFFECTS OF SALTS AND HCl ON PLATING RATE IN AQUEOUS MEDIUM:

The addition of NaCl, KCl and $BaCl_2$ to bronze immersion plating solution enhances plating rate. However, the additon of HCl retards plating rate as shown in Figures 4.7 - 4.10 and Tables 1 - 4 (Appendix 1).

All the three salts have about the same effect in promoting plating rate.

The above observation may be explained in terms of common ion effect. Common ion effect causes a shift in equilibrium already established in the system towards the formation of solid particles (Pietrzyk and Frank, 1979), or the depletion of Cu^{2+} or Sn^{2+} ions; hence, promoting plating rate.

eg. $CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^{-1} + Cl^{-1}$ 5.1

$SnCl_2 \rightleftharpoons Sn^{2+} + 2Cl^{-1} + Cl^{-1}$ 5.2

HCl addition retards plating rate. It would be noted that the newly formed deposit is simultaneously being attacked by the acid.

Also, the above argument is supported by the relative stabilities of copper and tin in mineral acids. Metals more electronegative than hydrogen, eg zinc, tin, iron, etc., react with dilute hydrochloric acid (HCl) with the liberation of hydrogen gas. This is shown schematically by the electrochemical reactions:

$$Fe(s) \longrightarrow Fe^{2+} + 2e \quad \ldots\ldots 5.3$$

$$2H^{+} + 2e \longrightarrow H_2(g) \quad \ldots\ldots 5.4$$

$$\text{Net: } Fe + 2H^{+} \rightarrow Fe^{2+} + H_2(g) \quad \ldots\ldots 5.5$$

$$Sn(g) \longrightarrow Sn^{2+} + 2e \quad \ldots\ldots 5.6$$

$$2H^{+} + 2e \longrightarrow H_2(g) \quad \ldots\ldots 5.7$$

$$\text{Net: } Sn(s) + 2H^{+} \longrightarrow Sn^{2+} + H_2(g) \quad \ldots\ldots 5.8$$

However, metals more electropositive than hydrogen, such as copper are not attacked by mineral acids.

Hence, hydrochloric acid leaches out the tin in bronze deposit, leaving a porous copper deposit. The acid then contacts the basis steel metal and attacks it. Hence, there is a cycle of plating of bronze, leaching out tin and leaching the basis metal.

This may explain the erratic weight gain curves in hydrochloric acid media. During the bronze plating segment of the cycle, there is increasing weight gain which may be followed by weight loss during the leaching segment of the cycle. Since the porous copper deposit remains attached to the substrate, there is always a positive coating thickness, no matter how thin as reflected in coating thickness measurements.

5.3 STRIPPING EFFECT ON PLATING RATE:

The effect of stripping was examined. Initially plated coatings from solutions containing 20 g/L $SnCl_2.2H_2O$ and 10 g/L $CuCl_2.2H_2O$ with addition of sodium chloride were stripped and replated three times (Fig. 4.8). Stripping enhances plating rate. The second cycle of coating stripping produced weight gain up to a maximum of 0.6 mg/cm^2 versus the corresponding addition of sodium

chloride within 3 minutes. A cleaner surface phenomenon may account for the above observation. The more the coatings are stripped (peeled off) the fresher and cleaner is the substrate's surface. It is expected to be free from oxide layers and other impurities (including second phases) thus, attracting higher plating rate.

5.4 EFFECT OF ADDED SALTS AND HCl ON PLATING RATE IN ALCOHOLS:

KCl, NaCl and $BaCl_2$ are effective in that order upon improving plating rate in alcohol (methanol, propanol and butanol) media. However, the difference between the three salts on plating rate enhancement is not so remarkable as earlier observed. KCl, NaCl and $BaCl_2$ are only slightly soluble in pure alcohols. However, the three salts relatively dissolve more in alcohol solutions containing hydrated stannous and cupric chlorides than pure alcohols because of the formation of complexes, which promotes plating rate.

However, the difference in the solubilities of the three salts in alcohols may account for the observed effects on plating rate (Figures 4.11 - 4.19). HCl addition is a nuisance as already explained.

5.5 EFFECT OF ADDED SALTS ON PLATING RATE IN 'AKAMU' MEDIUM:

NaCl, KCl and $BaCl_2$ are all effective in enhancing plating rate in akamu medium (Figures 4.20 - 4.22). However, NaCl and KCl are more effective than $BaCl_2$.

Solubility and ion solvation effects may account for the relative plating rates. For example, smaller ions are more solvated than larger ones:

$\therefore \quad K^+ > Na^+ > Ba^{2+}$

The effect of solvation on the available solvent is of reverse order.

ie $\quad Ba^{2+} > Na^+ > K^+$

Solvation effect increases in order: $Ba^{2+} \longrightarrow Na^+ \longrightarrow K^+$

Available solvent decreases in order: $Ba^{2+} \longrightarrow Na^+ \longrightarrow K^+$

Hence, viscosity increases: $Ba^{2+} \longrightarrow Na^+ \longrightarrow K^+$

Hence plating rate decreases: $Ba^{2+} \longrightarrow Na^{+} \longrightarrow K^{+}$. Hence viscosity increases due to solvation effects, tend to reduce plating rate while reduced solubility due to decrease in available solvent enhances it. Hence, the observed plating rate is the difference between both effects. Since all the salts enhance plating rate; therefore, the reduced solubility effect appears to be more dominant.

Like in aqueous medium, the three salts (ie NaCl, KCl and $BaCl_2$) are all soluble in akamu. However, the plating rate is lower in akamu compared to the other media.

The low plating rate observed in 'akamu' may be explained in terms of obstruction to ionic diffusion. The colloidal particles in 'akamu' (suspension) probably obstruct free ionic diffusion from bulk solution to the plating sites on substrate's surface, thereby slowing down plating rate.

5.6 MEDIA AND ADDED SALTS EFFECTS ON PLATING RATE (COATING THICKNESS):

An attempt has already been made in this work (sections 5.1 - 5.5) to explain the various effects of added salts: NaCl, KCl and $BaCl_2$ in aqueous, alcohols and 'akamu' media. A similar pattern is observed when sodium chloride (Figures 4.23 - 4.27) and potassium chloride (Figures 4.28 - 4.29) are added to plating solutions when classifying the effects of plating media.

The results show that higher plating rates are obtained in lower molecular weight than in higher molecular weight alcohols. Thus, the plating rates are higher in methanol and ethanol than in propanol and butanol media approximately in that order of decreasing plating rate (Figures 4.23 - 4.29). The explanation to the above observation could be that the lighter the alcohol (low viscosity) the higher the plating rate.

The plating rate in aqueous medium is higher than the rates obtained from butanol and 'akamu' media (Figure 4.9). The explanation to this is that although NaCl, KCl and $BaCl_2$ are soluble in aqueous and akamu media, the difference in plating rate may be due to the fact that aqueous medium presents less resistance to ionic diffusion during plating compared to 'akamu' medium. Akamu particles are impediments to free ionic migration.

Since NaCl KCl and $BaCl_2$ are less soluble in butanol compared to methanol and ethanol, their effect on plating rate are less in this medium, and it may account for the lower plating rate.

5.7 PLATING RATES IN DIFFERENT MEDIA:

As earlier observed, higher plating rate is promoted in lower molecular weight alcohols than in akamu (Figures 4.30 - 4.31). Reasons have already been advanced for the above observations.

The coating thickness increases with plating time before reaching steady conditions after which the thickness remains fairly constant.

The increase in coating thickness with plating time is fairly linear at the initial stage, but approaches a steady value after about 2 to 3 minutes of plating. The above observation is an indication of the end-point of actual plating.

In most cases, the thickness is hardly over 1.0μm irrespective of plating media.

Worthy of note is the difficulty in detemining the increment in coating thickness at the initial stages of plating ($0<t<5$ seconds). hence, the coating thickness at zero time can only be obtained by interpolation in the negative direction.

5.8 MEDIA, HCl AND SODIUM DITHIONATE EFFECTS ON PLATING RATE:

In all of the Figures (4.32, 4.34, 4.36, 4.38, 4.40 and 4.42), the addition of HCl retards plating rate; its addition is clearly a nuisance due to its leaching effect. Conversely, plating rate is promoted in acid-free solutions irrespective of plating media (solvents).

The addition of sodium dithionate in acid-free solutions promotes plating rate.

As earlier observed, higher plating rate is favoured in lower molecular weight alcohols and some explanation has already been advanced in respect of that observation. The plating rate is highest in methanol medium in which maximum weight gain of 0.8 mg/cm^2 versus the corresponding addition of sodium

dithionate is obtained as against 0.41 mg/cm^2 obtained in butanol plating medium. Thus, the plating rate decreases with increase in molecular weight of the alcohol.

The plating rate in aqueous medium is greater than in 'akamu', but it is about the same as in butanol medium. An explanation to this has already been given. Colloidal particles obstruct the migration of ions in akamu compared to aqueous medium.

Two mechanisms of immersion plating exist:

(i) Displacement plating: $Fe \longrightarrow Fe^{2+} + 2e$ 5.9

$Sn^{2+} + 2e \longrightarrow Sn$ 5.10

(ii) Chemical plating: $Sn^{2+} + 2e \longrightarrow Sn$ 5.11

Reducing agent $\longrightarrow$ Oxidized + 2e 5.12

In bronze plating, copper is more noble than tin, thus, the reaction below cannot ordinarily take place simultaneously: (Lowenheim, 1978)

$Cu + Sn^{2+} \longrightarrow Sn + Cu^{2+}$ 5.13

However, the electrode potential of copper can be made more negative by the addition of a complexing agent into the bronze plating solution. Thiourea and other reducing agents such as sodium dithionate and L-cysteine form stable complexes with copper. They enhance solution stability, lower copper potential; hence, promoting the codeposition of the two metals onto the substrate's surface. Since the two metals are codeposited, more coating thickness or higher plating rate is obtained than from solutions containing no complexing agents.

5.9 MEDIA, CONCENTRATION AND SODIUM DITHIONATE EFFECTS ON PLATING RATE:

The effects of media and dithionate on plating rate enhancement as shown in Figures 4.33, 4.35, 4.37, 4.39, 4.41 and 4.43 have already been explained in section 5.8.

The plating rate also increases with the conrresponding increase in copper ion (Cu^{2+}) concentration in solution when stannous ion concentration is kept constant. This is because Cu^{2+} is easier to plate than Sn^{2+} from free energy point of view. Consequently, the more the cu^{2+} in solution the higher is

the plating rate.

Also, it is observed that the plating rate increases with the addition of sodium dithionate in solution. Chemical plating is increased hence the observation. Complexing agent promotes solution stability, narrows the codeposition potential, hence promoting plating rate.

The highest plating rate with respect to sodium dithionate addition is obtained in solutions containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$ as against the lowest plating rate obtained from solutions containing 8 g/L $SnCl_2.2H_2O$ and 4 g/L $CuCl_2.2H_2O$ irrespective of plating medium.

The magnitude of the highest plating rate obtained in methanol medium versus the corresponding sodium dithionate addition is 0.80 mg/cm^2 as against the lowest plating rate of 0.40 mg/cm^2 obtained in butanol medium. The two solutions contain 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$. The respective solubilities of cupric and stannous chlorides in the alcohols and their viscosities could account for the observed differences in plating rates in alcohols.

The gain in coating thickness versus the addition of L-cysteine is higher in methanol and is about 810mμm(Fig. 46) as against 450mμm obtained in butanol medium (fig. 4.52).

5.10 MEDIA, HCl AND L-CYSTEINE EFFECTS ON COATING THICKNESS:

From all the Figures (4.44, 4.46, 4.48, 4.50, 4.52, and 4.54), HCl addition retards the gain in coating thickness as earlier observed.

The Addition of L-cysteine in the plating solution enhances plating rate (gain in coating thickness). The explanation to this is the fact that L-cysteine like sodium dithionate is a reducing agent.

5.11 MEDIA, CONCENTRATION AND L-CYSTEINE EFFECTS ON COATING THICKNESS:

Lower molecular weight alcohols favour plating rate as earlier observed. The addition of L-cysteine between 4 - 20 g/L in the plating solutions promotes coating thickness growth (Figures 4.45, 4.47, 4.49, 4.51, 4.53 and 4.55).

The plating rate or coating thickness increases with the corresponding

increase in Cu^{2+} concentration in solution as the stannous chloride concentration is kept constant.

The highest plating rate is obtained from solutions containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$. Conversely, the least coating thickness is obtained from solutions containing 8 g/L $SnCl_2.2H_2O$ and 4 g/L $CuCl_2.2H_2O$ irrespective of plating medium; thereby, supporing Fick's diffusion Law.

For the alcohols, the highest coating thickness growth of 810mμm with respect to L-cysteine level is obtained in methanol medium (Fig. 4.47) and the lowest coating thickness of 450mμm is obtained from butanol medium (Fig. 4.53) containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$.

The plating rate is higher in butanol than in aqueous and akamu media. The viscosity of butanol is less than that of water and 'akamu', and could account for the slight difference on plating rate.

5.12 MEDIA, HCl AND THIOUREA EFFECTS ON COATING THICKNESS:

Lower molecular weight alcohols promote coating thickness growth as earlier observed.

The addition of HCl retards plating rate as earlier observed. (Fig. 4.56, 4.58, 4.60, 4.62, 4.64 and 4.66).

The addition of thiourea promotes coating thickness growth in acid-free solutions. This is because thiourea is a reducing agent. It catalyses the reduction of ions in bulk solution into metallic form which is subsequently plated onto the substrate's surface. The reaction takes place very rapidly and it could be less than 2 minutes. Also, thiourea is very soluble in aqueous and alcohol media. Hence, a high amount of thiourea is in solution catalysing the reduction reaction resulting in higher plating rate.

The plating rates are higher in lower molecular weight alcohols as earlier observed. Coating thickness growth up to 950mμm and 700mμm with respect to thiourea addition are obtained in methanol and ethanol media respectively (Fig. 4.58 and 5.60).

5.13 MEDIA, CONCENTRATION AND THIOUREA EFFECTS ON COATING THICKNESS:

Plating rate increaseswith corresponding increase in copper ion concentration in solution (4 - 8 g/L $CuCl_2.2H_2O$) as stannous chloride concentration is kept constant. The reason for this observation has already been given.

The addition of thiourea to plating solution between 4 - 20 g/L promotes coating thickness growth as earlier observed (Fig. 4.59, 4.61, 4.63, 4.65 and 4.67). An explanation has already been given on the effect of thiourea in promoting plating rate. P. J. Proll (1972) in his work on copper and nickel plating, has observed that the addition of thiourea to the electroplating solutions promoted higher plating rates, which supports this work.

The highest coating thickness with respect to thiourea additon is 950mμm obtained in methanol medium (Fig. 4.59) as against the lowest coating thickness of 265mμm obtained from akamu medium (Fig. 4.67) all from solutions containing 8 g/L $SnCl_2.2H_2O$ and 8 g/L $CuCl_2.2H_2O$. Viscosity and solubility effects have already been used to provide an explanation to the above observation.

5.14 MEDIA (WATER/ALCOHOL) CONCENTRATION AND SODIUM DITHIONATE EFFECTS ON COATING THICKNESS:

Higher alcohol concentration in aqueous solutions favours plating rate with respect to the corresponding addition of sodium dithionate (Fig. 4.68 - 4.71).

The plating rate is moderate in 50% alcohol medium compared to a relatively lower plating rate obtained from 25% alcohol. However, the plating rate is higher in 75% alcohol and highest in pure alcohol. However, because of high cost of pure alcohol, plating in (mixed) alcohol may be commercially exploited. Coating thickness up to 750mμm and 615mμm versus the corresponding addition of sodium dithionate are obtained in mixed methanol and ethanol respectively as against 450 mμm obtained in mixed propanol or butanol of 75% concentration.

5.15 MEDIA (WATER/ALCOHOL) CONCENTRATION AND L-CYSTEINE EFFECTS ON COATING THICKNESS:

Coating thickness growth is promoted in higher alcohol concentration with respect to the addition of L-cysteine in plating solution (Fig. 4.72 - 4.75).

The plating is more effective in solution containing 75% alcohol compared to solutions containing 25% alcohol as earlier observed.

Mixed methanol and mixed ethanol promote higher plating rate compared to mixed propanol or butanol media. An explanation to that has already been given.

Coating thickness growth up to 700mμm and 610mμm versus L-cysteine addition have been obtained in 75% methanol and ethanol respectively (Fig. 4.72 - 4.73).

The addition of L-cysteine in the plating solution of concentration eg. $2 \leq$ [L-cysteine] $\leq$ 20 g/L promotes coating thickness growth irrespective of the type of alcohol. The solubility of L-cysteine and its ability to stabilize the plating solution have already been given as an explanation to the above observation.

5.16 MEDIA (WATER/ALCOHOL) CONCENTRATION AND THIOUREA EFFECTS ON COATING THICKNESS:

As earlier observed, coating thickness growth is promoted in higher alcohol concentration with respect to the corresponding level of added thiourea (Fig. 4.76 - 4.79). Hence plating is better in solutions containing 75% alcohol compared to solutions containing 25% alcohol. The explanation to this could be the relative solubilities of alcohol and aqueous medium put together and the effects of their relative viscosities as earlier explained in this work.

The addition of thiourea to the plating solution of concentration eg. $2 \leq$ [thiourea] $\leq$ 20 g/L enhances coating thickness growth. The explanation to this has earlier been given.

5.17 EQUATIONS OBTAINED FROM LINEAR CURVES:

Two hundred and four equations have been obtained from the linear plots of this work. They include equations on solubility, bronze immersion plating and bronze electroplating. These equations will assist in relating the relevant parameters in the various ranges investigated.

Under controlled conditions, it is possible to obtain the solubility of cupric or stannous chloride in aqueous, alcohols or in mineral and vegitable oils, by simply varying the temperatures as shown in equations 4.3 to 4.18.

Similarly, for immersion plating, we can obtain any plating rate or coating thickness of interest by simply varying the concentration of NaCl, KCl, $BaCl_2$, sodium dithionate, L-cysteine and thiourea in the plating solution as given in equations 4.19 to 4.161.

Also, for bronze electroplating, it is possible to obtain any coating thickness or plating rate by simply varying the plating time as shown in equations 4.162 to 4.206.

5.18 CONCLUSIONS:

(1) NaCl, KCl and $BaCl_2$ addition to bronze immersion plating solutions promotesplating rate.

(2) Reducing agents such as sodium dithionate, L-cysteine and thiourea promote plating rate approximately in that order during immersion plating.

(3) Lower molecular weight alconols such as methanol, ethanol promote faster plating rate compared to aqueous and butanol media.

(4) HCl addition to bronze immersion plating solutions retards plating rate.

(5) Acid addition to electroplating solutions (eg. nitric, acetic and formic) increases plating rate approximately in that order.

(6) Bronze electroplating in 50% water/acetone and 37% formaldehyde media promotes faster plating rate compared to 99% acetone medium.

(7) Higher current densities (10 - 30 A/m^2) increase coating thickness. However, lower current densities produce finer and brighter coatings.

(8) Solution agitation favours plating rate.

5.19 SUGGESTION:

From the results of this investigation the following suggestions are made:-

(1) Bronze immersion plating could be commercially exploited in mixed lower molecular weight alcohols (methanol and ethanol), aqueous and akamu media. The mixed alcohols (water/alcohol) are cheaper than pure alcohols, but produce plating rate comparable to pure alcohols.

Akamu medium is suggested because of its fine bright coatings. Akamu is also cheaper than alcohols in terms of cost and its readily available.

(2) NaCl, KCl, $BaCl_2$ could be added in that order to bronze immersion plating solutions in order to enhance plating rate.

(3) Thiourea, L-cysteine and sodium dithionate should be used as reducing agents during bronze immersion plating in cyanide-free solutions. They promote faster plating rate even at very low solution concentration.

(4) Moderate current densities (eg. 5 - 15 A/m^2) should be employed during bronze electroplating in order to obtain moderate plating rate as well as fine coatings.

5.20 RECOMMENDATION FOR FURTHER WORK:

Further work is required in the following areas:

(i) Work is required to establish the composition of the bronze immersion plated coatings.

(ii) Heat treatment of the immersion plated coatings in order to effect interatomic diffusion between coatings and substrate resulting to mechanical 'keying' at the interfaces.

(III) Plating could be exploited in vegetable and/or engine oils.

(IV) The effects of 'mixed' reducing agents (eg. dithionate/thiourea, dithionate/L-cysteine, L-cysteine/thiourea, etc) on plating could also be exploited.

REFERENCES:

Atkins, P.W., Physical Chem., 2nd End, Oxford Univer. Press (1982), 313-373.

Aylward, G.H., and Findlay, T.J.V, S.I. Chem. Data, 2nd Edn. John Wiley & Sons (London) (1974) 61-110.

Bard, A.J.. and Faulkner, L.R., Electrochemical Methods, Fundamental and Applications., 1st Edn., John Wiley and Sons, New York (1980) 5-21.

Bennett, H., Ed., The Chem. Formulary, Vol. III, Van Nostraud, New York (1936) 275-286.

Blum, W. and Hogaboom, G.B. Princ. of Electroplating and Electroforming,3rd Edn., Reihold, New York (1967) 192-194.

Braley, J.C., U.S. Patent (1942) 2, 282, 513.

Brant, W.T. and Langein, G., Electrodeposition of metals, 8th Edn. Henry Carey Baird and Co, New York (1920) 613-621.

Brenner, A., Electrodeposition of Alloys (2Vols.), Academic Press, New York (1963) 11-17.

Britton, S.C., Tin and Tin Alloys, Tin Research Int. (1952) 27-33.

Burns R.M. and Bradley, W.W., Prot. Coatings for Metals, 3rd Edn. Reinhold, New York (1954) 259-269.

Canning, W., Canning Handbook of Electroplating (1970) 10-15.

Chemicals, M and T, Inc., Tin Coatings in Industry, Tech. Data Sheet (1952) 105-110.

Chemicals M and T, Inco. Immersion Tinning of Bronze, Copper and Brass, Tech. Data Sheet (1960) 17-25.

Costain W, and Terry B.W.H., Imp. Chem. Ind. Ltd. (1972) 17-21.

Dean, J.A. Langes Handbook of Chem. 12th Edn, Mc Graw-Hill (1972) 117-223.

Drobne J.R. and Ceresa, M., U.S. Patent (1959) 2, 891.

Field, S. and Weil, A.D. Electroplating, 5th Edn., Pitman, New York (1945) 368-371.

Gabe, D.R., Princ. of Met. Sur. Treat. and Prot., 2nd Edn., Perg. Press, London (1978) 19-79.

Graham, Elect. Handbook, 2nd., Chapman & Hall (1962) 18-25.

Gould, E.S., J. Amer Chem. Soc, 96, 2373 (1974) 19-28.

Ho Tam, Z.C. and Amis, E.S., J. Inorg Nucl Chem., 28 (1966) 38-45.

Kern, E.F., Trans. Amer. Electro. Soc. (1913) 24, 192-198.

Kitaigorodskii, A.I., Org. Chem. Cryst., Cons. Bureau, New York (1955) 112-127.

Kohan, L.R., Met. Ind. (1959) 451.

Kohan, L.R., Met. Finish. (1959) 618.

Krochler, W.A. and Creighton, H.J., Princ. and Appl. of electrochem., 2nd Edn., Vol. II, Willey, New York (1944) 41-68.

Lowenheim, F.A. and Forman, H.B., U.S. Patent (1956), 2, 861, 891.

Lowenheim, F.A. Electroplating, First Edn., McGraw-Hill New York (1978), 210-315.

Lowenheim, F.A., Plating (1964) 50, 551.

Melton, S.L., Wear, T.O., T. Inorg. Nucl. Chem. 17, 317 (1961) 17-24.

Oguta, M., and Mikio, J., Ind. Prod. Res. Inst., Tokyo, Japan, Kinzoku Hyomen Giyutsu (1975), 26, (12), 292-296.

Ollard, S.A. and Smith, E.B., Handbook of Ind. Electroplating, Iliffe (1954), 17-25.

Pavlish, A.E., and Sullivan, J.D., Metals and Alloys (1949) 11, 135.

Pietrzyk, D.J. and Frank, C.W., Analy. Chem., 2nd Edn., Acad. Press, Inc., New York (1979) 106-121.

Price, E., The Chem. of Non-Aqueous Solvents, Vol. I., Edn Logowski, J.J. Acad. Press (1966) 70.

Proll, P.J., In Comprehensive Chem. Kinetics; Vol.7, Elsevier (1972) 157-168.

Raub, E. and Muller, K., Fundamental of Metal Deposition, Elsevier (1967) 17-21.

Reutor, O., Theoret. Princ. of Org. Chem., MIR Publishers, Moscow (1970) 7-11.

Saubestre, E.B., Plating (1972) 59, 563.

Shipley, L., U.S. Patent 3,303 (1967) 50, 551.

Sullivan, J.D. and Pavlish, A.E., U.S. Patent (1939) 2, 159, 510.

Takahanshi, T. and Kozawa A. J. Met. Finish. Society, Japan (1969) 11, 301.

Vegranmyan, A.T. and Soleveva, Z.A., Tech. of Electrodeposition, Draper (1962) 13-21.

Wilson, J.K. and Wright, O., Contact Tin Plate, Electroplating (1951) 15-23.

Wranglen, E., An Intro. to Corr. and Prot. of Met., 1st Edn., Butler and Turner Ltd., Rome and London (1972) 174-180.

Wright, O. and Wilson, J.K., Electroplating Met. Finish. 4 (1951) 274.

Wright, O. and Wilson, J.K., Met. Finish. 2, (1953) 50.

Wright, O. and Wilson, J.K., Aircraft Prod., Vol. 15 (1953) 329.

Wright, O. and Rapson, H.D.C., Immersion Tinning of Steel by Internal Electrolysis, Electrodeposition Tech. Soc. (1965) 3-7.

APPENDIX 1:

TABLES OF

BRONZE IMMERSION PLATING.

NaCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml /l HCl	20 ml/l HCl
0	0.050	-0.010	0.030
4	0.110	0.000	0.020
8	0.150	0.075	0.010
12	0.225	0.040	0.025
16	0.325	0.02	0.025
20	0.425	0.04	0.015

TABLE 1: Addition of NaCl and HCl effects on bronze immersion plating in distilled water containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C.

NaCl (g/l)	Weight Gain (mg/cm^2)		
	0 Stripping	1st Stripping	2nd Stripping
0	0.000	0.0150	0.040
4	0.030	0.075	0.100
8	0.045	0.100	0.175
12	0.075	0.150	0.250
16	0.115	0.250	0.400
20	0.145	0.350	0.600

TABLE 2: Addition of NaCl and stripping effects on bronze immersion plating in distilled water containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C.

KCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.25	0.00	0.10
4	0.35	0.30	0.30
8	0.40	0.50	0.20
12	0.50	0.00	0.60
16	0.60	-0.10	0.65
20	0.80	0.60	0.30

TABLE 3: Effects of KCl and HCl on bronze immersion plating in distilled water containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

$BaCl_2$ (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml./l HCl	20 ml/l HCl
0	0.10	0.00	0.10
4	0.20	0.30	0.40
8	0.30	0.20	0.20
12	0.50	0.10	0.10
16	0.55	0.30	0.30
20	0.65	0.50	0.20

TABLE 4: Effects of $BaCl_2$ and HCl on bronze immersion plating in distilled water containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

NaCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.200	-0.05	-0.15
4	0.250	0.00	0.10
8	0.450	0.20	-0.10
12	0.650	0.10	0.00
16	0.800	0.30	-0.20
20	1.0	0.10	0.1

TABLE 5: Effects of NaCl and HCl on bronze immersion plating in methanol medium containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

KCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.200	-0.100	-0.150
4	0.350	0.000	0.100
8	0.400	-0.150	0.000
12	0.500	0.30	0.300
16	0.600	0.00	0.100
20	0.700	0.100	0.150

TABLE 6: Effects of KCl and HCl on bronze immersion plating in methanol containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated for 5 minutes at 25°C.

$BaCl_2$ (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.200	0.00	-0.10
4	0.500	0.10	0.00
8	0.400	-0.10	-0.10
12	0.500	0.20	0.30
16	0.900	0.30	0.10
20	1.000	0.15	0.10

TABLE 7: Effects of $BaCl_2$ and HCl on bronze immersion plating in methanol medium containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

NaCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.10	-0.05	0.00
4	0.15	0.20	-0.15
8	0.30	0.00	0.30
12	0.60	-0.10	-0.10
16	0.65	0.30	0.30
20	0.80	0.40	0.20

TABLE 8: Effects of HCl and NaCl on bronze immersion plating in propanol medium containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

KCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.00	0.00	-0.10
4	0.20	-0.10	0.20
8	0.25	0.30	0.00
12	0.40	0.20	0.30
16	0.60	0.10	-0.10
20	0.80	0.40	0.10

TABLE 9: Effects of HCl and KCl on bronze immersion plating in propanol medium containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

$BaCl_2$ (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.20	0.00	-0.15
4	0.10	0.20	0.10
8	0.30	0.00	0.30
12	0.35	-0.10	-0.10
16	0.50	0.30	0.20
20	0.70	0.20	0.30

TABLE 10: Effects of $BaCl_2$ and HCl on bronze immersion plating in propanol medium containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

NaCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.05	0.00	-0.15
4	0.10	0.20	0.30
8	0.30	-0.10	0.00
12	0.30	0.30	-0.10
16	0.50	0.15	-0.10
20	0.70	0.20	0.20

TABLE 11: Effects of NaCl and HCl on bronze immersion plating in butanol medium containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

KCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.2	0.00	-0.10
4	0.1	0.30	-0.10
8	0.30	-0.10	0.20
12	0.35	0.00	0.10
16	0.50	0.20	-0.10
20	0.65	0.10	0.20

TABLE 12: Effects of KCl and HCl on bronze immersion plating in butanol medium containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

$BaCl_2$ (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.00	0.00	-0.10
4	0.20	0.30	0.00
8	0.30	-0.10	0.20
12	0.35	0.00	0.30
16	0.60	0.40	0.10
20	0.65	0.10	0.20

TABLE 13: Effects of $BaCl_2$ and HCl on bronze immersion plating in butanol containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

NaCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.00	0.00	0.10
4	0.10	0.10	0.00
8	0.10	0.10	-0.10
12	0.30	0.20	0.00
16	0.50	0.00	0.00
20	0.70	0.10	0.10

TABLE 14: Effects of NaCl and HCl on bronze immersion plating in akamu containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

KCl (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.00	0.10	0.00
4	0.00	0.00	-0.10
8	0.20	0.00	0.20
12	0.40	0.10	0.00
16	0.30	0.00	0.10
20	0.60	0.20	0.10

TABLE 15: Effects of KCl and HCl on bronze immersion plating in akamu containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

$BaCl_2$ (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.20	0.00	0.00
4	0.00	0.10	0.00
8	0.00	0.10	0.10
12	0.15	0.00	-0.10
16	0.40	0.10	0.10
20	0.55	0.20	0.00

TABLE 16: Effects of $BaCl_2$ and HCl on bronze immersion plating in akamu containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

NaCl (g/l)	Coating Thickness (um)		
	0 HCl	10 ml/1 HCl	20 ml/1 HCl
0	0.075	0.025	0.075
4	0.110	0.050	0.060
8	0.150	0.075	0.051
12	0.225	0.040	0.051
16	0.325	0.025	0.051
20	0.450	0.040	0.030

TABLE 17: Effects of NaCl and HCl on bronze immersion plating in distilled water containing 20 g/l $SnCl_2.2H_2O$ and 10 $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

NaCl (g/l)	Coating Thickness (um)		
	0 HCl	10 ml/1 HCl	20 ml/1 HCl
0	0.200	0.05	0.01
4	0.210	0.10	0.20
8	0.430	0.30	0.05
12	0.575	0.20	0.10
16	0.800	0.40	0.01
20	1.000	0.20	0.20

TABLE 18: Effects of NaCl and HCl on bronze immersion plating in methanel containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 mimutes.

NaCl (g/l)	Coating Thickness (um)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.2	0.10	0.10
4	0.25	0.30	0.02
8	0.40	0.10	0.40
12	0.70	0.05	0.05
16	0.75	0.40	0.40
20	0.90	0.50	0.25

TABLE 19: Effects of NaCl and HCl on bronze immersion plating in propanol containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

NaCl (g/l)	Coating Thickness (um)		
	0 HCl	10 ml/l HCl	20 ml/l HCl
0	0.10	0.10	0.00
4	0.20	0.30	0.40
8	0.40	0.05	0.10
12	0.40	0.40	0.05
16	0.60	0.20	0.05
20	0.80	0.30	0.30

TABLE 20: Effects of NaCl and HCl on bronze immersion plating in butanol containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

NaCl (g/l)	Coating Thickness (um)		
	0 HCl	10 ml /l HCl	20 ml /l HCl
0	0.10	0.10	0.20
4	0.20	0.20	0.10
8	0.20	0.20	0.05
12	0.40	0.30	0.10
16	0.65	0.10	0.10
20	0.75	0.20	0.20

TABLE 21: Effects of NaCl and HCl on bronze immersion plating in akamu containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

KCl (g/l)	Coating Thickness (um)			
	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH
0	0.30	0.20	0.10	0.30
4	0.45	0.35	0.30	0.30
8	0.50	0.50	0.35	0.40
12	0.60	0.675	0.50	0.45
16	0.88	0.700	0.70	0.60
20	1.00	0.93	0.90	0.80

TABLE 22: Comparison of the effects of KCl and media in acid free solution on bronze immersion plating in solutions containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

KCl (g/l)	Coating Thickness (um)	
	Water	Akamu
0	0.35	0.10
4	0.43	0.10
8	0:50	0.30
12	0.60	0.50
16	0:70	0.45
20	0.85	0.65

TABLE 23: Comparison of the effects of KCl and media in acid free solution on bronze immersion plating in solutions containing 20 g/l $SnCl_2.2H_2O$ and 10 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Time (min)	Coating Thickness (um)			
	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH
0.5	0.30	0.20	0.20	0.15
1.0	0.50	0.40	0.25	0.20
1.5	0.65	0.55	0.45	0.25
2.0	0.80	0.60	0.55	0.35
2.5	0.92	0.70	0.65	0.45
3.0	0.96	0.75	0.70	0.55
3.5	0.98	0.80	0.72	0.65
4.0	0.99	0.86	0.75	0.73
4.5	1.00	0.92	0.80	0.75
5.0	1.00	0.93	0.80	0.75

TABLE 24: Plating rate of bronze immersion plating in various media from acid free solutions containing 20 g/l $SnCl_2.2H_2$, 10 g/l $CuCl_2.2H_2O$ and 20 g/l NaCl, operated at 25°C.

Time (min)	Coating Thickness (μm)	
	Water	Akamu
0.5	0.20	0.15
1.0	0.35	0.20
1.5	0.50	0.30
2.0	0.60	0.40
2.5	0.65	0.50
3.0	0.70	0.50
3.5	0.73	0.55
4.0	0.75	0.57
4.5	0.80	0.60
5.0	0.80	0.60

TABLE 25: Plating rate of bronze immersion plating in various media from acid free solutions containing 20 g/l $SnCl_2.2H_20$, 10 g/l $CuCl_2.2H_20$ and 20 g/l NaCl, operated at 25°C.

Dithionate (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	5 ml /1 HCl	10 ml/1 HCl
0	0.100	-0.010	-0.01
4	0.250	0.010	-0.10
8	0.300	0.020	0.07
12	0.320	-0.100	0.04
16	0.350	0.025	-0.06
20	0.390	0.100	-0.03

TABLE 26: Effects of sodium dithionate and HCl on bronze immersion plating in distilled water containing 8 g/l $SnCl_2.2H_20$ and 8 g/l $CuCL_2.2H_20$, operated at 25°C for 5 minutes.

Dithionate (g/l)	Weight Gain (mg/cm^2)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	0.10	0.075	0.030
4	0.25	0.120	0.080
8	0.30	0.175	0.125
12	0.32	0.250	0.175
16	0.35	0.275	0.230
20	0.375	0.310	0.250

TABLE 27: Effects of concentration and sodium dithionate on bronze immersion plating in distilled water containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	0.15	-0.05	-0.07
4	0.28	0.00	-0.03
8	0.45	0.08	0.03
12	0.56	0.02	0.10
16	0.68	0.14	0.00
20	0.80	0.20	0.13

TABLE 28: Effects of sodium dithionate and HCl on bronze immersion plating in methanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2 2H_2O$, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	0.15	0.10	0.05
4	0.28	0.18	0.12
8	0.45	0.25	0.18
12	0.56	0.39	0.28
16	0.68	0.58	0.38
20	0.80	0.63	0.43

TABLE 29: Effects of concentration and sodium dithionate on bronze immersion plating in methanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	0.100	-0.05	-0.07
4	0.280	0.01	-0.05
8	0.400	0.02	0.00
12	0.510	0.03	0.03
16	0.580	0.08	0.035
20	0.680	0.06	0.035

TABLE 30: Effects of sodium dithionate and HCl on bronze immersion plating in ethanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	0.10	0.10	0.05
4	0.28	0.18	0.10
8	0.40	0.30	0.15
12	0.50	0.41	0.20
16	0.58	0.41	0.25
20	0.63	0.45	0.30

TABLE 31: Effects of concentration and sodium dithionate on bronze immersion plating in ethanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	0.10	-0.02	-0.03
4	0.15	-0.01	-0.05
8	0.30	0.05	-0.01
12	0.38	0.02	0.05
16	0.46	0.05	0.03
20	0.60	0.04	0.03

TABLE 32: Effects of sodium dithionate and HCl on bronze immersion plating in propanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	0.10	0.08	0.060
4	0.15	0.10	0.080
8	0.30	0.18	0.100
12	0.40	0.22	0.120
16	0.50	0.28	0.150
20	0.60	0.32	0.200

TABLE 33: Effects of concentration and sodium dithionate on bronze immersion plating in propanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	0.075	-0.075	-0.050
4	0.125	-0.030	-0.050
8	0.210	0.00	0.060
12	0.275	0.075	0.00
16	0.375	0.100	-0.04
20	0.410	0.040	0.04

TABLE 34: Effects of sodium dithionate and HCl on bronze immersion plating in butanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	0.075	0.040	0.05
4	0.125	0.100	0.075
8	0.22	0.175	0.100
12	0.30	0.17	0.155
16	0.375	0.25	0.25
20	0.42	0.35	0.30

TABLE 35: Effects of concentration and sodium dithionate on bronze immersion plating in butanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	0.03	-0.04	-0.05
4	0.11	-0.03	-0.03
8	0.15	0.00	-0.020
12	0.21	0.03	0.00
16	0.27	0.02	0.02
20	0.325	0.02	0.01

TABLE 36: Effects of sodium dithionate and HCl on bronze immersion plating in akamu containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Weight Gain (mg/cm^2)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	0.020	0.025	0.015
4	0.120	0.080	0.056
8	0.150	0.120	0.076
12	0.220	0.175	0.120
16	0.270	0.250	0.170
20	0.320	0.275	0.200

TABLE 37: Effects of concentration and sodium dithionate on bronze immersion plating in akamu containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	80	40	25
4	105	75	48
8	200	100	51
12	270	100	75
16	290	120	85
20	310	130	94

TABLE 38: Effects of L-cysteine and HCl on bronze immersion plating in aqueous solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	77	70	60
4	101	92	75
8	201	135	80
12	275	175	84
16	290	201	90
20	300	250	101

TABLE 39: Effects of concentration and L-cysteine on bronze immersion plating in aqueous solution containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	100	50	35
4	250	90	50
8	480	145	75
12	605	180	100
16	750	210	102
20	800	290	165

TABLE 40: Effects of L-cysteine and HCl on bronze immersion plating in methanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/1)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	100	85	65
4	250	200	90
8	475	260	160
12	610	410	210
16	750	470	290
20	810	510	380

TABLE 41: Effects of concentration and L-cysteine on bronze immersion plating in methanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

L-cysteine (g/1)	Coating Thickness (mum)		
	0 HCl	5 ml/1 HCl	10 ml /1 HCl
0	100	40	20
4	190	70	45
8	310	110	80
12	450	160	115
16	540	200	130
20	650	210	140

TABLE 42: Effects of L-cysteine and HCl on bronze immersion plating in ethanol containing 8 g/1 $SnCl_2.2H_2O$ and 8 g/1 $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	100	80	40
4	190	95	70
8	310	160	95
12	450	210	140
16	540	290	180
20	650	340	220

TABLE 43: Effects of concentration andL-cysteine on bronze immersion plating in ethanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	75	50	20
4	190	70	40
8	280	100	50
12	350	120	60
16	480	170	70
20	560	210	80

TABLE 44: Effects of L-cysteine and HClon bronze immersion plating in propanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	80	70	45
4	180	100	75
8	270	160	100
12	350	210	150
16	475	275	200
20	565	360	270

TABLE 45: Effects of concentration and L-cysteine on bronze immersion plating in propanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	80	30	25
4	150	75	30
8	285	110	40
12	350	175	45
16	400	200	70
20	440	220	100

TABLE 46: Effects of L-cysteine and HCl on bronze immersion plating in butanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°c fof 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	80	60	50
4	155	95	75
8	280	150	110
12	350	180	150
16	400	210	219
20	450	275	225

TABLE 47: Effects of concentration and L-cysteine on bronze immersion plating in butanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	60	49	20
4	110	90	50
8	180	120	50
12	220	185	55
16	290	200	60
20	310	210	90

TABLE 48: Effects of l-cysteine and HCl on bronze immersion plating in akamu containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	52.5	50	50
4	115	100	90
8	185	170	125
12	220	195	165
16	300	250	200
20	320	290	225

TABLE 49: Effects of concentration and L-cysteine on bronze immersion plating in akamu containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	150	80	48
4	370	100	70
8	450	120	100
12	550	180	140
16	650	210	160
20	700	220	170

TABLE 50: Effects of thiourea and HCl on bronze immersion plating in aqueous solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/1)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	$Sn^{2+}Cu^{2+}$=8/4
0	150	104	85
4	400	200	120
8	540	300	200
12	600	400	220
16	670	450	260
20	730	500	350

TABLE 51: Effects of concentration and thiourea on bronze immersion plating in aqueous solution containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Thiourea (g/1)	Coating thickness (mum)		
	0 HCl	5 ml/1 HCl	10 ml/1 HCl
0	180	100	50
4	350	150	90
8	540	210	150
12	680	240	170
16	820	310	200
20	950	350	210

TABLE 52: Effects of thiourea and HCl on bronze immersion plating in methanol containing 8 g/1 $SnCl_2.2H_2O$ and 8 g/1 $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	150	100	80
4	370	230	150
8	530	300	260
12	730	380	350
16	800	400	400
20	950	580	450

TABLE 53: Effects of concentration and thiourea on bronze immersion plating in methanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating thickness (mum)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	130	90	70
4	270	100	100
8	350	170	120
12	430	200	150
16	600	300	200
20	700	340	220

TABLE 54: Effects of thiourea and HCl on bronze immersion plating in ethanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/1)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	130	110	90
4	270	210	150
8	390	290	190
12	450	340	240
16	600	390	290
20	700	440	320

TABLE 55: Effects of concentration and thiourea on bronze immersion plating in ethanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Thiourea (g/1)	Coating Thickness (mum)		
	0 HCl	5 ml/1 HCl	10 ml/1 HCl
0	120	70	51
4	220	150	90
8	270	170	120
12	330	220	175
16	360	275	200
20	460	320	240

TABLE 56: Effects of thiourea and HCl on bronze immersion plating in propanol containing 8 g/1 $SnCl_2.2H_2O$ and 8 g/1 $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	110	95	75
4	210	177	105
8	260	210	165
12	320	280	210
16	355	305	280
20	450	350	300

TABLE 57: Effects of concentration and thiourea on bronze immersion plating in propanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	0 HCl	5 ml/l HCl	10 ml/l HCl
0	80	55	40
4	130	100	80
8	210	150	100
12	285	195	120
16	385	210	170
20	380	235	200

TABLE 58: Effects of thiourea and HCl on bronze immersion plating in butanol containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	80	80	65
4	130	100	95
8	210	178	130
12	290	230	180
16	335	280	220
20	410	325	270

TABLE 59: Effects of concentration and thiourea on bronze immersion plating in butanol containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	0 HCl	5 ml /l HCl	10 ml /l HCl
0	52	45	25
4	80	52	55
8	125	90	75
12	170	115	90
16	200	140	100
20	230	152	110

TABLE 60: Effects of thiourea and HCl on bronze immersion plating in akanu containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	Sn^{2+}/Cu^{2+}=8/8	Sn^{2+}/Cu^{2+}=8/6	Sn^{2+}/Cu^{2+}=8/4
0	60	50	35
4	95	70	70
8	140	100	80
12	180	130	130
16	225	180	150
20	260	210	170

TABLE 61: Effects of concentration and thiourea on bronze immersion plating in akamu containing hydrated cupric and stannous chlorides, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Coating Thickness (mum)		
	75% CH_3OH	50% CH_3OH	25% CH_3OH
0	100	90	70
4	200	200	190
8	395	400	300
12	570	525	450
16	660	620	570
20	750	700	650

TABLE 62: Effects of sodium dithionate and methanol concentration on bronze immersion plating from solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$ operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Coating Thickness (mum)		
	75% C_2H_5OH	50% C_2H_5OH	25% C_2H_5OH
0	96	96	70
4	180	210	150
8	300	250	280
12	430	390	390
16	580	530	470
20	630	550	480

TABLE 63: Effects of sodium dithionate and ethanol concentration on bronze plating from solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Sodium Dithionate (g/l)	Coating Thickness (mum)		
	75% C_3H_7OH	50% C_3H_7OH	25% C_3H_7OH
0	70	75	50
4	160	210	100
8	270	230	200
12	300	300	210
16	400	430	280
20	450	440	300

TABLE 64: Effects of sodium dithionate and propanol concentration on bronze immersion plating from solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$.

Sodium Dithionate (g/l)	Coating Thickness (mum)		
	75% C_4H_9OH	50% C_4H_9OH	25% C_4H_9OH
0	70	70	50
4	150	210	100
8	275	235	200
12	310	300	205
16	415	450	275
20	450	435	300

TABLE 65: Effects of sodium dithionate and butanol concentration on bronze immersion plating in solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	75% CH_3OH	50% CH_3OH	25% CH_3OH
0	95	60	25
4	200	170	100
8	320	280	180
12	510	390	250
16	620	480	300
20	700	560	320

TABLE 66: Effects of L-cysteine and methanol concentration on bronze immersion plating from solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	75% C_2H_5OH	50% C_2H_5OH	25% C_2H_5OH
0	70	50	40
4	180	160	100
8	310	300	180
12	460	330	280
16	580	340	300
20	610	470	360

TABLE 67: Effects of L-cysteine and ethanol concentration on bronze immersion plating in solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	75% C_3H_7OH	50% C_3H_7OH	25% C_3H_7OH
0	100	80	70
4	190	110	140
8	280	260	210
12	370	320	290
16	450	380	310
20	500	460	380

TABLE 68: Effects of L-cysteine and propanol concentration on bronze immersion plating in solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

L-cysteine (g/l)	Coating Thickness (mum)		
	75% C_4H_9OH	50% C_4H_9OH	25% C_4H_9OH
0	52	50	40
4	170	100	100
8	230	140	140
12	290	230	170
16	310	280	180
20	390	300	210

TABLE 69: Effects of L-cysteine and butanol concentration on bronze immersion plating in solution containing 8 g/l $SnCL_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	75% CH_3OH	50% CH_3OH	25% CH_3OH
0	100	80	50
4	210	180	90
8	410	160	170
12	510	440	280
16	680	580	390
20	740	610	410

TABLE 70: Effects of thiourea and methanol concentration on bronze immersion plating in solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	75% C_3H_5OH	50% C_3H_5OH	25% C_3H_5OH
0	80	70	60
4	190	175	130
8	260	260	200
12	400	370	260
16	490	450	350
20	570	510	380

TABLE 71: Effects of thiourea and ethanol concentration on bronze immersion plating in solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Thiourea (g/l)	Coating Thickness (mum)		
	75% C_3H_7OH	50% C_3H_7OH	25% C_3H_7OH
0	100	75	75
4	190	155	125
8	240	240	160
12	300	280	180
16	350	300	185
20	400	350	205

TABLE 72: Effects of thiourea and propanol concentration on bronze immersion plating in solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

APPENDIX 2:

TABLES OF

BRONZE ELECTROPLATING OF IMMERSION

PLATED SUBSTRATES.

Thiourea (g/l)	Coating Thickness (mum)		
	75% C_4H_9OH	50% C_4H_9OH	25% C_4H_9OH
0	51	45	30
4	125	100	90
8	170	130	100
12	206	170	120
16	230	180	140
20	250	200	151

TABLE 73: Effects of butanol concentration and thiourea on bronze immersion plating in solution containing 8 g/l $SnCl_2.2H_2O$ and 8 g/l $CuCl_2.2H_2O$, operated at 25°C for 5 minutes.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	5.5	3.0	2.0
10	8.5	5.5	2.4
15	10	7.0	3.0
20	12.4	8.5	4.0
25	14.0	9.5	4.6
30	15.0	10.0	5.0

TABLE 74: Effects of currrent density and plating time on bronze electroplating in distilled water of immersion plated substrate. The electroplating solution contained 50 ml/l HCl, 100 g/l $SnCl_2.2H_2O$ and 100 g/l $CuCl_2.2H_2O$.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
0	5.0	4.6	3.5
10	9.0	8.5	4.4
15	12.0	10.6	4.7
20	13.5	11.0	4.8
25	14.5	11.5	5.0
30	15.5	12.0	5.5

TABLE 75: Effects of current density and plating time on bronze electroplating in distilled water of immersion plated substrate. The electroplating solution contained 60 ml/L HCl, 100 g/l $SnCl_2.2H_2O$ and100 g/l $CuCl_2.2H_2O$, operated at 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	8.0	7.0	5.0
10	12.0	8.5	5.8
15	13.5	10.5	6.8
20	15.5	11.5	7.0
25	17.5	12.8	7.5
30	18.0	13.0	8.0

TABLE 76: Effects of current density and plating time on bronze electroplating in methanol of immersion plated substrate. The electroplating solution contained 50 ml/L HCl, 100 g/l $SnCl_2.2H_2O$ and 100 g/l $CuCl_2.2H_2O$ and operated at 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	8.5	6.50	5.00
10	13.0	10.50	6.50
15	15.55	11.00	6.80
20	16.40	12.00	7.00
25	18.00	13.00	8.00
30	18.00	13.50	8.50

TABLE 77: Effects of current density and plating time on bronze electroplating in methanol of immersion plated substrate. The plating solution contained 60 ml/L HCl, 100 g/l $SnCl_2.2H_2O$, and 100 g/l $CuCl_2.2H_2O$ and was operated at 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	10.00	6.00	3.50
10	13.00	8.50	5.00
15	14.50	9.80	5.50
20	15.00	10.60	5.80
25	16.80	11.50	6.20
30	17.00	12.00	6.60

TABLE 78: Effects of current density and plating time on bronze electroplating in ethanol of immersion plated substrate. The electroplating solution contained 50 ml/L HCl, 100 g/l $SnCl_2.2H_2O$ and 100 g/l $CuCl_2.2H_2O$, and was operate at 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	10	6.4	4.0
10	13.5	8.0	5.0
15	14.8	10.0	5.8
20	15.4	10.8	6.0
25	16.0	12.5	6.5
30	16.5	13.0	7.0

TABLE 79: Effects of current density and plating time on bronze electroplating in ethanol of immersion plated substrate. The electroplating solution contained 100 g/l $SnCl_2.2H_2O$, 100 g/l $CuCl_2.2H_2O$ and 60 ml/L HCl. The plating temperature was maintained at 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	5.0	4.0	2.0
10	7.0	6.0	2.5
15	8.5	7.4	3.5
20	10.8	9.4	4.0
25	13.0	11.0	4.5
30	14.0	12.5	5.0

TABLE 80: Effects of current density and plating time on bronze electroplating in propanol of immersion plated substrate. The electroplating solution contained 100 g/l $SnCl_2.2H_2O$, 100 g/l $CuCl_2.2H_2O$ and 50 ml/L HCl. The plating temperature was maintained at 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	6.0	4.5	2.5
10	8.0	6.5	3.4
15	10.0	8.8	3.8
20	12.0	10.5	4.4
25	14.0	12.0	5.4
30	14.4	13.0	5.8

TABLE 81: Effects of current density and plating time on bronze electroplating in propanol of immersion plated substrate. The electroplating solution contained 100 g/l $SnCl_2.2H_2O$, 100 g/l $CuCl_2.2H_2O$ and 60 ml/L HCl, and was operated at a temperature of 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	3.5	2.5	1.5
10	5.5	4.5	2.5
15	7.5	5.8	3.0
20	9.5	6.8	3.5
25	11.5	7.5	3.8
30	12.0	8.0	4.0

TABLE 82: Effects of current density and plating time on bronze electroplating in butanol of immersion plated substrate. The electroplating solution contained 100 g/l $SnCl_2.2H_2O$, 100 g/l $CuCl_2.2H_2O$ and 50 ml/L HCl and was operated at a temperature of 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	3.0	2.0	1.2
10	6.0	4.0	2.5
15	9.0	6.0	3.5
20	12.0	7.5	4.5
25	13.5	9.5	5.2
30	14.0	10.0	5.6

TABLE 83: Effects of current density and plating time on bronze electroplating in butanol of immersion plated substrate. The electroplating solution contained 100 g/l $SnCl_2.2H_2O$, 100 g/l $CuCl_2.2H_2O$ and 60 ml/L HCl, and was operated at 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	3.0	2.0	1.0
10	5.0	3.0	1.5
15	7.0	4.0	1.8
20	8.5	5.0	2.4
25	9.5	5.5	2.8
30	10.0	6.0	3.0

TABLE 84: Effects of current density and plating time on bronze electroplating in akamu of immersion plated substrate. The electroplating solution contained 100 g/l $SnCl_2.2H_2O$, 100 g/l $CuCl_2.2H_2O$ and 50 ml/L HCl, and was operated at 35°C.

Time (min)	Coating Thickness (um)		
	30 A/m^2	20 A/m^2	10 A/m^2
5	4.5	4.0	1.8
10	6.0	4.8	2.6
15	7.5	5.2	2.8
20	8.5	6.0	3.5
25	9.4	6.8	3.80
30	9.8	7.0	4.00

TABLE 85: Effects of current density and plating time on bronze electroplating in akamu of immersion plated substrate. The electroplating solution contained 100 g/l $SnCl_2.2H_2O$, 100 g/l $CuCl_2.2H_2O$ and 60 ml/L HCl, and was operated at a temperature of 35°C.

Time (min)	Coating Thickness (um)		
	50 ml/L Nitric Acid	50 ml/L Acetic Acid	50 ml/L Formic Acid
5	4.3	2.0	1.5
10	7.3	4.5	3.8
15	10.0	6.8	6.0
20	12.4	10.5	10.0
25	14.5	12.5	11.5
30	15.0	13.5	12.0

TABLE 86: Effects of acids (nitric, acetic and formic) and plating time on bronze electroplating in distilled water of immersion plated substrate. The plating solution contained 100 g/l $SnCl_2.2H_2O$ and 100 g/l $CuCl_2.2H_2O$. The plating took place at a temperature of 35°C, with current density of 20 A/m^2.

Time (min)	Coating Thickness (um)		
	50 ml/L Nitric Acid	50 ml/L Acetic Acid	50 ml/L Formic Acid
5	4.0	2.5	2.0
10	7.5	4.8	4.8
15	9.5	7.0	8.0
20	13.5	10.8	11.5
25	16.5	14.5	13.3
30	17.0	16.00	14.0

TABLE 87: Effects of acids (nitric, acetic and formic) and plating time on bronze electroplatingin methanolof immersion plated substrate. The plating solution contained 100 g/1 $SnCl_2.2H_20$ and 100 g/1 $CuCl_2.2H_20$. The plating took place at a temperature of 35°C with a current density of 30 A/m^2.

Time (min)	Coating Thickness (um)		
	50 ml/1 Nitric Acid	50 ml/1 Acetic Acid	50 ml/1 Formic Acid
5	2.5	2.0	1.8
10	5.0	5.0	3.5
15	7.0	6.5	4.0
20	8.5	7.5	5.0
25	9.5	8.5	6.0
30	10.0	9.0	6.6

TABLE 88: Effects of acids (nitric, acetic and formic) and plating time on bronze electroplating in akamu of immersion plated substrate. The plating solution contained 100 g/1 $SnCl_2.2H_20$ and 100 g/1 $CuCl_2.2H_20$. The plating took place at a temperature of 35°C with a current density of 20 A/m^2.

Time (min)	Coating Thickness (um)		
	50% Acetone/water	37% Formaldehyde	99% Acetone
5	2.5	2.0	1.6
10	4.8	3.5	2.5
15	6.8	5.8	3.5
20	8.5	7.0	3.8
25	9.5	9.0	5.5
30	10.0	9.5	6.0

TABLE 89: Effects of solvents (50% Water/acetone, 37% formaldehyde and 99% acetone) and plating time on bronze electroplating of immersion plated substrate from solutions containing 100 g/l $SnCl_2.2H_2O$ and 100 g/l $CuCl_2.2H_2O$, operated at a temperature of 35°C with a current density of 20 A/m^2.

Time (min)	Coating Thickness (um)		
	50% Acetone/water	37% Formaldehyde	99% Acetone
5	2.0	2.5	1.5
10	3.00	3.6	2.0
15	3.5	3.9	2.5
20	4.6	4.4	2.8
25	5.8	4.8	3.3
30	6.0	5.0	3.5

TABLE 90: Effects of solvents (50% Water/acetone, 37% formaldehyde and 99% acetone) and plating time on bronze electroplating of immersion plated substrate from solutions containing 100 g/l $SnCl_2.2H_2O$ and 100 g/l $CuCl_2.2H_2O$, operated at a temperature of 35°C with a current density of 30 A/m^2.